

Wolfgang Tress

Organic Solar Cells

Theory, Experiment, and Device
Simulation



Springer

Springer Series in Materials Science

Volume 208

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Organic Solar Cells

Theory, Experiment, and Device Simulation

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ISSN 0933-033X ISSN 2196-2812 (electronic)
ISBN 978-3-319-10096-8 ISBN 978-3-319-10097-5 (eBook)
DOI 10.1007/978-3-319-10097-5

Library of Congress Control Number: 2012953251

Springer Cham Heidelberg New York Dordrecht London

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Preface

We owe our children similar chances as we had when we started exploiting the resources the earth is offering us. This does not mean that we should not use what the earth provides. It neither implies that we should not change the earth's appearance. Exactly that is the aspiration of humankind. However, to allow this quest to grow also in future generations, we have to act in what we call a sustainable way. One huge impact on the (non-) sustainability of current human actions is related to the supply of energy for nowadays' society. The large-scale exploitation of fossil and nuclear resources conflicts with the idea of sustainability, as those resources were generated during millions or even billions of years. Their rapid consumption depletes them quickly and causes global changes which might be too rapid to be coped with by humankind in a fair way. Regarding energy "consumption", the most sustainable way of living is to harvest the energy flux continuously provided by the sun.

This book describes the fundamentals regarding the conversion of solar energy into electricity. It focuses on a relatively novel type of solar cell based on organic materials, where the term "organic" refers to molecules based on hydrocarbons, which are synthesized in the framework of organic chemistry. These solar cells show many advantages and peculiarities compared to their inorganic counterparts. Organic photovoltaics covers and combines three interesting, important, and challenging fields: basic theory of solar energy conversion, materials science on novel semiconductors, and physics and technology applied to the energy sector.

With this book I aim to address a broad readership with background in electrical engineering, physics, or materials science. The book should provide students in those fields with a solid introduction and a broad overview of organic photovoltaics. The main focus of the book is on the device physics and working principle of organic solar cells. The textbook-like character of several chapters makes the book also valuable for readers from other disciplines like chemistry or mathematics.

Apart from students searching for introductions, professionals in the field are addressed as well. This book offers parallel to the didactic part a comprehensive discussion of the state of the art. It studies questions of general interest using modeling and experimental data. However, these parts are not organized in a

reporting way but rather an explanatory way. In general, intuitive approaches are preferred to rigorous derivations in case of very complex problems. Note that it is not the scope of this book to give a complete review of the literature regarding organic solar cells.

The prevailing book is based on my Ph.D. thesis, however, faced a complete revision. Especially the introductory parts are strongly extended to give them very general textbook-like characteristics. The second part is reorganized and new data are added. I want to thank all the individuals mentioned in the acknowledgments of my thesis without explicitly repeating the text here. I wrote the book while working as a researcher in the groups of Prof. Dr. Karl Leo and Prof. Dr. Olle Inganäs, who are acknowledged for the freedom they gave me. Moreover I want to thank Ivan Ramirez, Prof. Dr. Horst Hartmann, Dr. Koen Vandewal, Dr. Feng Gao, Johannes Widmer, and Armantas Melianas for inspiring discussions regarding parts of the book. Prof. David Haviland, Torben Menke, Beatrice Beyer, Christian Körner, Selina Olthof, Dr. Lars Müller-Meskamp, Martin Hermenau, and Dr. Mingtao Lu are acknowledged for reading and commenting on sections of the book. I thank Jonas Bergqvist and Dr. Mattias Andersson for comments on the last chapter, Dr. Scott Maugers, Prof. Dr. Sean Shaheen, Dr. Bertrand Tremolet de Villers, and Dr. David Paul Ostrowski for carefully reading the manuscript and detecting inconsistencies and language mistakes. I kindly acknowledge support by the Reiner-Lemoine foundation during my Ph.D. work, the BMBF (Germany), and the Wallenberg foundation (Sweden).

I hope that this book will be of use for many people who want to understand how organic solar cells work. Multiplied by the brains and hands of those, I am sure that this book will contribute to the efforts toward a sustainable energy supply.

Lausanne

Wolfgang Tress

Contents

1	Introduction	1
1.1	Energy Supply and Climate Change	1
1.2	Development of (Organic) Photovoltaics	4
1.3	Scope and Structure of This Book.	7
	References.	9

Part I Basics

2	Photovoltaic Energy Conversion	15
2.1	Fundamentals of Solar-Thermal Energy Conversion	16
2.1.1	The Solar Spectrum	16
2.1.2	Black-Body Radiation	19
2.1.3	Maximum Power-Conversion Efficiency	20
2.2	Basics of Semiconductor Physics	23
2.2.1	Band Structure, Electrons and Holes	23
2.2.2	Quasi-Fermi Levels and Electrochemical Potentials	30
2.3	Transformation of Thermal Radiation into Chemical Energy.	39
2.4	From Chemical Energy to Electric Energy	40
2.5	Possible Realizations of Solar Cells.	45
2.5.1	The p-n Junction.	45
2.5.2	Heterojunction and Dye Solar Cells.	51
2.5.3	The p-i-n Concept with Wide-Gap Transport Layers.	52
2.6	Maximum Efficiency of Solar Cells Based on Semiconductors	53
2.6.1	The Shockley-Queisser Limit	53
2.6.2	Approaching the Radiative Efficiency Limit.	56

2.7	Novel Concepts and Classification of Solar Cells	60
2.8	Answers to the Initial Questions and Further Reading	61
	References.	63
3	Organic Solar Cells.	67
3.1	Energetics of Organic Molecular Materials.	67
3.1.1	From Atoms to Molecules	68
3.1.2	From Single Molecules to a Molecular Solid	83
3.2	Energy and Charge Transport in Organic Semiconductors	87
3.2.1	Exciton Transport	87
3.2.2	Transition Rates and Marcus Theory	89
3.2.3	Charge Transport—Gaussian Disorder Model	93
3.3	Working Principle of Donor-Acceptor Heterojunction Solar Cells.	99
3.3.1	Particle Losses, Quantum Efficiency, and Photocurrent.	100
3.3.2	Energy Losses, Potential Energy, and Photovoltage. . .	105
3.3.3	Maximum Power-Conversion Efficiency	130
3.3.4	Understanding the <i>J-V</i> Curve in the MIM Picture	134
3.3.5	Introduction to Analytical Models Describing the Photocurrent	137
3.4	The Charge-Transfer State in Experiment.	146
3.4.1	Absorption.	147
3.4.2	Luminescence.	148
3.4.3	Driving Force for Charge Transfer	149
3.4.4	Dependence on Temperature and Electric Field.	149
3.4.5	Transient Pump-Probe Spectroscopy	151
3.4.6	The Binding Energy of the CT State	153
3.4.7	Hot CT states.	154
3.4.8	From Photon Absorption to Free Charges—Alternative Views.	156
3.5	Metal-Organic Interfaces	157
3.5.1	Conventional Metal-Semiconductor Interfaces: Barriers and Schottky Contacts.	157
3.5.2	Metal-Organic Interfaces: Disorder and ICT	160
3.6	Experimental Realization of Organic Solar Cells.	161
3.6.1	Deposition and Coating Techniques	161
3.6.2	Solar-Cell Stacks	164
3.6.3	Materials	167
3.6.4	Morphology of the Bulk Heterojunction.	185
3.6.5	Degradation	187
3.6.6	Exemplary Details of a Lab-Scale Vacuum Fabrication System	188

3.7	Basic Characterization Methods	191
3.7.1	Current-Voltage Characteristics.	191
3.7.2	Spectrally Resolved Measurements	193
3.7.3	Transient Electrical Measurements	194
3.8	Answers to the Initial Questions and Further Reading	195
	References.	197
4	Modeling	215
4.1	Overview.	215
4.2	The Drift-Diffusion Model in General	217
4.2.1	Derivation and Conditions	217
4.2.2	The Einstein Relation	221
4.2.3	Poisson's Equation	223
4.2.4	Differential Equation System	223
4.3	Implementation of a Drift-Diffusion Algorithm.	225
4.3.1	Basics of the Algorithm and Discretization.	225
4.3.2	Calculation of the Electric Field	227
4.3.3	Calculation of Rates of Change	227
4.3.4	Calculation of the Time Step	230
4.3.5	Detection of Steady State and Transient Currents	230
4.4	Models for the Individual Processes	232
4.4.1	Charge Carrier Mobility.	232
4.4.2	Recombination	234
4.4.3	Traps.	238
4.4.4	Gaussian Density of States.	240
4.5	Contacts as Boundary Conditions	241
4.6	Organic-Organic Interfaces.	244
4.6.1	Charge Transport	245
4.6.2	Generation and Recombination.	248
4.7	Optical Modeling: Transfer Matrix Approach	250
4.8	Exemplary Devices: Analytical and Numerical Solutions	257
4.8.1	Single-Carrier Devices and SCLC	257
4.8.2	The p-n Junction.	260
4.9	Experimental Determination of Material Properties	263
4.10	Summary of the Main Input Parameters for a Drift-Diffusion Model	268
4.11	Answers to the Initial Questions and Further Reading	269
	References.	271

5 Simulation Study on Single-Layer Bulk-Heterojunction

Solar Cells	277
5.1 Device Structure and Definitions.	277
5.2 On the Optimum Mobility, Contact Properties, and the Open-Circuit Voltage.	280
5.2.1 Investigated Mobility and Recombination Models	280
5.2.2 Recombination only in the BHJ Guaranteed by Selective Contacts	282
5.2.3 Recombination (also) at Electrodes Due to Non-selective Contacts.	290
5.2.4 Injection Barriers	293
5.3 Bending of Energy Levels and the Open-Circuit Voltage	297
5.4 Photocurrent and Characteristic Points of the J - V Curve. . . .	298
5.4.1 Negligible Recombination in the Bulk	299
5.4.2 Photocurrent Limited by Recombination in the Bulk.	301
5.4.3 Photocurrent Transients	305
5.5 Fill Factor, Absorber Thickness, and Mobility Imbalance. . . .	308
5.6 Summary	310
References.	311

Part II Joint Experimental and Simulation Studies

6 Interplay Between Electrodes and Active Materials:

The Open-Circuit Voltage and S-shaped J-V Curves	315
6.1 Methodological Approach	315
6.2 Current-Voltage Data	319
6.2.1 Characteristic Parameters	319
6.2.2 Current-Voltage Characteristics Under Illumination . . .	321
6.3 Detailed Microscopic Explanations	323
6.3.1 Injection Barriers	323
6.3.2 Extraction Barriers	328
6.3.3 Comparison Between Flat and Bulk Heterojunction. . .	329
6.4 Current-Voltage Curves on a Logarithmic Current Scale	330
6.5 Characterizing an Organic-Organic Interface with Photoelectron Spectroscopy.	331
6.6 Ways to Distinguish Between Extraction and Injection Barriers	336
6.6.1 Dependence of the J - V Curve Shape on Layer Thicknesses	336
6.6.2 Temperature Dependent Measurements	340

6.6.3	Transient Photocurrent Measurements	342
6.6.4	Intensity Dependent Measurements	349
6.7	Summary	353
	References.	354
7	Further Origins of S-shaped J-V Curves	359
7.1	Imbalanced Mobilities in Planar Heterojunction Solar Cells . . .	359
7.1.1	Imbalanced Mobilities in Simulation	360
7.1.2	Experimental Verification	364
7.2	Field-Dependent Exciton Dissociation	369
7.3	Kinks in Forward Direction	370
7.4	Kinks for Voltages Below Open Circuit.	372
7.5	Summary	374
	References.	375
8	The Model System ZnPc:C₆₀	377
8.1	Open-Circuit Voltage and Mixing Ratio.	377
8.2	Optimizing the Morphology Using Graded Junctions.	382
8.3	Correlation of Fill Factor with Absorption Profile and Imbalance in Mobilities	384
8.3.1	Idea and Solar-Cell Design	384
8.3.2	Absorption Data	386
8.3.3	Simulated Generation Profiles.	388
8.3.4	Current-Voltage Data	389
8.3.5	Monochromatic J - V Curves	391
8.3.6	External Quantum Efficiency as a Function of Voltage	392
8.4	Recombination	394
8.4.1	Exponential Region of Dark J - V Curves	395
8.4.2	J - V Data Dependent on Illumination Intensity.	397
8.5	Comparison with Simulations.	403
8.6	Summary	408
	References.	409

Part III Summary and Outlook

9	Device Physics in a Nutshell	413
9.1	Brief Guidelines for Understanding Trends in Current-Voltage Curves	413
9.2	Which Property Influences the J - V Curve in What Way?	418
9.3	Organic Solar Cells and Drift-Diffusion Simulation: Final Remarks	422

10 Organic Photovoltaics—Quo Vadis?	427
10.1 Towards Higher Efficiencies.	427
10.1.1 Tandem Solar Cells.	428
10.1.2 Optimization of the Bulk Heterojunction	432
10.1.3 Engineering of Interfaces	434
10.1.4 Light Management	435
10.1.5 Material Design	436
10.2 The O-Factor	437
10.3 Towards Large-Scale Application	441
10.3.1 Stability.	442
10.3.2 Economics	444
10.3.3 Sustainability	447
10.4 Summary and Answers to the Initial Questions.	450
References.	451

Part IV Appendix

11 References	457
11.1 Details on the Simulation.	457
11.2 Contributions	457
Index	459

Symbols

a	Lattice constant (nm)
a	Initial distance of geminate pair (nm)
$a(\hbar\omega)$	Absorptance
A	Area (cm^2)
α	Absorption coefficient (cm^{-1})
β	Direct/bimolecular recombination constant ($\text{cm}^3 \text{s}^{-1}$)
β_r	Radiative recombination constant ($\text{cm}^3 \text{s}^{-1}$)
β_L	Direct/bimolecular Langevin recombination constant ($\text{cm}^3 \text{s}^{-1}$)
c	Speed of light (m s^{-1})
c_t	Capture coefficient ($\text{cm}^3 \text{s}^{-1}$)
d	(Device) thickness (nm)
D	Diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
D_γ	Photonic density of states ($\text{cm}^{-3} \text{eV}^{-1}$)
e_γ	Energy per unit volume (eV cm^{-3})
E	Energy (eV)
$\mathbf{E}$	Electro-optical field vector (V m^{-1})
E_B	(CT) Exciton binding energy (eV)
E_C	Conduction band edge (eV)
E_{CT}	Energy of the CT state (eV)
E_{et}	Electron transport level $\approx$ LUMO (eV)
E_F	Fermi energy/level (eV)
E_F^n	Electron quasi-Fermi level (eV)
E_F^p	Hole quasi-Fermi level (eV)
E_g	Energy gap (eV)
E_g^{DA}	Effective energy gap between IP^{donor} and $\text{EA}^{\text{acceptor}}$ (eV)
E_{ht}	Hole transport level $\approx$ HOMO (eV)
E_T	Energy of trap level (eV)
E_V	Valence band edge (eV)
E_{Vac}	Vacuum level (eV)
ϵ_r	Dielectric constant

η	Power-conversion efficiency
η_n	Electrochemical potential for electrons (eV)
η_p	Electrochemical potential for holes (eV)
η_i	Quantum efficiency
$f(E)$	Occupation probability
F	Electric field (V m^{-1})
FF	Fill factor
$g(E)$	Density of states ($\text{cm}^{-3} \text{ eV}^{-1}$)
G	Optical charge carrier generation rate ($\text{cm}^{-3} \text{ s}^{-1}$)
γ	Poole-Frenkel factor ($\text{cm/V})^{1/2}$
I	Power (W)
I	Intensity (mW cm^{-2})
I	Electrical current (A)
I_S	Entropy flux (W K^{-1})
$j_{\gamma, \Omega}$	Radiance ($\text{W m}^{-2} \text{ sr}^{-1}$)
j_E	Energy flux density, intensity (W m^{-2})
j_γ	Particle fluxes ($\text{m}^{-2} \text{ s}^{-1}$)
$\partial j_E / \partial \hbar \omega$	Spectral irradiance ($\text{W m}^{-2} \text{ eV}^{-1}$)
$\partial j_E / \partial \lambda$	Spectral irradiance ($\text{W m}^{-2} \text{ nm}^{-1}$)
J	Electrical current density (mA cm^{-2})
J_{dark}	Current density in the dark (mA cm^{-2})
J_{illu}	Current density under illumination (mA cm^{-2})
J_{photo}	Photocurrent density (mA cm^{-2})
J_s	Diode dark saturation current density (mA cm^{-2})
J_{sat}	Saturated photocurrent density (under reverse bias) (mA cm^{-2})
J_{sc}	Short-circuit current density (mA cm^{-2})
k	Wave number (cm^{-1})
κ	Extinction coefficient
k_{diss}	Dissociation rate constant of CT states (s^{-1})
k_{relax}	Relaxation rate constant of CT states (s^{-1})
k_{SRH}	Recombination rate constant <i>via</i> traps (s^{-1})
l	Drift length (nm)
L	Box length (nm)
L_D	Diffusion length (nm)
λ	Wavelength (nm)
m	Mass (kg)
m^*	Effective mass (kg)
m	Spectral mismatch factor
Δm	Discretization distance (nm)
μ	Charge carrier mobility ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)
n	Electron density/concentration (cm^{-3})
n	Refractive index
n_D	Diode ideality factor
n_0	Equilibrium electron density (cm^{-3})
n_i	Intrinsic electron/hole density/concentration (cm^{-3})

n_t	Trapped electron density (cm^{-3})
N	Total number of states
N_A^-	Concentration of ionized acceptors (cm^{-3})
N_C	Effective density of states in the conduction band (cm^{-3})
N_D^+	Concentration of ionized donors (cm^{-3})
N_T	Trap density (cm^{-3})
N_V	Effective density of states in the valence band (cm^{-3})
ν	Frequency (Hz)
ω	Angular frequency (s^{-1})
Ω	Solid angle
p	Momentum (kg m s^{-1})
p	Hole density/concentration (cm^{-3})
p_0	Equilibrium hole density (cm^{-3})
p_t	Trapped hole density (cm^{-3})
P	Probability of jump over barrier
P	Probability of CT-exciton dissociation
P	Polarization energy (eV)
ϕ	Electric potential (V)
ϕ	Angle of incidence
φ	Phase
φ	Energy barrier (eV)
φ_{injec}	Injection barrier (eV)
φ_{extra}	Extraction barrier (eV)
Φ	Work function (eV)
$\mathbf{r}$	Position (nm)
Q	Dissipation of electro-optical energy (W m^{-3})
$r_{i,j}$	Reflection coefficient
R	Resistance (Ω)
R	Charge carrier recombination rate ($\text{cm}^{-3} \text{s}^{-1}$)
R_{sep}	Exciton separation rate (at D/A interface) (s^{-1})
ρ	Space-charge density (A s cm^{-3})
s	Surface-recombination velocity (m s^{-1})
s	Exciton density (cm^{-3})
σ	Cross section (cm^2)
σ	Specific conductivity (S cm^{-1})
σ	Width of a Gaussian density of states (eV)
t	Time (s)
$t_{i,j}$	Transmission coefficient
T	Temperature (K)
τ	Lifetime (s)
v	Velocity (m s^{-1})
V	Volume (cm^3)
V	Voltage (V)
V_0	Compensation voltage, where $J_{\text{photo}} = 0$ (V)
V_{bi}	Built-in potential (V)

V_{bias}	Applied bias voltage (V)
V_{oc}	Open-circuit voltage (V)
x	Spatial coordinate (nm)
X	CT state density (cm^{-3})
ζ	Chemical potential (eV)
Z	Force (N)

Constants

c_0	Vacuum speed of light ($3 \times 10^8 \text{ m s}^{-1}$)
e	Elementary charge ($1.602 \times 10^{-19} \text{ A s}$)
ϵ_0	Vacuum permittivity ($8.854 \times 10^{-12} \text{ F m}^{-1}$)
h	Planck's constant ($6.626 \times 10^{-34} \text{ m}^2 \text{ kg s}^{-1}$)
$\hbar$	Planck's constant divided by 2π ($1.055 \times 10^{-34} \text{ m}^2 \text{ kg s}^{-1}$)
k_B	Boltzmann constant ($1.38 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$)
σ	Stefan–Boltzmann constant ($5.67 \times 10^{-8} \text{ J m}^{-2} \text{ s}^{-1} \text{ K}^{-4}$)

Acronyms

AC	Alternating current
AM	Air mass
BHJ	Bulk heterojunction (solar cell)
BOS	Balance of system
CT	Charge transfer
CV	Cyclic voltammetry
D/A	Donor/acceptor (interface)
D-A	Donor-acceptor
DC	Direct current
DOS	Density of states
EA	Electron affinity
EPBT	Energy payback time
EQE	External quantum efficiency
ERF	Energy return factor
ETL	Electron transport layer
FD	Fermi-Dirac
FHJ	Flat/planar heterojunction (solar cell)
GDM	Gaussian disorder model
HOMO	Highest occupied molecular orbital
HTL	Hole transport layer
IP	Ionization potential
IPES	Inverse photoemission spectroscopy
IQE	Internal quantum efficiency: EQE divided by absorption efficiency
ITO	Tin-doped indium oxide
LUMO	Lowest unoccupied molecular orbital
MM	Spectral mismatch
OPV	Organic photovoltaics
QCM	Quartz crystal monitor
SC	Semiconductor

SCLC	Space-charge-limited current
SOMO	Single occupied molecular orbital
SRC	Standard reporting conditions
SRH	Shockley-Read-Hall
UPS	Ultraviolet photoelectron spectroscopy
UV	Ultraviolet
WF	Work function

Chapter 1

Introduction

1.1 Energy Supply and Climate Change

Photovoltaics and in particular organic photovoltaics are fields of applied research whose support by the society is based on the insight that this technology can significantly contribute to worldwide electricity generation by conversion of solar energy into electrical energy. Apart from wind energy, photovoltaic energy conversion is the most promising among the emerging “renewable” energy technologies due to its large theoretical potential, which is given by the solar energy flux hitting the earth surface. This potential is estimated to be 6,000 times larger than the global annual energy consumption of $\approx 12,000$ million tons of oil equivalent (≈ 15 TW mean power) in 2010. Note that the global energy demand roughly doubled within the last thirty years and keeps growing as shown in Fig. 1.1a.

The technical potential of solar energy conversion is very large as well: A rough estimation demonstrates that an area of less than 6 % of the Sahara¹ would be enough to satisfy the world energy demand with today’s technologies. However, this estimation neglects distribution and storage issues. Currently, energy is provided to a large extent (> 80 %) by fossil fuels due to economic and traditional technical reasons [2].

Mainly two issues arise from fossil-powered energy conversion. First, fossil resources are finite and their distribution on the earth surface is very unbalanced. Second, burning fossil fuels is accompanied by carbon dioxide (CO_2) emission which results in climate change, because CO_2 acts as a greenhouse gas. The greenhouse effect is caused by the atmosphere reflecting (infrared) heat radiation from the surface of the earth back to it. This effect is essential for the development of life on earth, because the radiation balance between the sun, atmosphere, and the earth surface yields a mean earth’s surface temperature of $\approx 14^\circ\text{C}$ which would be -15°C [3] without the greenhouse effect. The temperature was very stable in the last millennia and the global temperature distribution created climate zones with their characteristic

¹ Assumptions: area $9 \times 10^6 \text{ km}^2$, mean irradiation 285 W/m^2 [1], power-conversion efficiency 10 %.

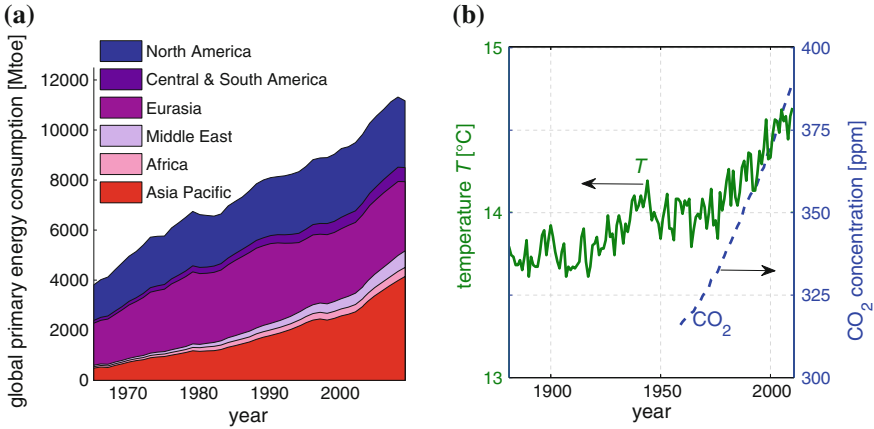


Fig. 1.1 **a** Development of the regional distribution of primary energy demand in million tons of oil equivalent (1 Mtoe $\approx$ 42 PJ). *Source* BP [5]. **b** Annual mean CO_2 concentration in the atmosphere from measurements at the Mauna Loa Observatory, Hawaii [6]. In pre-industrial times the CO_2 concentration was 280 ppm [4]. The development of the mean global temperature in the last century is plotted as well [7]. Both curves describe a significant increase

flora and fauna, which are very sensitive to temperature. An increased greenhouse gas concentration in the atmosphere disturbs this equilibrium and leads to a higher global temperature, which has been observed within the past decades (Fig. 1.1b). In recent years it became broad consensus in science and politics that this rise in temperature is anthropogenic and correlates with the amount of CO_2 in the atmosphere, which has increased significantly compared to pre-industrial times (Fig. 1.1b) [4].

The impacts of global warming are very severe and potential consequences are a rise in sea level due to a thermal expansion of ocean water and the melting of on-shore ice shields. Furthermore, desertification and water shortages are becoming more likely and even collapses of whole ecosystems and changes of ocean currents being essential for the global balance of living nature are expected. The last point represents one of the many non-linear effects which are hard to predict, but contain a high risk of a rapid change. Although nature is not a static system, but continuously in change, development, and assimilation, the survival of a certain species is in danger upon a fast change of the environment. How fast, to what extent, and at which sacrifice modern man is capable to adapt is unknown. On the one hand, besides biological adaption, he has technological and medical means to support him. On the other hand, he is very vulnerable. His economic wealth and the survival of societies and dense populations heavily rely on technological large-scale food production and globalized markets.

Based on the elaborations of several researchers, summarized in IPCC reports [4], the issues of global change are continuously discussed by policy makers on international summits on climate change. In 1992 during the Earth Summit in Rio de Janeiro, the United Nations Framework Convention on Climate Change (UNFCCC) was initiated with the aim of reducing the impacts of global warming. On a succeeding summit the Kyoto Protocol (1997) was adopted which contains reduction targets

for CO₂ emissions. However, it is not ratified on a global scale. Also the common 2-degree-target was only recently officially agreed on in Cancun (2010). This target demands for a maximum global mean temperature rise of 2 °C compared to pre-industrial times. Two degrees is a number that was chosen because the consequences of a rise of mean earth surface temperature by this value are supposed to be in a manageable range. For a higher increase in temperature non-linear effects become more likely.

To fulfill this 2 °C target (which is not very likely given the current trajectory) the energy sector has to be decarbonized completely within the next three decades. Renewable energies are the most sophisticated and most developed kind of technology which can contribute to a quick decarbonization. The main obstacle are their electricity-generation costs which are currently higher than those of conventional energy technologies. This is, however, to a large extent due to the fact that the external costs of the conventional technologies are not internalized. Consequently, the long-term damages caused by these technologies have to be carried by the broad world population.

This cost problem was recognized by policy makers. Here, Germany is mentioned as an example, as it was one of the first countries with a legislation that actively supported renewable energies. In 2000 the German parliament initiated a feed-in tariff, where in their electricity bill all customers support the introduction of renewable energies. In the meantime many other countries followed this model. On the one hand, supporting photovoltaics in Germany is a very expensive way of reducing carbon-dioxide emissions, and the feed-in tariff has shown the problem of over subsidizing and the risk of favoring non-economic concepts also on the long run. On the other hand, this concept was very successful in bringing costs down, which significantly reduced the time until photovoltaics will be an economic and CO₂-saving way of electricity generation in southern countries. It lead to installed capacities of 31 GW (wind) [8] and 32 GW (photovoltaics) [9] at a total installed electrical capacity of ≈170 GW [10] in Germany in 2012. These data are nominal capacities, which represent peak values (W_p) in the case of the renewable technologies. They show that in Germany solar and wind energy can already now provide from 0 to 50 % of the instantaneous power² dependent on the weather, season, and demand. It is obvious that grid extensions and/or an increase in the electricity-storage capacity will become very important for a further extension of renewable energy technologies. As these measures introduce additional costs and drops in the overall energy-conversion efficiency, they require very cost-effective solar and wind energy harvesting units.

In 2012 renewable energy technologies had a share of 26 % (5.3 % photovoltaics) in Germany's electricity generation [9]. The costs, especially of photovoltaics, have decreased significantly, following a learning curve due to economy of scale and technological improvements. Today, photovoltaic electricity generation is already economical in off-grid systems and attractive for self-consumption in southern countries (grid parity) [12]. Consequently, large power plants are built all over the world, with

² In Germany the typical Sunday peak load around noon is approximately 60 GW [11].

the first ones operating economically without subsidies. Therefore, the cumulated, globally installed capacity rose to 100 GW at the beginning of 2013 [9].

1.2 Development of (Organic) Photovoltaics

The first silicon solar cell with an efficiency of around 4 % was invented in the Bell Laboratories in 1953, six years after the discovery of the p-n junction by William B. Shockley, Walter H. Brattain, and John Bardeen, who were awarded by the Nobel price in physics for the discovery of the transistor effect in 1956. Five years after the invention of the silicon solar cell, the first solar module was used in space. The term “module” describes a set of solar cells that are electrically connected and packaged. In the 1960s commercial modules were available for terrestrial use and showed cell efficiencies of 14 %. At the end of the seventies an annual production of 500 kW_p was reached. The modules powered remote telecommunication systems (e.g. in the Australian Outback) with an estimated cost of 100 EUR/W_p. Prices decreased due to incentives during the oil crisis in the seventies, the German 1000 and 100,000 “Dächer (roofs) Programm” in the 1990s, and the feed-in tariff starting in the year 2000. The prices are still decreasing, e.g. on the German market from 5 EUR/W_p in 2006 to 1.7 EUR/W_p in 2013 [13] (system price for roof top installation). This drop in prize together with an increase of module efficiency beyond 15 % (cell efficiency beyond 20 %) made the tremendous growth of the installed capacity possible and maintained a high market share of silicon solar cells (80–90 %).

The working principle of every solar cell is based on the (inner) photoelectric (“photovoltaic”) effect, first discovered by the physicist Alexandre E. Becquerel (1839) with electrolytic cells [14]. Photoconductivity was shown for selenium by Smith [15] in 1873, and the outer photoelectric effect was systematically investigated by Hertz and Hallwachs in 1886 [16]. In 1904 the physicist and Nobel Prize laureate Lenard [17] discovered the role of the frequency of light regarding the energy of the emitted electrons. His results were theoretically explained by Einstein [18] who was awarded by the Nobel Prize for this work in 1921. The photoelectric effect is very interesting from a technological point of view, as it allows for the most direct conversion of sun light into electricity. This process simply requires a planar solid-state device (i.e. solar module) aligned to the sun. A solar module does not contain any chemical liquids or mechanical wear parts like conventional generators with rotating elements. Therefore, long-term stability and low maintenance costs are inherent and big advantages of solar modules compared to conventional means of electricity generation.

From the findings at the end of the nineteenth century it was still a long way to solar cells based on silicon (1953), which is nowadays the most common industrial semiconductor material for several kinds of applications. In the meantime, a variety of materials was investigated and electronically characterized. Amongst those were organic materials, which are based on hydrocarbon molecules. First investigations of the electronic properties of organic molecular solids were reported for anthracene at

the beginning of the 20th century [19–21]. In the 1970s (semi)conducting polymers were discovered [22]. Allan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa received the Nobel Prize in chemistry in 2000 for the discovery and development of these conductive polymers. In the 1980s high electroluminescence efficiencies were reached in organic materials. This achievement led to the development of organic light emitting diodes (OLEDs) [23, 24] as first broad application of organic electronics. Today, OLEDs can be found in efficient flat panel displays [25] and are about to become an alternative large-area light source with a high efficiency and a pleasant irradiation spectrum [26].

The first photocurrent in an organic semiconductor was observed also in anthracene by Kalman and Pope in 1959 [27]. In the following two decades, several organic photovoltaic devices were developed. They consisted of a metal-organic junction which showed efficiencies of less than 0.1 % (for a contemporary review, see [28]). The first major breakthrough in the deployment of organic semiconductors in solar cells has been made by Ching Tang who developed the donor-acceptor solar cell and reported an efficiency of 1 % [29] in 1986. Tang's cell comprised a junction of two materials, one electron and the other hole accepting and transporting (a perylene tetracarboxylic derivative and copper phthalocyanine). The second major step was the invention of the bulk heterojunction which is a mixed layer of donor and acceptor, fabricated by a co-deposition of the two molecules. This approach was firstly reported in [30, 31]. A detailed overview of the development of organic photovoltaics can be found in [32].

After these achievements the amount of publications rose nearly exponentially in the last decade. Efficiencies recently reached 12 % (Fig. 1.2) [33, 34], also pushed by several spin-offs and established companies turning focus on this topic. The reason for this boom is found in the expected high potential of organic semiconductors, which

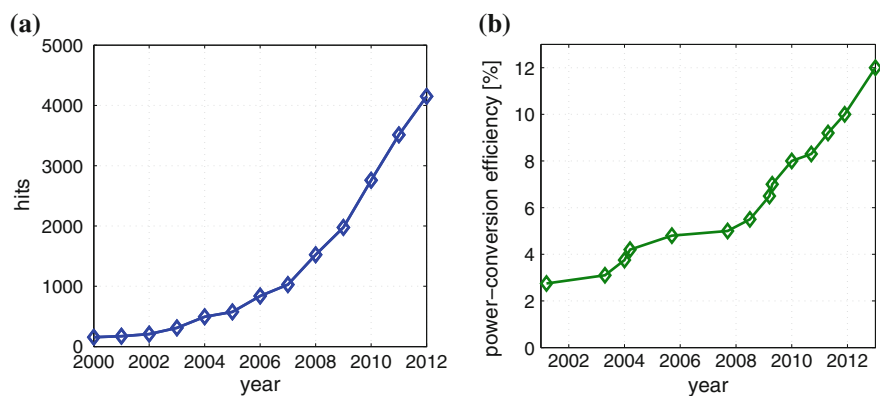


Fig. 1.2 **a** Hits of a search in the database “Web of Science” regarding organic photovoltaics (search string: Topic = (“organic photovoltaic” OR “organic photovoltaics” OR “organic solar cell” OR “organic solar cells” OR “polymer solar cell” OR “polymer solar cells”). Search performed on 26.08.2013). **b** Development of the maximum power-conversion efficiency for organic solar cells on the laboratory scale during the last decade

are either (vacuum or solution processed) small molecules or (casted or printed) polymers.

The main advantages of organic solar cells are:

- Potentially cheap production by high-throughput roll-to-toll printing or other low-temperature deposition techniques
- Low energy payback times due to a fabrication process avoiding expensive purification methods or energy-intensive steps
- High versatility and efficiencies due to the toolbox of organic chemistry
- High energy yield due to a good low-light performance and a positive temperature coefficient of the power-conversion efficiency
- Non-toxicity and low consumption of abundant absorber materials (a few grams per square meter)
- New products containing and merging with photovoltaics, e.g. in architecture due to a tunability of color and (semi-)transparency
- Application in novel and mobile devices (e.g. consumer electronics) due to mechanical flexibility and low weight (Fig. 1.3)

One major challenge from the economic point of view is a realization of these potential properties within the next few years. Here, the main difficulty is the competition with established technologies. As already mentioned, crystalline silicon photovoltaics showed a tremendous reduction of production costs in the last decade. Furthermore, the developments in inorganic thin-film photovoltaics reveal the potential of these technologies to cover several of the mentioned advantages of organic photovoltaics as well, e.g. mechanical flexibility. Regarding organic solar cells, first

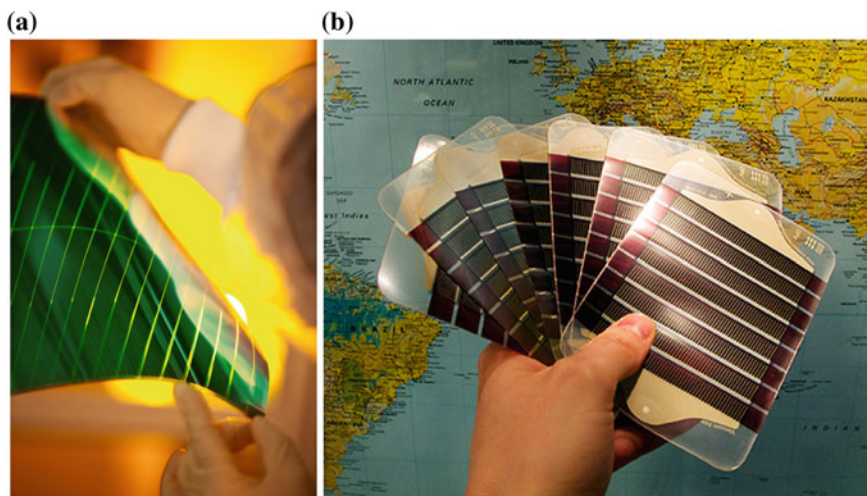


Fig. 1.3 **a** Example of a flexible solar foil (picture Heliatek GmbH). **b** Demonstrator modules with an efficiency of 1.8 % currently shipped worldwide [35] (picture DTU Energy Conversion)

pilot lines are installed in order to demonstrate a feasible transition from product innovation to process innovation. Currently, printed demonstrator modules are shipped worldwide for free (Fig. 1.3b) [35]. Product innovation and development are still crucial as an increase in solar-cell efficiencies beyond 12–15 % will enhance the ability of organic photovoltaics to compete with the established technologies. However, process development is very important at the current stage. It is required to verify that the performance and the lifetime, which have already been achieved, can be transferred to large-scale devices with ≈ 5 % efficiency at the anticipated costs. On the long run and on the terawatt scale, the criteria of material abundance favor mainly two technologies, namely silicon and carbon-based photovoltaics [36]. The success of organic photovoltaics depends strongly on the current investments, making this technology capable of finding its market a side of silicon and possibly in the future even in competition.

This book focuses on the research and development of organic solar cells, as the physics of these devices is far from being completely understood. However, a further improvement of efficiencies and stability, increasingly demands for a detailed understanding of the processes limiting the device performance. Whereas in the first years, research was mainly based on trial-and-error experiments and simple material screening, in recent years modeling and simulations became more important (e.g. large-scale computational screening projects [37]). On the one hand, many results obtained from microscopic theories are far from experimental results. On the other hand, theoretical considerations in particular on the device level considerably improved the understanding of the working principle of the complete solar cell. That is why the working principle of organic solar cells is the topic of the prevailing book, giving insights into theory, simulations, and experiments.

1.3 Scope and Structure of This Book

The scope of this book is to give the interested reader a comprehensive insight into the device physics of organic solar cells. It is an attempt to bridge the gap between experimentalists and theoreticians or computational physicists. It is suited for readers with background in physics, electrical engineering, materials science, and chemistry. The book covers a broad spectrum from fundamental theory to applied methods and technology to the latest results in the research field of organic photovoltaics. Many topics go beyond organic solar cells and are, therefore, interesting for readers working with different kinds of solar cells. The strategy of the book is to repeatedly pick up important characteristics shifting the perspective. Therefore, many topics once introduced based on very fundamental theories are revisited in the context of organic solar cells and subsequently applied to explain experimental data in a further chapter.

This book focuses on teaching on organic solar cells. Its scope is not to provide a complete review on the field of organic photovoltaics. That is why in particular

the bibliography is not intended to be an exhaustive list of the major publications on organic solar cells.

The chapters of this book are grouped in three main parts I–III distinguishing the main scope of the chapters belonging to a respective part. Part I containing Chaps. 2–5 gives a broad introduction to the topic of organic solar cells in a textbook like format. It is well suited as starting point for students who are about to work in the field of organic solar cells. It presupposes some basic knowledge in solid state physics and describes the general ideas of solar thermal energy conversion independent of the chosen material system. In some cases intuitive explanations are preferred to rigorous mathematical derivations for the sake of comprehension. However, the major physics relevant for solar cells is introduced in detail acquainting the reader with the basic concepts. The main focus is the working principle of solar-cell devices. It is elaborated starting from general considerations of solar-thermal energy conversion and semiconductor physics in the first chapter. Here, the practically oriented reader can skip the detailed derivations based on thermodynamics. Important are the main principles, which will be applied to organic solar cells in the subsequent chapter. There, the basics of organic chemistry are briefly reviewed in an intuitive way to provide the reader with the background necessary to understand the semiconductive properties of organic molecules.

Chapter 3 continues with the working principle of donor-acceptor heterojunction solar cells, focusing on the open-circuit voltage, the photocurrent, metal-organic interfaces, and the charge-transfer state. In particular, ongoing discussions on the latter demonstrate that the understanding of photocurrent generation in organic materials is not completely settled. Hence, some parts of this chapter give a review on the most recent theoretical and experimental approaches for characterizing the photophysics of organic solar cells without giving a final conclusion. The chapter closes with more practical aspects regarding materials and the experimental realization and characterization of organic solar cells.

In Chap. 4 an electrical model based on drift-diffusion and an optical model based on the transfer-matrix approach are presented. The content covers several descriptions of charge carrier transport and recombination. One part of the chapter focuses on a possible realization of a drift-diffusion simulation. This part is dedicated to computational physicists and might be skipped by other readers who may wish to go back to it if necessary when digesting explanations based on these simulations in subsequent chapters.

The last chapter (5) of Part I contains a detailed theoretical study based on drift-diffusion simulations. Showing the interplay between properties of the absorber and the contacts, it provides explanations on major processes and parameters influencing photovoltaic energy conversion.

Part II (Chaps. 6–8) focuses on systematic experimental studies which have been performed mainly during the PhD work of the author. Each chapter of this part is organized in a way that the reader can follow it without having read all previous chapters. Although elaborated on experimental and simulation data of selected material systems, most of the conclusions of this part are of general nature. Thus, they may be helpful for scientists who are dealing with the interpretation of current-voltage

data of (organic) solar cells in general. The first chapters (6–7) of this part contain discussions on the origin and limiting processes regarding the open-circuit voltage and give explanations for distorted J - V curves which follow S-shaped characteristics. The last chapter (8) contains detailed investigations on a selected model system, which is the most common small-molecule solar-cell system zinc phthalocyanine (ZnPc)—fullerene C₆₀. In particular, the effect of the mixing ratio, a gradient in the active layer, the role of the absorption profile, and dominating recombination mechanisms are discussed. The results provide a detailed picture of the interplay between energy levels, charge carrier mobilities, and recombination mechanisms in organic solar cells in general.

Part III (Chaps. 9 and 10) contains a summary and wrap-up of the general conclusions drawn in the second part. This summary is arranged in a catalog of guidelines on how to interpret experimental current-voltage curves from the drift-diffusion point of view. A variety of schematic drawings based on simulation results visualize the influence of several material parameters and physical mechanisms on the current-voltage characteristics of solar cells. The last chapter gives an outlook with a survey on the major challenges of organic solar cells regarding efficiency, stability, ecology, and economics.

Each chapter begins with a brief abstract containing a list of questions. The intended purpose of these questions is twofold: First, they provide a table of contents, which is oriented at problems. Therefore, the reader gets a quick idea which problems are addressed in the prevailing chapter. Second, they serve as means of control to the reader allowing him or her to check whether he or she has grasped the main messages of the chapter. That is why short versions of the answers are provided at the end of each chapter including a list of literature as suggestion for further reading.

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Part I

Basics

Chapter 2

Photovoltaic Energy Conversion

Abstract This chapter provides an introduction to the basic principles of solar energy conversion including its thermodynamic limits. We discuss the optical and electrical requirements for an ideal photovoltaic device and show examples of possible realizations based on semiconductors. To recall the basics, a brief review on semiconductor physics with emphasis on the p-n junction is given. We discuss the role of the electrochemical potential as driving force for the conversion of sunlight into electricity. We conclude with estimations on the maximum power-conversion efficiency for a single band-edge absorber and introduce approaches for achieving it or even going beyond it. Readers without any background in solid state physics might consider consulting an introductory textbook while reading this chapter. If the reader comes to the conclusion that his/her background in physics is not sufficient, he might consider to skip this chapter and directly start with Chap. 3, as a detailed understanding of thermodynamics is not required to follow most of the elaborations on the working principle of organic solar cells in subsequent chapters. The reader interested in the fundamental laws of solar energy conversion should follow this chapter and be able to answer the following questions afterwards: (a) What is the thermodynamic limit of solar-thermal energy conversion with a device located on the earth surface? What is the role of entropy? (b) Why is the power-conversion efficiency of a solar cell based on a single semiconductor limited to 33 %? What tradeoffs have to be made? (c) Where is the “maximum” of the solar spectrum located? What are possibilities of expressing spectra (e.g. from the sun) considering energy versus wavelength or photon fluxes versus intensity fluxes (irradiance)? (d) What are the main optical and electrical properties of semiconductors and how can they be derived? (e) What are the relations between Fermi levels and charge carrier densities? (f) What are the driving forces for the movement of charge carriers? What is the concept of quasi-Fermi levels? (g) What is the effect of recombination on the photovoltage of a solar cell? Which loss processes are unavoidable? (h) How does a p-n junction solar cell work? Are there alternative architectures? (i) What are the basic requirements for a solar cell? Consider the role of selective contacts and the built-in electric field. (j) Why should a good solar cell show a high electroluminescence quantum yield, i.e. large emission? (k) What are the main concepts for overcoming the so-called Shockley-Queisser limit?

2.1 Fundamentals of Solar-Thermal Energy Conversion

2.1.1 The Solar Spectrum

Every solar energy converter should be designed to optimally harvest the energy emitted by the sun. This energy is released through a nuclear fusion reaction of hydrogen into helium taking place in the core of the sun. It reaches the surface of the earth around 8 min after having been emitted as thermal radiation from the solar surface. As solar radiation provides the energy that we want to convert into useful energy, we briefly discuss its properties. Most important is the spectrum of a light source, which contains information on the contribution of each energy to the overall energy of the light. It can be expressed as a spectrally resolved intensity, which is energy per time and area or in other words an energy flux density. The spectral energy flux density (also denoted as spectral irradiance) $dj_E/dh\omega$ emitted by the sun and measured at distance sun-earth is the so-called solar spectrum. It is plotted in Fig. 2.1 (blue line) as a function of energy expressed by the frequency ν of light multiplied by Planck's constant h . Alternatively, $\omega = 2\pi\nu$ and $\hbar = h/2\pi$ are used. The maximum of this irradiance spectrum is found in the infrared range at 1.4 eV (880 nm, 340 THz).

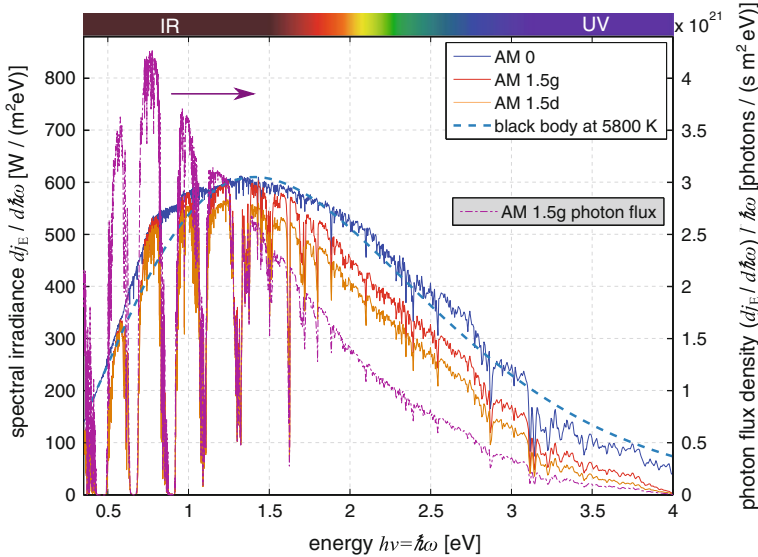


Fig. 2.1 Solar spectrum and spectral photon flux density as a function of the frequency ν of light multiplied by Planck's constant h . Data are from ASTM [1] and represent air mass (AM) spectra. The solar spectrum outside the atmosphere (AM0) follows approximately the radiation of a black body at 5,800 K

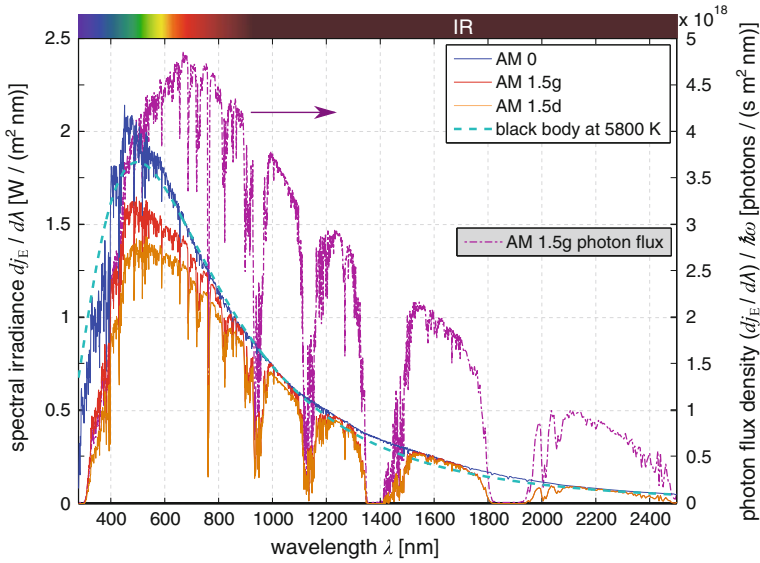


Fig. 2.2 Solar spectrum and spectral photon flux density as a function of the wavelength λ . In contrast to Fig. 2.1, the quanta are displayed per unit wavelength. Data are from ASTM [1]

Spectra are commonly plotted also as a function of the (vacuum) wavelength λ of light instead of as a function of energy. Such a plot of $dj_E/d\lambda$ of the solar spectrum as a function of the wavelength $\lambda = c/\nu$ with the vacuum velocity of light c is shown in Fig. 2.2. Although the spectra in both figures are the same, the positions of the maximum in the two plots are different. In Fig. 2.2 the maximum is located in the middle of the visible spectral range at 500 nm (600 THz, 2.5 eV). This is because the first spectrum describes the light intensity per unit energy (frequency) and the second spectrum the light intensity per unit wavelength. With $\lambda = \frac{2\pi c}{\omega}$ and consequently $\frac{d\lambda}{d\hbar\omega} = -\frac{1}{\hbar} \frac{2\pi c}{\omega^2}$, the wavelength interval $d\lambda = -\frac{2\pi c}{\hbar\omega^2} d\hbar\omega = -\frac{\lambda^2}{\hbar c} d\hbar\omega$ does not correspond to a constant energy interval $d\hbar\omega$. This causes an ambiguity when pointing out the maximum of the solar spectrum.

The discussed spectrum is measured outside the earth atmosphere and is denoted as air mass (AM) 0 with an overall radiant energy flux density of 1,353 W/m². This number is called the solar constant. The air mass describes the distance that a sun ray travels through the atmosphere in multiples of the radial extension of the atmosphere. Thus, the AM of a sunray is one or larger when measured on the earth's surface. AM1 denotes the case of perpendicular incidence. On the earth's surface, AM can be calculated as $1/\cos(\alpha)$ with the angle of incidence α measured to the vertical as sketched in Fig. 2.3a. Absorption of the compounds in the atmosphere is the main reason for distinguishing several AM spectra.

AM1.5, corresponding to an angle of incidence of 48°, is chosen as standard spectrum for solar-cell characterization. This value is approximately reached, e.g., in

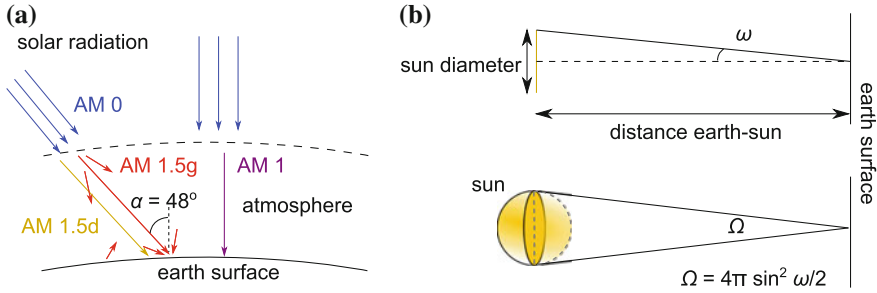


Fig. 2.3 **a** Illustration of the definition of air-mass spectra. **b** Visualization of the solid angle Ω subtended by the sun seen from the earth

Münsingen in southern Germany at noon at an equinox, i.e. on the 21st of March and the 23rd of September. The integral over AM 1.5, i.e. the total energy flux density, is reduced compared to the solar constant due to absorption in the earth atmosphere. It is defined as $1 \text{ kW/m}^2 = 100 \text{ mW/cm}^2$ for the standard AM 1.5 spectrum. In Germany an average annual energy flux density of $\approx 1,000 \text{ kWh/(m}^2 \text{ a)}$ is observed. This number corresponds to an average intensity of 115 W/m^2 and to around 1,000–2,000 sunshine hours (intensity $> 120 \text{ W/m}^2$) dependent on the location [2]. These values can be doubled in desert regions closer to the equator [3].

AM 1.5 spectra are shown in Figs. 2.1 and 2.2 as well. Some parts of the AM 0 spectrum, especially in the infrared, are filtered out by absorption of molecules in the atmosphere like water vapor, carbon dioxide, and methane. Oxygen and in particular ozone are well known as UV shields, absorbing in the ultraviolet part of the spectrum. The AM 1.5 spectrum can be further specified in AM 1.5g and AM 1.5d. The first is the global spectrum including direct light from the sun and diffuse light due to reflection and scattering. The latter only describes the direct beam from the sun including a 2.5° circumsolar component. This spectrum is chosen when characterizing solar concentrator devices. These are optimized for a specific angle of incidence, which during the course of a day and year is kept as constant as possible by a tracking system.

For the AM 1.5g spectrum, Figs. 2.1 and 2.2 show the quantity $\frac{dj_E/d\hbar\omega}{\hbar\omega}$ and $\frac{dj_E/d\lambda}{\hbar\omega}$, respectively (right axis). As we will see later, this number correlates with the maximum photocurrent that can be harvested at a particular energy (wavelength).

Apart from the atmospheric absorption lines, the AM 1.5 spectrum follows approximately a black-body radiation spectrum with a temperature of 5,800 K. This black-body spectrum is also plotted as dashed line in the figures. The temperature of 5,800 K is supposed to be found at the surface of the sun although the temperature of its core is much higher. In the following section we will discuss the black-body radiation in more detail. There, we will further deal with the nature of light, shifting from the picture of an electromagnetic wave towards the particle picture according to the wave-particle duality.

2.1.2 Black-Body Radiation

The solar spectrum is a thermal one and can be approximated by a black-body spectrum as mentioned previously. Hence, we briefly introduce the properties of black-body radiation. A black body is defined as an idealized body that completely absorbs incoming light of every wavelength, which means an absorptance $a(\hbar\omega) = 1$ for all ω . It can be realized by a black box with a small hole or by a real body that is sufficiently thick and non-reflecting. According to Kirchhoff's law of thermal radiation, a black body (as perfect absorber) is also a perfect emitter. This law is a result of energy conservation.

Black-body emission is characterized by the surface temperature of the body and can be described by Planck's law, which is a consequence of the quantized nature of light. These quanta of light, the photons, obey Bose-Einstein statistics and show a density of states limited by the Heisenberg uncertainty principle. Their energy E_γ is $\hbar\omega$ and allows only discrete multiples of this value for the energy of an electromagnetic wave at frequency ω . The energy per unit volume and per unit energy interval $d\hbar\omega$ in a solid angle interval $d\Omega$ can be written as product of density of states $D_{\gamma,\Omega}$, occupation probability f_γ , and photon energy $E_\gamma = \hbar\omega$:

$$\frac{d\rho_{E\gamma}(\hbar\omega)}{d\hbar\omega} = D_{\gamma,\Omega} \cdot f_\gamma \cdot E_\gamma = \frac{(\hbar\omega)^2}{4\pi^3 \hbar^3 c^3} \cdot \frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1} \cdot \hbar\omega d\Omega. \quad (2.1)$$

Here, k_B denotes the Boltzmann constant and T the absolute temperature. We will sketch a derivation of $D_{\gamma,\Omega}$ when discussing the density of states for electrons in Sect. 2.2.1.

Multiplying the spectral energy density $\frac{d\rho_{E\gamma}(\hbar\omega)}{d\hbar\omega}$ in (2.1) with the velocity of the photons (light) c gives a spectral energy flux density, called spectral radiance $dj_E(\nu)/d\nu d\Omega$ ($dj'_E(\lambda)/d\lambda d\Omega$). This quantity describes the emitted power per unit area, per unit solid angle, and per unit frequency or wavelength (if ν is expressed by λ). Replacing ω by $2\pi\nu$ and using $\frac{d\hbar\omega}{d\nu} = \frac{d\hbar\nu}{d\nu} = h$ yields the common formulations of Planck's law:

$$\begin{aligned} \frac{dj_E(\nu)}{d\nu d\Omega} &= \frac{2h\nu^3}{c^2} \frac{1}{e^{\frac{h\nu}{k_B T}} - 1}; \\ \frac{dj'_E(\lambda)}{d\lambda d\Omega} &= \frac{2hc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda k_B T}} - 1}. \end{aligned} \quad (2.2)$$

These equations describe a spectral radiance of a black body. This spectrum shows a maximum at a certain frequency, which depends on T , and consequently a drop towards lower and higher frequencies. The decrease for low frequencies is due to the first factor ν^3 resulting from the density of states and the photon energy (2.1) increasing with ν . The ultraviolet catastrophe (spectral radiance $\rightarrow \infty$ for $\nu \rightarrow \infty$) predicted by classical mechanics (Rayleigh-Jeans law) is avoided by the exponential

decay of the occupation statistics f_γ , saying that the occupation of higher energies (number of active modes) decreases exponentially. Figures 2.1 and 2.2 show $\frac{dj_E(\nu)}{d\nu}$ and $\frac{dj'_E(\lambda)}{d\lambda}$ for $T = 5,800$ K. The maximum of the spectrum is located at $\hbar\omega_{\max} = h\nu_{\max} = 2.82k_B T$ (1.41 eV for $T = 5,800$ K) and at $\lambda_{\max} = \frac{hc}{5k_B T} \rightarrow h\nu = 4.97k_B T$ (2.48 eV for $T = 5,800$ K), respectively. An integration over all photon energies and a hemisphere ($\Omega = 2\pi$, effectively π for a planar surface element [4]) leads to the Stefan-Boltzmann law, which describes the total emitted energy flux density (black-body irradiance) as a function of temperature:

$$j_E = \frac{\pi^2 k_B^4}{60\hbar^3 c^2} T^4 = \sigma T^4. \quad (2.3)$$

Here, the natural constants are combined into the Stefan-Boltzmann constant σ . Equations (2.2) and (2.3) directly connect the spectrum of a black body to its temperature. Therefore, the spectrum of a black body (e.g. of the sun) allows for a determination of its (surface) temperature. An operating incandescent light bulb is based on glowing metal and emits a black-body spectrum with temperatures around 3,000 K. The black-body radiation is the reason for characterization light sources by their color temperature, although the terms warm (reddish, hence low λ and T) and cold (blueish, higher λ and higher T) are used the other way round based on psychological reasoning.

Having introduced the concept of photons, we identify the additional curve $\frac{dj_E/d\hbar\omega}{\hbar\omega} = dj_\gamma/d\hbar\omega$ in Fig. 2.1 ($\frac{dj_E/d\lambda}{\hbar\omega} = dj_\gamma/d\lambda$, Fig. 2.2) with the spectral distribution of photons emitted from the sun per unit time and area. As convention, we use the index E for energy flux densities with unit W/m^2 and the index γ for photon, i.e. particle, flux densities in number of photons/ $(\text{m}^2 \text{ s})$. In the wave picture each photon carries a quantum of energy proportional to the frequency of the electromagnetic wave it corresponds to. The number of photons of a certain energy being transported in a light beam is proportional to the overall light intensity. The photon flux from the sun shows a broad maximum shifted to the red/infrared compared to the solar (intensity) spectrum $dj_E/d\hbar\omega$ ($dj_E/d\lambda$). The reason is that a certain intensity for higher λ originates from a larger number of low-energy photons. We will see later on that it is the photons that have to be harvested by a solar cell converting the photon flux into an electron flux.

2.1.3 Maximum Power-Conversion Efficiency

Now we estimate the maximum power-conversion efficiency of a terrestrial solar-thermal energy converter. This efficiency is limited by thermodynamic considerations. We derive it by building an ideal thermal engine as suggested by Würfel [4, 5]. Before doing so, we want to calculate the solid angle Ω_S at which the sun appears to an observer located on the earth surface. The derivation is illustrated in Fig. 2.3b,

first calculating the aperture ω via trigonometric functions knowing the diameter of the sun and the distance between earth and sun. The solid angle Ω_S subtended by the circular cone of the opening angle is then 6.8×10^{-5} . Knowing this value we can directly estimate the temperature T_{BB} of a black body irradiated by the sun and located outside of the earth atmosphere. We assume that the planar surface of this body radiates the whole power received from the sun back into a complete half space according to the Stefan-Boltzmann law. In equilibrium the energy flux has to be balanced and we find $T_{BB} = 123^\circ\text{C}$ when using (2.3) in

$$j_E^{\text{Abs}} = \frac{\Omega_S}{\pi} \sigma T_S^4 = j_E^{\text{Em}} = \sigma T_{BB}^4. \quad (2.4)$$

Here, we took into account that the fraction of solar emission that reaches the planar body is $\frac{\Omega_S}{\pi}$ compared to the emission predicted by the Stefan-Boltzmann law. The same result is obtained when setting the solar constant equal to j_E^{Em} . If we fully concentrate the sun light on a black body, we also focus the emitted light due to the reversibility of the optical path. This means that the absorber will reach T_S in case of maximum concentration. A further concentration is not possible as this would directly violate energy conservation or would mean destroying entropy. Considering the principles of imaging [4], the maximum concentration factor (in vacuum) is $\pi/\Omega_S \approx 1/\sin^2 \omega = 46,200$ [6].

To avoid parasitic emission, the ideal thermal engine requires a black body as absorber, which is arranged in a way that it sees only the solar (black-body) radiation (from the solid angle Ω_S) and itself. Such an arrangement can be imagined as an absorber in a cavity with perfect mirrors on the wall and a hole with a lens to couple in the solar radiation (Fig. 2.4a). This setup represents the condition of maximum concentration.

As long as power is not extracted, the absorber is in equilibrium with the sun and its temperature T_A reaches the temperature of the sun T_S . When extracting

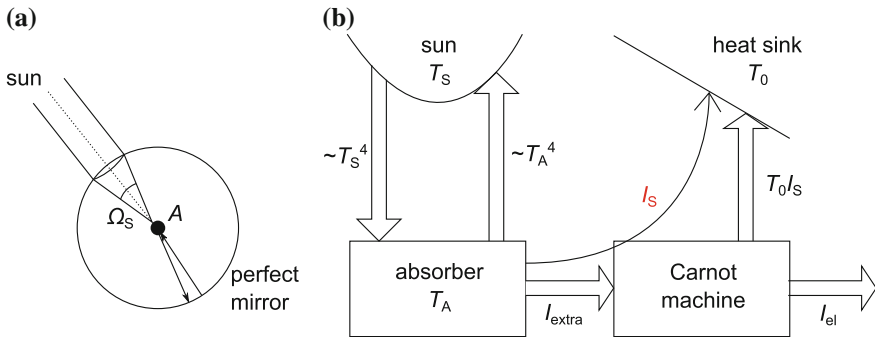


Fig. 2.4 **a** Arrangement of absorber with area A within a perfect mirror and a lens to couple in and concentrate solar radiation. **b** Energy (large arrows) and entropy (I_S) flux diagram of an ideal solar-thermal engine

power (energy flux I_{extra}) from the absorber with area A , its temperature decreases. The extracted energy is the difference of the absorbed (I_{abs}) and emitted radiation according to the Stefan-Boltzmann law (2.3): $I_{\text{extra}} = \frac{\Omega_S}{\pi} \sigma (T_S^4 - T_A^4) A$. This results in a power-conversion efficiency of

$$\eta_{\text{extra}} = \frac{I_{\text{extra}}}{I_{\text{abs}}} = 1 - \frac{T_A^4}{T_S^4}. \quad (2.5)$$

The efficiency η_{extra} increases with a decreased temperature of the absorber. However, the heat energy flux I_{extra} is accompanied by an entropy flux of $I_S = I_{\text{extra}}/T_A$ as illustrated in Fig. 2.4b. Entropy is a measure of a system's disorder, which, according to the second law of thermodynamics, cannot decrease for an isolated system. We can intuitively understand why a $T_A < T_S$ increases the disorder. If the heat is transferred to another emitter and completely emitted as black-body radiation at lower temperature than T_S , this implies a larger solid angle like in (2.4). A lower concentration of the photons means a higher degree of disorder due to the higher number of available states for a larger solid angle. Alternatively, one can state that it is impossible to cool the absorber to $T_A < T_S$ by only adding electric energy and without releasing heat.

As discussed, entropy cannot be destroyed according to the second law of thermodynamics. Thus, it has to be at least conserved and then released. The Carnot machine as ideal thermal engine provides a conservation of entropy. This machine extracts work when operating between two different heat reservoirs with temperature T_A and T_0 . The transformation of heat into work occurs at finite efficiency, as the entropy released at T_0 demands for a release of the heat energy flux $T_0 I_S$. Hence, the entropy-free energy “work” flux, which can be electric power I_{el} , is the difference between the heat flux, accepted and released by the machine. In case of the conservation of entropy, we can write $I_{\text{el}} = I_{\text{extra}} - T_0 I_S = T_A I_S - T_0 I_S$. Consequently, the efficiency becomes

$$\eta_C = \frac{I_{\text{el}}}{I_{\text{extra}}} = 1 - \frac{T_0}{T_A}. \quad (2.6)$$

This equation describes the Carnot efficiency, which increases with temperature difference. As T_0 is the ambient temperature, T_A should be high. Equation (2.6) in combination with (2.5) leads to a tradeoff for the overall efficiency η resulting in a maximum value of

$$\eta_{\text{max}} = \eta_{\text{extra}} \cdot \eta_C = 0.85 \quad (2.7)$$

for $T_A = 2,478 \text{ K}$ ($T_S = 5,800 \text{ K}$, $T_0 = 300 \text{ K}$).

In the following sections we review fundamentals of semiconductors. These materials are well suited as absorbers because, in contrast to a black body, they provide absorption and emission of high energy radiation at low temperatures and therefore with a minimum creation of entropy. We will see that on the one hand, they

can convert monochromatic light into work with the Carnot efficiency. On the other hand, they are not well suited to efficiently harvest broad spectra. Naturally, also the efficiency of semiconductor-based solar energy converters is limited by thermodynamics. However, they show a major advantage compared to a thermal absorber: High values for the efficiency can be obtained at low temperatures of the absorber. This advantage is of practical importance as an operation around ambient temperature is beneficial for many applications.

2.2 Basics of Semiconductor Physics

This book focuses on solar cells based on organic materials. Although this class of materials shows significant differences compared to conventional crystalline semiconductors, its physics has to follow the same fundamental principles. Especially a self-consistent (numerical) simulation of organic semiconductor devices has to obey the principle of detailed balance and the laws of statistical and quantum mechanics. Furthermore, many terms of classical solid state physics are reused when describing organic semiconductors. A brief introduction to classical semiconductor physics is therefore given here. As the style of this section is very compact, a reader without background in solid state physics is referred, e.g., to [7–9] for a detailed introduction to the topic. Several items of this section will be revisited and further discussed in Chap. 3.

2.2.1 Band Structure, Electrons and Holes

Bandgap

Semiconductors are characterized by an energy gap E_g in the range of 0.5–4 eV. This gap in the electronic energy landscape separates the valence band, which is fully occupied by electrons for $T \rightarrow 0$ K, from the conduction band, which is completely empty for $T \rightarrow 0$ K. Electrons can be promoted into the conduction band when gaining thermal energy at higher temperatures. However, electron energies within the gap are forbidden.

The existence of an energy gap can easily be explained imagining a free electron with parabolic dispersion (energy (E)-momentum (p) relation) in a periodic crystal (Fig. 2.5a). The parabolic dispersion is equivalent to the common expression for the kinetic energy of a (non-relativistic) mass particle

$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} \quad (2.8)$$

with velocity v and momentum p .

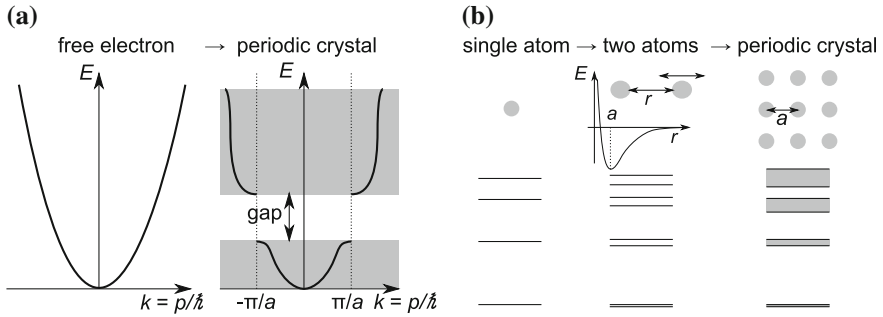


Fig. 2.5 Schematic explanations for the existence of bands and bandgaps. Energy band diagrams are commonly drawn using the reciprocal space k as abscissa, which scales with the crystal momentum p . **a** Free-electron approximation with parabolic dispersion relation of a free electron, which is modified when the electron faces the periodic potential of the crystal atoms. **b** Tight-binding-model: discrete degenerate atomic levels split, when atoms interact with each other. This leads to a quasi-continuum of states

Due to wave-particle duality, the electron constitutes a de Broglie wave of wave number $k = 2\pi/\lambda = p/\hbar$. For an electron in a crystal, this wave faces Bragg reflections at the lattice if $\lambda/2 = Na$ with $N \in \mathbb{N}$ and the distance a between atoms in the simple one-dimensional lattice of Fig. 2.5a. This reflection inverts the direction of propagation and leads to interference. In general, a superposition of waves with $\pm k$, i.e. waves propagating to the right and to the left, results in two standing waves. Their potential energies are, dependent on the sign of superposition, lower and higher than the middle energy of a free electron as propagating wave. This implies a region of forbidden energies and hence an energy gap close to $k = \frac{\pi}{a}N$.

Another approach for making the existence of bands plausible starts from single atoms whose electrons occupy discrete states (Fig. 2.5b). These states are calculated by applying the Schrödinger equation to an atom. The solution describes discrete allowed energy values for the electrons in the shell of an atom. Bringing the atoms close to each other leads to interactions and electron-wave-function overlap (tight-binding approach). The equilibrium interatomic distance a , i.e. lattice constant for primitive lattices, is given by the minimization of the total energy of the crystal. In Fig. 2.5b this equilibrium position is found at the minimum of the potential well of the Lennard Jones potential which is a result of long-range attracting (dipole-dipole) forces and shorter range (Pauli) repulsive forces. The band structure results from the coupling of all atoms in a periodic crystal and is mainly a consequence of the Pauli exclusion principle for fermions, which forbids that more than two electrons with spin up and down occupy one state. Therefore, the discrete and between isolated atoms degenerate atomic energy levels shift and split. These levels form a quasi-continuum of states for the electrons, which are delocalized over the complete assembly of atoms. This distribution of states is called a band, with a total density of states equaling twice the number of all atoms due to the spin degeneracy.

Two bands can be separated by the bandgap E_g , as is the case for valence and conduction band in a semiconductor. Bands can also be partly occupied as is the case in metals. Furthermore, valence and conduction band can overlap for some values of the momentum p giving the material quasi-metallic properties. They are therefore named metalloids.

A quantum mechanical treatment of the multi-particle system “crystal” means solving a Schrödinger equation with wave functions of states containing the coordinates of every particle. The Born-Oppenheimer (also called adiabatic) approximation allows for separate treatments of the atom cores (nuclei with core electrons) and the valence electrons, because their masses and consequently their energy eigenvalues differ strongly. An approximated solution of the Schrödinger equation for the complete atoms as quantum mechanical harmonic oscillators leads to the phonons as vibrational states of the lattice. The wave function of a single electron (the many-body problem is reduced to a single-particle problem) in a periodic crystal is a Bloch wave and can be assigned a quasi or crystal momentum and a wave vector $\mathbf{k} = \mathbf{p}/\hbar$. Due to the periodicity, the energy dispersion can be fully described by taking into account the first Brillouin zone only, which is the reciprocal unit cell (Wigner-Seitz cell) of a lattice.

Only incompletely occupied bands contribute to charge transport, because an empty band does not contain an electron which can be moved. In a fully occupied band there is no room to shift electrons or in other words the momentum (and energy respectively) of an electron cannot be changed continuously. This means that the electron cannot receive energy from an applied electric field F . An explanation in the quantum mechanical picture (Fig. 2.6) starts from the inversion symmetry $E(k) = E(-k)$, which guarantees that the overall momentum of all electrons is zero as long as current does not flow. It comes along with a uniform time averaged occupation probability of states with wave vector k and $-k$. Applying a field in combination with lattice scattering results in a dk . In a not-fully occupied band (Fig. 2.6b) this means an asymmetric occupation of the states with respect to $k = 0$. This situation represents an effective force and thus current with group velocity

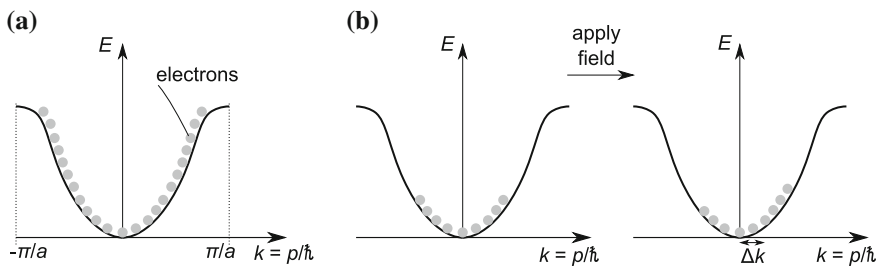


Fig. 2.6 Electric current in k -space. Shown is the energy dispersion of the first Brillouin zone. **a** Fully occupied band. **b** Partly occupied band: in contrast to a fully occupied band it receives a change in crystal momentum Δk upon the application of an electric field F and scattering of electrons at the lattice

$v = \frac{\partial \omega}{\partial k} = \frac{\hbar dk}{m^*}$, where m^* is the effective mass (see next section) of the quasi-free electrons. In a fully occupied band, however, shifting electrons by dk out of the first Brillouin zone means shifting them into the zone at the “other side”. Effectively, dk and consequently the electron velocity are zero.

Occupation Statistics

Analogously to the photon density of a black body (2.1), the occupation of the bands in thermal equilibrium is described by the integral in energy over the product of density of states (DOS) $g(E)$ (unit $\text{m}^{-3} \text{eV}^{-1}$) and the probability of occupation $f(E)$:

$$\int_{\text{band}} g(E) \cdot f(E) dE. \quad (2.9)$$

In other words, the total number of electrons in a band is the sum of all electrons having their individual energy. For each energy interval dE there is a number of available positions, called states. Whether these states are really occupied is described by $f(E)$. This probability of occupation for electrons as half-integer spin particles is given by the Fermi-Dirac statistics (FD function) when neglecting mutual interaction of the particles:

$$f(E) = \frac{1}{e^{\frac{E-E_F}{k_B T}} + 1} \quad \begin{matrix} E-E_F > 3k_B T \\ \approx e^{-\frac{E-E_F}{k_B T}} \end{matrix}. \quad (2.10)$$

The FD function can be approximated by a Boltzmann term for $E - E_F > 3k_B T$, as illustrated in Fig. 2.7a. Here, E_F is the Fermi level which is defined as the energy where the FD function is $1/2$. In a metal ($g(E_F) \neq 0$), for $T \rightarrow 0 \text{ K}$, E_F describes the energy of the highest occupied electron state and is then called Fermi energy. The transition of the FD function from 1 to 0 at E_F is broadened in energy when increasing the temperature. The reason is that the probability of occupying energetically higher states increases with T due to the higher thermal energy in the system.

The density of states $g(E)$ can be a complicated function. Assuming parabolic band minima (at E_C) or maxima (at E_V) (like in the energy dispersion of a free electron in Fig. 2.5a), this function depends on the square root of the energy in a three-dimensional semiconductor and on the effective mass m^* , which is proportional to the reciprocal curvature of the energy dispersion:

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k^2}. \quad (2.11)$$

The effective mass is an operand, which replaces the free-electron mass (e.g. in the equation of motion) and incorporates the electronic interactions with the lattice. In

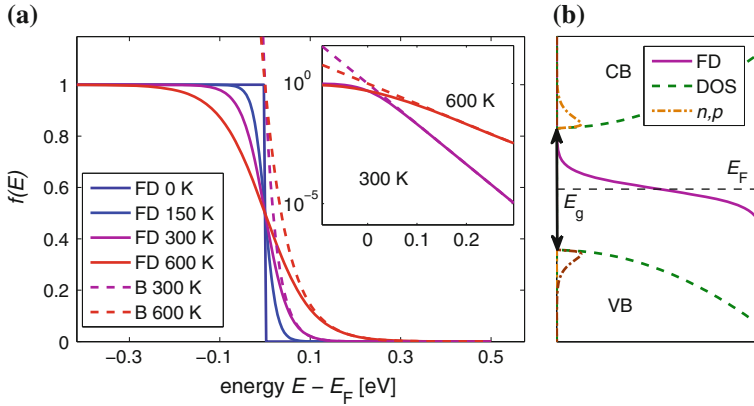


Fig. 2.7 **a** Fermi-Dirac (FD) function for different temperatures and Boltzmann approximation (B) in a linear and logarithmic (*inset*) plot. **b** Fermi-Dirac distribution, density of states (DOS), and electron and hole densities in the parabolic conduction (CB) and valence band (VB), respectively, at $T > 0$ K

case of a parabolic energy dispersion, m^* is constant like for a free electron. However, for typical semiconductors m^* is smaller than the free electron mass.

To give an idea about the shape of $g(E)$, we elaborate a simple derivation of the DOS of a free electron gas in three-dimensional space. We know from the solution of the stationary Schrödinger equation of an electron in a box with edge length L in real space that the wave number in each spatial direction has to fulfill $k_{x,y,z} = N\pi/L$ with $N \in \mathbb{N}$. This result meaning $\lambda = 2L/N$ is intuitively expected for a potential well with infinite barriers, where the wave function has to be zero at the edges. The $k_{x,y,z}$ are equidistantly spaced with the difference between $k_{x,y,z}(N)$ and $k_{x,y,z}(N+1)$: $\Delta k_{x,y,z} = \pi/L$. Hence, the volume of one allowed k -value in three dimensions is $(\pi/L)^3$. Imagining a sphere in k -space, the number of states N in this volume is the ratio between the volume of the sphere and the volume of one k -value multiplied by two due to the spin degeneracy:

$$N(k) = 2 \cdot \frac{1/8 \cdot 4/3\pi k^3}{(\pi/L)^3} = \frac{V}{3\pi^2} k^3. \quad (2.12)$$

Here, $V = L^3$ is the volume of the crystal (in real space). The factor 1/8 is introduced as we discuss only 1/8th of the volume of the sphere, where k_x , k_y , and k_z are positive. Alternatively, we could have assigned the double volume to each $|k_{x,y,z}|$. Replacing k by the dispersion relation of an electron $E(k) = \frac{\hbar^2 k^2}{2m^*}$ leads to the number of states dN per energy interval dE :

$$\frac{dN}{dE} = \frac{d\left(\frac{V}{3\pi^2} \cdot \left(\frac{2m^*E}{\hbar^2}\right)^{3/2}\right)}{dE} = \frac{V}{2\pi^2} \cdot \left(\frac{2m^*}{\hbar^2}\right)^{3/2} E^{1/2} =: g(E)V. \quad (2.13)$$

In this context we can explain the expression used in (2.1) for the photon density of states: Applying the dispersion of a photon $|\mathbf{p}| = \hbar|\mathbf{k}| = \hbar\omega/c$ delivers directly D_γ , which in (2.1) is given per solid angle and hence divided by 4π .

The integral in (2.9) can be approximately solved under the discussed assumptions. The result is the following expression for the electron density $n = N/V$ in the conduction band:

$$\begin{aligned} n &= \int_{E_C}^{\infty} g(E)f(E)dE = \int_{E_C}^{\infty} 4\pi \left(\frac{2m^*}{\hbar^2}\right)^{3/2} (E - E_C)^{1/2} \frac{1}{e^{\frac{E-E_F}{k_B T}} + 1} dE \\ &\stackrel{E-E_F > 3k_B T}{\approx} \int_{E_C}^{\infty} 4\pi \left(\frac{2m^*}{\hbar^2}\right)^{3/2} (E - E_C)^{1/2} e^{-\frac{E-E_F}{k_B T}} dE \\ &= N_C \exp\left(-\frac{E_C - E_F}{k_B T}\right). \end{aligned} \quad (2.14)$$

Here, we assumed that the conduction band ranges from the edge E_C to ∞ , like depicted in Fig. 2.7b. $N_C = 2 \cdot \left(\frac{2\pi m^* k_B T}{\hbar^2}\right)^{3/2}$ is the so-called effective density of states, which is a volume density (in cm^{-3}) having the energy dependency of the DOS $g(E)$ already included. One might think of it as a reduced DOS with value N_C located only and directly at the band edge with its occupation described by Boltzmann statistics ($E_C - E_F > 3k_B T$). This idea is only for an intuitive illustration as it directly contradicts the Pauli principle. However, the concept of N_C is correct and a rather formal one which is very useful for the calculation of charge carrier densities avoiding an integration over $g(E)f(E)$ each time.

Holes as Defect Electrons

We describe charge transport in the valence band via hole densities p , because it is much easier to follow fewer particles. Holes are missing (or defect) electrons and carry the charge $+e$ (elementary charge). Consequently, the occupation probability for holes is $1 - f(E)$, which is equal to the FD function of $-E$ [i.e. $f(-E)$] due to its symmetry with respect to E_F (2.10). Having in mind Fig. 2.7, it follows analogously to (2.14):

$$p = \int_{-\infty}^{E_V} g(E)[1 - f(E)]dE = N_V \exp\left(-\frac{E_F - E_V}{k_B T}\right). \quad (2.15)$$

Consequently, the product

$$n_0 p_0 = n_i^2 = N_C N_V \exp\left(-\frac{E_g}{k_B T}\right) \quad (2.16)$$

is independent of the position of E_F . Thus, (2.16) is valid in equilibrium (will be defined later) denoted by the index 0 even if electron and hole densities are not equal. It is a result of the law of mass action. In chemistry, this law predicts the concentrations of educts (A and B) and products (C and D) of a reversible reaction which is in dynamic equilibrium. According to this law, the ratio between the product of the educt concentrations and the product of the product concentrations is constant (2.17). It can be explained with the aid of kinetics: We assume that the rate towards the products is proportional to the “availability”, i.e. concentration c , of the educts, and for the products the other way around. In dynamic equilibrium, the rates are balanced and:

$$A + B \rightleftharpoons C + D: k_1 c_A c_B = k_2 c_C c_D \Rightarrow \frac{c_A c_B}{c_C c_D} = \frac{k_2}{k_1} = \text{const.} \quad (2.17)$$

Here, k_1 and k_2 denote the rate constants for forward and reverse reaction. From (2.17) it is not obvious why (2.16) is called law of mass action, but formally it can be derived similarly to (2.17), whose derivation was only sketched here in a simplified way. In a semiconductor, as we will discuss in the next sections, electrons and holes can be seen as educts that can reversibly “react” e.g. to photons by the processes of generation and recombination. There, (2.16) guarantees the equilibrium between absorption and emission of ambient photons. Anyway, the law of mass action is very fundamental and can be discussed in a more involved way using thermodynamics.

In a pristine, so-called intrinsic semiconductor, electrons in the conduction band can only result from a thermal activation of valence electrons. This process is identical to a creation of holes in the valence band, leading to $n = p = n_i = p_i$. Here, the index i means intrinsic. For common and optically interesting values of the bandgap (1.0–3.5 eV), n_i is low at room temperature. For example, n_i is $1.45 \times 10^{10} \text{ cm}^{-3}$ for silicon ($E_g = 1.12 \text{ eV}$) at room temperature, which is very low compared to the density of atoms ($5 \times 10^{22} \text{ cm}^{-3}$) [7]. As the electrical conductivity scales with the free charge carrier densities [will be discussed at (2.34)], it is very poor for intrinsic semiconductors and increases with temperature. This behavior of the conductivity is a characteristic property of a semiconductor. However, it is technologically challenging to reach intrinsic properties due to the required high material purity and perfect crystallinity of the semiconductor. Impurities can increase n_0 or p_0 by donating free charges. This mechanism, exploited in a controlled way, is called doping as discussed in the following paragraph.

Doping

To manipulate and improve conductivity, doping is applied by replacing some crystal atoms (commonly less than 0.1 %) by atoms having one excess valence elec-

tron which does not enter a covalent bond (e.g. doping phosphorus into silicon). The additional electron can approximately be described by the hydrogen problem, replacing the free electron mass by the effective mass and considering the polarizability of the surroundings in the dielectric constant ϵ_r of the semiconductor. In a rough estimation the binding energy is predicted in the range of $13.6 \text{ eV} \cdot \frac{m}{m^*} \cdot \frac{1}{\epsilon_r^2} \approx 13.6 \text{ eV} \cdot \frac{1}{10} \cdot \frac{1}{10^2} = 13.6 \text{ meV}$. This value is by a factor of 1,000 lower than the binding energy of the hydrogen electron. Hence, at room temperature this electron is released from the nucleus and increases the number of free electrons n in the crystal. As this treatment is an approximation not considering the effect of the other electrons of the doping atom, measured values for the binding energy depend on the doping element and are in the range of several 10s of meV. The described electron delivery to the crystal is called n-doping, and the guest atom is a donor. The same argumentation holds for p-doping, where atoms with one missing valence electron are inserted. These so-called acceptors increase the hole density p . The dominating type of charge carriers is called majorities in contrast to the minorities. According to (2.14) and (2.15) a change in n and p is related to a change in E_F . The Fermi level shifts towards E_C in case of n-doping and towards E_V for p-doping.

The concentration of free charge carriers increases with temperature, because the ionization of the dopant atom demands for breaking the binding energy. Hence, the conductivity is temperature activated at low temperatures. Commonly, at room temperature, the saturation regime, which is characterized by the ionization of all dopant atoms N_D , is already reached. For example, in the case of n-doping with $N_D \gg n_i$, good approximations for the charge carrier densities are $n \approx N_D$ (majorities) and with (2.16) $p \approx n_i^2/N_D$ (minorities).

2.2.2 Quasi-Fermi Levels and Electrochemical Potentials

Absorption

As long as the semiconductor is in equilibrium, the occupation of valence and conduction band can be described by a single Fermi distribution. Under illumination with photons with energy $\hbar\omega \geq E_g$, however, electrons from the valence band can be excited into the conduction band (Fig. 2.8a, b). Consequently, additional quasi-free electrons and holes are created. This results in values of n and p which are simultaneously larger than n_i . That is the difference to doping, which increases either n or p . Even the simultaneous presence of donor and acceptor atoms does not increase n and p but leads to a (partial) compensation. The semiconductor whether doped or undoped is in equilibrium, and (2.16) is valid. In contrast, upon absorption of a photon, the semiconductor is not in equilibrium. However, a minimization of the energy of the photogenerated charge carriers leads to a fast ($< \text{ps}$) thermalization to the band edge. Consequently, charge carriers have the temperature of the crystal and their distribution within the band is again described by an FD function considering the Pauli

principle. The thermalized electrons have a certain lifetime (typically μs), before they release their energy, ideally via photons, when recombining with holes. This difference in timescale between (intra-band) relaxation and (band-band) recombination results from quantum mechanical transition rates according to Fermi's Golden Rule (cf. 3.2), which will be discussed in detail in Sect. 3.1.1. A variety of states exists within the band and possible interactions of charge carriers with low-energy phonons are very likely as the phonons are capable of absorbing small quantities of energy in several subsequent steps. In contrast, band-band recombination requires an interaction between the electron and a photon with the large energy of the bandgap. Consequently, the recombination process is less probable and in turn much slower than intra-band relaxation.

Therefore, upon illumination both thermalized electrons and holes in their respective bands follow FD statistics. However, n and p are much larger than their values in equilibrium, i.e. in the dark. As the electrons are thermalized, their temperature is the one of the crystal. Hence, according to (2.14) and (2.15), E_F is shifted towards the conduction band for properly describing the distribution of electrons and towards the valence band for properly describing the distribution of holes. This can only be fulfilled by two distinct Fermi distributions and two Fermi levels E_F^n and E_F^p , one for each band (see Fig. 2.8a). They are called quasi-Fermi distributions and quasi-Fermi levels, respectively. Applying (2.14) and (2.15), the following holds:

$$n \cdot p = N_C \exp\left(-\frac{E_C - E_F^n}{k_B T}\right) \cdot N_V \exp\left(-\frac{E_F^p - E_V}{k_B T}\right) = n_i^2 \exp\left(\frac{E_F^n - E_F^p}{k_B T}\right). \quad (2.18)$$

The occupation of intra-gap (trap-)states between the quasi-Fermi levels would be described neither by E_F^n nor by E_F^p , but by the dynamics of occupation and release.

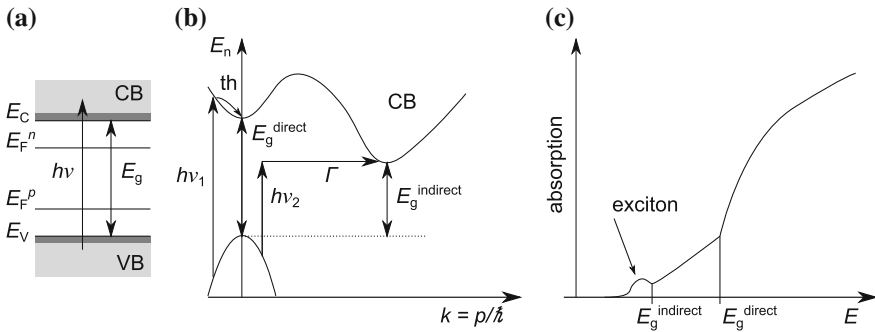


Fig. 2.8 **a** Sketch of the absorption of light with an energy $h\nu$ larger than the bandgap E_g . This process increases the electron and hole concentration in conduction and valence band (CB and VB), respectively. Combined with a fast thermalization within the bands, this leads to two separate quasi-Fermi levels for electrons (E_F^n) and holes (E_F^p). **b** Scheme of direct ($h\nu_1$, $\Delta k \approx 0$) and indirect ($h\nu_2$, phonon (Γ)-assisted) absorption processes and thermalization (th). **c** Schematic absorption of an indirect semiconductor as a function of photon energy

The creation of quasi-free charge carriers upon light absorption is called generation, which we denote by G . This process must obey the laws of conservation of energy and momentum as illustrated in Fig. 2.8b. Absorption of photons can occur either via direct or indirect transitions. A direct transition takes place at the same momentum or vector in k -space, whereas an indirect transition occurs between two points with different k -vector in the dispersion relation and, thus, requires a change of momentum. Because of the very low momentum of a photon (compare $p_\gamma = E_\gamma/c \approx 5 \times 10^{-28} \text{ N s}$ for $E_\gamma = 1 \text{ eV}$ and c the vacuum speed of light to $p = \hbar k = \hbar\pi/a \approx 3 \times 10^{-25} \text{ N s}$ for a transition from the center to the edge of the Brouillon zone), a direct transition has a much higher probability than an indirect transition. An indirect transition is a multi-particle process, where phonons as particles with low energy, but high momentum, have to deliver the required Δk , when they are created or absorbed. This is why silicon with an indirect bandgap (situation in Fig. 2.8b) has an orders of magnitude lower absorption coefficient for energies close to the bandgap than, e.g., gallium arsenide with a direct bandgap (global minima of conduction and valence band at the same k). Direct ($h\nu_1$) and indirect ($h\nu_2$ and phonons Γ) absorption processes are shown in Fig. 2.8b. The absorption spectrum of an indirect semiconductor is sketched in Fig. 2.8c, where the absorption onset is characterized by the (indirect) bandgap. Once the photon energy approaches the direct gap, absorption increases more strongly. The spectrum shows an additional feature below the (indirect) bandgap, which is attributed to a so-called excitonic absorption into a Coulombically bound electron-hole pair. Its binding energy is the distance of the excitonic absorption line to the band edge. Such excitonic states are usually seen as sharp peaks at lower temperatures, but will become important when we discuss organic materials in Chap. 3.

Radiative Recombination

The reverse process to generation is the annihilation of an electron-hole pair, which is called recombination R . In the dark and in equilibrium (index 0) R equals the generation G_0 caused by the thermal background radiation:

$$R_0 = \beta n_0 p_0 = G_0. \quad (2.19)$$

Here, R is proportional to the product of electron and hole density, as a recombination event requires a hole to meet an electron. The radiative recombination constant β with unit $\text{cm}^3 \text{ s}^{-1}$ represents a volume rate constant. R and G are rates per volume. Thus, the generation rate G_0 is given by the absorbed number of photons, which is the product of the photon flux incident to a volume element and the absorption coefficient α with unit cm^{-1} . Using $dj_\gamma/d\hbar\omega = dj_E/(\hbar\omega d\hbar\omega) = c \cdot d\rho_E/(\hbar\omega d\hbar\omega)$ from (2.1), G_0 can be expressed by:

$$G_0 = \int_0^\infty \alpha(\hbar\omega) \frac{dj_\gamma^0(\hbar\omega)}{d\hbar\omega} d\hbar\omega = \frac{\Omega}{4\pi^3 \hbar^3 c^2} \int_0^\infty \frac{\alpha(\hbar\omega) (\hbar\omega)^2}{e^{\hbar\omega/k_B T_0} - 1} d\hbar\omega. \quad (2.20)$$

The absorption coefficient $\alpha(\hbar\omega)$ for a semiconductor becomes significant for $\hbar\omega > E_g$; $dj_\gamma^0(\hbar\omega)/d\hbar\omega$ is the ambient spectral photon flux which is black body radiation at the temperature T_0 of the surrounding (2.1). The quantity $c = c_0/n$ describes the velocity of light in the medium, i.e. semiconductor with refractive index n , and is reduced compared to the velocity in vacuum c_0 or air. This means that c decreases if we imagine an energy flux from air into a semiconductor. As the energy flux at the interface air/semiconductor has to be conserved, a lower c requires a smaller solid angle Ω in the medium. This condition is equivalent to Snell's law, describing refraction towards the vertical when a light beam enters an optically denser medium. Knowing α and n_i ($n_0 p_0 = n_i^2$), β can be calculated with (2.19) and (2.20). It is independent of the doping concentration as long as doping does not change α . $R_0 = G_0$ is fulfilled for every $\hbar\omega$ according to the theory of detailed balance, where at thermal equilibrium every single process is balanced. Hence, absorption and emission at each wavelength even out. Thus, the emitted photon flux density (number of photons per second and m^2) in equilibrium can be expressed by

$$dj_\gamma^{\text{em},0}(\hbar\omega) = a(\hbar\omega) dj_\gamma^0(\hbar\omega) = \frac{\Omega}{4\pi^3 \hbar^3 c^2} \frac{a(\hbar\omega) (\hbar\omega)^2}{e^{\frac{\hbar\omega}{k_B T_0}} - 1} d\hbar\omega \quad (2.21)$$

for every ω . Here, $a(\hbar\omega)$ denotes the spectral absorptance, which describes the total fraction of energy absorbed by a body. Hence, its value is a number between 0 and 1 at each $\hbar\omega$. For an ideal thick bandedge absorber, $a(\hbar\omega) = 1$ for $\hbar\omega \geq E_g$ and 0 else.

In non-equilibrium, the charge carrier densities n_0 and p_0 are changed by absorption of photons or by injection and extraction of (additional) electrons. The recombination rate is simply modified using the actual charge carrier densities n and p in (2.19) and (2.18):

$$R = \beta np \stackrel{(2.19)}{=} \frac{G_0}{n_0 p_0} np \stackrel{(2.16)}{=} \frac{G_0}{n_i^2} np \stackrel{(2.18)}{=} G_0 \exp\left(\frac{E_F^n - E_F^p}{k_B T}\right). \quad (2.22)$$

This is allowed, because charge carriers still follow Fermi-Dirac statistics in their respective band and have the lattice temperature so that only the rate of the emitted photons changes, whereas the spectrum contained in G_0 (2.20) remains unmodified. This equation shows that an increased quasi-Fermi level splitting leads to higher recombination. We can write this equation also in spectral photon fluxes replacing the absorption coefficient by the total spectral absorptance $a(\hbar\omega)$ like in (2.21):

$$\frac{dj_\gamma^{\text{em}}(\hbar\omega)}{d\hbar\omega} = \frac{\Omega}{4\pi^3 \hbar^3 c^2} \frac{a(\hbar\omega) (\hbar\omega)^2}{e^{\frac{\hbar\omega}{k_B T_0}} - 1} \exp\left(\frac{E_F^n - E_F^p}{k_B T}\right). \quad (2.23)$$

Equations (2.22) and (2.23) contain some approximations (e.g. Boltzmann distribution). The exact result for the emitted photon flux is obtained using a more detailed derivation [10]:

$$dj_{\gamma}^{\text{em}}(\hbar\omega) = a(\hbar\omega) \frac{np}{n_i^2} dj_{\gamma}^0(\hbar\omega) = a(\hbar\omega) \frac{\Omega}{4\pi^3 \hbar^3 c^2} \frac{(\hbar\omega)^2}{e^{\frac{\hbar\omega - (E_F^n - E_F^p)}{k_B T}} - 1} d\hbar\omega. \quad (2.24)$$

This expression is called generalized Planck's law, describing thermal [compare to classical Planck's law in (2.1)] and luminescence radiation. The latter results from the presence of the bandgap or an energy gap in general, giving rise to long-living non-equilibrium n and p at the (low) lattice temperature. These charges recombine radiatively generating photons with an energy that is dominated by E_g rather than by T .

Radiative recombination requires an electron to meet a hole. Hence, this mechanism can be classified as *bimolecular* recombination with a net recombination rate of $R = \beta(np - n_i^2)$ which we will use later on. Bimolecular recombination is a process of order two, as R is proportional to the product of electron and hole density. We will also call this process direct recombination, as electron and hole recombine without any intermediate steps when encountering each other.

Non-radiative Recombination

Radiative recombination is an unavoidable result of the thermodynamic equilibrium of radiation between bodies at a certain temperature. Apart from radiative recombination other types of recombination can be present and play a significant role. They are sketched in Fig. 2.9. One such process is Auger recombination. Here, energy and momentum of a recombining electron-hole pair are transferred to another free electron in the conduction band. The excited electron thermalizes afterwards. Requiring a hole and two electrons (or vice versa), Auger recombination is a three-particle mechanism with $R_{\text{Aug}} = Cn^2p$. The excitation of the second electron provides the opportunity to accept also changes in momentum in contrast to radiative recombination where a photon is emitted. That is why Auger recombination is significant in indirect semiconductors where recombining electron and hole are located at the band extrema with different k values. There, the change in momentum of the recombining charges is compensated by the gain in momentum of the remaining electron. Auger recombination limits the performance of highly efficient silicon solar cells [11].

Another mechanism, dominant in many real (less pure) semiconductors, is recombination via intra-bandgap states. Such states, called traps, result from crystal defects, which could be dislocations, impurities, or surfaces. Recombination via these trap states can be described by the Shockley-Read-Hall (SRH) model as a two-step process [12]: At first a free electron (i.e. an electron in the conduction band) is captured by an intra-gap state and becomes immobile. This process can be described by a capture constant, which is a product of thermal velocity v and cross section σ of the trap with density N_T . The second step to complete the recombination process is the emission of the electron into the valence band, which is equivalent to a capture of a hole. SRH recombination is described by the following expression, which is found after a more involved derivation [12]:

$$R_{\text{SRH}} = \frac{np - n_i^2}{\frac{n + N_C \exp(-(E_C - E_T)/k_B T)}{N_T \sigma_p v_p} + \frac{p + N_V \exp(-(E_T - E_V)/k_B T)}{N_T \sigma_n v_n}}. \quad (2.25)$$

Examining the denominator of this equation shows that traps with energy E_T close to the center of the bandgap, so-called midgap traps, are most active as recombination centers. In this case the sum in the denominator is minimized giving the highest value of R_{SRH} . This sum is mainly governed by the exponential functions and gets larger, if E_T moves closer to E_C or E_V . Giving an intuitive picture, the occupation probability of a midgap trap is comparable for electrons and for holes. However, a charge carrier can easily escape thermally in the case of a shallow trap, which is located close to a band edge. A high escape probability decreases the recombination rate, e.g., of an electron trapped close to the conduction band edge with a hole. Consequently, midgap traps act as most efficient recombination centers.

SRH recombination is also called *monomolecular* recombination, as a free charge carrier recombines with a localized, trapped charge, and it roughly holds $R \propto n$. Thus, the expression “monomolecular” refers analogously to “bimolecular” to the order (here one) of the recombination process and has nothing to do with molecules.

A further source of recombination are surfaces. Surface recombination can be described by a surface recombination velocity s_n , leading to a surface recombination rate

$$R_{\text{sf}} = s_n(n - n_0). \quad (2.26)$$

The effect of G_0 and R_0 are already included by the subtraction of n_0 . R_{sf} is the net recombination rate, given as a recombination current density in units $\text{cm}^{-2} \text{s}^{-1}$ in contrast to the previous recombination and generation rates, which were given per unit volume. Therefore, R_{sf} is identical to extraction of charges. The term “surface recombination” is commonly used for the extraction of minority charges, which is a loss mechanism in solar cells as we will see later in this chapter. Equation (2.26)

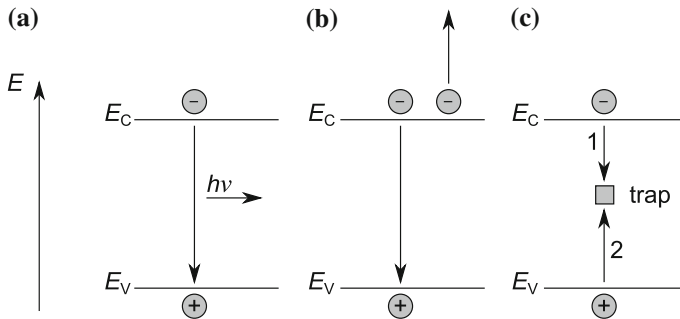


Fig. 2.9 Recombination processes between electron and hole: **a** radiative recombination, emitting a photon, **b** Auger recombination, transferring the energy to another electron in the conduction band, and **c** trap-assisted (indirect) recombination as a two-step process

is further discussed in Sect. 4.5. At a metal contact s_n is commonly very high for electrons and holes ($s_n \rightarrow \infty$). This implies that the contact is in equilibrium independent of the applied voltage or illumination. In this case, $n = n_0$ and $np = n_i^2$ are valid in the semiconductor at the interface to a metal.

Overall Recombination

A lifetime τ can be assigned to each recombination mechanism, because every recombination term (here shown for electrons) can be written as

$$\Delta R_j = \beta_j \Delta n = \frac{\Delta n}{\tau_j}. \quad (2.27)$$

However, τ is only a (constant) material property (including impurities and defects) for monomolecular recombination processes. In all other cases, τ depends also on the density of the other charge carrier type, here the holes p [cf. (2.19)]. In the case of a highly doped semiconductor, a minority lifetime can be defined, because the majority concentration is approximately independent of a small perturbation $\Delta n = \Delta p$ (e.g. for a p-doped layer $p_0 \gg \Delta p \Rightarrow p = p_0 + \Delta p \approx p_0 = \text{const.}$). The overall lifetime is the inverse of the sum of all inverse lifetimes, because all processes are running in parallel ($1/\tau_{\text{tot}} = \sum_j 1/\tau_j$).

Driving Forces

Until now we discussed the Fermi energy or more precisely the Fermi level only related to occupation statistics. Now we extend our discussions allowing variations in space and examining forces on electrons and holes. For simplicity we avoid vectors and use only one dimension with the coordinate x . We will find that a major driving force for the movement of charge carriers is a gradient in their respective quasi-Fermi level.

The basic concept is that forces and hence particle currents vanish, as soon as a system is in equilibrium. We have already used the term “equilibrium” several times. Now we specify it in more detail: A system can be in equilibrium with respect to each individual intensive variable [4]. Intensive variables are variables that do not depend on the amount of material, such as temperature, pressure, chemical and electric potential. Each variable reaches a constant value in space if the system is in equilibrium regarding the respective parameter. Dependent on the linking element of two subsystems, which allows exchange of heat but not particles, e.g., the system reaches thermal but not chemical equilibrium. Chemical equilibrium means that the concentrations of present species do not show a tendency to change with time.

Concerning semiconductors, we assume a constant temperature, neglect any magnetic or gravitational forces on the electrons, and consider only the electric (ϕ) and chemical (ξ) potential. These two potentials are most relevant for describing the motion and concentrations of charged particles in a semiconductor. Starting from the energy balance of a system and some thermodynamic considerations [4], the Fermi

level is found to be identical to the electrochemical potential η . We do not show the exact derivation here. However, we can make it plausible that a non-constant E_F describes a non-equilibrium situation. Imagine two different metals being adjacent to each other and showing a difference in E_F . The system will tend to reach the state of lowest energy, which means that electrons will flow from the metal where they had a higher energy to the metal where electrons with lower energy are located. This flow will stop as soon as the electron ensembles on both metals have the same energy which is equivalent to a constant E_F . We can write for the electrochemical potentials for electrons and holes:

$$\begin{aligned}\eta_n(x) &= -e\phi(x) + \xi_n(x) = E_F^n(x); \\ \eta_p(x) &= e\phi(x) + \xi_p(x) = -E_F^p(x).\end{aligned}\tag{2.28}$$

These equations show that $E_F(x)$ is constant in a semiconductor in equilibrium due to the equality of E_F and η . Consequently, a gradient in E_F denotes non-equilibrium and constitutes a force, which generates a particle current, as we will see in detail in the following sections.

Electron and hole face the same electric potential ϕ at each given position x_0 . The splitting of electron and hole quasi-Fermi levels $E_F^n(x_0) - E_F^p(x_0)$ represents the (entropy-) free or chemical energy of the electron-hole pair $\eta_n(x_0) + \eta_p(x_0) = \xi_n(x_0) + \xi_p(x_0)$ in an ensemble of particles. This energy has to be distinguished from the internal energy of the electron-hole pair, which is (roughly) the potential bandgap energy E_g . Here, we once more face the consequences of thermodynamics. The difference between internal and free energy ΔE is related to the entropy S via $\Delta E = TS$. As elaborated in Sect. 2.1.3 a flow in entropy is unavoidable when extracting work from a heat source. As the electric voltage is free of entropy, the energy related to the flow of entropy is the difference between free (quasi-Fermi level splitting) and internal (E_g) energy. Consequently, a lower temperature allows for a larger free energy and therefore a larger quasi-Fermi level splitting at a given electron and hole concentration. This is in accordance with the definition of the Fermi level and the relations given in (2.14), (2.15), and (2.18). In contrast to the electric work, which is limited to a value below E_g , the radiative recombination of the electron-hole pair generates a photon of energy E_g . The reason is that in a semiconductor emission and absorption at E_g are reversible processes which conserve the entropy if the solid angles of absorption and emission are the same.

Figure 2.10 summarizes all quantities in an energy diagram for electrons. This is what we also call band diagram, as E_C and E_V denote the edges of conduction and valence band, where excess electrons and holes are located. All energy levels are negative and referred to the vacuum level. Potentials for electrons (η_n , ξ_n) are also negative, whereas potentials for holes (η_p , ξ_p) are positive.

Non-equilibrium situations in space are shown in Fig. 2.11. In part (a) the electrochemical potential is tilted due to an applied (constant) electric field F , changing the electric potential $\Delta\phi = -\int F dx$. Subfigure (b) shows a change in the chemical potential due to a higher concentration of electrons and holes on the left.

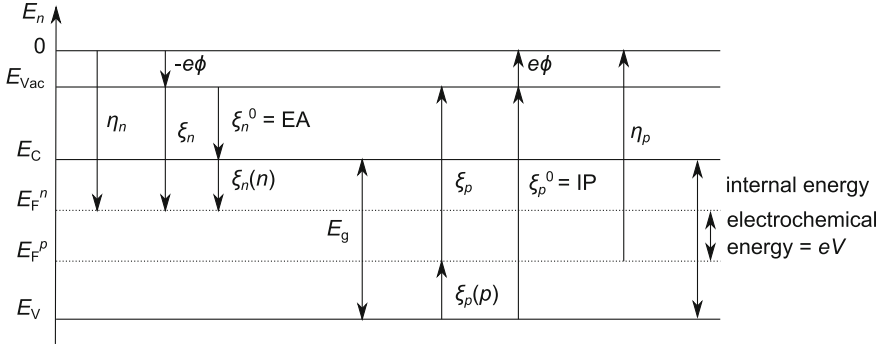


Fig. 2.10 Energy diagram for electrons (n) and holes (p). Shown are the relations between electric potential ϕ , chemical potential ξ , and electrochemical potential η compared to the quasi-Fermi levels E_F^n and E_F^p . ξ consists of a constant part ξ^0 , which is a material property (electron affinity EA , ionization potential IP), and a part, which is dependent on the charge carrier concentration. All energies are given with respect to the vacuum level E_{Vac} , which is shifted by the electric potential ϕ . (Reproduced after [4].)

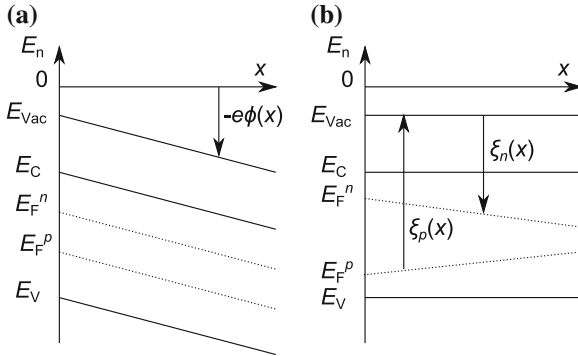


Fig. 2.11 Spatial (x) energy diagrams for **a** an electric potential difference and **b** a concentration gradient. Both result in a tilt of the quasi-Fermi levels E_F^n and E_F^p and consequently in currents for electrons and holes

Electrons and holes will flow independently towards the direction that provides a minimization of their electrochemical energy. This means for situation (a) that electrons flow to the right (η_n becomes more negative) and holes to the left (η_p (positive) becomes smaller). That is expected when applying a field to particles with inverse charge, as we will discuss in Sect. 2.4. In case (b), both, electrons and holes will flow towards the right to minimize their η . This is anticipated as well, as the high particle concentrations on the left will lead to a diffusion current which we will discuss also later.

2.3 Transformation of Thermal Radiation into Chemical Energy

We want to come back to the absorption of sun light in a solar energy converter based on semiconductors. A gedankenexperiment due to Würfel [4] divides photon absorption into two steps: In a first step electrons and holes are generated by absorption of light with an energy $h\nu > E_g$. Excluding scattering at the lattice, the charge carriers reach sun temperature T_S under maximum concentration. The average energy of an electron-hole pair is then $E_g + 2 \cdot \frac{3}{2}k_B T_S$ according to the theory of the thermal energy in a three-dimensional electron gas with three translational degrees of freedom. As the semiconductor is in thermal equilibrium with the sun, the Fermi level for electrons and holes is the same, and it holds according to (2.14) and (2.15):

$$E_C - E_F = k_B T_S \ln(N_C/n); \quad E_F - E_V = k_B T_S \ln(N_V/p). \quad (2.29)$$

After allowing scattering at the lattice in the second step, the electrons cool down to the lattice temperature T_0 . This thermalization is accompanied by the creation of entropy in the form of phonons. The remaining energy per electron-hole pair can be calculated using the same expression as (2.29) replacing T_S by T_0 and E_F by the respective quasi-Fermi level (2.18): $E_C - E_F^n = k_B T_0 \ln(N_C/n)$; $E_F^p - E_V = k_B T_0 \ln(N_V/p)$. This potential energy is the chemical energy ξ , which is represented by the quasi-Fermi level splitting. It can be summarized combining both equations and replacing the logarithms by the expressions of (2.29):

$$\xi_n + \xi_p = E_F^n - E_F^p = E_g \cdot (1 - T_0/T_S). \quad (2.30)$$

This equation allows an estimation of the maximum efficiency of the transformation of heat radiation into chemical energy. If we assume that we do not extract any charge carriers and there is no thermalization (i.e. monochromatic illumination with $h\nu = E_g$), the incoming photon energy is E_g and hence $\eta_{\max} = 1 - T_0/T_S$, which is the Carnot efficiency. Note that this expression derived from (2.30) includes also the condition of maximum concentration. In the recombination process the chemical energy is transferred to a photon, which is emitted at $T = T_0$ and has a chemical potential $\xi_\gamma = \xi_n + \xi_p \neq 0$. This type of radiation is called luminescence, in contrast to the heat or thermal radiation of the sun at $T = T_S$ and $\xi_\gamma = 0$.

In the situation discussed, all absorbed energy is re-radiated to the sun. If we want to extract an electron-hole (particle) current j_{Extra} , a difference is required between absorbed and emitted photon flux:

$$j_{\text{Extra}} = j_\gamma^{\text{abs}} - j_\gamma^{\text{em}} = j_\gamma^{\text{abs}} - j_\gamma^{\text{em},0} np/n_i^2 = j_\gamma^{\text{abs}} - j_\gamma^{\text{em},0} \exp\left(\frac{\xi_n + \xi_p}{k_B T}\right). \quad (2.31)$$

This expression is obtained by considering (2.28) and (2.23) to replace j_γ^{em} , where $j_\gamma^{\text{em},0}$ is the absorbed, i.e. emitted, photon flux if the semiconductor is in equi-

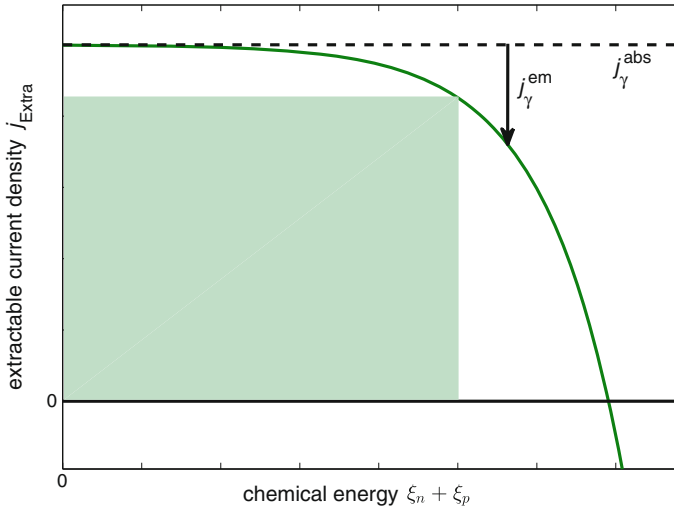


Fig. 2.12 Extractable (particle) current density j_{Extra} of electron-hole pairs as a function of their chemical energy $\xi_n + \xi_p$. The *rectangle* marks the maximum power density, which can be delivered as product of energy and current

librium with the background black-body radiation (2.21). A sketch of j_{Extra} as a function of $\xi_n + \xi_p$ is presented in Fig. 2.12. The power that can be extracted is the product of particle current j_{Extra} and energy per particle $\xi_n + \xi_p$. It can be visualized as a rectangular area below the curve as shown in the figure visualizing that the power reaches a maximum value for a certain current-energy pair. The reason is a tradeoff between number and energy of the collected electron-hole pairs due to thermodynamics. For low chemical energies, very few photons are emitted and almost all electron-hole pairs can be collected, however, at this low energy. With increasing energy, j_{Extra} decreases due to higher radiative recombination. The remaining question of how to extract these electrons and holes to get an electric current is addressed in the following section.

2.4 From Chemical Energy to Electric Energy

To extract the chemical energy of an electron-hole pair in terms of an electric current in an external circuit, electron and hole have to be collected at two different positions in the absorber, e.g., by metal contacts. In the optimum this requires selective contacts. Here, selectivity is a property of the contact and refers to the type of charge carrier. This means that the electron (hole) contact only accepts electrons (holes) and blocks the other type of charge carrier, i.e. holes (electrons). We will see later how this property of selectivity can be realized. Independent of the contact's selectivity

charge carriers have to reach the contact driven by forces acting on them. These forces are discussed in an intuitive way here. A detailed derivation is sketched in Chap. 4. Again, we exclude gravitation, magnetism, and temperature gradients as driving forces acting on the charged particles, and focus on the electric field and the concentration gradient.

Drift Current

The force Z acting on an electron due to the electric field F is given by $Z = -eF$. Inserting this expression as driving force into the equation of motion (Newton's second law) and assuming friction due to scattering with the average scattering time τ_r , leads to the differential equation:

$$-eF = Z = m^* \cdot (dv/dt + v/\tau_r). \quad (2.32)$$

Here we consider the electron being exposed to the crystal potential by using the effective mass m^* . The scattering term v/τ_r increases with velocity resulting in an average v , where the energy dissipation due to friction is balanced by the energy gained due to the accelerating force Z . Thus, we can write for the drift velocity v of the electron in steady state ($dv/dt = 0$):

$$v = -\frac{e\tau_r}{m^*} F = -\mu F \quad (2.33)$$

with the introduction of the mobility μ defining the achievable charge carrier velocity for a particular electric field. In other words, v increases linearly with F and the pre-factor μ . The higher μ , the more mobile are charge carriers and the faster is their average velocity for a given electric field.

The electric current density j , i.e. transported charge per second and area, is the product of particle density, average velocity, and charge. Charges that contribute to the current in a semiconductor are electrons n in the conduction band and holes p in the valence band. The electric field causes holes (positive) to flow in the opposite direction compared to electrons. However, they transport also a reverse, i.e. positive charge. Thus, the contribution from electrons and holes adds up as summarized in microscopic Ohm's law:

$$j_{\text{drift}} = (-env_n + epv_p) = e \cdot (n\mu_n F + p\mu_p F) = \sigma F = \frac{1}{\rho} F. \quad (2.34)$$

Here, the conductivity σ (resistivity ρ) is defined as proportionality constant relating the current to the electric field. Note that in general j and V are vectors and μ and σ are tensors. We have already mentioned the conductivity when we discussed doping, which increases the charge carrier density contained in (2.34). The conductivity of an ohmic rectangular or cylindric sample is easily accessible when measuring the current I as a function of applied voltage V :

$$I = Aj = A\sigma \frac{V}{d} = \frac{A}{\rho d} V = \frac{1}{R} V. \quad (2.35)$$

Here A is the cross-sectional area, d the length, and R the resistance of the sample. The semi-classical picture of band theory is in accordance with (2.34), for metals first postulated by Drude, because Newton's dynamics are valid for the description of electrons in a solid. In a crystal $d(\hbar k)/dt = eF$ holds, where k represents the crystal momentum. The parabolic energy dispersion of a free electron is replaced by that of an electron in a crystal $E(k)$. As already mentioned, $E(k)$ is symmetric and periodic with any inverse lattice vector. This means that accelerating an electron by an electric field without scattering leads to a fast acceleration of the electron out of a band minimum, which is followed by a retardation due to a reversed curvature of the dispersion relation (negative effective mass, cf. Fig. 2.6). This leads to oscillations between the minimum and maximum energy of a band and hence to an average dk of zero and subsequently a v of zero. In such a situation current does not flow in real space. The electrons perform so-called Bloch oscillations [13], which have been observed in semiconductor superlattices [14]. Thus, scattering is essential for an electric current in a periodic crystal, because it provides an equilibrium dk . This change in the momentum of the crystal electrons upon the application of an electric field is $\hbar dk = \tau \cdot (-eF)$ with the average relaxation time τ . For an electron located in a parabolic band minimum with a constant effective mass, we can write $d(\hbar k) = m^* dv = -e\tau F$, which is identical to (2.33).

Diffusion Current

A non-constant (charged) particle density leads to an additional (electric) current, according to Fick's law:

$$j_{\text{diff}}^n = -(-e)D\nabla n; \quad j_{\text{diff}}^p = -(+e)D\nabla p. \quad (2.36)$$

This law states that chemical equilibrium is reached in the absence of other forces if the concentration gradient vanishes. It assumes a current which is proportional to the negative gradient of the particle density with the diffusion constant D as pre-factor. The microscopic reason for the diffusion current is a thermal (Brownian) motion of the electrons in the electron gas. Despite its random character, this motion tends to equilibrate inhomogeneous concentrations. The number of collisions makes the particles effectively diffusing against the concentration gradient.

To bring (2.36) into a form comparable to (2.34), one uses a mathematical trick and replaces ∇n by $n \frac{\nabla n}{n} = n \nabla (\ln n/N_0 - \ln N_C/N_0) = n \nabla \ln \left(\frac{n}{N_C} \right) = n \frac{\nabla \xi}{k_B T}$. N_0 was only introduced to keep the argument of the logarithm free of units. Furthermore, (2.28) and (2.14) have been applied to introduce the chemical potential ξ .

Using the Einstein relation

$$\frac{D}{\mu} = \frac{k_B T}{e}, \quad (2.37)$$

the diffusion coefficient can be replaced by an expression containing only the mobility as a material parameter. This results in the following equation for the total diffusion current:

$$j_{\text{diff}} = n\mu_n \nabla \xi_n - p\mu_p \nabla \xi_p. \quad (2.38)$$

The origin and applicability of the Einstein relation is discussed in Chap. 4 in detail, as it is not given a priori for each type of semiconductor. For now we accept that the diffusion constant can be expressed as a function of mobility and temperature, as scattering limits both diffusion and drift current.

Total Current

The total current is the sum of diffusion and drift current. Combining (2.38) with (2.34) and expressing the electric field as the gradient of the electric potential ϕ ($F = -\nabla \phi$), we get:

$$\begin{aligned} j_n &= j_{\text{drift}}^n + j_{\text{diff}}^n = -n\mu_n e \nabla \phi + n\mu_n \nabla \xi_n = n\mu_n \nabla E_F^n; \\ j_p &= j_{\text{drift}}^p + j_{\text{diff}}^p = -p\mu_p e \nabla \phi - p\mu_p \nabla \xi_p = p\mu_p \nabla E_F^p. \end{aligned} \quad (2.39)$$

Here we merged drift and diffusion current into one expression, which shows that the gradient of the electrochemical potential, or the quasi-Fermi level (2.28), is the driving force as already postulated in Sect. 2.2.2.

We illustrate the benefit of examining quasi-Fermi levels for the example of a metal-insulator-metal (MIM) device with thickness d . Such a device consists of an intrinsic material (insulator (can be seen as wide-gap semiconductor) or semiconductor) sandwiched between two metal contacts. The metals shall have different work functions WF, where work function in general is another word for Fermi level referred to the vacuum ($\text{WF} = -E_F$). The work function is a material (surface) property which describes the energy required to eject an electron from a metal into vacuum. We choose a high-WF (noble) metal for the left and a lower WF metal for the right contact as shown in the inset of Fig. 2.13a.

Bringing all three materials together, the electrochemical potential and consequently E_F have to align, as they are constant in equilibrium. The alignment happens by an exchange of electrons between the metals, either through an external connection or the semiconductor. Electrons from the low-WF metal (on the right) are transferred to the high-WF metal until equilibrium is reached. The resulting band diagram is shown in Fig. 2.13a. Comparing it with Fig. 2.11a we identify a difference in electric potential between left and right. It equals $\Delta \text{WF}/e$ and is associated with a built-in field, which can be seen at the tilting of the bands. This field is directly accompanied by a diffusion gradient, resulting from the spatially varying distance between the Fermi level and the band edges [compare (2.14) and (2.15)]. Close to the left (right) metal we have more holes (electrons) than in the intrinsic semiconductor before being in contact with the metals. In steady state, field and diffusion current cancel each other. More precisely, the net force as superposition of the forces of

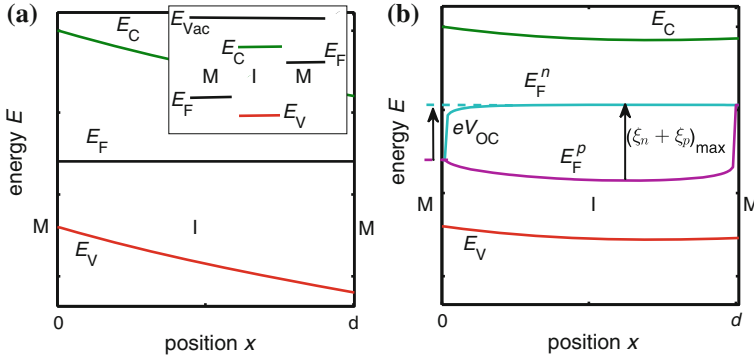


Fig. 2.13 **a** Equilibrium band diagram of a MIM device cross section with hole contact at $x = 0$ and electron contact at $x = d$. The band tilt represents a built-in field caused by a lower work-function contact on the right compared to the one on the left. The *inset* shows the situation before contact of the materials. **b** The device under illumination with split quasi-Fermi levels and a eV_{OC} lower than the maximum chemical potential of an electron-hole pair due to surface recombination

the diffusion gradient and the field on the ensemble of electrons and holes is zero. Consequently, there are not two particle currents flowing in opposite directions and balancing each other. Note that there is simply no current as there is no effective force. This is intuitively clear because an electric current implies energy dissipation due to the resistivity of the material caused by charge carrier scattering. The result would be a continuous generation of heat, which is not allowed in thermodynamic equilibrium by the law of conservation of energy.

If we take the MIM device of Fig. 2.13a and assume that the (intrinsic) semiconductor absorbs light, we might get a quasi-Fermi level splitting at open circuit, which looks like the one depicted in Fig. 2.13b. The voltage measurable from the outside is the difference of the respective electrochemical potential at electron and hole contact. The reason is that the voltage V represents the electric (thus entropy-free) energy eV of one extracted charge carrier pair of the total ensemble. As we are investigating the situation of open circuit, where current does not flow, V is the so-called open-circuit voltage V_{OC} . The sketched gradients in the electrochemical potentials show that the electric energy eV_{OC} is lower than the chemical energy, which is found in the maximum splitting of the quasi-Fermi levels located in the center of the device. The gradients in the quasi-Fermi levels originate from significant surface recombination at the electrodes and cause an internal current flow at open circuit. However, open circuit is defined as the situation where no net-current flows. This situation under illumination demands for a (this time physically real) compensation of electron and hole current by identical particle currents in the same direction. Such compensating currents are represented according to (2.39) in an inverse gradient of E_F^p and E_F^n at each position x . This equation also explains the different amount of the bending of E_F^n and E_F^p due to different gradients, depending on charge carrier density and mobility. In Fig. 2.13b ∇E_F^n is larger close to the left contact due to the much lower

electron density there. Additionally, E_F^p is less constant in space compared to E_F^n . The reason is that a lower hole mobility assumed for the calculation of the band diagram requires a larger ∇E_F^p to provide a hole current equal to the electron current (2.39).

This simple example demonstrates how an ideal solar cell would function: Additional sources of recombination (to the processes present in the absorber anyway, determining the chemical energy) should be avoided and especially contacts should be selective. With selective contacts we hinder electrons from flowing to the left and holes to the right contact. If this is fulfilled, the maximum chemical energy will be completely transferred via flat quasi-Fermi levels to electric energy at open circuit: $\xi_n^{\max} + \xi_p^{\max} = eV_{oc}$. However, this condition is not sufficient for highly efficient solar cells. As already discussed for the chemical potential (cf. Fig. 2.12), power extraction is not possible at open circuit, but requires a current flow. This involves a gradient in the electrochemical potential and leads to ohmic losses in the case of low-conductivity absorber materials or transport layers. In other words, the electrodes have to be capable of receiving (almost) the maximum quasi-Fermi level splitting (chemical potential) for every applied voltage. Under this condition the chemical energy is converted completely into electric energy. The subject of the next section will be technological realizations targeting the ideal solar-cell structure before we want to estimate the maximum power-conversion efficiency of terrestrial solar cells based on semiconductors.

2.5 Possible Realizations of Solar Cells

2.5.1 The p-n Junction

The p-n junction is the best-known realization of a photovoltaic device, because it is employed in the most common type of solar cells, which consists of crystalline silicon. It therefore makes sense to introduce it first. In the ideal case, its current-voltage characteristics can be calculated analytically according to the Shockley equation which we derive in the following. This equation is often used to describe organic solar cells as well, although their working principle is not based on a conventional p-n junction as we will see in the next chapter. Therefore, it is important to be aware of the conditions and approximations applied for the derivation of the Shockley equation to judge whether and to what extent this equation is applicable to organic solar cells.

We start with the behavior of the p-n junction in dark. A p-n junction consists of a p-doped and an adjacent n-doped region. The doping concentrations are N_A and N_D . We assume that all dopants are active, which gives for the equilibrium hole (electron) densities in the p-(n-)region $p_p^0 = N_A$ ($n_n^0 = N_D$). The position of the Fermi levels is according to (2.15) and (2.14) close to the valence band edge for p-doping and close to the conduction band edge for n-doping. Bringing both regions

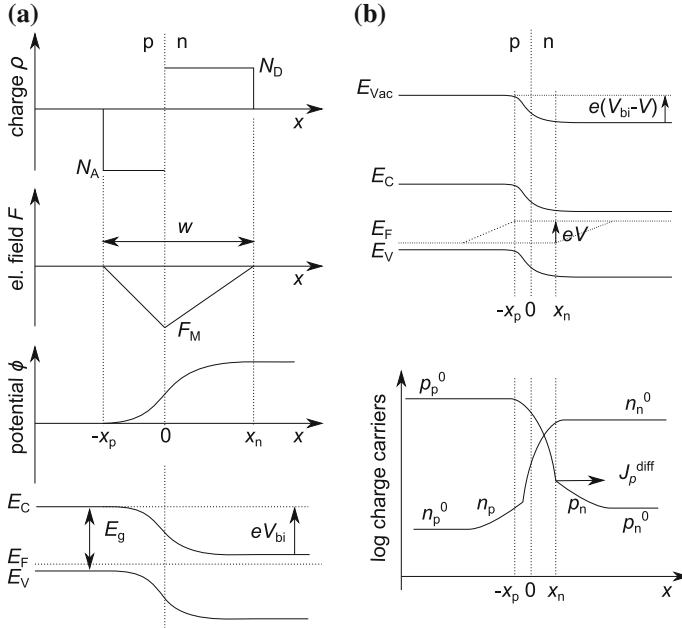


Fig. 2.14 **a** Space charge ρ , electric field F , potential V , and band diagram of a p-n junction in equilibrium. The width of the space-charge region is $w = x_n + x_p$. **b** Band diagram and free charge carrier densities under an applied forward bias voltage V

into contact, the electrochemical potential must be constant in equilibrium and hence, E_F aligned. The resulting band diagram is shown at the bottom of Fig. 2.14a. Reaching equilibrium after contact demands for a redistribution of free charge carriers. The concentration gradients of electrons and holes between p- and n-region cause a diffusion of electrons towards the p-doped and holes towards the n-doped semiconductor, where they recombine. Since the overall semiconductor is neutral, immobile ionized doping atoms remain (top of Fig. 2.14a). They build up a space-charge (ρ) region, which creates a field according to Poisson's equation. This field opposes the diffusion current and stops it in equilibrium, which is represented by a constant E_F . The potential difference is called the built-in potential V_{bi} . For the MIM device in the previous section, it was the difference between the work functions of the metals. Here, it is the difference between the Fermi levels of the neutral n- and p-doped regions, which can be expressed by the equilibrium charge carrier concentrations n_n^0 and p_p^0 according to (2.15) and (2.14) (index specifies the region, n-doped or p-doped, respectively, superscript 0 individual equilibrium in n- or p-doped layer):

$$\begin{aligned}
eV_{\text{bi}} &= E_{\text{F},n}^0 - E_{\text{F},p}^0 = E_{\text{g}} - k_{\text{B}}T \ln\left(\frac{N_{\text{C}}}{n_n^0}\right) - k_{\text{B}}T \ln\left(\frac{N_{\text{V}}}{p_p^0}\right) \\
&= k_{\text{B}}T \ln\left(\frac{N_{\text{C}}N_{\text{V}}}{n_n^0 p_p^0}\right) - k_{\text{B}}T \ln\left(\frac{N_{\text{C}}N_{\text{V}}}{n_n^0 p_p^0}\right) \approx k_{\text{B}}T \ln\left(\frac{N_{\text{A}}N_{\text{D}}}{n_i^2}\right). \quad (2.40)
\end{aligned}$$

Assuming the Schottky or depletion approximation, i.e. an abrupt end of the space-charge region (cf. Fig. 2.14a), the peak electric field F_{m} is simply given according to Poisson's equation by integrating the space charge ρ :

$$F_{\text{m}} = \int_{-x_p}^0 \rho_p dx = -\frac{eN_{\text{A}}}{\epsilon_0\epsilon_{\text{r}}}x_p = -\int_0^{x_n} \rho_n dx = -\frac{eN_{\text{D}}}{\epsilon_0\epsilon_{\text{r}}}x_n. \quad (2.41)$$

Integrating the linear electric field distributions from $-x_p$ to x_n gives the potential, which is equal to V_{bi} :

$$V_{\text{bi}} = \frac{eN_{\text{A}}}{\epsilon_0\epsilon_{\text{r}}} \frac{x_p^2}{2} + \frac{eN_{\text{D}}}{\epsilon_0\epsilon_{\text{r}}} \frac{x_n^2}{2} = \frac{1}{2}F_{\text{m}}x_p + \frac{1}{2}F_{\text{m}}x_n = \frac{1}{2}F_{\text{m}}w. \quad (2.42)$$

We used (2.41) and defined w as the length of the space-charge region. Applying both equations, w can be expressed as a function of doping concentrations, dielectric constant, and V_{bi} :

$$w = \sqrt{\frac{2\epsilon_0\epsilon_{\text{r}}}{e} \frac{N_{\text{A}} + N_{\text{D}}}{N_{\text{A}}N_{\text{D}}} V_{\text{bi}}}. \quad (2.43)$$

Here, V_{bi} can be replaced using (2.40). Thus, w depends, apart from material parameters, only on the temperature. The reason for the increase of w with T can be easily understood, considering the mentioned drift-diffusion equilibrium: The diffusion current increases with T due to the dependence of D in (2.37) on T . Therefore, it has to be compensated by a higher drift current, which demands for a higher field and hence a larger space charge provided by an increased w .

A p-n junction under applied bias voltage shows rectifying behavior and is therefore called a diode. Biasing the device in reverse [(+) at n-side and (−) at p-side] attracts the charge carriers in the doped neutral regions towards the electrodes. This increases the (depleted) space-charge region, where no mobile carriers are located. Therefore, only an extremely small current (carried by thermally generated charges) can flow under reverse bias. In forward bias (Fig. 2.14b), this region is flooded by charge carriers and after reaching a certain threshold, a significant current flows.

Neglecting generation and recombination in the space-charge region (low n and p), the current-voltage characteristics can easily be calculated resulting in the Shockley equation. Additional preconditions are Boltzmann statistics (as in the whole chapter), an abrupt end of the depletion region with extensions x_n and x_p , and operation in

the low-injection regime. This means that injected minority concentrations are much lower than the amount of majorities resulting from doping. In steady state, electron and hole current in the space-charge region must be constant due to the exclusion of recombination in this region. Hence, we can select the most simple position to calculate the current. This is the boundary of the space-charge region to the n-doped layer x_n for the hole current and x_p for the electron current, respectively (Fig. 2.14b). We choose the hole current J_p at $x \geq x_n$ to demonstrate the derivation of the diode current. As the region $x \geq x_n$ is field free, only diffusion of holes, being minorities, p_n into the n-doped region has to be considered (2.36):

$$J_p(x) = -eD_p \frac{dp_n(x)}{dx}. \quad (2.44)$$

A constant hole current for $x < x_n$ postulates an almost constant E_F in the space-charge region. A significant gradient would result in a current [cf. (2.39)], which is not constant due to the strong variation of p within the space-charge region, as shown in the bottom graph of Fig. 2.14b. This would only be possible if charges recombine within the depletion region. We excluded this process due to the low charge carrier densities there. Consequently, an applied voltage changes directly the distance between E_F^p and E_V at x_n as visualized in the band diagram in Fig. 2.14b. E_F^p moves closer to E_V compared to the equilibrium situation. This increases the hole concentration at x_n . According to (2.18) we can correlate p_n under bias and the equilibrium hole density p_n^0 in the following way:

$$p_n(x_n) = p_n^0 \exp\left(\frac{eV}{k_B T}\right). \quad (2.45)$$

As the additional holes $p_n - p_n^0$ are subject to minority diffusion into the n-region accompanied by recombination R with electrons, the following continuity equation must be solved, where (2.44) and (2.27) are applied:

$$\frac{dp}{dt} = -\frac{1}{e} \frac{dJ_p}{dx} - R = D \frac{d^2(p_n(x) - p_n^0)}{dx^2} - \frac{p_n(x) - p_n^0}{\tau} \stackrel{\text{steady state}}{=} 0 \quad (2.46)$$

Note that we used (2.27) and defined a lifetime τ , as $p_n \ll n_n \approx n_n^0$. The steady-state solution of the differential equation (2.46) gives an exponential decay of the hole density with the minority carrier diffusion length $L_p = \sqrt{D_p \tau_p}$:

$$p_n(x) - p^0(x) = (p_n(x_n) - p_n^0) e^{-(x-x_n)/L_p} \stackrel{2.45}{=} p_n^0 (e^{eV/k_B T} - 1) e^{-(x-x_n)/L_p}. \quad (2.47)$$

Using this expression for the excess charge carriers in (2.44) and evaluating it at $x = x_n$ leads to

$$J_p(x_n) = \frac{eD_p p_n^0}{L_p} (e^{eV/k_B T} - 1). \quad (2.48)$$

Finally, this term in sum with the analog result for electron diffusion into the p-side (evaluated at x_p) delivers the Shockley equation:

$$J = J_p + J_n = \left(\frac{eD_p p_n^0}{L_p} + \frac{eD_n n_p^0}{L_n} \right) (e^{eV/k_B T} - 1) = J_S (e^{eV/k_B T} - 1). \quad (2.49)$$

Here, J_S is the saturation current, which is proportional to $n_i^2/N_{D/A}$, if one uses (2.16) to replace the minority charge carrier density p_n^0 or n_p^0 . This leads to an exponential temperature dependence of $J_S \propto e^{-E_g/k_B T}$. Commonly, the so-called diode ideality factor n_D is introduced in the exponential function $\exp(eV/n_D k_B T)$. This factor accounts for recombination in the space-charge region and is 2 in case of SRH recombination [cf. (2.25)]. Real diodes show a superposition of both effects, giving rise to $1 \leq n_D \leq 2$ and a modified J_S . The closer n_D is to 1, the more ideal (diffusion-limited) is the diode. We will discuss n_D further when dealing with recombination in organic solar cells (Sect. 8.4.1).

Let us consider the p-n junction under illumination now. Photogenerated electrons and holes are extracted by a drift current, as soon as they enter the depletion region. At short circuit the gradients of the quasi-Fermi levels in the space-charge region are dominated by V_{bi} as shown in Fig. 2.15a. Therefore, electrons flow towards the right and holes towards the left. Thus, this photocurrent J_{photo} is reverse compared to the forward current of the diode. Assuming J_{photo} to be independent of the field, which means that every charge carrier in this region is always extracted, allows its subtraction from the diode dark current of (2.49):

$$J = J_S (e^{eV/k_B T} - 1) - J_{\text{photo}}. \quad (2.50)$$

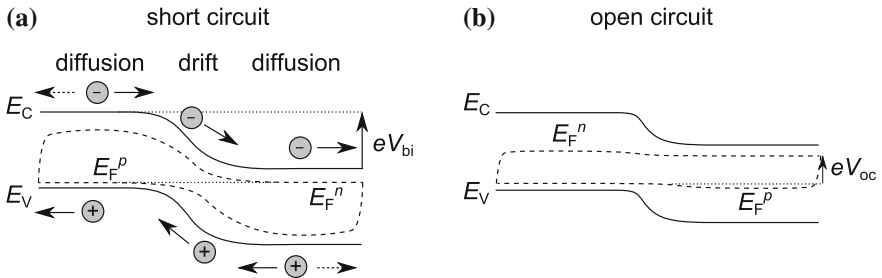


Fig. 2.15 The band diagram of a p-n junction under illumination at **a** short circuit and **b** open circuit. The *dashed arrows* represent losses due to diffusion of minority charge carriers to the “wrong” electrode. The voltage measurable at the contacts is the difference between hole quasi-Fermi level on the *left* and electron quasi-Fermi level on the *right*

Here, we assumed that dark and photocurrent can simply be superimposed. Therefore, J_{photo} is identical to the current measured at short circuit ($V = 0$ V). The open-circuit voltage V_{oc} can be calculated by setting J to zero:

$$V_{\text{oc}} = \frac{k_B T}{e} \left(\ln \frac{J_{\text{photo}}}{J_S} + 1 \right) \approx \frac{k_B T}{e} \ln \left(\frac{J_{\text{photo}}}{J_S} \right) \quad J_S = J_{S0} e^{-\frac{E_g}{k_B T}} \frac{E_g}{e} - \frac{k_B T}{e} \ln \left(\frac{J_{S0}}{J_{\text{photo}}} \right). \quad (2.51)$$

Here, we used the condition $J_S \ll J_{\text{photo}}$. Assuming not too high illumination intensities, the photocurrent scales linearly with light intensity. Thus, according to (2.51) V_{oc} increases logarithmically with intensity. Furthermore, due to the temperature activated J_S and $J_{S0} \gg J_{\text{photo}}$, V_{oc} decreases linearly with T . It is evident that a high J_S decreases V_{oc} .

Equation (2.51) is formally identical to (2.31) [and to (2.22) adding a G_{abs}], which contain the maximum $V_{\text{oc}}^{\text{max}}$ in the chemical energy or quasi-Fermi level splitting, when optical generation and (radiative) recombination are equal, i.e. the extracted current is 0:

$$V_{\text{oc}}^{\text{max}} = \frac{k_B T}{e} \ln \frac{j_{\gamma}^{\text{abs,photo}} + j_{\gamma}^{\text{abs,0}}}{j_{\gamma}^{\text{em,0}}} = \frac{k_B T}{e} \left(\ln \frac{j_{\gamma}^{\text{abs,photo}}}{j_{\gamma}^{\text{em,0}}} + 1 \right). \quad (2.52)$$

Here, we replaced the absorbed photon flux j_{γ}^{abs} in (2.31) by the sum of non-equilibrium photogeneration $j_{\gamma}^{\text{abs,photo}}$ and the equilibrium absorption of the background black-body radiation $j_{\gamma}^{\text{abs,0}}$, which equals the equilibrium emission $j_{\gamma}^{\text{em,0}}$. The coincidence between (2.51) and (2.52) is not necessarily expected as (2.52) results from a recombination current of photogenerated charge carriers, i.e. a photocurrent which is non-constant in voltage. Equation (2.51), however, is derived from a diffusion current of injected (dark) minorities into the majority charge carrier region (2.47), which balances the (constant) photocurrent. Nevertheless, the coincidence is not casual. Instead of defining a diffusion lifetime, we can take the minority carrier density at the edge of the space-charge region (2.45) and assume that this charge carrier density recombines bimolecularly with the electron density $\approx n_n^0$:

$$R = \beta \cdot p_n(x_n) \cdot n_n(x_n) = \beta p_n^0 \exp \left(\frac{eV}{k_B T} \right) n_n^0 \stackrel{(2.16)}{=} \beta n_i^2 \exp \left(\frac{eV}{k_B T} \right). \quad (2.53)$$

If the bimolecular recombination runs at its radiative limit, it holds $\beta n_i^2 = G_0$ according to (2.19). Hence, (2.53) is identical to (2.22) or (2.31). Therefore, the diode with a current-voltage characteristics of (2.50) is an ideal solar cell, if all absorbed photons are transformed to electrons and the saturation current is identical to the current due to radiative emission:

$$J_{\text{photo}} = J_{\text{sc}} = e j_{\gamma}^{\text{abs,photo}}; \quad J_S = e j_{\gamma}^{\text{em,0}}. \quad (2.54)$$

As it holds $j_{\gamma}^{\text{em},0} = j_{\gamma}^{\text{abs},0}$, the equality of J_S with $e j_{\gamma}^{\text{em},0}$ means that the current flowing in an ideal reversed biased diode (2.49) is given by thermally activated charge carriers, i.e. $j_{\gamma}^{\text{abs},0}$, as long as charges are not injected (or created by so-called diode-breakdown processes like tunneling or avalanche ionization effects). Then, for $V \rightarrow -\infty$ the absorbed photon flux from the thermal background radiation is completely extracted as electric current instead of decaying radiatively.

In reality, the p-n junction shows some drawbacks with respect to an ideal solar cell [15]: Minorities have to reach the space-charge region via diffusion, as absorption takes place also beyond the space-charge region. If their diffusion length is too low, they recombine ($J_{\text{photo}} < e j_{\gamma}^{\text{abs,photo}}$). Additionally, the contacts are not selective and constitute recombination centers for minorities, which reach the contact instead of the space-charge region (dashed arrows in Fig. 2.15a). This additional recombination reduces the maximum quasi-Fermi level splitting obtainable and gives rise to electron and hole currents towards both electrodes. These currents compensate each other at open circuit (Fig. 2.15b) comparable to the situation discussed for the MIM device in Fig. 2.13b. Technological solutions like doping profiles, generating a so-called back-surface field [16], and surface passivation can reduce these negative effects. Furthermore, in silicon the radiative limit is not reachable due to Auger recombination [11, 17]. As we will see in the following, more sophisticated concepts exist, which provide some requirements for an ideal solar cell already as a built-in property.

2.5.2 Heterojunction and Dye Solar Cells

The term heterojunction denotes a junction of two different materials. The p-n junction we discussed previously is called homojunction as it consists of the same material (e.g. silicon), having apart from the doping concentration (approximately) the same properties, e.g. regarding E_C and E_V . That is not the case for heterojunctions where usually band discontinuities exist at the junction (Fig. 2.16a). Solar cells based on these junctions are heavily investigated. Most of the potentially low-cost thin-film photovoltaics and in particular efficient organic solar cells are exclusively of this type. A p-n heterojunction works in a similar way to a homojunction and has the same drawbacks. However, if the built-in potential introduced by doping is low or doped layers are not used, the band offsets at the heterojunction assist a directive extraction of charge carriers. An electron, created or having once reached the n-side, faces the energy barrier and cannot flow (back) to the p-side as illustrated in Fig. 2.16a. This effect will be important for so-called flat or planar heterojunction organic solar cells, where charge carriers are directly generated at the junction and therefore located separately on their respective side of the junction. Consequently, the device is intrinsically selective regarding charge transport.

Another comparable realization is the dye (sensitized) solar cell (DSSC), where the absorber consists in the extreme case of a monolayer of dye molecules, which are located between an electron and hole conducting material [18, 19] (Fig. 2.16b).

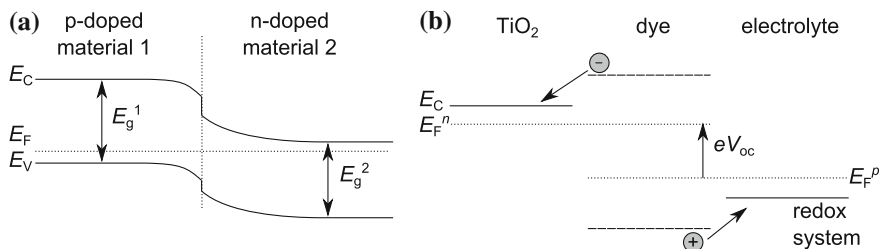


Fig. 2.16 **a** Sketch of the band diagram of a p-n heterojunction with band discontinuities at the junction. **b** Sketch of the energy levels of a dye solar cell at V_{oc} . Photons are absorbed on the dye and after charge transfer electrons and holes are transported in separated media

In these devices a nanostructured interface is essential to achieve a sufficiently large absorption in the dye monolayer. After excitation of the dye, the electron is transferred to a porous titanium dioxide (TiO_2) film, whereas the hole is transported by ions in a (polymeric or liquid) electrolyte. If recombination between the electrons on TiO_2 and the positive charge of the ions can be suppressed, this structure provides a built-in selectivity.

2.5.3 The p-i-n Concept with Wide-Gap Transport Layers

A more sophisticated solar cell architecture consists of three layers: an intrinsic absorber layer sandwiched between n- and p-doped wide-gap charge transport layers. An energy diagram of this structure is sketched in Fig. 2.17 in equilibrium (a) and under illumination in the open-circuit situation (b). Band offsets (ΔE_C , ΔE_V) at the interface between absorber and charge transport layers cause high energy barriers for electrons (holes) at the p-contact (n-contact). They guarantee the selectivity of the contacts and avoid recombination of charge carriers at the “wrong” electrode. The highly doped transport layers are responsible for an excellent collection of the Fermi levels and avoid losses due to voltage drops in the case of current flow. As a by-product the doped layers introduce a built-in field similar to the field in a p-n junction (Sect. 2.5.1) or the MIM device (Fig. 2.13). The p-i-n concept can be seen as ideal solar-cell architecture [4], which provides a high freedom of choice and arrangement of the absorber. It is realized, e.g., in crystalline-amorphous silicon heterojunction solar cells, where the absorber consists of crystalline silicon and the p- and n-regions are realized by amorphous silicon with a higher bandgap [20, 21]. Also many of the organic solar cells described in this book employ this approach [22].

We already mentioned the built-in field in the p-i-n device due to the doped transport layers. However, this field is not necessarily required to achieve the conditions shown in Fig. 2.17b. The same situation characterized by flat electrochemical poten-

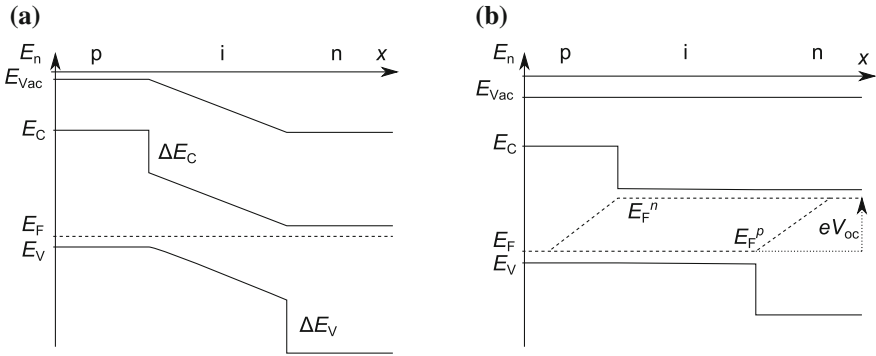


Fig. 2.17 **a** Sketch of the band diagram of a p-i-n device with wide-gap transport layers in equilibrium. **b** The p-i-n device as ideal solar-cell structure at open circuit. The quasi-Fermi levels are constant within the intrinsic absorber. This condition is required for the maximum open-circuit voltage V_{oc}

tials, which means charge carrier collection without creating further entropy, can be realized by imagining a constant E_{Vac} in (a) with a continuous change in the electron affinity and ionization potential of the intrinsic material [4]. E_{Vac} in (b) would then rise from the p- to the n-region, representing a field due to the photogenerated charges. A similar condition of flat quasi-Fermi levels at V_{oc} is given in a MIM device without V_{bi} but completely selective contacts, as we will discuss in Sect. 3.3.2 (Fig. 3.29).

2.6 Maximum Efficiency of Solar Cells Based on Semiconductors

2.6.1 The Shockley-Queisser Limit

So far we have discussed the thermodynamic efficiency limit of an ideal photovoltaic energy converter working at maximum concentration of sunlight. Now we address the more realistic scenario of a terrestrial semiconductor-based solar cell operating at moderate solar concentrations. To derive its maximum efficiency, the so-called Shockley-Queisser limit, we assume an ideal single-gap solar cell, which does not exhibit extrinsic losses caused by series resistances or by reflection and transmission of light due to detrimental properties of the surface or overly thin absorbers. We consider only physical (“intrinsic”) losses, which are unavoidable.

At the beginning of this chapter we found the thermodynamic limit of solar-thermal energy conversion to be 85 %. A terrestrial solar cell based on semiconductors cannot reach this limit, because it is not working under maximum concentration

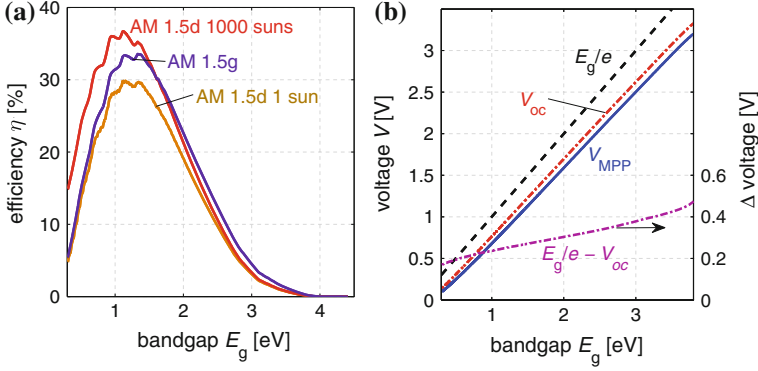


Fig. 2.18 **a** Maximum power-conversion efficiency of a single-gap absorber as a function of the bandgap E_g for different illumination spectra (AM 1.5 direct and global) and concentrations. **b** V_{oc} and V_{MPP} as a function of the bandgap. They are lower than E_g/e due to radiative recombination. The difference between E_g/e and V_{oc} refers to the right scale. All data are shown for $T = 300$ K

of the sun light. Additionally, thermalization losses are unavoidable. This means that photogenerated electron-hole pairs are harvested at one energy, although the average energy of the absorbed photons originating from the broad emission of the sun was significantly larger (cf. Fig. 2.1). Furthermore, photons below the bandgap are not absorbed (cf. Fig. 2.8). Shockley and Queisser [23] calculated the maximum efficiency for a single-bandgap semiconductor as a function of the bandgap approximating the sun as a black body. Henry refined the data using the AM1.5 spectrum [24]. Figure 2.18a shows the ideal efficiency η as a function of the bandgap at $T = 300$ K. The maximum efficiency at 1 sun is around 30 % and increases to 36 % for a concentration factor of 1,000 (AM 1.5d). AM 1.5g gives a value of 33 %. The ideal bandgap is between 1.1 and 1.6 eV. Lower bandgaps lead to a decrease in η due to high thermalization losses resulting in a low V_{oc} . Higher bandgap semiconductors do not absorb photons with energies lower than the bandgap. This tradeoff and additionally unavoidable radiative recombination [cf. (2.24)], which limits V_{oc} below E_g/e , result in the curve.

We want to have a closer look at the efficiency limits using Fig. 2.19 to give a graphical illustration of the losses. Plotted is the photon flux density j_γ , which can be absorbed by a one-band-edge absorber with a band edge at a particular E_g , which is the abscissa. The absorber is assumed to be sufficiently thick to absorb every photon larger than E_g ($a(\hbar\omega) = 1 \forall \hbar\omega > E_g$). So, every value of j_γ at E_g is the result of an integration over the spectral photon distribution shown in Fig. 2.1 from E_g to infinity:

$$j_\gamma^{\text{abs,photo}}(E_g) = \int_{E_g}^{\infty} \frac{d j_E^{\text{AM 1.5g}} / d \hbar\omega}{\hbar\omega} d \hbar\omega = \int_{E_g}^{\infty} d j_\gamma^{\text{AM 1.5g}}(\hbar\omega). \quad (2.55)$$

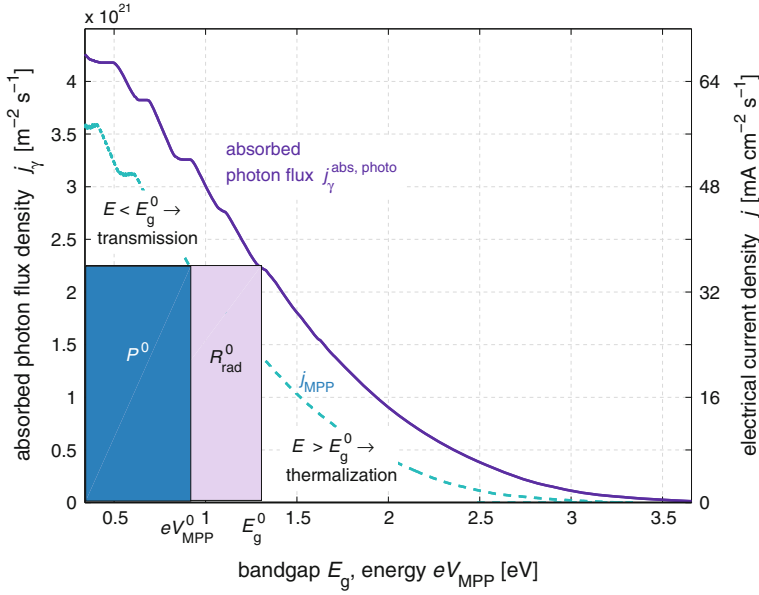


Fig. 2.19 Solar photon flux density $j_{\gamma}^{\text{abs,photo}}$ that can be harvested as a function of the bandgap E_g of a band-edge absorber. The *right* axes denotes the respective current density. The area *below the curve* describes the total energy of the photon flux. The maximum power which can be harvested by a single-bandgap absorber is the product of j_{MPP} and the energy $eV_{\text{MPP}}^0 < E_g^0$ of the extractable electron-hole pairs. This is represented by the area of the *rectangle* marked with P^0

Consequently, $j_{\gamma}^{\text{abs,photo}}(E_g = 0)$ is the total photon flux from the sun. Thus, the solid line in Fig. 2.19 visualizes losses due to non-absorbed photons for an increasing E_g . The area under this curve represents the total intensity emitted from the sun. The largest rectangle with area $E_g^0 \cdot j_{\gamma}(E_g^0)$ would be the maximum intensity that can be harvested by a single-bandgap absorber with E_g^0 , ignoring any recombination. The area to the right of the rectangle at higher energy is lost due to thermalization, because these photons are collected at energy E_g^0 instead of using their total energy. The area above the rectangle represents losses due to the transmission of photons with too low energy.

We have already discussed the thermodynamics of a band-edge absorber and the unavoidable radiative recombination. This recombination limits the electric energy of an extracted electron-hole pair to a value below E_g . The emitted flux $j_{\gamma}^{\text{em},0}$ due to radiative recombination can be calculated integrating (2.21) with $\Omega = \pi$ for a flat device emitting only from one surface:

$$j_{\gamma}^{\text{em},0}(E_g) = \frac{1}{4\pi^2 \hbar^3 c^2} \int_{E_g}^{\infty} \frac{(\hbar\omega)^2}{e^{\frac{\hbar\omega}{k_B T_0}} - 1} d\hbar\omega. \quad (2.56)$$

Recall that we treated the semiconductor as a band-edge absorber, which means an absorptance $a(\hbar\omega)$ of 1 for energies larger than E_g and 0 for smaller energies. With (2.23) or (2.31) we can calculate the ideal current-voltage characteristics as difference between absorbed and re-emitted photon flux, which is equivalent to the curve in Fig. 2.12:

$$\begin{aligned} J(V, E_g) &= e \cdot \left(j_{\gamma}^{\text{abs,photo}}(E_g) + j_{\gamma}^{\text{abs},0}(E_g) - j_{\gamma}^{\text{em},0}(E_g) \cdot e^{\frac{eV}{k_B T}} \right) \\ &= e \cdot \left(j_{\gamma}^{\text{abs,photo}}(E_g) + j_{\gamma}^{\text{em},0}(E_g) \cdot \left(1 - e^{\frac{eV}{k_B T}} \right) \right). \end{aligned} \quad (2.57)$$

Here, J is the electric current density.

The maximum power can then be calculated by numerically finding the maximum of the electric power $J \cdot V$. The current at this maximum power point (MPP) is plotted as a function of the voltage at the MPP in Fig. 2.19 (dashed line). Figure 2.18b illustrates that the difference between both curves in Fig. 2.19 is due to a decreased voltage at the MPP compared to E_g/e and also at open circuit [obtained by setting $J(V, E_g) = 0$ in (2.57)]. Consequently, the maximum power-conversion efficiency is represented by the area marked with P^0 in Fig. 2.19. It is reached for $E_g^0 \approx 1.1 \dots 1.4$ eV and represents 33 % of the whole area under the curve. Radiative recombination accounts for 30 % relative loss, i.e. 13 % total loss. The use of concentrators to enhance the photon flux of the sunlight would shift the j_{MPP} -curve closer to j_{γ} .

For an ideal absorber at the bandgap of silicon with $E_g = 1.12$ eV, the following values are obtained: $V_{\text{oc}} = 0.87$ V, $J_{\text{sc}} = 44$ mA/cm², and $\eta = 33.3$ %. More detailed calculations of the recombination losses, including device geometry and the equilibrium between absorption, emission, and reabsorption can be found in [23, 24]. Experimentally realized efficiencies with silicon solar cells are in the range of 20 % (commercial module) to 25 % (record cell) [25]. This is a high value for silicon as indirect semiconductor where Auger recombination dominates, which was estimated to limit the theoretical maximum to close to 30 % [11, 17]. We will further discuss the effects of recombination on V_{oc} when treating the photovoltage of organic solar cells in Sect. 3.3.2.

2.6.2 Approaching the Radiative Efficiency Limit

The Shockley-Queisser limit demands for a complete absorption of the incoming photons with energy larger than the bandgap and considers only radiative recombination losses. Although silicon as most abundant semiconductor fits the optimum gap well and can be processed at a high purity to avoid recombination at defects (traps), it shows a weak absorption (close to its band edge) because it is an indirect semiconductor. Therefore, a rather thick absorber layer is required. Due to conservation of momentum (cf. Sect. 2.8), Auger recombination is significant.

Direct semiconductors are in general better suited as absorbers. However, also a device based on these materials, which are electrically close to ideal ones, has to be optimized regarding optics to avoid what we called extrinsic optical losses in the previous section. These basically cover reflection of incident sunlight at the surface air-semiconductor and parasitic absorption eventually present in a rear back reflector.

Reflection of electromagnetic waves at an interface of materials with varying index of refraction n can be described applying the Fresnel equations [cf. (4.82) and (4.83)] based on Maxwell's laws. We do not derive them here, but simply recall that for a dielectric material the reflectance R under normal incidence can be written as:

$$R = \frac{I_{\text{reflected}}}{I_{\text{incident}}} = \left(\frac{n - 1}{n + 1} \right)^2. \quad (2.58)$$

Here, I_{incident} denotes the normally incident and $I_{\text{reflected}}$ the reflected light intensity. Equation (2.58) predicts that around 30 % of the incoming light of perpendicular incidence is reflected for a material like silicon with a refractive index of $n \approx 3.5$. Therefore, it is essential to decrease the reflectivity. One option is coating a material with thickness of a quarter of the wavelength. This leads to destructive interference of incoming and reflected light which decreases the reflectivity to a value close to zero. However, this idea is only applicable for a specific wavelength. Another approach working for a broad wavelength range is index matching. Here, the semiconductor is coated with an optically thick transparent layer with refractive index between the one of air and the one of the semiconductor. According to (2.58), the transmission $1 - R$ of light from air into silicon covered with a glass or plastic layer with $n = 1.5$ is $(1 - R_{\text{air-IM}})(1 - R_{\text{IM-SC}})(1 + R_{\text{IM-SC}}R_{\text{air-IM}} + \dots) \approx 0.8$, where IM denotes the index matching layer and $\dots$ account for a repeated bouncing of the light beam in the IM layer. Therefore, the reflectivity is reduced to 20 %.

If the transmission of light is significant due to a too thin absorber, a mirror on the backside of the absorber will increase the absorption. The effect of the mirror can further be enhanced by the approach of light trapping (Fig. 2.20b). This can be

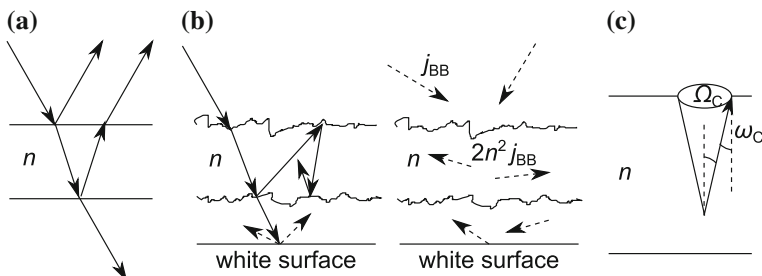


Fig. 2.20 **a** Solar cell with refractive index n without light trapping. The path of an incident light beam faces refraction at the planar surfaces according to Snell's law. **b** Surface texturing traps light. The intensity can be enhanced up to a factor of $2n^2$. **c** Escape cone of light emitted in an optically dense material. Ω_c is limited by total internal reflection

done by texturing the back surface of the semiconductor. A distribution of light rays hitting this surface is in the extreme case completely randomized by the reflection at the rough surface. This means the correlation between the angle of incidence and reflection is completely lost. The effect of this texturing can be explained in a simple picture treating light as rays: Assume rays with perpendicular incidence. Hitting the textured back surface randomizes the directions of reflected rays. Thus, in average this light will have a second longer path through the semiconductor and the reflection at the top surface will be increased as well, as some beams will exploit the effect of total internal reflection. Also a structuring of the front surface can cause this effect if this surface is coated by a layer for index matching. Then the light will be trapped in this (transparent) layer. The trapped light will sooner or later be absorbed in the adjacent semiconductor.

To quantify this effect of light trapping in case of an isotropic black-body radiation, we can use (2.20) or (2.21). There, we said that the solid angle at an interface of media with different n has to change according to Snell's law to conserve the energy flux. If, however, the solid angle is completely randomized within the semiconductor, the intensity has to increase. Assuming the same solid angle in air and in the semiconductor gives directly an enhancement of the intensity by a factor of n^2 . With a mirror at the backside this value is doubled to $2n^2$, which is known as the Yablonovitch limit. Yablonovitch derived this limit of maximum concentration by light trapping also for non-black-body radiation applying statistical mechanics [26].

The presented concept of light trapping is directly intuitive as it decreases reflection and enhances absorption by a longer optical path in the semiconductor. Less intuitive and at first glance contradictory is the statement that a good solar cell should be optimized to outcouple as much light as possible. This implies a high emissivity in particular at open circuit, where electric current is not extracted. Of course, close to the maximum power point, we want to have a luminescence which is reduced by the flux of extracted charges.

Having followed this chapter so far, the demand for a high luminescence yield is not astonishing, because high emission means:

- proportionally high absorptivity due to the basic thermodynamic considerations in Kirchhoff's law;
- less non-radiative recombination processes which would decrease the efficiency below the Shockley-Queisser limit;
- a minimization of parasitic absorption in mirrors etc.

According to [27] it is not sufficient to use a material with a high internal luminescence yield for recombining charges, but a high outcoupling efficiency of the solar cell. The outcoupling efficiency can be estimated applying the condition of total internal reflection according to Snell's law ($\sin \omega_c = 1/n$). Using the equation in Fig. 2.3 we can calculate the solid angle Ω_c of the escape cone visualized in Fig. 2.20c. The escape probability of light isotropically emitted within the absorber is then the ratio between Ω_c and the total solid angle 4π . Including a factor of 0.5 for the backside mirror, the probability for outcoupling is $1/(4n^2) = 2\%$ for silicon. The remaining light faces a high probability of reabsorption: Photons are recycled and new

electron-hole pairs are generated. At first glance, this looks beneficial for solar-cell performance. However, each generation event is followed by a new chance for non-radiative recombination, decreasing the overall luminescence yield compared to the internal luminescence yield (e.g. a 95 % internal yield arrives at approx. $0.95^5 = 0.77$ assuming four reabsorption events). This idea means we prefer that a photon generated by radiative recombination escapes the device instead of being reabsorbed [27]. Without doubt that is desired at open circuit. However, when extracting charge, one should also consider that a reabsorbed photon has a second chance to generate an electron-hole pair which might be extracted. Therefore, the photocurrent at the MPP might be enhanced by reabsorption. Nevertheless, reported data [27] indicate that the gain in V_{oc} dominates the efficiency. This effect is expected when consulting Figs. 2.18 and 2.19. These figures show that the energy loss at the MPP compared to the product of electric current and potential energy $e j_{\gamma}^{abs} \cdot E_g / e$ is mostly due to a voltage V_{MPP} at the MPP which is significantly lower than E_g / e . The current density at the MPP j_{MPP} compared to j_{γ}^{abs} is barely reduced as the curves in Fig. 2.19 are more or less shifted horizontally.

An ideal back mirror is required to make use of a second path of transmitted light through the absorber. Most common is a metal mirror, as it combines a high reflectivity with a high conductivity. Thus, the metal provides additionally the function of the electric back contact. The high specular reflectance of a metal is due to the fact that electric fields are screened by free electrons close to the metal surface and do not significantly penetrate the metal. These electrons screen the field due to resonant oscillations and generate a reflected electromagnetic wave. This works as long as the light frequency is below the plasma frequency of the metal. Then the metal surface appears shiny. However, the electromagnetic field penetrates the surface (approx. 50–100 nm for visible light), which gives rise to absorption. The absorbed energy is transformed into heat and cannot be used to generate electric energy. In general, absorption, not taking place in the absorber itself, but in peripheral elements of the solar cell, is not useful. It is called parasitic absorption.

To avoid parasitic absorption, a non-absorbing mirror should be used. We know that dielectric high-bandgap materials show a low absorption coefficient in the visible range. To avoid transmission, a microdispersion of this material with another material of different refractive index is required. This layer with sufficient thickness acts than as a highly scattering (dielectric) mirror, appearing white (cf. white paint or snow) [28]. Assuming a perfect mirror, a solar cell based on a thin absorber and light trapping can provide a higher efficiency than a device consisting of a thick absorber of the same material. In both cases, roughly all incident photons with $h\nu \geq E_g$ are absorbed. However, in case of the thin device they are absorbed in a smaller volume increasing the charge carrier densities and thus the quasi-Fermi level splitting and in turn V_{oc} [(2.18) and (2.31)]. Therefore, light trapping is equivalent to the geometric concentration of the incident light, which we already mentioned. Based on these considerations, the record efficiency for a solar cell consisting of a single absorber was recently reported to a value close to 29 % [27, 29] measured under AM1.5g. The employed material is gallium arsenide (GaAs) which is a direct semiconductor with a bandgap of 1.4 eV.

2.7 Novel Concepts and Classification of Solar Cells

Several ideas for overcoming the Shockley-Queisser limit have been proposed [30–32]. The simplest approach is the stacking of solar cells with different bandgaps creating a multi-junction device. Here, the low-bandgap cell is positioned at the back contact and absorbs light which is transmitted through the front cell(s) as sketched in Fig. 2.21a. Thermalization losses are reduced compared to a single (low-bandgap) junction, because high-energy photons are harvested by the high-bandgap cell(s) which deliver(s) a higher V_{oc} . The power output of a tandem cell can be represented in Fig. 2.19 by two rectangles, potentially covering a larger area than a single rectangle. This is illustrated in Fig. 2.21b. The theoretical efficiency maximum of a tandem cell is 42 % ($E_g^1 = 1.0$ eV; $E_g^2 = 1.9$ eV) [33] rising to 50 % at 1,000 suns [24]. Henry also calculated the maximum efficiency of a 36-gap cell to 72 % at 1,000 suns [24]. Technically, multi-junction cells are usually realized monolithically on a common substrate. This technology results in a series connection of the single sub-cells, which increases V_{oc} , but requires current matching. The most recently reported record efficiency for a GaInP/GaAs/GaInNAs triple junction solar cell measured at 942 suns is 44 % [25].

There are several other concepts to overcome the Shockley-Queisser limit. They include the extraction of hot carriers to avoid thermalization losses or the insertion of intra-gap states, which are not active as recombination centers, but allow a two-step absorption. Another approach is using multiple electron-hole pair generating absorbers or up- and down conversion materials to make better usage of the photon energy. However, these approaches have not yet lead to highly efficient solar cells. They belong to the third generation of photovoltaics [30]. According to this

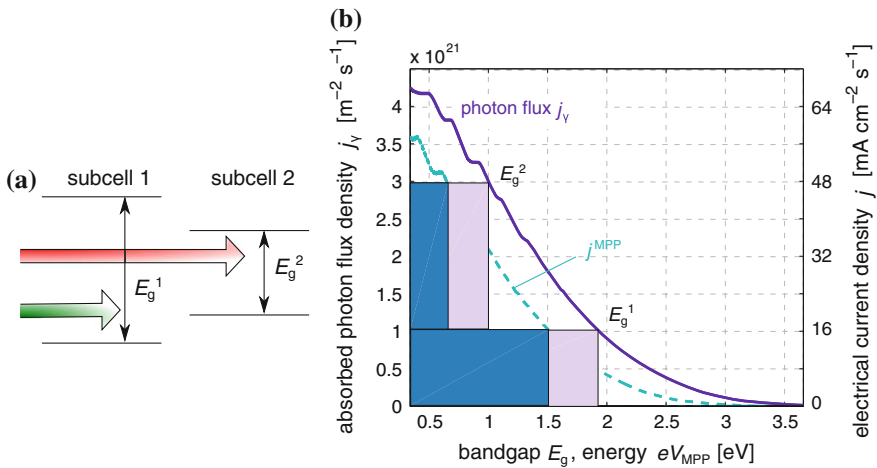


Fig. 2.21 Tandem solar cells. **a** Sketch of the arrangement of two subcells with different bandgaps. **b** The same plot as in Fig. 2.19 for a tandem solar cell where a part of the transmitted energy of the wide-gap cell with E_g^1 is harvested by the other subcell with E_g^2

classification the first generation consists of the conventional single or poly-crystalline (mostly Si) solar cell, which is energy intensive and expensive in production. The second generation is said to consist of cheap thin-film technologies (e.g. cadmium telluride (CdTe), copper indium gallium selenide (CIGS), or thin-film silicon) employing less crystalline (and less pure) absorbers and providing moderate efficiencies.

Another classification describes the third generation of solar cells as cheap and efficient. Organic photovoltaics showing the potential of low-cost production technologies are sometimes ranked among this field. According to present-day knowledge, no significantly stricter theoretical limits are to be expected with organic photovoltaics beyond those discussed in this chapter, although the energy conversion requires additional steps. The development in the last years has shown an increase in organic-solar-cell efficiencies of around 1% per year recently reaching 12% [29, 34]. Consequently, 15% should be within reach in the next years. These results are promising and a deeper discussion of the principles of organic photovoltaics is given in the subsequent chapter.

2.8 Answers to the Initial Questions and Further Reading

- *What is the thermodynamic limit of solar-thermal energy conversion with a device located on the earth surface? What is the role of entropy?*

The maximum efficiency is roughly 85% (assuming full concentration of the sun light) and is solely a function of the temperatures of the sun (surface), the absorber, and the surroundings. During this conversion the entropy contained in the black-body heat flux from the sun, has to be at least conserved. The energy to be used, however, is work or electricity, which is free of entropy. Thus, the entropy flux requires a heat (energy) flux which limits the maximum power-conversion efficiency.

- *Why is the power-conversion efficiency of a solar cell based on a single semiconductor limited to 33%? What tradeoffs have to be made?*

The solar spectrum is broad but the semiconductor is a band-edge absorber. All absorbed photons create electron-hole pairs which are extracted at an energy related to the band edge. The excess energy is lost in form of heat due to so-called thermalization. From this perspective a high bandgap is desired. However, only photons with energies above the bandgap are absorbed. This leads to a tradeoff, and a bandgap at around 1.1–1.4 eV is optimum to harvest the broad solar spectrum.

- *Where is the “maximum” of the solar spectrum located? What are possibilities of expressing spectra (e.g. from the sun) considering energy versus wavelength or photon fluxes versus intensity fluxes (irradiance)?*

Spectra express either energy or photon fluxes as a function of the frequency of light. That is why the maximum of the photon flux spectrum is shifted to lower energies compared to the irradiance. A definition of the energy of maximum radiance/photon flux is difficult as spectra contain energies or number of photons per interval. Commonly, the unit of this interval is either nm (unit wavelength)

or eV (energy, frequency), which are not linearly related. Consequently, these intervals differ along the spectrum. That is why, the maximum of the irradiance (photon flux) per unit wavelength is in the green (red) spectral range, and per unit energy in the infrared. Latter is more physical, as it is the energy that propagates with the electromagnetic wave.

- *What are the main optical and electrical properties of semiconductors and how can they be derived?*

Semiconductors are characterized by an energy gap, resulting in a sharp absorption onset, and a low conductivity, as only thermally activated charge carriers contribute to the conductivity, which increases with temperature. These properties are best described with energy bands resulting from the wave-function overlap of a periodic crystal lattice. Adding more free charge carriers in a controlled way (so-called doping) is technologically relevant for applications.

- *What are the relations between Fermi levels and charge carrier densities?*

The Fermi energy describes the energy to which states are filled at temperatures approaching 0 K. The Fermi level of a semiconductor is found in between conduction and valence band. It describes the energy, where the probability of occupation is $1/2$ according to Fermi-Dirac statistics. The higher the temperature, the broader is the distribution. And the closer the Fermi level to the valence (conduction) band, the more holes (electrons) are in the material. The relation between the position of the Fermi level relative to the band edge and charge carrier densities is exponential (Boltzmann approximation).

- *What are the driving forces for the movement of charge carriers? What is the concept of quasi-Fermi levels?*

Charge carriers try to minimize their energy, which is expressed in the electrochemical potential of an ensemble of charge carriers. This potential is equal to the Fermi level. In quasi-equilibrium (e.g. under illumination), two quasi-Fermi levels can be defined which separately represent the electrochemical potential of electrons and holes. Therefore, spatial gradients in the quasi-Fermi levels constitute a driving force. Two intuitive forces enter the electrochemical potential: one due to an electric field (drift) and the other one due to a concentration gradient (diffusion).

- *What is the effect of recombination on the photovoltage of a solar cell? Which loss processes are unavoidable?*

The photovoltage under open circuit results from a dynamic equilibrium between photogeneration and recombination of charge carriers, as every generated charge carrier has to recombine in average if it is not extracted: the stronger the recombination, the lower the voltage. Radiative recombination is unavoidable due to thermodynamic considerations. It guarantees the radiation equilibrium between bodies, here the solar cell and the ambient.

- *How does a p-n junction solar cell work? Are there alternative architectures?*

Absorption takes place in p- and n-doped regions of the solar cell. Minority charge carriers diffuse to the junction, which provides the asymmetry for a directive extraction of positive and negative charges. P-i-n structures or (doped and intrinsic) heterojunctions are alternative architectures.

- *What are the basic requirements for a solar cell? Consider the role of selective contacts and the built-in electric field.*

Absorbed photons need to generate long-living electron-hole pairs, which can be extracted before they recombine. The chemical energy stored in these pairs has to be transformed into electrical energy by a collection of electron and hole at different contacts. Therefore, a selective device architecture is required. This can be provided by selective contacts, one letting pass only electrons and the other one only holes. A built-in electric field is not necessarily required but introduces a beneficial source of selectivity.

- *Why should a good solar cell show a high electroluminescence quantum yield, i.e. large emission?*

This condition refers to open circuit, where all photogenerated charge carriers have to recombine. As radiative recombination is unavoidable, a high luminescence yield indicates a weak non-radiative recombination, which would be an additional loss.

- *What are the main concepts for overcoming the so-called Shockley-Queisser limit?*

This limit of 33 % describes the maximum efficiency of a solar cell based on one semiconductor as absorber. Concentrating the sun light or stacking several absorbers each with different bandgap can increase the efficiency. Avoiding thermalization in one material or benefiting from two-particle processes (up and down conversion) is also a (so far rather theoretical) way to go.

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Chapter 3

Organic Solar Cells

Abstract This chapter starts with a description of the characteristic electronic structure and charge transport properties of organic semiconductors. These introductory parts are followed by detailed elaborations on the working principles of organic solar cells based on the considerations of Chap. 2. The discussions focus on processes which limit the quantum efficiency and the maximum extractable energy. Beginning with a description of the general steps involved in energy conversion, the chapter shifts focus towards real structures and materials. It concludes with more experimental aspects concerning fabrication and characterization. Whereas the first sections review very basic chemistry knowledge, the solar-cell section gives a detailed evaluation of currently used models and ideas to explain the current-voltage characteristics of organic solar cells. Some basic questions addressed are: (a) What are the major prerequisites for organic materials to show semiconducting properties? (b) What happens when molecules form a solid? What are the main differences between organic and crystalline inorganic semiconductors? (c) What is the role of the reorganization energy considering optical and electrical properties of organic semiconductors? (d) What approaches exist to describe the charge-carrier mobility in organic solids? (e) What are the steps of energy conversion in an excitonic solar cell? What is the role of the bulk heterojunction? (f) How can different recombination mechanisms be distinguished experimentally? (g) What is (the role of) the charge-transfer state? (h) Can the open-circuit voltage be related to other optical and electrical quantities accessible by experiment? (i) Does a stricter limit exist for the maximum power-conversion efficiency of organic solar cells compared to their inorganic counterparts? (j) Why does a single-layer organic solar cell show diode behavior? (k) What determines the fill factor? (l) What is the role of metal electrodes? What kind of energetic situations are possible when a metal-organic contact is formed? (m) What are common solar-cell stacks? How can they be fabricated? (n) What are the remaining challenges for making organic solar cells competitive?

3.1 Energetics of Organic Molecular Materials

The main difference of organic semiconductors compared to semiconductors consisting of single atoms is the presence of separate molecules, which maintain most of their characteristics also when forming a solid. These characteristics of the

single molecule are reflected in the optical properties of the solid such as absorption and luminescence. They also rule the electrical properties like transport gaps and the localization, separation, and transport of charge carriers. The latter strongly depend on the arrangement of the molecules in a solid film. Such films are mostly amorphous or nanocrystalline. Before addressing the properties of the solid, we briefly introduce single molecules. Their electrical properties are discussed in an intuitive way here. This treatment has to be judged as an introduction to the physics of conjugated molecules for non-chemists.

3.1.1 From Atoms to Molecules

We have seen in the previous chapter that a basic requirement for electrical conductivity is the presence of delocalized electrons capable of receiving energy from an external electric field. The delocalization is much less pronounced in an organic solid compared to a crystalline semiconductor. The electron wave-function overlap in a crystalline semiconductor gives rise to energy bands which can be occupied by delocalized conducting electrons. In organics, the delocalization is given on a smaller length scale by the so-called π -system of molecules which are the subunits of an organic solid.

In the following, we derive the formation of molecular orbitals by assembling the molecules from single atoms. As we are dealing with organic chemistry, the main component is the element carbon (C) having six electrons including four valence electrons. The electrons are organized in shells around the core. Each shell consists of orbitals representing the wave functions, whose square moduli describe the probability function for finding an electron at a certain location. A visualization of orbitals can be done depicting a spatial region, within which an electron is located with a certain probability (commonly about 90 %). Each orbital can host two electrons with different spins. Carbon has the electronic configuration $1s^2 2s^2 2p^2$, which means that the s-orbitals of the first and second shell are fully occupied by two electrons. The two remaining electrons are found in two of the three degenerate p-orbitals, which can host up to six electrons, and are each filled by one electron first according to Hund's rule. These orbitals are known from the solution of the Schrödinger equation for the hydrogen problem and correspond to particular quantum numbers. The principle quantum number describes the shell ($N = 1, 2, \dots$), and the angular momentum quantum number is represented by the letters s, p, d, ... Figure 3.1a shows the shape and orientation of the rotationally symmetric s- and the three dumbbell-shaped p-orbitals.

For chemical bonds, only valence electrons play a role, which are the electrons of the outer shell ($N = 2$ for C). To make a stable bond with another atom, the atom tries to achieve a noble gas configuration. This configuration is characterized by eight valence electrons (two for hydrogen with $N = 1$) and results from an energy minimization (octet rule). If the electrons are shared between both atoms, this bond is called covalent, in case of a complete electron transfer it is called ionic (e.g. sodium chloride, Na^+Cl^-). Note that a covalent bond between two atoms with different

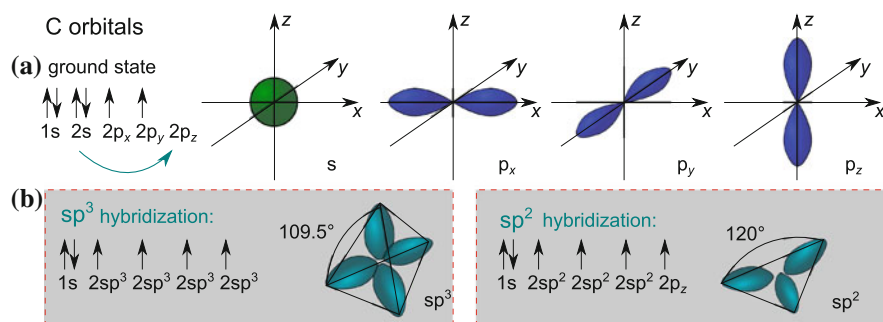


Fig. 3.1 **a** Electron configuration and molecular orbitals of a single carbon (C) atom. **b** Hybridization, where the three (two) 2p orbitals and the 2s orbital form four sp^3 (three sp^2) hybrid orbitals

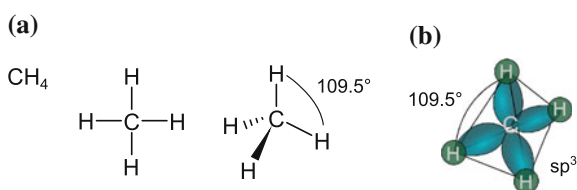
electronegativity gives rise to a dipole due to partial charge transfer (e.g. in H_2O). We will make use of this polarity when discussing the design of absorber materials in Sect. 3.6.3.

Conjugated Systems

We start our study of covalent bonding with a simple hydrocarbon, the methane CH_4 : The central carbon atom with four valence electrons shares one with each hydrogen, also delivering one electron for the bond, which is represented by a line in the Lewis structure of Fig. 3.2a. This results for both, H and C, in a noble gas configuration (He and Ar). The four bonds represent overlapping orbitals and the equilibrium angle between the bonds is 109.5° . In this configuration, the H atoms have the maximum possible distance from each other, such that a symmetric tetrahedron is formed. The tetrahedron also guarantees the optimum location of the (repulsive) electron orbitals according to valence shell electron pair repulsion (VSEPR) theory [1].

The four bonding orbitals cannot result from a simple overlap of the three orthogonal p-orbitals and the single symmetric s-orbital of the binding partners. They constitute four new orbitals, called sp^3 (Fig. 3.1b), because they result from an overlap of the s- and the three p-orbitals of the C atom. This effect is called hybridization where the four sp^3 orbitals are occupied by one electron each. It implies that one C valence electron from the s-orbital and three electrons from the p-orbital have each entered an sp^3 -orbital. The energy required for the rearrangement and repopulation

Fig. 3.2 Methane (CH_4) molecule: **a** compact Lewis structure and **b** visualization of the bonding orbitals and the bonding angle



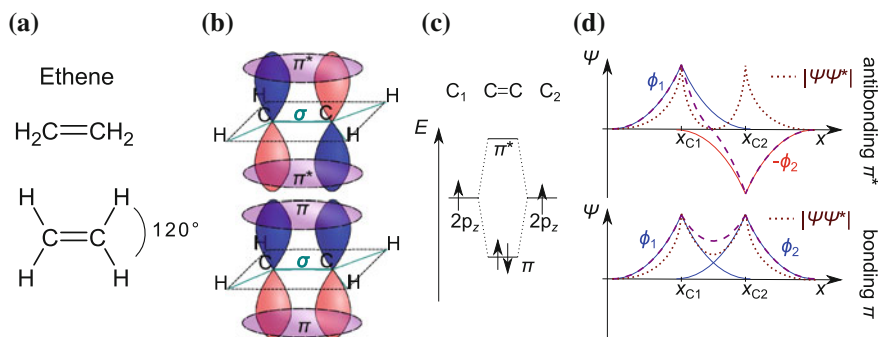


Fig. 3.3 a–c Ethene (C_2H_4) molecule: **a** compact Lewis structures, **b** visualization of bonding and antibonding π -orbitals and **c** their energies. Colors of the orbitals denote the phase of the wave function as sketched in **(d)**. An antibonding orbital lies higher in energy than the occupied bonding orbital. **d** Linear combination of atomic orbitals (solid lines) with the cores located at $x_{\text{C}1}$ and $x_{\text{C}2}$ defining the molecular electron wave function (dashed) and probability distribution (dotted)

of the orbitals is compensated by the formation of bonds to the H atoms. They are so-called σ (sigma) bonds, consisting of two electrons in the overlapping $\text{sp}^3(\text{C})$ - $\text{s}(\text{H})$ orbital shared between C and H (Fig. 3.2b). In the quantum-mechanical picture, these bonds are approximately formed by linear combinations of the single-atom orbitals (LCAO method [2]), leading to a splitting of the energy eigenvalues. Depending on the sign (or the phase) of the two overlapping wave functions ϕ , bonding and antibonding (high energy) states Ψ are formed. The principle is illustrated in Fig. 3.3d for another example which we will discuss next. Bonding orbitals are characterized by a lower energy than antibonding orbitals and a high probability of finding an electron between the atoms. Due to symmetry reasons only these two combinations are allowed. If one imagines a bond between two identical atoms, this is directly plausible, because the probability distribution $\Psi\Psi^*$ remains symmetric only in these two cases. In a relaxed, i.e. equilibrium, state, only the bonding orbital is expected to be occupied.

Proceeding with a more complex molecule, ethene C_2H_4 , we find a double bond between the two C atoms, so that every C atom has only three neighbors (Fig. 3.3a). This constellation results from one s- and two p-orbitals hybridizing to three new sp^2 orbitals, which are occupied by one electron each (Fig. 3.1b). The optimum occupation of space leads to a configuration with angles of 120° between the bonds, which lay within one plane. The perpendicular p-orbital (p_z) of each C atom remains unchanged. These p-orbitals of the two C atoms overlap in a region out of the plane and form a so-called π (pi) bond, which is again dependent on the sign of the combination, bonding (π) or antibonding (π^*). Thus, a double bond, indicated by two lines in the Lewis structure, consists of a σ bond due to two overlapping sp^2 (line in Fig. 3.3b) and a π bond established by two overlapping p_z -orbitals. A triple bond would have two π bonds.

The ethene molecule is planar. The location of the π -orbital is shown in Fig. 3.3b. In principle it is the result of electrostatic forces on the π electron gas. Attraction from the

positive carbon cores and repulsion from the C–C and C–H σ bonds favor a location of the π -orbital out of the plane of the σ bonds, however close to the positive cores.

The discussed chemistry of covalent bonding is also present in inorganic semiconductors, e.g. diamond or silicon with the same sp^3 tetragonal binding angles. Such a three-dimensional configuration leads to stable intrinsic materials, showing semiconductive properties due to their band structure and due to a high delocalization of additionally inserted electrons. Organic semiconductors consist of (covalently bound) hydrocarbon molecules as their basic units, which develop only weak bonds between each other. Among this class of molecules, aromatic compounds are very interesting, because they show extended π -systems, which are capable of electron transport due to a high delocalization. Aromatics are planar ring molecules with each atom providing one p-orbital perpendicular to the plane. The number of these π electrons has to fulfill $4n + 2$ with $n \in \mathbb{N}$ according to Hückel's rule [3].

The simplest aromatic compound is benzene, consisting of six C atoms in a ring, each forming a bond with one H and a double and single bond with the neighboring C atoms [4]. Two possible realizations, so-called resonant (mesomeric) structures, can be imagined and are shown in Fig. 3.4a, where neither configuration is preferred due to symmetry reasons. In reality, energy minimization leads to the same length of each bond (≈ 140 pm = 1.4 Å) [5], which is found between the length of a single (146–148 pm) and a double bond (130–135 pm) [6]. One might draw a circle in the Lewis structure, which has the disadvantage that electrons cannot be counted.

In the molecular orbital picture, every C atom forms three sp^2 -orbitals (σ bonds) and one perpendicular p_z -orbital (Fig. 3.4b). The overlap results in six π -orbitals with different energies depending again on the phase overlap, which means on the number of “nodes” as shown in Fig. 3.4c. The six electrons occupy the 3 lower-lying bonding π -orbitals, whereas the 3 antibonding π^* -orbitals are unoccupied when the molecule is in its ground state. The difference between the highest occupied molecular orbital (HOMO, highest π) and the lowest unoccupied molecular orbital (LUMO, lowest π^*)

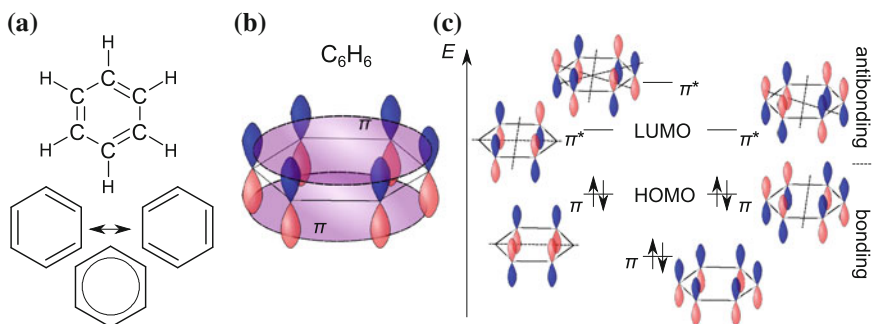


Fig. 3.4 Benzene: **a** Kekulé structure, consisting of two resonance structures (mesomerism). **b** Visualization of the location of the lowest bonding π -orbital. **c** The position of the six energy levels resulting from the overlap of the six p_z orbitals. The more nodes are found in the wave function, the higher is the energy

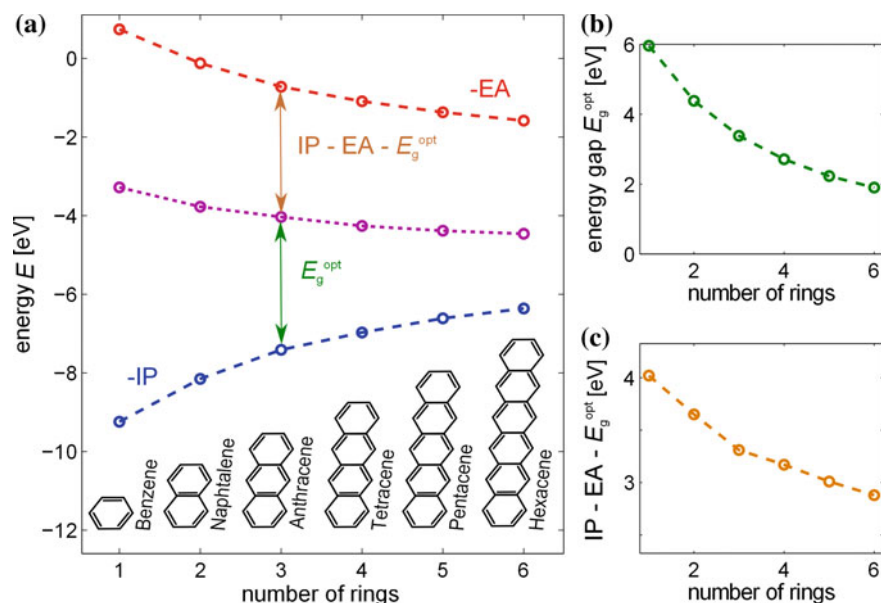


Fig. 3.5 Energy levels related to the π frontier orbitals of oligoacetenes as a function of the number of rings. **a** Ionization potential (IP) and electron affinity (EA) determined by photoelectron spectroscopy, **b** optical gap E_g^{opt} , i.e. HOMO $\rightarrow$ LUMO transition, determined by absorption measurements, **c** difference between optical and electrical ($IP - EA$) gap. Both gaps decrease and EA and IP tend to converge with a larger number of rings, i.e. a larger π -system. Data are from [8, 9] measured in gas phase with photoelectron and UV/vis absorption spectroscopy. The EA is deduced from half wave reduction potentials measured in aprotic (non hydrogen-donating) solvents

of benzene is in the range of 6 eV, which corresponds to a UV photon wavelength of 250 nm [7].

An extension of the π -system by, e.g., adding more rings, leads to a further spreading of single energy levels and delocalization of the π electrons, which decreases the HOMO-LUMO distance as visualized at a decreased optical gap in Fig. 3.5b. For example, the HOMO-LUMO gap of pentacene (5 rings) is 2.2 eV (560 nm) [7]. This trend in the HOMO-LUMO gap can be illustrated considering an electron in the π -system as particle in a box [10] whose size represents the extension of the π -system. The solution of the Schrödinger equation of this system directly results in a decreased distance between the energy eigenvalues for a larger box size. The adjustability of the gap provides tunable optical transitions, also in the visible spectral range. This property paired with the formation of an extended π -system makes aromatic compounds very interesting for optoelectronic applications. That is why many molecules employed in organic electronics are based on aromatic or similar π -conjugated systems. Also non-aromatic systems can show alternating double and single bonds, so-called conjugated bonds, which are the condition for a delocalization of the π electrons. Instead of stopping with the ethene (ethylene) molecule, we could imagine a longer carbon chain. The result could for instance be a

conjugated- $\text{C}=\text{C}-\text{C}=\text{C}-\text{C}=\leftrightarrow=\text{C}-\text{C}=\text{C}-\text{C}=\text{C}$ -chain where each C atom contributes one π electron (cf. polyacetylene in Fig. 3.57).

One important material class of conjugated molecules are polymers. These macromolecules are characterized by a basic unit called monomer. A chain of repeated identical monomers, which are covalently bound, makes up the compound. The conjugation can be localized on the monomer or it can be spread over several monomers depending on the nature of bonding and the monomer itself. Comparable to the series in Fig. 3.5, the positions of the frontier orbitals converge for a sufficiently large number of conjugated monomers meaning that adding further monomers does not (significantly) influence the optical properties of the material. This threshold value of monomers (in the order of 10) defines whether the compound is called polymer (above threshold) or oligomer (below threshold). We will discuss examples of molecules that are relevant for organic solar cells in Sect. 3.6.3.

Electron Configurations

In the previous section, we have already mentioned the electron configuration of carbon. We have introduced how molecular orbitals are formed when a molecule is assembled of several atoms. For this purpose we applied the LCAO method which predicts molecular orbitals as a result of overlapping atomic orbitals. Now, we study the principles that determine how molecular orbitals and in general atomic orbitals are occupied by electrons.

The “filling” of the orbitals follows energy minimization and is described by so-called electron configurations. Here, the spin of the involved electrons is of particular importance. It can be regarded as a kind of quantized angular momentum of spinning electrons. However, it is a much more general quantum mechanical property of all elementary particles. We do not go into detail here and refer to textbooks on this topic [11, 12]. All we have to know or accept is that electrons are fermions. They are half-integer spin particles. The spin can be described by a linear combination of two eigenstates called spin up and spin down, $s = +1/2$ and $s = -1/2$. Imagine a projection of the spin vector onto a selected axis in space. As the quantum mechanical spin only contains the direction (no angular velocity), the projection allows for two options: Either a rotation in forward (spin up) or in reverse (spin down) direction regarding the selected axis. These two quantum states have to be considered as an additional degree of freedom that an electron can occupy obeying the Pauli principle. We have already made use of that principle when, e.g., introducing the Carbon atom with an inner shell that is occupied by two electrons ($1s^2$), i.e. the $1s$ shell is occupied by two electrons, one with spin up and one with spin down.

In quantum chemistry a commonly used parameter related to the spin is the spin multiplicity which is defined as:

$$\text{multiplicity} = 2S + 1, \quad S = \left| \sum_i s_i \right|. \quad (3.1)$$

The multiplicity is a measure of the number of particles with unpaired spin in a (multi-particle) system. To calculate S for a molecule with several electrons, we can simply count all unpaired electrons and multiply the obtained number by $1/2$. If we apply it to CH_3 for example, we find that the orbitals are occupied by two electrons with paired spins. Consequently, the multiplicity of this electron configuration (in the ground state) is 1 ($S = 0$).

In general, the electron configuration of atoms and molecules can be described by the Aufbau principle and Hund's rule. The former states that the states with lowest energy are filled first. The latter postulates that in case of degenerate orbitals, the configuration with the highest multiplicity has the lowest energy and, therefore, results in the most stable atomic or molecular configuration. Recall that we drew the electron configuration for a Carbon atom according to this principle, when we placed two electrons in two different degenerate p-orbitals for $N = 2$ (cf. Fig. 3.1).

Now we briefly introduce the nomenclature of states with different multiplicity with the aid of Fig. 3.6. We arbitrarily select a molecule that has four π electrons (could also be an atom with four valence electrons). We call the molecule M and depict the electron configuration of its ground state in (a). As we do not have energetically degenerate energy levels, the electrons occupy the two π -orbitals in pairs. The multiplicity is one and the state is called singlet, denoted by the superscript 1: $^1M_0$. The 0 in the index indicates the ground state. When we remove one electron (b), the molecule becomes a radical cation with multiplicity 2 and is thus called doublet $^2M^+$. Note that the electronic state is the same, i.e. a cation with only one electron in the π_0 orbital, but there are two different electron configurations dependent on the spin of this electron. A doublet can also be formed when an electron is added (d). Then the molecule becomes a radical anion $^2M^-$. The term "radical" indicates that these configurations with unpaired electrons are very reactive as they tend to reach a closed-shell configuration.

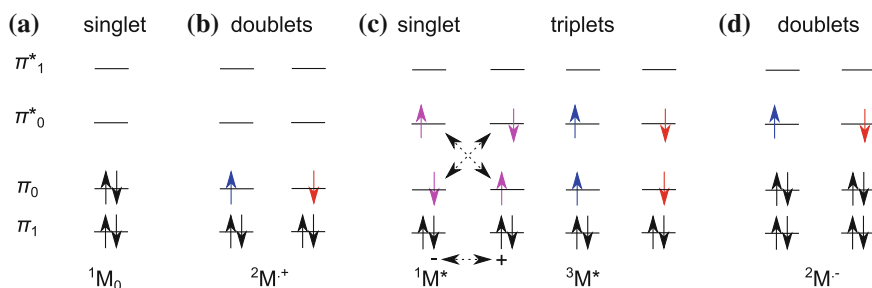


Fig. 3.6 Electron configurations of a molecule describing singlet, doublet, and triplet states. Note that in (c) a combination of two electrons in different orbitals (here one in π_0 and one in π_0^*) allows for four different permutations regarding the spin. The new wave function (including the spin) has to be constructed from the single-electron wave functions obeying the quantum mechanical picture of the indistinguishability of two electrons. That is why linear combinations (symbolized by the dashed arrows) of the two spin wave functions depicted in magenta have to be taken, which result dependent on the sign in one singlet (*minus*) and one triplet state (*plus*) **a** ground state **b** radical cation **c** singlet/triplet excited state **d** radical anion

We can change the configuration also without changing the number of electrons. We can remove one electron from the π_0 orbital and place it in a π_0^* orbital (c). This configuration represents an excited state of the molecule, which is not in its lowest energy state. Consequently, it is not stable, but has a certain lifetime before it relaxes back to the ground state. The excited state can be created imagining four different combinations of two electrons with either spin up or down, one located in the π_0 and the other one in the π_0^* orbital. Their spins can be either anti-parallel or parallel. The multiplicity is either one (singlet) or three, which is called triplet. Let us assume that we combine two electrons with uncorrelated spin, when forming the excited state. To determine the ratio between singlet and triplet, we have to consider that the four permutations mentioned are single-particle states. The new wave function is the product of these single particle states. According to quantum mechanics the wave function $\Psi(1, 2)$ of two fermions 1 and 2 has to be anti-symmetric, i.e. $\Psi(1, 2) = -\Psi(2, 1)$ [for bosons symmetric $\Psi(1, 2) = \Psi(2, 1)$]. Both conditions satisfy the indistinguishability of elementary particles demanded by quantum mechanics, because the measurable probability density function is the square modulus of the wave function $|\Psi(1, 2)|^2 = |\Psi(2, 1)|^2$.

Wave functions which depend on several parameters are commonly approximated by a product of independent functions (product ansatz). Here, we can treat the spatial $\Psi_r(1, 2)$ and the spin part $\Psi_s(1, 2)$ separately. Multiplying both demands for either the spatial part or the spin part to be antisymmetric. Let us look at $\Psi_s(1, 2)$ for the four possible permutations of two electrons in different orbitals as shown in (c): If we combine two spin-up or two spin-down electrons, the multiplicity is three (triplets) and we cannot distinguish them regarding their spin (two states on the right). The resulting spin wave function is the same independently of which electron is called number 1 or 2. In contrast, if we combine one spin-up and one spin-down electron in two different orbitals, an interchange results in a different situation, i.e. different spin wave functions. This result is artificial and not allowed. We, therefore, make them indistinguishable by linear combinations of the two single-particle wave functions, which are for particle number 1 $\Psi_s^+(1)$ and $\Psi_s^-(1)$ for spin up and spin down, respectively. For particle number 2 we write $\Psi_s^+(2)$ (spin up) and $\Psi_s^-(2)$ (spin down).

The resulting spin wave functions can be calculated using so-called Slater determinants. For two electrons, we get two new wave functions depending on the sign in the linear combination. An addition of the products ($\Psi_s(1, 2) = 1/\sqrt{2} (\Psi_s^+(1) \cdot \Psi_s^-(2) + \Psi_s^-(1) \cdot \Psi_s^+(2))$), $1/\sqrt{2}$ is a normalization factor) results in a symmetric spin wave function. Hence, the spins are unpaired and the multiplicity is three. A subtraction ($\Psi_s(1, 2) = 1/\sqrt{2} (\Psi_s^+(1) \cdot \Psi_s^-(2) - \Psi_s^-(1) \cdot \Psi_s^+(2))$) describes an antisymmetric wave function, meaning that the spins are paired. Consequently, the multiplicity is one. We recognize that triplets demand for an antisymmetric spatial part of the wave function. In contrast, singlets require a symmetric spacial part of the wave function to guarantee the anti-symmetry of $\Psi(1, 2) = \Psi_r(1, 2) \cdot \Psi_s(1, 2)$. In sum we have three distinguishable triplet configurations, but one singlet configuration. Consequently, when statistically forming excited states using electrons with uncorrelated spins, the ratio between singlets and triplets is 1:3. This ratio is

important in organic light-emitting diodes where electrons and holes are injected and form singlet and triplet states, whose optical properties (emission wavelength and in particular emission yield) differ strongly as we will describe in the next section.

Note that (neutral) molecules in the ground state are not necessarily singlet. For instance, oxygen (O_2) is triplet in its most stable form due to two unpaired electrons, which explain the paramagnetic behavior. However, we presuppose in the following discussions that the conjugated molecules that make up our semiconductor are in a singlet ground state.

Both, molecular orbitals and electron configurations, are not observables. What can be observed for instance is their interaction with photons, which we discuss in the following.

Absorption and Emission

A photon can stimulate the transition of electrons between different molecular orbitals. In a typical absorption spectrum of a single molecule (measured in a molecular ensemble in gas phase), $\pi - \pi^*$ transitions are expected to be observed as sharp lines. These lines are superimposed by vibrational, rotational and translational manifolds increasing the energy of an electronic state. The energy levels of excited states introduced in Fig. 3.6c and possible transitions are summarized in Fig. 3.7, which shows an extended Jablonski diagram for valence electrons of a molecule.

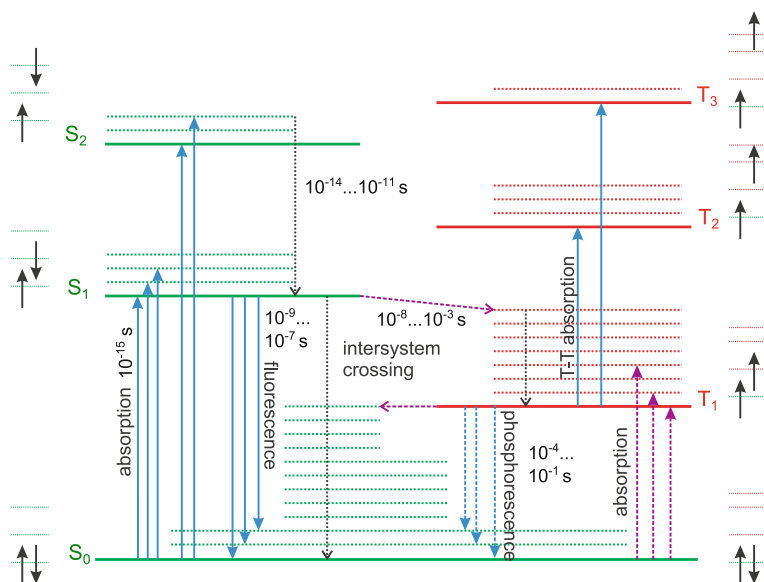


Fig. 3.7 Jablonski scheme with singlet (S) and triplet (T) states and their vibrational manifolds (dotted). Solid lines denote exemplary optical transitions, dashed lines spin-forbidden transitions (intersystem crossing), and dotted lines non-radiative internal conversion paths (redrawn after [7, 13]). The numbers indicate typical timescales of the individual processes

Electronic states are plotted as solid lines and vibrational states are dashed. Typically, the vibrational manifolds show a characteristic spacing of around 100 meV, each superimposed by rotational and translational sublevels of energies in the range of 10 meV.

In the Jablonski diagram the excited states are categorized by their multiplicity, singlet states on the left and triplet states on the right. The ground state of a molecule usually shows multiplicity of one, which we called singlet, because all orbitals up to the HOMO are occupied by paired electrons. They have opposite spins, leading to an overall spin of zero (3.1).

The ground state with energy 0 is denoted as S_0 . Excited (singlet) states are called $S_1, S_2 \dots$. The energy related to the absorption or emission of a photon between S_0 and S_1 is $E(^1M^*) - E(^1M_0)$ using the nomenclature we introduced for electron configurations. Two electrons in different orbitals with unpaired (i.e. parallel) spins are triplets $T_1, T_2 \dots$. The energy related to a $S_0 \rightarrow T_1$ transition is $E(^3M^*) - E(^1M_0)$. Triplet energies are commonly found to be lower than singlet energies. The reason is the Pauli exclusion principle, allowing a larger wave function overlap (some overlap is needed for a transition) of electrons with antiparallel spins in two different orbitals. Hence, on average, electrons with antiparallel spins (singlets) are found closer together, which causes a larger Coulombic repulsive energy. Consequently, singlets have a higher energy than triplets [13]. Note that this is a rather intuitive picture. More rigorously, the difference between triplet and singlet energies is predicted by the so-called exchange interaction, which is a purely quantum mechanical property. It is related to the indistinguishability and the requirements for either symmetric or antisymmetric wave functions. In the previous section we found that a symmetric spin part (triplet) demands for an antisymmetric spatial part and vice versa. Although the exchange interaction depends on the symmetry of the spatial part, it is directly linked to the spin part due to the requirements for an antisymmetric overall wave function. According to this theory, triplet states exhibit a lower energy than singlet states.

Singlet-triplet transitions are spin-forbidden, but can occur due to spin-orbit coupling. This interaction between the spin and the angular momentum of the electron allows for intersystem crossing (dashed in Fig. 3.7). As this process is not very likely, a T_1 state, which decays to S_0 , has a much longer lifetime (commonly milliseconds) than an S_1 state (typically μs -ns) [7, 13]. The probability for intersystem crossing is enhanced when a heavy atom is included in the molecule as done for iridium-based emitters in organic light-emitting diodes. Less planar molecules also show stronger intersystem crossing as out-of plane vibrations of the π -system lead to an enhanced π - σ interaction, which increases spin-orbit coupling [14].

Higher excited states ($S_{2,3} \dots T_{2,3} \dots$) show very short lifetimes and relax to the first excited state by internal conversion within picoseconds (dotted lines). Internal conversion is a non-radiative process giving off the energy to vibrational modes, whereas transitions (according to Kasha's rule mainly from S_1 and T_1) to the ground state can be radiative [15]. This luminescence radiation from singlets is called fluorescence and from the longer living triplets phosphorescence. The photoluminescence signal is commonly shifted to larger wavelengths ("red shift") compared to

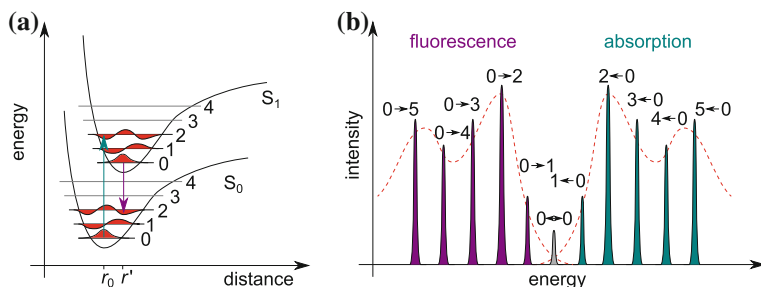


Fig. 3.8 Franck-Condon shift due to vibronic transitions: **a** sketch for a two-atomic molecule where the interatomic distance differs between excited (r') and ground state (r_0). **b** Absorption and fluorescence emission between vibrational ground states and vibrational manifolds of S_0 and S_1 , respectively. The $2 \leftrightarrow 0$ peak is largest due to the favored vertical vibronic transition resulting from a larger overlap in wave functions as shown in (a). In solution or solid phase the peaks of the spectrum in gas phase are broadened (dashed line). (Redrawn after [7, 13])

the absorption spectrum (Stokes shift) due to structural relaxations, minimizing the electronic energy of the excited state.

The probability of optical transitions between different electronic levels considering their vibrational sublevels is explained by the Franck-Condon principle. It describes so-called vibronic transitions, which are characterized by a simultaneous change of electronic and vibrational states. The Franck-Condon principle states that an optical transition is most probable for a vertical transition, where a motion of the much heavier (roughly 1,000 times) and thus slower nuclei is not required. Such a transition usually does not occur between two vibrationally relaxed states, because they exhibit different equilibrium positions of the nuclei. Quantum mechanically spoken, the most probable (vibronic) transition is the one with the highest wave function overlap between electronic ground and excited state, as sketched in Fig. 3.8 for a two-atomic system. In this example absorption happens predominantly from the relaxed S_0 state into a non-relaxed S_1 state. After a fast internal conversion, emission is most likely from the (vibrationally) relaxed S_1 state into a non-relaxed S_0 state.

The Franck-Condon principle presupposes the Born-Oppenheimer approximation discussed for inorganic materials in Sect. 2.2.1. The Born-Oppenheimer approximation states that nuclear and electron motion can be separated to solve the Schrödinger Equation for a system consisting of several atoms. The Franck-Condon principle (Condon approximation) additionally demands that electronic transitions occur at timescales much faster than nuclear motion. These transitions are then of vibronic nature.

Whereas the Bohr model explains the spectral lines of an atom, the introduction of quantum mechanics allowed for a quantitative description of the different brightness, i.e. absorption and emission strength of transitions. In case of a weak electronic coupling between the states, we can apply perturbation theory to describe the absorption of a molecule via transition probabilities. A very general expression of the transition

probability T between states i and j is:

$$T_{i \rightarrow j} = \frac{2\pi}{\hbar} |\langle \Psi_j | H' | \Psi_i \rangle|^2 \rho. \quad (3.2)$$

This equation is known as Fermi's golden rule although it was mainly discovered by Dirac. It is very general and can be applied to describe a variety of transitions between different quantum-mechanical states. Here, $\langle \Psi_j | H' | \Psi_i \rangle$ is called the matrix element of the perturbation with the initial eigenstate $|\Psi_i\rangle$ and the final eigenstate $|\Psi_j\rangle$. H' is the Hamiltonian describing the physical interaction caused by stimulation due to a photon having the energy $E_j - E_i$; ρ is the density of final states.

The transition probability is proportional to the strength of the electromagnetic field (density of photons), which is included in the Hamiltonian. From the classical treatment of absorption it is known that we can use the (approximated) model of electric dipole transitions to describe absorption. The dipole moment μ equals $e\mathbf{r}$ with the displacement vector $\mathbf{r}$ between the charges $\pm e$. Thus, we can use the dipole operator μ to express the matrix element:

$$\mu = \mu_e + \mu_c = -e \sum_k \mathbf{r}_k + e \sum_l Z_l \mathbf{R}_l. \quad (3.3)$$

Here, we summed the contributions from k electrons at position $\mathbf{r}_k$ and all l nuclei at position $\mathbf{R}_l$ with charge eZ_l . According to the product-ansatz we separate the wave functions Ψ^i and Ψ^j in an electronic and vibrational contribution:

$$\Psi = \Psi_e(\mathbf{r}) \Psi_v(\mathbf{R}), \quad (3.4)$$

where the first depends on the position of the electrons and the second on the position of the cores. The probability amplitude is then proportional to:

$$\begin{aligned} \langle \Psi_j | \mu | \Psi_i \rangle &= \langle \Psi_e^j \Psi_v^j | \mu | \Psi_e^i \Psi_v^i \rangle \\ &= \langle \Psi_e^j \Psi_v^j | \mu_e | \Psi_e^i \Psi_v^i \rangle + \langle \Psi_e^j \Psi_v^j | \mu_c | \Psi_e^i \Psi_v^i \rangle \\ &= \underbrace{\langle \Psi_v^j | \Psi_v^i \rangle}_{\text{Franck-Condon factor}} \cdot \underbrace{\langle \Psi_e^j | \mu_e | \Psi_e^i \rangle + \langle \Psi_e^j | \mu_c | \Psi_e^i \rangle}_{\text{orbital selection}} \quad (3.5) \end{aligned}$$

Here, we ignored the spin wave functions which can be added as a third factor to (3.4) and will result in an additional selection rule. The first factor in (3.5) is the Franck-Condon factor describing the different absorption strength for different vibronic transitions in Fig. 3.8 due to vibrational wave function overlap. The second factor describes the electronic orbital selection. To separate these two contributions, we assumed that the scalar product describing the electronic orbital selection is

independent of the coordinates of the nuclei (Condon approximation). Note that this is only approximately given. The second summand is 0 as electronic wave functions between two different states i and j are orthogonal.

The dipole matrix element can be related to the oscillator strength f , originating from the semi-classical description of the electron-nucleus interaction described by a Lorentz oscillator. There, f as a dimensionless quantity describes the strength of an electronic transition:

$$f_{i,j} = \frac{2}{3} \frac{m_e}{\hbar^2} (E_j - E_i) |\langle \Psi_j | H' | \Psi_i \rangle|^2 \quad (3.6)$$

with the electron mass m_e .

The oscillator strength can be expressed by a so-called absorption cross section σ :

$$\sigma_{i,j} = \frac{\pi e^2}{m_e c} f_{i,j} = \frac{2}{3} \frac{\pi e^2}{c \hbar^2} (E_j - E_i) |\langle \Psi_j | H' | \Psi_i \rangle|^2. \quad (3.7)$$

The absorption cross section has the unit of an area. Multiplying σ of a molecule with the molecular density N_M in a solution or thin film gives the absorption coefficient α per unit length (e.g. cm^{-1}):

$$\alpha_{i,j} = \sigma_{i,j} N_M. \quad (3.8)$$

The absorption coefficient is the commonly used quantity to describe absorption in a macroscopic material parameter: It is a function of the wavelength λ and experimentally accessible when measuring transmission and reflection spectra of a sample with a given thickness [cf. (4.77)]. Note that the measured $\alpha(\lambda)$ contains not only one transition but a superposition of all accessible optical transitions in the material at each λ . We have used α already when discussing absorption and emission of a semiconductor in Sect. 2.2.2 and we will use it further when characterizing organic molecules.

Ionization Potential and Electron Affinity

According to Koopmans' theorem [16], the HOMO level is approximately equal to the energy needed to ionize the molecule, which is called ionization potential ($\text{IP} = -\text{HOMO}$). Note the compact way of writing, where we simply set the orbital term HOMO to an energy instead of writing $\text{IP} = -E_{\text{HOMO}}$, which would be more correct. Using the electron configurations of our molecule M , the IP is defined as the energy difference between ground state and the radical cation state: $\text{IP} = E(^1M_0) - E(^2M^+)$. In chemistry, the IP is also called oxidation potential. The energy gained when adding an additional electron to a neutral molecule, then forming an anion, is the electron affinity ($\text{EA} = -\text{LUMO}$) as illustrated in Fig. 3.9. Note that we defined EA as a positive value according to the sign convention of semiconductor physics. The EA can be expressed as $\text{EA} = E(^2M^-) - E(^1M_0)$, which is equal to the reduction potential of the molecule.

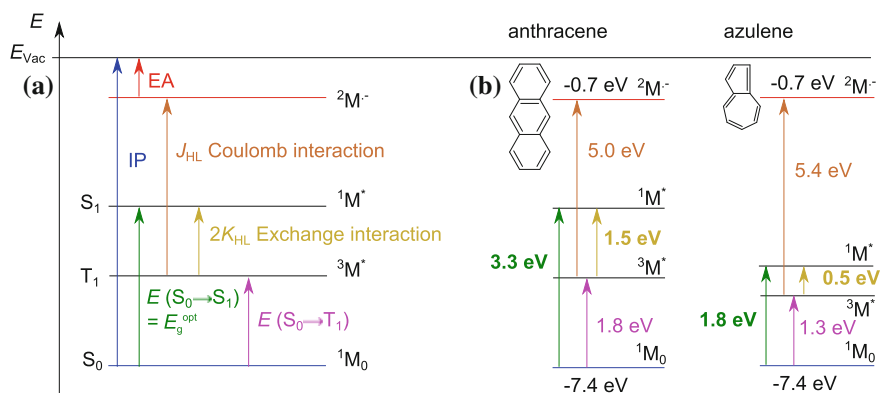


Fig. 3.9 The energies of ground state, first excited singlet and triplet state, and IP and EA: **a** in general and **b** for selected molecules. The comparison between anthracene and azulene shows that the energy for a HOMO $\rightarrow$ LUMO transition E_g^{opt} can differ significantly although IP and EA are the same. This difference is due to the Coulomb and exchange interaction. That is why anthracene is colorless whereas azulene is blue [17]

One major question is how IP and EA are related to the energies of excited states seen in optical transitions. The approximation $h\nu_{(\text{HOMO} \rightarrow \text{LUMO})} = \text{IP} - \text{EA}$, derived in Chap. 2 for inorganic semiconductors is not valid for a molecule. Within the molecule interactions between electrons in different orbitals are much stronger than for electrons in conduction and valence band of an inorganic semiconductor. We address two major contributions to these interactions: One was discussed when we explained the energy difference between singlet and triplet states (singlet-triplet splitting) seen in the Jablonski diagram (cf. Fig. 3.7). It is the exchange interaction K , a quantum-mechanical property which decreases the energy of triplet states. The second quantum-mechanical contribution is the electron repulsion integral J . This energy is basically due to the classical electrostatic repulsion force given by Coulomb's law [11, 12]. The resulting energies of the different states are depicted in Fig. 3.9a, showing that Coulomb J_{HL} and exchange K_{HL} interactions of electrons in HOMO and LUMO give rise to a significant difference between excited and ionized state.

With part (b) of the figure, we illustrate the consequences of the differences following Michl et al. [17] who compared anthracene with azulene, two molecules with similar IP and EA, but different color. Both molecular structures and the respective energy levels are shown in the figure. The difference between the optical HOMO $\rightarrow$ LUMO transition ($E_g^{\text{opt}} = E(S_0 \rightarrow S_1)$) and $\text{IP} - \text{EA}$ is around 5 eV. This difference is also obvious in Fig. 3.5a and is mainly due to J_{HL} . The intuitive reason for this difference becomes clear when we compare the following two situations: (i) We place one (additional) electron on the LUMO of the molecule forming $^2M^-$. (ii) We first remove one electron from the molecule and put one onto the LUMO afterwards. In (i) we gain simply EA. In (ii) we first need IP and when putting the electron back we gain more than EA as the Coulomb repulsion is reduced due to the missing electron

in the HOMO. As case (ii) is in a first approximation equivalent to a direct optical $\text{HOMO} \rightarrow \text{LUMO}$ excitation, the energy of this transition is much smaller than $\text{IP} - \text{EA}$.

Although J_{HL} explains the reduced optical gap, it cannot explain the differences in colors of anthracene and azulene. Here, the influence of K_{HL} becomes significant, which defines the singlet-triplet splitting and is much larger for anthracene than for azulene. As the color is dominated by the spin-allowed transition $S_0 \rightarrow S_1$, anthracene with an optical gap of 3.3 eV (375 nm) is colorless and azulene which absorbs around 1.8 eV (685 nm) is blue. The reason for this difference in K_{HL} is that the exchange interaction depends strongly on the spatial distributions of HOMO and LUMO on the molecule. Intuitively, we can state that the weaker the spatial overlap, the smaller is the exchange interaction. Whereas HOMO and LUMO are similarly distributed in anthracene (cf. benzene in Fig. 3.4), this is not the case for azulene [17].

We mentioned that J is similar for both molecules. In general, as a rule of thumb, J decreases with molecule size as a larger molecule contains more electrons which are more delocalized. This trend is reflected in Fig. 3.5c showing the difference between $E_{\text{g}}^{\text{opt}}$ and $\text{IP} - \text{EA}$.

What happens if we further ionize a cation? The neutral molecule holds a pair of electrons (with opposite spin) in the HOMO and provides a place for a pair of electrons in the LUMO. For both of the two electrons in the HOMO the energy required for ejection into vacuum is the (same) IP. However, the molecule becomes charged after having ejected or received one electron. Cation or anion are radicals, as they have an unpaired electron in the former HOMO or LUMO of the neutral molecule. Alternatively, one can say that the unpaired electron occupies the single occupied molecular orbital (SOMO), which is a half-filled HOMO (and thus also a kind of LUMO) of the radical.

How do the energy levels of a cation look like compared to those of the neutral molecule? Theoretically, the ionization potential of the cation, which equals the second oxidation potential of the neutral molecule, should increase due to one missing electron, leaving behind a positive net-charge. The difference would be the Coulomb interaction J_{HH} between two electrons in the HOMO. Thus, it holds: $\text{IP}(^2\text{M}^+) = \text{EA}(^1\text{M}^{2+}) = \text{IP}(^1\text{M}^0) + J_{\text{HH}}$, where J_{HH} is in the order of several eV for typical π -conjugated molecules. Commonly, however, differences in that range are not observed experimentally. For larger π -systems (>20–30 electrons) $\text{IP}(^2\text{M}^+)$ and $\text{IP}(^1\text{M}^0)$ almost coincide. This observation is not fully understood as it has not been completely verified by theoretical predictions. Possible reasons are a stabilization of the excited molecule by the surroundings or a reorganization of the radical, as we will discuss in the context of polarons in the next section. Furthermore, a formation of a complex between anion and a neutral molecule in the surroundings $^2(\text{M} - \text{M})^+$ could occur, which could have an IP similar to the neutral molecule [18]. A cation, especially if the molecule is oxidized twice, usually has a lower optical gap than the neutral molecule, as commonly the difference between two π -orbitals (cf. π_0 and π_1 in Fig. 3.6) is lower than the difference between π and π^* orbital. Analogous observations regarding energy gaps exist for a further reduction of an anion.

3.1.2 From Single Molecules to a Molecular Solid

Now we address what happens if molecules are brought together forming solutions or a solid. The main difference between a covalently bound solid (characterized by a high melting point, brittleness, and low intrinsic conductivity) and a molecular solid is found in the weak van der Waals bonds between molecules. These bonds are promoted by fluctuating charges. Such fluctuations induce temporary dipoles, resulting in an attractive force. Commonly, no other type of intermolecular bond can be formed due to a closed shell of each molecule. An exception are some semiconductive organic molecules which form hydrogen bonds [19]. The weak van der Waals bonds are the reason for the low rigidity and melting point of organic solids. Due to the low interactions, organic solids are classified as soft matter. The main spectroscopic properties of the solid coincide to a large extent with those of the single molecule. That is why the terms HOMO and LUMO are also used for the solid. Absorption edges are usually shifted to lower energies due to intermolecular interactions. For a highly ordered molecular crystal, the energies of excited states split due to wave function overlap and form (comparable to inorganics) narrow excitonic bands. As the films of materials commonly applied in organic solar cells do not form single crystals, but are rather amorphous, we do not discuss the properties of molecular crystals any further. The interested reader is referred to [7]. Amorphous layers do not show long-range order and the concept of delocalized crystal waves and energy bands is not suitable. The absorption spectrum of an amorphous solid is comparable to a solution spectrum, where the molecular absorption peaks are shifted. This is called solvent shift and results from a changed polarizability of the surroundings, e.g. induced by the polarity of the solvent (in a solution) or the presence of other polarizable molecules (in a solid). As polarities of ground and excited state can differ, they will be influenced in a different way by the polarity of the surroundings. Furthermore, spectra of an amorphous solid are strongly broadened due to a distribution of intermolecular distances as we have already visualized with the dashed line in Fig. 3.8b.

We want to draw an energy diagram for conducting electrons and holes in an organic solid comparable to the band diagrams of Chap. 2. There, the energy scale refers to the potential of an electron in the film. We call this approach a single-particle picture. This description is not directly compatible with the excitonic picture, shown in the Jablonski diagram of Fig. 3.7 [20], where the energies of excited states are shown. The main difference is in the choice of the reference. In the single-particle picture we choose the vacuum level and in an excited-state diagram the energy of the ground state as reference. On the one hand, we can still compare the energies of excited and ionized states as we have done in Fig. 3.9. On the other hand, we cannot depict the energy levels of excited states in the classical energy level diagram, where energy levels of electrons and holes are depicted, because these energy levels cannot be related to an energy of an electron and hole forming the excited state.

Nevertheless, Fig. 3.10 is an attempt to visualize all energy levels within one picture, where we fix the ground state S_0 of the molecule at the HOMO. The HOMO is referred to the vacuum level (black energy scale), whereas the excited state energies

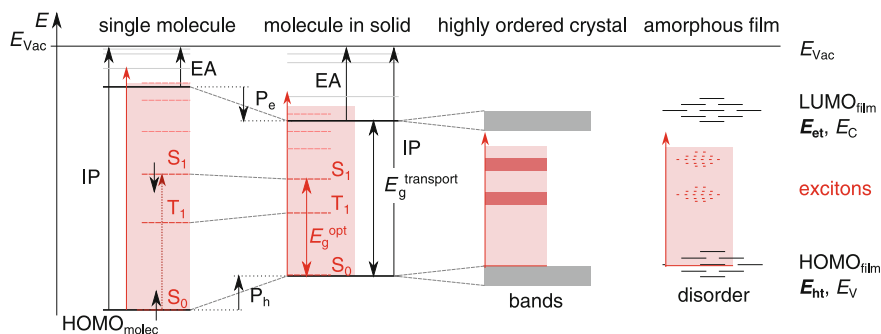


Fig. 3.10 The evolution of the energy levels of a molecular solid from single-molecule levels. Gaps are decreased due to a polarization (P) of the surroundings. Excited states are plotted on a separate scale (in *red*), where the ground state S_0 is placed at the position of the HOMO. Strong interactions in a crystal create bands (as discussed in Sect. 2.2.1) whereas disorder results in a statistical distribution of the energy levels of hopping sites

refer to the ground state (red scale). In this diagram we can still compare energy differences between the two scales. However, e.g. the level of the excited states and the EA cannot be related as the zero value for excited-state energies was arbitrarily set to the HOMO.

Phenomenologically spoken, the charge transport levels of a solid consisting of many molecules are the ionization potential (IP) for a positive charge (hole) and the electron affinity (EA) for a quasi-free electron, as defined in the previous section. In the orbital picture, a mobile electron is located in the LUMO, whereas a hole is transported in the HOMO. This is an approximation and not completely true, as we have put an additional electron onto the molecule or removed one electron completely in case of a hole. More precisely in case of a strong localization of the charge on one molecule, the electron (hole) is located in the SOMO of the anion (cation). We have already mentioned that the SOMO is observed to be close to the LUMO (HOMO) of the neutral molecule, which holds true especially for a molecule located within a film as we will discuss subsequently.

Figure 3.10 shows what happens with the molecular HOMO and LUMO levels, when a solid is formed out of several single molecules: The values shift, decreasing gaps and giving rise to the solvent shift which we have already mentioned in the context of absorption spectra. Polarization effects, resulting from an electrostatic screening, change energy levels, as the charges of neighboring molecules are redistributed, in particular in the presence of an ion. Therefore, it is easier to remove an electron from a molecule in a solid as the electrons of the surroundings partly screen the positive charge of the core. Consequently, the HOMO-LUMO transport gap of a solid is significantly lower than the one expected from a single molecule (Fig. 3.10). The polarization energy P_h can be determined by (ultraviolet) photoelectron spectroscopy (UPS, cf. Sect. 4.9), comparing the IPs of a single molecule and a solid. In

a first approximation, the polarization is independent of the sign of the charge. This implies that P_e equals P_h .

Additionally to the electrical polarization, structural or lattice relaxations contribute to a further slower polarization. The hole or electron in combination with this polarization due to changes in the surroundings is commonly called a positive or negative polaron respectively. This quasi-particle was introduced for ionic [21] and molecular crystals [22] and describes a moving electron carrying the lattice distortion with it (Fig. 3.11a). Nowadays the term polaron is also applied to charges moving in amorphous solids (no lattice defined there) accompanied by structural relaxations of the surroundings. For convenience we will also use the term electron and hole, keeping in mind that polaronic effects are already included in these terms. The formation of the polaron implies a reduction of the energy of the electron (or hole). Consequently, the frontier orbitals of cation and anion, stabilized by the surroundings, are found within the HOMO-LUMO gap of the neutral molecule [23, 24], decreasing the IP and increasing the EA, respectively as depicted in Fig. 3.11b. Note that this sketch emphasizes the additional relaxation, but does not want to imply that a further oxidation of the cation (reduction of the anion) requires less energy than the oxidation (reduction) of the neutral molecule, as we did not consider the Coulomb repulsion interactions here.

The energy gained from the reorganization also results in an optical gap of radical ions which is decreased in comparison to the ground state absorption of the neutral molecule (see e.g. in [25, 26]).

The concept of a polaron is not only related to an abstract environment, but can be illustrated on a molecular level by using a dithiophene molecule as example (Fig. 3.12). Consisting of two thiophene rings, it belongs to the material class of aromatics, which can be verified using Hückel's rule, considering that one of the two lone electron pairs of sulfur is located in the p-orbital of sulfur that contributes to the π -system of the ring. Then, each ring is planar and contains 6 ($=4n + 2$ with

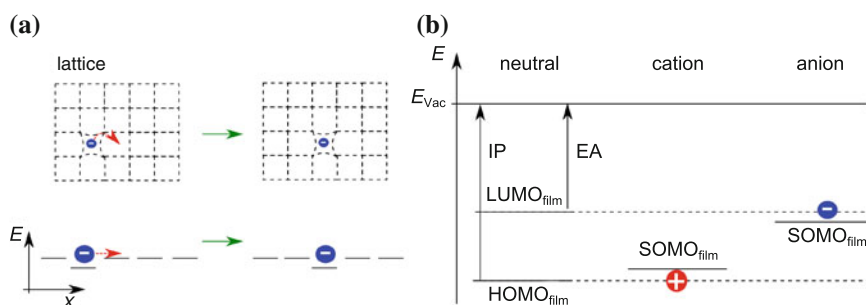


Fig. 3.11 **a** Sketch of the idea of a polaron, which is a charge dragging a lattice distortion with. This energy minimization decreases the energy of a polaron compared to the energy an electron would have in an undistorted lattice. **b** Sketch of ionization potential and electron affinity of a neutral molecule in a solid. Ionized molecules including their environment undergo a reorganization decreasing the energy of a hole on a cation and an electron on an anion

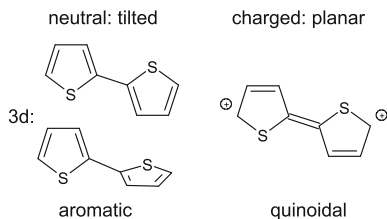


Fig. 3.12 The polaronic effect demonstrated at a dithiophene molecule. Upon being positively charged (here twice, charges are drawn for illustrative purposes only), it changes its structure from an aromatic to a quinoidal form. The first shows torsion between the two rings, whereas the second is planar

$n = 1$) π -electrons like the benzene ring. However, the repulsion of the π -electrons gives rise to a torsion angle >0 between the two rings. The single bond between the two rings allows for this torsion angle. If the molecule is positively charged, a new equilibrium situation occurs, where a double bond is located between the two rings. Then, the molecule changes its shape and becomes planar. Thus, charging of the molecule is accompanied by a structural change. If the charge moves to a neighboring dithiophene or along a polythiophene chain, it drags the distortion with it.

Note that the terms HOMO and LUMO contain some ambiguity. Originally we introduced HOMO and LUMO as orbitals of a neutral molecule, where the first allowed optical transition occurs between HOMO and LUMO. Then, we distinguished between this HOMO $\rightarrow$ LUMO transition and the energy level we want to denote as HOMO and LUMO defining the HOMO as $-IP$ and the LUMO as $-EA$ of the molecule (Koopmans' theorem). This definition is maintained for molecules in an organic film, where LUMO or HOMO refer to the energies where an (additional) electron or hole is located. However, the values obtained for a single molecule are changed when it is embedded in a film due to (electrical polarization) screening effects. Hence HOMO and LUMO levels of the single molecules shift and follow a distribution dependent on the disorder in the film. Their values can be measured employing the outer photo effect. Finally, the presence of a charge induces a further shift due to distortions in the surrounding which give rise to the formation of a polaron. As changes in the coordinates of nuclei is slower than the process of electron emission, photoelectron spectroscopy of uncharged material cannot be used to address the polaron energy (SOMO).

Regarding optical transitions, we avoid the terms HOMO and LUMO from now and call them excitonic denoted by S_x or T_x according to their multiplicity (cf. Jablonski scheme in Fig. 3.7). Furthermore, to avoid confusion, we call the energy levels of the charge carriers **transport energies** E_{et} and E_{ht} , when discussing charge-transport simulations of films. For practicality reasons we set $E_{et} \approx LUMO_{film}$ and $E_{ht} \approx HOMO_{film}$ (Fig. 3.10), where HOMO and LUMO are determined by photoelectron spectroscopy. Applying this approximation later for device simulation, we do not explicitly consider the polaronic properties of moving charge.

In the case of a highly ordered crystal, E_{et} and E_{ht} of Fig. 3.10 are not single levels. The degenerate levels split and form bands as discussed for classical semiconductors in Chap. 2, where we defined band-edge energies. Here, however, bands are narrow (several 100s of meV) due to the low wave function overlap [7]. Thin films employed in solar cells are, as already mentioned, mostly amorphous. Consequently, bands are not formed. Though, the energy levels of the solid cannot be described by single numbers but are commonly assumed to follow a Gaussian distribution consisting of the single energy levels of each molecule in the solid. The reason for this broadening are local changes in polarization energy due to disorder in the amorphous solid. Typical values of the width σ of the distribution are in the range of 50–150 meV. Additionally, trap states within the transport gap can emerge from regions with significantly higher polarization energies due to impurities, regions with a higher crystallinity, or grain boundaries in nano-crystalline materials. Models for the transport mechanisms of excitons and polarons and the role of the energy levels are discussed in the following section. Note that excitons and polarons can interact, which usually results in exciton quenching (non-radiative relaxation).

3.2 Energy and Charge Transport in Organic Semiconductors

Energy (here via excitons) and charge (via polarons) transport in a highly ordered molecular crystal at low temperatures are comparable to the processes in conventional semiconductors described in the previous chapter. These quasi-particles are coherently transported in energy bands with a crystal momentum k . The coherence time is the time until scattering at a defect occurs. If the distance covered by the particle during this time is reduced to the range of the lattice constant or intermolecular distance, coherence is completely lost and transport can be described by hopping from site to site, where a site is a π -conjugated system, i.e. a conjugated (small) molecule or a segment of a polymer contributing to charge transport. This kind of transport is dominant in organic thin films employed in solar cells, because they are commonly nanocrystalline or amorphous.

3.2.1 Exciton Transport

An excited state can be seen as a quasi-particle, which is called an exciton. This exciton can be transferred to a neighboring molecule providing an energy transport by migration. An exciton can be delocalized in case of strong intermolecular interactions as present in a highly crystalline solid. It is then called a Wannier exciton, which can be found in crystalline semiconductors like silicon. Such a large amount of delocalization is commonly not the case in disordered organic materials, where the exciton is mainly located on one (small) molecule or chromophore (conjugated segment of a polymer) and can be treated as an electrically neutral quasi-particle

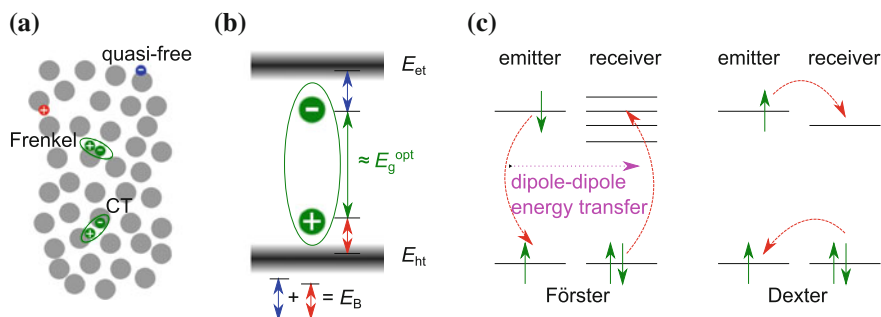


Fig. 3.13 **a** Visualization of a quasi-free charge carrier pair, Frenkel exciton, and charge-transfer (CT) exciton in a molecular solid. **b** Visualization of an exciton (e.g. S_1) as excited state with exciton binding energy E_B in a potential diagram for one electron (single-particle picture). **c** Exciton transport: resonant Förster (only singlet transport) and hopping Dexter transfer (also triplet)

with polaronic nature, called Frenkel exciton (Fig. 3.13a). Such a Frenkel exciton can be regarded as a tightly bound electron-hole pair with the exciton binding energy as difference between its energy and the internal energy of a completely separated electron-hole pair. The binding energy E_B is material dependent and typically in the range of several 100 meV [7], because the dielectric constant of common organic materials is relatively low ($\epsilon_r = 3 \dots 6$) compared to typical inorganic semiconductors ($\epsilon_r = 13 \dots 16$ [27]). Visualizing this energy in an energy-level diagram with transport levels, which is a potential diagram for electrons, leads to the already mentioned difficulty of representing excited states in such a diagram. In this book, an exciton is symbolized by an ellipsoid around an electron and hole located in the energy gap, as shown in Fig. 3.13b. The vertical distance between electron and hole represents the energy of the exciton, which can be expressed as $E_{et} - E_{ht} - E_B$. If the two charges are located on separate neighboring molecules (or molecular segments), the exciton is called a charge transfer (CT) exciton, which can also be found between different molecular species, as we will see later.

The transport of a Frenkel exciton as neutral quasi-particle can be described by a diffusive motion from one molecule (emitter) to a second molecule in the surroundings (receiver). According to Fermi's golden rule (3.2), the transition probability is given by a matrix element with a perturbation Hamiltonian, including electrostatic and electron-exchange interaction potentials. The former is responsible for so-called Förster and the latter for Dexter energy transfer. They are visualized in Fig. 3.13c.

Förster transfer is based on a dipole-dipole interaction, characterized by the spectral overlap of emission and absorption spectrum of emitter and receiver. It decays with distance R^{-6} and is typically long-range (several nm). The energy is transferred by a radiationless but resonant process conserving the spin of both emitter and receiver. Hence, it allows only for singlet transfer, as molecules in the ground state are typically singlets. Förster energy transfer is a near-field effect in contrast to an emission plus reabsorption event, where a real photon is exchanged up to macroscopic distances.

Dexter transfer does not require allowed transitions between emitter and receiver. Electrons can be exchanged by a wave function overlap between nearest neighbors with a rate exponentially decreasing with distance (e^{-R}). This decay limits the distance range to typically 1–2 nm. It can be regarded as a simultaneous transfer of electron and hole between neighboring molecules, which is comparable to hopping charge transport. All transitions which conserve the total spin of the involved molecules are allowed. These include triplet-triplet transitions. Organic solar cell materials show energy migration occurring in the range of 5–40 nm [28, 29], which is much larger than the range where a single Dexter transfer happens. Thus, exciton transport can be described by a multi-step diffusion process. Also Förster energy transfer might be important for solar cells.

Energy migration can be experimentally observed by sensitized fluorescence in a mixed guest-host system, where most of the incident light is absorbed by the host, constituting, e.g., more than 99 % of the film [7]. However, emission is predominantly observed from the guest with a lower S_1 energy, which favors energy transfer onto the guest compared to the reversed direction. The large signal of the emission of the guest can only be explained by an energy transfer to the guest after exciton diffusion in the host. Other methods to prove exciton migration use a luminescence quencher at a location in a defined distance from the location of absorption. The photoluminescence efficiency as a function of the distance between quencher and absorber allows for determining the exciton diffusion length. Furthermore, excitonic processes can be exploited, for instance exciton annihilation, when two excitons meet after diffusion (cf. Sect. 4.9).

3.2.2 Transition Rates and Marcus Theory

In this section, we briefly introduce a theoretical way of describing electron transfer from an initial to a final state, e.g. for hopping transport from one molecule to another. This theory, which is very common in chemistry, can be applied to describe charge transport between equal molecules as well as for charge transfer between different molecules. Both will play an important role in further discussions of the working principle of solar cells. Assuming that the electron transfer is fast compared to the motion of nuclei, we can apply again the Condon approximation. This time, energy of the electron has to be conserved because we discuss charge transport in the dark without having a photon providing/absorbing the energy. Comparable to Fig. 3.8 a diagram with the (Gibb's) free energy $G = U + pV - TS$ can be drawn as a function of the reaction coordinate. The reaction coordinate includes the position and movement (translational, vibrational) of all atomic nuclei of the system. G is a thermodynamic quantity containing also an entropic term (TS with entropy S). If a system changes between two states, ΔG describes the maximum work that is exchanged at a constant pressure p (V is the volume). For describing electron transfer, commonly, changes of the entropic term in the free energy are neglected. Thus, ΔG (at constant pressure) equals the change of the internal energy U only, which in this case is the potential

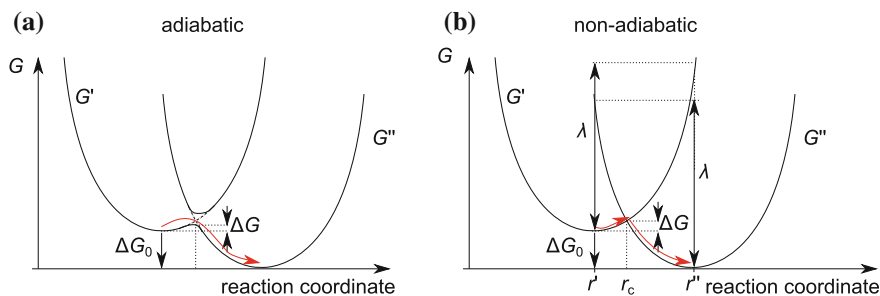


Fig. 3.14 Free energy of educt G' and product G'' state as a function of the reaction coordinate for two cases: **a** adiabatic charge transfer, where the system remains on a low-energy curve, **b** non-adiabatic (hopping) charge transfer, where the interaction between the two states is too weak to change the energy surfaces. Red arrows indicate how the transfer from the equilibrium position of G' to the equilibrium position of G'' occurs

energy E . This energy of the system can be illustrated by a parabola as shown in Fig. 3.14 assuming a harmonic oscillator.

For an intuitive description of the reaction coordinate, we can assign a distance to it, imagining a simple molecule consisting of two atoms joined by a vibrating bond (recall Hooke's law for a spring). Let's say that the left parabola in the figure describes G' of the educts (e.g. situation before charge transfer) and the second parabola G'' of the products (situation after charge transfer). As the system in reality is three-dimensional, G' and G'' are called potential energy surfaces.

How can a transition from G' to G'' occur? On the one hand, a transition between both states can only occur horizontally due to the conservation of energy (this means at resonance). On the other hand, it can only occur vertically due to the Franck-Condon principle. Thus, the transition can only happen at an intersection of the two curves.

There is a certain probability for the system in the initial state to jump into the final state if both states are electronically coupled. If this coupling between both states is strong, the energy surfaces will split up at the intersection as visualized in Fig. 3.14a. Then, the system follows the low-energy curve during the transition and ΔG is an activation energy. It needs to be overcome thermally in the classical picture or via quantum-mechanical tunneling in a semi-classical theory. This transfer happening on one common potential energy surface is called adiabatic. The term "adiabatic" originates from thermodynamics and says that there is no exchange of heat with the environment. Here, it means that a quantum-mechanical jump does not occur, the rate of electron transfer is given by the product of the probability of occupation and the rate of (thermally) crossing this point. A tunneling process would lead to a modification of the transfer rate, as ΔG is not required to be (completely) overcome.

In case of weak interaction, the splitting at the intersection is negligible and the system tends to remain in the educt state, even in cases where the (thermal) fluctuations in the reaction coordinate and energy are larger than r_c and ΔG at the point of intersection, respectively. If charge transfer occurs, it is a non-adiabatic process, saying that a quantum jump is required. We want to derive the probability for this process using Fig. 3.14b. For doing so, we assume the same curvature of both parabolas, i.e. an equal stiffness k if we think of harmonic oscillators and Hooke's law. We, furthermore, allow for different values of the minimum free energy of both states. The difference between the minima is denoted with $\Delta G_0 = G''(r'') - G'(r')$, which is negative for a down-hill process, such as the one in Fig. 3.14b. At the point of intersection r_c , the parabola equations can be compared:

$$\begin{aligned} \frac{1}{2}k(r_c - r')^2 - \Delta G_0 &= \frac{1}{2}k(r_c - r'')^2 \\ \Rightarrow r_c &= \frac{r'' + r'}{2} + \frac{\Delta G_0}{k(r'' - r')}. \end{aligned} \quad (3.9)$$

Plugging r_c into the equation for the parabola with minimum at r' and correcting for ΔG_0 yields:

$$\Delta G = \frac{1}{2}k(r_c - r')^2 = \frac{1}{2}k\left(\frac{r'' + r'}{2} + \frac{\Delta G_0}{k(r'' - r')} - r'\right)^2. \quad (3.10)$$

We introduce the quantity $\lambda = 1/2 \cdot k \cdot (r' - r'')^2$ which is the excess energy of G' at the equilibrium position r'' of G'' (or vice versa). This is the excess energy of an activated educt state, which has the same nuclear configuration as the product state in equilibrium, i.e. the energy gained by the system without charge transfer. Using λ allows for a compact expression of ΔG :

$$\Delta G = \frac{(\Delta G_0 + \lambda)^2}{4\lambda}. \quad (3.11)$$

As ΔG is an activation energy, we can say classically that the transition probability is proportional to:

$$\exp\left(-\frac{\Delta G}{k_B T}\right), \quad (3.12)$$

if we assume Boltzmann statistics. Now, we can take Fermi's golden rule (3.2) and consider (3.12) when expressing ρ . This is possible when treating the vibrational contributions classically. Then, we can describe the electron transfer simply between an electronic two-level system (with difference ΔG_0) and summarize all vibrational contributions weighted by the thermal distribution in ρ [30]. According to (3.5) we can separate the matrix element into an electronic coupling I_{ij}^2 term and a vibrational one called Franck-Condon factor which can be expressed via λ (without derivation

here: $\sqrt{\frac{1}{4\pi\lambda k_B T}}$, [30]). The transition rate probability is then:

$$\nu_{ij} = \frac{|I_{ij}|^2}{\hbar} \sqrt{\frac{\pi}{\lambda k_B T}} \exp\left(-\frac{(\Delta G_0 + \lambda)^2}{4\lambda k_B T}\right). \quad (3.13)$$

This equation is known as the semi-classical non-adiabatic Marcus expression which is only valid for finite temperatures. It has to be modified for temperatures approaching zero Kelvin ($T \rightarrow 0$ K) to describe the ν_{ij} observed in experiment. Rudolph A. Marcus developed his theory in 1956 [31]. In 1992 he received the Nobel Prize in Chemistry for it. The electronic coupling I_{ij}^2 depends on the orbital overlap, e.g. HOMO-HOMO (LUMO-LUMO) overlap for electron transfer in the respective orbitals. $|I_{ij}|^2$ decreases strongly with distance, commonly following an exponential decay.

The quantity λ is called reorganization energy. As visualized in Fig. 3.14b, it is the energy required to convert the nuclear configuration of the products into that of the educts without electron transfer. It results from changes in the local dielectric properties, where Marcus distinguishes two main contributions: First, a change in inner shell vibrational modes and, second, solvent effects resulting from the polarizability of the local environment. The intramolecular effects decrease with further delocalization of the charge and depend on the stiffness of bonds (related to k). These contributions also include conformational reorganization of molecules.

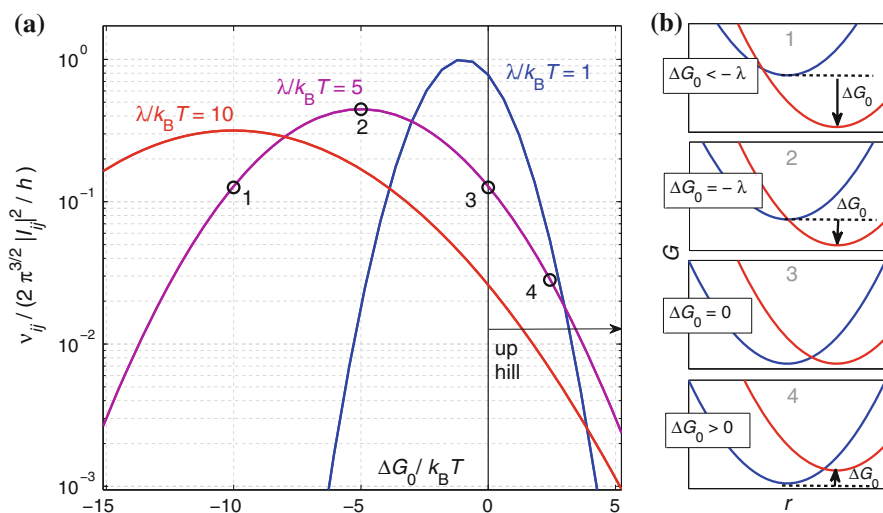


Fig. 3.15 a Marcus rate ν_{ij} rescaled from (3.13) as a function of the offset energy ΔG_0 . Different curves represent different values of the reorganization energy λ . The rate is reduced for uphill processes ($\Delta G_0 > 0$). Interestingly, the rate decreases also for downhill processes with a large $|\Delta G_0|$, i.e. a $\Delta G_0 < -\lambda$. This region is called the inverted regime. The circles mark situations shown in (b), where $G(r)$ for educt (blue) and product (red) states are sketched

In Fig. 3.15a, the Marcus rate normalized by the prefactor and with energies as multiples of $k_B T$ is plotted as a function of ΔG_0 for different values of λ . The rate decreases for uphill transitions, i.e. a positive ΔG_0 , as intuitively expected. However, there is a maximum in ν_{ij} followed by a decrease for further downhill process (negative ΔG_0), as soon as $\Delta G_0 < -\lambda$. This is the so-called inverted regime, which could indeed be observed in later experiments [32]. The reason is an increasing activation energy due to a crossing of the parabolas with an r_c which is not in between the two equilibrium positions r' and r'' as visualized in the top right figure of Fig. 3.15b. A larger λ reduces the differential dependence of the rate on ΔG .

In amorphous organic solids, charge transport from molecule (segment) to molecule (segment), i.e. site to site, is commonly treated by non-adiabatic Marcus theory, describing a hopping process between weakly coupled sites. Modeling of this hopping process will be topic of the following section.

3.2.3 Charge Transport—Gaussian Disorder Model

In an organic semiconductor electrons are delocalized on an intramolecular (within a molecule) scale in π -electron systems. However, in amorphous organic solids, they are localized on an intermolecular (between molecules) scale. Thus, each molecule—or more precisely π -system—constitutes a hopping site with a transition probability to a neighboring π -system, which is in the first approximation proportional to the square modulus of the overlap of the two adjacent π -orbitals (HOMOs) for hole transport or two π^* -orbitals (LUMOs) for electron transport. On a more detailed level, the polarization effect of the hole (electron) should be considered, and depending on the screening capability of the surroundings, the transport is better described as hop from the SOMO of the ion to the HOMO (LUMO) of a neutral molecule. In less densely packed amorphous films, the low overlap results in charge carrier mobilities which are several orders of magnitude lower compared to crystalline semiconductors. Furthermore, they show a “reverse” temperature dependence around room temperature: In organic semiconductors, the mobility increases with temperature due to thermally activated hopping, whereas in case of band transport it decreases due to increased phonon scattering. Additionally, disorder leads to a dispersive transport, complicating experimental determination of a single mobility value. Therefore, in many cases the mobility of a material is not described by a single value. In the extreme case, this puts the applicability of the (theoretical) material parameter mobility (2.33) into question.

The most common model for a theoretical description of hopping is the Bässler model [33], also called Gaussian disorder model (GDM), which will be introduced in the following and is illustrated in Fig. 3.16a:

Although the energy levels of charge transport are not directly measurable by optical spectroscopy due to the discussed favored excitonic transitions, the Gaussian shape of the excitonic transitions seen in absorption and fluorescence are expected to apply to charge transport levels as well. Thus, we can write for the density of states (DOS):

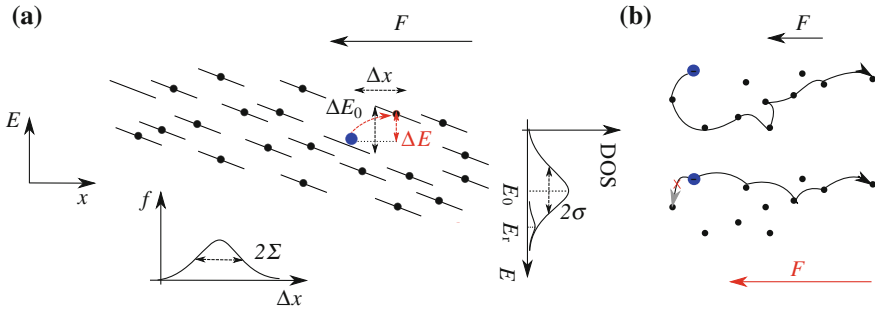


Fig. 3.16 Sketch of hopping transport from site to site (*dots*): **a** illustration of diagonal (σ) and off-diagonal Σ disorder and the effect of an electric field F (visualized by the *tilted lines*) on the effective barrier ΔE , **b** negative field effect for large spatial disorder: the most probable electron path is suppressed by a higher field. This reduces the mobility

$$g(E) = \frac{N_{\text{sites}}}{\sqrt{2\pi}\sigma} \exp\left(-\frac{(E - E_0)^2}{2\sigma^2}\right). \quad (3.14)$$

Here, E_0 is the center of the DOS and the energies of the discrete hopping sites with density N_{sites} follow a Gaussian distribution with width σ . The reason is the already discussed change in polarization energy due to disordered surroundings. This approach assumes that the energies of adjacent sites are uncorrelated, i.e. adjacent molecules influence the energy levels of each other purely randomly, which is not necessarily true.

The jump rate ν_{ij} from site i to j is assumed to be of Miller-Abrahams type [34]:

$$\nu_{ij} = \nu_0 \exp(-2\gamma\Delta R_{ij}) \cdot \begin{cases} \exp\left(-\frac{E_j - E_i}{k_B T}\right); & E_j > E_i \\ 1; & E_j < E_i. \end{cases} \quad (3.15)$$

The first exponential term of this equation describes the wave function overlap and represents a tunneling probability, dependent on the site distance ΔR_{ij} and the wave function decay parameter γ which is in the order of 10^{10} m^{-1} . The prefactor ν_0 is the attempt frequency ($\approx 10^{13} \text{ s}^{-1}$) with which the electron tries a jump. With these parameters, a ΔR_{ij} of 1 nm results in ≈ 10 downward jumps per millisecond, while a ΔR_{ij} of 0.5 nm yields ≈ 1 jump per nanosecond. This change of ν_{ij} in the order of five magnitudes shows the strong sensitivity of the hopping rate on ΔR_{ij} . Energetic upward jumps follow a Boltzmann factor with an effective energy offset $E_j - E_i$, which can be lowered by a macroscopic electrical field F pointing from $\mathbf{r}_j$ to $\mathbf{r}_i$. This field is assumed to be constant between $\mathbf{r}_i$ and $\mathbf{r}_j$ and gives

$$E_j - E_i = E_j^0 - E_i^0 - eF |\mathbf{r}_j - \mathbf{r}_i|. \quad (3.16)$$

Downward jumps are assumed not to be influenced by the field. Equation (3.15), also known as the Mott formalism [35] includes already some assumptions such as $E_j - E_i > k_B T$. Polaronic effects are neglected, but sufficient electron-phonon interactions are presupposed to guarantee a dissipation of the energy in case of a downward jump. To make this approach compatible with the principle of detailed balance, also the exact occupation probabilities governed by the chemical potential have to be considered. A thorough overview can be found in [36].

In addition to the distribution of E the hopping distance ΔR_{ij} and hence the overlap factor is also affected by the disorder and assumed to follow a Gaussian distribution with width Σ (off-diagonal disorder).

From the theoretical perspective there is a significant difference between nearest neighbor and variable-range hopping. Commonly, the tunneling term in (3.15) decays very quickly with distance (see example in previous paragraph), making jumps to non-nearest neighbors unlikely. However, for strong localization, small density of sites, or low temperatures the energetic term might limit the hop rates to the nearest neighbor and the probability of a transition to non-nearest neighbor j with a smaller $E_j - E_i$ becomes more likely. Then, the dominating type of transport is variable-range hopping.

The Miller-Abrahams equation neglects polaronic effects as already mentioned. We recall the Marcus model (3.13) as an appropriate theory to describe electron transfer in a hopping regime with weak interactions between sites:

$$\nu_{ij} = \frac{I_{ij}^2}{\hbar} \sqrt{\frac{\pi}{\lambda k_B T}} \exp\left(-\frac{(E_j - E_i + \lambda)^2}{4\lambda k_B T}\right). \quad (3.17)$$

The Miller-Abrahams equation can be seen as a simplified expression of the Marcus equation, which additionally contains the reorganization energy λ covering polarization effects upon charging/discharging a molecule. Both (3.15) and (3.17) have been used to model hopping transport in organic semiconductors.

The probability of a jump from site i to j is finally given by the jump rate divided by the total jump probability including all potential destination sites j' in the neighborhood of site i :

$$p_{ij} = \frac{\nu_{ij}}{\sum_{j', j' \neq i} \nu_{ij'}}. \quad (3.18)$$

To extract some information from this model, Bässler performed Monte Carlo simulations, placing one particle at an arbitrary energy for a random walk in a three-dimensional solid with the dimensions of $70 \times 70 \times 70$ sites. Together with the distribution in site energy, one can call the calculation space a four-dimensional hopping space [37].

The first result Bässler obtained is a relaxation of the excess charge carrier to a Gaussian equilibrium distribution with a maximum E_0^{relax} , which lies below E_0 :

$$E_0^{\text{relax}} = E_0 - \sigma^2 / k_B T. \quad (3.19)$$

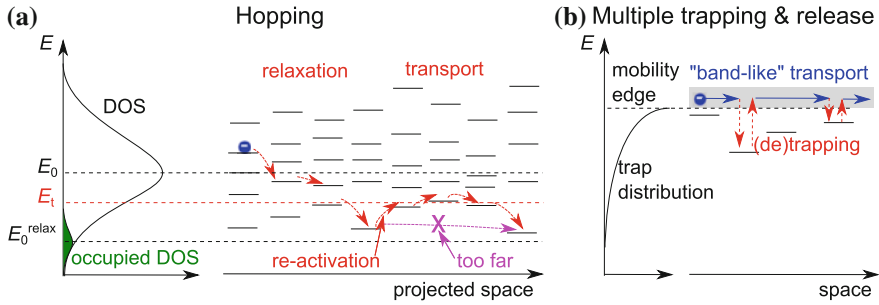


Fig. 3.17 **a** Sketch of hopping transport and the concept of a transport energy E_t , higher than the average energy of completely relaxed charges. The low density of states in the tail makes it necessary to thermally activate the charge carrier to reach a hopping site in its vicinity. **b** Sketch of the multiple-trapping-and-release model: Charge transport happens in a quasi-continuum of states and is hindered by trapping events requiring a (thermal and possibly field-assisted) detrapping for further transport

This is a considerable value, if we assume, e.g., $\sigma = 50$ meV, E_0^{relax} would be 100 meV below the center of the DOS at room temperature. Such a relaxation is difficult to determine experimentally. Note that Fermi-Dirac statistics are not important in Bässler's model, because only one charge carrier travels in an otherwise empty DOS. This represents the condition of low charge carrier densities, where electron-electron interactions are negligible and either a site is occupied by one electron or it (including its surroundings) is empty.

Interestingly, in the GDM the electron does not relax completely but into a finite mean energy E_0^{relax} , determining a dynamic equilibrium of the hopping electron. Consequently, the relaxation of a number of non-interacting carriers results in a Gaussian distribution of the occupied DOS as sketched in Fig. 3.17a. As a relaxed charge carrier is trapped in the "tail" of the DOS, its transport requires a thermal activation to higher lying states. Their energy is called the transport energy E_t . Giving a distinct value for E_t is not simple. For the Gaussian DOS described in (3.14), its position depends on N_{sites} , $\sigma/k_B T$, and γ [38]. It is located between E_0^{relax} and E_0 . Phenomenologically, the transport energy first introduced in [39] is similar to the mobility edge if we think of mobile (above) and trapped (below the mobility edge) charges.

Whereas E_0^{relax} can be calculated analytically, the following expression for mobility (μ) is not a theoretically derived formula, but results from fits of selected analytical equations to numerical Monte Carlo simulation results:

$$\mu(\sigma, \Sigma, F, T) = \mu_0 \exp\left(-\left(\frac{2\sigma}{3k_B T}\right)^2\right) \cdot \begin{cases} \exp\left(C \cdot \left(\left(\frac{\sigma}{k_B T}\right)^2 - \Sigma^2\right) \sqrt{F}\right); & \Sigma \geq 1.5 \\ \exp\left(C \cdot \left(\left(\frac{\sigma}{k_B T}\right)^2 - 2.25\right) \sqrt{F}\right); & \Sigma < 1.5. \end{cases} \quad (3.20)$$

This equation with the empirical constant $C = 2.9 \times 10^{-4} \sqrt{\text{cm/V}}$ summarizes the field and temperature dependence of μ considering both disorder parameters σ and Σ . A strong temperature dependence of μ is expected, because hopping is a thermally activated process. Equation (3.20) describes an $\exp(-1/T^2)$ dependence instead of the common thermal activation following $\exp(-1/T)$. In general, the exponent n in the $\mu \propto \exp(-1/T^n)$ law depends on the shape of the DOS, the hopping process, and the position of the Fermi level [40]. The limited temperature region commonly accessible by experiment makes a distinction between the mobility following $\exp(-1/T^2)$ or the Arrhenius-like behavior difficult. The temperature dependence of μ is contained in the temperature dependence of the conductivity as well according to (2.34). Modeling studies including charge carrier densities predict for hopping conductivity $\sigma \propto \exp(-T^{-1/4})$ [37, 41].

The $\exp \sqrt{F}$ behavior in (3.20) coincides with phenomenological equations previously found to describe $\mu(F)$ in organic solids. It is formally identical to the result from the Poole-Frenkel effect [42], used to characterize charge transport via shallow traps ($\epsilon_r \epsilon_0$ is the absolute permittivity of the material):

$$\mu \propto \exp \sqrt{\gamma F}; \quad \gamma = \gamma_{\text{PF}} = e^3 / \pi \epsilon_r \epsilon_0. \quad (3.21)$$

This coincidence is anticipated, because a macroscopic field increases the electron jump or escape probability in both models. However, the Poole-Frenkel effect considers a quasi-free electron in the Coulomb potential of a positively charged (trap) state located at $x = 0$ in Fig. 3.18a. When applying a constant field F , the two potentials are overlaid:

$$E(x) = E_{\text{Coulomb}}(x) + E_{\text{field}}(x) = -e^2 / (4\pi \epsilon_r \epsilon_0 x) - eFx. \quad (3.22)$$

Consequently, the effective barrier for leaving the Coulomb potential is reduced by $\Delta\phi$, which can be calculated as the maximum of the superposition of the two potentials by setting $\frac{dE}{dx}$ to zero:

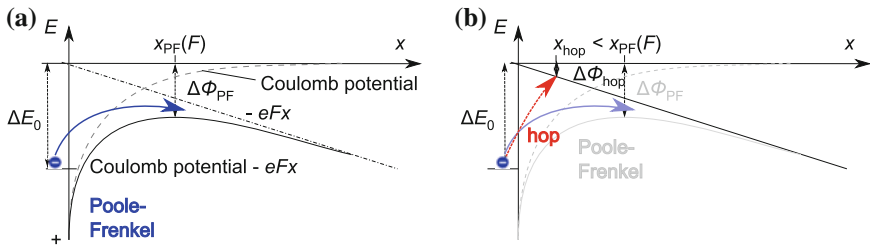


Fig. 3.18 Comparison between Poole-Frenkel effect **a** with a field dependent barrier lowering ($\Delta\phi_{\text{PF}}(F)$) at a long-range distance $x_{\text{PF}}(F)$ and hopping **b** with a short fixed distance x_{hop} . In case of the Poole-Frenkel effect, the barrier is lowered due to a superposition of the Coulomb potential and the potential $-eFx$ resulting from an external field. In case of hopping, the barrier is lowered due to a tunneling when the electron jumps from position 0 to x_{hop}

$$\Delta\phi_{\text{PF}}(x_{\text{PF}} = \sqrt{e/4\pi\epsilon_r\epsilon_0 F}) = e\sqrt{eF/\pi\epsilon_r\epsilon_0}. \quad (3.23)$$

However, the distance x_{PF} for reasonably strong fields $F = 10^5$ – 10^6 V/cm is in the range of several nm and thus significantly larger than the distance covered by a jump ($x_{\text{hop}} \approx 0.5$ – 1 nm). This difference in distances leads to a lower $\Delta\phi$ in case of hopping as depicted in Fig. 3.18b. Consequently, the classical derivation of the Poole-Frenkel effect including γ_{PF} in (3.21) is not generally applicable to hopping transport. For hopping transport, the parameter γ can be derived either by using the theoretical equation (3.20) or by fitting of experimental data in case of a phenomenological description.

Interestingly, (3.20) proposes also regions with a negative field dependence caused by a high Σ . Figure 3.16b illustrates the reason for this effect in an intuitive picture: The high off-diagonal disorder increases the probability of a non-straight electron traveling path (i.e. not in the direction of the (negative) field, but even partially in reverse direction) being the one with the highest hopping rates. This implies some jumps that do not occur in the direction of the applied negative field. These jumps are suppressed by the field and the otherwise positive effect of the field on the direct path is overcompensated by the elimination of the favored indirect path. In particular, such an effect could be important for films consisting of a mix of different materials [43].

Since its introduction by Bäessler, the Gaussian disorder model (GDM) has undergone many refinements and addenda. A very compact extension was given by Pasveer et al. [44] who introduced the extended GDM (EGDM). This model also considers the dependence of the mobility on charge carrier density. The main result is an increase of μ with higher charge carrier density. The larger the charge carrier density, the more higher lying sites of the Gaussian DOS are filled. Electrons located on these sites require lower activation energies for hopping and are thus more mobile than electrons occupying deeper (shallow-trap like) states. This explanation is valid as long as the DOS is less than half-filled which is an assumption that is implicit for all common discussions of hopping transport as a DOS that is more than half-filled is completely irrelevant for all applications.

In contrast to the physically justified Gaussian distribution of the energetic disorder (normal distribution of energy levels around a mean value), the description of the geometrical (off-diagonal) disorder with a Gaussian distribution is not well-justified and other models are proposed (see [45]). Furthermore, it was found that a spatial correlation of energetic disorder can be of importance when describing mobility [46]. Spatial correlation means that the energy of adjacent sites is not independent of each other. Imagine e.g. a charged site which influences its polar surroundings. Considering the correlation allows for a more appropriate description of the $\sqrt{F}$ behavior over the entire field range. Microscopic reason for correlations could be long-range interactions of charges with randomly distributed permanent electric dipole moments, e.g. from polar molecules, that change the potential energy and hence the site energy considerably. This interaction leads to a correlation of energies E_i and E_j of neighboring sites. Also a short-range order of non-completely randomly amorphous semiconductors can give rise to spatial correlations. An additional

consideration of the influence of the charge carrier density lead to the extended correlated disorder model (ECDM) [47].

A variety of further approaches can be applied to describe charge transport in disordered solids, which can in general be seen as a problem for percolation theory [48]. Instead of a Gaussian DOS, an exponential density of states ($\propto \exp(-E)$) is used as well. As in the GDM charges are mainly located in the tail of the Gaussian ($\propto \exp(-E^2)$), an exponential tail yields similar results. We mentioned already the role of the transport energy representing a kind of mobility edge. This concept of mobility edge leads us to simplified models where one distinguishes between mobile and completely immobile, i.e. trapped, charges depending on their energetic position in the DOS. This means charges located below the mobility edge are immobile. Then the mobile charges might be described by a constant (band-like) mobility and the trap distribution by an exponential tail. The charge carrier dynamics are separated into horizontal (i.e. transport) processes and vertical (i.e. energy related trapping) processes, as sketched in Fig. 3.17b. The effective long-range charge carrier transport rate is then limited by trapping and detrapping events. Those govern the dependence of charge transport on temperature and field. That is why this description is called multiple-trapping and release model [49]. It is obvious that it is very similar to a hopping model predicting qualitatively the same phenomenological trends. However, the physics behind both models are very different.

Charge transport is one of the crucial mechanisms in the complete sequence of photovoltaic energy conversion. Electron-hole pairs, which are photogenerated in the bulk, have to be transported towards the contacts. In the following, we will simply characterize charge transport by mobility keeping in mind that it might be a complicated function of several parameters (temperature, electric field, charge carrier density, etc.) rather than a material constant.

3.3 Working Principle of Donor-Acceptor Heterojunction Solar Cells

This section provides an overview of the general working principle of an organic solar cell. We discuss main parameters and mention common theories. In the first section, we follow (quasi-)particles and define quantum efficiencies of the individual processes resulting in the photon-to-electron-hole-pair conversion efficiency. In the second part, we examine energy losses and photovoltage. We comment on the maximum achievable efficiency and finally present some analytical models for the current-voltage characteristics. A detailed summary regarding the present knowledge of the initial processes of photogeneration is found in a subsequent section (Sect. 3.4).

3.3.1 Particle Losses, Quantum Efficiency, and Photocurrent

Photocurrent is generated by the absorption of a photon, which is finally extracted as an electron-hole pair, whereby the electron has to be collected at another position of the solar cell than the hole (see Sect. 2.4). Compared to inorganics, organic solar cells show one important peculiarity: light absorption does not lead instantaneously to free charge carriers, but, as discussed in Sect. 3.2.1, to localized excited states or highly bound excitons with binding energies $E_B \gtrsim 0.3$ eV (cf. Fig. 3.13). These excitons have to be separated in a subsequent step. However, efficiencies for a spontaneous separation and free charge carrier generation via (temperature activated) autoionization are commonly below several percent [7]. Therefore, the so far most successful approach consists of the application of a donor-acceptor (D-A) heterojunction [50]. Such a junction comprises an arrangement of two different molecules with an electronic structure that favors charge transfer instead of, e.g., energy transfer (Fig. 3.19). Consequently, one molecule is of electron donating type and the other one shows strong electron-accepting properties. This means in the molecular orbital picture (Figs. 3.19b and 3.20) a difference in LUMO and HOMO values, which makes it favorable for e.g. an electron of an excited donor state (S_1 , π^* orbital) to jump onto the acceptor. After the charge transfer, donor and acceptor are charged, remaining hole and transferred electron occupy the SOMO of the cation and anion, respectively.

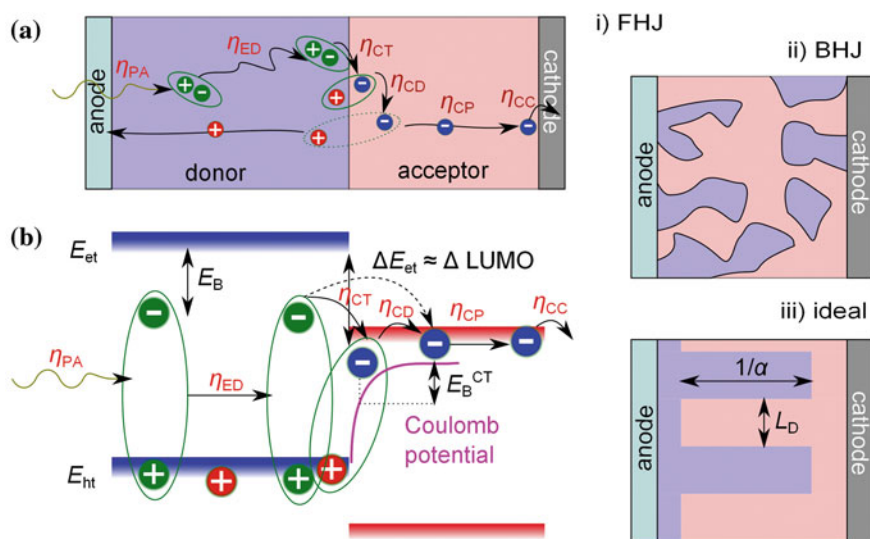


Fig. 3.19 Donor-acceptor concept: **a** possible realizations: flat/planar heterojunction (FHJ, bilayer), bulk heterojunction (BHJ, blend), comb-like structure, **b** steps of energy conversion with associated quantum efficiencies η_i in the one-electron picture where $\Delta LUMO$ is the driving force to overcome the exciton binding energy E_B . The Coulomb attraction of charges residing at the heterointerface is visualized by the Coulomb potential of a fixed positive charge acting on an electron located at different distances from the interface

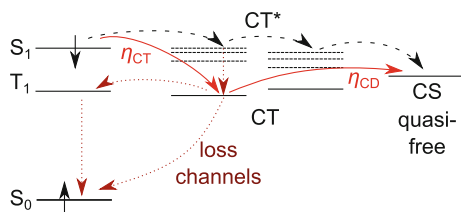


Fig. 3.20 Donor-acceptor concept in an excited-state diagram. *Solid arrows* show the dissociation of a singlet exciton S_1 via charge-transfer (CT) states. The *dashed lines* represent an alternative path via hot CT states directly to charge separated (CS) states. *Dotted lines* show loss channels via relaxation of CT states or via a back transfer of energy to a triplet state T_1 on the donor, which is a likely process if T_1 lies below CT

The energies of these orbitals are expected to be close to the levels of HOMO and LUMO of the neutral molecules as discussed previously (cf. Fig. 3.11). Similarly, a hole can be created on the donor after the splitting of an exciton resulting from absorption on the acceptor.

Considering the energy levels for charge transport in a molecular solid (Fig. 3.19b), a D-A heterojunction is characterized by sufficiently large steps in ionization potential (absorption on acceptor) $\Delta IP/\Delta HOMO$ and electron affinity (absorption on donor) $\Delta EA/\Delta LUMO$. The “intrinsic” offsets resulting from the assumption of vacuum level alignment can be influenced and modified by eventually occurring dipoles at the heterojunction [51] (for dipoles at interfaces cf. Sect. 3.5.1).

The whole energy conversion chain can be divided into the following steps [52], each with a quantum conversion efficiency η_i as illustrated in Fig. 3.19:

- Photon absorption with efficiency $\eta_{PA}(\lambda)$. It depends on the absorption coefficient $\alpha(\lambda)$ (3.8) of the absorber molecule, which shows (usually narrow) peaks. Additional to transmitted photons, reflected ones are lost. Since the thicknesses of the layers of organic solar cells are in the range of the coherence length of the sun light, not only the thickness of the absorber determines $\eta_{PA}(\lambda)$ but its position within the optical field distribution dominated by interference effects. As we will see later, optical interference mainly results from the employment of a reflective electrode at the backside of the solar cell. Hence, an optimization of η_{PA} means finding molecules with high absorption in the desired spectral range and a tailoring of the solar-cell stack regarding optics.
- Exciton diffusion with efficiency η_{ED} . The exciton has to reach a D-A interface to be split. During this process, diffusion and relaxation are competing. A high diffusivity characterized by the diffusion constant D and lifetime τ lead to a large exciton diffusion length $L_D = \sqrt{D\tau}$. Thus, η_{ED} is mainly determined by the ratio of L_D to the thickness of the absorber layer. Common values of L_D of amorphous organic films are in the range of 10 nm [52]. A device optimization leads to a trade-off with η_{PA} , requiring layers with thicknesses of 50–200 nm (for $\alpha \approx 10^5 \text{ cm}^{-1}$). This means that the amount of harvested excitons is low compared to the amount

of incident photons in a planar arrangement of donor and acceptor (bilayer) as shown in Fig. 3.19a.i.

To overcome this problem, the planar arrangement is changed to a volume structure by mixing (or blending) donor and acceptor to form a bulk heterojunction (Fig. 3.19a.ii) [53–55]. In the optimum case this film is mixed in the 10 nm length scale to guarantee an efficient exciton harvesting even for thick layers.

Parasitic absorption in regions that are not electrically active decreases the exciton harvesting efficiency as well and can either be assigned to exciton losses (η_{ED} , e.g. if excitons are generated in transport layers) or to absorption losses (η_{PA} , e.g. if light is absorbed in a metal electrode), as absorption does not take place in the designated material.

Results from transient measurements indicate that in bulk heterojunctions excitons reach the D-A interface in a timescale which is too short for a diffusion process. Based on this observation, we will comment on the latest discussions about the role of exciton diffusion in state-of-the-art solar cells at the end of Sect. 3.4.

- Charge transfer with efficiency η_{CT} . This process is known to be very efficient and fast for several donor-acceptor combinations (45 to several hundreds of femtoseconds) [56–60]. An efficient charge transfer is commonly observed if there is an energetic driving force towards a charge-transfer or a charge-separated state.
- Dissociation of the electron-hole pair with efficiency η_{CD} . This step is seen as the essential process in an organic solar cell. It is not yet completely understood and a matter of controversial discussions (for reviews, see [61, 62]). The main question is whether the dissociation happens via an intermediate state, a so-called charge-transfer (CT) exciton which is the first excited state of a charge-transfer complex at the heterojunction. The other proposal is that the energy gained from the energy level offset is used to directly generate free charge carriers via hot states.

A discrimination of both mechanism is only important if the CT state is a bound state. Otherwise, obviously in the very early timescale the transferred charge must be hot due to the step in potential energy. Afterwards this state relaxes and forms a pair of almost free charges at the heterojunction, which are in a state, i.e. a charge-transfer state, that can be probed by direct transitions from the ground state of this charge-transfer complex to the CT state.

Let us discuss the implications if the CT exciton is a bound electron-hole pair, or an electron in the Coulomb potential of a localized positive charge, as depicted in the potential energy diagram for a quasi-free electron in Fig. 3.19b [63]. A complete dissociation of this pair into free charge carriers is then temperature activated and field dependent. Furthermore, it is in competition with the relaxation of the CT state. This process is called geminate recombination. The photocurrent yield is then commonly described by the Onsager-Braun theory [64, 65] (details in Sect. 4.4.2). Some calculations showed good agreement with the high $\eta_{CD}(F, T)$ measured [66–68], although mostly either the lifetimes of the CT states are strongly overestimated or the binding energies underestimated when compared to spectroscopic measurements [69]. In other cases this theory could not describe the field dependence of the photocurrent [70]. According to [71] the Onsager-Braun theory applied to an electron-hole pair at a donor-acceptor heterojunction requires

some modification. In [72] it is suggested based on Monte Carlo simulations that the high dissociation yield is due to a high delocalization of charges on polymer chains. The idea of a fast delocalization of the charges over several nm and very weak binding energies in the range of meV is proposed to describe efficient charge carrier generation despite geminate recombination processes, which happen on a timescale of 1–100 ns [73, 74]. Debate and research on this topic are still ongoing.

A description of the CT state may be preferred and even more accurate using an excited-state diagram (cf. Fig. 3.7) shown in Fig. 3.20 instead of regarding the CT state as Coulombically bound electron-hole pair. If allowed, radiative transitions between ground state and CT state should be observable. In recent years they have been reported for several donor-acceptor combinations in absorption [75], external quantum efficiency [76], photoluminescence [77], and electroluminescence [78, 79] measurements. Sensitive measurement techniques are required due to a very low cross section [80]. An observed reduction of η_{CD} for a heterojunction exhibiting a low difference between CT and S_1 [81] gives evidence for the importance of the CT state. Also the importance of the donor triplet energy T_1 compared to the CT energy is a clear hint for the participation of the CT state at photocurrent generation [82]. Veldman et al. showed that well working solar cells possess a T_1 above the CT state energy. Otherwise, η_{CD} suffers significantly because, assuming a large intersystem-crossing probability of the CT state [26], a T_1 lower than the CT state favors back transfer of the energy to the donor with a subsequent relaxation of the triplet state (Fig. 3.20). Such a triplet state does not necessarily lead to a decreased device performance. A long lifetime and delocalization might favor a re-dissociation of the triplet as proposed in [83]. The role of ΔLUMO was investigated in [84, 85] showing the irrelevance of further excess energy (above a certain threshold) for η_{CD} . There, the temperature and field dependence of the photocurrent for excitations above the optical gap and below the gap (direct CT excitation) were similar. The authors concluded that in both cases, free charge carrier generation happens via CT states. Their implicit assumption is that the temperature dependence of the dissociation of CT states ($\eta_{\text{CD}}(T)$) limits the total η . They did not see any dependence of η_{CD} on the photon energy, indicating that an excess energy does not increase the dissociation probability. This independence of η_{CD} of photon energy is commonly observed [86].

Although the existence of the CT state is undoubted, the efficient dissociation mechanism of this geminate pair with commonly stated binding energies between 0.2 and 0.5 eV is still unclear (cf. Sect. 3.4). The obvious unlikelihood of a dissociation supports the idea of an instantaneous separation and complete dissociation of excitons reaching the interface. In this process the excess energy from the energy offsets is directly used for overcoming the Coulomb attraction via hot CT excitons CT^* (dashed path in Figs. 3.19b and 3.20). Thus, an internal conversion into a CT first excited (i.e. non-hot) state, which has to be reactivated for a later dissociation, is omitted. Evidence for the excess energy being important is reported by Ohkita et al. who found that η_{CD} scales with the difference between the S_1 state and the

energy difference between the IP of the donor and the EA of the acceptor [87]. Note that this observation can also be explained by the formation of a non-hot CT state followed by a repopulation of states on the donor as already discussed for triplet states. The probability for this repopulation increases with a higher IP-EA gap giving rise to a reduced η_{CD} . Recent studies point towards the relevance of hot CT states as well [88–91].

In conclusion, as long as quantitative results are not reported, the question remains whether (non-hot) CT excitons are the exclusive path of exciton dissociation. Furthermore, the nature of the CT state seen in optical experiments has to be clarified, investigating whether the idea of a bound electron-hole pair is applicable or whether the CT state is a purely resonant state. In principle, sufficiently long lifetimes of CT states or entropic contributions can yield high dissociation probabilities despite binding energies which are larger than $k_{\text{B}}T$. A quantification of the binding energy of the CT state is highly desired to judge the relevance of the controversial discussions on the dissociation of the CT state. We will further focus on the processes at the D/A interface reviewing results from various measurement techniques in Sect. 3.4.

- Charge transport with efficiency η_{CP} . Once separated, charges have to be transported to the electrodes. The only possible loss mechanism is recombination between electrons and holes. In a planar heterojunction, the recombination probability of once separated charges should be low, because electrons are located on the acceptor and holes on the donor. Hence, they are spatially separated from each other. In a bulk heterojunction, however, electrons and holes can meet each other during extraction and recombine non-geminately. A common measure for η_{CP} is the mobility-lifetime ($\mu\tau$) product, which expresses the average distance a charge carrier travels at a fixed electric field before it recombines (cf. Sect. 3.3.5). However, as already discussed in Sect. 2.2.2, assigning a τ to a charge carrier in an ambipolar device is difficult. In general, η_{CP} depends on the present field and the diffusion gradient (cf. Chap. 2), which will be the topic of subsequent sections and Chaps. 5 and 6. The increased recombination probability which comes along with the bulk heterojunction concept is unfavorable for a high η_{CP} . Hence, the optimum donor-acceptor solar cell structure is supposed to be comb-shaped with lateral dimensions in the order of L_{D} and vertical dimensions in the order of $1/\alpha$, as depicted in Fig. 3.19a:iii.
- Charge collection at the electrodes with efficiency η_{CC} . This is only a direct loss path for particles if contacts are not selective and a charge carrier reaches the “wrong” contact, where it is extracted, i.e. recombines with charges of the contact material (cf. Fig. 2.13, p. 44). Selective contacts inhibit this particle loss, and consequently η_{CC} is unity. Though, as charge collection is also in competition with recombination within the device, a very low charge carrier collection rate could lead to a pile-up of charge carriers at the electrode, which then effectively reduces η_{CP} or η_{CD} . This effect is the topic of Chap. 6.

The overall efficiency (so-called external quantum efficiency, EQE or incident-photon-to-electron conversion efficiency, IPCE) as a function of wavelength λ , applied voltage V (influencing the electric field F), and temperature T is the product of the single efficiencies:

$$\begin{aligned} \text{EQE}(\lambda, V, T) &= \eta_{\text{PA}}(\lambda) \cdot \text{IQE}(\lambda, V, T) \\ &= \eta_{\text{PA}}(\lambda) \eta_{\text{ED}}(T) \eta_{\text{CT}}(T) \eta_{\text{CD}}(F, T) \eta_{\text{CP}}(F, T) \eta_{\text{CC}}(F, T). \end{aligned} \quad (3.24)$$

The EQE divided by η_{PA} is called internal quantum efficiency (IQE) and contains only the electric processes within the device. Absorption of light in other components of the solar cell (e.g. electrodes, encapsulation layers) apart from the real absorber layer makes a definition of IQE ambiguous. It remains undefined whether this so-called parasitic absorption is already considered as a loss in η_{PA} . A reasonable definition of IQE depends on the object of study. If the IQE is used to evaluate the processes after absorption only in the active (i.e. absorber) layer, which is the usual case, η_{PA} should already be corrected for parasitic absorption. The parasitic absorption cannot be measured directly but has to be determined by optical simulations (cf. Sect. 4.7). The IQE might then be called effective $\text{IQE}^{\text{active}}$ [92].

3.3.2 Energy Losses, Potential Energy, and Photovoltage

In the previous section, we examined the quantum efficiency describing the conversion of photons to electrons in the causal direction. The result was a number of electron-hole (e-h) pairs that can be extracted for a number of incident photons. Now, we investigate the energy carried by one extracted e-h pair. To estimate the maximum energy, we directly start at the point of charge collection. As discussed in Sect. 2.3 in detail, the maximum free energy of a photogenerated e-h pair as part of a charge carrier ensemble is found when it is not extracted, i.e. at open circuit. Hence, in the following we discuss several approaches describing and investigating the open-circuit voltage of organic solar cells.

Radiative Recombination Limit

The free energy of an e-h pair is represented by the quasi-Fermi level splitting or chemical potential difference $\xi_n + \xi_p$, which is in the ideal case present at the contacts in form of the measurable open-circuit voltage V_{oc} (cf. Sect. 2.4). To define electrochemical potentials or quasi-Fermi levels for electrons and holes, we assume that electrons and holes are in equilibrium within their density of states. Otherwise we would have a hot-carrier device and cannot define quasi-Fermi levels. As there is no clear experimental evidence for hot carriers in organic solar cells, we can write according to (2.52):

$$eV_{\text{oc}}^{\text{max}} = E_{\text{F}}^n - E_{\text{F}}^p = \xi_n + \xi_p = k_{\text{B}}T \ln \left(\frac{j_{\gamma}^{\text{abs}}}{j_{\gamma}^{\text{em},0}} \right). \quad (3.25)$$

This is the maximum open-circuit voltage which is limited by thermodynamic laws. V_{oc} is set by the ratio of the absorbed photon flux j_{γ}^{abs} and the equilibrium recombination flux $j_{\gamma}^{\text{em},0}$. This radiative recombination is unavoidable due to the absorption and consequently emission of photons when the solar cell is not illuminated by the sun and at 0 V applied bias. In this case the solar cell is in equilibrium with the black-body radiation from the surroundings at $T \approx 300$ K, as we discussed in detail in Sects. 2.2.2 and 2.3. We will come back to (3.25) when we consider the reciprocity between photovoltaic and electroluminescence quantum efficiency. For now we focus on an alternative expression of (3.25), where we use charge carrier densities instead of photon flux densities.

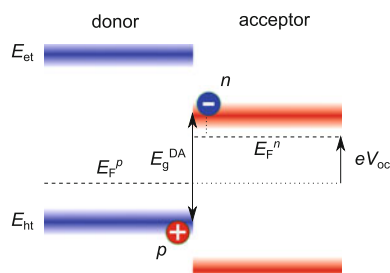
Semiconductor with Effective Energy Gap

As free charge carrier generation and recombination happen at the donor-acceptor heterojunction, one can assume that the processes limiting V_{oc} take place at this junction. An energy diagram neglecting recombination losses in the pure phases is depicted in Fig. 3.21. In this case, we replace $E_{\text{F}}^n - E_{\text{F}}^p$ in (3.25) using (2.18). This approach yields:

$$eV_{\text{oc}} = E_{\text{F}}^n - E_{\text{F}}^p = E_{\text{g}}^{\text{DA}} - k_{\text{B}}T \ln \frac{N_{\text{C}}N_{\text{V}}}{np}. \quad (3.26)$$

Here, the quasi-Fermi level splitting is expressed by the charge carrier densities np at the heterojunction assuming that the electron is located on the acceptor and the hole on the donor. The energy gap of this effective two-component semiconductor is then an effective donor-acceptor gap E_{g}^{DA} . It is defined as the difference between the electron transport level ($E_{\text{et}} \hat{=} -\text{EA} \approx \text{LUMO}$) of the acceptor and the hole transport level ($E_{\text{ht}} \hat{=} -\text{IP} \approx \text{HOMO}$) of the donor. Commonly, a bulk heterojunction is characterized by an intimate intermixing between donor and acceptor material. Then, we are allowed to use the volume densities n and p in (3.26), assuming that their recombination is completely determined by the widespread donor-acceptor

Fig. 3.21 Visualization of the quasi-Fermi level splitting at an illuminated donor-acceptor heterojunction and definition of the effective donor-acceptor gap E_{g}^{DA} .



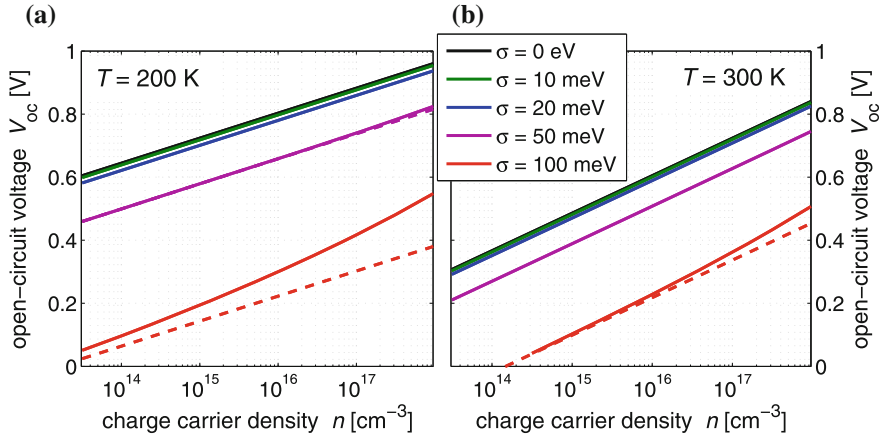


Fig. 3.22 Open-circuit voltage as a function of charge carrier density for different values of the width σ of a Gaussian DOS in HOMO and LUMO. It is calculated using Fermi-Dirac statistics (solid lines) or (3.27) (dashed). The energy gap E_g^{DA} is 1.2 eV (changes ΔE_g^{DA} directly result in an equal $e\Delta V_{\text{oc}}$) and $N_C = N_V = 10^{21} \text{ cm}^{-3}$. For a temperature of **a** 200 K and **b** 300 K

interface. The effective gap E_g^{DA} of the blend might be slightly changed compared to the prediction from the energy levels of the pure materials, as polarization energies might be different due to a changed (amount of) crystallinity etc. (cf. Sect. 8.1).

Equation (3.26) predicts that V_{oc} scales with E_g^{DA} , but does not reach E_g^{DA}/e at $T > 0 \text{ K}$ as np is supposed to be smaller than the product of all available states for electrons and holes $N_C N_V$. This limit of V_{oc} in case of radiative recombination was visualized for a band-edge absorber in Fig. 2.18b when we discussed the Shockley-Queisser limit. If recombination is enhanced compared to the radiative limit, np and therefore V_{oc} will be further reduced.

It is necessary to comment on N_C and N_V in (3.26). These parameters were introduced as effective densities of states in (2.14). Their derivation is based on common semiconductor theory under the assumption of energy bands with parabolic band minima. The occupation of these bands is assumed to follow Boltzmann statistics. Especially the first assumption is not given for a disordered semiconductor. Therefore, the values of $N_{C,V}$ might be adjusted to represent a modified density of states. However, the characteristic dependence of V_{oc} on temperature and charge carrier densities remains valid, if electrochemical potentials and quasi-Fermi levels can be defined. All experimental data indicates that this is the case, as a linear scaling of V_{oc} with $-T$ and values of $\approx 0.3\text{--}0.6 \text{ eV}$ for the last term in (3.26) are observed [93] ($T = 300 \text{ K}$, 1 sun illumination). These values are in the expected range under the assumption of typical charge carrier densities at 1 sun illumination ($10^{16}\text{--}10^{17} \text{ cm}^{-3}$ [94]) and $N_{C,V} = 10^{20}\text{--}10^{21} \text{ cm}^{-3}$ (cf. Fig. 3.22).

The Effect of a Gaussian DOS Resulting from Disorder

One can use a Gaussian density of states to derive the relation between charge carrier density and the Fermi level in (2.14). This Gaussian DOS is motivated by a broadening of the molecular energy levels due to a distribution of hopping sites in a disordered solid given by (3.14). After the integration of (2.14) using a Gaussian DOS and the Boltzmann approximation, we find the following expression reported by Garcia-Belmonte [95]:

$$eV_{\text{oc}} = \underbrace{E_{\text{g}}^{\text{DA}} - \frac{\sigma_n^2 + \sigma_p^2}{2k_{\text{B}}T}}_{\tilde{E}_{\text{g}}^{\text{DA}}\left(\frac{1}{T}\right)} - k_{\text{B}}T \ln \frac{N_{\text{C}}N_{\text{V}}}{np}. \quad (3.27)$$

Here, E_{g}^{DA} is the difference between the maxima of the Gaussian shaped HOMO and LUMO and $N_{\text{V,C}}$ are the total densities of available states in HOMO and LUMO. Their values correspond to the number of available hopping sites, i.e. the densities of molecule(segment)s or π -systems. When discussing V_{oc} at a fixed temperature, we recognize that (3.27) and (3.26) show the same trend with charge carrier densities. The only difference is that E_{g}^{DA} of the band-edge absorber (3.26) is replaced by $E_{\text{g}}^{\text{DA}} - \frac{\sigma_n^2 + \sigma_p^2}{2k_{\text{B}}T}$. Here, σ is the width of the DOS, giving rise to an effective energy gap that is lower than E_{g} in case of a sharp band edge. We recognize in $\sigma^2/k_{\text{B}}T$ a similar expression as found for the relaxation of charge carriers in a Gaussian DOS (3.19).

Figure 3.22 depicts V_{oc} as a function of $n = p$ for two temperatures. At high T or moderate σ , (3.27) (dashed lines) yields a very good approximation for V_{oc} compared to the real value calculated numerically with Fermi-Dirac statistics (solid lines). A filling of a narrow DOS theoretically leads to an increase of V_{oc} which is superlinear with $\ln(np)$, as seen for $\sigma = 100$ meV. The reason is that the increase of the chemical potential due to the higher concentration is accompanied by an increase in the average potential energy, effectively increasing E_{g}^{DA} for charges at higher states. This effect becomes visible as soon as n is sufficiently large to significantly fill the DOS with additional charge carriers occupying higher-energy states. Note that this requires a high σ and a low T , which are usually not found under working conditions of a realistic organic solar cell.

Examining the temperature dependence of V_{oc} , we observe a difference between (3.26) and (3.27). Whereas (3.26) predicts a linear dependence of V_{oc} with $-T$ and a $V_{\text{oc}}(T \rightarrow 0 \text{ K}) = E_{\text{g}}^{\text{DA}}/e$, (3.27) describes a decreased (non-constant) temperature coefficient of V_{oc} with T . Data calculated for a Gaussian DOS are depicted in Fig. 3.23 for different values of σ . V_{oc} flattens out for lower T with increased σ (solid lines). The reason is that charges are further relaxed at lower T and effectively the transport gap decreases. Equation (3.27) (dashed) compared to the numerical solution (solid) is a good approximation as long as $3k_{\text{B}}T \gtrsim \sigma$. Figure 3.24 shows the same data as a

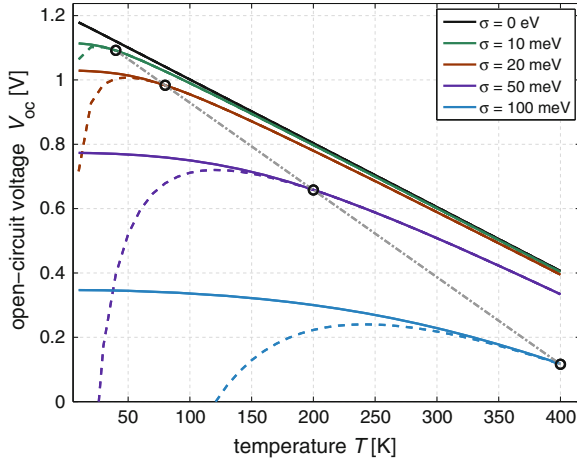


Fig. 3.23 Open-circuit voltage as a function of temperature T for different values of the width σ of a Gaussian DOS in HOMO and LUMO. It is calculated using Fermi-Dirac statistics (*solid lines*) or with (3.27) (*dashed*). The *dash-dotted* line connects the points where $3k_B T$ equals σ . The higher T , the lower is the effect of σ on V_{oc} . The charge carrier density is selected to $n = p = 10^{16} \text{ cm}^{-3}$

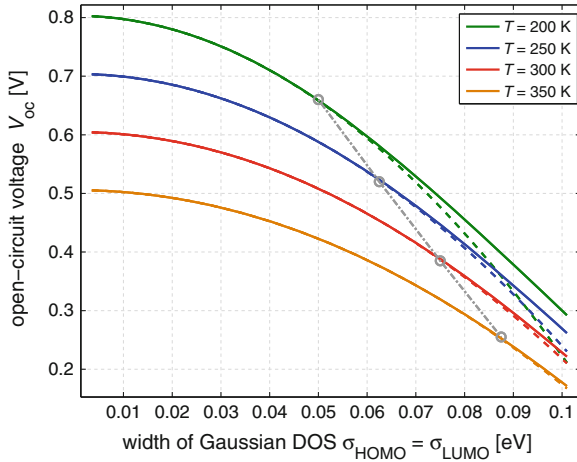


Fig. 3.24 Open-circuit voltage as a function of the width σ of a Gaussian DOS in HOMO and LUMO for different temperatures T . It is calculated using Fermi-Dirac statistics (*solid lines*) or with (3.27) (*dashed*). The *dash-dotted* line connects the points where σ equals $3k_B T$. The higher T , the lower is the effect of σ on V_{oc} . The charge carrier density is selected to $n = p = 10^{16} \text{ cm}^{-3}$

function of σ and T as parameter. The larger σ the lower is the effect of temperature on V_{oc} .

Deviations from a linear scaling of V_{oc} with $-T$ have indeed been observed for organic solar cells [96], although other reasons besides a Gaussian DOS play a role

as well. The electrodes might limit V_{oc} as we will discuss at the end of this section, or np might be significantly reduced, if excitons cannot be dissociated for lower T . Then, V_{oc} can even decrease (cf. Fig. 3.26b). In the next section we will see that np depends on the recombination rates of charge carriers. If e.g. the rate constant for direct/bimolecular recombination [β in (2.22)] is a function of temperature, this will give rise to a non-linear relation between V_{oc} and $-T$ [cf. (3.29)]. Finally, E_g^{DA} can also show a dependence on temperature, although this effect is expected to be weak. For inorganic semiconductors the bandgap slightly increases with a decreased temperature. The reason is found in reduced atomic vibrations at low T , which increase the interatomic spacing. A larger spacing reduces interatomic interactions and consequently decreases the band width, which in turn demands for a larger bandgap (for silicon: $E_g(T = 0 \text{ K}) - E_g(T = 300 \text{ K}) = 0.045 \text{ eV}$). Organic semiconductors show rather a slight decrease in the bandgap with temperature, e.g. explained by interchain interactions [97], and also seen at a slight decrease of the energy of the charge-transfer state E_{CT} ($\approx 50 \text{ meV}/100 \text{ K}$) [98].

Identifying Dominating Recombination Mechanisms at Open Circuit

Excluding losses at the contacts (i.e. demanding for selective contacts), all photogenerated charge carriers recombine in the absorber at open circuit. If this recombination is purely radiative, (3.25) describes V_{oc} . However, if further non-radiative recombination mechanisms are present, they cannot be observed in the emitted photon flux. Nevertheless, their effect is reflected in V_{oc} by a reduced charge carrier density, which decreases V_{oc} below the radiative limit. An investigation of V_{oc} as a function of illumination intensity can give insights into the dominating recombination mechanism. In the following we want to treat the effect of direct and trap-assisted recombination on V_{oc} .

Direct recombination of electrons and holes was introduced as bimolecular recombination in (2.22), where $R = \beta np$. Here, β is the recombination constant for direct recombination, which might be significantly enhanced compared to its value for the radiative recombination limit. We will discuss models for β in organic materials in the next chapter (Sect. 4.4.2).

For a simple analytical treatment we assume a spatially homogeneous photogeneration G of electrons and holes in the absorber. As already mentioned, we exclude losses at the electrodes. Therefore, at V_{oc} we do not expect any diffusion-driven electron and hole (particle) current in the same direction, which might lead to a recombination R depending on the location within the absorber. This allows us to set $R(x)$ at V_{oc} equal to $G(x)$ at each position x of the device:

$$R(x)|_{V_{oc}} = \beta n(x)p(x)|_{V_{oc}} = G. \quad (3.28)$$

With a constant G , $R(x)$ becomes independent of x . Then we can replace np in (3.26) by (3.28), which gives for V_{oc} :

$$eV_{oc} = E_g^{DA} - k_B T \ln \frac{N_C N_V}{G/\beta} = E_g^{DA} - k_B T \ln N_C N_V \beta G_0 + k_B T \ln G/G_0, \quad (3.29)$$

where G_0 is an arbitrary constant with unit $\text{m}^{-3} \text{s}^{-1}$ to keep the argument of the logarithm free of units. This equation shows that V_{oc} scales logarithmically with light intensity because the generation rate G is proportional to the light intensity. The slope of V_{oc} in a graph, where the illumination intensity is plotted in the logarithm to the base 10, is $k_B T / \log e^1 \approx 2.3 k_B T \approx 59 \text{ mV/decade}$ ($T = 300 \text{ K}$).

Another recombination mechanism in semiconductors is indirect recombination of electrons with holes via traps. This process can be described by Shockley-Read-Hall (SRH) theory. There, the recombination rate is given by (2.25). This equation contains many parameters which are commonly unknown for organic materials. For simplicity we assume that the capture coefficients for electrons and holes are the same. We further assume that we have deep traps which means $E_C - E_T \gg k_B T$ and $E_T - E_V \gg k_B T$. Then we can simplify (2.25) in the following way:

$$R_{SRH} = \frac{np - n_i^2}{\frac{n + N_C \exp(-(E_C - E_T)/k_B T)}{N_T \sigma_p v_p} + \frac{p + N_V \exp(-(E_T - E_V)/k_B T)}{N_T \sigma_n v_n}} \approx c_t N_t \frac{np}{n + p}. \quad (3.30)$$

with $c_t = \sigma_p v_p = \sigma_n v_n$. We also neglected the intrinsic charge carrier densities which are much smaller than those generated by light. If the majority of the charge carriers is photogenerated ($n_{ph} = p_{ph}$), this equation results in $R \approx c_t N_t n_{ph}/2 = c_t N_t p_{ph}/2$. Thus, with $R = G$, it holds $n_{ph} \propto G$. This proportionality is also valid close to the contacts, where a high background density (n_d, p_d) of one charge carrier species may exist, e.g. $n_d \gg n_{ph} = p_{ph} \gg p_d \rightarrow G \approx c_t N_t p_{ph}$.

Replacing np in (3.26) yields in the case of SRH recombination:

$$eV_{oc} = E_g^{DA} - k_B T \ln \frac{N_C N_V}{G^2 C} = E_g^{DA} - k_B T \ln N_C N_V C^{-1} G_0 + 2k_B T \ln G/G_0. \quad (3.31)$$

Here, C is a constant containing c_t and N_t . The slope of V_{oc} is $(2.3) \cdot 2k_B T$ in a plot of V_{oc} as a function of the (common) logarithm of G . Hence, the slope is doubled compared to the case of bimolecular recombination. This difference in the slope was discussed in a similar derivation by Cheyns et al. for flat-heterojunction solar cells [99]. It was applied e.g. in [100–102] and previously derived for amorphous silicon solar cells by Schiff [103]. We will make use of it when investigating small molecule solar cells in Sect. 8.4.2.

If C and β do not significantly change with the illumination intensity, we expect that SRH recombination will dominate at lower intensities whereas bimolecular recombination becomes visible at higher intensities as sketch in Fig. 3.25a. The reason is that the probability for bimolecular recombination increases with n^2 , whereas it is linear with n for SRH recombination. A typical plot of measured values for V_{oc} as a function of intensity might look like the one sketched in Fig. 3.25b. It shows

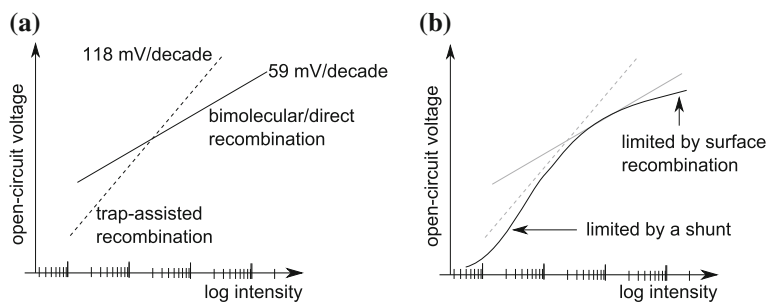


Fig. 3.25 Open-circuit voltage as a function of the logarithm of the illumination intensity: **a** the slope is determined by the prevailing recombination mechanism and the temperature (here 300 K). For higher intensities direct recombination is expected to dominate, **b** a possible realistic shape, where limits due to a finite shunt resistance at low intensities and due to surface recombination at a higher V_{oc} are visible

that the observed dependence of V_{oc} on intensity is superimposed by parasitic effects like a shunt (cf. Fig. 3.37), which reduces V_{oc} for lower light intensities, as it acts as a partial short cut. Higher values of V_{oc} (observed at higher intensities) might be limited by surface recombination at the electrodes (Fig. 3.30a).

The Role of the Charge-Transfer State

When discussing the generation of photocurrent, we mentioned the (possible) role of the CT state limiting the quantum efficiency η_{CD} . The question arises whether the energy E_{CT} of this state influences or even governs V_{oc} . In the picture presented so far, at first glance, a direct correlation of E_{CT} and V_{oc} is not expected, because the CT state energy is the internal energy of an excited state which has to be separated to form free charge carriers. And it is only the free charge carriers that can generate a voltage, as the CT state has to be seen as a bound electron-hole pair which is neutral. However, it is required to have a directive force on electrons and holes, which shift them in opposite directions to induce a voltage. These charge carriers occupy the transport levels when they are collected at the electrodes. Therefore, one could assume that the CT binding energy $E_B = E_g^{DA} - E_{CT}$ is not relevant. It had to be overcome to result in free charge carriers, which define the quasi-Fermi level splitting giving rise to V_{oc} according to (3.26). However, we also know that np in this equation is set by the equilibrium between recombination and generation. If recombination via the CT state is significant, it will act as a modified recombination channel for electrons and holes. Therefore, the properties and in particular the lifetime of the CT state can set np and thus V_{oc} . This recombination probability is then ruled by rate equations describing the transitions between the states rather than by the energy of the CT state.

However, if charge carrier densities and the occupation of the CT state, which is the excited charge-transfer complex, are in equilibrium, one can derive a relation between E_{CT} and V_{oc} . It is difficult to give a theoretical proof for this assumption.

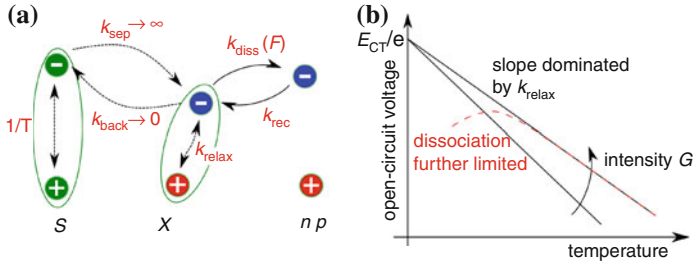


Fig. 3.26 **a** The CT state (X) as an intermediate state on the way of excitons (s) to free charge carriers (n, p) and the other way around. **b** In the case of recombination via CT states, the open-circuit voltage is dominated by the energy E_{CT} of the CT state and its lifetime $1/k_{relax}$

We can argue that transitions between n, p and the CT state are much faster than the relaxation of the CT state (decay into the ground state) due to binding energies which are significantly smaller than E_{CT} . Recall that we used this reasoning when we introduced the quasi-Fermi levels in Sect. 2.2.2, where we assumed that charge carriers are in equilibrium within their respective DOS after fast thermalization. Now, we extend this idea of quasi-equilibrium regarding n and p including the CT state.

Considering the CT state we can modify the treatment of bimolecular recombination presented in the previous section. There, we assumed that recombining electrons and holes vanish after the recombination event. Now, we assume that they do not release their complete energy, but form a bound CT state with a certain lifetime. We want to explicitly consider the properties of this state as an intermediate state on the way towards a complete recombination event. Such a recombination path is basically the reversed mechanism to a generation process, where the CT state is an intermediate state for photocurrent generation on the way towards a complete exciton dissociation at the donor-acceptor interface (Fig. 3.26a). Charges having entered this state have a chance to dissociate again. We consider this effect by modifying generation and recombination terms in (3.28). We define a probability P for the generation of free charge carriers from CT states [104]. Thus, the effective generation rate of free charge carriers $\tilde{G}$ is

$$\tilde{G} = GP \quad (3.32)$$

and the effective recombination rate $\tilde{R}$ is

$$\tilde{R} = R(1 - P). \quad (3.33)$$

Both rates are reduced, because not every generated exciton leads to a free charge-carrier pair and not every recombining e-h pair is lost, as some of them are regenerated by the dissociation of the CT state. Assuming that the CT state either dissociates or relaxes, as sketched in Fig. 3.26a, P can be expressed by dissociation k_{diss} and relaxation k_{relax} rate:

$$P = \frac{k_{\text{diss}}}{k_{\text{diss}} + k_{\text{relax}}}. \quad (3.34)$$

The dissociation rate can be related to β considering the situation in equilibrium. In this case charge carrier densities and the amount of occupied CT states X_0 do not change. The principle of detailed balance requires that recombination of charges into the CT state and its dissociation are in equilibrium:

$$X_0 k_{\text{diss}} = \beta n_i^2. \quad (3.35)$$

As n_i^2 is given by the equilibrium for direct thermal excitations, it is supposed to be independent of the dynamics of the CT state. Therefore, we can conclude that the dissociation rate scales with β . Furthermore, thermal equilibrium requires (under the assumption of Boltzmann statistics) that $k_{\text{diss}} \propto \exp\left(-\frac{E_B}{k_B T}\right)$. A detailed discussion based on the theory of detailed balance is found in Kirchartz et al. [105]. With these assumptions we can write for k_{diss} :

$$k_{\text{diss}} = \beta e^{-\frac{E_B}{k_B T}} f(F, E_B), \quad (3.36)$$

where $f(F, E_B)$ contains a possible dependence of the dissociation rate on the electric field F or further parameters. We will comment on $f(F, E_B)$ in Sect. 4.4.2, when discussing the modeling of the dissociation of the CT state according to Onsager-Braun theory. Now, we consider the case of open circuit, where $\tilde{R}$ equals $\tilde{G}$. With (3.32) and (3.33) we get:

$$\begin{aligned} \tilde{G} &= GP = \tilde{R} = R(1 - P) \\ \Rightarrow G &= R \frac{1 - P}{P} \stackrel{(3.34)}{=} R \frac{k_{\text{relax}}}{k_{\text{diss}}} \stackrel{(3.36)}{=} R \frac{k_{\text{relax}}}{\beta e^{-\frac{E_B}{k_B T}} f(F, E_B)}. \end{aligned} \quad (3.37)$$

The free charge carrier recombination R is given according to (3.28). Inserting this equation into (3.37) results in

$$G = np \frac{k_{\text{relax}}}{e^{-\frac{E_B}{k_B T}} f(F, E_B)}. \quad (3.38)$$

This equation shows that the equilibrium between generation and recombination becomes independent of β . Replacing np in (3.26) by (3.38) yields:

$$\begin{aligned}
eV_{\text{oc}} &= E_{\text{g}}^{\text{DA}} - k_{\text{B}}T \ln \left(\frac{N_{\text{C}}N_{\text{V}}}{G} \frac{k_{\text{relax}}}{e^{-\frac{E_{\text{B}}}{k_{\text{B}}T}} f(F, E_{\text{B}})} \right) \\
&= \underbrace{E_{\text{g}}^{\text{DA}} - E_{\text{B}}}_{E_{\text{CT}}} - k_{\text{B}}T \ln \left(\frac{N_{\text{C}}N_{\text{V}}k_{\text{relax}}}{G \cdot f(F, E_{\text{B}})} \right).
\end{aligned} \tag{3.39}$$

This expression is very similar to the equation we found for bimolecular recombination (3.29). The energy gap is replaced by the energy of the CT state and the temperature dependence is governed by its lifetime $1/k_{\text{relax}}$ replacing β . Therefore, V_{oc} as a function of temperature might follow a curve as the one sketched in Fig. 3.26b. V_{oc} can leave the linear scaling and show a maximum at finite temperatures (dashed line) if the temperature dependence of $f(F, E_{\text{B}})$ limits the generation of free charge carriers. Effectively, this effect is equivalent to a lower light intensity for lower temperatures. In Sect. 5.2.2 we will discuss results of numerical calculations dealing with the dependence of V_{oc} on temperature and illumination intensity.

A correlation of E_{CT} with V_{oc} was observed in several experiments [76, 79, 82].

General Reciprocity Between Absorption and Emission

We already introduced the radiative recombination limit with (3.25) at the beginning of this section. Equation (3.25) can be rewritten assuming that every absorbed non-ambient photon contributes to the short-circuit current density $J_{\text{sc}} = ej_{\gamma}^{\text{abs,photo}} = ej_{\gamma}^{\text{abs}} - ej_{\gamma}^{\text{abs},0}$:

$$eV_{\text{oc}}^{\text{max}} = \xi_n + \xi_p = k_{\text{B}}T \ln \left(\frac{J_{\text{sc}}}{ej_{\gamma}^{\text{em},0}} - 1 \right). \tag{3.40}$$

Here, the superscript 0 denotes equilibrium, where absorbed $j_{\gamma}^{\text{abs},0}$ and emitted $j_{\gamma}^{\text{em},0}$ photon fluxes balance each other. Previously, we calculated $j_{\gamma}^{\text{abs},0} = j_{\gamma}^{\text{em},0}$ under the assumption of a band-edge absorber (2.56). Now, we want to consider the absorption of the CT state as well. Therefore, we can write:

$$j_{\gamma}^{\text{em},0} = \frac{1}{4\pi^2 \hbar^3 c^2} \int_{\approx E_{\text{CT,onset}}}^{\infty} (a_{\text{CT}}(\hbar\omega) + a_{\text{S}}(\hbar\omega)) \frac{(\hbar\omega)^2}{e^{\frac{\hbar\omega}{k_{\text{B}}T_0}} - 1} d\hbar\omega. \tag{3.41}$$

Here, a_{CT} is the absorptance of the CT state and a_{S} the absorptance in the neat materials of the blend leading to (singlet) excited states. The remaining terms describe the black-body radiation (photon flux) at the temperature T_0 of the surroundings. As the black-body spectrum at $T = 300$ K is strongly dominated by the exponential function in the denominator for energies in the visible range, the absorption onset at the lowest energies determines $j_{\gamma}^{\text{em},0}$. In case of a working solar cell, this is the absorption (and emission) of the CT state, because its energy is supposed to be

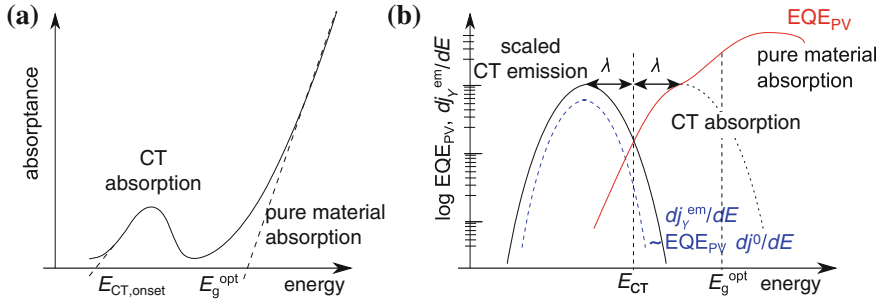


Fig. 3.27 **a** Absorbance of a blend layer showing the molecular (S_1) absorption of the pure material with E_g^{opt} and a weak sub-bandgap absorption of the CT state at a donor/acceptor interface. **b** Photovoltaic external quantum efficiency (EQEPV) and emitted photon flux ($\frac{dj_Y^{\text{em}}}{dE}$). The energy of the CT state E_{CT} is defined according to (3.62) with the reorganization energy λ . The reciprocity between EL and PV processes demands for $\frac{dj_Y^{\text{em}}(\hbar\omega)}{d\hbar\omega} \propto \text{EQEPV}(\hbar\omega) \frac{dj^0(\hbar\omega)}{d\hbar\omega}$

red-shifted compared to the energy of singlet excitons in the neat material as sketched in Fig. 3.27a.

In (3.41) the emission is formally given in terms of a decay of an excited state (CT to ground state, singlet to ground state). This is a difference to the situation discussed in Sects. 2.2.2 and 2.3, where an electron met a hole at different chemical potentials. That is why we briefly outline how the chemical potential of such a state is connected to emission where we follow [106]. Assume a certain concentration c of charge-transfer complexes CTC, which are formed by interacting donor and acceptor molecules. An excitation of the CTC results in what we called CT state. We can also denote the CT state as an excited charge-transfer complex CTC*. Analogously to the illustration for electrons and holes in Fig. 2.10, which we could call the photoelectric picture, the chemical potential of each state in the molecular photochemical view [107] is

$$\xi_{\text{CTC}} = \xi_{\text{CTC}}^0 + k_B T \ln(c_{\text{CTC}}); \quad \xi_{\text{CTC}^*} = \xi_{\text{CTC}^*}^0 + k_B T \ln(c_{\text{CTC}^*}). \quad (3.42)$$

We recognize a concentration independent part and an entropic term, as we had for the electrons and holes.

In equilibrium, the chemical potentials for CTC and CTC* have to be the same and we get for the ratio of the equilibrium (superscript 0) concentrations:

$$\frac{c_{\text{CTC}^*}^0}{c_{\text{CTC}}^0} = \exp\left(-\frac{\xi_{\text{CTC}^*}^0 - \xi_{\text{CTC}}^0}{k_B T}\right) = \exp\left(-\frac{E_{\text{CT}}}{k_B T}\right). \quad (3.43)$$

The equilibrium densities considering thermal excitations are described by a Boltzmann distribution. Here, E_{CT} is the internal energy difference between the two states, i.e. the free energy for $T \rightarrow 0$ K. It is the energy of a photon absorbed/released upon

a transition between both states. This interaction with a photon can be quantum-mechanically described by Fermi's golden rule (3.2). However, we do not choose this approach here, but refer to Einstein's considerations for transitions induced at a two-level system in the presence of an electromagnetic field. Einstein introduced a simple rate equation for changes of the concentration of atoms (here molecular complexes) in the ground state:

$$\frac{dc_{\text{CTC}}}{dt} = \underbrace{A_{21}c_{\text{CTC}^*}}_{\text{spontaneous emission}} - \underbrace{B_{12}\rho(\hbar\omega)d(\hbar\omega)c_{\text{CTC}}}_{\text{absorption}} + \underbrace{B_{21}\rho(\hbar\omega)d(\hbar\omega)c_{\text{CTC}^*}}_{\text{stimulated emission}}. \quad (3.44)$$

This equation means that the concentration of molecules in the ground state is increased by spontaneous emission being proportional to c_{CTC^*} and stimulated processes being proportional to the energy density $\rho(\hbar\omega)d(\hbar\omega)$ of the electromagnetic field at E_{CT} and the states they are acting on. The coefficients are called Einstein coefficients. We can directly state their values examining the system in steady state ($d/dt = 0$) and in equilibrium with a black-body radiation. In this case, the black-body radiation describes $\rho(\hbar\omega)d(\hbar\omega)$, as (3.44) has to be fulfilled for all kinds of ρ and in particular for a black-body radiation.

We rearrange (3.44) to be able to directly compare it with (2.1)

$$\rho(\hbar\omega)d(\hbar\omega) = \frac{A_{21}}{B_{12}\frac{c_{\text{CTC}}}{c_{\text{CTC}^*}} - B_{21}} \stackrel{(3.43)}{=} \frac{A_{21}}{B_{12}\exp\left(\frac{E_{\text{CT}}}{k_{\text{B}}T}\right) - B_{21}}. \quad (3.45)$$

Comparing the coefficients between both equations demands for:

$$\begin{aligned} B_{12} &= B_{21} \\ A_{21} &= \frac{E_{\text{CT}}^3}{\pi^2 \hbar^3 c^3} B_{12}. \end{aligned} \quad (3.46)$$

Assuming that out of equilibrium the spectral shape of the emission is not changed and the coefficients are maintained, we end up with Wülfel's generalized Planck's law [cf. (2.24), $\Omega = 2\pi$, effectively π for a planar surface element]:

$$dj_{\gamma}^{\text{em,CT}}(\hbar\omega) = \frac{1}{4\pi^2 \hbar^3 c^2} \frac{a_{\text{CT}}(\hbar\omega) (\hbar\omega)^2}{e^{\frac{\hbar\omega - (\xi_{\text{CTC}^*} - \xi_{\text{CTC}})}{k_{\text{B}}T}} - 1} d\hbar\omega \stackrel{(2.23)}{\sim} \exp\left(\frac{(\xi_{\text{CTC}^*} - \xi_{\text{CTC}})}{k_{\text{B}}T}\right). \quad (3.47)$$

Thus, we can relate the amount of emission, i.e. relaxation events of the CT state, exponentially to the difference in chemical potential between excited state and ground state CT complexes, which is related to the concentrations according to (3.42) and (3.43):

$$\xi_{\text{CTC}^*} - \xi_{\text{CTC}} = E_{\text{CT}} - k_{\text{B}}T \ln \frac{c_{\text{CTC}}}{c_{\text{CTC}^*}}. \quad (3.48)$$

Both states are electrically neutral. However, we want to relate this chemical energy to an electrical energy, i.e. the open-circuit voltage. This was straight forward in Sect. 2.4 where we discussed an electron-hole pair delivering an elementary charge when electron and hole reach their respective electrode. To do so here, we should examine the interaction between CT states and free charge carriers. We have already performed this treatment from a different point of view in the previous section. The basic assumption is that CT states and free charge carriers are in equilibrium even in the non-equilibrium situation of illumination. This assumption of extended quasi-equilibrium is difficult to prove, however reasonable for high and fast interactions between CT states and free charge carriers. Then, we can write with the CT state binding energy $E_{\text{B}} = E_{\text{g}}^{\text{DA}} - E_{\text{CT}}$ and the overall density of CT complexes $N_{\text{CTC}} = c_{\text{CTC}} + c_{\text{CTC}^*}$:

$$\frac{np}{N_{\text{C}}N_{\text{V}}} = \frac{c_{\text{CTC}^*}}{N_{\text{CTC}}} \exp\left(-\frac{E_{\text{B}}}{k_{\text{B}}T}\right). \quad (3.49)$$

Thus:

$$eV_{\text{oc}}^{\text{max}} = \xi_{\text{n}} + \xi_{\text{p}} \stackrel{(3.26, 3.49)}{=} E_{\text{g}}^{\text{DA}} - k_{\text{B}}T \ln \frac{N_{\text{CTC}}}{c_{\text{CTC}^*}} - E_{\text{B}} \stackrel{(3.48), N_{\text{CTC}} \approx c_{\text{CTC}}}{=} \xi_{\text{CTC}^*} - \xi_{\text{CTC}}. \quad (3.50)$$

Here, we replaced N_{CTC} by the concentration of ground CTCs assuming that only a very small fraction of CTCs is excited. Equation (3.50) states that the chemical energy of the CT state is completely transferred to chemical energy of the electron-hole pair. Equation (3.49) shows that the dynamic equilibrium between np and c_{CTC^*} can be largely shifted towards the free charge carriers even in case of a significant E_{B} . The reason is the difference in the densities of states: If $\sqrt{N_{\text{C}}N_{\text{V}}} \gg N_{\text{CTC}}$, most CT states split to free charge carrier pairs. This entropic driving force might explain why even a bound CT state might split into free charge carriers giving high internal quantum efficiencies (at short circuit).

Now, we want to consider what happens if the solar cell shows further loss mechanisms additional to radiative recombination. These losses are seen in a luminescence efficiency which is smaller than unity and a photovoltaic external quantum efficiency $[\text{EQE}_{\text{PV}}, (3.24)]$ which is smaller than the absorptance. This implies an internal quantum efficiency $\text{IQE} < 1$. For such a situation, Rau derived a general reciprocity relation between photovoltaic and electroluminescence quantum efficiency [108]. This approach requires additional assumptions, which are the reciprocity in charge transport and the superposition principle applied to current in the dark and under illumination. We made use of this principle when deriving the current-voltage characteristics of the p-n junction under illumination (2.50). In his derivation Rau makes the same assumption that demands for a photocurrent independent of applied voltage, which can be superimposed with a dark current due to injection of charge carriers. This

condition is not necessarily fulfilled in an organic solar cell. Hence, we allow for a voltage dependence of the $\text{EQE}_{\text{PV}}(V)$, although this might violate the original reciprocity relation to a minor extent. Nevertheless, we will see that if $J_{\text{sc}} \gg e j_{\gamma}^{\text{em},0}$, variations of J_{photo} with voltage are not crucial when determining V_{oc} . However, they are critical when considering the maximum power-conversion efficiency as we will see later.

We modify the expression of (2.55) considering a finite external quantum efficiency EQE_{PV} , which contains both losses due to insufficient absorption and an internal quantum efficiency smaller than unity:

$$J_{\text{photo}}(V) = e \int_0^{\infty} \text{EQE}_{\text{PV}}(V, \hbar\omega) d j_{\gamma}^{\text{AM1.5g}}(\hbar\omega). \quad (3.51)$$

Equation (3.51) holds also in the case of equilibrium with the thermal black-body radiation, as $\text{EQE}_{\text{PV}}(0, \hbar\omega)$ does not depend on the photon source. As the intensity of the ambient black-body radiation is much weaker than solar illumination, we assume that $\text{EQE}_{\text{PV}}(0, \hbar\omega)$ is independent of the intensity of the incoming light, i.e. the solar cell response is linear in intensity. Replacing the solar photon flux spectrum in (3.51) by the black-body photon flux spectrum of the ambient results in an equilibrium current J_0 . When we discussed the case with $\text{EQE}_{\text{PV}}(V, \hbar\omega) = a(\hbar\omega)$, we saw that this current is not present as electrical current but the absorbed photon flux is completely emitted in form of photons. Also for an $\text{IQE} < 1$, the absorbed photon flux is completely emitted at equilibrium. As sketched in Fig. 3.28a, we want to formally distinguish between electron-hole pairs that have the potential to be extracted, i.e. those contributing to the IQE , and those that do not. The former give rise to the current in (3.51). Naturally, in equilibrium, net-current does not flow.

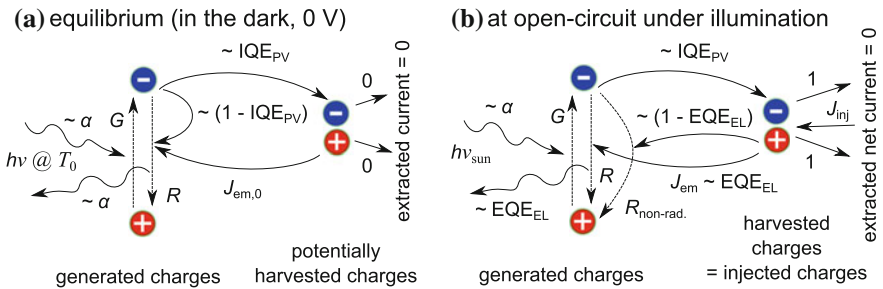


Fig. 3.28 Sketch of the general reciprocity between photovoltaic and electroluminescence quantum efficiency: **a** in equilibrium with the ambient black-body radiation at T_0 , which generates electron hole pairs (G). They recombine (R) radiatively to maintain equilibrium. $J_{\text{em},0}$ is introduced to balance the conversion of photogenerated electron-hole pairs into electron-hole pairs which can potentially be harvested (share of IQE_{PV}), **b** Under illumination at open-circuit: The harvested electron-hole pairs are compensated by an injection current J_{inj} . Due to an $\text{EQE}_{\text{EL}} < 1$, only a share of the injected charges recombine radiatively

Formally, however, we can say that J_0 has to be counterbalanced by a microscopic injection current $J_{\text{em},0}$ into the volume element, where the absorption happened, which created J_0 . This current leads to emission of photons to maintain equilibrium with the ambient. The idea of a counterbalancing electric current in equilibrium is a bit counterintuitive as we previously explained that real current does not flow in equilibrium. Such a current would require scattering events and therefore energy dissipation. So we should not think of $J_{\text{em},0}$ as a macroscopic current flowing in the device, but as a formal approach which allows to relate absorption and emission in non-equilibrium.

We can write for J_0 :

$$J_0 = e \int_0^\infty \text{EQE}_{\text{PV}}(0, \hbar\omega) dj_\gamma^0(\hbar\omega) = J_{\text{em},0}. \quad (3.52)$$

Here, according to (2.21), the ambient black body radiation is expressed as a spectral photon flux density: $dj_\gamma^0 = \frac{1}{4\pi^2 \hbar^3 c^2} \frac{(\hbar\omega)^2}{e^{k_B T_0} - 1} d\hbar\omega$ for a more comprehensive style of expression.

Now we assume that the injected current under an applied bias voltage, which leads to (luminescence) emission, increases exponentially with voltage:

$$J_{\text{em}}(V) = e \int_0^\infty \text{EQE}_{\text{PV}}(V, \hbar\omega) dj_\gamma^0(\hbar\omega) \exp\left(\frac{eV}{k_B T}\right) - J_{\text{em},0}. \quad (3.53)$$

We see that this equation guarantees that the real current injected into the device is zero at $V = 0$ V. Its further validity for $V \neq 0$ is given for many systems and based on reciprocity relations of charge transport [108, 109]. The reader is referred to the original work for a detailed derivation of this equation. Here, we allow for an $\text{EQE}_{\text{PV}}(V, \hbar\omega)$, which might change with voltage, and assume that the injected emissive current scales with the EQE. We accept the exponential rise of J_{em} with V , as it can indeed be observed for organic solar cells [79].

Now we can relate the overall injected current $J_{\text{inj}}(V)$ to the injected current leading to emission $J_{\text{em}}(V)$ by introducing a quantum efficiency for electroluminescence $\text{EQE}_{\text{EL}}(V)$, which describes the share of injected charges that recombine radiatively:

$$J_{\text{em}}(V) = \text{EQE}_{\text{EL}}(V) J_{\text{inj}}(V). \quad (3.54)$$

Inserting this expression into (3.53) yields:

$$J_{\text{inj}}(V) = \frac{1}{\text{EQE}_{\text{EL}}(V)} \left(e \int_0^\infty \text{EQE}_{\text{PV}}(V, \hbar\omega) dj_\gamma^0(\hbar\omega) \exp\left(\frac{eV}{k_B T}\right) - J_{\text{em},0} \right). \quad (3.55)$$

This equation describes the current-voltage characteristics in the dark (device operates as an LED) as an exponential function of V , photovoltaic and electroluminescence EQEs, and the thermal background radiation.

Finally, we superimpose the current $J_{\text{photo}}(V)$ generated by an additional, non-equilibrium light source [e.g. the sun, (3.51)] with the dark curve. At open circuit, photogenerated and injected current have to be equal as visualized in Fig. 3.28b:

$$e \int_0^{\infty} \text{EQE}_{\text{PV}}(V_{\text{oc}}, \hbar\omega) dj_{\gamma}^{\text{AM1.5g}} \hbar\omega = \frac{1}{\text{EQE}_{\text{EL}}(V_{\text{oc}})} \left(e \int_0^{\infty} \text{EQE}_{\text{PV}}(V_{\text{oc}}, \hbar\omega) dj_{\gamma}^0(\hbar\omega) \exp\left(\frac{eV_{\text{oc}}}{k_{\text{B}}T}\right) - J_{\text{em},0} \right). \quad (3.56)$$

Rearranging the equation and replacing $J_{\text{em},0}$ with the aid of (3.52) gives for the open-circuit voltage:

$$eV_{\text{oc}} = k_{\text{B}}T \ln \frac{\left(\int_0^{\infty} \text{EQE}_{\text{PV}}(V_{\text{oc}}, \hbar\omega) dj_{\gamma}^{\text{AM1.5g}}(\hbar\omega) + \frac{1}{\text{EQE}_{\text{EL}}(V_{\text{oc}})} \int_0^{\infty} \text{EQE}_{\text{PV}}(0, \hbar\omega) dj_{\gamma}^0(\hbar\omega) \right)}{\frac{1}{\text{EQE}_{\text{EL}}(V_{\text{oc}})} \int_0^{\infty} \text{EQE}_{\text{PV}}(V_{\text{oc}}, \hbar\omega) dj_{\gamma}^0(\hbar\omega)}. \quad (3.57)$$

We assume that the spectral shape of the EQE_{PV} does not significantly change with applied voltage. This assumption is reasonable for a spatial absorption profile independent of wavelength, as in this case a correlation of photon energies with recombining charges is not expected. The charges do not remember the energy of the photon they were created from. We introduce the factor $m \leq 1$ defined via: $\text{EQE}_{\text{PV}}(V_{\text{oc}}, \hbar\omega) = m \text{EQE}_{\text{PV}}(0, \hbar\omega)$. Equation (3.57) can then be rewritten:

$$eV_{\text{oc}} = k_{\text{B}}T \ln \frac{\left(\text{EQE}_{\text{EL}}(V_{\text{oc}}) \int_0^{\infty} m \text{EQE}_{\text{PV}}(0, \hbar\omega) dj_{\gamma}^{\text{AM1.5g}}(\hbar\omega) + \int_0^{\infty} \text{EQE}_{\text{PV}}(0, \hbar\omega) dj_{\gamma}^0(\hbar\omega) \right)}{\int_0^{\infty} m \text{EQE}_{\text{PV}}(0, \hbar\omega) dj_{\gamma}^0(\hbar\omega)}. \quad (3.58)$$

With (3.51) and (3.52) we obtain our final result:

$$eV_{\text{oc}} = k_{\text{B}}T \ln \left(\text{EQE}_{\text{EL}}(V_{\text{oc}}) \frac{J_{\text{sc}}}{J_{\text{em},0}} + \frac{1}{m} \right). \quad (3.59)$$

Obviously, this equation is only valid under the condition, it was derived for. Hence, it presupposes an exponential injection current that balances the photogenerated current at V_{oc} . An exponential rise of the dark curve is observed for good organic solar cells if losses at the contacts are prohibited. If this is not the case (cf. approach by Sokel and Hughes in Sect. 3.3.5), V_{oc} is not dominated by recombination in the bulk

but by a balance of photogenerated charges leaving right and left electrode. This means $\text{EQE}_{\text{PV}}(V_{\text{oc}}) \rightarrow 0$ and thus $1/m \rightarrow \infty$, and $\text{EQE}_{\text{EL}}(V_{\text{oc}}) \rightarrow 0$. Such a situation means that V_{oc} cannot be predicted using (3.59). Therefore, although including non-radiative losses, (3.59) requires selective contacts to guarantee a conversion of chemical energy into electrical energy with an efficiency of 100 %. Equation (3.59) might also be problematic if V_{oc} is strongly limited by the dissociation of CT states, which also decreases m significantly.

An experimental indication for the applicability of (3.59) is an investigation of the point of intersection between the current-voltage curve under illumination and in the dark. We will focus on this point of intersection in Sect. 5.4. For now, we note that the further it is away from V_{oc} , the higher is the chance of an applicability of (3.59). For the ideal p-n junction, the point of intersection does not exist, as $J_{\text{photo}}(V) = J_{\text{sc}}$ is independent of the applied voltage. Therefore, the current-voltage characteristics under illumination is obtained by a subtraction of a constant value (J_{sc}) from the dark curve [cf. (2.50)]. The $\text{EQE}_{\text{PV}}(V_{\text{oc}})$ is expected to be the same as at short circuit. In organic solar cells this is not a priori given, as already discussed when introducing the factor m .

Assuming that $1/m$ in (3.59) is negligible, we can write for V_{oc} :

$$eV_{\text{oc}} \approx \underbrace{k_{\text{B}}T \ln \frac{J_{\text{sc}}}{J_{\text{em},0}}}_{\text{radiative limit}} - \underbrace{k_{\text{B}}T \ln \frac{1}{\text{EQE}_{\text{EL}}(V_{\text{oc}})}}_{\text{non-radiative loss}}. \quad (3.60)$$

This equation already reported by Ross [107] is very interesting as it connects V_{oc} to macroscopic properties of a solar cell which are experimentally accessible. V_{oc} can be calculated when $\text{EQE}_{\text{PV}}(\hbar\omega)$ (in $J_{\text{em},0}$ and J_{sc}) and EQE_{EL} are known.

The differential form of (3.55) in energy yields the following proportionality at a given V :

$$dj_{\gamma}^{\text{em}} \frac{(V, \hbar\omega)}{d\hbar\omega} \propto \text{EQE}_{\text{PV}}(V, \hbar\omega) \frac{dj_{\gamma}^0(\hbar\omega)}{d\hbar\omega}. \quad (3.61)$$

This relation holds for each wavelength and follows the principle of detailed balance. Therefore, checking this equation with experimental data gives good evidence for the applicability of (3.60). We sketch this relation in Fig. 3.27b, where even a Stokes shift between emission and absorption is well covered. Due to the fast decay of dj_{γ}^0 with energy, the absorption of the CT state dominates the emission of the blend. This was shown by Vandewal et al. [79].

Vandewal et al. went further and came up with an equation relating $J_{\text{em},0}$ to molecular properties by giving an expression for the absorption cross section of a CT state according to [110]:

$$\sigma(\hbar\omega) = \frac{f_{\sigma}}{\hbar\omega\sqrt{4\pi\lambda k_{\text{B}}T}} \exp\left(-\frac{(E_{\text{CT}} + \lambda - \hbar\omega)^2}{4\lambda k_{\text{B}}T}\right). \quad (3.62)$$

This equation describes approximately a Gaussian absorption spectrum with a maximum located at $E_{CT} + \lambda$ (Fig. 3.27b), where λ is the reorganization energy, which we have discussed when having introduced electron transfer via Marcus theory [111] (cf. Sect. 3.2.2). This reorganization gives rise to a change of the orbitals when a molecule (here the charge-transfer complex) is excited. The reasons are vibrational and structural relaxations of the molecule complexes. The reorganization energy related to the CT state, i.e. the excited CTC, gives rise to a Stokes shift between absorption and emission. Emission occurs at a higher wavelength, because the excited state has reached a state of lower energy after reorganization. The maximum of the emission peak of the CT state would then be expected at $E_{CT} - \lambda$ [110]. The reorganization energy determines the width of the peak, where a higher λ and a higher T give rise to broadening according to (3.62). The overall transition probability decreases according to Fermi's Golden rule with the energy difference. The prefactor f_σ is determined by the electric coupling between ground and excited state.

Knowing σ we can roughly estimate the photovoltaic external quantum efficiency originating from the absorption of CT states:

$$EQE_{PV}(\hbar\omega) = IQE_{PV}\alpha(\hbar\omega)l \stackrel{(3.8)}{=} IQE_{PV}\sigma(\hbar\omega)N_{CTC}l, \quad (3.63)$$

where we used the definition of the internal quantum efficiency from (3.24). N_{CTC} is the volume density of charge transfer state complexes that can be excited. The length l represents the path of the light through the solar cell including an attenuation of the intensity of the incident light due to absorption. Vandewal et al. assumed that l can be approximated by the double value of the thickness d of the absorber. The reason is that α of the CT states is so weak that the light intensity (incident plus once reflected at the back electrode) will hardly be changed upon absorption.

Replacing EQE_{PV} in $J_{em,0}$ (3.60) by the expression in (3.63) and integrating over all energies gives (detailed derivation in the appendix of [98]):

$$eV_{oc} \approx E_{CT} - k_B T \ln \left(\frac{f e 2\pi (E_{CT} - \lambda)}{J_{sc} h^3 c^2} \right) - k_B T \ln \left(\frac{1}{EQE_{EL}} \right). \quad (3.64)$$

Here, we summarized some variables in f with $f = IQE_{PV} f_\sigma N_{CT} \cdot 2d$, where f_σ does not depend on energy. Equation (3.64) relates the energy of the CT state to V_{oc} comparable to (3.39). It contains a significant (theoretical) difference to the one for a band-edge absorber [cf. (2.52)]. There, the radiative limit of V_{oc} was given by a trade-off between absorption and emission connected to recombination of charges at the band edge. If the absorbed photon flux and therefore J_{sc} was increased by a higher absorption coefficient, the emission was increased proportionally to the absorption due to the principle of detailed balance. That is not necessarily the case here, as J_{sc} can be modified independently of f . The reason is that the first depends on an excitonic absorption in the pure material, whereas the emission depends on the emissivity and therefore the absorptance of the CT state. This means that the argument of the first logarithm in (3.64) can reach values smaller than 1. Consequently, the second

summand becomes negative describing a V_{oc} which is larger than E_{CT}/e in the radiative limit and for $T > 0$ K. Thus, in the extreme case independent of the difference between the energy E_g^{opt} of the S_1 state of the absorbing molecule and the CT state, V_{oc} can follow the radiative limit given by absorption (and emission/recombination) via the S_1 state. However, a V_{oc} larger than E_{CT}/e has not yet been observed, as it requires an almost complete occupation of all CT states in the case of a significant difference between E_g^{opt} and E_{CT} . V_{oc} would then decrease with T for low T [112]. This trend requires that electrons on the acceptor and holes on the donor cannot recombine with each other (f_σ low and non-radiative processes less pronounced). They have to be injected into a pure material to form the exciton. As this injection requires energy (for a significant difference between E_g^{opt} and E_{CT}), a very low density of CT states N_{CTC} compared to the density of S_1 states is required to make this process probable.

Vandewal et al. demonstrated good agreement of (3.64) with experiment. However, detecting the weak transitions of the charge transfer complex requires some experimental effort and seems not feasible for every material system. Knowing the rough order of magnitude of the EQE or the other parameters except E_{CT} is sufficient to predict V_{oc} quite accurately due to the logarithmic functions with relatively small prefactor. Further studies are required to give closer insights, e.g., including a verification of the temperature dependence of (3.62).

The Role of the Built-In Field and the Electrodes

So far we discussed the chemical potential in the absorber, which can be completely transformed into electrical energy (at open circuit) under the assumption of ideal, i.e. selective contacts. These contacts prevent recombination of charge carriers at the “wrong” electrode, as elaborated when discussing the ideal solar-cell structure in Sect. 2.5.3. For an organic bulk heterojunction solar cell as sketched in Fig. 3.19, this is not necessarily given. This architecture represents a metal-insulator-metal structure which we have already introduced in Fig. 2.12. Commonly, surface recombination velocities at metal electrodes are high for both electrons and holes. Therefore, this structure suffers from “minority” carrier loss. That is why in experiment blocking layers between absorber and electrode are inserted.

If the surface recombination velocities for both charge carriers are the same at the electrode and inhomogeneities in the bulk heterojunction do not exist, only one driving force for a directive charge extraction remains. This force is due to the built-in potential resulting from the difference of the electrode work functions $eV_{bi} = \Delta WF$. In this case, V_{oc} is limited by V_{bi} and cannot exceed it. On the contrary, if the electrodes are selective, V_{oc} will be defined by the chemical potential in the bulk independently of V_{bi} , even if V_{bi} is 0. Energy level diagrams for both extreme cases are shown in Fig. 3.29a and b. The first case (a) represents a situation of flat energy levels (“flat band”), where V_{oc} is limited by V_{bi} . The chemical potential, which is the quasi-Fermi level splitting in the bulk is reduced due to surface recombination (cf. Fig. 2.13b). The second case (b) shows that V_{oc} is reached despite a large reversed field in the device.

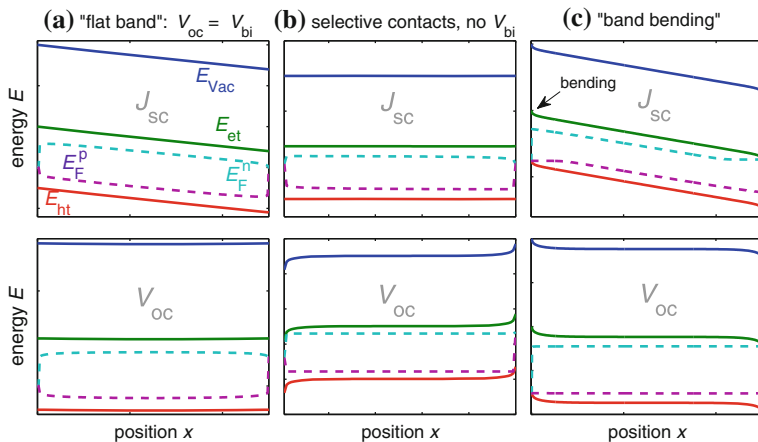


Fig. 3.29 Energy level diagram at short and open circuit for three different cases. The anode collecting holes is located on the left and the cathode collecting electrons on the right of each diagram. **a** A difference in the work functions of the electrodes gives rise to a built-in potential V_{bi} seen in the tilt of the energy levels at J_{sc} . The maximum V_{oc} is limited by recombination at the electrodes and reaches V_{bi} ("flat band"). **b** Selective contacts: Although $V_{bi} = 0$ V, a V_{oc} is found where the field in the device is reversed. **c** Very high charge carrier concentrations at the electrodes give rise to space charge and a bending of the energy levels, which, however, does not influence V_{oc}

The independence of V_{oc} on V_{bi} for flat-heterojunction devices, which contain already an intrinsic selectivity due to the spatial separation of donor and acceptor, can be shown analytically. Cheyns et al. [99] solved the drift and diffusion equations in this case. We do not need to do this here, as we know that the electrochemical potential is constant if there are no additional sources of recombination at the electrodes. Therefore, V_{oc} is independent of V_{bi} . We will investigate the interplay between V_{bi} and V_{oc} in Chap. 6 using experimental data.

Note that the limitation of V_{oc} by V_{bi} in case of non-selective contacts might not be reached under 1 sun illumination and at 300 K. However, this limit might be approached for higher intensities and/or lower temperatures, where the chemical potential increases. Then V_{oc} deviates from the predictions of (3.26) and tends to saturate with lower temperatures [113] or higher intensities as visualized in Figs. 3.30a and 3.25b.

We want to come back to the MIM picture and assume that the device shows the maximum V_{bi} possible, which means that the work functions of the metals match the charge transport levels (for details on metal-organic interfaces, see Sect. 3.5.2). Combined with a high density of states, we expect high charge carrier densities close to the electrodes, as the Fermi level approaches the charge transport level [cf. (2.14)]. They give rise to a large space charge which causes a bending of the energy levels. This space-charge effect can be described by Poisson's equation as we did when deriving the potential distribution of a p-n junction. The bending implies a higher field close to the electrodes. Therefore, it reduces the built-in field in the middle of the device below V_{bi}/d with the thickness d of the absorber layer. This case is

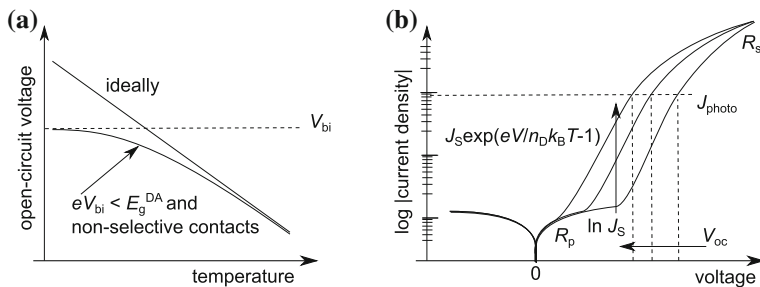


Fig. 3.30 **a** The open-circuit voltage V_{oc} as a function of temperature for ideal contacts and for non-selective contacts. In the latter case, V_{oc} is limited by the built-in potential V_{bi} determining the saturation of V_{oc} at lower temperatures. **b** J - V curves in the dark in a logarithmic current scale. In case of a decreased J_0 , the curves in the exponential region shift downwards. This leads to an increased V_{oc} assuming that V_{oc} is mainly given as the voltage, where the photocurrent J_{photo} equals the injection current

sketched in Fig. 3.29c. It was suspected that this bending is the reason for a decrease of eV_{oc} below eV_{bi} which is equal to E_g^{DA} in this configuration [82, 114]. From our consideration of the electrochemical potentials we directly understand that the bending does not influence the quasi-Fermi levels, which define the voltage. The bending increases rather the selectivity of the contacts due to the large field there. If the chemical potential of the photogenerated electron-hole pairs in the absorber allows, V_{oc} can be higher than expected from the field in the bulk (cf. Fig. 3.29b). This situation implies that the field in the bulk has already changed sign at V_{oc} . In Sect. 5.3 we will show by numerical calculations in detail that a decrease in V_{oc} for higher N_C/V is due to a decreased quasi-Fermi level splitting and decoupled from the charge carrier density and energy level bending at the contacts, which can be an accompanying phenomenon.

Relating the Dark Forward Current of a Diode to V_{oc}

Previously we determined $j_{\gamma}^{em,0}$ in (3.40) from electro-optical measurements. Now, we want to consider the J - V curve in the dark as given by (3.55) assuming that EQE_{EL} is independent of voltage. In this case, (3.55) describes an injection current which increases exponentially with applied voltage like the current of an ideal diode (2.49). Hence, $e j_{\gamma}^{em,0} = J_S$ can be directly determined by fitting an exponential function (cf. Sect. 3.3.5) to the J - V curve in the dark. In case of non-radiative recombination, J_S does not only include $j_{\gamma}^{em,0}$, but also all non-radiative recombination processes (3.59). In general, J_S is determined by E_g^{DA} and the recombination parameters. It decreases with an increased E_g^{DA} and/or decreased recombination rate constants.

We can visualize the relation between J_S (independent of its origin) and V_{oc} in a plot of the (absolute) dark current-voltage curve, where the current is plotted in a logarithmic scale (Fig. 3.30b). There, a change of J_S shifts the exponential region of the J - V curve vertically. This is indicated by the different J - V curves in the figure, where also series R_s and parallel R_p resistances are included, which we will

discuss in Sect. 3.3.5 (Fig. 3.37). Under the assumption of an absorption and an EQE independent of voltage, the dark current at V_{oc} is approximately constant and equals J_{photo} , which is visualized by the horizontal line in the figure. Consequently, V_{oc} (i.e. the point of intersection where $J_{inj}(V_{oc}) = J_{photo}$) follows the shift of the dark curve and decreases with J_S . In case of a known or a fixed E_g^{DA} , differences in recombination probabilities can directly be observed in a change of J_S and subsequently V_{oc} . However, this approach only works if the rise of the dark curve is not limited by other processes than recombination (e.g. injection of charges cf. Sect. 6.4). Potschavage et al. showed the validity of this approach for devices, where the current is dominated by recombination at the donor-acceptor interface [115, 116].

Determining V_{oc} via Lifetime Measurements

Coming back to (3.25) describing V_{oc} of an ideal solar cell, we recall that for calculating V_{oc} it is sufficient to know the incoming absorbed photon flux and the photon flux emitted in equilibrium. However, as most of the recombination in organic solar cells is non-radiative, this ideality is not applicable. Nevertheless, this balance equation holds for non-radiative recombination as well if the emitted photon flux is divided by the quantum efficiency for electroluminescence (3.59). Therefore, V_{oc} can be predicted if the total recombination flux $J_{rec,0}$ is known. Previously we determined $J_{rec,0}$ via EQE_{EL} and EQE_{PV} .

The recombination flux can also be deduced from transient photovoltage decay and charge extraction measurements (details on the experimental methods in Sect. 3.7.3). The first provides the lifetime τ and the second the charge carrier density n at a given V_{oc} . Assuming a homogeneous absorption profile in an absorber with thickness d and a specific recombination model, verified by intensity dependent measurements, allows to determine the recombination current [117] at V_{oc} :

$$J_{rec} = edR(n) = ed\beta(n)n^2 \stackrel{(2.27)}{=} ed \frac{1}{\tau(n)n} n^2. \quad (3.65)$$

This equation describes direct recombination of electrons and holes ($n = p$), allowing for a dependence of β on the charge carrier density itself. Extrapolating J_{rec} towards $V_{oc} \rightarrow 0$ yields the recombination flux $J_{rec,0}$.

From measurements of τ and n it was found that the following equations hold [94, 117]:

$$\tau = \tau_0 n^{-\lambda}; \quad n = n_0 \exp\left(\frac{eV_{oc}}{k_B T n_D}\right). \quad (3.66)$$

Here, λ is the negative slope of τ plotted in a double logarithmic scale as a function of n . Such a plot is shown in Fig. 3.31. For purely bimolecular recombination, β is independent of n and therefore λ is 1 (3.65). The equation relating n and V_{oc} contains a logarithmic scaling of V_{oc} with charge carrier density, which is a prerequisite for the applicability of the approach here. Therefore,

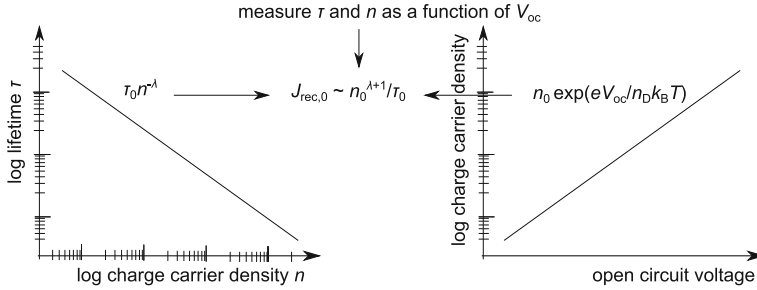


Fig. 3.31 Approach of reconstructing the open-circuit voltage V_{oc} via measurements of the lifetime τ and the charge carrier density n as a function of illumination intensity or alternatively as a function of V_{oc} , which directly translates into a certain intensity

$$J_{rec,0} = J_{rec}|_{V_{oc} \rightarrow 0} = ed \frac{1}{\tau(n_0)n_0} n_0^2 = ed \frac{1}{\tau_0 n_0^{-\lambda} n_0} n_0^2 = ed \frac{n_0^{\lambda+1}}{\tau_0}. \quad (3.67)$$

Replacing the equilibrium recombination current in (3.25) by $J_{rec,0}$ and considering the non-ideality of the exponential rise of V_{oc} with intensity, represented by the diode ideality factor n_D , gives for V_{oc} :

$$eV_{oc} = n_D k_B T \ln \left(\frac{J_{sc}}{J_{rec,0}} \right). \quad (3.68)$$

Here, as previously, we assumed that the photogenerated current equals the short-circuit current density. This approximation is acceptable even for a not completely saturated photocurrent at short circuit because V_{oc} depends logarithmically on J_{sc} . A change of J_{sc} (or $J_{rec,0}$) by a factor of 10 modifies V_{oc} only by $n_D \cdot 60 \text{ mV}$ ($T = 300 \text{ K}$).

Applying (3.67) and (3.68), Maurano et al. [117] were able to predict V_{oc} very accurately measuring n and τ as a function of illumination intensity and subsequently approximating $J_{rec,0}$. Investigating several donor-acceptor heterojunctions with varied E_g^{DA} , they could explain slight deviations in the linear scaling of V_{oc} with E_g^{DA} . The authors found that the deviations are due to changed recombination probabilities of free charge carriers. This observation is identical to a variation of the last term in (3.26) for different material systems.

The D/A Interface as a Two-Level System

Nelson et al. [118] examined V_{oc} of organic solar cells from a slightly different point of view by balancing excitation and relaxation rates at a donor-acceptor heterojunction as a two level system. They included also the effect of charge transfer and transport limiting the efficiency and calculated charge transfer rates using Marcus theory. Applying the theory of detailed balance they found (for the derivation, see the original paper):

$$eV_{oc} = E_g - k_B T \ln \left(\frac{K_g}{G_s + G_0} + 1 \right). \quad (3.69)$$

Here, K_g is a coefficient of recombination, G_s is the absorbed photon flux from the sun and G_0 is the absorbed photon flux from the ambient, both per unit volume. A high recombination constant will reduce V_{oc} in this equation as well.

Introducing a chromophore as the absorber (which is somehow analog to the CT state) they find that a too fast transfer rate from the chromophore to the adjacent donor and acceptor molecules is detrimental for a high V_{oc} . The reason is that this high rate (described by Marcus theory) comes along with a high backtransfer of the charge into the ground state of the chromophore, which means a high recombination rate. In other words, a low charge transfer rate is beneficial as it increases the charge carrier density on the chromophore (at the heterojunction). V_{oc} is then given by the (radiative and non-radiative) generation-recombination equilibrium on the chromophore and is not limited by interfacial recombination. However, too low transfer rates reduce the probability of charge extraction and thus affect the maximum electrical power which can be delivered by the solar cell.

The Correct Gap and Quasi Equilibrium

In the previous sections we used E_g^{DA} to describe the electrical gap of an organic solar cell. We related it to the energies of the HOMO and the LUMO of donor and acceptor. Cravino [23] postulates that taking the single occupied molecular orbital (SOMO) instead of the HOMO level to calculate the effective gap decreases the difference between E_g^{DA} and eV_{oc} (at 1 sun and at 300 K) to very low values. The reason is that the SOMO as polaronic level is supposed to lie higher than the HOMO, because it includes the polarization energy of a positively charged molecule (cf. Sect. 3.1.1, Fig. 3.11). This example shows the ambiguity regarding the energy value that should be assigned to the hole transport level: the HOMO of the molecule, the SOMO, or the ionization potential (IP)? How is the correct gap defined? By peak to peak values, onsets, the CT state energy? Experimental verifications are very difficult as the experimental errors when determining these energy values are commonly in the range of hundreds of meV. The broadening of the energy levels, which is introduced by disorder and found in a similar energy range, makes it problematic to state a discrete E_g^{DA} . However, when discussing V_{oc} , variations in the range of 10 meV are already of significance.

For the calculations shown in this book, as already mentioned, the (negative) IP of molecules in a (blended) thin film is supposed to be the transport energy level for holes E_{ht} . The IP, as measured by photoelectron spectroscopy, includes electronic polarization effects of the film and is the best approximation for the energy level a hole is transported on. For electrons, the electron affinity (EA) in a thin film is chosen for E_{et} , which, unfortunately, is hard to accurately determine in experiment. Of course, energies of the CT state can also be considered, using a consistent theory with clearly defined parameters.

All equations for V_{oc} in this chapter have been given under the assumption of the validity of detailed balance. Charge carriers have been assumed to be relaxed in their density of states (quasi equilibrium). The good agreement of V_{oc} calculated and experimentally determined indicates that this assumption is valid. Thus, an organic solar cell is not a kind of hot-carrier device (at least at V_{oc}). This might be assumed when thinking of the photogenerated charges being injected into a Gaussian DOS at elevated positions. In this case the Bässler model predicts a relaxation of charges during hopping, e.g. a relaxation in time and space (cf. Sect. 3.2.3). This effect implies an effective gap which depends on the number of hops, i.e. the distance charges travel. Therefore, e.g. a V_{oc} as a function of device thickness would be expected, if the relaxation is in the length scale of device dimensions (10s of nm). In particular when examining planar heterojunction devices, V_{oc} should decrease with a larger thickness. Quasi-Fermi levels cannot be defined in this case. However, such observations have not yet been reported.

3.3.3 Maximum Power-Conversion Efficiency

The absolute EQE ($\lambda, 0\text{ V}$) multiplied by the number of incident photons at λ (cf. dash-dotted line in Fig. 2.2) integrated over the (solar) illumination spectrum gives the short-circuit current density J_{sc} of a solar cell (3.51). Note that in this case the EQE has to be measured at conditions similar to solar illumination, which requires an applied background light of similar intensity that is absorbed by the solar cell. Background illumination is not required if the solar cell's response is linear in intensity, which means that the EQE does not depend on the illumination intensity. However, this is not the case for significant bimolecular recombination at 0 V.

In short circuit, as well as at V_{oc} , power cannot be extracted (cf. Sect. 2.3). The optimum operation point is the so-called maximum power point (V_{MPP} , J_{MPP}), where the product of current and voltage is maximized, as illustrated in Fig. 3.32.

The power-conversion efficiency (η) as the product of V_{MPP} and J_{MPP} divided by the illumination intensity P_γ can be rewritten as a function of J_{sc} and V_{oc} with the fill factor FF as new proportionality constant describing the ratio between $V_{MPP} \cdot J_{MPP}$ and $V_{oc} \cdot J_{sc}$:

$$\eta = \frac{V_{MPP}J_{MPP}}{P_\gamma} = \frac{V_{oc}J_{sc}FF}{P_\gamma}. \quad (3.70)$$

The FF can be seen as a quality factor, measuring the squareness of the J - V curve. All quantum efficiencies introduced in Sect. 3.3.1 that show a dependence on voltage influence the FF . Thermodynamics sets the ultimate limit of the FF , which is reached in case of an ideal solar cell. Equation (2.57) predicts a higher FF for a reduced recombination flux. Then, the exponential rise of the current with voltage is sharper. Taking the values used in Sect. 2.6.1 to derive the Shockley-Queisser limit (SQ) for a silicon solar cell we calculate a maximum FF of 87 %.

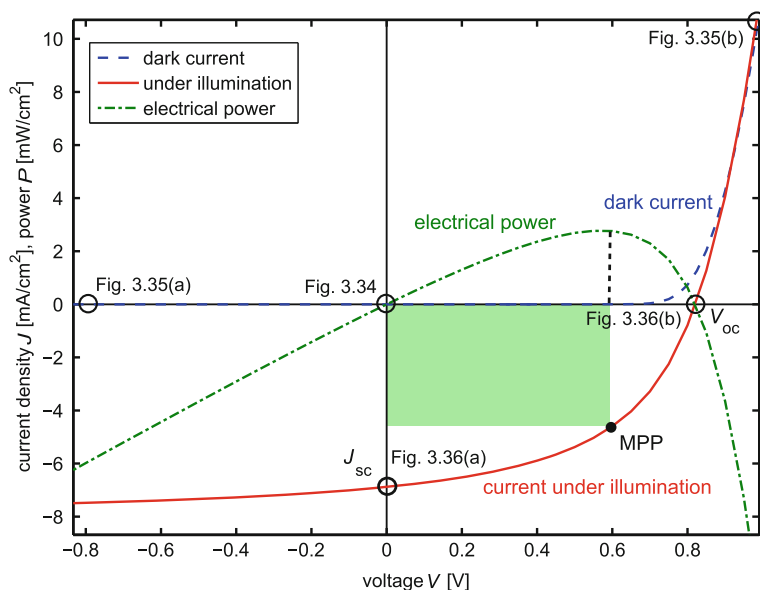


Fig. 3.32 Current-voltage characteristics of a solar cell in the dark and under illumination. In the fourth quadrant, electric power is provided with a maximum at the maximum power point (*MPP*)

There, we found that the maximum power-conversion efficiency of a single band-edge absorber is given by this limit with radiative recombination as the only loss mechanism. In principle, this upper limit holds also for organic solar cells. Theoretically, it should be achievable if the energy offset between the LUMOs in case of absorption only in the donor is adjusted to cover exactly the exciton binding energy. This means that the values of optical and electrical (effective) gap are identical and the maximum efficiency is given by the radiative lifetime of the exciton. However, optical and electrical gap differ in a real organic solar cell. This difference introduces an additional complexity when applying the SQ limit to a given donor-acceptor system. The analysis by Shockley and Queisser is based on the definition of the electrochemical potentials for electrons and holes. Their difference defines both the radiative recombination rate and the voltage measurable at the contacts. The quantities that recombine radiatively are identical to those being extracted. This is not the case for an organic semiconductor where radiative transitions are excitonic and charge transport is polaronic. Therefore, deriving a maximum efficiency for the two-component material system donor-acceptor is not straight forward.

Nevertheless, a thermodynamic approach can be applied to relate the radiative recombination to the limit of V_{oc} . We have done so in the previous section, where we found that V_{oc} can reach the value of the SQ limit if “sub-bandgap” emission from the CT state can be avoided. If the CT-state emission is significant, the energy of the CT state E_{CT} will set the maximum V_{oc} [98, 105], related with a loss in energy due to the thermalization of exctons from the S_1 state into the CT state. In this situation,

the (significant) absorption onset is E_g^{opt} . Recombination, however, happens at E_{CT} . Thus, the Shockley-Queisser limit cannot be reached.

If the emission of the CT state is weak [i.e. long lifetime compared to pure material emission or in other words a low absorption coefficient in (3.63)], the SQ limit for V_{oc} can be approached [112] independently of the energy offsets between E_g^{opt} (S_1), E_{CT} (CT state), and E_g^{DA} (free charges), as long as the CT state or free charges do not constitute a significant source of recombination. From this point of view one should not use the donor-acceptor approach, but simply fabricate a single-material device. Indeed, devices consisting of a pristine (donor) absorber usually show a significantly higher V_{oc} than devices where this donor is combined with an acceptor. However, the overall efficiency of these devices is low as J_{sc} and FF are low due to low quantum efficiencies in charge separation.

We conclude that the arrangement first mentioned is the one which can approach the SQ limit: An overlap of S_1 and CT-state spectra, with a CT state binding energy approaching 0. Then the field dependence of the photocurrent is weak and the donor-acceptor interface will have simply the function of delocalizing the excited state.

However, there is one fundamental difference between inorganic and organic semiconductors, namely a significant reorganization energy. This energy leads to an energetic relaxation of excited states or upon charge transfer (cf. Marcus theory). Thus, it results in a Stokes shift between absorption and emission of S_1 or CT states. This means that the onset of emission is red-shifted compared to the onset of absorption. In this case the SQ limit cannot be reached with a realistic solar cell, as this difference in energy is lost. The reorganization process is comparable to thermalization of electrons in energy bands of a conventional semiconductor. Recall, that thermalization is the most severe energy loss, contributing to the reduction of the theoretical thermodynamic limit to the SQ limit. In case of organic materials, the lost energy is due to a vibrational or structural relaxation of an excited molecule which leads to dissipation of heat. This entropy rich energy is not accessible for the generation of a photovoltage. Therefore, it constitutes a loss inherent to molecular semiconductors and limits the electrical gap below the optical one. For high efficiencies, this reorganization energy should be minimized [119]. Further ways towards higher efficiencies will be discussed in the last chapter of this book.

Analogous to the reorganization energy, intragap tail states introduced by disorder decrease the maximum efficiency due to a further thermalization of charges or additional paths for recombination [120]. In state-of-the-art devices, too narrow absorption bands, non-radiative charge carrier and/or CT exciton loss paths at the heterojunction, and low mobilities in combination with bimolecular recombination limit the power-conversion efficiency to a value below 10 % [121].

We can roughly estimate a realistic value of the maximum power-conversion efficiency which might be achievable without reaching a new working regime for organic solar cells. Note that this estimation is based on empirical values which are derived from a literature survey and the feeling for what seems feasible when doing slight modifications, further optimizations, and engineering of the molecules and the

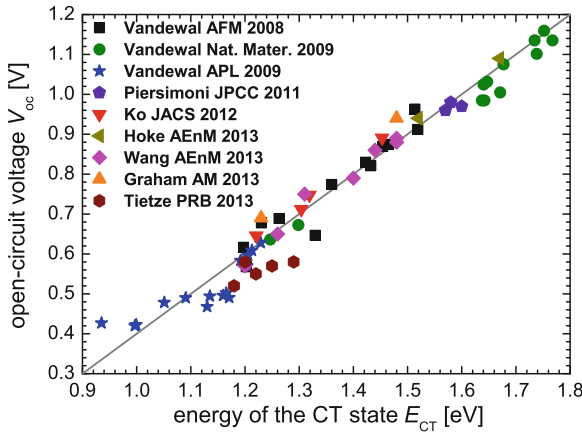


Fig. 3.33 The open-circuit voltage V_{oc} as a function of the energy of the CT state E_{CT} for several material systems including polymers and small molecules: overview of data from [76, 79, 122–128]

device. We estimate η according to (3.70) and assume the following for the individual parameters:

- V_{oc} : As shown in Fig. 3.33, a difference of around 0.6 V is observed between V_{oc} and E_{CT}/e . This value is much larger than the theoretical one but seems to be general for organic solar cells due to strong non-radiative recombination. Thus:

$$V_{oc} \approx E_{CT}/e - 0.6 \text{ V}. \quad (3.71)$$

For an efficient charge transfer and dissociation at the heterojunction, we postulate a required energy difference of 0.1 eV between E_{CT} and E_g^{opt} . The latter denotes the absorption onset. This number of 0.1 V describes a realistic value for a well-optimized D/A heterojunction. Now, let us choose a value for E_g^{opt} . When deriving the Shockley-Queisser limit, we found that the optimum bandgap for a single-bandgap absorber is in the range of 1–1.5 eV. Looking at Fig. 2.18b, we see that the difference between eV_{oc} and E_g does not change significantly for $E_g = 1\text{--}1.5$ eV. Thus, even for a reduced V_{oc} compared to the SQ limit, we can approximately consider the shape of the efficiency curve in Fig. 2.18a to select the optimum gap. We choose $E_g^{\text{opt}} = 1.5$ eV, which results in a V_{oc} of 0.8 V. Despite yielding similar efficiencies, a larger gap is preferred compared to a lower value (e.g. 1.1 eV) due to the following reason: A lower gap requires a higher photocurrent for the same efficiency and thus demands for a broad absorption, which is commonly hard to achieve with organic dyes. Furthermore, high currents lead to larger ohmic losses in electrodes (cf. Sect. 3.6.3).

- J_{sc} : According to Fig. 2.19, a bandedge absorber with an optical gap of 1.5 eV can absorb a maximum photon flux equivalent to an electrical current of 28 mA/cm². Let's assume that the absorption is really broad and losses due to reflection and a

limited internal quantum efficiency reduce this current by only 20 % resulting in 22 mA/cm^2 .

- *FF*: We postulate that an optimization of the morphology and materials with high mobility can deliver a *FF* of 80 %.

Combining these values in (3.70) results in an efficiency of around 14 %. This value, which is rather low, shows that a further reduction of losses is essential, in particular regarding V_{oc} . Note that several 10s of (relative) percent are commonly lost, when going from a champion solar cell to an industrially produced module. A comparison on how close solar cells and modules of different existing technologies come to the Shockley-Queisser limit can be found in [129].

3.3.4 Understanding the *J-V* Curve in the MIM Picture

We introduced the metal-insulator-metal (MIM) picture in Sect. 2.4 (Fig. 2.13). We have already applied it when examining the role of the electrodes on V_{oc} in Fig. 3.29. Here, we want to discuss it in more detail to understand the rectifying behavior of an organic solar cell. This property is the origin of a photovoltaic behavior, which has to be distinguished from a solely photoconductive effect. The following qualitative discussions hold as well for a p-i-n structure with highly (p and n) doped transport layers and the intrinsic layer consisting of a bulk heterojunction absorber. Whether the solar cell is experimentally realized as MIM or p-i-n device depends on the technology used. In general, a p-i-n architecture provides higher flexibility (see Sect. 3.6.2).

Figure 3.34 shows the energy diagram of a MIM device in thermodynamic equilibrium, which means in the dark and at 0 V applied bias. The work functions of the metals are chosen to match the IP and EA of the blend, respectively. This configuration has two main properties: First, only holes can be injected at the anode and only electrons at the cathode due to high injection barriers for the “other” charge carrier. Note that the anode is defined as the electrode where holes are injected, and the cathode as the electrode where electrons are injected. The voltage in all *J-V* plots throughout this book is defined as the electrochemical potential at the anode minus the electrochemical potential at the cathode. The selective injection/blocking directly leads to a rectifying behavior, because dependent on the sign of the applied voltage, electrons and/or holes reverse their direction of flow, and hence change the contact where they are injected.

Second, this structure has a built-in potential V_{bi} like the p-n junction discussed in Sect. 2.5.1. Here, eV_{bi} is simply the difference between the work functions of the two contacts and equals the effective energy gap in this case of matched contact work functions. The resulting electric force on charge carriers in the semiconductor has to be compensated in equilibrium (0 V applied bias in the dark) to guarantee that electric current does not flow. The opposing force is provided by the concentration gradient of free charge carriers. Consulting (2.14) and (2.15) we know that the energetic distance of the Fermi level to the conduction band and to the valence band is a

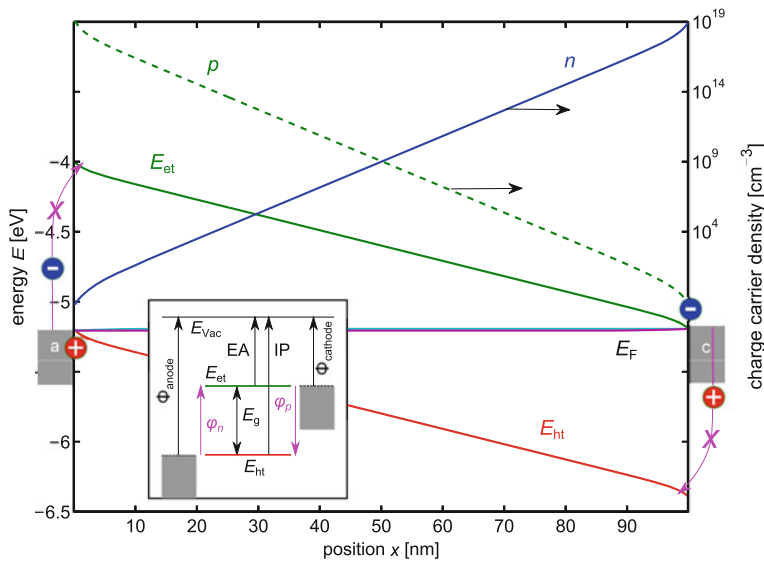


Fig. 3.34 Energy level diagram and charge carrier densities (n and p) of a metal-insulator-metal (MIM) device in electrochemical equilibrium (in the dark at 0 V). The work function Φ of each contact matches the respective charge transport level. Electron (hole) injection at the anode (cathode) is suppressed by a high energy barrier φ . The inset shows the energy levels before contact

measure for the electron and hole concentrations, which increase exponentially with decreasing distance. Thus, in the MIM device the hole (electron) concentration at the anode (cathode) is very high and very low at the cathode (anode), causing a diffusion force opposing the electric field. Concentrations of electrons and holes are shown in Fig. 3.34 as well.

If the MIM device is negatively biased, which means a negative anode potential relative to the cathode potential, a significant current does not flow. Due to the negative potential, electrons (and/or holes) are supposed to be injected at the anode (cathode), which is not possible due to the high injection barrier φ_n (φ_p). Instead, the potential attracts the equilibrium charges pulling holes towards the anode and electrons towards the cathode. The result is a strong depletion of free charges as shown in Fig. 3.35a.

For low applied forward bias, electrons are injected at the cathode and holes at the anode. However, the electric field due to V_{bi} counteracts the current flowing against the built-in field. Hence, this forward current is very small. For applied voltages below the built-in voltage it is a diffusion current, as the applied bias decreases the field and the diffusion gradient stays mainly the same assuming the contacts in equilibrium. Thus, in a first approximation this current can be described like the one in a p-n junction by a general exponential function $\exp(eV/n_D k_B T)$ with the ideality factor n_D , which has already been introduced in Sect. 2.5.1. The threshold where the MIM diode turns on depends then mainly on V_{bi} and the charge carrier concentrations

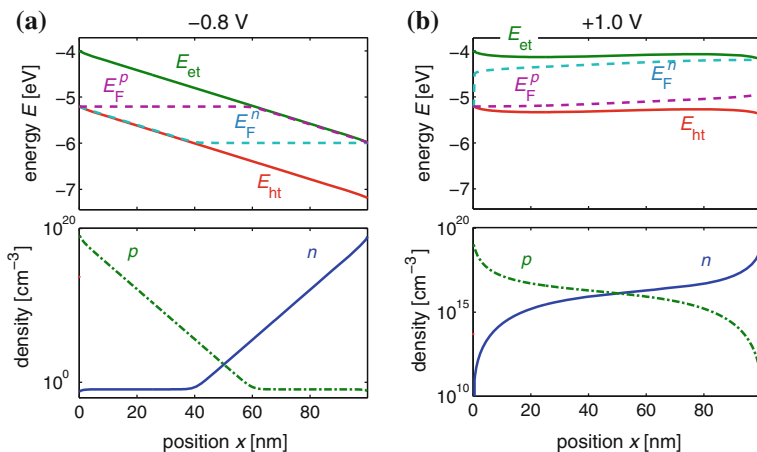


Fig. 3.35 Energy level diagram and charge carrier densities of a MIM device **a** in reverse (-0.8 V), where electrons and holes are pulled out of the device and a significant current does not flow (apart from thermally generated charge carriers) and **b** in forward (1 V), where electrons flow from right to left and holes from left to right. The applied bias is found in the difference between the Fermi levels at the contacts

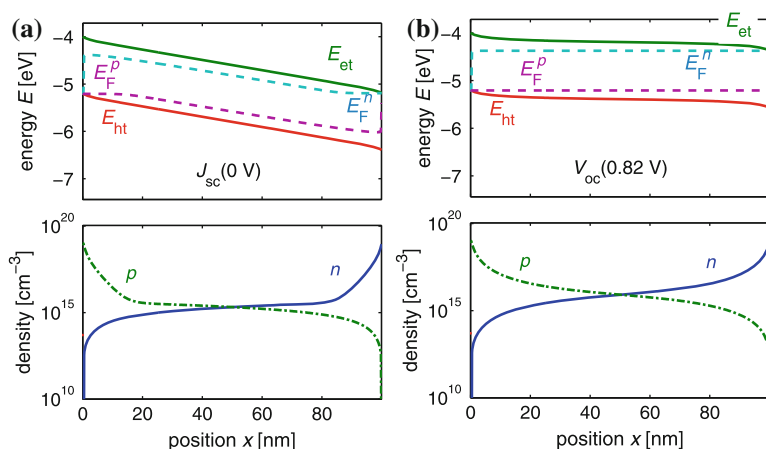


Fig. 3.36 Energy level diagram with split quasi-Fermi levels and charge carrier densities of a MIM device under illumination **a** at short circuit and **b** at open circuit (0.82 V). The voltage measurable between the contacts is the difference between the Fermi levels at the contacts

at the contacts defined by the density of states. For larger forward bias, as shown in Fig. 3.35b, charge carrier densities are strongly increased and the field in the bulk of the layer has already changed sign (reverse tilt of the energy levels), giving rise to large forward currents limited by the resistivity of the material.

If we consider the device under illumination (Fig. 3.36), charge carriers are generated in the intrinsic layer, which is either a bulk heterojunction (as in the figure) or a bilayer of donor and acceptor (flat heterojunction). These additional charge carriers are then driven by the field and constitute a current in a direction which is reverse compared to the direction of forward injection current. That is analog to the photocurrent generated in the space-charge region of a p-n junction (Sect. 2.5.1). The current-voltage characteristics under illumination are then a superposition of both contributions leading to a J - V curve showing a J_{sc} and a V_{oc} . This is the characteristic difference to a photoconductor, which only shows a decreased resistivity upon illumination, but no electric power generating regime. The main difference between a MIM device and the conventional p-n junction is the invalidity of the assumption of a constant photocurrent. Therefore, other models have been proposed which are discussed briefly in the next section. Although V_{bi} is essential in the discussed MIM device, we know from Sects. 2.4 and 3.3.2 that a built-in field is not necessarily required for solar-cell behavior. We will demonstrate this experimentally in Chap. 6 with the aid of devices exhibiting a built-in diffusion gradient. These are flat-heterojunction solar cells or devices with selective contacts. Such organic solar cells, however, show poor performance due to poor charge transport properties seen in low fill factors.

3.3.5 Introduction to Analytical Models Describing the Photocurrent

Analytical models describing the whole J - V curve or voltage dependence of the photocurrent are very useful for a quick interpretation of measured data. However, such models include several assumptions, which are not necessarily fulfilled in an organic solar cell. For example, space-charge effects are mostly neglected, which play a crucial role in low-conductive organic materials. More complicated shapes of J - V curve including inflection points cannot be described by simple analytical equations. Nevertheless, we want to briefly introduce a few approaches used in the literature, which are equivalent-circuit models, the concept of the $\mu\tau$ -product, and the description of the photocurrent by an equation derived by Sokel and Hughes [130].

Equivalent Circuit

The equivalent-circuit model is characterized by a very high level of abstraction, because physics is represented by ideal electrical components like resistors, diodes, and current sources. They result from the interplay of several physical processes. The basic assumption of an equivalent-circuit model with a diode and a (photo)current source as main components (Fig. 3.37a) is the applicability of the Shockley equation (2.49 and 2.50), derived for an ideal p-n junction. This approach might be legitimate in a first approximation if one assumes that an organic solar cell can be described in the previously depicted MIM picture with a built-in potential and a

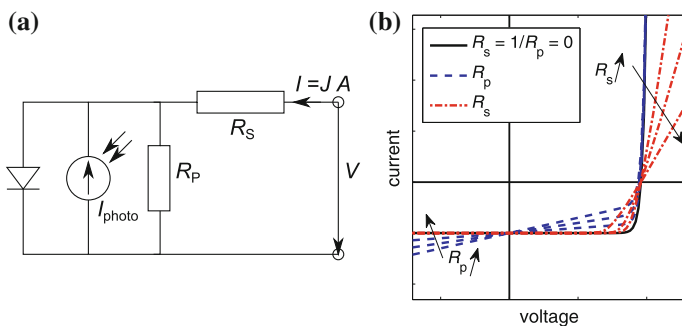


Fig. 3.37 **a** Simple equivalent circuit of a real solar cell. It contains a diode, a photocurrent source and parallel and series resistances. **b** Influence of series resistance R_s and parallel resistance R_p on the current-voltage curve. The resistances mainly reduce the fill factor

diffusion-driven forward current. Then, (2.49) can be applied to describe the diode in the equivalent circuit of Fig. 3.37. This equation is modified by the introduction of a diode ideality factor n_D , which represents recombination in the space-charge layer of the p-n junction. As the space-charge layer of a p-n junction corresponds to the intrinsic bulk heterojunction absorber layer of an organic solar cell, recombination in the bulk is expected or, if contacts are selective, even necessary for driving a forward current. Thus, the ideality factor, which modifies the slope of the exponential diode current, is capable of giving some information about the dominant recombination mechanism in an organic solar cell (cf. Sect. 8.4.1). Including all components, the current density in the circuit of Fig. 3.37a is described by:

$$J = J_S(e^{(V-JAR_S)/n_D k_B T} - 1) + \frac{V - JA R_S}{R_p} - J_{\text{photo}}(V). \quad (3.72)$$

This equation takes into account losses due to a macroscopic series resistance R_s lowering the effective voltage at the junction by $R_s JA$ (area A), and a parallel/shunt resistance R_p , comprising a leakage current path. The characteristic influence of these resistivities is shown in Fig. 3.37b. Both decrease the FF , whereas R_s does not affect V_{oc} , because the voltage dropping at a resistor without a current is 0. The same holds for R_p and J_{sc} , because the voltage and consequently the current at R_p is 0 in this case.

Equation (3.72) describes real diodes quite well. It has also been frequently used to fit the dark current of organic solar cells [131–135]. However, it is very challenging to correctly identify the saturation behavior and determine the saturation current. Another unresolved issue are too high values of n_D , which are difficult to explain physically. To describe more complicated solar cell structures or to include additional recombination mechanisms, the model can be arbitrarily extended, adding more diodes and resistors [136]. Although adequate fits to measured dark curves have

been obtained, the benefit of such models for a deeper physical understanding of organic solar cells remains questionable.

The $\mu\tau$ -product

We assumed the photocurrent J_{photo} to be independent of voltage when discussing the p-n junction (Sect. 2.5.1). Experiments clearly show that this assumption cannot be maintained for most of the organic solar cells, where a strong dependence of the photocurrent on voltage is observed. A clear hint for this behavior is a commonly seen crossing of the dark J - V curve and the one under illumination at a voltage slightly higher than V_{oc} .

A simple approach to describe the dependence of J_{photo} on voltage is the $\mu\tau$ product, where it is assumed that a charge carrier within the blend has a certain lifetime before it recombines. Thus, the expression $\mu F \tau = v \tau = l$ describes the average distance l (drift length) that the charge carrier travels at a certain electric field F (Fig. 3.38). If this distance is smaller or in the range of the device thickness d , J_{photo} will show a dependence on voltage. Under the assumption of a spatially constant generation rate of electron-hole pairs $G = \text{absorbed photon flux density}/d$ and a constant field $F = (V_{\text{bi}} - V_{\text{bias}})/d$ in the device, $J_{\text{photo}} = |J_{\text{illu}} - J_{\text{dark}}|$ under an applied bias V_{bias} can be expressed by [137, 138]:

$$J_{\text{photo}}(V) = \begin{cases} eG\mu\tau \cdot (V_{\text{bi}} - V_{\text{bias}})/d; & l \leq d \\ eGd; & l > d. \end{cases} \quad (3.73)$$

As shown in Fig. 3.38a, a photo-active region exists at each electrode, limited by the $\mu\tau$ product of holes at the cathode and electrons at the anode.

If τ is known, the charge carrier density can be calculated as $G\tau$ and the conductivity of the layer as $eG\tau\mu$. One can directly see that this approach is based on

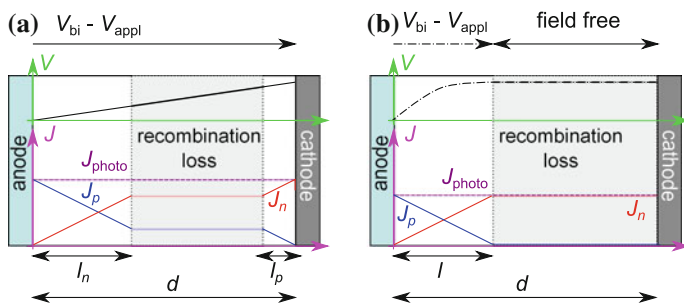


Fig. 3.38 Collection of electron and hole current (J_n and J_p) as assumed by the $\mu\tau$ approach: only the regions (white) within the drift lengths l_n and l_p close to the contacts contribute to the photocurrent. In case of $\mu_p \tau_p \ll \mu_n \tau_n$ (b), a space charge builds up and the voltage completely drops over l (dash-dotted). The photocurrent can then be described by a space-charge-limited current (SCLC)

averaging. A space charge is not considered, because the field is assumed to be constant. Furthermore, the generation rate G is assumed to be spatially constant as well. The lifetime τ is assumed to be a material property, which is only valid for minority carriers or for non-direct/non-bimolecular recombination. Otherwise, as discussed in Sect. 2.2.2, τ depends on the concentration of the other charge carrier type. We will see throughout this book (e.g. Chap. 8) that these assumptions are not always valid for real devices.

Extension to Space-Charge Limit

In case of imbalanced transport ($\mu_p \tau_p \ll \mu_n \tau_n$), a space-charge region builds up in the device, because charge carriers of the slower type (here holes) accumulate in the device. To avoid infinite charging of the device, only one electron (albeit fast) can be extracted for each hole (slow) in steady state. That is why the region at the other contact (here cathode) remains field-free, reducing the electron current (Fig. 3.38b). In a first approximation the photocurrent is only generated in the space-charge region, as in the field-free region photogenerated electrons and holes recombine. Furthermore, the total electric potential drops over the space-charge region, which means that the device thickness d in (3.73) has to be exchanged by the length of the space-charge region. Thus, it holds $l = \mu_p \tau_p \cdot (V_{bi} - V_{bias})/l$ and

$$J_{\text{photo}}(V) = eGl = eG \cdot (\mu_p \tau_p)^{1/2} \cdot (V_{bi} - V_{bias})^{1/2}. \quad (3.74)$$

Goodman and Rose [139] discussed this case and found that in the electrostatic limit J_{photo} equals the space-charge-limited current $J_{\text{SCLC}} = 9/8 \cdot \varepsilon_0 \varepsilon_r \mu_p V^2 / l^3$ (derivation of J_{SCLC} in Sect. 4.8.1). Using this expression to replace l in (3.74) yields for the current:

$$J_{\text{photo}}(V) = e \left(\frac{9\varepsilon_0 \varepsilon_r \mu_p}{8e} \right)^{1/4} G^{3/4} (V_{bi} - V_{bias})^{1/2}. \quad (3.75)$$

This result is very interesting, because it predicts a $G^{3/4}$ -dependence of J_{photo} , which was indeed shown for a certain material system by Mihailetschi et al. [104]. Furthermore, it contains only one material property, namely μ . However, this extended analysis also assumes non-injecting contacts and considers only drift currents.

The Hecht Equation

Commonly, the photocurrent is not linear with voltage as predicted by (3.73). Therefore, a more detailed derivation of the current as a function of voltage is required as presented by Crandall for p-i-n solar cells consisting of amorphous silicon [140]. The derivation starts with the continuity equation, here given for electrons:

$$\frac{\partial n(x)}{\partial t} = -\frac{1}{e} \frac{\partial J_n(x)}{\partial x} + G - R(x). \quad (3.76)$$

This equation describes that the electron density p changes with time due to generation (G), recombination (R), or a gradient in the current density J . We consider a spatial dependence of these quantities only in a direction (x) perpendicular to the device surface as previously and we assume a homogeneous generation G , a constant electric field F , and neglect diffusion currents. Then, we can simplify (3.76) in steady state $\frac{\partial n(x)}{\partial t} = 0$:

$$\frac{1}{e} \frac{\partial J_n(x)}{\partial x} = \mu_n F \frac{\partial n(x)}{\partial x} = G - R(x), \quad (3.77)$$

where we used the expression $J_{n,\text{drift}} = en\mu_n F$ for the drift current according to (2.34).

Next, we characterize the recombination by a lifetime τ_n (2.27):

$$R = \frac{n}{\tau_n}. \quad (3.78)$$

This approach is valid for recombination via traps according to Shockley-Read-Hall theory (3.30). The reader can easily verify that an integration of the partial differential equation (3.77) yields for the electron density:

$$n = G\tau_n \cdot \left(1 - \exp\left(-\frac{x}{l_n}\right)\right), \quad (3.79)$$

where we again used the drift length

$$l_{n,p} = \mu_{n,p} F \tau_{n,p}. \quad (3.80)$$

Equation (3.79) is valid in the region, where the electrons are minorities (on the left side in the device of Fig. 3.38a). This condition is presupposed when defining τ_n according to (3.78). In the other region, which means closer to the opposite electrode, we can solve the same equations for holes:

$$p = G\tau_p \cdot \left(1 - \exp\left(-\frac{d-x}{l_p}\right)\right) \quad (3.81)$$

with the thickness d of the absorber.

Electron and hole densities are plotted as solid lines in Fig. 3.39b, where (3.79) is valid on the left and (3.81) on the right side. The asymmetry between n and p originates from the assumption of $l_n/l_p = 20$. We want to define a cross-over point x_c . At this point, both equations are supposed to be valid, and we can calculate the overall current as sum of electron and hole current at this point. Note that the overall current has to be constant with x in steady state and we can choose the most appropriate x to calculate it as we did when deriving the current-voltage relation for the p-n junction. As both equations are (approximately!) valid at x_c , both describe R : $R(x_c) = \frac{p}{\tau_p} = \frac{n}{\tau_n}$ (dashed lines). Considering this condition in (3.81) and (3.79), we find:

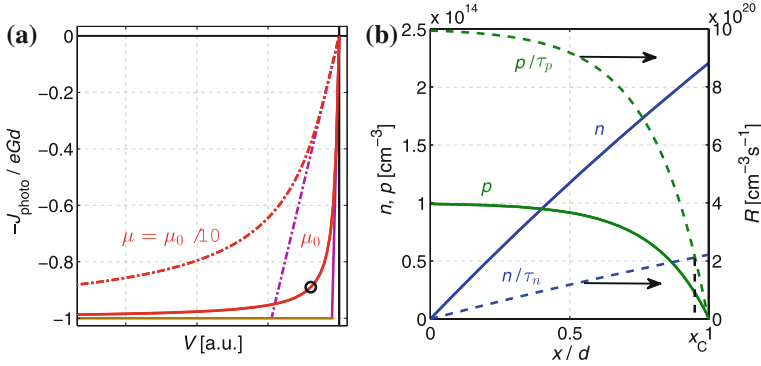


Fig. 3.39 **a** Photocurrent as a function of voltage according to the Hecht equation (3.83) for two different mobilities. *Solid lines* show approximations based on (3.73). **b** Distribution of charge carrier densities within the absorber at the voltage point marked as a *circle* in (a). We assumed $\tau_n = 10^{-6} \text{ s}^{-1}$, $\tau_p = \tau_n/10$, $l_n/l_p = 20$, and $G = 10^{21} \text{ cm}^{-3}$

$$x_c = \frac{d}{1 + l_n/l_p}. \quad (3.82)$$

Plugging x_c into (3.81) and (3.79), we can write for the drift current at x_c :

$$J_{\text{photo}} = eF \cdot (\mu_p p + \mu_n n) = eG \cdot (l_p + l_n) \cdot \left(1 - \exp\left(-\frac{d}{l_p + l_n}\right)\right). \quad (3.83)$$

This equation is called Hecht equation, because it was previously derived by Hecht for the photocurrent of insulating crystals [141]. It converges to (3.73) for large fields, where J saturates at its maximum value $J = eGd$. It also matches (3.73) for low fields, where $l_p + l_n < d$. As for the simple $\mu\tau$ -approach, we can calculate the drift length by either assuming a constant field $F = (V_{\text{bi}} - V_{\text{bias}})/d$ or by considering the case of space-charge-limited current. The latter implies strongly different $\mu\tau$ products for electrons and holes resulting in $F = (V_{\text{bi}} - V_{\text{bias}})/l$.

Figure 3.39a shows J_{photo} calculated with (3.83) in comparison to the very rough approximation for the photocurrent predicted by (3.73). The Hecht equation was successfully applied to the photocurrent of organic solar cells by Street et al. [142] and others [143].

Photocurrent According to Sokel and Hughes

The simple $\mu\tau$ ansatz completely ignores diffusion-driven currents. A more complicated approach, sometimes used to evaluate the photocurrent [66, 68, 134, 135, 144, 145], is proposed in a paper by Sokel and Hughes [130]. On the one hand, they perform a numerical analysis of the photoconductivity of insulators. On the other hand, they derive an analytical equation for the photocurrent under the following

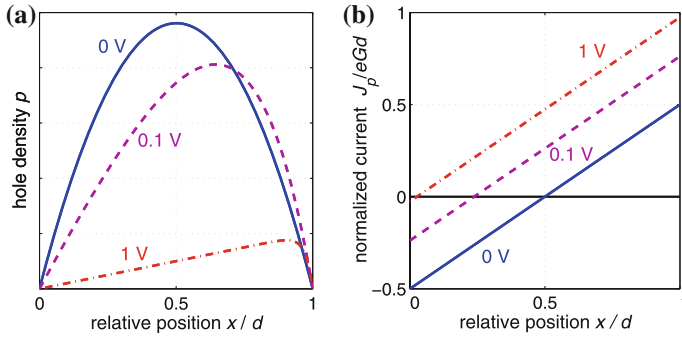


Fig. 3.40 Model for the photocurrent according to Sokel and Hughes: **a** hole density within the absorber calculated with (3.85) dependent on the applied voltage. Charge carrier extraction upon an applied voltage reduces the charge carrier density, **b** hole current, which is in case of 0 V only a diffusion current to both electrodes (zero net current) and in case of a positive applied voltage directed towards the right contact. The electron current (not shown) is equivalent to the hole current, mirrored at $x/d = 0.5$

assumptions: first, a constant generation rate; second a constant electric field as in the (non space-charge limited) approaches discussed previously; third, diffusion is allowed and very important. Fourth, however, recombination of charge carriers in the bulk material is neglected. The continuity equation for holes is then simply:

$$\frac{\partial p}{\partial t} = -\frac{1}{e} \frac{\partial J_p}{\partial x} + G. \quad (3.84)$$

This equation expresses that a change in p with time is either due to a generation G of holes or due to a gradient in the current, causing some redistribution of holes. Replacing J_p by the drift-diffusion equation [$J_p = e\mu_p pF - \mu_p k_B T \frac{\partial p}{\partial x}$, (2.39)] and the electric field F by the applied bias $V = F/d$ yields a differential equation containing only p as variable which is dependent on x . The solution is in steady state ($\frac{\partial p}{\partial t} = 0$) and under the condition of vanishing charge carrier densities at the contacts ($p(0) = p(d) = 0$):

$$p(x) = \frac{Gd^2}{\mu_p V} \cdot \left(\frac{x}{d} - \frac{e^{V/k_B T} \frac{x}{d} - 1}{e^{V/k_B T} - 1} \right); \quad V > 0. \quad (3.85)$$

We leave it to the reader to stepwise derive this equation by integrating (3.84) considering the mentioned assumptions. The hole density expressed in (3.85) is plotted in Fig. 3.40a.

Inserting (3.85) and its derivative into the drift-diffusion equation (2.39) gives the hole current, which is plotted in Fig. 3.40b. It is linear with x because R is zero and G is constant in (3.84), which predicts a slope which is governed by G independent

of x and V . For 0 V, half of the photocurrent is extracted on the left and half on the right, yielding a net current of 0. If $V \neq 0$, the spatial current profile shows an offset. Obviously, the current profile for electrons has to be the mirror image of the current profile for holes, mirrored at $x/d = 0.5$. The final result for the total current, which is independent of x in steady state, is

$$J = J_p + J_n = eGd \cdot \left(\frac{e^{\frac{eV}{k_B T}} + 1}{e^{\frac{eV}{k_B T}} - 1} - \frac{2k_B T}{eV} \right); \quad V > 0. \quad (3.86)$$

For high voltages V , the last expression of (3.86) approaches zero and the first one 1, giving a current $J = eGd$, which means that all generated charge carrier pairs are extracted. In the case of an organic solar cell, where a built-in potential V_{bi} is present (cf. Sect. 3.3.4), V is again replaced by $V_{bi} - V_{bias}$. Here and in this whole section, V_{bi} is implicitly assumed as the point where the photocurrent becomes zero (see discussion about V_0 in Sect. 5.4).

Mihailetchi et al. [66] extended this model, introducing a field dependent generation rate of free charge carriers:

$$G = G_0 \cdot P(F, T). \quad (3.87)$$

The introduction of the probability $P(F, T)$ is motivated by a strong dependence of photocurrent on high applied negative voltages. It is justified by the proposed presence of bound CT states and their relaxation, i.e. geminate recombination (cf. 3.32). The temperature and field dependence of the dissociation of the Coulombically bound electron-hole pair might be described by Onsager-Braun theory [64, 65] (for details, see Sect. 4.4.2). This approach of representing most of the dependence of the photocurrent on voltage by a $P(F)$ (η_{CD} in Sect. 3.3.1) gives acceptable results in some cases. In other cases it seems to be inadequate to describe the J - V curve [70]. The reason for this is that on the one hand geminate recombination does not play a role in all material systems. On the other hand, if geminate recombination is significant, the correct $P(F, T)$ might be unknown.

Apart from the discussion of the presence and relevance of a CT state and the correct modeling of its dissociation probability [71], this approach shows two main drawbacks. First, recombination between charge carriers is not included ($\eta_{CP} = 1$). The original approach by Sokel and Hughes assumes that every photogenerated charge carrier leaves the device at every applied voltage. Losses are then only caused by a diffusion to the “wrong” contact ($\eta_{CC} < 0$). Well working organic solar cells, however, employ selective contacts (cf. Figs. 2.17a and 3.49b). The second assumption states that only photogenerated charge carriers are present in the device and charge carrier concentrations at the contacts are zero. However, especially in the low-voltage regime, where diffusion is dominant, the diffusion gradient is altered by the presence of the dark carriers, starting to deliver forward current.

Both the method developed by Goodman and Rose and the one after Sokel and Hughes, were originally intended for the description of photoconductivity in

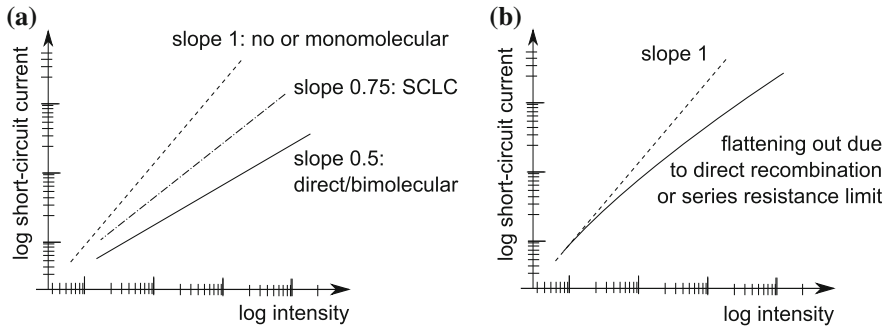


Fig. 3.41 Short-circuit current as a function of the illumination intensity in a double logarithmic scale. **a** The slope of the curves can give indications for the recombination process dominating at short circuit. For good solar cells the recombination at short circuit is weak and a linear scaling of the current with intensity (slope 1) is expected independent of recombination mechanism. **b** Realistic curve, where direct recombination becomes visible at higher illumination intensities. Another reason for a flattening of the curve can be a macroscopic series resistance

insulators with non-injecting contacts. We will show in Sect. 5.4 by comparison of analytical and numerical solutions of the transport equations for a MIM device that subtracting the dark current and correcting the applied bias for V_{bi} does not in general convert the photovoltaic device into a simple photocarrier-extracting device. Thus, the applicability of the presented analytical equations to solar cells, which show high forward currents, is limited. They could be best employed to solar cells without transport layers at the contacts and with high injection barriers. In this case contacts are not selective, which means that electrons and holes can flow to both contacts. Furthermore, the conditions $n(0/d) \approx 0$ and $p(0/d) \approx 0$ are valid.

Intensity Dependence of the Photocurrent

The photocurrent scales linearly with the generation rate ($G = \text{absorbed photon flux density}/d$ with the absorber thickness d) in most of the equations derived previously. One exception is the space-charge limited photocurrent (3.75). Let us investigate J_{sc} , which is the photocurrent at short circuit. A linear scaling of J_{sc} with intensity is commonly observed in experiment for moderate to even high light intensities. This is particularly the case when (almost) all of the photogenerated charges can be extracted at J_{sc} . In case of a J_{sc} limited by recombination, the intensity dependence of J_{sc} might give some indications on the order of the prevailing recombination mechanism. In this case J_{sc} is the difference between generated and recombining electron-hole pairs ($J_{sc} = ed(G - R)$). If R scales linearly with intensity like for geminate recombination or other monomolecular mechanisms like trap-assisted recombination, J_{sc} will also scale linearly with intensity (Fig. 3.41a).

If the recombination is of higher order, it increases superlinearly with intensity and gives rise to a non-linear and therefore reduced increase of J_{sc} with intensity. In the limit of high recombination, we can say that the majority of charges recombine. For

simplicity we assume a homogeneous G and a homogeneous charge carrier distribution ($n = p$) like we did in Sect. 3.3.2 (3.28). In case of bimolecular recombination we can write $G = R = \beta n^2$. Therefore, $n = \sqrt{G/\beta}$. If we assume that J_{sc} scales with n as it is the case for a drift current, J_{sc} will scale with the intensity to the power of 0.5:

$$J_n = e\mu_n nF = e\mu_n \sqrt{G/\beta} V_{bi}/d. \quad (3.88)$$

However, for state-of-the-art solar cells recombination is not that significant at J_{sc} and slopes of 0.8 to 1 are observed. A high background charge carrier density (e.g. at the electrodes or introduced by doping), which is independent of the illumination intensity, partially hides the square root dependence of J_{sc} on G . Then, even bimolecular recombination results in a monomolecular appearance, because e.g. for a high hole density p_0 it holds $R = \beta n(G)p_0$ with $p_0 \gg n(G)$. Figure 3.41 visualizes the extreme cases of $J_{sc}(G)$ dependent on the recombination mechanism, where the slope for the space-charge limited case (SCLC) is based on (3.75).

As shown at realistic data in Fig. 3.41b, a transition towards a sublinear behavior is expected for higher light intensities where direct recombination starts to dominate. However, in this regime a macroscopic series resistance R_S can limit J_{sc} as well, because a voltage loss at the series resistance scales with the photocurrent: $V_{R_S} = R_S J_{photo}$.

3.4 The Charge-Transfer State in Experiment

We have already discussed the implications of the CT state on the quantum efficiency and the open-circuit voltage. We also mentioned that the existence of this state is a possible reason for a photocurrent which depends on the electric field and, therefore, the applied voltage. We furthermore stated that the origin of the CT state is supposed to be a Coulombically bound electron-hole pair at a donor-acceptor heterojunction. We found that the energy of this state can be described in a Jablonski-like diagram. Then we think of the CT state as an excited state of the charge-transfer complex. This complex results from the interaction of valence states (π, π^* -orbitals) of adjacent donor and acceptor molecules. Such complexes can also be formed between two identical molecules in a film as we will see when discussing the optical properties of absorber materials in Sect. 3.6.3. In that case the absorption spectrum of the single molecule in a film is modified due to interactions of two neighboring molecules, in the extreme case giving rise to so-called dimer absorption. Also the newly generated (CT) state at a heterojunction between two different molecules, namely donor and acceptor, might allow for optical transitions. We have already introduced those transitions when deriving the radiative limit for V_{oc} in Sect. 3.3.2. Therefore, the CT state created upon blending donor and acceptor should be seen in absorption and luminescence measurements, if its optical cross section is sufficiently large (Fig. 3.43a).

3.4.1 Absorption

The absorption of the CT state in a working donor-acceptor combination is expected to be (slightly) red-shifted compared to the absorption of the pure materials (cf. Figs. 3.20 and 3.27). One might call this new absorption feature sub-bandgap absorption, assigning the term bandgap to the optical gap (absorption onset) of the pure materials. The optical cross section of the charge transfer complex is, however, very low, as the wave function overlap between different molecules is not very strong. In a simple picture, we might imagine such an absorption event requiring the excitation of an electron in the HOMO of the donor directly into the LUMO of the acceptor. The probability for such an event is expected to be much lower compared to an excitation event of the single molecule. We recall that we try to avoid this simple picture, as we want to see the CT complex as a new quantum-mechanical state with its own energy levels for excitations instead of referring back to the orbitals of the single donor and acceptor molecule.

Due to the low cross section, the absorption of the CT state is commonly not seen in the absorption spectra derived from simple transmittance and reflectance measurements. However, sensitive measurements of the absorption such as photothermal deflection spectroscopy [84, 146] are capable of visualizing the absorption of the CT state. Usually, absorption spectra of the pure components are measured separately and subsequently compared to the spectrum of the blend. The difference is attributed to CT state absorption, which is usually seen at an additional shoulder at high wavelengths in the absorption spectrum of the blend. Instead of detecting the absorption directly, one can measure the spectral photocurrent response (SR) of the solar cell. The SR or EQE, respectively, as a function of wavelength is the product of absorption and internal quantum efficiency [cf. (3.24)]. A sensitive measurement of the SR is Fourier-transform photocurrent spectroscopy (FTPS) [80]. This technique is based on Fourier-transform infrared spectroscopy (FTIR), which is commonly used to study optically weak sub-bandgap transitions. The high sensitivity is obtained by generating the absorption spectrum via a Fourier transformation of an interferogram obtained from a white-light source illuminating moving mirrors and the sample. In FTPS, the photodetector required for FTIR is replaced by the solar-cell sample, acting as both absorber (specimen) and electrical current generator (detector).

Sub-bandgap absorption for polymer-fullerene blends is commonly observed and was e.g. reported in [147]. There, the authors propose several reasons including CT state absorption or a modified absorption of fullerenes close to interfaces or in polymer-rich phases. These suggestions demonstrate that an additional shoulder in the absorption spectrum of a blend is not necessarily related to a CT state, especially if the (nano-)crystallinity of the compounds and the amount of disorder is changed upon blending.

3.4.2 Luminescence

We remember from the considerations of detailed balance in the current and the previous chapter that an absorbing state has to show emission as well. Due to the Stokes shift, we expect the emission to be red-shifted compared to the absorption as already depicted in Fig. 3.27b. Although the CT state emission is commonly very weak, it can be experimentally detected, e.g. in a sensitive photoluminescence (PL) measurement, where absorbing molecules are excited by a light source, which is usually a laser or a light bulb with a monochromator. Also here, the PL of the CT state is found comparing PL spectra of films consisting of the pure materials with the spectrum of a blend. Commonly, pure (donor) materials themselves show a strong PL signal. Upon blending with an acceptor, the PL can be quenched, partly or almost completely, whereas the absorption is only slightly changed. The quenching is due to an exciton dissociation upon a fast charge transfer to the acceptor (or the other way around).

For some material combinations, a weak emission signal arises in the blend, which is commonly red-shifted compared to the emission of the pure materials and attributed to PL from the CT state. This observation implies an energy transfer from the optically excited singlet state of the pure material to the CT state. It was observed for many material combinations [81, 82, 148–152]. However, it can be difficult to experimentally detect CT PL as it is very weak (low yield) and can be covered by the (broad) emission of the pure materials themselves. If the CT state is of significance for photocurrent generation, its PL is a loss mechanism and should be decreased under reverse bias. A CT PL quenching dependent on the applied reverse bias voltage was indeed reported [81, 153]. However, it is not straight-forward how to relate the quenching efficiency to the extraction of photocurrent.

The working principle of organic light-emitting diodes is based on injected electrons and holes recombining radiatively upon formation of singlet or triplet excitons, which show luminescent or phosphorescent emission when decaying. An organic solar cell without illumination behaves like a diode, as discussed in Sect. 3.3.4. In the ideal device, the forward current consists of electrons and holes that are injected into the blend at their respective electrode and recombine at a donor-acceptor interface. At least one recombination path should contain the CT state as intermediate step. Hence, a CT state seen in PL should also show electroluminescence (EL) if populated by injected charges. EL was indeed observed for several material combinations [78, 81, 154, 155] in the same spectral range as PL from the CT state. For some material combinations, the EL peak was found to be slightly shifted towards lower energies (≈ 0 –100 meV) [156]. One reason might be that injected electrons and holes form lower-energy CT states as charge transport occurs predominantly via ordered regions representing the low-energy states of the blend. Furthermore, the EL peak was found to slightly depend on the applied voltage or forward current [81]. Further studies looking e.g. into the field and temperature dependence of PL and EL are required for a complete picture.

3.4.3 Driving Force for Charge Transfer

Previously, we have postulated that efficient charge transfer at the donor-acceptor heterojunction requires a driving force, which we found in the LUMO-LUMO (HOMO-HOMO) offset (cf. Fig. 3.19) or the difference in the energy of S_1 (E_g^{opt}) and CT state (E_{CT}) (cf. Fig. 3.20). There, the LUMO (HOMO) referred to the transport energy E_{et} (E_{ht}) of an additional electron (hole) in the acceptor (donor). The demand for an offset in the energy levels was motivated by the exciton binding energy E_B , which has to be overcome upon charge transfer. Estimated values for the offset are in the range of >0.35 eV [157]. However, it is not easy to define and accurately measure E_{et} and E_B . Therefore, it is preferred to examine $\Delta E_{\text{ct}} = E_g^{\text{opt}} - E_{\text{CT}}$ for a more accurate quantification of the required differences in energy. Here, E_g^{opt} and E_{CT} should be determined in the same way due to the broad energy distribution of both states.

Many experiments have been performed to identify whether an energetic driving force is required and how large it should be. All experiments indicate that the driving force should be larger than zero. However, a clear correlation was not found between the value of the respective energy offset and the efficiency of exciton dissociation, which should be seen in changes in the photocurrent, i.e. internal quantum efficiencies as a function of the energy offset. An empirical minimum value for ΔE_{ct} of around 100–150 meV was reported for a variety of material systems [82, 125, 158]. One major problem discussing energy values in the range of 100 meV or even lower is that all optical transitions are rather broad and a determination of E_{CT} can be ambiguous. Nevertheless, this low value indicates that on the one hand not much potential energy is lost when forming a CT state. On the other hand, the offset energy is not required to drive charge dissociation against the Coulomb attraction in the picture of an electron and hole tightly bound and localized at the D/A interface. In that picture the energy required for a separation is expected to be larger.

When discussing the energetic driving force from excitons to free charges, one has to consider the energy of further states close to the D/A interface as well. Most critical are triplet states, which commonly have an energy below the energy of the optically generated singlet excitons (cf. Fig. 3.7). It was observed that triplet states on the donor molecule with energies lower than E_{CT} can be occupied via the CT state, which shows a high probability for intersystem crossing. Instead of being dissociated, the singlet CT state is then converted into a triplet, which jumps back onto the donor and subsequently decays non-radiatively [26, 82]. This process decreases the internal quantum efficiency and leads to devices with poor efficiencies.

3.4.4 Dependence on Temperature and Electric Field

So far we discussed the driving force for charge transfer. Now we look into the complete separation of the charges. When deriving the EQE in Sect. 3.3.1, we already mentioned that additional energy might be required to dissociate a CT state. If we

assume that electron and hole are located within a distance of 1–2 nm, the Coulomb binding energy is 360–180 meV ($\epsilon_r = 4$). This energy has to be overcome to generate photocurrent if a relaxed, tightly bound CT state is a precursor for free charge carriers. Temperature and electric field are supposed to be possible sources for providing this energy.

The thermal energy at room temperature is much lower than the estimated binding energy. Nevertheless, some studies address the effect of the temperature on the dissociation efficiency. Such studies are difficult as a changed temperature results in modified hopping rates of charge carriers as well. Hence, the effect of overcoming the Coulomb binding energy is hard to distinguish from the influence of an enhanced mobility. Nevertheless, a temperature activated CT dissociation was reported for a polymer-polymer blend [66] and is supported by spectroscopic studies (e.g. [159]).

The influence of the electric field can be studied in an experiment where the PL of a solar cell is measured as a function of the applied voltage. Indeed, a quenching efficiency that depends on the applied bias was reported for a blend with low driving force [81, 156]. If the voltage dependence of the PL quenching efficiency follows the photocurrent, one can conclude that the emissive CT state is essential in the generation of free charge carriers (Fig. 3.42a). However, one cannot unambiguously conclude whether the electric field is required to dissociate the CT state or whether simply a faster extraction of charges reduces the probability for (bimolecular) recombination seen in less luminescence. Such emissive non-geminate recombination should give rise to a delayed PL signal which has been observed for donor polymers blended with non-fullerene acceptors [160].

Another method employed very recently to investigate the role of the electric field is the time-delayed-collection-field technique [161] (Fig. 3.42b). This approach exploits the different time scales on which CT dissociation and charge transit are supposed to occur. The experiment is conducted as follows: The sample is kept at a certain pre-bias while illuminated by a laser pulse. After a certain delay time in the range of 10 ns, the applied voltage is switched quickly from the initial pre-bias to the extraction voltage. A variation of initial and extraction voltages and a comparison with the steady-state J - V curve allows to identify a different field dependence of initial and later processes. The initial processes are assigned to a (possibly) field dependent CT-state dissociation, whereas charge extraction (competing with bimolecular recombination) is supposed to be seen at later times. Therefore, this method relies on a definition of a clear threshold time. The results obtained so far depend on the materials. For P3HT, the influence of the initial field was found to be weak [162], whereas it was significant for PCPDTBT and MDMO-PPV [163, 164] (for details on the materials see Sect. 3.6.3). The main drawback of this method is a correct choice of the time to switch between pre- and extraction voltage, as lifetimes of the CT states are reported in the range of 10 ns and charge extraction times can also be found in the range of 1 to 100 ns at short circuit or negative applied voltage.

A further method is based on the measurement of charge carrier densities and their lifetimes. Assuming that the photocurrent as a function of voltage can be expressed as the difference between photogenerated and recombination current, it is possible to reconstruct the J - V curve when knowing recombination mechanism, charge carrier

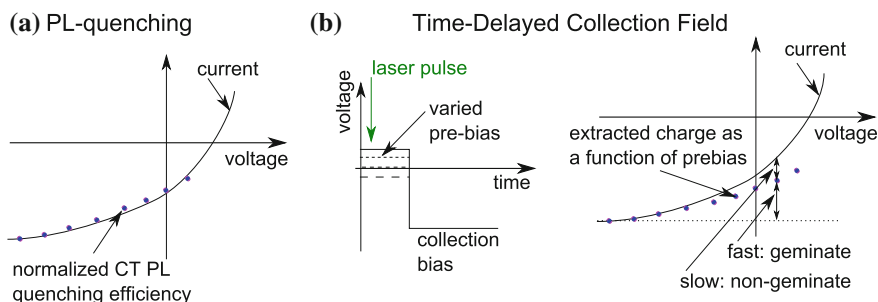


Fig. 3.42 Probing the relevance of the electric field on the dissociation of the CT state: **a** PL quenching: if it scales with the photocurrent (as *sketched here*), this is an indication that the radiative decay of the CT state is of importance for recombination. **b** Time-delayed collection field: the voltage-dependence of the charge-carrier collection efficiency is separately probed for short and long timescales, as the voltage is switched upon a light pulse after a time delay in the range of 10 ns. The dependence of the collection efficiency on the pre-bias is supposed to result from a field dependence in the dissociation of the CT state

density, and charge carrier lifetime at each bias point. These parameters can be determined by charge extraction and transient photovoltage decay measurements as we have mentioned when discussing V_{oc} in Sect. 3.3.2 on p. 127. Such measurements provide information about the recombination of free charge carriers. The difference of the predicted and measured J - V curve is then attributed to geminate recombination being dependent on the electric field [165].

3.4.5 Transient Pump-Probe Spectroscopy

Many spectroscopic studies have been performed to address the dynamics of excited states. These states are generated by the absorption of a light pulse and subsequently probed by a second (probe) pulse [166]. This method is sketched in Fig. 3.43b. Comparing the absorption (commonly transmission is detected) of the probe pulse with and without pump gives information about the presence of different species dependent on their spectral fingerprint. For a significant pump intensity, a decrease in ground state absorption (of the probe light) can be observed, which is called ground-state bleaching. On the other hand, new absorption bands occur due to the presence of charge carriers or excited states generated by the pump pulse. These states are then further excited to higher energy levels due to photon absorption of the probe pulse. By varying the delay between pump and probe pulse, a transient absorption spectrum can be recorded as done in transient absorption spectroscopy (TAS) [167–171]. This technique belongs to the field of photoinduced absorption (PIA) spectroscopy. Apart from directly investigating the transient signal, analyses in the frequency domain can also be performed to extract lifetimes [26, 159, 172]. In this case, chopped light sources are used to provide a harmonic excitation intensity. The

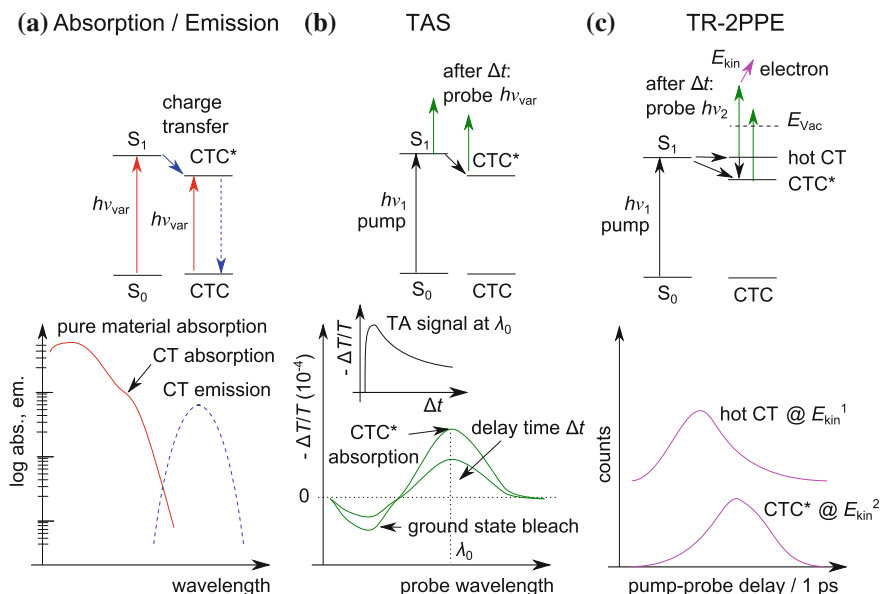


Fig. 3.43 Experimental approaches to spectroscopically probe the CT state: **a** measurement of direct absorption and emission of the charge-transfer complex (CTC) via FTPS, EL, and PL, **b** pump-probe spectroscopy (PIA, TAS): the absorption of probe light is measured optically in the change of transmission ΔT . ΔT reveals the presence of excited states previously generated by a pump pulse, and **c** time-resolved two-photon photoemission (TR-2PPE), where the energy distribution of emitted electrons originating from excited states is measured. Assigning the correct transition to the energy, where a TA or TR-2PPE signal is observed, is not trivial, as a variety of excited states (cations, anions, CT, T_1 , S_1) is usually probed

main challenges of these methods are the inherently weak absorption signals of low densities of excited states. That is why usually high pump intensities are required. Assigning the spectral regions where a change in absorption is detected to a specific state is not straight-forward, as the absorption spectra of excited states (e.g. S_1 to S_x , CT to CT^* , T_1 to T_x , cation to cation*, free charges, etc.) are commonly not known and might overlap. Often, quantum-chemical calculations assist the identification of the respective transitions. One of the main advantages is that non-emissive species can be probed and timescales can vary from fs to ms.

Transient absorption spectroscopy is also possible on complete solar cells, which allows for studies on the influence of the electric field. It was, e.g., found that the electric field does not influence the μs TAS signal from polarons in a PCPDTBT:PC₇₁BM blend [173], which is surprising, as at least the sweep-out time depends on the electric field. Neither an effect of temperature on the TAS signal in the 100 ps range was seen for P3HT:PCBM [174]. Many studies are still ongoing.

3.4.6 The Binding Energy of the CT State

Several times we mentioned the binding energy E_B of an electron-hole pair forming a (tightly-bound) CT state and postulated some numbers which are regarded as reasonable. Note that so far mainly estimates of E_B exist. These are based on Coulomb's law:

$$E_B = \frac{e^2}{4\pi\epsilon_0\epsilon_r a}. \quad (3.89)$$

Here, E_B depends on two unknown parameters which have to be estimated by measurements and/or calculations: first, the dielectric constant ϵ_r , which is assumed to be the macroscopic value of the surroundings ($\epsilon_r \approx 3\text{--}4$); second, the distance a between positive and negative charge, which is expected in the range of 1 nm. This distance is a typical spatial extension of small molecules employed in organic solar cells including fullerenes. These assumptions yield the discussed values of 0.2–0.5 eV for E_B . Quantum-mechanical calculations and data from two-photon photoemission spectroscopy for a pentacene surface as a model system predict values of 0.4 eV [88, 175]. Obviously, the dissociation efficiency of an electron-hole pair with this binding energy is expected to be low, as this energy is in the same range as the binding energy of an exciton in the pure material. There, the efficiency for autoionization is known to be low giving rise to the employment of a donor-acceptor interface. Therefore, such high values for E_B seem implausible if a relaxed and tightly-bound CT state is the path for free charge carrier generation.

If the relaxed CT state is important, E_B according to (3.89) is overestimated. To reduce E_B we can either increase the distance or the screening. The first is done by proposing a delocalization of the charge over several nanometers [72–74]. A delocalization might be favored by the polymer chain or by fullerene nano-crystallites in the blend. A higher screening seems likewise plausible because summarizing the polarizability of the surroundings by a macroscopic dielectric constant ϵ_r is an oversimplification. If the dimension of the localization of the charges is in the range of the molecule size, ϵ_r is not a good approximation for the polarizability of the surroundings. Here, quantum-chemical calculations describing several molecules might give new insights. A further suggestion is that disorder allows for the dissociation of the CT state. In this approach the CT state upon charge transfer is treated as bound electron and hole which are both not relaxed in their densities of states. Therefore, during a stepwise separation of electron and hole, downward jumps exist, which overcompensate for the Coulomb interaction as shown in [176]. This means that the binding energy of the CT state compared to the potential energy of free carriers is negative. However, such a process would imply that disordered semiconductors show higher dissociation yields than more ordered ones. Furthermore, the relaxation on long time and length scales should be visible in the open-circuit voltage, which cannot be described by the approach of quasi equilibrium at the junction as we did in Sect. 3.3.2. Further experimental evidence for such a process has to be collected.

The third option to resolve the CT-state dilemma is assuming that charge carrier generation happens via so-called hot CT states.

3.4.7 Hot CT states

Hot CT states are further excited states of the charge-transfer complex. These states are weakly bound and therefore easy to dissociate. Electrons entering the relaxed CT state will hardly be dissociated according to this theory. A lot of experimental effort is undertaken to detect hot CT states, which are expected to be formed upon charge transfer with energies dependent on the driving force and possibly the energy of the absorbed photon. The question is whether a direct dissociation of these states can compete with the relaxation/internal conversion time of the CT state which is in the range of ps or even below. Therefore, the measurement setup must be capable of resolving this timescale. In the following we review selected studies based on ultrafast spectroscopy.

An indirect probe of the influence of the excess energy is reported in a TAS study in [87]. There, the authors investigate a series of polythiophene-fullerene blends. They observe that the yield in free charge carrier generation does not scale with the quenching efficiency of the singlet PL. The PL quenching is always efficient as soon as fullerene is added to the polythiophene. The polaron pair generation, however, depends on the driving force, which the authors defined as the difference between E_g^{opt} and E_g^{DA} . Therefore, charge transfer responsible for the PL quenching and complete charge dissociation seem to be two different processes. This observation can be regarded as an indication for the relevance of the excess energy giving rise to thermally hot states.

Zhu et al. [88] probed CT states at a pentacene surface as model system for the donor/acceptor interface. The technique they used is time-resolved two-photon photoemission (TR-2PPE) spectroscopy with two femtosecond pulses of photons with energy commonly below the work function of the material (Fig. 3.43c). The first (pump) pulse populates excited CT states, which are then probed by the slightly delayed (here femtoseconds) pulse, photoemitting the electron. These electrons are collected by a detector analyzing their kinetic energy. Knowing the energy of the probe pulse, the energy distribution of the excited states can be calculated similar to conventional photoelectron spectroscopy. Manifolds of excited (including hot) CT states are detected similar to the energy levels found for the hydrogen problem. The authors think that those hot CT states at a pentacene surface should be formed at a D/A interface as well due to several reasons: The existent excess energy, a delocalization due to initially high charge carrier mobilities in crystalline domains, an increased electronic coupling as hot CT states are energetically closer to the singlets and therefore more resonant, and the existence of a high local electric field. Whether this model system can be transferred to a D/A interface remains to be proven with experiments on a solar cell.

Bakulin et al. [89, 177] performed an electro-optical pump-push experiment, where they measure the change in photocurrent as a function of the delay of the push pulse. The pump pulse excites singlets on the absorber, charge transfer at the D/A interface occurs and CT states are formed. They observe that the photocurrent signal is enhanced upon the push pulse in the IR range (0.5 eV), which is supposed to re-excite relaxed CT states. For a reduced HOMO or LUMO offset, the signal is larger. The authors speculate that the push pulse lifts a localized CT state and generates hot CT states/delocalized band states with lifetimes smaller than 1 ps. These delocalized states are said also to be formed directly after charge transfer at the D/A interface and are, therefore, responsible for the high dissociation yields.

Recently, further publications pointed towards the relevance of hot CT states [178]. Jailaubekov and co-workers [90] investigated CuPc/C₆₀ solar cells by applying two ultrafast non-linear techniques, TR-2PPE and time-resolved second harmonic generation (TR-SHG). TR-SHG probes the appearance of a transient electric field upon charge separation. The experiment works as follows: S₁ states are populated by a pump pulse, followed by charge transfer at the D/A interface. Instead of monitoring the transmission/absorption of the probe pulse directly, the second harmonic (at half wavelength) is detected. Such a second harmonic light signal is generated in the presence of dipoles. That is why selectively CT states instead of excitons or polarons are probed. The authors found a very fast population of the CT states (<100 fs), not significantly decaying within 10 ps. With TR-2PPE, they monitored the time evolution of the energy distribution of the CT states and observed hot states with energies around 0.3 eV higher than the relaxed CT state. The energy of these hot states is close to that of S₁ states, i.e., close to resonance. The hot state shows a decay time of around 1 ps. The authors concluded that this is the time window, where a complete separation of charges has to occur to avoid trapping of the charge in the Coulomb potential.

A synchronous probe of polaron states showing that they are indeed (only) created in this time window although relaxed CT states live much longer would have been the perfect proof for a hot mechanism. Unfortunately, this observation has not been reported.

Grancini et al. [91] tried to address hot CT states as well with TA spectroscopy resolving a time range of 10 fs and varying the wavelength of the probe pulse to monitor excitons, CT states, and polarons. They found that free charges are generated within 40–100 fs and CT states are populated dependent on the excitation energy within 20–40 fs. The higher the excess energy, the faster is the charge transfer and charge generation. They observed that the IQE depends on wavelength and increases by a factor of two for higher energies compared to the absorption onset. Consequently, they claim that the relaxed CT states do not contribute to free charge carriers.

We cannot provide a final conclusion regarding the CT state at the time given. What we know is that processes and timescales vary significantly between different material systems. Experimental proof was given for the same internal quantum efficiency for singlet and direct non-hot CT excitations [84, 85]. This fits into common findings of an internal quantum efficiency that does not significantly depend on

photon wavelength. This observation is the simplest, however, most direct proof compared to spectra from transient fs ...ps (absorption) spectroscopy which are not straight-forward to understand. As long as IQEs that significantly depend on the photon energy are not reported, a separate consideration of hot CT states, which either relax or dissociate, is not essential. The speculation of the author of this book is that most likely the CT state binding energy ($\text{HOMO} - \text{LUMO} - E_{\text{CT}}$) is much lower than the simple estimate of 0.3–0.5 eV, especially for efficient and fullerene based acceptors. The reason is that the CT state does not result from the combination of a donor and an acceptor molecule but from the interaction of a rather delocalized pair of electron and hole in the bulk heterojunction. Then, a discrimination between hot and relaxed CT states is not critical. More and more very recent results seem to confirm this idea [179–181].

3.4.8 From Photon Absorption to Free Charges—Alternative Views

In Sect. 3.3.1 we sketched the common view on the chain of energy conversion in donor-acceptor solar cells. The sequence started with photon absorption creating an excited state, followed by exciton diffusion to a D-A interface, and a subsequent dissociation into charge carriers, which are finally collected at the contacts. Interestingly, the exciton diffusion length for a variety of materials employed in organic solar cells is mostly found in the range of 5–10 nm and, therefore, not strongly dependent on the material. In contrast, charge carrier mobilities of organic materials show huge variations. This observation questions the relevance of exciton diffusion in organic solar cells. Especially diffusion on the length scale of several nm complicates a proper definition of a diffusion length. Furthermore, as discussed in the previous sections, charge transfer is observed in the fs range and can happen before the internal conversion of S_x states into the S_1 state [91]. This time range is not accessible for exciton diffusion over several nm, which is expected in the ps to ns time scale. Therefore, the idea of excitons being delocalized over several nm came up [182]. Directly after the absorption, the exciton is assumed to be delocalized and charge transfer can occur without a hopping process of excitons from molecule (segment) to molecule (segment). Such a delocalization should be seen in the optical properties of the film. This is, however, not the case as absorption spectra hardly change (except for the solvent shift) when molecules form a film. Furthermore, the fast response seen in the transient experiments might only reflect absorption events in the direct vicinity of a heterojunction. An alternative explanation for the fast photoresponse are phases in the bulk heterojunction that are not pure and contain a fraction of the other component. Hence, regarding the role of exciton diffusion, there is room for further systematic (e.g. experiments with well-defined bilayers) and more quantitative investigations, which are required to address the question of the different processes after photon absorption.

The on-hand section about the CT state (Sect. 3.4) demonstrates the preliminary character of the state-of-the-art knowledge of processes at the D/A interface, where new insights are expected in the coming years. Now, we move on towards a more established field, which are metal-semiconductor interfaces.

3.5 Metal-Organic Interfaces

To collect the charge carriers photogenerated inside a solar cell, metal electrodes or metal-like (degenerate) highly doped transparent conductive oxides are attached to the organic layers. These interfaces determine the collection efficiency η_{CC} defined in Sect. 3.3.1. Therefore, a brief overview of metal-organic interfaces is given. We start with conventional metal-semiconductor interfaces.

3.5.1 Conventional Metal-Semiconductor Interfaces: Barriers and Schottky Contacts

In case of an intrinsic semiconductor attached to a metal, the work function within the semiconductor close to the interface is defined by the metal, as shown in Fig. 3.44a. We know from Chap. 2 that the Fermi level in an intrinsic semiconductor is close to the middle of the energy gap. However, when attaching a metal, the Fermi level has to align in equilibrium. As the intrinsic semiconductor does not contain sufficient charge, the Fermi level in the semiconductor will be determined by the metal for typical device thicknesses.

As electrons in the metal occupy states up to the Fermi edge, the distance between E_F and the hole (electron) transport level describes the injection barrier for holes φ_p (electrons, φ_n). For vacuum level alignment (Schottky-Mott theory), φ_p (φ_n) can be predicted as difference between metal work function Φ_M and the ionization potential (electron affinity) of the semiconductor. The injection barrier can be changed by interface dipoles (D), which act as modifiers of the effective surface work function Φ_M^{eff} of the metal (Fig. 3.44b). The field between the two dipole charges is mainly located between them and manifests itself in the potential (according to Poisson's equation, imagine a space charge with infinitesimal extensions in Fig. 2.14) by an offset in the vacuum level and a following shift of all energy levels. Such dipoles can occur undesiredly or are introduced intentionally, e.g., by monolayers of polar molecules. If the work function of the metal is higher (lower) than the IP (EA) of the semiconductor, an interface dipole is commonly formed, resulting in a pinning of E_F to E_{et} or E_{ht} , as shown in Fig. 3.44c. The reason is that E_F would be within the band without this pinning, constituting a degenerate semiconductor with very high electron or hole concentrations. This is usually a non-equilibrium situation which

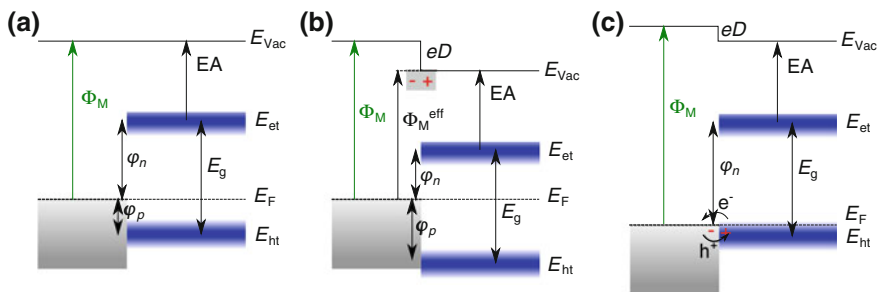


Fig. 3.44 Sketches of energy-level diagrams for metal-organic interfaces assuming an intrinsic semiconductor and considering **a** vacuum level alignment, **b** an interface dipole D , and **c** Fermi-level pinning at E_{ht} , which occurs if the work function Φ_M of the metal is larger than the sum of electron affinity (EA) and gap E_g of the semiconductor. In this case charge transfer is energetically favorable giving rise to an interface dipole D

drives free-charge transfer from the metal into the semiconductor. The redistributed charge at the interface constitutes the dipole leading to the pinning.

Relevant conventional metal-semiconductor interfaces are produced by using doped layers. They contain free and localized charges, which can force the semiconductor to its own equilibrium at a particular distance to the interface. This equilibrium is characterized by a certain position of E_F determined by the active doping concentration (2.14). Dependent on the work function offsets and the type of doping, so-called ohmic or Schottky contacts are formed. Figure 3.45 gives an overview. Considering an n-type semiconductor, a lower metal work function leads to an ohmic contact (a), whereas a higher metal work function results in a Schottky contact (b). Such a contact is characterized by the already defined electron injection barrier and a built-in potential V_{bi} due to the work function difference, which causes a bending of E_{et} comparable to a p-n junction. For a p-doped semiconductor the situation is the other way around.

A Schottky contact shows rectifying behavior, because electrons (holes in case of p-doping) cannot be injected from the metal. A significant forward current flows after the applied voltage has reached a certain negative value at the n-doped side (positive value in case of p-doping). This is comparable to the diffusion current in a p-n junction. The common approach of making a Schottky contact ohmic, i.e. not rectifying, consists of using a very high doping concentration at the contacts, which reduces the width of the space-charge region and allows for a high tunneling probability for electrons in both directions (Fig. 3.45c). This approach is also applied in the organic p-i-n type solar cells described in Sect. 3.6.2.

Figure 3.46a shows a sketch of the barrier height φ_n dependent on the metal work function Φ_M . The linear regime within the bandgap (solid line) is described by the Schottky-Mott [183, 184] law:

$$\varphi_n = \Phi_M - EA_{sc} \quad (3.90)$$

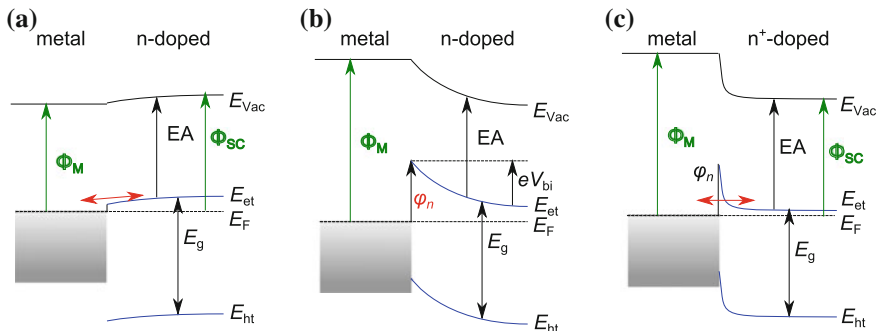


Fig. 3.45 Metal-organic interfaces with n-doped semiconductor: **a** $\Phi_M < \Phi_{SC}$ forms an ohmic contact and **b** $\Phi_M > \Phi_{SC}$ forms a Schottky contact with electron injection barrier φ_n . **c** A high doping concentration allows for a tunneling current through the barrier

The slope $d\varphi_n/d\Phi_M$ is unity for Φ_M within the bandgap. However, in experiment lower slopes have been reported [185], which can be attributed to interface states as proposed by Bardeen [186]. In the simplest case one might assume a continuum of interface states [187] within the bandgap, where a characteristic energy, called the charge neutrality level (CNL), defines the polarity of the interface (Fig. 3.46c). An E_F equal to the CNL represents a net surface charge of zero. If there is a difference, the amount of surface charge is proportional to this difference. The reverse charge is then located on the metal and a dipole layer is formed. This leads to a modification of (3.90), decreasing the slope $d\varphi_n/d\Phi_M$ due to the additional dipole, which lowers φ_n .

A very high density of intragap states would lead to a pinning of E_F to the CNL and thus a φ_n independent of Φ_M as already discussed for the pinning at the band edges. Several microscopic models exist like the metal-induced gap state model, where the states are formed by the decaying complex wave functions of metal electrons [188],

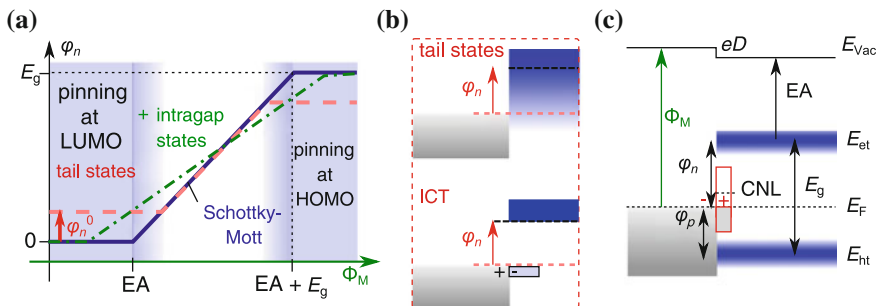


Fig. 3.46 Metal-organic interfaces: **a** electron injection barrier height φ_n as a function of the metal work function Φ_M . Without tail states the barrier depends on Φ_M as long as $EA < \Phi_M < EA + E_g$ and does not exceed E_g , **b** illustration of Fermi-level pinning at tail states or at a polaronic level and **c** surface states not filled up to the charge neutrality level (CNL) cause an interface dipole

which penetrate the semiconductor. However, there are several other simpler mechanisms that contribute to intragap states, like surface states of the finite semiconductor crystal abruptly ending at the interface (for an overview, see [189]). A very elaborate review focusing on a quantum-mechanics-based picture of metal-semiconductor interfaces can be found in [190].

3.5.2 Metal-Organic Interfaces: Disorder and ICT

In principle, the previously described effects hold for organic semiconductors as well. For example, the CNL approach is applied to describe metal-organic interfaces [191]. However, organics introduce additional complexities, as described in the reviews by Ishii et al. and Hwang et al. [192, 193]. The main differences to conventional semiconductors are found (i) in a low screening within organic materials and (ii) in the presence of significant disorder. The former (i) changes the position of E_{et} and E_{ht} close to the interface [194]. The gap close to the metal becomes smaller due to the much higher screening capability of the metal, which increases the polarization energy (cf. Fig. 3.10).

The latter (ii) implies a high occupation of intragap/tail states, which cause a pinning of E_{F} to values within the energy gap away from the charge transport level. A treatment of this effect is comparable to the defect model in inorganic semiconductors, describing intragap interface states (Fig. 3.46b). Fermi level pinning within the electrical gap is commonly observed experimentally in photoelectron spectroscopy studies. Here, typical values between the ionization potential and E_{F} are in the range of 0.3–0.5 eV [195]. A second theory to explain this pinning is the integer charge transfer (ICT) model [196–199], which assumes polaronic or bipolaronic states at the metal-organic interface (Fig. 3.46b). These states are further relaxed states due to the screening of the metal electrons. Therefore, they lie within the energy gap. As soon as the work function of the metal reaches this polaronic level, a charge transfer to the electrode is favorable and, consequently, an interface dipole is created.

The described effects should rather result in an interface dipole than in a bending of the energy levels, because a bending can only originate from localized, but spatially extended charges (i.e. a space charge region) like ionized dopant molecules. Free charge carriers face the field and pile up directly at the interface. A spatial extension of the free charge carriers could only be possible in the case of a very low density of states, which hinders the relocation of all charge carriers to an interfacial monolayer. Blakesley and Greenham [200] tried to distinguish between the impacts of ICT and tail states on the bending of energy levels, comparing simulation and photoelectron spectroscopy measurements. They found that both theories can fit the experimental data.

Furthermore, chemical effects exist that change the interface properties. Some organic molecules react with the metal and form metal-organic complexes, as it was observed, e.g., in [201, 202]. If these complexes are electrically active, they constitute interface states ruling the energy level alignment. Metal atoms evaporated

onto organic material can diffuse into the organic film and create gap states [203] or lead to a doping of the semiconductor. Energy level alignment is also affected by the push-back effect: Commonly, the electron wave function extends out of a metal surface into vacuum. When depositing an organic film on the surface, these electrons are pushed back by the repulsive force of occupied electron orbitals of the deposited material. Therefore, molecules deposited on a metal surface change the surface work function of the metal.

A verification of these theories and the identification of the dominating process is complicated, because the additional levels (polaronic, CN, or tail states) are hard to determine experimentally. The mechanisms governing the final energy level alignment are intensely researched on by combining experimental techniques like sophisticated photoelectron spectroscopy and scanning tunneling microscopy with quantum-mechanical calculations to describe the electronic structure and dynamics at metal-organic interfaces [204–206].

3.6 Experimental Realization of Organic Solar Cells

So far we have treated the theory of several mechanisms prevailing in organic materials and solar cells. Now we address the experimental realization of devices focusing on device architectures. Furthermore, we give examples for molecules employed as absorbers. We start with deposition techniques of thin films consisting of those molecular materials.

3.6.1 *Deposition and Coating Techniques*

Organic solar cells can be divided by material class into polymer based and small-molecule organic solar cells, where small molecules cover oligomers or molecules with a molar weight which is roughly $\lesssim 1,000$ g/mol. Whereas polymers are exclusively solution processable, small molecules can also be deposited via desublimation in a vacuum system.

Solution Processing

Solution processing requires a molecule soluble in a specific solvent. The solvent has to evaporate after the deposition of the layer. In laboratory setups the solution is usually spin-coated onto the substrate. There, a few droplets of solution are deposited onto a substrate mounted on the chuck of a spin coater. Subsequently, the rotation of the sample is started with a speed of a few hundreds to thousands rpm. The result is a relatively homogeneously spread solution over the substrate. Commonly, the film dries within seconds to a few minutes during the rotation dependent on the boiling

point of the solvent. The thickness of the film can be adjusted by the speed of rotation and the concentration of the molecules in the solution etc.

This laboratory scale deposition technique cannot be transferred to large-scale production. Instead, inkjet printing, screen printing [207, 208], slot-die coating [209], gravure coating, and other coating technologies are under investigation [210, 211]. They are shown schematically in Fig. 3.47. In *inkjet printing* (a), the organic material has to be dissolved in a solvent, forming an ink or colloid, which can be printed in a similar way as the inks from color cartridges in an office printer. The ink in the printing head is contained in a reservoir and ejected at a nozzle in form of small droplets. These droplets can be generated either by increasing the pressure in a tiny chamber at the nozzle via a piezoelectric crystal or by thermal evaporation due to resistive heating. The droplets hit the substrate, where patterns are formed while moving substrate and/or the cartridge. Commonly, a cartridge contains a number of nozzles to increase the speed of printing. This contactless approach allows for a high resolution. The printing pattern can be complicated as it is controlled by software, which results in a low waste of ink. However, the requirements to the formulation of the ink are high. It usually contains several components to reach the desired viscosity and surface tension of the tiny droplets. *Spray coating* is a similar process, where the solution is transferred to the substrate via an aerosol, consisting of a carrier gas and single droplets.

Screen printing (b) is a well-established technology for printing, e.g., posters. It is also applied in the fabrication of printed circuit boards to deposit the resist which masks i.e. protects the copper film during edging the uncovered regions. This technology is interesting for printing organic solar cells because of its large-scale nature. The ink is deposited on a woven mesh (metal grid or some fabrics), where the pattern is generated by areas covered by a stencil, which blocks the ink. The woven mesh is brought into close contact to the substrate, and the ink is pressed through the

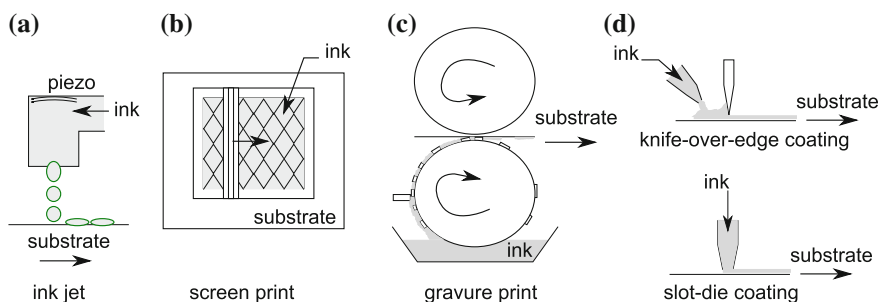


Fig. 3.47 Selected deposition techniques from solution: **a** ink jet printing, where the ink is deposited via troplets, **b** screen printing (*top view*), where the ink is squeezed through a woven mesh (here planar, but could be a cylinder as well), **c** gravure printing, where the ink fills the slots engraved into the surface of a cylinder and **d** Knife-over-edge coating, which provides a complete coverage of the surface comparable to doctor blading; slot-die coating, which allows for the deposition of stripes

mesh by moving a squeegee along the mesh. A high viscosity and a low volatility of the ink are required for a good result, because the thickness of the wet film is large.

A simple method to coat a wet film of defined thickness is *doctor blading* or blade coating. There, the solution is cast in front of a sharp blade, which is located some 10s or 100s of μm from the substrate. This distance roughly defines the thickness of the wet film, which is much larger than the final thickness of the dried film. Then, the blade is moved along the substrate and gives a film which dries afterwards. Instead of moving the blade, the substrate can be moved as well. Then this technique is called knife-over-edge coating (d), completely covering a substrate with solution. A more sophisticated version is *slot-die coating*, which allows to print stripes. The solution is kept in a container with a slot at the bottom, which is brought in close vicinity to the substrate. When moving the substrate with a defined speed, material is deposited with a defined thickness. Another method to print stripes is *gravure coating* (c), where a cylinder with engraved pattern transfers the ink from a supply onto the substrate.

These printing technologies can be integrated into a roll-to-roll facility to coat flexible substrates. A high throughput and fabrication at ambient conditions promise a huge potential for a fast and cost-efficient device fabrication. However, solution processing of multilayer stacks requires orthogonal solvents not to dissolve the underlying layer. Surface energies have to be adjusted for a good wetting of a surface, which might be more hydrophobic or hydrophilic. Furthermore, the high precision considering layer thicknesses in the range of 100 nm and the homogeneity of the electrically active layers is a challenging task when using printing methods.

Vacuum Processing

Vacuum processing is based on the evaporation (or sublimation) of the raw materials from a heated crucible. The evaporated molecules spread through the vacuum and reach the substrate which is located at some distance from the opening of the crucible. In lab setups (cf. Sect. 3.6.6), point sources are used, which give rise to a radial distribution of the flux due to the escape cone. An upscaling of this method is straight forward by replacing the point source with a linear evaporation source which provides a homogeneous flow of molecules in the area, where the substrate passes during a roll-to-roll deposition process.

As a technology based on evaporation requires vacuum chambers, it is regarded as more complex and cost-intensive than printing. This assumption mainly considers the initial investments, although these costs should not be the main issue for a high-throughput technology, where the main costs are given by the operation costs of the tools and the prices and usage of the required raw materials. At the moment material costs are dominated by the price of the transparent electrode tin-doped indium oxide [212] (cf. Sect. 3.6.3). Sophisticated printing machines, which are required for high-performance organic solar cells, will be expensive as well, however provide a faster coating than vacuum-based methods.

The main advantages of vacuum processing are a higher purity of the deposited films, which are free of any remaining solvent in contrast to solution processed films. Aside from the solvents, small molecules show a higher degree of purity compared to

polymers with long chains, which are more difficult to isolate from remaining reaction byproducts. In an evaporation approach, a controlled deposition of multilayer stacks is readily achieved by consecutive evaporation steps. Almost all solar cell devices discussed in this book are processed by vacuum sublimation.

3.6.2 Solar-Cell Stacks

Standard Architecture

From Fig. 3.19 and the discussions of the metal-insulator-metal device, we know that the simplest realization of an organic solar cell is a bulk heterojunction sandwiched between two metal-like electrodes. The most common layer sequence, called stack, is sketched in Fig. 3.48a. It is referred to as normal geometry in so-called superstrate configuration, characterized by an illumination of the solar cell through the substrate. The solar cell is “super-substrate”, i.e. on top/on the other side of the substrate referred to the path of incident light. The normal stack has been used for decades, as glass or plastic substrates coated with tin-doped indium oxide (ITO) are commercially available. ITO is well suited as electrode material due to its low roughness, high transparency (cf. Fig. 3.59) and acceptably low sheet resistance to be able to carry the current laterally for several mm. Hence, it is broadly used in thin-film displays like liquid crystal displays (LCD). The thickness of the ITO layer is commonly in the range of 100 nm. The active layer (20–300 nm) is deposited on top of the ITO, either as a bilayer or a blend. Finally a reflective metal cathode is evaporated on top of this stack. In case of solution processing of the blend layer, only one spin-coating step is required.

As metal-organic interfaces demand for an adjustment of the work function, interlayers between electrode and active material are inserted. Commonly, the ITO substrate is coated with a conductive polymer with a low work function to match the HOMO/ E_{ht} of the donor. Mostly PEDOT:PSS (see Sect. 3.6.3) is used, which is coated in aqueous solution, whereas organic (non-polar) solvents are used for the blend (e.g. toluene, chloroform, chlorobenzene, orthodichlorobenzene (ODCB), or xylene). It was found that coating the metal directly on top of the intrinsic organic material is detrimental for device performance. That is why (sacrificial) buffer layers like lithium fluoride (LiF), bathocuproine (BCP) or bathophenanthroline (BPhen) are inserted. They guarantee an ohmic contact to the cathode, as they protect the organic layer during evaporation of the metal electrode. The exact working principle of these interlayers is not completely understood yet. Usually their nominal thickness is in the range of several nm only.

Inverted Geometry

The main drawback of the conventional architecture is the employment of ITO, which does not allow for a large-scale production due to the scarcity and therefore high price

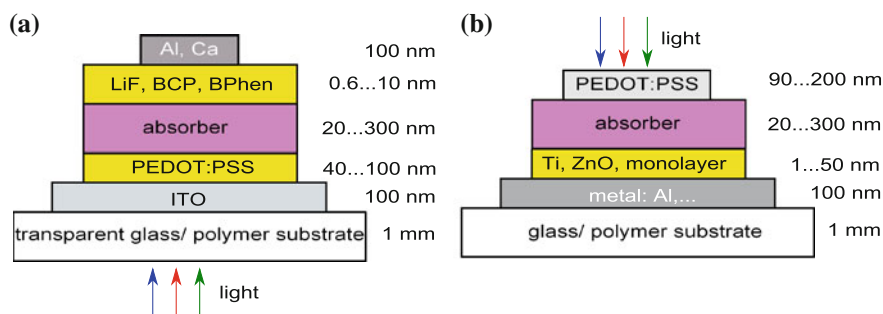


Fig. 3.48 Commonly used solar-cell stacks: **a** conventional geometry in superstrate configuration with illumination through the substrate and **b** inverted geometry in substrate configuration (illumination from top) and with interchanged anode and cathode. Frequently, inverted stacks are constructed also in superstrate configuration on an ITO-coated substrate covered by zinc oxide and with a molybdenum oxide (MoO_3)/silver anode

of indium. From the production point of view, an inverted layer sequence might be interesting, starting with a metal-coated substrate. Glatthaar et al. [213] introduced this configuration, shown in Fig. 3.48b. The stack is called substrate configuration, as the illumination is not incident through the substrate, but from the top of the stack. The transparent electrode is realized in the optimum case by a PEDOT:PSS layer with high conductivity, eventually supported by a metal grid.

Note that the term “inverted” is ill-defined. It can also refer to an interchange of the function of the electrodes, i.e. a change of anode and cathode, without changing from superstrate to substrate configuration. Additional interlayers between active material and electrodes are used for inverted devices as well. A common stack for inverted lab-scale devices is ITO/ZnO/blend/ MoO_3 /Ag, where the MoO_3 /Ag anode can be replaced by PEDOT:PSS. Being able to modify the work function of the electrodes by monolayers introducing high dipoles, provides the freedom of using the same electrode material as anode and cathode. In this way, also semitransparent devices can be fabricated. The most flexible device layout is, however, based on doped charge transport layers as discussed in the following.

p-i-n Design

Highly efficient state-of-the-art small-molecule solar cells employ doped charge transport layers [214, 215]. This approach results in a p-i-n architecture [216, 217], which we introduced in Sect. 2.5.3 (Fig. 2.17) when having discussed possible realizations of the ideal solar-cell structure. It is stressed that in contrast to some publications of organic solar cells, where p and n refer only to the type of conductivity (hole or electron), here, p and n mean electrically p- and n-doped semiconductor layers as discussed in Sect. 2.2.1.

A p-i-n stack with typical layer thicknesses is depicted in Fig. 3.49a. The absorber which contains a donor-acceptor heterojunction is found in the middle of the stack

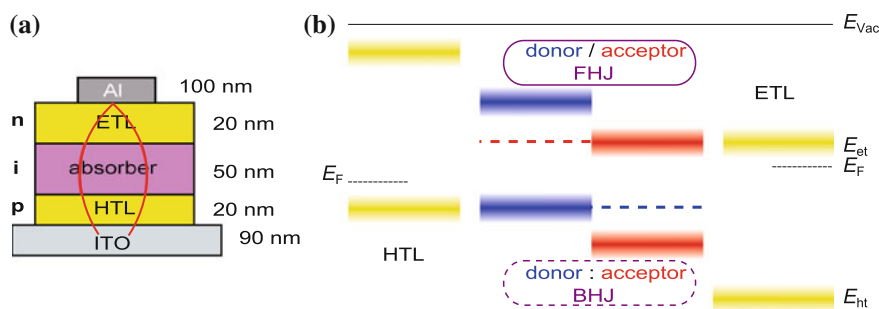


Fig. 3.49 p-i-n concept: **a** solar-cell stack with common layer thicknesses and a sketch of a standing electromagnetic wave, reflected at the Al contact, **b** energy levels with respect to the vacuum level, i.e. without contact of the materials. The position of the Fermi level E_F is close to the electron-transport level E_{et} in the n-doped electron-transport layer (ETL) and close to the hole-transport level (E_{ht}) in the p-doped hole-transport layer (HTL)

and can be realized either by a bilayer (flat heterojunction, FHJ) or by a co-evaporated material mixture (bulk heterojunction, BHJ). A combination of both leads to a hybrid heterojunction, comprising a BHJ sandwiched between intrinsic donor and acceptor layers [218, 219]. Attached are the doped transport layers, hole transport layer (HTL) and electron transport layer (ETL), optionally with some intrinsic HTL or ETL between absorber and doped transport layer. The purpose of this intrinsic layer is to keep dopants away from the absorber, because they are supposed to quench excitons [220]. Additionally, solar cells with improved long-term stability have been realized by this structure. The doped layers are supposed to fulfill the following functions, visualized in Fig. 3.49b:

- Selective contacts: A high LUMO (HOMO) offset between active material(s) and the HTL (ETL) blocks electrons (holes). Thus, these charge carriers are hindered in penetrating the HTL (ETL). Therefore, recombination or diffusion to the “wrong” contact is avoided. In terms of Sect. 3.3.1 this condition guarantees an $\eta_{CC} = 1$, as long as interface recombination is excluded.
- Optical spacer and exciton reflector: HTL and ETL are transparent due to the large optical gap of the employed materials. Therefore, they are sometimes called window layers, which are required because commonly the thickness of the absorber layer is limited due to transport constraints. Thus, the absorber should be positioned in the optical field maximum to optimize η_{PA} (cf. Fig. 4.14). The transparency of the layers implies that the excited states S_1 and T_1 of HTL and ETL are higher in energy than those in the absorber. Thus, energy transfer to the HTL/ETL is unlikely and excitons are hindered from passing through and being quenched at the metal contact. This provides a high η_{ED} .
- Ohmic contact to electrodes: The doped layers are highly conductive and a tunneling contact to the electrode is achieved as described in Sect. 3.5.1, independent of the work function of the electrode.

- Connection of tandem cells: A highly doped p-n junction can be used for a tandem cell as recombination contact, converting electron into hole current without losing energy (cf. Sect. 10.1.1).

In the classical p-i-n stack the HTL is deposited on a transparent glass substrate, covered by ITO. Aluminum (Al) is used as reflecting back contact. The n-doped layer can be interchanged with an intrinsic organic buffer layer in combination with Al (like in Fig. 3.48), often resulting in a very similar solar-cell performance as with n-doped layer. Devices of this type are then called p-i-metal structures. The mentioned properties of the transport layers imply that inverted structures can be realized without difficulty by exchanging HTL and ETL. The stack is then of n-i-p type. A switch from superstrate to substrate configuration is independent of the stack, but requires the deposition of a transparent electrode on top of the solar-cell stack.

3.6.3 Materials

In this section, materials are introduced that are employed to realize the various functions in an organic solar cell discussed so far (i.e. donor, acceptor, HTL, ETL). Following the basics of Sect. 3.1.1 and intuitive rules of chemistry, we describe the properties of these molecules.

The desired properties of a solar cell material differ depending on its function in the solar-cell stack. Charge transport layers should be transparent in the visible spectral range, HTLs should have a HOMO in the range of the HOMO of the absorber materials and ETLs a LUMO in the range of the LUMO of the absorber to guarantee efficient hole and electron transfer between absorber and HTL/ETL. Absorber layers are desired to grow as (micro-)crystalline phases. This yields a high exciton diffusion length and a high charge carrier mobility [221, 222], because grain boundaries are the main factor limiting transport [223]. Transport materials, however, are preferred to grow amorphous to result in smooth layers. The conductivity of these amorphous layers is still sufficient due to the employment of a high doping concentration.

Basically two main approaches are followed to manipulate these energetic and morphological properties: First, a variation of the size and arrangement of the aromatic systems that contribute to the π -system. The size mainly influences the HOMO-LUMO gap as discussed in Sect. 3.1.1. The three-dimensional structure of the molecule changes the morphology of the film. For example, side groups that are free to rotate activated by temperature reduce the tendency of the molecular film to crystallize.

The second approach is the application of functional groups, which are electronically active as electron donating or withdrawing groups. They define the absolute location of the orbitals and therefore the type of a molecule, or more precisely of its π -system, being a stronger donor or acceptor. Two major effects of functional groups on the energy levels can be distinguished: The first one is the inductive effect, which acts on a σ bond between two different atoms with different electronegativity. The

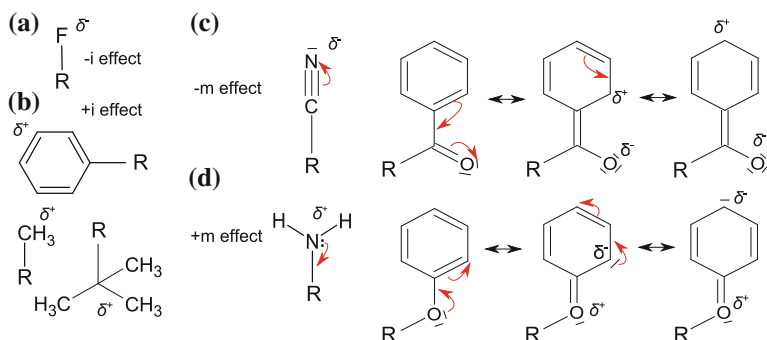


Fig. 3.50 Examples for typical functional electron withdrawing and electron releasing groups: **a**, **b** phenyl, fluorine, methyl, and tert-butyl groups with inductive effect, and **c**, **d** amine and nitrile (cyano) group showing a mesomeric effect. The mesomeric effect is also visualized by resonance structures of a π -system containing oxygen. *R* denotes the body of the molecule

higher the electronegativity of an atom or functional group [224], the higher is its electron withdrawing property and the higher is the positive partial charge remaining on the core of the molecule ($-i$ effect). As depicted in Fig. 3.50a, fluorine (F) shows the $-i$ effect, whereas methyl (CH_3) and phenyl (C_6H_5) displayed in Fig. 3.50b are electron releasing ($+i$ effect).

The second influence of functional groups is found in the so-called mesomeric effect, which acts on conjugated π bonds. Figure 3.50c shows an example for oxygen, where in one mesomeric resonant structure, four non-bonding valence electrons are located on the oxygen. Flipping bonds leads to other mesomeric resonant structures, revealing a partial negative charge ($-m$ effect) or in the case of 3.50d positive charge ($+m$ effect) on the oxygen. Other groups show this effect as well. A nitrile (cyano) group (CN), e.g., introduces a strong $-m$ effect, whereas an amine group (NH_2) shows a $+m$ effect.

A quantification of the electronic effects of substituents can be done using the Hammett constant, which is determined by a comparison of the dissociation constant of substituted ($\text{X}-\text{C}_6\text{H}_4-\text{COOH}$) and unsubstituted benzoic acid ($\text{C}_6\text{H}_5-\text{COOH}$) in water [225]. The higher the electron withdrawing properties of the substituent, the closer is the chemical equilibrium at the ionized form of the acid $\text{X}-\text{C}_6\text{H}_4\text{COO}^- + \text{H}^+$ which can be measured by the pK_a value of the solution.

Small-Molecule Absorber Materials

Figure 3.51 shows the absorber molecules used in the studies presented in the subsequent parts of this book. Zinc phthalocyanine (ZnPc) (3.51a), which is a relatively planar molecule with an extended aromatic system (calculations in Fig. 3.52), is the most common absorber in small-molecule solar cells [226, 227]. Its absorption coefficient is plotted in Fig. 3.53. The zinc as central metal atom can be interchanged with other elements. This modification can lead to a change in the energetic [228] and

absorption properties of the phthalocyanine molecule due to a large interaction of the metal atom with the π -system. For example, Sn [229], Pb, and Cl-Al [230] shift the absorption towards lower energies (infrared). Additionally, larger metal atoms (Sn, Pb) decrease the planarity of the molecule [231]. This leads to changes in the spatial structure and hence influences the stacking of molecules. ZnPc (and comparably CuPc) crystallizes in herringbone structure in different phases dependent on substrate and deposition conditions [232]. The HOMO of ZnPc in solution is around -5.4 eV, determined by an electrochemical measurement (cyclic voltammetry, CV). Ultraviolet photoelectron spectroscopy (UPS) measurements of a thin film deliver a HOMO value of -5.07 eV. This value is the onset (cf. Sect. 6.5 for details on UPS) of the HOMO, which we denote by $\text{HOMO}^{\text{UPS}} \approx -\text{IP}$. It lies higher than the HOMO in the solution due to polarization effects discussed in Sect. 3.1.2 (cf. Fig. 3.10).

The HOMO can be shifted by employing functional groups, e.g. the amount of fluorination ($-i$ effect) of the naphthyl groups at the corner of the molecule decreases the HOMO for F_4ZnPc to -5.46 eV (IP, UPS) [235] and for F_{16}ZnPc to -6.1 eV (CV) [236]. The same effect is observed for CuPc with an IP of 5.2 eV shifting to 6.3 eV for F_{16}CuPc [237]. Such approaches allow for an optimization of the $\text{HOMO}^{\text{Donor}} - \text{LUMO}^{\text{acceptor}}$ acceptor gap (E_{g}^{DA}), which governs the open-circuit voltage.

Furthermore, the IP can also depend on the molecular orientation, which is according to [238] 5.15 eV (5.65 eV) for lying CuPc (F_{16}CuPc) molecules and 4.75 eV (6.5 eV) for molecules standing upright on a graphite substrate. These findings indicate that the IP and therefore E_{g}^{DA} are properties of the film which cannot be predicted

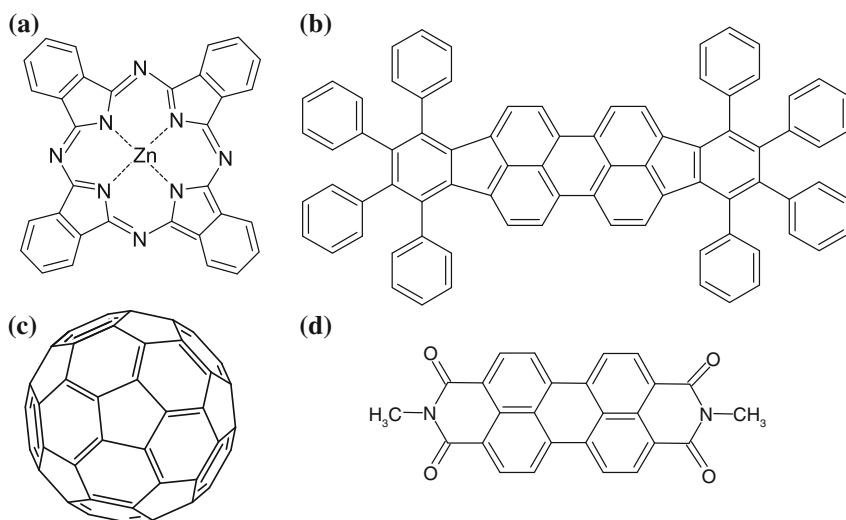


Fig. 3.51 Examples of absorber materials: donors (a) ZnPc and (b) Ph₄-Ph₄-DIP and acceptors (c) C₆₀ and (d) Me-PTCDI

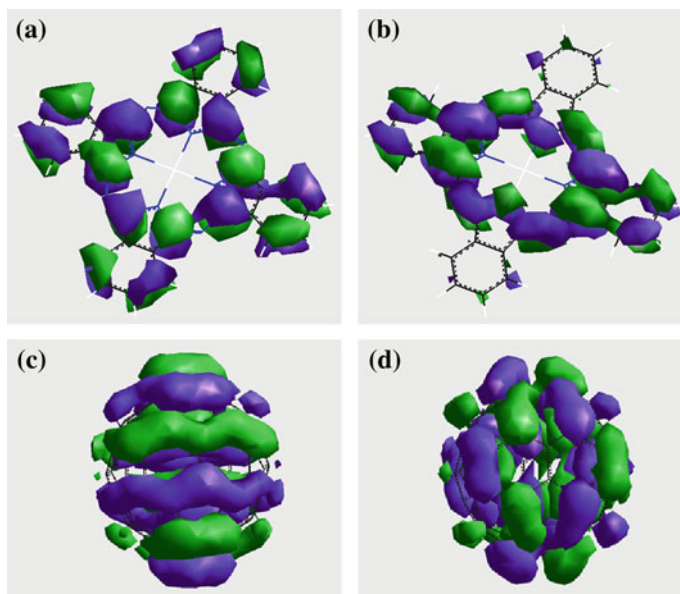


Fig. 3.52 Examples of the frontier orbitals of **a, b** ZnPc and **c, d** C₆₀. Shown are one HOMO (**a, c**) and LUMO (**b, d**) for each molecule calculated using a semi-empirical method (Austin Model 1) [233, 234]. The orbitals are delocalized over large parts of the molecule showing characteristic distributions of the probability to find an electron at a certain place. Note that the calculations predict several degenerate frontier orbitals with different shapes, whose appearances depend strongly on the perspective. The *two colors* indicate the sign of the wave function like in Figs. 3.3 and 3.4

directly from the HOMO of the single molecule. We will see in Sect. 8.1 that a mixture with the acceptor can also change the IP of the film.

Another class of absorbers shown in Fig. 3.51b, d are perylenes. The Ph₄-Ph₄-DIP, a di-indeno-perylene (DIP) with eight phenyl groups as substituents, exhibits the π -system located on the core [239]. Whereas unsubstituted DIP is completely planar and grows crystalline [240, 241], the phenyl groups rotate out of the plane and prevent a crystalline growth. The crystallinity of the pure DIP is supposed to give a large exciton diffusion lengths in the range of several 10s of nm (100 nm reported by [223]). Ph₄-Ph₄-DIP absorbs between 500 and 600 nm (see Fig. 7.4, p. 365), whereas Me-PTCDI shows an absorption maximum in the blue [242] due to the smaller π -system. Ph₄-Ph₄-DIP consisting only of hydrocarbons is ambipolar, whereas Me-PTCDI is an n-type molecule with lower lying molecular orbitals due to the electron withdrawing oxygens, making the π -system more acceptor-like. The prevailing type (donor or acceptor) can also be estimated from the average oxidation state of the carbon, which is negative in the Ph₄-Ph₄-DIP due to the positive hydrogens, whereas it is expected to be close to zero for the Me-PTCDI, because the effect of the hydrogens (oxidation number +I) is approximately compensated by the oxygen (−II).

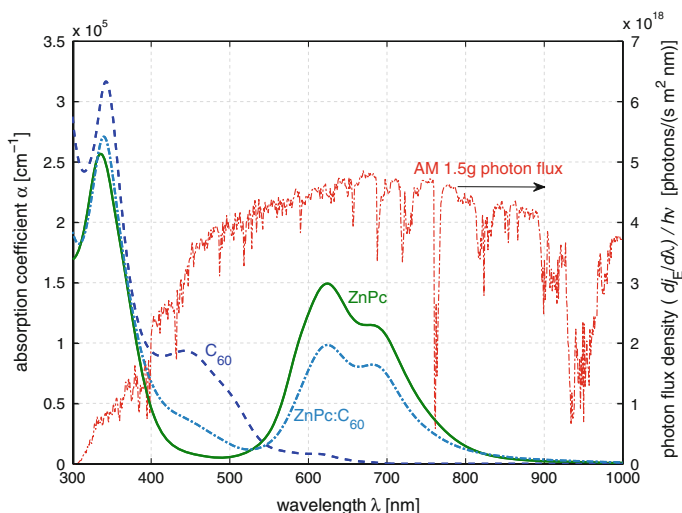


Fig. 3.53 Absorption coefficient $\alpha = 4\pi\kappa/\lambda$ of ZnPc, C₆₀, and a 1:1 blend with the extinction coefficient κ determined by reflectance and transmittance measurements of samples with varied layer thicknesses. The absorption of ZnPc shows a characteristic double peak between 600 and 700 nm. C₆₀ shows a peak at 450 nm. The absorption of the blend contains the fingerprints of both compounds. The AM1.5g photon flux is plotted for comparison

The oxidation state of zero also allows to understand the strong acceptor properties of the fullerene C₆₀ consisting of 12 pentagons and 20 hexagons with a carbon atom in each corner [243–245]. They constitute a spherical molecule (Fig. 3.51c), also called buckyball, with a nucleus diameter of 0.7 nm (average C–C bond lengths of 1.4 Å [246]), a van der Waals diameter of 1 nm, and a crystal lattice constant in a cubic system of 1.4 nm [247]. Examples of its frontier orbitals are shown in Fig. 3.52, where the LUMO level in a film is about –4 eV [248]. The absorption coefficient of C₆₀ is added to Fig. 3.53, showing complementary parts to ZnPc.

The absorption of ZnPc between 550 and 800 nm is called the Q-band, which is attributed to the first excitonic or $\pi-\pi^*$ transition [249]. The splitting of the Q-band into a low energy peak at 680 nm and a high energy peak at 625 nm can be explained by vibrational manifolds [250]. The broadening of the high-energy region at around 600 nm is attributed to dimer (or larger aggregate) absorption [251]. Dimer absorption is seen at the high-energy edge as it implies a charge transfer between two ZnPc molecules (similar to CT between donor and acceptor), giving a less-bound and therefore higher-energetic exciton. On the one hand, the dimer (or larger aggregate) absorption becomes more pronounced for films showing larger crystallinity. On the other hand, it decreases when blending ZnPc with C₆₀. This effect may explain the slightly different spectral shape of the absorption of ZnPc in the blend, where the shoulder at 580 nm is not visible and the peak at high energy is decreased more strongly than the low energy peak. In general, the absorption spectra of molecules in a film depend on the morphology of the film, which is influenced,

e.g., by the substrate material, the deposition temperature [249], and post-annealing [252], although the main spectral shape is commonly preserved.

The absorption coefficient of organic molecules depends strongly on the orientation of the polarization of the light with respect to the extension of the π -system, which is mostly planar, i.e. two-dimensional. The probability of a photon-electron interaction is much higher when the electric field oscillates within the plane of the π -system. A very illustrative explanation for the increased transition dipole moment in plane is the picture of the electric field of the electromagnetic (light) wave shaking an electron to lift it to an excited state. This is more probable within an iso-energetic region, which means within the lateral extension of the π -system. Thus, for thin film-solar cell applications it is favorable if ZnPc or DIP molecules form a flat-lying configuration on the substrate instead of standing upright. This arrangement means an orientation of their π -system parallel to the surface of the substrate and perpendicular to the direction of incidence of the light. Also the transport properties perpendicular to the substrate are supposed to be improved by the higher π orbital overlap of lying molecules. That is why much research focuses on getting molecules lying flat [253, 254].

The absorption coefficient of ZnPc (Fig. 3.53) and other organic dyes is much larger than the one of inorganic band-edge semiconductors close to the band edge. This can be explained by Fermi's golden rule (3.2), describing the transition probability T between ground and excited state. In Sect. 3.1.1 (p. 68) we found that T is proportional to the matrix element of the perturbation between the two states. This perturbation represents the interaction of the field of the electromagnetic wave with the transition dipole moment of the substance. Furthermore, T is proportional to the density of states. Due to the large interaction between atoms within a crystal, energy levels split strongly and form wide bands with a relatively low density of states (increasing with $\sqrt{E}$) close to the band edge. For example, silicon with an absolute density of states = atom density = $5 \times 10^{22} \text{ cm}^{-3}$ has an effective density of states $N_C = 3 \times 10^{19} \text{ cm}^{-3}$. Molecular solids show very narrow absorption bands, resulting in a much higher density of states and consequently in a high absorption coefficient in this narrow region. However, also the transition dipole moment can vary significantly between different organic molecules.

Transport Layers

Several hole transport materials are displayed in Fig. 3.54a–e. Characteristic are the nitrogen atoms with three single bonds called tertiary amines (NR_3), which lie roughly in one plane (C-N-C angle $\approx 120^\circ$). The π -system is disturbed by these single bonds between the ring systems. Single bonds in general allow rotations and therefore hinder the planarity of molecules. Non-planarity is energetically more favorable for the π -electron cloud, which results in an equilibrium torsional angle for an unsubstituted biphenyl $(\text{C}_6\text{H}_5)_2$ of 44.4° . In the depicted molecules, angles in the range of 40 – 50° are expected between the plane of N and its bonds with the plane of the attached rings. When depositing such a material, not every molecule is found in its equilibrium structure and hence an amorphous layer (supercooled melt) is formed.

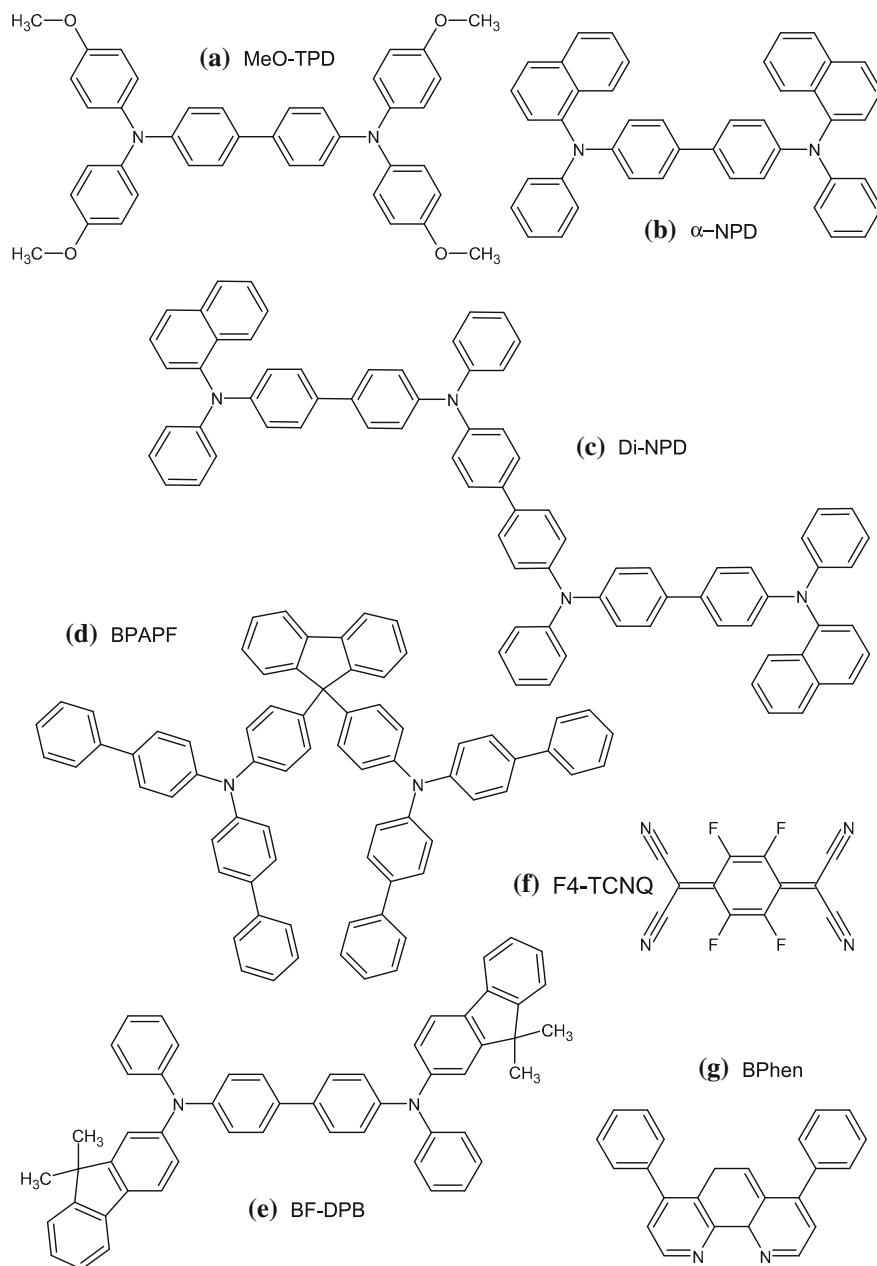


Fig. 3.54 Common molecules employed in charge transport layers: **a–e** hole transporting materials **a** MeO-TPD, **b** α -NPD, **c** Di-NPD, **d** BPAPF, **e** BF-DPB, **f** p-dopant F4-TCNQ, and **g** electron-transporting material BPhen

The difference in the HOMO^{UPS} of MeO-TPD (−5.1 eV) and α -NPD (−5.5 eV) can again be attributed to the impact of functional groups. The four methoxy groups (O–CH₃) employed at MeO-TPD are electron donating groups, which shift the orbitals upwards (+m and +i effect).

Organic chemistry offers a variety of conjugated molecules. The justification of employing exactly the depicted complicated molecular structures is found in the restrictions and procedures of organic chemistry, providing a set of common precursors and allowing only particular substitution reactions.

Charge transport layers are electrically doped to increase their conductivity. HTLs can be p-doped by dopant molecules, which are very strong acceptors with a LUMO in the range of the HOMO of the matrix. As example, F₄-TCNQ is shown (f), which has a very high electron affinity due to the cyano group and fluorine substituents. The doping process is comparable to inorganics (Sect. 2.2.1, review [255]) and results from an electron transfer, leaving a hole in the HTL material and a localized negative charge on the ionized dopant molecule (anion). Although doped HTLs become highly hole conductive, it is not entirely known to which extent the hole is free or bound in a charge-transfer state. The detailed mechanisms giving a relatively free hole and the efficiency of the doping process including the role of traps are still under research [195, 256–258].

N-doping of an electron transport layer (ETL) is more difficult to realize in the presented picture. It requires a dopant with a HOMO lying higher than the LUMO of the matrix material. This implies a LUMO of the dopant which is even higher. We know from (less noble) metals with a low work function (i.e. high Fermi level) that they oxidize easily. The same happens with organic molecules with a high HOMO. They are very reactive and can easily form bonds with oxygen. That is why n-dopants are not air-stable, although their stability increases when they are embedded in a film. Recently, research has begun to focus on the development of air-stable precursors for n-dopants [259, 260].

Doping itself is not further topic of this book. However, the devices that are discussed later on employ doped transport layers in a p-i-n stack (cf. Fig. 3.49) to provide good (ohmic) contact to the electrodes. For technical reasons (chamber contamination by F₄TCNQ) the proprietary dopants NDP2, NDP9, and NDN1 (Novaled AG, Dresden) are mostly used. We will focus on HTLs when examining variations of the charge transport layers. On the n-side, an n-doped ETL is commonly replaced by a thin (<10 nm) layer of BPhen, whose structure is shown in Fig. 3.54g. Its function is mostly a buffer protecting the absorber layers during metal evaporation.

More small-molecule absorber and transport materials are available and employed than described in the previous paragraphs. Mishra and Bäuerle compiled a recent review on the variety of small-molecule semiconductors in organic solar cells [261].

Polymer Absorbers

Currently, the majority of organic solar cells are based on polymers, although a new trend emerges towards solution processable small molecules. Commonly, a donor polymer (for a review see [262]) is blended with a C₆₀ based acceptor such

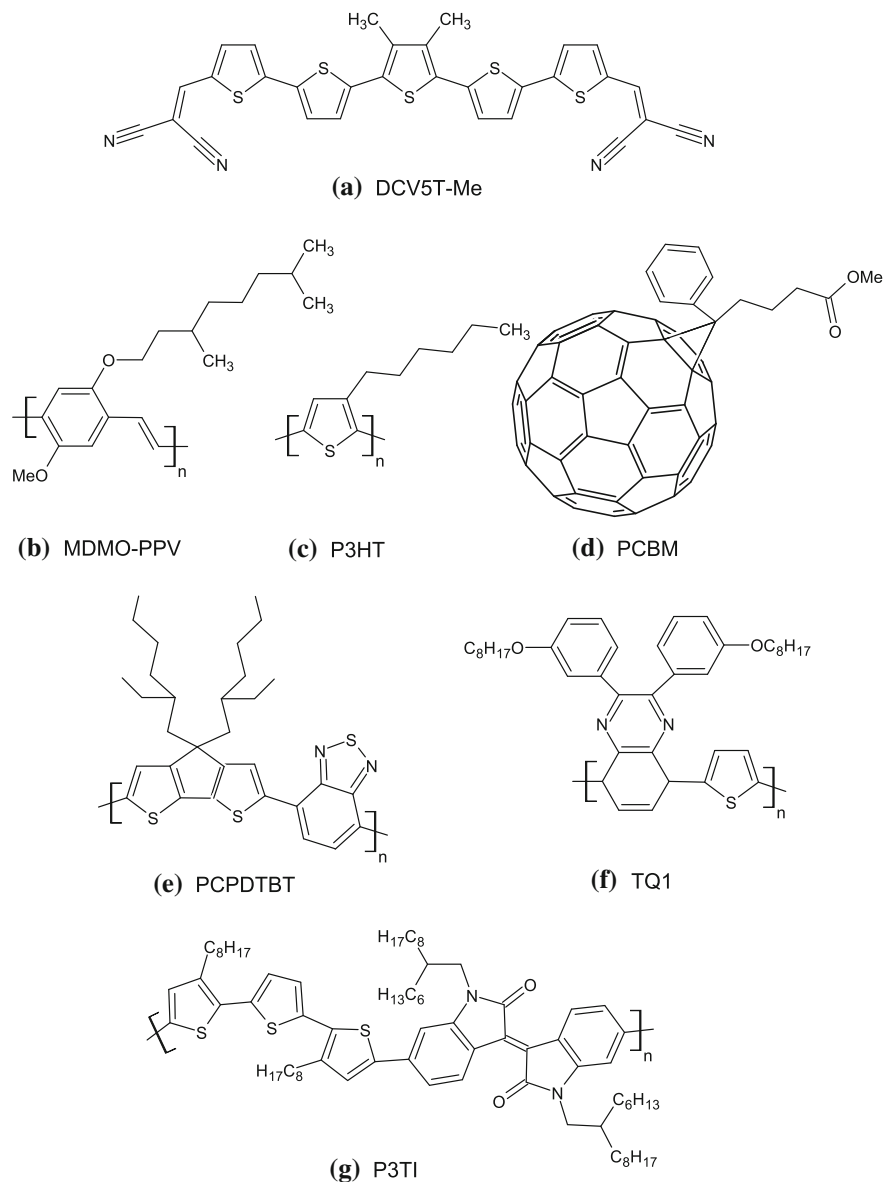


Fig. 3.55 Examples of further active materials employed in organic solar cells. **a** Oligomer: methyl-substituted dicyanovinylcapped quinquethiophene; **b**, **c** donor polymers poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylenevinylene] and poly(3-hexylthiophene); **d** acceptor: soluble fullerene derivative [6,6]-phenyl-C₆₁-butyric acid methyl ester; **e–g** donor copolymers poly[2,6-(4,4-bis-(2-ethylhexyl)-4*H*-cyclopenta[2,1-b;3,4-b']dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)], poly[2,3-bis-(3-octyloxyphenyl)quinoxaline-5,8-diyl-alt-thiophene-2,5-diyl], and poly[*N,N'*]-bis(2-hexyldodecyl)isobenzofuran-5,6'-diyl-alt-thiophene-2,5-diyl]

as [6,6]-phenyl- C_{61} -butyric acid methyl ester (PCBM) or other derivatives such as $PC_{71}BM$. These fullerenes are modified such that they become (more) soluble in organic solvents. E.g. for PCBM [263] a group consisting of a phenyl, connected at a carbon atom to a butyric acid methyl ester, is attached to C_{60} as shown in Fig. 3.55d.

C_{60} is replaced by C_{70} for highly efficient solar cells, because the absorption coefficient of C_{70} is larger due to a higher probability for HOMO-LUMO transitions (less forbidden transitions due to reduced symmetry) [264, 265]. The spectral range of absorption on the fullerenes is often complementary to the donors (Fig. 3.56). Therefore, C_{70} increases the external quantum efficiency between 400 and 600 nm. From a practical point of view C_{70} is supposed to be less relevant due to its high production costs. A bulk heterojunction that tolerates a mixture of different kinds of fullerenes (C_{60} , C_{70} , C_{84} , etc.) is perfect as it avoids expensive purification steps of the outcomes of the fullerene production, which contain a distribution of derivatives.

Commonly, the main absorber in polymer solar cells is the donor polymer analogously to the donor molecule in small-molecule devices. Polymers consist of a large number of monomers and, therefore, show a much higher molecular weight ($\approx 100,000 \text{ g mol}^{-1}$) than small molecules. Commonly, a compound is called polymer as soon as adding further monomers does not change the properties of the neat material. Polymerization is an additional step in material synthesis and the molecular weight is an additional parameter that influences device processing and the electrical properties of the solar cell. On the one hand, longer chains generally enhance charge transport due to the higher probability for longer conjugated segments. On the other hand, the solubility in a solvent and the miscibility with C_{60} can be negatively affected.

A historically important polymer absorber material is poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV). It belongs to the polyvinylenes employing the most common aromatic building block in its monomers, which is the benzene ring we discussed in Sect. 3.1.1. The structure of MDMO-PPV is shown in Fig. 3.55b. Employed in a blend with $PC_{61}BM$, efficiencies in the range of 3 % could be obtained for bulk heterojunction solar cells.

The by far most-studied donor and absorber is poly(3-hexylthiophene) (P3HT). Its structure is shown in Fig. 3.55c. It consists of thiophene (C_4H_4S) monomers which are aromatic conjugated systems like benzene rings. Thiophenes are also used as building blocks for small-molecule absorbers (oligomers) like the methyl-substituted dicyanovinylcapped quinquethiophenes (DCV5T) (Fig. 3.55a), which showed in a blend with C_{60} power-conversion efficiencies of close to 7 % [268]. The DCV5T in a film has an optical gap of 1.7 eV. Decreasing the number of thiophenes slightly increases the gap [269], as the extension of the π -system is reduced (cf. discussion on the polycyclic aromatic hydrocarbons). For P3HT mixed with $PC_{61}BM$ or $PC_{71}BM$, maximum values for the power-conversion efficiency of around 3.5–5 % are reported [270, 271]. Higher values (6.5 %) are achieved by employing an indene- C_{60} bisadduct as acceptor [272]. Due to its higher lying LUMO it gives a higher open-circuit voltage when blended with P3HT.

The monomers of P3HT are equipped with a side chain, which is an alkyl (hexyl) side chain at position 3 of the ring. This makes the polymer soluble in organic solvents

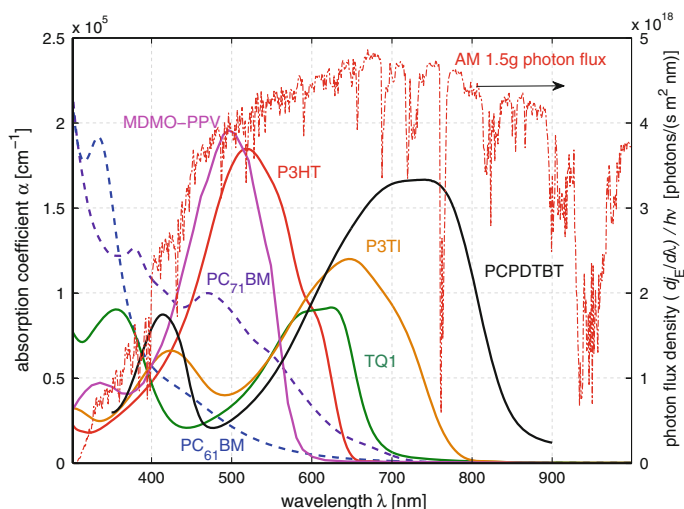


Fig. 3.56 Absorption coefficients of common donor polymers MDMO-PPV and P3HT and acceptors PC₆₁BM and PC₇₁BM. TQ1, P3TI, and PCPDTBT are selected as representatives of novel copolymers with an absorption spectrum shifted to the red. The molecular structures of all materials can be found in Fig. 3.55. The data are determined via ellipsometry at spin-cast thin films, except the data for MDMO-PPV which is from [266] and the data for PCPDTBT according to [267]. It is noted that the spectra depend also on the processing conditions due to changes in the orientation of anisotropic molecules and the degree of crystallization etc.

which facilitates solution processing. Although electronically inactive (because not π -conjugated), side chains affect the performance of a solar cell. They influence the mean distance between molecules and can therefore change the preferred orientation between molecules. This is seen in different stacking or enhanced or suppressed tendencies for crystallisation. One major aspect thoroughly investigated with P3HT is the regioregularity of the polymer, which is obtained if the polymerization reaction guarantees a linking of the monomers in a way that the side chain is always at the same position. In this case steric hindrance is minimized which allows longer conjugation lengths compared to regiorandom P3HT. Therefore, a lower optical bandgap is obtained together with the best charge transport and stacking properties.

The absorption coefficients of MDMO-PPV and P3HT are shown in Fig. 3.56 visualizing that a large part of the solar spectrum in the red and IR is not absorbed by these high-bandgap polymers. Hence, novel low-bandgap materials are developed to harvest more sun light [273–275]. We know from the discussion of the SQ limit that a bandgap of 1.1 to 1.4 eV is the optimum for a band-edge absorber. Although molecules show pronounced narrow absorption bands, it is desired to shift them to the IR, roughly maintaining the absorption strengths and possibly broadening the spectrum. Mainly two approaches in molecular design exist to reduce the energy of the absorption onset [276, 277].

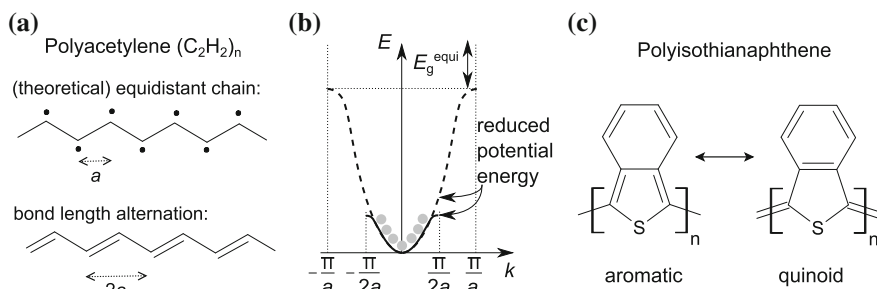


Fig. 3.57 Peierls effect: Bond length alternation doubles the length of the repeat unit (a) and reduces the potential energy (b) giving the conjugated polymer chain semiconductive properties. Consequently, a reduction of the bond length alternation reduces the bandgap. For polythiophene (c), the fusion of a benzene ring to the thiophene makes the quinoidal structure with a reduced alternation in bond length energetically more favorable and lowers the optical gap

The first one focuses on a reduction of the bond length alternation, which is responsible for the bandgap. To clarify this we take polyacetylene, which is a polymer consisting of a carbon chain with alternating single and double bonds (Fig. 3.57a). The monomer is therefore C_2H_2 . Each C is sp^2 hybridized (cf. Fig. 3.1 on p. 69) where three valence electrons form σ bonds with the two adjacent carbon atoms and the hydrogen atom. The fourth electron of the perpendicular p-orbital contributes to the π -system. If all carbon atoms were equidistantly spaced (with distance a) in this linear polymer, the π electrons would be completely delocalized along the chain, making the polymer metal-like. Consequently, the bandgap would vanish. Recalling the origin of the bandgap for a one dimensional crystalline semiconductor with a periodic lattice potential, we recognize an analogy between the periodic crystal and an equidistantly spaced carbon chain. In Sect. 2.2.1 we found that bandgaps occur at a wave number $k = \pi/a$ (Fig. 2.5). As every atom provides two allowed states (Pauli principle and spin) in a respective band, the band is half-filled, which is characteristic for metals.

However, this situation of equidistant spacing does not occur due to the so-called Peierls effect, which makes an equidistantly spaced chain of ions with one electron per ion not a stable situation. The reason is a reduction in the energy of the system for alternating distances, i.e. bond lengths. Alternating distances in the chain result in a periodicity which is twice the value compared to the case of equidistance (Fig. 3.57a). This periodicity causes bandgaps at $k = \pi/2a$ ($2a$ is now one period) as visualized in Fig. 3.57b. Consequently, the band is now fully occupied and the chain with alternating bond lengths shows the most fundamental property of a semiconductor which is a filled valence band (at $T = 0$ K). Using this explanation we extended the discussion on the semiconductive properties of conjugated systems introduced in Sect. 3.1.1.

The energy dispersion at the edge of the first Brillouin zone ($k = \pi/2a$) has to show a derivative dE/dk of 0 due to symmetry considerations combined with the condition of differentiability of $E(k)$ [cf. Sect. 2.2.1, Fig. 2.6 and (2.11)]. Therefore, the potential energy of electrons close to the bandgap is reduced compared to the

energy the electron would have in the equidistant chain at $k \approx \pi/2a$. This reduction of the potential energy of the π electrons overcompensates the elastic energy required for the rearrangement of the ions/C atoms.

How can the bond-length alternation be influenced by molecular design? For polythiophenes, for instance, the double-bond character of the linkages between the thiophenes can be strengthened [277]. As shown in Fig. 3.57c, a localization of the double bonds in the chain is a so-called quinoid structure which is energetically unfavorable in the polythiophene. Fusing, e.g., a benzene ring to the thiophene increases the probability of finding the polymer in the quinoid state. This polymer is then called poly(isothianaphthene) [278]. As consequence the bandgap is lowered, in this case by 1 eV [279].

The second approach for tuning the energy levels employs polymers with alternating donor-like (electron rich) and acceptor-like (electron deficient) building blocks [280]. Such polymers are also called push-pull copolymers. We have already mentioned that electron donating and withdrawing groups can be attached to molecules to modify the frontier orbital energies. In case of conjugated polymers, the HOMO-LUMO gap can be tuned by the degree of π overlap of the backbone influenced by steric interactions (cf. regioregular and regiorandom P3HT). For push-pull copolymers, the π -system consists of alternating electron donating and accepting monomers. Here, the expressions donor and acceptor should not be mixed up with the donor and the acceptor in a bulk heterojunction, which are two separate molecules. A push-pull copolymer is one compound which can e.g. be employed as the donor in a bulk heterojunction solar cell. The accepting monomer of the copolymer has lower lying orbital energies than the donating monomer. Combining both π -systems leads to orbital mixing comparable to the case we have discussed when deriving molecular orbitals starting from atoms (cf. Fig. 3.3 on p. 70 in Sect. 3.1.1). As shown in Fig. 3.58a, the levels split towards higher and lower energies, resulting in an effectively higher HOMO and lower LUMO than those of the monomers [280]. Or in other words, the donor roughly determines the HOMO and the acceptor sets the LUMO. Therefore, a π - π^* transition stimulated by the absorption of a photon can be seen as an intramolecular (partial) charge transfer. Effectively, the HOMO-LUMO gap of the new π -system is decreased.

One prominent example is poly[2,6-(4,4-bis-(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT) [281] consisting of a cyclopentadithiophene donor unit and a benzothiadiazole as acceptor unit (Fig. 3.55e). Its absorption spectrum is shown in Fig. 3.56. Compared to P3HT the absorption onset is shifted to the red although it is far from covering the IR. In combination with PC₇₁BM, efficiencies of 5.5 % [282] were reported.

Another molecule, employed in solar cells discussed in further chapters of this book, is poly[2,3-bis-(3-octyloxyphenyl)quinoxaline-5,8-diyl-alt-thiophene-2,5-diyl] (TQ1) [283, 284]. As visualized in Fig. 3.55f it is based on a thiophene (donor) and a quinoxaline (acceptor) unit. The absorption is shifted to the red compared to P3HT. Power conversion efficiencies in standard and inverted [285] geometry exceeding 5 to 6 % are reported. Poly[*N,N'*-bis(2-hexyldecyl)isoidindigo-6,6'-diyl-alt-thiophene-2,5-diyl] (P3TI) (Fig. 3.55g) is another example of a donor-acceptor

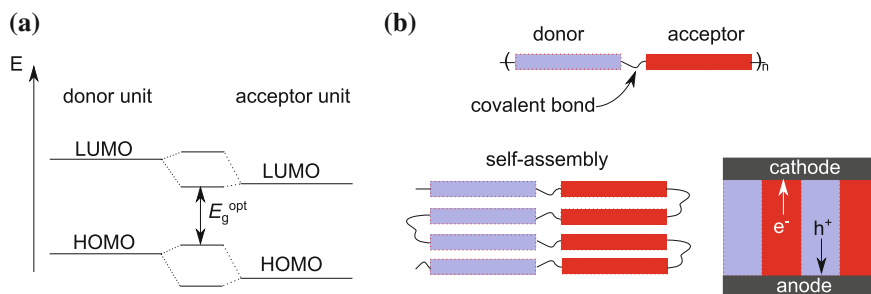


Fig. 3.58 **a** Orbital mixing decreases the optical gap of an absorber molecule (copolymer) consisting of donor and acceptor subunits (monomers). This approach of donor-acceptor (push-pull) copolymers enables low-bandgap absorbers employed as donors in organic solar cells. **b** Block copolymers, where the donor and acceptor are covalently bound via an electrically inert link. These macromolecules might enable a structured morphology supported by self-assembly

copolymer consisting of an electron rich teriophene (donor) unit and an electron withdrawing isoindigo (acceptor) unit. Due to an absorption also in the red spectral range (Fig. 3.56), P3TI:PC₇₁BM show high power-conversion efficiencies (> 6 %) [286].

Apart from tailoring the absorption (optical gap), the energy levels of the donor (polymer) are tuned to decrease the LUMO-LUMO offset to the fullerene acceptor and therefore optimize the donor-acceptor gap [275]. This electrical gap determines the open-circuit voltage independent of the optical gap as discussed in Sect. 3.3.2. Further design criteria include good charge transfer and charge transport properties. Those, however, are very difficult to predict.

One approach towards a self-assembled perfect morphology of the absorber layer is the idea of block copolymers [287]. These macromolecules consist of (now real heterojunction) donor and acceptor units which are covalently bound, but do not show a large orbital intermixing. The components might be a conjugated polymer with C₆₀ attached or two polymers (rod-rod configuration) as sketched in Fig. 3.58b. These molecules are supposed to form cable like structures, giving rise to parallel paths for electrons and holes towards the electrodes. However, so far the performance of solar cells based on block copolymers is far behind the efficiency of the best bulk heterojunctions.

Inorganic Electrode Materials

Electrodes establish an electric contact between the solar-cell stack (absorber plus potentially present charge-transport layers) and the outer circuitry. This implies that distances for charge transport in electrodes are much larger than in active materials. Whereas charges move some 10–100s of nm in the organic layers, they have to be transported laterally over mm and cm in the electrodes. Therefore, electrode materials are required to show a much higher conductivity than active materials.

If the conductivity is too low, current flow will be accompanied by a significant potential drop over the electrodes. Therefore, the electric field in the active material at a given current is reduced. In an equivalent circuit (cf. Sect. 3.3.5), this effect represents a series resistance decreasing the fill factor of the solar cell as shown in Fig. 3.37 (p. 138). More precisely, the organic solar cell at a given external bias has to be seen as a device consisting of several elementary donor/acceptor junctions connected via resistances representing the electrode as non-equipotential surface. These elements work at different voltages dependent on their distance to the outer circuitry, meaning that the macroscopic current-voltage relation does not represent the single junction. A simple correction for one macroscopic series resistance is not sufficient but a transmission line model has to be used. However, in lab-scale devices active areas are often smaller than the areas of the bars to the contact pads on the substrate (cf. Fig. 3.63). In this case, voltage losses at the bars dominate which can be considered as one macroscopic series resistance.

Commonly, metals like aluminum or silver are employed as reflective back electrodes. A thickness in the range of 100 nm is sufficient to transport photogenerated charges over centimeter distances. In commercial silicon solar cells a silver back electrode is screen-printed using a paste followed by a firing step ($>600\text{ }^{\circ}\text{C}$) to achieve a good contact between silicon and the electrode. For organic solar cells, flexible substrates with an evaporated metal layer are the technology of choice.

The main challenge is the front electrode, which has to simultaneously show high conductivity and high transparency. Materials with this combination of electro-optical properties are rare, as high conductivity requires a large density of free charge carriers, which gives rise to free-charge-carrier absorption in the near infrared. According to (2.34), a high conductivity demands for a high mobility as well.

The most common transparent electrode material is indium tin oxide (ITO) which shows the best trade-off between transparency in the visible spectral range and conductivity. Figure 3.59 displays the transmission of a glass substrate coated with a 100 nm thick ITO film. The sheet resistance R_S of this commonly employed configuration is $\approx 25\text{ }\Omega/\square$. Here, R_S is defined as the ratio between specific resistance ρ and layer thickness d (Fig. 3.60a):

$$R_S = \frac{\rho}{d} = \frac{1}{\sigma d}. \quad (3.91)$$

This value is a property of a thin film, whose thickness might not be known, and describes the resistivity of a square with arbitrary area l^2 when considering the lateral current $I = \frac{V}{R} = \frac{V}{\rho l/d} = \frac{V}{R_S}$. E.g. for $R_S = 25\text{ }\Omega/\square$, a current density of 10 mA/cm^2 , which flows through a 1 cm^2 sheet, would lead to a voltage loss of $V = RI = 250\text{ mV}$. Such a voltage loss considerably limits the FF of a high- FF

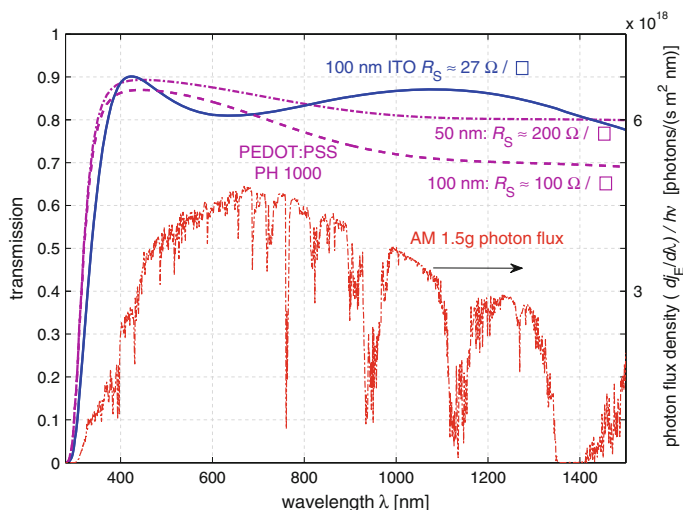


Fig. 3.59 Calculated transmission of 100 nm ITO and 50 or 100 nm of PEDOT:PSS (PH1000) on a 1 μm thick glass substrate. PEDOT:PSS shows sufficient transparency in the visible range whereas it absorbs significantly in the IR

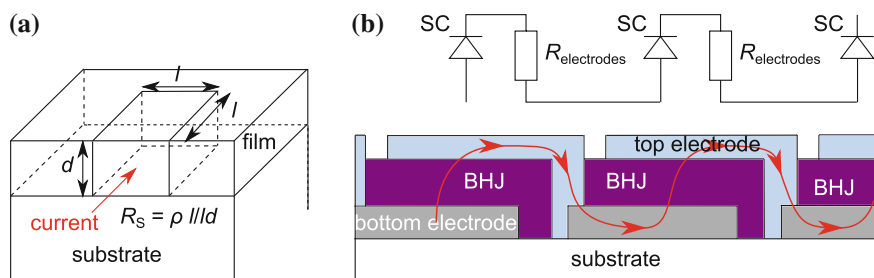


Fig. 3.60 **a** Visualization of the sheet resistance R_s , a parameter describing lateral transport through a thin film. **b** Equivalent circuit and sketch of a module consisting of solar cell (SC) stripes connected in series. In reality the lateral dimensions (≈ 1 cm) are much larger than the layer thicknesses ($< 1 \mu\text{m}$). The red line illustrates the electrical connection, and $R_{\text{electrodes}}$ summarizes the contributions from top and bottom electrodes and from contact resistances between electrode and semiconductor

organic solar cell. This example shows that a simple ITO electrode is not sufficient in modules, where larger areas are required. There, either a metal mesh could be used as is done in crystalline silicon solar cells, or several stripes of solar cells with a width of ≈ 1 cm could be connected in series as sketched in Fig. 3.60b. Solar cells employing a mesh suffer from losses of photoactive area due to shading and the contact resistance between deposited grid and semiconductor. A monolithical series connection is commonly preferred for solar modules based on thin film technologies. It requires patterning during deposition (e.g. printing) or post structuring e.g. by laser

ablation to realize the interconnects. Stripe dimensions are then optimized finding a trade-off between the limited conductivity of the electrode and the area and effort required for the interconnects. Note that the overall photocurrent does not have to be transported along the whole stripe width, as it is generated below the whole electrode and accumulatively collected towards the interconnect. That is why the losses for a module with e.g. 1 cm ITO stripes are acceptable and by far not as severe as our simple estimation in this paragraph might imply. A module based on a series connection of the sub cells delivers the accumulated voltage of all sub cells at low currents.

ITO is very successfully employed in the thin-film display (liquid crystal, LCD) and thin film photovoltaics industries. However, indium, which is mostly a byproduct of zinc mining, has become scarce. Consequently, the prices have risen and show high fluctuations. Furthermore, ITO is rather brittle and not very well suited for a flexible substrate. That is why alternatives are required (for an overview, see [288, 289]). Other transparent conductive oxides (TCO) like Al doped zinc oxides are under investigation. However, so far ITO as established technology dominates mainly because the fabrication of alternatives is not (yet) as easy and precise (regarding stability, roughness, structuring) as the deposition of ITO. Recalling Sect. 3.5.2, also the work function of the electrode has to be considered if doped transport layers are not employed.

Summarizing, wide-gap semiconductors like TCOs are most commonly employed as transparent electrodes so far. Metals either structured as grid or deposited as thin (≈ 10 nm) semitransparent layers are also investigated. For latter, an optical optimization (cf. Sect. 4.7) of the stack is essential to benefit from the micro-cavity effects created by top and bottom metal electrodes. Role-to-role processing on flexible substrates (cf. Sect. 3.6.1) requires non-brittle materials and rather low-temperature processes. Promising electrode candidates meeting these criteria are graphene [290], carbon nanotubes [291], and in particular (silver) nanowire meshes [292]. Most desirable would be a highly conductive polymer electrode, opening the way towards a (printed) all-organic solar cell. The so far most conductive and sufficiently transparent organic material is PEDOT:PSS.

PEDOT:PSS

Poly(3,4-ethylenedioxythiophene) [293] poly(styrenesulfonate) (PEDOT:PSS) is one of the most used and most developed conductive polymer blends consisting of two components. The respective structures are shown in Fig. 3.61. The polymerization of the thiophene based PEDOT can be done in aqueous solution with the polyelectrolyte PSS and employing sodium peroxodisulfate as an oxidant. Then, PEDOT is oxidized receiving a relatively mobile positive charge, which allows hole conduction. PEDOT itself is not soluble in water, but forms in combination with PSS a microdispersion. PSS delivers the counterion and keeps PEDOT dispersed. The PEDOT:PSS is a very stable complex [294]. Its synthesis was developed by the Bayer AG, Germany in the 1980s. It became a multi-ton product and has been distributed as BAYTRON[®] P, first used as antistatic coating in photographic films [295]. It

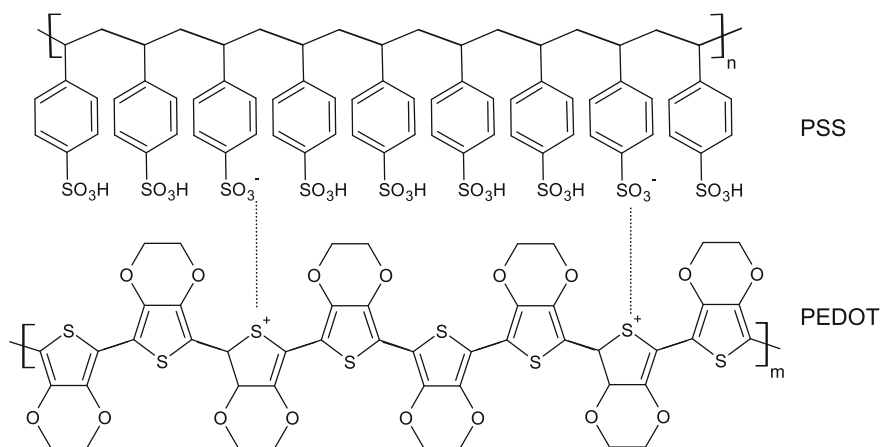


Fig. 3.61 Structure of the conductive polymer blend PEDOT:PSS. An electron is transferred to the PSS leaving a mobile hole on the PEDOT

can be bought as a dark-blue solution. The color results from the fact that PEDOT shows a higher absorption in the red (cf. Fig. 3.59). As water is a relatively high-boiling-point solvent, PEDOT:PSS commonly requires a post-heating step to release the water and form a conductive film.

Investigations of the structure of spin-cast PEDOT:PSS films revealed anisotropic properties. Ellipsometry measurements showed an anisotropy regarding the optical constants of PEDOT:PSS films, which can be described with metal-like models [296]. The high in-plane conductivity was explained by lamella-like PEDOT grains, adjacent to each other with low distances, whereas horizontally the grains are separated more strongly by insulating PSS regions [297]. It was found that the high conductivity for vertical transport can be described by variable-range hopping from PEDOT grain to PEDOT grain.

Many studies and engineering approaches have led to increases in the conductivity from $<1 \text{ S cm}^{-1}$ up to values larger than $3,000 \text{ S cm}^{-1}$. This high-conductivity PEDOT can be purchased as Clevios™ PH 1000. The reasons behind this increase are modifications of the morphology due to additives like diethylene glycol or dimethyl sulfoxide (DMSO), which are supposed to favor phase separation of PSS reducing the PSS concentration between conductive PEDOT regions [298–300] or leading to an increased interchain interaction of PEDOT [301].

These high conductivity values allow the employment of PEDOT:PSS not only as a thin interlayer (cf. Fig. 3.48), but as a lateral electrode in organic solar cells [302]. Its work function in the range of 5.2 eV makes it suitable as anode. Thin layers (in the order of 100 nm and R_S in the range of $100 \Omega/\square$) show sufficient transparency (Fig. 3.59) such that PEDOT:PSS can be used as a transparent electrode. Therefore, PEDOT:PSS might be a candidate to replace ITO as front electrode in organic solar cells. The feasibility of a PEDOT-only electrode was demonstrated [303] mostly

employing metal grids [213, 304] on the PEDOT:PSS film. Using a PEDOT electrode it is easily possible to fabricate flexible solar cells [305]. However, PEDOT-organic interfaces are also associated with issues related to the instability and acidity of PEDOT.

3.6.4 Morphology of the Bulk Heterojunction

Here, we want to briefly address a huge research area within the field of organic photovoltaics. It deals with the investigation of the phase structure of the donor-acceptor blend. This phase structure is called morphology [306]. In Sect. 3.3.1 and Fig. 3.19c we have already claimed the prerequisites for an ideal morphology, allowing on the one hand closed percolation paths for charge extraction and on the other hand sufficient donor-acceptor interfaces to separate excitons. The importance of the morphology became evident in the work by Shaheen et al. [307] who found that a change in solvent (from toluene to chlorobenzene) increased device performance by a factor of 3 for the same active materials (MDMO-PPV:PCBM). This effect is attributed to a change in the morphology of a spin-cast film. The formation of the final morphology from a wet film depends strongly on the solvent evaporation conditions and speed. It is obvious that the degree of donor-acceptor intermixing has strong implications on properties for charge transport, recombination, and even the CT state.

Up to now it is impossible to precisely predict the morphology. From the thermodynamics point of view, the grade of intermixing is determined by a minimization of the free energy, which contains the entropy and the enthalpy/potential energy. Whereas the entropy (grade of disorder) always favors a homogeneous mixing of donor and acceptor, the potential energy could increase or decrease upon mixing two components. That depends on the interaction energies between donor molecules and acceptor molecules among themselves and among each other, i.e. whether donor and acceptor are rather repulsive or attractive. The thermodynamic equilibrium should be independent of the processing conditions. However, the morphology upon deposition is usually not in an equilibrium state. This frozen morphology is required for an intermixing in the 10 nm length scale, as commonly donor and acceptor tend to phase separate. Therefore, the morphology can change during operation of the solar cell at higher temperatures or simply when storing it over time. However, if the temperatures are below the so-called glass transition temperature, the morphology remains frozen. Consequently, a theoretical description of the morphology has to take into account the method of deposition as well. It also has to consider the interactions between non-spheric molecules dependent on their orientation to each other.

As it is difficult to model the morphology, it is neither easy to experimentally adjust it in a tailored way. Main processing conditions influencing the morphology are [308–310]:

- Mixing ratio of donor and acceptor

- In case of solution processing: Choice of solvent(combination)s [307] and additives like alkane dithiols (for PCPDTBT octanedithiol (ODT DIO) [282, 311] selectively dissolving PCBM and having a higher boiling point to establish larger fullerene phases)
- Concentration and molecular weight [312] of components in the solution
- Drying conditions of the film
- In case of deposition in vacuum: Heating of the substrate during deposition [313, 314]
- Post-annealing via tempering [315, 316] or low-level illumination before tempering [317]
- Pretreatment of the substrate including a deposition of a monolayer with template function.

It remains open and has to be individually examined, which of these methods lead to a better performance for a specific material combination. The desired morphology depends on the device geometry as well. That is why a vertical phase separation can be beneficial in some cases and detrimental in other cases.

Investigating the morphology is challenging as the blend consists of molecules mainly containing carbon. This gives rise to a weak material contrast. The crucial dimensions of the phases are in the range of 10 nm, which is a challenging length to resolve. The most common and simplest method to get an idea about the morphology is a topography image obtained by atomic force microscopy (AFM) [318]. This technique employs a cantilever with a tip to scan the surface of a specimen. Dependent on the tip and the precision of the instrument lateral resolutions in the range of 3 nm and a vertical resolution in the sub-nanometer regime can be obtained. Although this method gives only information about the surface, the measured roughness and topographic structure can be seen as an indicator for a more or less intermixed or crystalline film. Dynamic modes AFM [319] offers studies of material contrasts due to a sensitive detection of surface forces.

A further step for investigating the morphology is transmission electron microscopy (TEM), based on the same working principle as optical microscopy, however, capable of resolving structures in the sub-nm range by using electrons instead of (visible) photons. These electrons with energies in the range of 100 keV are characterized by a de Broglie wavelength smaller than 1 nm. A TEM image contains a projection of the 3-d morphology onto a 2-d picture. As transmission properties of carbon-based molecules are similar, energy filtering techniques based on specific excitations of plasmons or core-levels are applied allowing for a better material contrast [320].

Another technique is scanning transmission X-ray microscopy (STXM) providing resolutions in the sub-10 nm length scale [321]. Compositional contrast can be deduced from the differences in the near edge X-ray absorption fine structure (NEXAFS) spectra of the carbon 1 s absorption edge.

The so far most sophisticated approach of imaging the morphology is TEM tomography [322]. Employing this technique, many pictures are taken for a variety of angles and a 3-d picture is reconstructed using software. If the material contrast is sufficient,

different phases can be identified in the bulk-heterojunction. However, it is very difficult to tell whether the phases are pure or consist of a mixture of donor and acceptor with a different stoichiometry compared to other domains.

There are considerably more methods addressing the morphology, e.g. X-ray diffraction techniques to monitor the crystallinity of phases.

In the following, we do not explicitly consider the morphology and assume that the absorber is a well and homogeneously intermixed film. Such a film can be described as a new effective material with its own material parameters more or less connected to those of the single components.

3.6.5 Degradation

Organic solar cells stored or processed under ambient conditions suffer from a reduction of their performance with time [323, 324]. This is mostly related to the electrical properties of the device rather than to the optical ones. Here, two main device components being subject to degradation can be distinguished: The interfaces to the electrodes and the bulk heterojunction itself.

The conductivity of metal-organic interfaces decreases strongly during aging. The reason is that a metal-insulator contact shows good charge transport properties only if the orbital energies are aligned (E_{ht} , E_{et}) to the work function of the metal (Sect. 3.5.1). A misalignment or the formation of a thin insulating interlayer is detrimental. The charge carrier cannot easily tunnel through this insulating layer. This is in contrast to conventional (doped) metal-semiconductor interfaces, where a tunneling process guarantees low-ohmic contact (cf. Fig. 3.45).

An insulating layer is commonly formed upon oxidation of the metal surface. The employment of low work function metals like Al and Ca favors this oxidation process in the presence of water or oxygen. This kind of degradation due to oxidation is an example of so-called *chemical degradation*. It is relatively independent of whether the device ages under operation or not. However, it can be efficiently reduced by avoiding oxygen contamination during processing and avoiding exposure to water vapor and oxygen during operation, where water vapor seems to be most harmful [325, 326]. Blocking undesirable compounds is achieved by barrier films for encapsulation which can increase the lifetime of solar cells up to 1000s of hours [327]. It is also suspected that low work function metals can directly react with the organic molecules, forming a metal-carbon bond. That is a reason why inverted structures or devices with specific interlayers can be more stable than the normal device.

The absorber itself and the charge-transport materials can degrade as well. A majority of these molecules is in particular sensitive to water and oxygen. The higher the HOMO, the higher is the probability of an electron transfer to an oxygen molecule resulting in a covalent bond. Excited molecules, having an electron in the LUMO, are prone for electron transfer. Such photochemical reactions in the presence of oxygen were observed e.g. for MDMO-PPV [328]. Blending the polymer with PCBM reduced the degradation kinetics possibly due to a fast electron

transfer to the PCBM. The oxidation affects mainly the electrical properties like conductivity and interface energetics, which commonly result in a decrease of solar-cell performance. Molecular oxygen is also known to p-dope ZnPc [220], which is a less harmful and to some extent reversible process. Under illumination P3HT is supposed to form reversible charge-transfer complexes with oxygen. P3HT not embedded into a blend shows a fast photo-oxidation, seen in a bleaching. This effect is strongly reduced in a blend with PCBM as the electron of the excited state is quickly transferred to PCBM. Ultraviolet light is another source of degradation [329]. It causes photochemical reactions, because the UV energy is sufficiently high to break up the molecules with bond dissociation energies of a carbon single bond of around 3.5 eV and for a double bond of around 6.2 eV. If other reaction partners are available, the broken bonds can be replaced by bonding to other substances. Some interlayers like ZnO [330] or electrode layers like ITO [331] and PEDOT:PSS suffer from (UV) light-induced degradation as well. However, in recent years more stable materials have been found.

It was observed that the presence and amount of charge carriers themselves causes degradation [332, 333], as charged molecules are radical ions with unpaired electrons possibly increasing the reactivity of the substances. Elevated temperatures commonly increase degradation rates. This fact is exploited when performing accelerated aging experiments.

Apart from these fundamental processes, *physical degradation* might play a role, changing the morphology of the blend if it is not in thermodynamic equilibrium and shows a low glass transition temperature. *Mechanical degradation* such as a delamination of the electrode or pinholes in the electrodes and barrier films are further technological challenges. Nevertheless, long lifetimes were demonstrated for lab-scale small-molecule solar cells with glass-glass encapsulation not showing any significant degradation after 2000 h in operation [334].

3.6.6 Exemplary Details of a Lab-Scale Vacuum Fabrication System

This section describes how a lab-scale fabrication system for small-molecule organic solar cells could look like. The vacuum systems located at Dresden University are chosen as example as they were used to fabricate most of the devices discussed in the following parts of this book. These systems allow for a fabrication of a complete series of solar cells within one evaporation run including systematic variations of, e.g., layer thicknesses. Therefore, a very accurate and reproducible comparison of devices fabricated in one run is possible. All devices employ the same material batches and exactly the same substrate treatment. And all layers are deposited under the same evaporation conditions. This is very important, as quality and purity of materials from different suppliers or batches vary in a certain range. Although a common purity of, e.g., $\geq 99\%$ is high in terms of chemical properties, the remaining

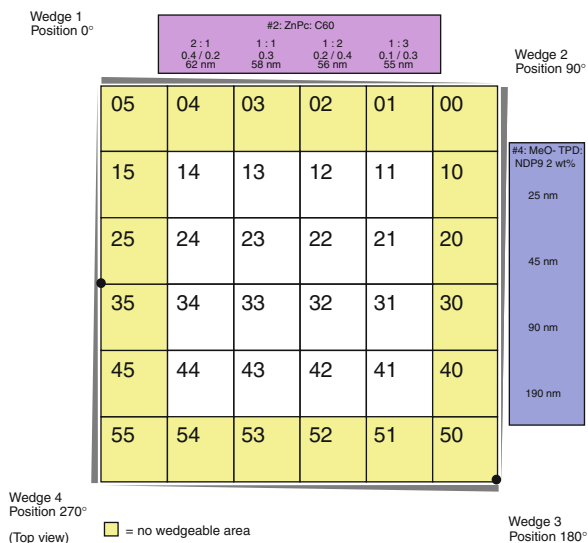


Fig. 3.62 Example of a wafer layout: the $15 \times 15 \text{ cm}^2$ wafer consists of 36 samples. Single columns (and rows) are addressable by wedges shading the remaining parts of the wafer during the deposition process

impurities can be crucial for electrical effects like doping and traps. The evaporation tool consists of a custom-made single vacuum chamber from K. J. Lesker company, equipped with 11 organic and several metal sources. Hence, it allows to fabricate complicated structures without breaking the vacuum. It handles glass wafers with $15 \times 15 \text{ cm}^2$, consisting of 36 substrates ($25 \times 25 \text{ mm}^2$) arranged in six rows and columns (Fig. 3.62). Due to technical reasons mostly only the inner four are available, resulting in 16 devices per wafer. During evaporation, single columns are addressed by wedges, which can be positioned to shadow designated columns. By rotating the wafer by 90° relative to the wedge, also single rows can be addressed. This geometry allows, e.g., variations in layer thicknesses or all mutual combination of two layers, each consisting of different materials. This variation scheme is often reflected in the experimental data presented later which consist of 4×4 matrices.

As already mentioned the wafer consists of up to 36 substrates. Each substrate contains four single solar cells, called pixels, with a nominal area of $2.54 \times 2.54 \text{ mm}^2 = 6.44 \text{ mm}^2$. This area is defined as geometrical overlap between the pre-structured ITO contact and the top metal contact which is a common contact for all four pixels, as shown in Fig. 3.63. The deposition areas are defined by separate shadow masks for organic and metal layers. The purpose of the metal stripes covering the ITO is a reinforcement of the ITO fingers to decrease the parasitic series resistance of the device, which is then found in the range of 30–50 Ω .

The definition of the active area via a geometrical overlap of electrodes is difficult, because the active regions extend slightly over the edges and contribute to the overall photocurrent by lateral currents from the surroundings which is illuminated as well.

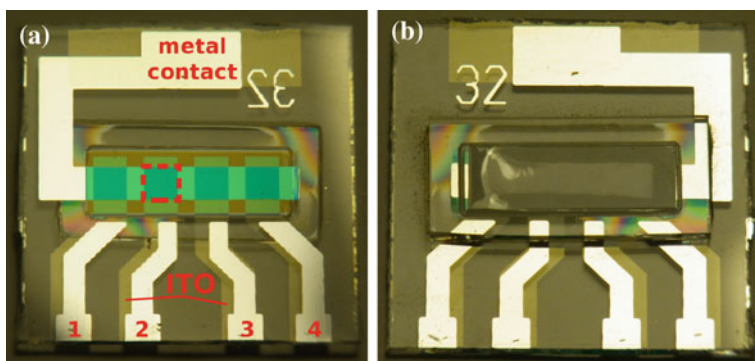


Fig. 3.63 Photograph of a sample containing four solar cell pixels (blue, one is marked by a dashed rectangle). Their area is defined by the overlap of the ITO (yellow) and the metal electrode (shiny). The four ITO fingers are reinforced by metal. **b** Top view, showing getter and encapsulation glass with interference fringes due to thickness variations in the glue which have been caused by mechanical stress. Usually this indicates a failure of the encapsulation

This effect depends strongly on the lateral conductivity of the layers. Assuming additional electrically active areas extending the edges by less than $1\text{ }\mu\text{m}$, this effect is expected to be less significant than the effect of slightly misaligned shadow masks during evaporation. Using an aperture to exactly define the illuminated area during a measurement increases the accuracy on the one hand, but includes the effect of a dark solar cell in parallel on the other hand. Thus, the aperture should be taken as area calibration by measuring the short-circuit-current density only. This value is then used to scale the current-voltage (I - V) curve, which is measured without aperture, to the correct current density versus voltage (J - V) curve. As the focus of this book is not on measuring exact solar-cell efficiencies, all I - V measurements are done without aperture. The current density J is obtained by dividing the measured current by the nominal device area of 6.44 mm^2 .

The sample preparation procedure is as follows: The ITO-coated and pre-structured glass substrate is cleaned with acetone and afterwards kept in a N-Methyl-2-pyrrolidone (NMP) bath for 20 min. These processes are followed by a rinse under deionized (DI) water and by ultra sonic baths in DI water and acetone (10 min each). Finally, the substrate is treated by an oxygen plasma (10 min).

Organic materials are commonly purified by vacuum gradient sublimation [335, 336], where the material is placed in a tube with a temperature gradient. After the cleaning, the material can be collected at a certain position in the tube, being separated from impurities which exhibit different sublimation temperatures. This treatment is repeated up to three times. The purified material is filled into crucibles, surrounded by resistive heating wires, constituting the evaporation source. All layers are evaporated subsequently at a base pressure of $\lesssim 10^{-7}$ mbar and with typical rates of $0.1\text{--}0.5\text{ }\text{\AA}/\text{s}$. Although it is possible to heat the substrate during evaporation to assist the rearrangement of arriving molecules on the surface, all samples

discussed in this book are fabricated at room temperature. The wafer is rotating during evaporation with a speed of 10 rpm to increase homogeneity.

Bulk heterojunctions or doped layers are processed by co-evaporation of both materials. Layer thicknesses are measured via independent quartz crystal monitors, which detect the mass of the evaporated material. As these monitors cannot directly be located at the substrate position, a tooling factor has to be determined, describing the proportionality factor between expected material at the substrate and actually measured material at the position of the monitor. The densities of the materials have to be known for thickness calculations. Density values of 1.34 g/cm^3 for ZnPc and 1.54 g/cm^3 for C_{60} are used, although recent X-ray diffraction measurements result in slightly different values. Stating errors in layer thickness is very difficult due to errors in the material density and a dependence of the tooling factor on the filling of the crucibles. A significant uncertainty is introduced for bulk heterojunctions due to the mostly unknown density of mixed films. However, relative variations in thickness are expected to be less than 10 %, including an inhomogeneity of $\approx 2 \%$ on one single wafer [337].

After processing, every $2.5 \times 2.5 \text{ cm}^2$ substrate is encapsulated with a cover glass, which is fixed by UV hardened epoxy glue. Additionally, a moisture getter (Dynic Ltd., China) is placed between cover glass and solar cell. Organic electronic devices degrade rapidly under exposure to air (especially oxygen and water vapor, see previous section). That is why a good encapsulation is essential for a reliable characterization of organic solar cells, which is described in the next section.

3.7 Basic Characterization Methods

We briefly address the setups commonly used for a basic electro-optical characterization of solar cells in steady state and for electrical transients. In particular, we comment on the issue of the spectral mismatch. Further measurements giving access to important properties of organic materials and devices are listed in Sect. 4.9 including brief descriptions.

3.7.1 Current-Voltage Characteristics

The most important characterization method is the measurement of the current-voltage characteristics (I - V curve), delivering the power-conversion efficiency η (3.70). Ideally, this measurement should be performed under real solar illumination and at a well-defined temperature. Standard reporting conditions for solar cell characterization are the AM1.5g spectrum (cf. Fig. 2.1) and $T = 25^\circ\text{C}$. For practicability reasons, laboratory setups employ a solar simulator. It consists of a light source, mostly a Xenon lamp with a specific gas mixture and filters, which emulate the real solar spectrum. Unless stated otherwise, the experimental I - V curves shown in the following of this book are measured under illumination with the solar simulator

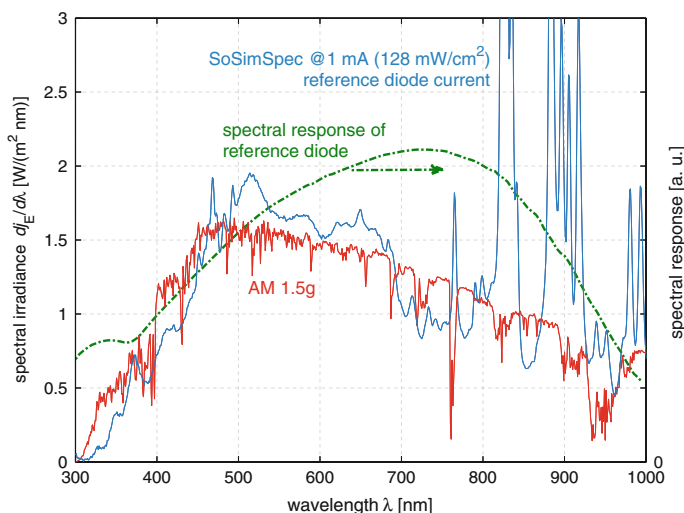


Fig. 3.64 Spectrum of a solar simulator in comparison to AM1.5g. The peaks for wavelengths larger than 800 nm result in a mismatch factor for ZnPc:C₆₀ solar cells smaller than 1 (≈ 0.7 – 0.8). The reason is that ZnPc:C₆₀ solar cells mainly absorb below 800 nm (cf. Fig. 3.53), whereas the spectral response of the silicon reference diode extends to $\approx 1,100$ nm

16S-002 by Solar Light Co., USA, whose spectrum is shown in Fig. 3.64. The illumination of the sample is provided via fiber optics with a spot of several millimeters in diameter. The light intensity is measured by a calibrated silicon reference photodiode. It can be varied by adjusting the power supply of the lamp, employing neutral density filters (fine metal grids), or varying the distance between fiber and sample. To record the I - V data, a voltage sweep is applied and the current is measured by a source measuring unit (Keithley 2400).

The main source of errors is the deviation of the solar simulator spectrum from AM1.5g, as visualized in Fig. 3.64. Considering this spectral mismatch is very important for a correct determination of η , especially for (organic) solar cells with spectrally narrow absorption bands. The intensity monitored by the silicon reference diode is the overall intensity, integrated over all wavelengths (smaller than the wavelength corresponding to the silicon bandgap energy). It averages the positive and negative deviations of the simulator spectrum compared to the AM1.5g spectrum. If, e.g., the positive deviations are located in the spectral region, where the test (organic) solar cell mainly absorbs, the efficiency will be overestimated. Therefore, the spectral mismatch factor has to be taken into account, describing the ratio between the intensity seen by the organic solar cell and the one measured by the reference cell. The spectral response of the solar cell has to be known to carry out the mismatch correction.

3.7.2 Spectrally Resolved Measurements

External Quantum Efficiency and Spectral Mismatch

The spectral photocurrent response describes the current density per unit wavelength and incoming intensity in the unit mA/(mW nm). Converting the incoming intensity into a number of photons (division by $h\nu$) and the current into the number of electrons (division by elementary charge), the external quantum or incident photon to collected electron efficiency (EQE / IPCE) can be obtained. The spectral mismatch (MM) for an illumination with spectrum $\text{SoSim}(\lambda)$ given as spectral photon flux density (γ) can then be calculated as:

$$\text{MM}(V) = \frac{\int \text{EQE}(\lambda, V) \cdot \text{SoSim}^\gamma(\lambda) d\lambda / \int \text{SoSim}^{\gamma/P}(\lambda) d\lambda}{\int \text{EQE}(\lambda, V) \cdot \text{AM1.5g}^\gamma(\lambda) d\lambda / \int \text{AM1.5g}^{\gamma/P}(\lambda) d\lambda}. \quad (3.92)$$

It is a measure of the sensitivity of the solar cell with respect to the illumination spectrum, i.e. the dependence of the EQE on λ in spectral regions, where the spectra show differences. Thus, it is in particular important for organic solar cells with distinct features in the EQE. The normalization in (3.92) can be done with respect to the photon number (γ) or more commonly to the incident intensity (P).

In general, the MM depends on the applied voltage due to the dependence of the EQE on the applied bias. However, this dependence is expected to be weak as we will see at an example in Sect. 8.3. Therefore, the MM is commonly calculated at $V = 0$. As the photocurrent of a reference diode is used to adjust the intensity of the sun simulator, the overall correction factor m is needed. It describes the ratio between the current to select $J_{\text{set}}^{\text{ref}}$ and the current J_0^{ref} , which is known from the calibration of the reference diode to correspond to a defined intensity, e.g., one sun under AM1.5g illumination. Hence, instead of normalizing to the overall intensity (3.92), the EQE of the reference cell has to be considered as well:

$$m = \frac{J_0^{\text{ref}}}{J_{\text{set}}^{\text{ref}}} = \frac{\int \text{EQE}^{\text{ref}}(\lambda) \cdot \text{AM1.5g}^\gamma(\lambda) d\lambda}{\int \text{EQE}^{\text{ref}}(\lambda) \cdot \text{SoSim}^\gamma(\lambda) d\lambda} \cdot \frac{\int \text{EQE}(\lambda, V) \cdot \text{SoSim}^\gamma(\lambda) d\lambda}{\int \text{EQE}(\lambda, V) \cdot \text{AM1.5g}^\gamma(\lambda) d\lambda}. \quad (3.93)$$

It is equivalent to replace the EQE by the spectral response of the solar cell and use the irradiance spectra (P) instead of photon fluxes (γ).

The EQEs shown in this book are recorded under monochromatic light generated by a Xenon arc-lamp (Oriel Apex Illuminator, Newport, USA) in combination with a monochromator (Cornerstone 260 1/4m, Newport, USA). The light is chopped and the current response of the sample is detected by a lock-in amplifier (7265 DSP Signal Recovery, UK). The lock-in technique increases the signal to noise ratio, as the lock-in amplifier only measures the signal at the chopping frequency. Consequently, parasitic signals and noise having another frequency (distribution) are filtered out. The calibration of the setup is done by measuring a silicon reference diode with known

spectral response. In doing so, the spectral photocurrent response of the reference cell is used to calculate the spectral intensity distribution that reaches the sample. The EQE can also be measured under a bias illumination or bias voltage applied to the sample.

Absorption

As already discussed in Sect. 3.3.1, the internal quantum efficiency of a solar cell is an interesting physical quantity, which can be calculated as ratio between EQE and spectral absorptance. In principle, the absorptance can be measured comparably to the EQE by using monochromatic light and detecting reflected and transmitted light. If the device is highly scattering, an integrating sphere might be used to collect all the reflected light.

The absorptance of an opaque solar cell can be measured in reflectance mode, as a transmission of light is not expected. This approach is applied for obtaining the data shown in this book, where a combined Deuterium and Halogen light source (Avalight-DH-S-BAL, Avantes, The Netherlands) and a spectrometer (OMT-ct60, OMT, Germany) are employed. Here, a reference spectrum has to be recorded to characterize the spectral distribution of the light source, the transmission performance of the optical setup, and the sensitivity of the spectrometer channels. The here investigated samples (layout see Fig. 3.63) show some regions that are covered by aluminum only. The reflectance of this reference can be calculated by optical simulations of 1 mm glass covered by 100 nm Al. Then the reflectance of the solar cell is calculated by dividing the spectrum from the sample by the reference spectrum and multiplying it with the calculated reflectance of the reference. Finally, the absorptance of the solar cell is obtained by subtracting the measured reflectance from unity.

3.7.3 Transient Electrical Measurements

Transient measurements of the photocurrent and photovoltage can reveal details on the dynamics of processes by providing characteristic response times. Photocurrents are measured by an oscilloscope with a low-impedance input (commonly 50 Ω) and voltages using a high-impedance input (commonly 1 M Ω). The excitation is provided by a light pulse generated by a light-emitting diode driven by a pulse generator. The data shown in this book was collected using the pulse generator HP 8114A (100 V/2 A) and the oscilloscope HP infinium (500 MHz/1 Gs). The illumination was provided by white Lumitronix Luxeon high power LEDs.

The photocurrent response can be measured at a varied bias voltage provided by a low-noise source, e.g., a battery with a resistive voltage divider (potentiometer).

The transient photovoltage (TPV) method provides access to charge carrier lifetimes [338]. Here, the device is kept at open circuit applying a constant bias illumination. The decay of the voltage, which is induced by a small-signal illumination pulse, is measured by the oscilloscope set to high-impedance input. A variation of the illumination intensity can be done by changing the current which drives bias

and probe LED. Combined with a charge-carrier extraction measurement, TPV can reveal information about recombination (Sect. 3.3.2). In this method, the voltage at the device is switched from open-circuit to short-circuit or even reversed bias, allowing for an extraction of (almost) all carriers in the device. Integrating the measured current pulse gives an approximation of the charge carrier density at open circuit.

3.8 Answers to the Initial Questions and Further Reading

- *What are the major prerequisites for organic materials to show semiconducting properties?*

Some valence electrons have to be delocalized on the molecules, where they occupy π orbitals. Conjugated systems with alternating single and double bonds between carbon atoms provide this property. The Peirls effect gives conjugated molecules that incorporate a carbon chain their semiconductive properties. Optical transitions from the highest occupied π orbital (valence states) to the lowest unoccupied (so-called π^*) orbitals (conduction states) can be in the visible range. An overlap of wave functions allows for a transport of charge from molecule to molecule.

- *What happens when molecules form a solid? What are the main differences between organic and crystalline inorganic semiconductors?*

Energy levels shift due to polarization effects (solvent shift). In inorganic semiconductors the delocalization of electrons gives rise to energy bands and therefore completely modified optical properties. This is commonly not the case for a disordered, amorphous organic solid, where charge transport is governed by a thermally activated hopping mobility. Characteristic molecular absorption bands albeit shifted are still visible in a film.

- *What is the role of the reorganization energy considering optical and electrical properties of organic semiconductors?*

Upon excitation or charge transfer, the system reorganizes. Potential energy surfaces change. This leads to a Stokes shift between absorption and emission. The energy dissipated when the molecular structure and the surroundings change is lost in a solar cell. The probability for intermolecular electron transfer is commonly reduced with a higher reorganization energy according to Marcus theory.

- *What approaches exist to describe the charge-carrier mobility in organic solids?*

Commonly, band transport of quasi-free electrons, characterized by the existence of an effective mass, long mean free paths, and scattering events at the lattice is not applicable. Instead, hopping models are applied, where electrons jump from site to site. The Bässler model considers disorder in a Gaussian distribution of the hopping sites. An alternative approach is a multiple-trapping-and-release model. Both models describe a mobility which is activated by temperature and dependent on the electric field and charge carrier densities.

- *What are the steps of energy conversion in an excitonic solar cell? What is the role of the bulk heterojunction?*

Incident photons are absorbed and create an excited state (exciton), which diffuses

and is subsequently split at an interface. The resulting charge carriers drift and diffuse to their respective electrode where they are collected. The difference to a conventional solar cell is the photogeneration of an exciton, i.e. a bound electron-hole pair, which has to be split at an additional structure/interface. This interface is called donor/acceptor interface. As the diffusion length of excitons is limited, donor and acceptor molecules are blended forming a so-called bulk heterojunction.

- *How can different recombination mechanisms be distinguished?*

The slope of the open-circuit voltage as a function of illumination intensity can be used to distinguish between direct and trap-assisted recombination. A linear scaling of the photocurrent-voltage curve with intensity indicates a monomolecular recombination mechanism (trap-assisted or geminate). Deeper insight is provided by transient photovoltage decay and charge extraction measurements.

- *What is (the role of) the charge-transfer state?*

The charge-transfer state describes the excitation of the charge-transfer complex at a donor/acceptor interface. A population of this state, which can alternatively be regarded as a bound electron-hole pair at the acceptor/donor interface, can be an intermediate step in the energy conversion from excitons to free charge carriers. Then, its dissociation and relaxation influences the photocurrent and determines the open-circuit voltage.

- *Can the open-circuit voltage be related to other optical and electrical quantities accessible by experiment?*

According to the general reciprocity between absorption and emission, the open-circuit voltage can be calculated when knowing the photovoltaic external quantum efficiency and the electroluminescence efficiency close to the open-circuit voltage.

- *Is there a stricter limit for the maximum power-conversion efficiency of organic solar cells compared to their inorganic counterparts?*

No, a more fundamental limit is not known. The exciton binding energy was never provided by a photon. Experiments indicate that the energetic driving force at a donor/acceptor interface can be small. State-of-the-art devices suffer from high non-radiative recombination. The reorganization energy provides a fundamental limitation, whose maximum reduction by molecular design cannot yet be predicted.

- *Why does a single-layer organic solar cell show diode behavior?*

The intrinsic organic (bulk heterojunction) layer is sandwiched between electrodes. Matching their work functions to the hole and electron transport level, respectively, allows injection of only one type of charge carrier at the metal-organic interface. That is why the device is rectifying. In forward an exponential diode current is expected as charge carriers diffuse against the (with increasing bias lowered) built-in potential, originating from the difference in electrode work functions.

- *What determines the fill factor?*

In the ideal solar cell the fill factor is limited by recombination only. In organic solar cells it is the competition between extraction (low mobility) and recombination of charges. A field-assisted dissociation of Coulombically bound electron-hole pairs can influence the fill factor as well.

- *What is the role of metal electrodes? What kind of energetic situations are possible when a metal/organic contact is formed?* The electrodes are supposed to selectively collect electrons or holes. Due to different work functions between cathode and anode, they provide a built-in potential increasing the probability of charges to reach their respective electrodes. Work functions in the energy gap of the semiconductor give rise to injection barriers for charges. Dipoles and surface and/or tail states can pin the Fermi level at a certain value.
- *What are common solar-cell stacks? How can they be fabricated?*
In the standard geometry, the active layer is deposited onto a substrate with a transparent anode. The stack completes with a reflective metal cathode. In inverted stacks, anode and cathode are interchanged. The illumination can also be incident from the top. Usually interlayers are inserted between electrode and active material, leading to a p-i-n structure with doped charge transport layers. Devices can be fabricated by desublimation in vacuum or by solution processing. Latter includes spin-coating and other solution-based coating or printing techniques.
- *What are the remaining challenges for making organic solar cells competitive?*
The development of novel absorber materials covering a broader spectral range and showing decent charge-transport properties. Engineering of the solar cell (morphology) and the module, delivering an optimized device which is highly efficient, long-term stable, and (roll-to-roll) fabricated in an economic way.

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Further Reading

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- 347. Comprehensive and well-explained review on the design approaches of donor polymers: Zhou, H., Yang, L., You, W.: Rational design of high performance conjugated polymers for organic solar cells. *Macromolecules* **45**, 607–632 (2012)
- 348. Review focusing on morphology of polymer-polymer blends for organic light emitting diodes and solar cells: McNeill, C.R., Greenham, N.C.: Conjugated-polymer blends for optoelectronics. *Adv. Mater.* **21**, 3840–3850 (2009)
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Chapter 4

Modeling

Abstract After having discussed general principles of solar energy conversion and the elementary processes in organic solar cells, we focus on modeling and simulation in this chapter. The first part deals with drift-diffusion simulation in general including the Einstein relation. In the second part, specific models for physical processes are discussed, which range from mobility and recombination models to the description of CT states, traps, interface barriers, and a Gaussian-shaped density of states. In a third part, an optical thin-film model based on the transfer-matrix approach is described. The final part contains discussion on exemplary devices visualized by simulation results. Readers, who are not interested in the details of drift-diffusion simulation, can simply skip the technical parts. However, they are encouraged to follow the descriptions of the ideas and models, as almost all analytical approaches to understand the current-voltage relation of organic solar cells are based on special cases of these equations. In particular, this chapter should help the reader to answer the following questions: (a) Which approaches exist to model organic solar cells? (b) What are the main assumptions for a drift-diffusion model? Where are difficulties in applying it to organic solar cells? (c) What are the basic equations and input parameters? (d) Charge carrier mobility and recombination in organic semiconductors: How can they be described? Are they interrelated? (e) What is the role of the contacts—mathematically and physically? (f) Why is the Lambert-Beer law incapable of describing absorption in organic solar cells? What is coherence? (g) What is the basic idea of the transfer-matrix model? (h) What are the different working regimes of a single-carrier device?

4.1 Overview

Modeling and in particular numerical simulations can fulfill several tasks which range from theoretical discussions of physical mechanisms to the assistance in the interpretation of experiments. The latter implies parameter extraction by fitting of (quantitative) experimental data or a (qualitative) explanation of dominating processes in the experiment. As state-of-the-art simulations of organic semiconductor devices are not yet predictive, the content of this book focuses mainly on the last point.

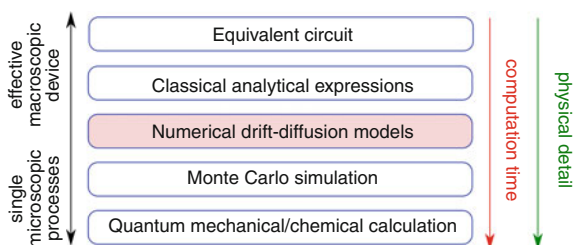


Fig. 4.1 Overview of approaches for organic semiconductor (device) modeling. In this book, we focus on numerical drift-diffusion simulations, which are categorized between microscopic and macroscopic models

Simulation of semiconductors and organic solar cells in particular can be performed on different scales of abstraction (Fig. 4.1). In the previous chapter, models with a very high level of abstraction have already been discussed, like the equivalent-circuit model. Such models are characterized by effective parameters rather than by physical processes, whose characteristic variables can be measured independently with other techniques than a current-voltage measurement. On the other hand, when reviewing the Bässler model, we discussed results of a Monte Carlo simulation, which is a more microscopic modeling approach. It is commonly applied in charge-carrier transport simulations of disordered and blended materials [1–6] and for geminate-pair dissociation [7–9]. Within this technique, charge carrier interaction and transport are described by rate equations. The path of a single charge carrier through a three dimensional solid is calculated by evaluating the probabilities for particular hops, considering disorder within the stochastic calculations. The final result is obtained as an average of a sufficiently large number of simulation runs. The main advantage of this method is the description of charge-carrier transport and mobilities within a semiconductor, correlating these properties to disorder parameters and the electric field. However, extending this method to a large solid, which means many hopping sites, or to several charge carriers, requires significant computational time. Thus, it has not often been used to simulate a whole set of I – V curves. Another reason is that the I – V curve and especially V_{oc} are, as discussed previously, a function of charge carrier densities and diffusion gradients within the device, which can hardly be modeled by a single carrier's hops.

Although being microscopic, Monte Carlo simulation requires several input parameters, which cannot be derived directly from chemical or physical structure data obtained by measurements or from the knowledge of single-molecule properties. Therefore, models which are even more microscopic are necessary. Recently, simulations have been developed that include a complete simulation chain to describe organic solar cells (almost) *ab initio* (Fig. 4.2) [4]. This chain involves multiscale models, considering different time and length scales. The energy levels and wave functions of the molecules can be calculated by quantum chemical electronic structure methods like the Hartree Fock approximation or (time dependent) density functional theory. These methods deliver an approximated numerical solution of the

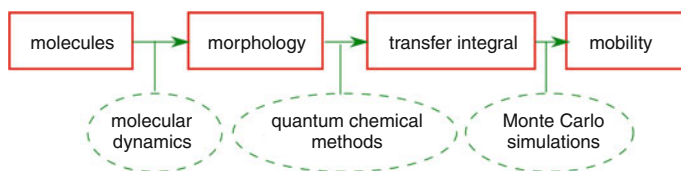


Fig. 4.2 Steps and methods for microscopic charge-transport simulations in organic semiconductors covering the whole chain from properties of single molecules to the mobility of a solid

electronic Schrödinger equation of a molecule. A further step includes atomistic molecular dynamics simulations for calculating atomic and molecular movements due to interatomic(-molecular) interactions. They deliver as result an arrangement of molecules (“molecular packing”) in a film, which can be called morphology. This structure is the starting point for quantum chemical techniques to calculate the parameters of the charge transfer rate equation according to non-adiabatic Marcus theory (3.17). The parameters include site energies, reorganization energies, and electronic transfer integrals resulting from molecular orbital overlap. These data are used as input for kinetic Monte Carlo simulations of hopping transport, finally resulting in a mobility value or function for the molecular film or in current-voltage characteristics of a device.

Apart from these very time-consuming simulations, drift-diffusion models are commonly applied in semiconductor device simulation and in particular, in the simulation of organic light-emitting diodes [10, 11] and solar cells [12–18]. In Fig. 4.1 they are ranked between the microscopic and the macroscopic approaches and are a trade-off between physical depth on the one hand and computational cost on the other hand. They provide I – V simulations of multilayer devices consisting of complicated structures. Both effective parameters for the description of not yet well understood processes and the implementation of explicitly known processes, can be combined into the framework of drift and diffusion currents. The main condition is the existence of quasi-free particles (electrons and holes) without mutual interactions, carrying charge, and obeying a continuity equation. It is discussed in the following section whether it is also legitimate to use such a continuum approach in organic semiconductors.

4.2 The Drift-Diffusion Model in General

4.2.1 Derivation and Conditions

Drift and diffusion currents have already been introduced when we discussed the transformation of chemical energy into electrical energy in the second chapter (Sect. 2.4). We have also applied continuity equations when describing recombination and diffusion of minorities in a p-n junction (Sect. 2.5.1). Within this chapter,

a microscopic derivation of these equations and the accompanied conditions are briefly discussed to give an idea where the drift-diffusion approach theoretically originates from. The reader is referred to textbooks, e.g. [19], for a more involved derivation.

Continuity and drift-diffusion equation are contained in the Boltzmann equation, whose derivation according to [19] is sketched in the following: The basic idea is a so-called distribution function $f(\mathbf{r}, \mathbf{v}, t)$, which completely describes the state of a (semi-)classical particle ensemble. The expression $f(\mathbf{r}, \mathbf{v}, t)d\mathbf{r}d\mathbf{v}$ denotes the number of particles around position $\mathbf{r}$ and with velocity around $\mathbf{v}$ at time t . Thus, an integration over $\mathbf{r}$ and $\mathbf{v}$ gives the total number of particles N . An integration over only $\mathbf{v}$ at a certain position $\mathbf{r}$ results in the charge carrier density $n(\mathbf{r}, t)$ at $\mathbf{r}$.

To investigate the variation of f with time, we discuss the one dimensional case: Assume a parallelepiped in $x - v_x$ space as shown in Fig. 4.3a, where x denotes the position in space and v_x the velocity in x -direction and $d\sigma$ the extension of the parallelepiped in direction of v . The number of particles entering (or leaving) the sketched infinitesimal area from the left is $f(x, v_x)v_x dt d\sigma$. The number of particles leaving (or entering) the depicted area at position dx is $f(x + dx, v_x)v_x dt d\sigma$. Consequently, the change of particles in x -direction is given by the difference between both:

$$(\partial N)_x = (\partial f(x, v_x)d\sigma dx)_x = -\frac{f(x + dx, v_x) - f(x, v_x)}{dx} dx v_x dt d\sigma. \quad (4.1)$$

Here, we expanded the right expression by dx/dx . It directly follows that the rate of change of f due to particles moving in x -direction is:

$$\left. \frac{\partial f}{\partial t} \right|_x = -\frac{\partial f}{\partial x} v_x. \quad (4.2)$$

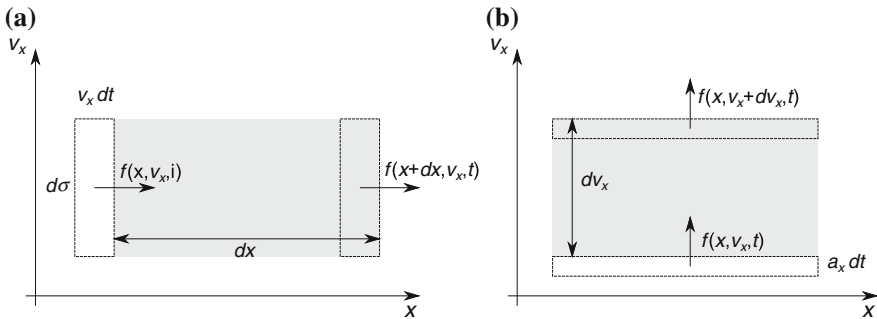


Fig. 4.3 An area in $x - v_x$ space, where *horizontal lines* represent constant velocities v_x and *vertical lines* constant locations x ; f is the distribution function defining the state of particles. The visualizations of **a** a change of position dx and **b** a change of velocity dv are used for the derivation of the Boltzmann equation

The same treatment can be done for particles crossing the horizontal lines of the parallelepiped as shown in Fig. 4.3b. This case represents a change in the velocity. Comparable to the fact that velocity changes the position of particles (4.2), an acceleration a is the reason for a change in the velocity of particles:

$$\left. \frac{\partial f}{\partial t} \right|_{v_x} = - \frac{\partial f}{\partial v_x} a_x. \quad (4.3)$$

The overall change of the distribution function with time is the sum of both contributions including all three space coordinates:

$$\frac{\partial f}{\partial t} + \mathbf{v} \nabla_{\mathbf{r}} f + \mathbf{a} \nabla_{\mathbf{v}} f = 0. \quad (4.4)$$

This expression is called Boltzmann equation, which is a very general equation in physics. For charge transport within a crystal, $\mathbf{v}$ might be replaced by an expression containing the crystal momentum $\mathbf{k}$.

If there are perturbations due to collisions, these additional processes changing $\mathbf{v}$ have to be added to (4.4) by replacing the right hand side by $\partial f / \partial t|_{\text{coll}}$.

To derive the continuity and drift-diffusion equation based on (4.4), the momentum method is used, where the Boltzmann equation is multiplied by powers α of the velocity (or momentum) with a subsequent integration over the velocity:

$$\int \mathbf{v}^\alpha \left(\frac{\partial f}{\partial t} + \mathbf{v} \nabla_{\mathbf{r}} f + \mathbf{a} \nabla_{\mathbf{v}} f \right) d\mathbf{v} = \int \mathbf{v}^\alpha \left. \frac{\partial f}{\partial t} \right|_{\text{coll}} d\mathbf{v}. \quad (4.5)$$

Setting α to zero results in the following four expressions (three addends on the left side and one on the right side) to evaluate: The first one as integration over all velocities of the derivative in time of the distribution function results simply in the change of the particle density $n(\mathbf{r})$ with time:

$$\int \frac{\partial f(\mathbf{r}, \mathbf{v}, t)}{\partial t} d\mathbf{v} = \frac{\partial}{\partial t} n(\mathbf{r}). \quad (4.6)$$

The second one can be rewritten, knowing that $\mathbf{v}$ and $\mathbf{r}$ are independent:

$$\int \mathbf{v} \nabla_{\mathbf{r}} f(\mathbf{r}, \mathbf{v}, t) d\mathbf{v} = \int \nabla_{\mathbf{r}} (f(\mathbf{r}, \mathbf{v}, t) \mathbf{v}) d\mathbf{v} = \nabla_{\mathbf{r}} \int \mathbf{v} f(\mathbf{r}, \mathbf{v}, t) d\mathbf{v}. \quad (4.7)$$

With the definition of the mean value of a quantity, here $\mathbf{v}$, $\langle \mathbf{v}(\mathbf{r}) \rangle = \frac{\int \mathbf{v} f d\mathbf{v}}{\int f d\mathbf{v}} = \frac{\int \mathbf{v} f d\mathbf{v}}{n(\mathbf{r})}$, (4.7) becomes:

$$\nabla_{\mathbf{r}} \int \mathbf{v} f(\mathbf{r}, \mathbf{v}, t) d\mathbf{v} = \nabla_{\mathbf{r}} (n(\mathbf{r}) \langle \mathbf{v}(\mathbf{r}) \rangle) = \nabla_{\mathbf{r}} \mathbf{j}(\mathbf{r}). \quad (4.8)$$

Here, $\mathbf{j}(\mathbf{r})$ is the particle current density. The third term under an applied field $\mathbf{F}$ is proportional to

$$\int_{-\infty}^{\infty} \mathbf{F} \nabla_{\mathbf{v}} f d\mathbf{v}. \quad (4.9)$$

This integral is zero, because f is evaluated at infinity, where it has to be zero. The collision integral on the right-hand side of (4.5) is also zero because it consists of an integration over all scattering-in and scattering-out events for each velocity. As a scattering-in at a certain velocity means a scattering-out at another velocity, an integration over all velocities gives a zero net-scattering term. Thus, the first two expressions of (4.5) remain and result in the following equation:

$$\frac{\partial}{\partial t} n(\mathbf{r}) + \nabla_{\mathbf{r}} \mathbf{j}(\mathbf{r}) = 0, \quad (4.10)$$

which is known as the continuity equation.

An evaluation of the first-order momentum [$\alpha = 1$ in (4.5)] results after a longer derivation [19] in the drift-diffusion equation:

$$n\mu\mathbf{F} - D\nabla_{\mathbf{r}} n = \mathbf{J} \quad (4.11)$$

with the diffusion constant D and the charge carrier mobility $\mu = e\tau/m$, where τ is the scattering time (average time between scattering events) and m the mass of the particle. In a semiconductor m is given by the effective mass (2.11).

We briefly summarize the conditions used in the presented derivation in order to estimate whether these equations are applicable to organic semiconductors:

- Low particle densities and no mutual interactions;
- Collisions which are described by scattering at the lattice with an average time of a scattering event smaller than the time between scattering events;
- A small $d\mathbf{r}$ on a macroscopic scale which is, however, large on a microscopic scale. Latter is required to guarantee that $d\mathbf{r}$ contains a sufficient number of particles;
- The existence of $f(\mathbf{r}, \mathbf{v}, t)d\mathbf{r}d\mathbf{v}$ completely describing the macroscopic situation of the system.

When we consider electrons located on single molecules and hopping from site to site, the jump time is expected to be much smaller than the time the charge is localized on the molecule. Additionally, very thin layers consisting only of some 10s of molecules complicate a definition of $f(\mathbf{r}, \mathbf{v}, t)$. This makes the applicability of such a continuum approach and the definition of the mobility via lattice scattering questionable.

However, electrons and holes are located on molecules and consist a charge carrier density n and p , when averaged over many molecules. The device dimensions are much larger than the hopping distance, and the lifetime of charge carriers is in a range that allows them to perform several hops before recombining. Thus, charge transport occurs via a multistep hopping process of charge carriers. This current can

be described by the laws of drift and diffusion despite the localization of charges. Especially in steady-state, it is assumed that these densities averaged over several hopping sites can be described by a DOS and Fermi-Dirac statistics (or the Boltzmann approximation) as discussed in Sect. 2.2.1.

As consequence, one has to be aware of the fact that the drift-diffusion approach is a rather macroscopic model for organic semiconductors. This implies that the parameters (μ and D) in (4.11) have to be handled as effective parameters, which cannot be rigorously connected to physical processes known from conventional semiconductor physics. Either they have to be found from experiment, or they can be related to novel theories describing the microscopic processes within organic semiconductors (cf. Bäessler model [1]). Despite this peculiarity, it is shown in the following parts of this book that drift-diffusion simulations are very powerful means of describing the current-voltage characteristics of organic solar cells.

4.2.2 The Einstein Relation

The diffusion coefficient D can be related to the charge carrier mobility μ . This correlation is called the Einstein(-Smoluchowski) relation. It can be derived applying an intuitive approach as sketched in the following: Considering a semiconductor layer in equilibrium, drift and diffusion forces must cancel each other. Thus, an electric field, if present, leads to a redistribution of charges. Similarly, a diffusion gradient causes an initial diffusion current, which stops after a compensating field has been built up. This was discussed for the p-n junction and the MIM device in the previous chapters. Equilibrium implies the following condition for each space coordinate (here shown for x) according to (4.11):

$$n\mu F = D \frac{\partial n}{\partial x}. \quad (4.12)$$

Using (2.28) for the electrochemical potential η , one obtains the generalized Einstein relation:

$$\frac{D}{\mu} = \frac{nF}{\frac{\partial n}{\partial x}} = \frac{nF}{\frac{\partial n}{\partial \eta} \frac{\partial \eta}{\partial x}} = \frac{n}{e \frac{\partial n}{\partial \eta}}. \quad (4.13)$$

We were able to eliminate the electric field by the explicit x -dependence of the electric potential $d\phi = eFdx$, which is included in η (2.39). In other words, the motion of an electron by dx causes a change in the electrochemical potential (quasi-Fermi level) which is proportional to $eFdx$. Assuming Boltzmann statistics, (4.13) can be further simplified because $n \propto e^{\eta/k_B T}$:

$$\frac{D}{\mu} = \frac{k_B T}{e}. \quad (4.14)$$

This equation is known as the classical Einstein relation, which is commonly used in semiconductor device simulations.

If the Boltzmann approximation is not valid, the generalized form has to be applied (4.13). That equation is fulfilled independent of statistics and shape of the DOS in quasi-equilibrium. Otherwise, zero current in equilibrium is not guaranteed and self-consistency of the model is lost. Several studies exist on the applicability of the Einstein relation in disordered semiconductors [20–25]. Roichman and Tessler [20] computed D/μ as a function of charge carrier density which is equivalent to a certain distance of the electrochemical potential to the charge-transport level. They assumed a quasi-equilibrium situation (chemical potential defined and Fermi-Dirac statistics applicable) for charge carriers within a Gaussian density of states (DOS). For this case they found that the classical Einstein relation is valid for a realistic width of the DOS (< 100 meV) and for charge carrier densities four orders of magnitude lower than the total density of states. This situation corresponds to a chemical potential with a difference of 0.5 eV ($T = 300$ K) measured to the center of the Gaussian DOS. The mentioned conditions are commonly fulfilled in organic solar cells as we will see in Part II of this book. On the other hand, Harada et al. [21] proposed the non-validity of the classical Einstein relation as reason for the temperature dependence of the diode ideality factor in organic p-n junctions. However, the injection current of a diode is sensitive to recombination mechanisms and the presence of traps, making the identification of the diffusion component of free charge carriers difficult. Correcting for the influences of traps, Wetzelaer et al. [25] conclude that the classical Einstein relation is sufficient to describe charge transport in organic solar cells.

Neumann et al. [23] have shown theoretically that the classical Einstein relation is valid even for the whole range of charge carrier densities that is experimentally relevant. Their main assumption was a mobility edge [26] located at the center of the Gaussian DOS. Mobility edge means that charge carriers in the DOS below this energy are trapped and do not contribute to charge transport at all. Consequently, the mobility is defined as an average value of the mobility of charges above the mobility edge. Such a definition naturally decreases the effect of a broad DOS. Li et al. [24] proposed a more realistic assumption for the mobility edge, declaring charge carriers between the Fermi level and a so-called transport energy as free charge carriers. Their result is that the generalized Einstein relation has to be considered for charge carrier densities as present in field-effect transistors or highly doped layers. In summary, the debate reflects the general discussion about the disputable definition of the charge carrier mobility in disordered organic semiconductors.

In a drift-diffusion simulation either the classical or the generalized Einstein relation can be applied, dependent on the statistics (Boltzmann approximation or Fermi-Dirac) and density of states that are assumed.

4.2.3 Poisson's Equation

We have already noticed when discussing the p-n junction that space-charge effects are very important. This observation holds in particular for low-mobility semiconductors, where apart from localized ionized dopants also the “free” charge carriers can pile up and create a space charge ρ . Such a space charge causes a spatial change (i.e. gradient ∇) in the electric field $\mathbf{F}$ according to Maxwell's first equation (Gauss's law):

$$\nabla \mathbf{F} = \frac{\rho}{\epsilon_0 \epsilon_r}. \quad (4.15)$$

The electric field in turn modifies the electric potential, which can be directly related to space charge by Poisson's equation of electrostatics:

$$\Delta \phi = \nabla^2 \phi = -\frac{\rho}{\epsilon_0 \epsilon_r}. \quad (4.16)$$

4.2.4 Differential Equation System

The following system of (coupled) differential equations has to be solved for a one-dimensional drift-diffusion simulation including space-charge effects:

$$\frac{\partial n}{\partial t} = G - R - \frac{1}{-e} \frac{\partial J_n}{\partial x} \quad (4.17)$$

$$\frac{\partial p}{\partial t} = G - R - \frac{1}{e} \frac{\partial J_p}{\partial x} \quad (4.18)$$

$$J_n = en\mu_n F - (-e)D_n \frac{\partial n}{\partial x} \quad (4.19)$$

$$J_p = ep\mu_p F - eD_p \frac{\partial p}{\partial x} \quad (4.20)$$

$$\frac{\partial^2 \phi}{\partial x^2} = -\frac{e}{\epsilon_0 \epsilon_r} (p - n + N_D^+ - N_A^- + \dots) \quad (4.21)$$

$$\frac{\partial s}{\partial t} = G_{\text{opt}} - \frac{s}{\tau} - R_{\text{Sep, Quench}} + \frac{L_D^2}{\tau} \frac{\partial^2 s}{\partial x^2}. \quad (4.22)$$

Here, x denotes the variable of space, which is perpendicular to the surface of the sample. This one-dimensional treatment is justified as the lateral device dimensions are about 10^5 times larger than the device thickness.

Equations (4.17) and (4.18) are the continuity equations for electrons (n) and holes (p), including generation (G) and recombination terms (R). Both equations can be interconnected, e.g., by a direct recombination term. The current densities J_n (4.19) and J_p (4.20) are expressed by drift and diffusion currents with the charge

carrier mobility μ , electric field F and the diffusion constant D . D is replaced using the Einstein relation (4.14) which yields $D = \mu k_B T / e$ in the case of Boltzmann statistics. Equation (4.21) is Poisson's equation (4.16), where the space charge is given by the free charge carrier densities and localized ionized dopant densities N_D^+ and N_A^- . Other sources of charges such as trapped charge carriers can be added as well.

The last equation (4.22) is the continuity equation for excitons s . This equation is decoupled from the others, as long as exciton-electron interactions are neglected. However, such interactions like exciton quenching at free charge carriers are possible. In this case, the rate equations for charge carriers and excitons are coupled, which requires a simultaneous solution of (4.22) with the overall equation system. We do not further consider such interactions because they are supposed to be negligible for charge and exciton concentrations resulting from illumination intensities smaller than a few suns.

According to (4.22), changes in exciton density occur via an optical generation term G_{opt} , via a relaxation of the excited state with lifetime τ , and via exciton separation or quenching terms R . Furthermore, a gradient in the diffusion current changes s , where the (one dimensional) exciton diffusion length $L_D = \sqrt{D\tau}$ is introduced. The separation (quenching) rate can be assumed to be zero for all x apart from exciton splitting (quenching) interfaces like a donor-acceptor (D-A) interface. The generation term is obtained by optical simulations according to a transfer matrix algorithm, including interference effects. Here, calculating the gradient in the Poynting vector from the simulated optical field distribution within the solar-cell stack yields directly the absorption profile. This profile is identical to the exciton generation profile under the assumption that each absorbed photon (in a given spectral range) creates one exciton. The transfer matrix algorithm [27, 28] is described in detail in Sect. 4.7. The idea of this thin-film model is to treat the layers coherently and describe the properties of interfaces and of the bulk layers by matrices for forward and backward running waves. A multiplication of all matrices gives the overall reflection, transmission, and absorption. These matrices contain the complex refractive indices of the materials. Therefore, this method requires apart from layer thicknesses the optical constants (complex refractive index $n + i\kappa$) of each material/layer as input. The simulation gives reasonable results as long as layer thicknesses are not too small ($n\kappa$ might differ for very thin (few nm) layers), the device stack is not too thick (coherence), and interfaces are smooth (scattering negligible). Although these assumptions are not valid for every employed organic material (combination), they are mostly given for organic thin-film solar cells [29, 30].

Considering the one-dimensional continuity equation for excitons (4.22) makes only sense in the case of a flat heterojunction device, where R_{sep} at the D-A interface enters the charge carrier generation term G in (4.17) and (4.18). In case of a homogeneously intermixed blend, exciton diffusion is not considered and G is set to cG_{opt} , where c accounts for a mean exciton loss within the domains. Reported values of IQEs close to unity [31] indicate that c is close to unity as well in weakly phase-separated blends. Considering charge transport, the blend itself is treated as

one effective medium. This means that the two-component material system is seen as a new material which is described by new parameters.

4.3 Implementation of a Drift-Diffusion Algorithm

Equations 4.17–4.22 constitute a system of coupled quasilinear partial differential equations, where (4.21) is of elliptic type and (4.17) with (4.19) (4.18 with 4.20) is of parabolic type. They can only be solved numerically. The main challenge are non-linearities introduced by the expressions for recombination and mobility, which are in general non-linear functions in n , p , and F . This problem has been treated for decades and solved in various ways. Yet, this section outlines how to construct a simple drift-diffusion solver. Note that the presented approach is rather intuitive and of didactic quality. It is far from an optimized algorithm. Nevertheless, the results presented in this book are obtained employing such a self-made solver. The author preferred this approach to the application of available solvers due to several reasons: Apart from technical advantages, allowing customized parameter variations and automations more easily than commonly available free semiconductor simulation tools, the knowledge and control over the physics is rated very important. Until now, validated solvers containing a comprehensive implementation of the peculiarities of organic materials do not exist. Additionally, many processes are still under discussion. Thus, the development of a simple self-made solver allows for detailed insights into the physics and for flexibility regarding the implemented models.

4.3.1 Basics of the Algorithm and Discretization

Although we are mainly interested in the steady-state solution of the differential equation system represented by (4.17)–(4.22), a transient algorithm is presented. On the one hand, it additionally enables a simulation of photocurrent transients (see Sect. 4.3.5) and on the other hand, it allows for a simple description of processes via time-dependent rate equations. The basic solution procedure is oriented at the work by Staudigel et al. [10], who presented a numerical model for the simulation of organic light-emitting diodes. Although the model presented here includes several improvements and additional processes, the algorithm of finding the steady-state solution is the same. It is sketched in Fig. 4.4 giving an overview on how to reach the solutions for the variables of state n , p , and F . Starting from initial values, these variables are modified within an iterative loop, which contains the calculation of the electric field according to Poisson's equation, the calculation of rates of change, the determination of a maximum time step, and subsequently the calculation of the new charge carrier concentrations:

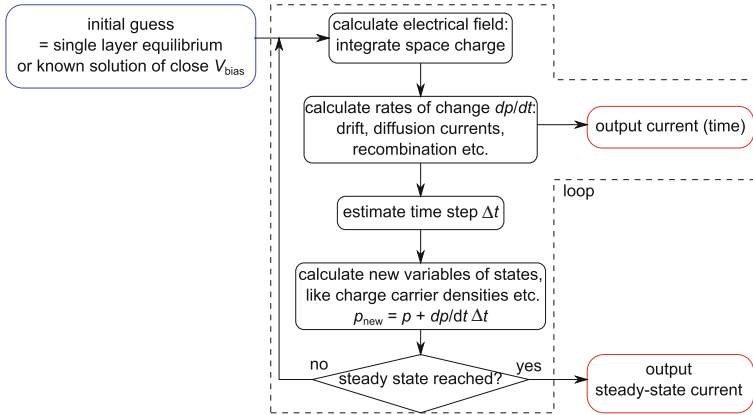
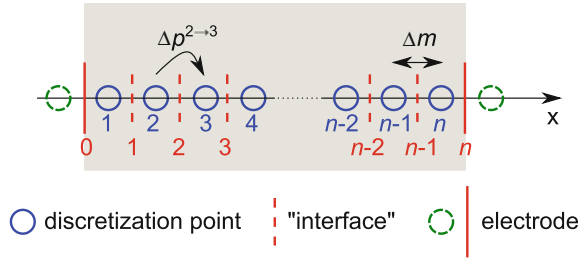


Fig. 4.4 Flowchart of the iterative algorithm for solving the drift-diffusion problem. The loop terminates as soon as steady state is reached. An output of the current during the iteration loop allows for a description of transient currents

Fig. 4.5 Sketch of the discretization scheme with the distance Δm between adjacent points of a one-dimensional mesh



$$F(x_i) \propto \int (-n + p + \dots) dx; \quad n(x_i)^{t+\Delta t} = n(x_i)^t + \frac{\partial n}{\partial t}(n, p, F, \dots) \Delta t \quad (4.23)$$

As these calculations cannot be done analytically, they are performed numerically at discrete values of x . We choose an adjustable, however constant discretization interval Δm , which can be set to an arbitrary value before the iterative algorithm starts (Fig. 4.5). It is then fixed over the whole x -range and kept constant during the whole calculation. Although Staudigel et al. identified this interval with the spacing of molecules and set it to 1 nm, here, a reliable solution is characterized by its independence of the discretization interval. This requirement seems more appropriate than using a fixed spacing in combination with a continuum approach. Furthermore, charges localized on a molecule occupy molecular orbitals with extensions even larger than the hopping distance. Figure 4.5 clarifies the numbering of grid points and the “interfaces” in between.

Mathematically spoken, the subsequently elaborated solution procedure is a finite difference method with discretization in space and time. The solution is found by an explicit Euler solver, which is a non-optimized, however very intuitive and stable method. Its single steps within each iteration are content of the next sections.

4.3.2 Calculation of the Electric Field

The electric field is obtained employing Poisson's equation (4.16). Discretization results in the following equation for the electric field F_{if}^i between two grid points i and $i + 1$:

$$F_{if}^i = \frac{\Delta m}{2\epsilon_0} \left(\sum_{j=1}^i \frac{\rho^j}{\epsilon_r^j} - \sum_{j=i+1}^N \frac{\rho^j}{\epsilon_r^j} \right) + \frac{\rho^{\text{anode}}}{\epsilon_0 \epsilon_r^i}. \quad (4.24)$$

Here, ϵ_r is the dielectric constant and ρ^i the local space charge, consisting of the sum of all charged species at position i :

$$\rho^i = p^i - n^i + N_D^{+i} - N_A^{-i} + p_t^i - n_t^i + \dots \quad (4.25)$$

The electric field F^i at a grid point i is in the simplest case calculated by a linear interpolation:

$$F^i = \frac{F_{if}^{i-1} + F_{if}^i}{2}. \quad (4.26)$$

An integration, which means a summation in discretized space, over the electric field results in the potential difference between anode and cathode. This potential difference is defined by the superposition of the applied bias V and the built-in voltage V_{bi} originating from metal electrodes with different work functions. Thus, the following equation has to be fulfilled:

$$\sum_{i=1}^N F^i \Delta m = V - V_{bi}. \quad (4.27)$$

This boundary condition determines the anode surface charge ρ^{anode} in (4.24). The anode is selected arbitrarily and ρ^{anode} is identical to a negative cathode charge.

4.3.3 Calculation of Rates of Change

To update charge carrier densities, their rates of change $\partial/\partial t \approx \Delta/\Delta t$ have to be calculated. The respective procedure is exemplary shown for holes. The transition rate for the hole density $\Delta p^{i \rightarrow i+1}/\Delta t$ from position i to position $i + 1$ is proportional to the charge carrier density itself and to the velocity divided by the distance the charge carrier travels. In other words, the amount of holes $\Delta p^{i \rightarrow i+1}$ traveling from position i to $i + 1$ within the time Δt is given by their velocity v multiplied by Δt and divided by the distance between i and $i + 1$:

$$\frac{\Delta p^{i \rightarrow i+1}}{\Delta t} \approx \frac{\partial p^{i \rightarrow i+1}}{\partial t} = \frac{v^i}{\Delta m} p^i. \quad (4.28)$$

Inserting the drift velocity for v gives:

$$\frac{\partial p_{\text{drift}}^{i \rightarrow i+1}}{\partial t} = \begin{cases} \frac{\mu_p^i F^i}{\Delta m} p^i, & F^i > 0 \\ 0, & F^i \leq 0 \end{cases} \quad (4.29)$$

The case differentiation ensures a drift current of holes only in the direction of the electric field.

Using the diffusion velocity

$$v_{\text{diff}} = \frac{D_p^i}{\Delta m} = \frac{\mu_p^i k_B T}{e \Delta m} \quad (4.30)$$

including the classical Einstein relation (4.14), yields an equation for the hole transition rate due to diffusion:

$$\frac{\partial p_{\text{diff}}^{i \rightarrow i+1}}{\partial t} = \frac{\mu_p^i k_B T}{e(\Delta m)^2} p_i. \quad (4.31)$$

When necessary, the generalized Einstein relation is used, which means a modification of v_{diff} according to (4.13). Due to the undirected nature of diffusion, it holds:

$$\frac{\partial p_{\text{diff}}^{i \rightarrow i+1}}{\partial t} = \frac{\partial p_{\text{diff}}^{i \rightarrow i-1}}{\partial t}. \quad (4.32)$$

The question arises whether a field-dependent mobility, as found, e.g. by Bäessler (3.20), implies any conceptual changes of the equations mentioned. Intuitively, the rates of change of charge carrier densities in the direction of the electric field should be increased by the field-dependent term describing a field-assisted hopping. A modification of the drift current (4.29) can easily be done replacing μ_p by $\mu_p(F)$, as drift occurs only in the direction of the field. However, the diffusion current described in (4.31) occurs in both directions, parallel and anti-parallel to the electric field. Due to the Einstein relation, it contains the mobility as well. Staudigel et al. [10] decided to use $\mu(F)$ for diffusion in the direction of the electric field and $\mu(F = 0)$ against the field. In the implementation here, it is preferred to use $\mu(F)$ for both diffusion directions. Using the field dependence only in one direction would result in a quasi-Fermi level splitting and hence a net driving force at zero applied bias in a device with a built-in field. This means that the Einstein relation is violated and the resulting current at zero applied bias is an unphysical situation.

The approach presented in (4.26) is based on a linear interpolation of the electric field between two “interface” grid points to calculate the electric field used in (4.29). Scharfetter and Gummel [32, 33] proposed a local solution of the drift-diffusion problem under the assumption of a constant electric field between mesh points:

$$\frac{\partial p_{\text{drift+diff}}^{i \rightarrow i+1}}{\partial t} = \frac{1}{\Delta m} \cdot \frac{F_{\text{if}}^i \mu_p}{1 - \exp(-e F_{\text{if}}^i \Delta m / k_B T)} p_i. \quad (4.33)$$

This expression allows the selection of a larger discretization distance Δm compared to the linear approximation and still yields converging results. Note that the values for field and mobility are chosen at the interface instead of taking an averaged value of the field at the discretization point according to (4.26).

The continuity equation (4.18) states that Δp^i can be additionally changed by trapping, recombination or generation. Thus, the overall change of p at position i is:

$$\begin{aligned} \Delta p^i = & -\Delta p_{\text{drift}}^{i \rightarrow i+1} - \Delta p_{\text{drift}}^{i \rightarrow i-1} - \Delta p_{\text{diff}}^{i \rightarrow i+1} - \Delta p_{\text{diff}}^{i \rightarrow i-1} \\ & + \Delta p_{\text{drift}}^{i-1 \rightarrow i} + \Delta p_{\text{drift}}^{i+1 \rightarrow i} + \Delta p_{\text{diff}}^{i-1 \rightarrow i} + \Delta p_{\text{diff}}^{i+1 \rightarrow i} \\ & - \Delta p_{\text{rec}}^i + \Delta p_{\text{gen}}^i - \Delta p_{\text{trap}}^i + \Delta p_{\text{detrap}}^i. \end{aligned} \quad (4.34)$$

Here, the additional rates depend on the used models and are described in the next sections. Electrons follow an analogous expression. The overall electrical (particle) current density J can be simply calculated by

$$J^i = J_n^i + J_p^i = e \cdot \left(\frac{\partial p^{i \rightarrow i+1}}{\partial t^i} - \frac{\partial p^{i+1 \rightarrow i}}{\partial t^i} - \frac{\partial n^{i \rightarrow i+1}}{\partial t^i} + \frac{\partial n^{i+1 \rightarrow i}}{\partial t^i} \right) \Delta m. \quad (4.35)$$

Considering discretization, the continuity equation of excitons (4.22) is similarly treated as the one of the charge carriers. The same expression as (4.31) is found for the diffusion, where the exciton diffusion constant D_s is replaced by the one dimensional exciton diffusion length L_D and the exciton lifetime τ :

$$\frac{\partial s_{\text{diff}}^{i \rightarrow i+1}}{\partial t} = \frac{v_s}{\Delta m} s^i = \frac{D_s}{(\Delta m)^2} s^i = \frac{L_D^2}{\tau \cdot (\Delta m)^2} s^i. \quad (4.36)$$

A drain for excitons is the relaxation simply described by a rate constant which is the inverse of τ . Exciton interactions like annihilation and quenching at impurities or free charge carriers can be added if interaction rates and reaction cross sections are available. The overall change of exciton densities including optical generation $\Delta s_{\text{gen\_opt}}^i$ reads:

$$\Delta s^i = -\Delta s_{\text{diff}}^{i \rightarrow i+1} - \Delta s_{\text{diff}}^{i \rightarrow i-1} + \Delta s_{\text{diff}}^{i-1 \rightarrow i} + \Delta s_{\text{diff}}^{i+1 \rightarrow i} - \frac{1}{\tau} s_i + \Delta s_{\text{gen\_opt}}^i - \Delta s_{\text{quench}}^i. \quad (4.37)$$

4.3.4 Calculation of the Time Step

To calculate the subsequent values of the variables of state in (4.23), the time step Δt has to be known. It is chosen according to the Courant-Friedrichs-Lewy condition (CFL condition) $\frac{v\Delta t}{\Delta x} \leq C$ to guarantee a stable iteration. The term $v/\Delta x$ with velocity v is a rate of change and C is a constant which in general depends on the differential equations and is chosen to unity here. An optimization of the time step is important, because too large time steps lead to instabilities and too small time steps increase the number of iteration steps and thus computing time. Hence, Δt is continuously adjusted by a recalculation within each pass of the iterative loop by choosing the inverse of the maximum relative rate of change. This conservative criterion can be written as:

$$\Delta t = \min_i \left(\frac{1}{\sum \frac{\partial p_{\text{drift,diff}}^i}{\partial t} / p^i}, \frac{1}{\frac{\partial p_{\text{rec}}^i}{\partial t} / p^i}, \frac{1}{\frac{\partial p_{\text{gen}}^i}{\partial t} / p^i}, \frac{1}{\frac{\partial p_{(\text{de})\text{trap}}^i}{\partial t} / p^i}, \dots \right). \quad (4.38)$$

Here, Δt is given by the minimum over all positions i . Equation (4.38) displays only the rates of change for the hole density (p). Naturally, the rates of change for all variables of state have to be considered to select Δt . They additionally include electrons, traps, and excitons.

Once having fixed Δt , the new values of the variables of state can be calculated by

$$p^{i,t_{j+1}} = p^{i,t_j} + \frac{\partial p^{i,t_j}}{\partial t} \Delta t^j, \quad (4.39)$$

where analog equations hold for n and s . The resulting densities $p^{i,t_{j+1}}$, $n^{i,t_{j+1}}$, and $s^{i,t_{j+1}}$ are the starting values of the subsequent iteration step, beginning again with the calculation of the electric field.

4.3.5 Detection of Steady State and Transient Currents

The iteration loop is supposed to terminate as soon as steady state has been reached. Steady state can be detected applying several criteria:

1. All relative rates of change of the variables of state are below a certain threshold value C_{max} : $\max_i \left(\frac{\partial n, p, s^i}{\partial t} \frac{1}{n, p, s^i} \right) < C_{\text{max}}$.
2. The charge-carrier current J as sum of hole and electron current is spatially constant: $1 - C < \left| \frac{J_i}{J_{i0}} \right| < 1 + C$, $\forall i$ and with an arbitrary reference current J_{i0} , $i_0 \in (0, n)$ and a relative threshold C .
3. The displacement current vanishes. This is identical to condition 2.

Criterion 2 turns out to be optimum for the charge carriers in combination with criterion 1 for the excitons.

Displaying the current over time is possible by using a time variable t and storing time/current pairs during the iteration. An introduction of perturbations in the generation rate (representing, e.g., light pulses) allows for a simulation of a transient photocurrent experiment. Changing V_{bias} sinusoidally and monitoring the current gives a value for the impedance of the device dependent on frequency. Such transient situations imply that steady state is not reached. Consequently, the particle current within the device is not constant and the electric field shows a variation with time. This variation $\partial F/\partial t$ causes a displacement current which has to be added to the electrical particle current to obtain the total current J_{total} measurable from outside:

$$J_{\text{total}} = J_n^i + J_p^i + J_{\text{displ}}^i = J_n^i + J_p^i + \epsilon_0 \epsilon_r \frac{\partial F^i}{\partial t} \approx J_n^i + J_p^i + \epsilon_0 \epsilon_r \frac{F^{i,t_{j+1}} - F^{i,t_j}}{\Delta t}. \quad (4.40)$$

According to Maxwell's fourth equation the overall current at an arbitrary time has to be constant within the device. The integral formulation of this Maxwell equation is Ampère's circuital law:

$$\oint_c H dS = \iint_S J_{\text{total}} dA \quad (4.41)$$

with the magnetic field H . It says that the path integral of H over a closed curve is equal to the overall current flowing through an area A enclosed by S . Imagining S being a fixed circle around the device and in plane with the device, the position x , where A crosses the device can be arbitrarily chosen (Fig. 4.6). As current is only flowing through the part of A , where A is crossing the device ($A_1^{\text{active}} = A_2^{\text{active}}$ which are $\gg \Delta x^2$), it holds for the homogeneous current density $J_1 = J_2 = J$.

Delivering current transients is the main advantage of a transient solver, extending its capability for simulating also time-dependent experiments. Another advantage of the chosen implementation is its vicinity to real physical processes. That is why the common scaling [34] of the equations is abandoned. The main drawback of a transient solver is a long computation time if processes of different timescales are involved. The maximum time step according to (4.38) is limited by the fastest process. However, steady state is reached after the slowest process has converged. This combination requires many iterations. An improvement could be achieved by separately updating selected processes dependent on their timescale [35]. This method allows for a separate treatment of fast processes. Computation time is saved by selectively updating the variables of state at positions where fast changes occur. Slower processes are updated less frequently. Combining fast and slow processes is a sophisticated task because an elaborate synchronization is required. As the focus of the following discussions is on physics, simply (4.38) is applied to calculate an overall time step. The exciton continuity equation can be solved separately, before handling the free charge carriers. As long as interactions between charge carriers and excitons are not

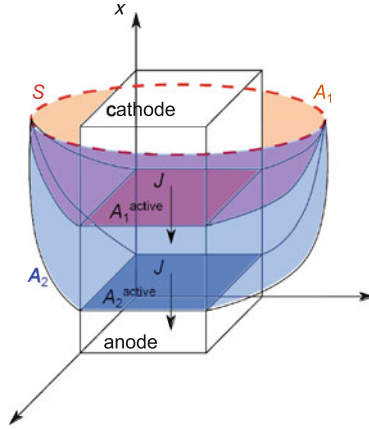


Fig. 4.6 Visualization of the application of Ampère’s circuital law to a device which is inhomogeneous only in x -direction. A_1 and A_2 are two arbitrary areas with the same active/effective area at different positions x in the device. Both areas have the same border curve S . This means that the current J including the displacement current is independent of x for all times

considered, (4.22) is independent of n and p and this approach does not result in any restrictions.

4.4 Models for the Individual Processes

In the previous chapters several mechanisms related to charge carrier transport and recombination have been mentioned. Here, we present equations to describe these processes in the framework of a device simulation. Note that the choice of models depends on the focus, depth, and complexity of the problem under investigation.

4.4.1 Charge Carrier Mobility

The charge carrier mobility is the fundamental parameter describing the property of charge carriers to move, either by drift due to an electric field or by diffusion according to the (generalized) Einstein relation. The mobility can theoretically be derived for crystalline semiconductors “going back” to the effective mass and scattering time of a quasi-free particle in a periodic crystal (cf. Sect. 2.4). These assumptions are not fulfilled for amorphous organic semiconductors. However, using the mobility as phenomenological parameter is still very convenient, where the simple definition of μ is applied (2.34). The mobility is the proportionality factor relating the electric field to the average charge-carrier velocity. Experimentally found [36–39] and theoretically motivated (hopping transport, etc. [1, 40, 41]) non-linearities between electric field

and current lead to a modification of μ , which itself becomes dependent on the electric field. Most common is the Poole-Frenkel behavior (Sect. 3.2.3, [42]), which is implemented in a drift-diffusion simulation with γ as an additional parameter:

$$\mu(F) = \mu_0 \exp\left(\gamma\sqrt{|F|}\right). \quad (4.42)$$

Typical values for γ are found in the range of $10^{-2} \dots 10^{-4} (\text{cm/V})^{1/2}$ [36, 39].

The temperature dependence of the mobility of organic semiconductors can be described by the following simple equation assuming a thermal activation of the transport properties:

$$\mu(T) = \mu_\infty \exp\left(-\frac{\Theta}{k_B T}\right). \quad (4.43)$$

Here, μ_∞ denotes the mobility for $T \rightarrow \infty$ and Θ represents the activation energy.

In case of a field and temperature dependence, we apply the following equation which allowed to fit experimental data of single carrier devices reasonably well [43]. Note that slight modifications exist [44]:

$$\mu(T, F) = \mu_\infty \exp\left(\frac{-\Theta + \gamma\sqrt{|F|}}{k_B T}\right). \quad (4.44)$$

Alternatively, the temperature dependence is reported to follow

$$\mu(T) = \mu_\infty \exp\left(-\left(\frac{2\sigma}{3k_B T}\right)^2\right), \quad (4.45)$$

which contains the width σ of the Gaussian DOS as a parameter and is consistent with an exponential $1/T^2$ dependence expected from the Bässler model (3.20).

The simulation is easily capable of dealing with other mobility models. The more variables of state (F , p , n) are involved and the more complex the interrelation, the more computing time is required.

For example, the Gaussian disorder model with a parameterization as proposed by Pasveer et al. [45] is considered as well. It additionally includes a dependence of μ on the charge carrier density, which has been motivated in Sect. 3.2.3 by a filling of the DOS starting with the deep low-mobility states. This unified model for the field, temperature, and charge-carrier density dependence of μ can be described by solely three material parameters, namely the width σ of the DOS, the average hopping distance, and an intrinsic hopping rate. For the complicated analytical equations, the reader is referred to the original paper [45]. It is noted that these equations have been obtained by fitting selected analytical expressions to Monte-Carlo simulations. Thus, they are only valid in a certain parameter space with a certain error. By performing simulations of a single-carrier device at a constant temperature, it is found that a reasonable fit of J - V curves is achievable using either a field dependence according

to (4.42) or the charge carrier dependence of the Pasveer model. A temperature series is required to distinguish between both effects. In the simulations presented in Part II, mainly a constant mobility or (4.42) are applied, which are found sufficient as long as there is no clear experimental evidence for a more complex behavior of μ . In particular, the dependence of μ on the electric field is not critical for solar cells with moderate electric fields around their operation point. In contrast, a proper description of the current in a transistor channel requires a mobility that depends on the electric field and the charge carrier density.

4.4.2 Recombination

The dominating recombination mechanism in organic solar cells is currently under debate. It seems that there is no distinct mechanism, but several processes dependent on the specific organic material and the morphology in the case of a mixed film. The models under discussion are the following.

Direct/bimolecular Recombination and Langevin Theory

The simplest mechanism is direct or bimolecular recombination of a mobile electron with a hole. The recombination probability is expected to be proportional to both charge carrier densities (that is why it is called bimolecular). The recombination constant β is commonly described by Langevin theory (β_L), although usually deviations are observed in experiment [46–48].

$$R = \beta \cdot (np - n_i^2); \quad \beta_L = \frac{e \cdot (\mu_n + \mu_p)}{\epsilon_0 \epsilon_r}. \quad (4.46)$$

Here, n_i is the intrinsic charge carrier density. Langevin theory [49] describes recombination of electrons with holes in low-mobility materials. Then, β is proportional to the sum of the charge carrier mobilities and to the inverse permittivity representing the screening capability of the material. Thus, the factor limiting recombination is the diffusion of charge carriers to each other and not the actual recombination process itself.

We can make the Langevin expression plausible assuming a fixed positive charge (hole) and a mobile electron. As the accelerating effect of the field on electron and hole differs only by the sign and the mobility, this assumption means only a specific selection of our coordinate system and $\mu = \mu_n + \mu_p$ describing the relative motion of the electron for a fixed position of the positive charge (hole). We say that in the absence of a macroscopic electrical field recombination happens as soon as the electron has come closer to the hole than the so-called Coulomb radius r_c , which is the distance where the Coulomb binding energy equals the thermal energy:

$$E_{\text{Coulomb}} = \frac{e^2}{4\pi\epsilon_r\epsilon_0 r_c} \approx k_B T. \quad (4.47)$$

As soon as the electron has entered the sphere with radius r_c , i.e. the distance $\tilde{r}$ to the hole is smaller than r_c , electron and hole inevitably recombine. If we assume that the Coulomb potential ϕ_{Coulomb} of the hole gives rise to a drift velocity v of the electron towards the hole, we can write:

$$v = \mu F = \mu \frac{d\phi_{\text{Coulomb}}}{dr} = \mu \frac{dE_{\text{Coulomb}}}{edr} = \mu \frac{e}{4\pi\epsilon_r\epsilon_0 \tilde{r}^2}. \quad (4.48)$$

As we are using volume densities in (4.46), we have to integrate v over the spherical area $4\pi\tilde{r}^2$ to find the overall rate constant for recombination:

$$\tilde{v} = 4\pi r_c^2 v = \frac{e\mu}{\epsilon_r\epsilon_0} = \beta_L. \quad (4.49)$$

That is the Langevin constant for recombination.

The advantage of Langevin theory from the simulations' point of view is the reduction of material parameters, as β is expressed by mobilities and the dielectric constant. This is essential because the charge carrier collection efficiency (cf. Sect. 3.3.1) and hence the shape of the J - V curve are dominated by the interplay between charge carrier extraction and recombination. As a further straight-forward description of β is not available, Langevin theory is broadly applied in reported simulations [10, 13]. It might be problematic in a simulation, where recombination only occurs if charge carriers meet at a discretization element, whose lateral extensions are much smaller than the Coulomb radius. In case of a one-dimensional simulation, β_L can be seen as describing diffusion limited recombination in the slices with an area parallel to the device surface. This approach might require modifications in the derivation of β .

Several efforts are made to motivate experimentally observed deviations from Langevin theory: Koster et al. [50] came up with the idea of replacing the sum in (4.46) by the minimum of μ in bulk heterojunction layers, because recombination is only possible if both, electron and hole, being present in the different material phases, meet each other at an interface. Hence, the mobility of the slower charge carrier is dominating, because figuratively spoken the faster charge carrier has to wait for the slower one to reach a heterointerface. However, this picture might underestimate recombination in a strongly intermixed bulk heterojunction with a large interfacial area, where the movement of charges parallel to the interface might become significant. Others introduced a pre-factor β_0 ($\beta = \beta_0\beta_L$) which is also attributed to the nanomorphology of the blend [46] or simply motivated by a problematic data analysis of the charge extraction measurement data as pointed out in [51]. Especially, an averaging over the complete device thickness is an issue, because charge carrier densities might change dramatically on the way from cathode to anode. More sophisticated modeling approaches exist which consider the fluctuations of the potential landscape of HOMO and LUMO as reason for a separation of electrons and holes and hence reduced recombination rate [52, 53]. The simplest explanation for the deviations

from Langevin theory observed in experiment is that the prevailing recombination process cannot be described by direct (Langevin) recombination between free charge carriers. Reasons are that other recombination mechanisms like, e.g., multiple trapping [54] dominate. In the simulation tool used throughout this book, the standard Langevin theory, the modification by Koster, a freely selectable pre-factor, and an arbitrary mobility-independent value of β are implemented. The consequences upon the choice of the recombination model are evaluated in Sect. 5.2.

Indirect/Trap-Assisted Recombination

Recently, the importance of traps in organic semiconductor devices became a research topic and it was proposed that trap-assisted recombination as described in Sect. 2.2.2 plays an important role [55–58]. The following equation is derived from (2.25), assuming capture rates $C_{n/p}$ for electrons and holes:

$$R = C_n C_p N_t \frac{np - n_i^2}{C_n(n + n_1) + C_p(p + p_1)}. \quad (4.50)$$

Here, n_1 and p_1 contain the energetic position of the trap state, which is defined here as fraction u of the energy gap E_g :

$$p_1 = N_V \exp\left(\frac{-uE_g}{k_B T}\right); \quad n_1 = N_C \exp\left(\frac{-(1-u)E_g}{k_B T}\right); \quad u \in (0 \dots 1). \quad (4.51)$$

Assuming midgap traps and the same capture coefficients for electrons and holes, the four parameters in (4.50) reduce to one, which is the product of trap density N_T and C . This is sufficient for a qualitative comparison of trap-assisted and direct recombination (cf. discussion on the open-circuit voltage in Sect. 3.3.2). If demanded by experimental data, all parameters can be chosen independently. Then, e.g., different charge carrier lifetimes can be examined by using different capture cross sections.

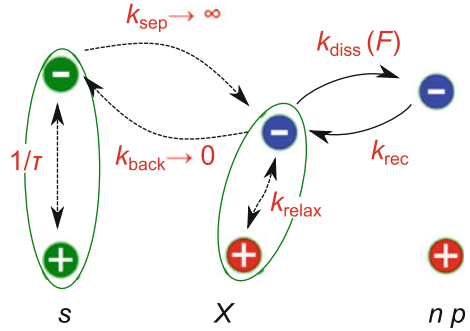
Geminate Recombination and Recombination via CT States

Geminate recombination, i.e. the recombination of an electron with a hole resulting from one photoexcitation, is discussed as a potentially important loss mechanism in organic solar cells (cf. Sect. 3.3.1). This process is equivalent to a relaxation of a charge transfer state (CT) at a donor-acceptor heterojunction. As depicted in Fig. 4.7 and discussed in Sect. 3.3.2, relaxation (k_{relax}) is in competition with dissociation k_{diss} , resulting in a free charge carrier generation probability of:

$$p = \frac{k_{\text{diss}}}{k_{\text{diss}} + k_{\text{relax}}}. \quad (4.52)$$

So far, predominantly the Onsager-Braun model is used to describe the field dependence and temperature dependence of the dissociation rate of a CT state. Onsager [59] developed his theory for the recombination of ions under the boundary condition

Fig. 4.7 Sketch of interaction rates between excitons (s), CT states (X), and free charge carriers (n , p) at a donor-acceptor interface. Geminate recombination is described by k_{relax} . The dissociation of the CT states can depend on the electric field (F)



that recombination occurs as soon as the distance between both ions is zero. Braun [60] refined the model under the assumption of a finite lifetime of a CT state, which allows a dissociation before a complete recombination/relaxation. This reversible property of forming a CT state, which allows recombining charges to make several attempts to be released, is expressed by the dissociation probability in (4.52).

Although good agreement with experiment has been demonstrated in some studies [61], the theory is under lively debate and modifications are proposed [62]. Especially for bulk heterojunctions, the description of a field enhanced dissociation is very questionable because the donor-acceptor interface is randomly orientated and not perpendicular to the electric field, which points simply from anode to cathode in a one-dimensional simulation. Nevertheless, the Onsager-Braun model is useful to qualitatively show the influence of a geminate recombination process on the J - V characteristics. The equation for the dissociation rate reads:

$$k_{\text{diss}} = \frac{3\beta}{4\pi a^3} e^{-E_B/k_B T} \frac{J_1(2\sqrt{-2b})}{\sqrt{-2b}}, \quad (4.53)$$

with the bimolecular recombination constant β , the Bessel function of first order $J_1 = 1 + b + \frac{b^2}{3} + \frac{b^3}{18} + \frac{b^4}{180} + \dots$, $b = e^3 F / (8\pi\epsilon_0\epsilon_r k_B^2 T^2)$, and the Coulomb binding energy $E_B = \frac{e^2}{4\pi\epsilon_0\epsilon_r a}$ (a denotes the initial distance between positive and negative charge). The proportionality of k_{diss} to β directly results from the detailed balance condition $k_{\text{diss}} X_0 = \beta n_i^2$ with the equilibrium densities for CT-states X_0 and free charge carriers n_i , which are defined by the relaxation/recombination dynamics of the single species at a certain temperature (cf. Sect. 3.3.2).

The rate of free charge carrier generation within a bulk heterojunction G in (4.17) is modified by (4.52) and the recombination R by $1 - p$, as recombination is assumed to form CT states, which reduce the effective recombination rate due to a certain probability for a re-dissociation [13]:

$$G = G_0 p; \quad R = R_0 \cdot (1 - p). \quad (4.54)$$

Here, G_0 is the generation rate of CT states and R_0 the recombination rate according to (4.46).

Motivated by disorder the initial distance and hence p might follow a distribution $f(a, x)$ around the nominal distance a , giving an overall dissociation probability of

$$P(a, T, F) = \int_0^{\infty} p(x, T, F) \cdot f(a, x) dx, \quad (4.55)$$

where Mihailetschi et al. [61] applied the distribution $f(a, x) = \frac{4}{\sqrt{\pi}a^3} x^2 e^{-x^2/a^2}$.

The application of p means an effective treatment of the CT state, changing G and R in the continuity equation for charge carriers (4.17) in an effective medium blend according to (4.54). The CT state is not explicitly included in the simulation. In case of a planar heterojunction, where the donor-acceptor interface is located between two mesh points (see Sect. 4.6), a continuity equation for CT excitons X can be applied, with the rates visualized in Fig. 4.7:

$$\frac{dX}{dt} = R_{\text{sep}} - k_{\text{relax}} X - k_{\text{diss}} X + R. \quad (4.56)$$

This equation contains the separation of excitons $R_{\text{sep}} \propto k_{\text{sep}}$ and the recombination of free charge carriers $R \propto k_{\text{rec}}$ as a source of CT states. Relaxation R to the ground state and dissociation are drain terms. A gradient in the current does not have to be considered as CT states are supposed to be located at the interface and hence immobile in x -direction. Equation 4.56 can be evaluated simply by replacing dX/dt by $\Delta X/\Delta t$. The CT states are assumed to constitute a bipolar space charge located at the discretization point left and right to the donor-acceptor interface. The situation at the interface can be extended by further states like triplets on one material, being generated by energy transfer from the CT state. This process would result in an additional drain term in (4.56).

4.4.3 Traps

Apart from constituting a recombination mechanism, filled traps, which are immobile states within the energy gap of a semiconductor, could yield a considerable amount of space charge. Thus, a description of the occupation of traps is required, where basically two approaches exist.

In the first approach, the occupation statistics are obtained similar to the one within the conduction states by using a Fermi-distribution with the Fermi level calculated from the free charge carrier density: Multiplying this distribution with the density of trap states and integrating the product over energy yields the trapped charge carrier density. This approach is only applicable in an equilibrium situation where one

Fermi level is defined. In case of two quasi-Fermi levels for electrons and holes, the occupation of the electron (hole) traps might be described using E_F^n (E_F^p).

In non-equilibrium, the second approach can be selected. Here, the occupation is described by trapping and detrapping rates (visualized in Fig. 4.8) according to the following equations for a single trap state under the assumption of Boltzmann statistics. We state exemplary for holes:

$$\left. \frac{\partial p_t}{\partial t} \right|_{\text{trap}} = C_{\text{trap}} p \cdot (N_{\text{pt}} - p_t); \quad \left. \frac{\partial p_t}{\partial t} \right|_{\text{detrap}} = C_{\text{detrap}} p_t \cdot (N_V - p). \quad (4.57)$$

As soon as a free hole (density p) is trapped, it is counted to the density of trapped holes p_t . Therefore, trapping is proportional to the amount of present holes and free trap states (N_{pt} is trap density) with C_{trap} as proportional constant. The detrapping rate scales with the amount of trapped holes and free valence states. Assuming a thermal detrapping mechanism, expressing C_{trap} by a cross section σ_t and a free hole velocity v_p , and including the trap energy E_{pt} , (4.57) results in

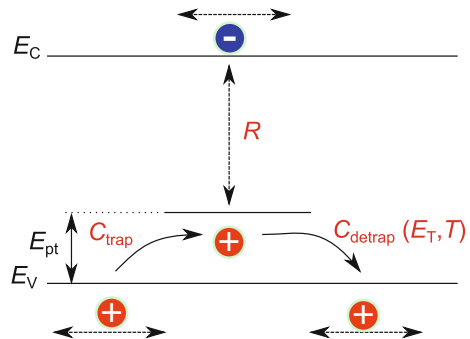
$$\frac{\partial p_t}{\partial t} = v_p \sigma_t \cdot \left(p \cdot (N_{\text{pt}} - p_t) - p_t \cdot (N_V - p) \cdot \exp\left(-\frac{E_{\text{pt}}}{k_B T}\right) \right). \quad (4.58)$$

In comparison to (4.57), C_{detrap} is related to C_{trap} by the steady-state condition, stating that trapping and detrapping rate have to be equal in equilibrium (detailed balance). A thermal activation for detrapping yields under the assumption of Boltzmann statistics with $1 - \exp\left(\frac{E_V + E_{\text{pt}} - E_F}{k_B T}\right) \approx 1$:

$$C_{\text{detrap}} = C_{\text{trap}} \exp\left(-\frac{E_{\text{pt}}}{k_B T}\right). \quad (4.59)$$

Staudigel et al. set v_p to the sum of drift and diffusion velocity $\mu \left(|F| + \frac{k_B T}{e \Delta m}\right)$, although usually the thermal velocity $\sqrt{3k_B T/m^*}$ [63] is used. Introducing a trapping constant $c_t = v_t \sigma_t$ as distinct parameter might be a pragmatic choice in the

Fig. 4.8 Sketch of trapping C_{trap} , detrapping C_{detrap} , and recombination R rates of a hole trap at energy E_{pt} . Detrapping is assumed to depend on the temperature T . A trapped hole can recombine with a free electron



case of hopping transport. A variation of this parameter allows already a traceable description of the competition between free charge carrier recombination, transport, and trapping. The described relation between trapping and release rates (4.59) guarantees an equilibrium trap occupation which is compatible with the one predicted by the first approach.

Within the approach of rate equations, we can easily add a further term, describing the recombination probability of a trapped charge (here hole) with a free charge carrier of opposite sign (here electron):

$$R_{pt,n} = \beta \cdot (p_t n - p_{t0} n_0) \stackrel{\text{Langevin}}{=} \frac{e\mu_n}{\epsilon_0 \epsilon_r} (p_t n - p_{t0} n_0). \quad (4.60)$$

The last expression results from the application of Langevin theory with $\mu_{pt} = 0$ and $R_{pt,n}$ adds as a drain term to the continuity equation for both n and p_t . By subtracting the product of equilibrium trap and charge carrier densities, detailed balance is guaranteed.

The described procedure, which we called second approach, can be easily implemented for a single trap state. Nonetheless, it can be extended by adding further trap energies or replacing the discrete energy level by a distribution. As the trapped charge carrier concentrations n_t and p_t are variables of state like n and p and their dynamics are described by the depicted rate equations, they have to be considered in the calculation of the time step as well.

To decrease computation time, the first approach of quasi equilibrium is implemented as well and can in particular be used in steady-state simulations of unipolar devices. Apart from a single-level trap-state, a Gaussian and an exponential distribution are implemented, where the first and latter allow for an analytical solution for p_t :

$$p_{t0} = \int t(E) f(E) dE = \begin{cases} \frac{N_t}{1 + \frac{N_V}{p} e^{-E_t/k_B T}}; E_F - (E_V + E_t) > 3k_B T & \text{discrete level} \\ N_t \left(\frac{N_V}{p} \right)^{-\frac{k_B T}{E_t}}; f(E) \approx 1 \forall E > E_F & \text{exponential} \\ N_t \int \frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{(E-E_t)^2}{2\sigma^2}} \frac{1}{e^{\frac{E-E_F}{k_B T}} + 1} dE; & \text{Gaussian} \end{cases} \quad (4.61)$$

4.4.4 Gaussian Density of States

The influence of disorder on charge transport is represented in the discussed expressions of the charge carrier mobility (Sect. 4.4.1), which depends on temperature, electric field, and charge carrier density [45]. In that approach, only the effect of the disorder on charge transport is represented while the energetics and statistics of

charge carrier densities are not considered. Therefore, an explicit representation of the Gaussian density of states (DOS) itself is desired in some cases. In a drift-diffusion simulation it can be implemented using a Gaussian density of states and Fermi-Dirac statistics to calculate the Fermi level from present charge carrier densities or vice versa. This approach is required when examining, e.g., the effect of a Gaussian DOS on the open-circuit voltage as discussed in Sect. 3.3.2. While this calculation cannot be done analytically, it requires a numerical integration at each mesh point and time step, which is very time-consuming. That is why tabulated data are used with an exponential (logarithmic) interpolation to find n from E_F (E_F from n). In this case of non-Boltzmann statistics, the diffusion constant is obtained from the generalized Einstein relation (4.13). As convention the parameters $\text{HOMO}/E_{\text{ht}}$ and $\text{LUMO}/E_{\text{et}}$ describe the maximum of the DOS with width σ .

Thus, the strategy of the simulation is to transfer the energetic disorder resulting from an energetic distribution of discrete hopping sites according to the Bässler model into a (narrow) Gaussian (DOS), present at each grid point. This derivation of the DOS is physically different to the one of Sect. 2.2.1 which resulted from the interaction of all atoms. In contrast, in the hopping model one position (site) corresponds to one discrete energy and the Gaussian DOS is given by the distribution of these sites. In the simulation, however, the Gaussian DOS is present at every position and charge carriers are assumed to fill up the DOS according to Fermi-Dirac statistics. The reason is simply that in the simulation charge carrier densities are discussed, which have to be seen as average values over several hopping sites. This description is reasonable due to the large lateral extensions of the device allowing a definition of the average charge carrier density in a plane with $x = \text{constant}$. Assuming quasi-equilibrium, a charge carrier density can be stated, which is statistically distributed in a Gaussian DOS.

It will be shown that in many situations the Gaussian shape of the DOS is not necessarily required to describe experimental data. In these cases, Boltzmann statistics and the approximation of an effective density of states at E_{ht} and E_{et} , which are supposed to be located close to the HOMO and LUMO onset, is used. E.g. $E_{\text{g}}^{\text{DA}*}$ can be set according to (3.27), which is valid for a large range of parameters as shown in Figs. 3.22–3.24.

4.5 Contacts as Boundary Conditions

A solar-cell device is sandwiched between metal(-like) electrodes, which provide the electrical contact to the outer circuitry. These contacts represent the starting and the end point of the spatial discretization grid of the simulation and require a special treatment to describe physical charge injection and extraction mechanisms and to guarantee a self-consistent model. In the mathematical nomenclature of differential equation systems, the contacts determine the so-called boundary conditions. Self consistent boundary conditions are very crucial, because the contacts as source of the built-in potential and the diffusion gradient significantly influence the current-voltage characteristics. A correct choice guarantees that the simulated current through the device in equilibrium (in the dark and at 0 V) is zero. The differential equation system

(4.17–4.21) demands for six boundary conditions. The first two are included within the potential drop (4.27) which is already applied in the calculation of the electric field. As only differences of the potential are physically defined, the potential at the anode is arbitrarily set to zero in the potential diagrams shown in the following parts of the book. Thus, the negative potential (in the electron picture) at the cathode is the applied bias voltage V_{bias} minus the built-in potential V_{bi} , given by the difference in work functions of the contacts:

$$V(0) = 0; \quad V(d) = V_{\text{bias}} - V_{\text{bi}}. \quad (4.62)$$

The four additional boundary conditions can be of Dirichlet or Neumann type, the first setting the charge carrier densities at the contacts and the second setting their derivatives.

A very basic and phenomenological physical equation for the description of the charge carrier (here electron) transfer to the electrode was given by (2.26):

$$J_{\text{sf}}^n = e s_n \cdot (n - n_0). \quad (4.63)$$

This equation represents a condition for a charge carrier extraction/injection current J_{sf}^n , characterized by a surface recombination velocity s_n and the equilibrium charge carrier density n_0 (here electrons). The latter guarantees self-consistency. An actual charge carrier density n exceeding n_0 results in charge carrier extraction and a lower n in charge carrier injection. Equation 4.63 implies that the metal-organic interface is not in equilibrium, which means that there is no common E_{F} between metal and semiconductor. Consequently two parameters s_n and n_0 are required. However, their experimental determination is difficult. For a normal metal contact, s_n is expected to be very large and the assumption of a current that is limited by s_n is only reasonable if there is experimental evidence of some thin insulating interlayer between metal and organics. Setting s_n to infinity leads to $n = n_0$, which characterizes a contact in equilibrium. Such a contact can be described by the commonly applied thermic injection as Dirichlet boundary condition, where n_0 is calculated by a simple Boltzmann factor with the injection barrier φ_{injec} defined as the difference between $E_{\text{ht}}/E_{\text{et}}$ and the negative metal work function $-\Phi_{\text{M}}$, which constitutes the Fermi level within the first monolayer of the semiconductor as well:

$$n_0(0/d) = N_{\text{C}} e^{-\frac{\varphi_{\text{injec}}^0(0/d)}{k_{\text{B}} T}} = N_{\text{C}} e^{-\frac{E_{\text{et}}(0/d) + \Phi_{\text{M}}(0/d)}{k_{\text{B}} T}}. \quad (4.64)$$

Whereas this expression assumes Boltzmann statistics and is only expected to be valid for $\varphi_{\text{injec}} > 3k_{\text{B}}T$, the charge carrier density is set according to the more general equation in the case of a Gaussian density of states:

$$\begin{aligned}
 n_0(0/d) &= \int \text{DOS}(E) \cdot f(E, E_F = -\Phi_M) dE \\
 &= \int \frac{N_C}{\sqrt{2\pi}\sigma} e^{\frac{(E-E_{\text{ct}})^2}{2\sigma^2}} \frac{1}{e^{\frac{E+\Phi_M}{k_B T}} + 1} dE.
 \end{aligned} \tag{4.65}$$

Analogous expressions hold for holes as well.

Assuming a positive image charge in the metal and a field (F) in the semiconductor, the superposition of the Coulomb potential and the external field (with a sign favoring injection) results in a lowering of the injection barrier similarly to the Poole-Frenkel effect discussed in Sect. 3.2.3. The only difference is a pre-factor of $1/2$, as the distance between electron (at position x) and image charge in the metal is $2x$ due to the nature of the image charge, being located at $-x$. For the Pool-Frenkel effect the distance between electron and localized positive core was simply x . Replacing x by $2x$ in the Coulomb potential expressed in Sect. 3.2.3, yields:

$$\Delta\varphi_{\text{injec}} = \sqrt{\frac{eF}{4\pi\epsilon_0\epsilon_r}} e. \tag{4.66}$$

This Richardson-Shockley [63] equation (4.64) with $\varphi_{\text{injec}} = \varphi_{\text{injec}}^0 - \Delta\varphi_{\text{injec}}$ describes thermionic emission under Boltzmann approximation and implies a lowering of the injection barrier. For realistic fields the maximum barrier occurs several nm away from the electrode due to a low ϵ_r (cf. Fig. 3.18). This distance makes the applicability of the thermionic injection model in organic devices very questionable due to two reasons: First, in case of low injection barriers, the field close to the contact is not constant in this region. However, this was presupposed for the derivation of (4.66). The reason is a large space charge. Second, the hopping distance is much smaller than the distance of the minimum barrier from the contact. Thus, the charge carrier cannot profit from the overall $\Delta\varphi_{\text{injec}}$ and consequently the barrier-lowering effect is overestimated. From the simulation point of view, issues arise as well: Barrier lowering can undermine self-consistency because it increases the charge carrier density of one species without changing the one of the other at a contact at the presence of a built-in field. This means that the equilibrium condition $np = n_i^2$ does not hold any more. In practice this is not crucial when simulating, e.g., realistic MIM devices, because the barrier lowering significantly affects charges in forward direction. Another problem is found in the fact that the boundary condition sets $n(0)$, although physically the injected charge is found at the position of the maximum of the superimposed potentials. This means rigorous self-consistency is lost, because the equilibrium between charge carrier density at the electrode and the potential difference is disturbed. Not taking this into account can lead to non-physical expressions, e.g., in analytical models for V_{oc} . A solution could be to set the majority carrier at the position of the potential maximum, set the minority carrier self consistently, and neglect space charge in the region between contact and the position where the charge carriers are set.

Scott and Malliaras [64] proposed a modification of the thermionic model by adding a recombination current, resulting in:

$$J = \frac{16\pi\epsilon_0\epsilon_r(k_B T)^2 \mu N_C}{e^2} \exp(-\varphi_B/k_B T) \exp(f^{1/2}) - n_c e S(F) \quad (4.67)$$

with a field dependent surface recombination velocity $S(F) = S(0)(1/\psi^2 - f)/4$ ($S(0) = 16\pi\epsilon_0\epsilon_r(k_B T)^2 \mu/e^3$), the reduced electric field $f = eFr_c/k_B T$ (r_c Coulomb radius), and $\psi(f) = f^{-1} + f^{-1/2} - f^{-1}(1 + 2f^{1/2})^{1/2}$. The velocity of the recombination current is set such that it becomes zero when there is no field applied. This condition, however, is not completely self-consistent in the case of a built-in field, because it creates an effective injection current. However, this effect may be negligible in case of photocurrent modeling.

In the following, the simulation is mainly applied to describe p-i-n solar cells, where highly doped layers are attached to the metal contacts. That is why the discussed injection processes (into an intrinsic semiconductor) are not directly applicable, because tunneling currents and the build-up of an interface dipole are expected. Although a theoretical description of this situation is difficult, doped layers make the simulation easier, because it is known from experiment that such a contact is not current-limiting. Additionally, energy level bending at the doped semiconductor-metal interface is restricted to several nm (<5 nm) which means that the bulk equilibrium situation of the doped layer with thicknesses larger than 20 nm is present in almost the whole layer [65, 66]. Thus, the boundary charge carrier density can be set to the effective doping concentration and V_{bi} can be set as difference between the Fermi levels of the p- and n-doped layer. Later we will see that it is not even necessary to know the exact doping concentration, because in the ideal case the J - V curve is independent of the doping concentration as long as it is sufficiently high.

4.6 Organic-Organic Interfaces

In the previous sections, the mechanisms within bulk layers—like charge transport and recombination—and the metal contacts as boundary conditions have been discussed. This is sufficient for a simulation of a single-layer device. Organic-organic interfaces, which are found in multilayer organic solar cells like flat heterojunction or p-i-n devices, require a separate treatment. The approach chosen here is a solution of (4.17–4.22) for the whole device and applying modifications of the bulk rates at interfaces. This concept is comparable to the description by Staudigel et al. [10]. Alternatively, multilayers could be treated as multiple boundary value problems, where each layer is dealt with separately and the boundary conditions of two adjacent layers are described by interface conditions and are matched during an iterative algorithm.

4.6.1 Charge Transport

There are two factors influencing charge transport at an organic-organic heterointerface: First, different mobilities and second, changes in the DOS, which mean changes in the parameters $N_{C/V}$, σ , and the absolute values of E_{ht} and E_{et} . The latter results in energy barriers φ at the interface.

The first one is simple, however requires some modification of the charge carrier transfer rates. The reason is the following: If (4.29) and (4.31) are applied for a charge carrier hop from left to right and from right to left, different mobilities will be used. That is in the first case the mobility of the left layer and in the second case the mobility of the second layer. This leads to a built-in selectivity of this interface, which means that this asymmetry is compensated by a higher charge carrier density in the material with the lower mobility. According to (2.28) a discontinuity in charge carrier density is equivalent to a step in the electrochemical potential at the interface in equilibrium, which is physically not allowed. To eliminate the selectivity, the same mobility has to be used for both jumps. One can choose the mobility of either the right or the left material or the average between both. Obviously it would be desired to know the jump rates (transfer integrals) between the two involved molecules. The influence of taking the average or selecting one or the other mobility is negligible (for $\varphi = 0$) as long as the number of discretization points within the layers is much larger than 1. This approach is quite intuitive because it is not the mobility in the material which determines the probability of a jump rate, but the transfer integral between two sites. Based on these considerations the question arises whether in case of a field dependent mobility, the field between two grid points should be selected instead of the field at the position of the grid point, where the charge carrier hop starts. This proposition is more rigorous and fits into the picture of self consistency although discrepancies are expected to be low in the case of a sufficiently small distance between discretization points.

Energy barriers represent a potential offset and result for holes from HOMO(E_{ht}) and for electrons from LUMO(E_{et}) offsets superimposed by the effect of interface dipoles. This means that the charge carrier gains potential energy, which is equal to the barrier height, if it crosses this barrier. The probability of such an upward jump is described by a Boltzmann factor as already discussed in Sect. 3.2.3 (3.15) for hopping. Thus, the charge carrier transition rate is modified according to the following equation:

$$\Delta n^{i \rightarrow i+1} = \Delta n_0^{i \rightarrow i+1} \exp\left(\frac{-\Delta E_{et}}{k_B T}\right). \quad (4.68)$$

Treating barriers in the case of a distribution of states (e.g. a Gaussian DOS) is more complicated (Fig. 4.9a). Staudigel et al. [10] calculate a rate of change by an integration over the densities of states at the origin and destination. That accounts for all possible hopping energy steps. They assume charge carriers equally distributed in the DOS, i.e. a probability function, which is simply constant in energy with a

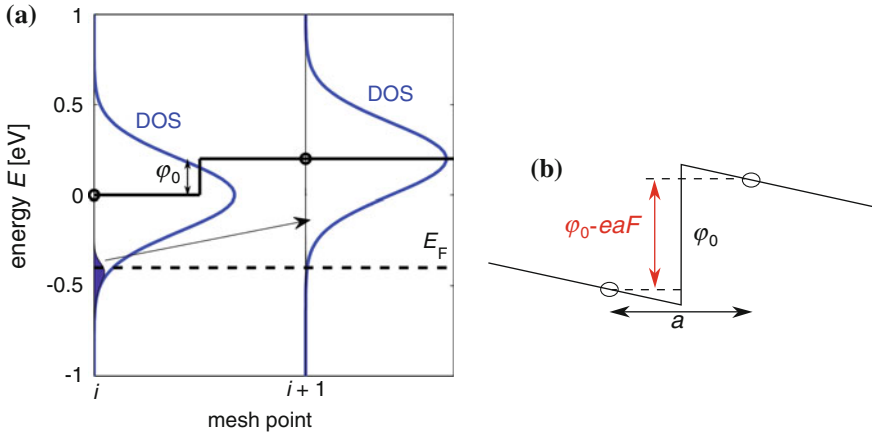


Fig. 4.9 **a** Sketch of the energy distribution at an organic-organic interface with barrier φ in the case of a Gaussian DOS, which influences the probability of an electron to cross the barrier. **b** An electric field F can lead to a hopping probability that is assisted by tunneling. The reason is a lowering of the effective barrier for a jump covering the distance a

value n/N_C . This assumption is motivated by the facts that relaxation according to the Bässler model (cf. 3.19) happens after a large number of hops and that charge carriers are supposed to be injected homogeneously into the DOS at the electrodes. The result is a much higher probability of barrier crossing compared to a Boltzmann factor with the distances between the maxima of $E_{\text{et}}/E_{\text{ht}}$ of the two adjacent materials. However, this approach is not self-consistent in the case of a drift-diffusion simulation, where the difference between the Fermi levels at the contacts is the applied bias voltage, because an increased probability for barrier crossing based on non-equilibrium conditions gives offsets in the electrochemical potential. These offsets can possibly be tolerated when describing a device far from equilibrium at several Volt applied bias. However, it is not allowed for solar-cell modeling, where each discontinuity in the (quasi-)Fermi level is directly found in changes of the open-circuit voltage. That is why we assume relaxed states, which can be described by Fermi-Dirac statistics. In case of a Gaussian DOS, the probability of interface crossing is calculated under the condition of a constant Fermi level at the interface. This means that the crossing rate is chosen in a way that the charge carrier density tends to fulfill this equilibrium condition:

$$E_F^{i+1} = E_F^i \quad (4.69)$$

which means for an upward-jump from left to right in the case of $\sigma \rightarrow 0$:

$$n^{i+1} = n^i \exp\left(-\frac{|\Delta E_{\text{et}}|}{k_B T}\right). \quad (4.70)$$

Otherwise, ΔE_{et} , σ^i , σ^{i+1} , n , and the Fermi-Dirac distribution define the crossing probability. This probability tends to 1 for a large σ , because ΔE_{et} becomes insignificant compared to the distribution of states. Figure 4.10 shows the influence of σ and n (via E_F) on the probability for barrier crossing depicted as a function of the energy barrier. It can be seen in Fig. 4.10a that the probability increases significantly with a higher σ , although not as strongly as proposed by Staudigel et al. (Fig. 3 in [10]). In case of different values of σ between origin and destination, probabilities larger than 1 can occur for a larger σ in the destination layer and a small barrier. Such a situation is treated by a probability smaller than one for the jump in reverse direction. This jump is effectively an upward jump due to the difference in σ overcompensating for the nominal barrier between the maxima of the DOS.

A change of $N_{V/C}$ is treated in the same way, which results simply in the condition

$$\frac{\Delta p^{i \rightarrow i+1}}{\Delta p^{i+1 \rightarrow i}} = \frac{\Delta p_0^{i \rightarrow i+1}}{\Delta p_0^{i+1 \rightarrow i}} \frac{N_V^{i+1}}{N_V^i} \quad (4.71)$$

at the interface. In case of non-equilibrium, (4.69) does not hold and steps in E_F can occur, e.g., due to interface recombination processes.

Additionally, a lowering of the barrier ($\Delta E_{\text{et}} = \varphi_0$) due to an electric field might be considered, if one assumes the charge carrier covering a distance a when crossing the interface (Fig. 4.9b). This distance can be identified with the hopping distance in (3.15) and φ is modified accordingly:

$$\varphi = \varphi_0 - eaF. \quad (4.72)$$

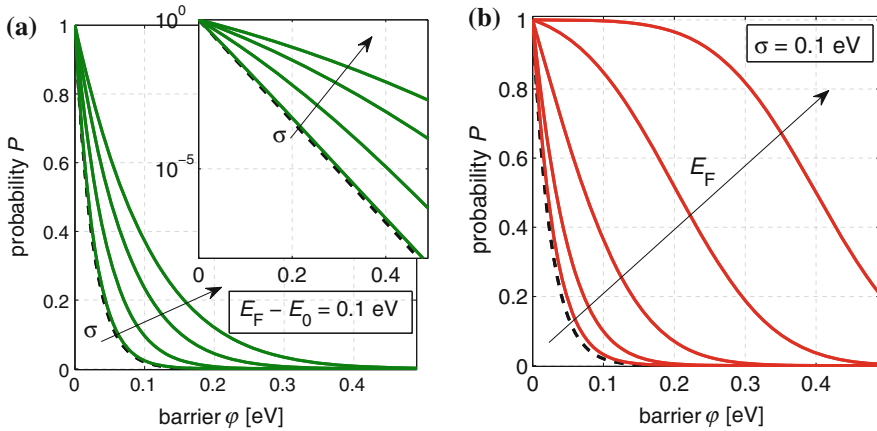


Fig. 4.10 Probability P of a jump over a barrier φ as a function of the barrier height **a** at varied width σ of the DOS ($\sigma = 0.1, 0.15, 0.2, 0.25$ eV) and **b** for a varied distance between E_F and the center of the DOS in the originating layer ($-0.4, -0.2, 0, 0.2, 0.4$ eV). This distance is correlated with the charge carrier density in front of the barrier. Dashed lines denote the probabilities in case of a discrete energy step

Note that the principle of detailed balance might be violated by this equation, if a is larger than the discretization distance and interface crossing of charges is only calculated between the adjacent discretization points.

4.6.2 Generation and Recombination

In a blend layer represented by an effective medium, the charge carrier generation (and recombination) rate is a bulk property. In case of a planar/flat heterojunction, generation and recombination occur at a spatially localized interface, which is found between two adjacent mesh points in the simulation. In this case, several rates have to be adjusted at the discretization points left and right to the interface. The simplest approach to identify an exciton-splitting donor-acceptor type heterojunction consists in an analysis of the offsets in $E_{\text{ht}}/E_{\text{et}}$. Comparing those with the transport gap and the exciton binding energy of the adjacent materials gives a rough estimate on how the simulator should treat the interface. If the offset in E_{ht} (E_{et}) is larger than the exciton binding energy, excitons from the acceptor (donor) are supposed to be separated. Of course, it is possible to consider more effects or to set the interface properties manually.

Exciton separation at a spatially localized D/A interface can be treated in two different ways: Either one uses the additional relaxation term R_{sep} in (4.22) assuming a certain (high) rate for exciton separation. Or one assumes that all excitons diffusing from the adjacent mesh point towards the interface at position i are quenched by forming a CT state or directly a free charge-carrier pair. The second approach represents the case of an infinitely high exciton separation rate. It is less sensitive to the choice of the discretization interval. If the quenched excitons form CT states, the charge of these states is assumed to be located at point i and the reverse one at $i + 1$. Their dissociation and relaxation is described via the Onsager-Braun theory similar to the situation in the bulk. When free charge carriers are generated, they are set to point $i - 1$ and $i + 2$, which means a discrete G in (4.17) and (4.18). As the creation of charge carriers from neutral excitons at an interface results in the occurrence of positive and negative charge at different locations (right and left of the D/A interface), this generation mechanism constitutes an electric current and is added to (4.35).

Recombination at an interface requires a separate treatment as well. On the one hand, it is essential to allow recombination between electrons and holes located on the right and left side of an interface, because it consists a physically important current path in the case of energy barriers. Simply spoken, electrons that face a barrier in their DOS at an interface do not have to cross it to recombine with holes located on the other side of the interface. They can directly recombine across the interface. On the other hand, such a process includes another complication, as recombining charge carriers travel a certain distance. In conventional semiconductor simulations, commonly surface recombination rates are set, which act in addition to bulk recombination processes.

In Staudigel et al. [10], the common bimolecular recombination is chosen with the recombining species located on the two sides of the interface: $R = \beta n^i p^{i+1} + \beta p^i n^{i+1}$. As long as discretization is not changed, this approach works, although there is a significant difference to bulk recombination (illustrated in Fig. 4.11), which is considered to occur only between charge carriers at the same mesh point in the simulation. In the bulk, treating electron-hole recombination only at the same position is not a severe restriction, because drift and diffusion can deliver the charges required for a recombination at the same position. However, it is not sufficient in the case of an interface with an energy barrier. Whereas recombination of charge carriers at the same position does not constitute a current (in x -direction), recombination of charges located on the two different sides of an interface constitutes a current. A current implies the definition of an average recombination distance a to guarantee that it is independent of the discretization distance. The necessity of a can be explained as follows: Current is according to (4.35) the product of a rate of change, the traveling distance, and the elementary charge:

$$J_{\text{interface}}^{pn} = eR\Delta m = ec\beta p^i n^{i+1} \Delta m. \quad (4.73)$$

Without adjusting c , the current scales with the discretization distance. Thus, c has to contain $1/\Delta m$. To maintain the unit of R as a rate of change for charge carrier densities ($\text{cm}^{-3}\text{s}^{-1}$), c has to contain a value of a length, which is the average recombination distance a . From the energetic point of view, the Coulomb radius might be used to define the average distance recombining charges travel. However, this value is in the range of 10 nm, which is too large for a direct recombination process because it exceeds the average hopping distance. It is most reasonable to take the average hopping distance (e.g. 1 nm) as average recombination distance.

As we are using net-recombination rates, e.g., in (4.46) describing recombination only of excess charge carriers, we consider the intrinsic charge carrier densities at the interface as well to guarantee self-consistency:

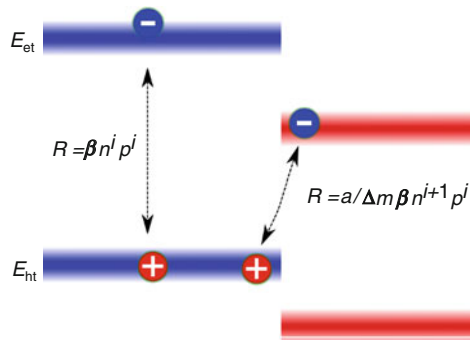


Fig. 4.11 Sketch of the difference between bulk ($R = \beta np$) and interface recombination. The latter requires a definition of the average distance a , which recombining charges travel. This causes an electric current at the interface

$$R_{np} = \frac{a}{\Delta m} \beta \cdot (n^i p^{i+1} - n_i^{j2} e^{-\varphi_p/k_B T}); \quad R_{pn} = \frac{a}{\Delta m} \beta \cdot (p^i n^{i+1} - n_i^{j2} e^{-\varphi_n/k_B T}). \quad (4.74)$$

The exponential terms are valid for Boltzmann statistics and are replaced by the probability of crossing the barrier in the case of a Gaussian DOS.

When CT states are considered, recombination at a D/A interface leads to CT states (cf. Fig. 4.7). Otherwise, recombined charge carriers are assumed to be gone. Analogously, a Shockley-Read-Hall recombination at the interface can be defined.

4.7 Optical Modeling: Transfer Matrix Approach

One important input into the continuity equations (4.17) and (4.18) is the generation rate $G = G_{n,p}$ of charge carriers. We discussed that this generation results from the splitting of excitons which reach a donor/acceptor interface. Therefore, it is desired to know the exciton generation rate G_s as a function of the spatial variable x . For a flat heterojunction (bilayer), we can apply the exciton diffusion equation (4.22) to calculate the amount of excitons reaching the D/A interface. For a well-mixed bulk heterojunction, the exciton generation profile can be set equal to the generation profile of charge-carrier pairs (or CT states), considering a given quantum efficiency η_{ED} due to some excitons, decaying before reaching a D/A interface:

$$G_{n,p} = \eta_{ED} G_s. \quad (4.75)$$

G_s equals the absorbed photon flux per unit volume in the wavelength range, where the incident light generates excited states of the molecule. This means that one absorbed photon generates one exciton. Multi-exciton processes are not covered here because they are not significant in state-of-the-art solar cells at an illumination of 1 sun and below.

If we consider a plane wave incident on a material, the absorbed intensity, i.e. energy dissipation Q per unit time (and volume), is supposed to be proportional to the intensity I in the volume element considered. Therefore, we can write:

$$Q = \frac{dI}{dx} = \alpha I \quad (4.76)$$

with the absorption coefficient α in units of cm^{-1} . The absorption coefficient is a function of the wavelength λ of the incident light and can be related to microscopic properties of the material via (3.6)–(3.8). The solution of the differential equation (4.76) is the well known Lambert-Beer law:

$$I(x, \lambda) = I_0(\lambda) e^{-\alpha(\lambda)x}. \quad (4.77)$$

Here, I_0 is the incident intensity and x the distance from the surface. Plugging (4.77) into (4.76) gives an expression for the dissipation profile $Q(x, \lambda)$. Dividing this number for each λ by the respective energy of the photons ($\hbar\omega$) and integrating it over the whole spectrum results in the number of absorbed photons at position x . This number is the quantity $G_s(x)$ we are interested in. Therefore, the absolute intensity spectrum or photon flux of the incident light has to be known to calculate G_s (cf. 4.98).

An approach based on (4.77) is applicable for optically thick layers or a (semi-transparent) solar cell consisting of one single layer. If the solar cell comprises several layers, reflections at the interfaces have to be considered, especially for a reflective back electrode (cf. typical stacks in Fig. 3.48). If the thicknesses of these layers are in the range of the wavelength of the incident light, the problem has to be treated coherently. Coherence means that there is a fixed relation between the phase of the two waves at a certain time and position. Although sun light is thermal radiation, where the single photons are emitted in a stochastically independent way, it behaves coherently on the length scale of the wavelength [67]. Consequently, incident and reflected wave of the same wavelength interfere. Interference means superposition, i.e. addition, of the electric field of forward and backward traveling electro-magnetic wave. Therefore, each wavelength has to be treated separately. Following Pettersson et al. [27] we can write for the electric field of a wave with specified wavelength and at a certain position x in the stack:

$$\mathbf{E}(x) = \mathbf{E}^+(x) + \mathbf{E}^-(x) \quad (4.78)$$

with $\mathbf{E}^+(x)$ ($\mathbf{E}^-(x)$) describing the electrical field of the forward (backward) propagating wave, as depicted in Fig. 4.12. As previously in the electrical model, we assume that the stack is homogeneous within the lateral dimensions. Therefore, all quantities show only a dependence on the vertical coordinate x . Remember that $\mathbf{E}(x)$ also depends on the time and can be expressed with the aid of the following equation for plane waves:

$$\mathbf{E} = \mathbf{A} \cos(\mathbf{k}\mathbf{r} - \omega t + \varphi) = \Re(\mathbf{A}e^{i(\mathbf{k}\mathbf{r} - \omega t + \varphi)}). \quad (4.79)$$

This equation describes the electromagnetic field as a quantity changing sinusoidally with time t and space $\mathbf{r}$. $\mathbf{A}$ represents the amplitude vector, $\mathbf{k}$ is the wave vector with $|\mathbf{k}| = 2\pi/\lambda$, ω is the frequency, and φ describes the phase. This wave equation directly results from a combination of Maxwell's Equations.

Looking at the stack of Fig. 4.12 we directly see that multiple reflections will occur as soon as the incident field $\mathbf{E}_0^+$ has entered the stack (here from the left). Therefore, it is not straight-forward to express (4.79) as a function of x . However, the approach of describing $\mathbf{E}(x)$ as sum of forward and backward propagating wave, allows us to apply the transfer-matrix approach. Consider the relation between $\mathbf{E}$ in layer i and j at the proximity of the interface i, j at x_0 : $\mathbf{E}_j^+(x_0)$ consists of the transmitted electric field from the previous layer and the reflected one of the backward propagating wave of layer j :

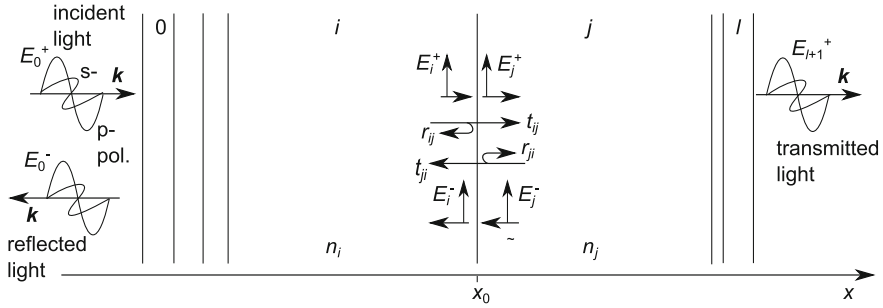


Fig. 4.12 Sketch of the transfer-matrix method. The optoelectric field in each layer $0, 1, \dots, i, j, \dots, l$ can be written as a superposition of the field of a forward E^+ and a backward E^- propagating wave. Sketched is the derivation of the interface matrix between layer i and j

$$E_j^+(x_0) = t_{i,j} E_i^+(x_0) + r_{j,i} E_j^-(x_0). \quad (4.80)$$

Analogously, we can write for the backward propagating wave in layer i :

$$E_i^-(x_0) = r_{i,j} E_i^+(x_0) + t_{j,i} E_j^-(x_0). \quad (4.81)$$

Here r and t are reflection and transmission coefficients at the interface i, j describing the change of the amplitude of the electric field upon reflection and transmission, respectively. They are given by the Fresnel Equations, resulting from the continuity conditions of the tangential component of the electric field and of the normal component of the electric displacement field considering Maxwell's equations in case of an interface without charge and current. They contain the complex refractive index $\tilde{n} = n + i\kappa$ with the real refractive index n and the extinction coefficient $\kappa = \frac{\alpha\lambda}{4\pi}$. To express r and t , we have to distinguish the polarization of the incoming light beam and decompose the electric field vector in s- and p-polarized light. For s-polarized light, where the electric field vector is perpendicular (German: "senkrecht") to the plane of incidence (illustration see on the left of Fig. 4.12), r and t can be written under the assumption of equal magnetic permittivities as:

$$r_{i,j}^s = \frac{\tilde{n}_i \cos(\phi_i) - \tilde{n}_j \cos(\phi_j)}{\tilde{n}_i \cos(\phi_i) + \tilde{n}_j \cos(\phi_j)}; \quad t_{i,j}^s = \frac{2\tilde{n}_i \cos(\phi_i)}{\tilde{n}_i \cos(\phi_i) + \tilde{n}_j \cos(\phi_j)}. \quad (4.82)$$

For p-polarized ("parallel") light r and t are:

$$r_{i,j}^p = \frac{\tilde{n}_j \cos(\phi_i) - \tilde{n}_i \cos(\phi_j)}{\tilde{n}_j \cos(\phi_i) + \tilde{n}_i \cos(\phi_j)}; \quad t_{i,j}^p = \frac{2\tilde{n}_i \cos(\phi_i)}{\tilde{n}_j \cos(\phi_i) + \tilde{n}_i \cos(\phi_j)}. \quad (4.83)$$

Here, ϕ is the angle of refraction at the interface, where ϕ_i and ϕ_j are related via Snell's law:

$$\frac{\tilde{n}_i}{\tilde{n}_j} = \frac{\sin \phi_j}{\sin \phi_i}. \quad (4.84)$$

Rewriting (4.80) and replacing $\mathbf{E}_i^+(x)$ in (4.81) yields:

$$\begin{aligned} \mathbf{E}_i^+(x_0) &= \frac{1}{t_{i,j}} \mathbf{E}_j^+(x_0) - \frac{r_{j,i}}{t_{i,j}} \mathbf{E}_j^-(x_0); \\ \mathbf{E}_i^-(x_0) &= r_{i,j} \left(\frac{1}{t_{i,j}} \mathbf{E}_j^+(x_0) - \frac{r_{j,i}}{t_{i,j}} \mathbf{E}_j^-(x_0) \right) + t_{j,i} \mathbf{E}_j^-(x_0). \end{aligned} \quad (4.85)$$

Using (4.82) and (4.83), we find that for both s- and p-polarized light $r_{j,i} = -r_{i,j}$ and $-r_{i,j}r_{j,i} + t_{i,j}t_{j,i} = 1$. Therefore, (4.85) can be rewritten in matrix form in the following way:

$$\begin{bmatrix} \mathbf{E}_i^+(x_0) \\ \mathbf{E}_i^-(x_0) \end{bmatrix} = \underbrace{\frac{1}{t_{i,j}} \begin{bmatrix} 1 & r_{i,j} \\ r_{i,j} & 1 \end{bmatrix}}_{I_{i,j}} \begin{bmatrix} \mathbf{E}_j^+(x_0) \\ \mathbf{E}_j^-(x_0) \end{bmatrix}. \quad (4.86)$$

We have defined an interface matrix I , which relates the electric field on the left side of the interface to the field on the right side.

The light passing through the material j with thickness d_j can also be expressed by a so-called layer matrix. As reflection does not occur within the layer itself, forward and backward waves propagate independently. Therefore, the off-diagonal elements of the layer matrix are zero. The diagonal elements relate the electric field on the right side of the left interface to the electric field on the left side of the right interface of the layer, considering a phase shift defined by n and an absorption ruled by κ . Therefore, in case of perpendicular incidence the phase shift is simply $\frac{2\pi}{\lambda} n_j d_j$ and the field is attenuated according to (4.77) by $\exp(-\frac{\alpha_j}{2} d_j) = \exp(-\frac{2\pi}{\lambda} \kappa_j d_j)$.

Figure 4.13a illustrates the case of non-perpendicular incidence. There, we have to calculate the difference in the optical path length $\Delta\Phi$ between point O and P:

$$\Delta\Phi = g\tilde{n}_j - h\tilde{n}_i \quad (4.87)$$

We apply trigonometric functions and Snell's law (4.84) to express g and h via d_j :

$$g = \frac{d_j}{\cos \phi_j}; \quad h = \sin \phi_i r = \frac{\tilde{n}_j}{\tilde{n}_i} \sin \phi_j \tan \phi_j d_j. \quad (4.88)$$

Plugging these expressions into (4.87) results in:

$$\Delta\Phi = \frac{d_j}{\cos \phi_j} \tilde{n}_j - \frac{\sin^2 \phi_j}{\cos \phi_j} d_j \tilde{n}_j = d \tilde{n}_j \cos \phi_j, \quad (4.89)$$

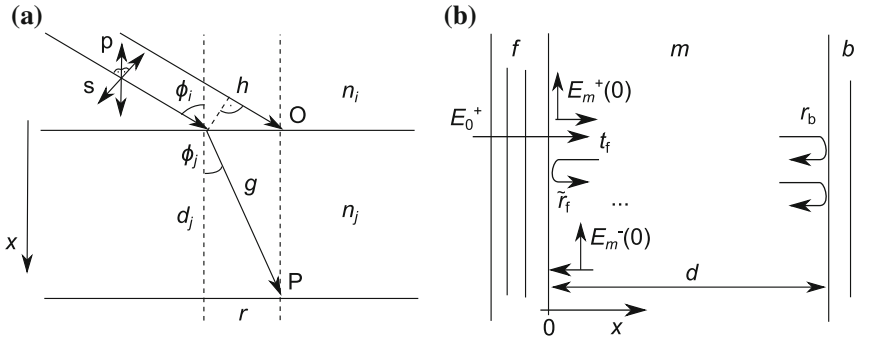


Fig. 4.13 **a** Illustration of the derivation of the layer matrix relating the electric field at position P to the one at O. **b** Derivation of the electric field distribution $E_m(x)$ within layer m , having combined the layers to the left into one stack in front of m and those to the right into one stack behind m . Their reflection and transmission coefficients are previously calculated by the transfer-matrix algorithm

where we used the identity $1 - \sin^2 \phi = \cos^2 \phi$.

Now we can write for the layer matrix:

$$L_j = \begin{bmatrix} e^{-i \frac{2\pi}{\lambda} \tilde{n}_j \cos \phi_j d_j} & 0 \\ 0 & e^{+i \frac{2\pi}{\lambda} \tilde{n}_j \cos \phi_j d_j} \end{bmatrix}. \quad (4.90)$$

L_j allows to calculate the electric field at the left side of layer j if the field on the right side of this layer is known.

If we want to relate the electric field of the incoming wave to the waves reflected and transmitted, we can multiply the matrixes of all l layers and interfaces:

$$\begin{bmatrix} E_0^+ \\ E_0^- \end{bmatrix} = \underbrace{I_{0,1} \prod_{i=1}^l L_i I_{i,i+1}}_{S = \begin{bmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{bmatrix}} \begin{bmatrix} E_{l+1}^+ \\ E_{l+1}^- \end{bmatrix}. \quad (4.91)$$

We directly see that the reflection and transmission coefficients of the complete stack for light incident from the left ($E_0^+ = E_{\text{incident}}$; $E_{l+1}^- = 0$) are:

$$r = \frac{E_0^-}{E_0^+} = \frac{S_{21}}{S_{11}}; \quad t = \frac{E_{l+1}^+}{E_0^+} = \frac{1}{S_{11}}. \quad (4.92)$$

We can also define r and t of subsystems to get access to $E(x)$ within a layer. Assume we are interested in layer m and have defined the reflection and transmission coefficients via (4.92) for the stack in front (index f) and behind (index b) layer m .

The locations refer to the light of incidence assumed from the left side only as shown in Fig. 4.13b.

The forward propagating electric field $\mathbf{E}_m^+(x_0 = 0)$ in layer m at the interface to stack f can be derived according to the optical path visualized in Fig. 4.13b. The field entering layer m from the stack f is $\mathbf{E}_0^+ t_f$. It is superimposed by the light passing through the layer, being reflected at stack b , once more passing through the layer and being reflected at stack f and subsequent loops:

$$\begin{aligned} \mathbf{E}_m^+(0) &= \mathbf{E}_0^+ t_f + \mathbf{E}_0^+ t_f r_b \tilde{r}_f e^{-2i \frac{2\pi}{\lambda} \tilde{n}_j \cos \phi_j d_j} + \mathbf{E}_0^+ t_f \left(r_b \tilde{r}_f e^{-2i \frac{2\pi}{\lambda} \tilde{n}_j \cos \phi_j d_j} \right)^2 + \dots \\ &= \frac{\mathbf{E}_0^+ t_b}{1 - r_b \tilde{r}_f e^{-2i \frac{2\pi}{\lambda} \tilde{n}_j \cos \phi_j d_j}}, \end{aligned} \quad (4.93)$$

where $\tilde{r}_f$ is the reflection coefficient of stack f for light incident from the right, i.e. $\tilde{r}_f = -S_{12}^f/S_{11}^f$ according to (4.91). We made use of the limes of the geometric series to find the final expression in (4.93). The electric field at the same position, propagating in the reverse direction is given by $\mathbf{E}_m^-(0)$ and one more loop within the layer excluding the reflection at the interface to stack f :

$$\mathbf{E}_m^-(0) = \mathbf{E}_m^+(0) r_b e^{-2i \frac{2\pi}{\lambda} \tilde{n}_j \cos \phi_j d_j}. \quad (4.94)$$

The total field is the sum of forward and backward propagating wave. This holds for each position in layer m . Therefore, we can express the electric field as a function of the incoming field:

$$\mathbf{E}_m(x) = \mathbf{E}_m^-(x) + \mathbf{E}_m^+(x) = \frac{\mathbf{E}_0^+ t_b}{1 - r_b \tilde{r}_f e^{-2i \frac{2\pi}{\lambda} \tilde{n}_j \cos \phi_j d_j}} \left(e^{i \frac{2\pi}{\lambda} \tilde{n}_j \cos \phi_j x} + r_b e^{i \frac{2\pi}{\lambda} \tilde{n}_j \cos \phi_j (2d_j - x)} \right), \quad (4.95)$$

where t and r can be expressed by the components of the stack matrices S_f , S_b of the layers in front and behind layer m .

Knowing the electric field distribution we can calculate the time-averaged energy dissipation (i.e. absorbed power) in layer m using (4.76):

$$Q(x, \lambda) = \alpha_m(\lambda) I(x, \lambda) = \frac{1}{2} c \epsilon_0 \alpha_m(\lambda) n_m(\lambda) |\mathbf{E}_m(x, \lambda)|^2. \quad (4.96)$$

Here, we applied the relation of I with $\mathbf{E}$ valid for an electromagnetic plane wave. We explicitly marked that $\mathbf{E}$ according to (4.95) was calculated for a specific wavelength λ .

Note that a more accurate approach to determine Q is to use the differential flux density of absorbed photons obtained calculating the x -component of the time-averaged Poynting vector [28].

Q can be transferred to an exciton generation profile, assuming that the wavelength region under consideration generates excitons with a quantum efficiency $\eta_{Q,s}$:

$$G_{\text{opt}}(x, \lambda) = \frac{\eta_{Q,s}}{\hbar\omega} Q(x, \lambda). \quad (4.97)$$

Usually, $\eta_{Q,s} = 1$ in the UV-vis spectral range of common absorber materials. Integrating $G_{\text{opt}}(x, \lambda)$ over the spectrum gives the total exciton generation profile:

$$G_{\text{opt,total}}(x) = \int_{\text{spectrum}} G_{\text{opt}}(x, \lambda) d\lambda = G_s(x). \quad (4.98)$$

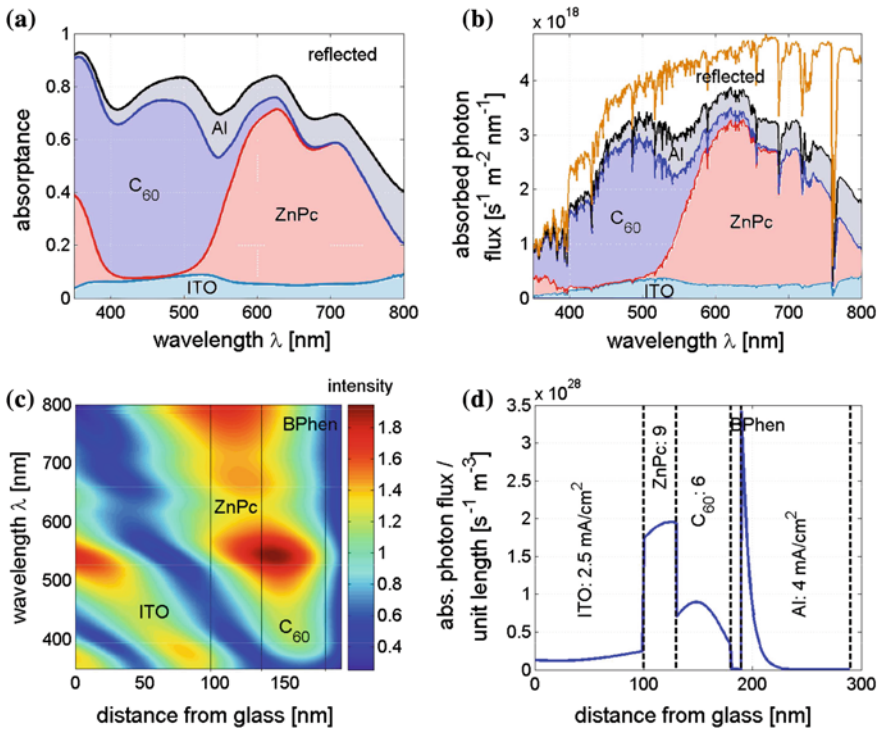


Fig. 4.14 Results from transfer-matrix modeling of the stack: glass (1 μm), ITO (100 nm), ZnPc (30 nm), C₆₀ (50 nm), BPhen (10 nm), Al (100 nm). **a** Absorbance of the separate layers; **b** absorbed photon flux of the AM1.5g spectrum in each layer; **c** intensity map (relative to the incoming intensity, which is set to unity for all wavelengths); **d** overall absorbed photon flux per unit length as a function of the position within the device. This plot represents the exciton generation profile under AM1.5g. The numbers following the name of the materials denote the total numbers of absorbed photon fluxes per layer converted into an electric current density

Figure 4.14 visualizes the outputs of a transfer matrix simulation of the exemplary stack glass (1 μm), ITO (100 nm), ZnPc (30 nm), C₆₀ (50 nm), BPhen (10 nm), and Al (100 nm). The absorption spectra of each layer shown as a stacked graph in (a) reflect the absorption features of the single materials (cf. Fig. 3.53). Multiplying the absorptance with the amount of photons at every wavelengths yields a spectrum of the absorbed photons per layer (b). Figure 4.14c displays the intensity as a function of the wavelength and distance to the glass. Interference effects are clearly visible, showing maxima and minima in the intensity dependent on the wavelength. The larger the wavelength, the further is the first interference maximum shifted to the left, i.e. away from the reflective back electrode. The weaker the absorption (see valleys in Fig. 4.14a at 550 nm, 670 nm, >800 nm) the higher is the intensity in the absorption maxima. Using these data in (4.96)–(4.98) we can calculate the absorbed photon flux per unit length, i.e. the exciton generation profile $G_s(x)$, shown in (d). The profile confirms that it is a good choice to position C₆₀ closer to the reflective electrode than ZnPc, as it absorbs in the low-wavelength range. The graph also illustrates that a considerable amount of photons are lost due to absorption in the metal.

4.8 Exemplary Devices: Analytical and Numerical Solutions

Before applying the drift-diffusion model to organic solar cells, we discuss some simple devices to demonstrate the convergence of the numerical simulations towards analytical solutions in special cases, where analytical solutions exist. This section also helps the reader to get acquainted with the diagrams used in the following to visualize results obtained from simulations.

4.8.1 Single-Carrier Devices and SCLC

First, a single-carrier device is simulated, where a sufficient injection of charge carriers (here holes) is assumed. The simulation data are compared to simple analytic data of Ohmic conductivity and space-charge-limited current (SCLC) according to the Mott-Gurney Law [68], which predicts a square-law current-voltage (J - V) dependence:

$$J = \frac{9}{8} \epsilon_0 \epsilon_r \mu \frac{V^2}{d^3}. \quad (4.99)$$

Here, d is the layer thickness and μ the mobility which is assumed to be independent of the electric field. The Mott-Gurney Law originates from an analytical solution of one-dimensional expressions of Poisson's equation (4.15) and the transport equation (4.19) neglecting diffusion currents and further space charge (e.g. originating from trapped charges):

$$\frac{\partial F}{\partial x} = \frac{e}{\epsilon_0 \epsilon_r} p; \quad J = ep\mu F. \quad (4.100)$$

Substituting n and integrating Poisson's equation yields:

$$\begin{aligned} \int_0^{F(x)} F dF &= \int_0^x \frac{J}{\epsilon_0 \epsilon_r \mu} d\tilde{x} \\ \Rightarrow \frac{F(x)^2 - F_0^2}{2} &= \frac{J}{\epsilon_0 \epsilon_r \mu} x \\ \Rightarrow F(x) &= \sqrt{\frac{2J}{\epsilon_0 \epsilon_r \mu}} x. \end{aligned} \quad (4.101)$$

Here, we used the condition that J is independent of x in steady state, and we set F_0 to zero as we are only interested in the potential dropping over the layer and we do not discuss surface charge at the metal-insulator interface. Hence the field, which is 0 in the metal electrode, yields an F_0 that is 0 as well. An integration of (4.101) over the layer thickness d yields:

$$-V = \int_0^d F(x) dx = \int_0^d \sqrt{\frac{2J}{\epsilon_0 \epsilon_r \mu}} x dx. \quad (4.102)$$

This equation results in (4.99). Since it contains only the charge carrier mobility, permittivity, and layer thickness, an SCLC experiment is commonly used to experimentally determine the mobility without knowing the charge carrier density. For high charge carrier densities n_0 within the device and low currents ($J \lesssim en_0\mu F$, $n_0 = \min \tilde{n}_0(x)$ is the minimum equilibrium charge carrier density in the layer), Ohmic conductivity is expected which follows (2.34) with $F = V/d$.

Figure 4.15 shows simulated J - V curves of hole-only devices together with analytical solutions in a double logarithmic plot. The simulation reproduces the analytical results dependent on the voltage range. For high voltages the space-charge region can be seen (slope 2), whereas for low voltages, or more precisely low currents, ohmic behavior is obtained due to charge carriers in the device in equilibrium (n_0). The additional curves shown in Fig. 4.15 are obtained assuming a doping density of $2 \times 10^{17} \text{ cm}^{-3}$ and 10^{18} cm^{-3} . The charge carriers introduced by doping increase the absolute current for lower voltages and the extension of the linear region of the J - V curves. For larger voltages and currents, the charge carrier density is not sufficient and current has to be driven by an injected space charge. The ohmic region seen in the simulation of the nominally undoped sample is due to a background charge carrier density provided by the electrodes, whose work functions are close to E_{ht} . In experiment, the linear region is also observed and can be caused additionally by charges generated through intragap states or a shunt/leakage current.

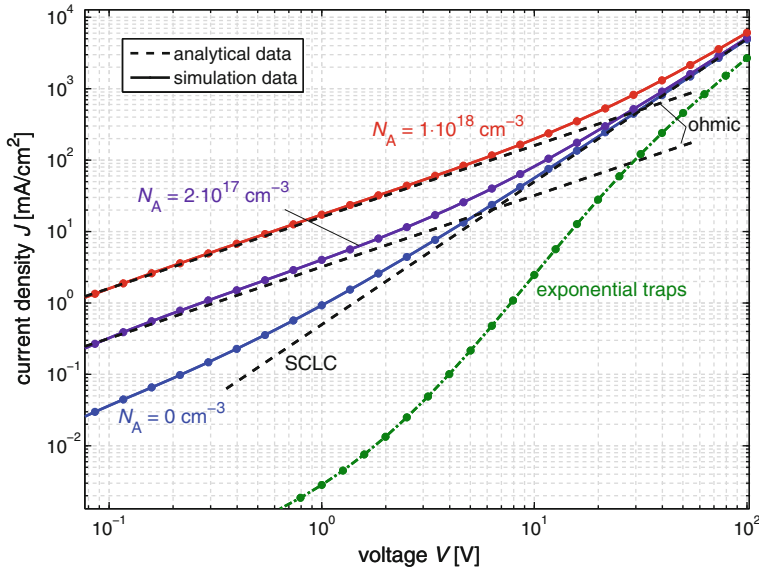


Fig. 4.15 Simulated J - V curves of a 100 nm thick hole-only device ($\mu_p = 10^{-6} \text{ cm}^2/\text{V s}$) with different doping concentrations N_A . Analytic solutions for ohmic (slope 1) and space-charge conductivity (SCLC) (slope 2) are shown as *dashed lines*. The simulation data (*symbols*) visualize the transition from the ohmic to the SCLC regime for higher currents. Trap-limited currents lead to higher slopes before reaching the SCLC case for higher voltages

Introducing exponentially distributed traps ($E_t = 0.1 \text{ eV}$) in the simulation yields an additional region in the J - V curve with a steep slope, as shown by the green dash-dotted line in Fig. 4.15. An analytical theory based on drift currents predicts a slope of $E_t/k_B T + 1 \approx 4.9$ in the ideal case of trap charge limited current [69]. As the simulation describes a superposition of all effects and the analytical equation ignores diffusion, a lower value of 3.6 is found for the slope at voltages around 10 V.

A higher slope compared to the SCLC case can also be caused by an injection limit, which is present in the region from 10 to 200 V of the plot in Fig. 4.16, where a barrier of 0.9 eV is assumed. The inset shows a logarithmic plot of the current as a function of the square root of the applied bias. There, the curve exhibits a linear part, which is expected from the thermionic injection model (4.66) plugged into (4.64) if the field in the device is constant and equals V/d as demonstrated in the following.

Figure 4.17 shows the electric field within the device for four situations at 10 V applied bias. In case of sufficient injection, F is constant for ohmic conductivity (solid line in Fig. 4.17a) or shows a square root dependence for the SCLC case (dashed line) as expected from (4.101). The overshoots close to the contacts are due to the large space charge introduced by the contacts. If the current is injection limited ($\phi_{\text{injec}} = 0.9 \text{ eV}$), F is either constant (dashed line in Fig. 4.17b), because the intrinsic device behaves mainly like a capacitor, or most of the potential drops

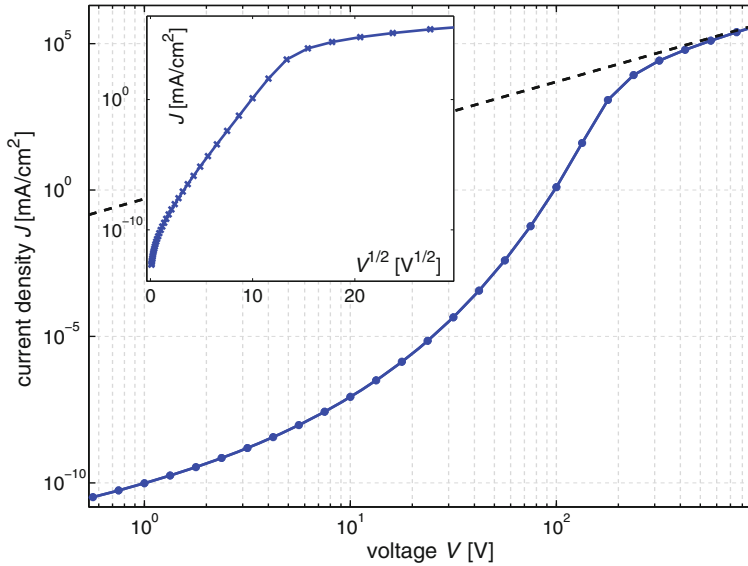


Fig. 4.16 Simulated J - V curve in the case of injection-limited current ($\varphi_{\text{injec}} = 0.9$ eV). The *inset* shows a linear behavior of $\exp(J \cdot \text{mA}^{-1} \text{cm}^2)$ plotted as a function of $\sqrt{V}$ in the injection limited region. This is expected from the thermionic injection model (4.66). The J - V curve reaches the SCLC limit (*dashed line*) for higher voltages where the injection barrier does not limit the current any more

in the space-charge region close to the contact in the case of a doped semiconductor (solid line) forming a Schottky contact (cf. Fig. 3.45).

These data demonstrate the reliability of the simulation. It is, in contrast to the analytical solutions, also capable of describing regions of transition between different dominating regimes in the J - V curve.

4.8.2 The p-n Junction

In Sect. 2.5.1 we discussed the classical p-n junction due to its relevance in conventional solar cells. Here, we apply the analytic equations from that chapter to verify the simulation of a $4 \mu\text{m}$ thick p-n junction as an example of a simple bilayer device. We use the material parameters of silicon ($E_g = 1.12$ eV, $\mu_n = 1,500 \text{ cm}^2/\text{Vs}$, $\mu_p = 450 \text{ cm}^2/\text{Vs}$, $N_C = 2.8 \times 10^{19} \text{ cm}^{-3}$, $N_V = 1.04 \times 10^{19} \text{ cm}^{-3}$, $\epsilon_r = 11.9$) and a doping concentration of $N_A = 10^{16} \text{ cm}^{-3}$ at the p-side and $N_D = 2 \times 10^{16} \text{ cm}^{-3}$ at the n-side. Simulated space-charge density, electric field and band diagram are shown in Fig. 4.18. The results obtained by using (2.41) and (2.43) are plotted as dashed lines. Simulated and analytic equations coincide in the way expected. The deviations

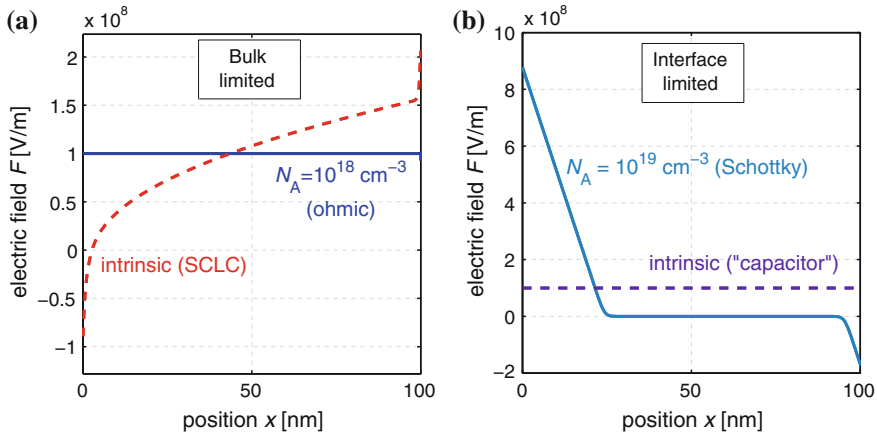


Fig. 4.17 Spatial profiles of the electric field F of a single-carrier device at 10 V and for four different cases ($\mu = 1 \text{ cm}^2/\text{V s}$, $\epsilon_r = 5$) **a** Bulk limit ohmic current-voltage relation with a constant F due to a high doping concentration (solid) or SCLC in case of an intrinsic semiconductor (dashed). **b** Injection limit ($\varphi_{\text{injec}} = 0.9 \text{ eV}$) doped semiconductor forming a Schottky contact to the left metal with a space-charge region for $x < 25 \text{ nm}$ (solid) or intrinsic semiconductor behaving like a plane capacitor (dashed)

are mainly due to approximations applied for the analytical solution. Especially, the abrupt end of the space-charge region is a quite severe approximation.

The simulated J - V curves under illumination and in the dark are plotted in Fig. 4.19, together with the photocurrent J_{photo} as difference between both. J_{photo} is found to be largely independent of the applied bias as expected from (2.50). As we know from the discussion of the drawbacks of the p-n junction (Sect. 2.5.1), this demands for a very large minority diffusion length. In the simulation a large diffusion length is given by the high mobility and the fact that Auger or trap assisted recombination are not considered. Additionally, contacts are set selective and are, therefore, not a source of (surface) recombination. Consequently, minorities are reflected at the respective contact. The semilogarithmic plot shown in the inset visualizes that the ideal slope of $e/k_B T \approx 1/26 \text{ mV}$ ($T = 300 \text{ K}$) according to the Shockley equation (2.49) is reproduced by the simulation.

To check whether the shape of the J - V curve under illumination and especially the calculated value for V_{oc} are reasonable, the fingerprints of the simulated curve are compared to the data from the theory of detailed balance (Sect. 2.6.1). However, only a rough comparison shall be done without considering the optics (absorption and re-absorption) in detail. Instead, we assume that every photon larger than the bandgap is absorbed in the $4 \mu\text{m}$ thick device and contributes to a spatially homogeneous generation rate. This condition implies an assumed absorption coefficient which is around 100 times larger than the real one of Si. As consequence, the radiative recombination constant of Si $\beta_r^{\text{Si}} = 3 \times 10^{-15} \text{ cm}^3/\text{V s}$ [70] has to be assumed 100 times larger in the simulation as well according to the detailed balance limit

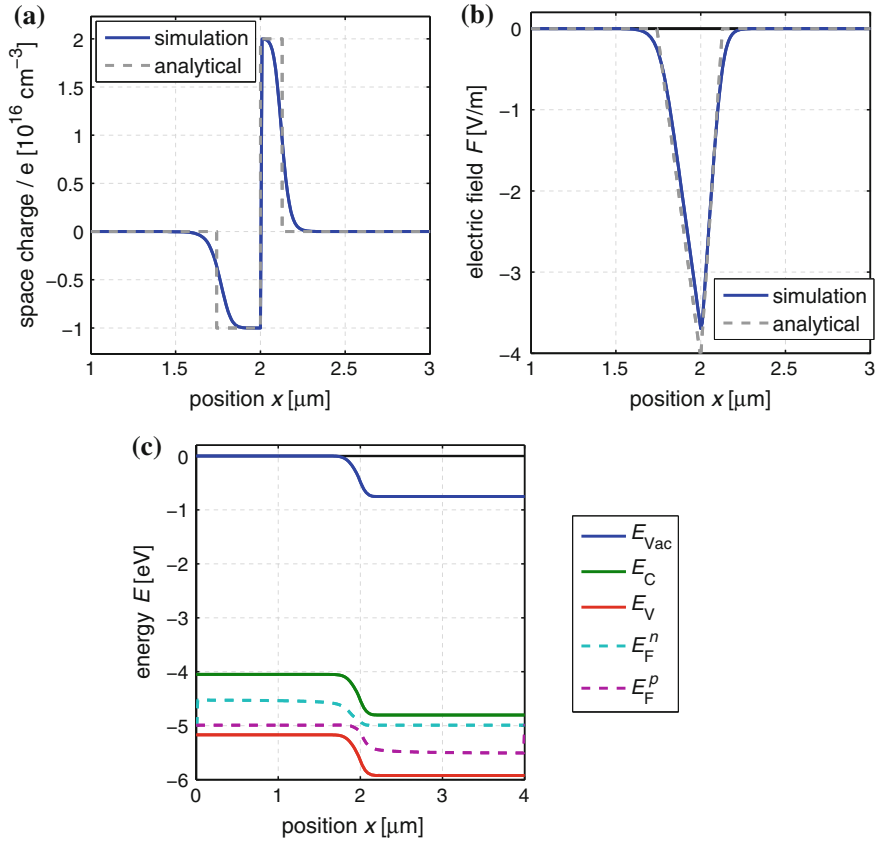


Fig. 4.18 Simulated data of an illuminated p-n junction at 0 V: **a** space charge (analytical solution *dashed*), **b** electric field F (analytical solution *dashed*), and **c** band diagram

(2.20). Plugging $100\beta_{\text{r}}^{\text{Si}}$ and a generation rate of $6.9 \times 10^{20} \text{ cm}^{-3} \text{ s}^{-1}$ into the simulation, results in a J_{sc} of 44 mA cm^{-2} , a V_{oc} of 0.82 V , and a FF of 0.84 , giving an η of 30% . These values are close to the theoretical maximum derived in Sect. 2.6.1 ($J_{\text{sc}} = 44 \text{ mA cm}^{-2}$, $V_{\text{oc}} = 0.87 \text{ V}$, $FF = 0.87$, and $\eta = 33.3\%$). The deviations are supposed to result mainly from the rough approximations for α and β . In conclusion, the data demonstrate that the simulation is well capable of also treating non-equilibrium and generation/recombination situations in accordance with the principle of detailed balance.

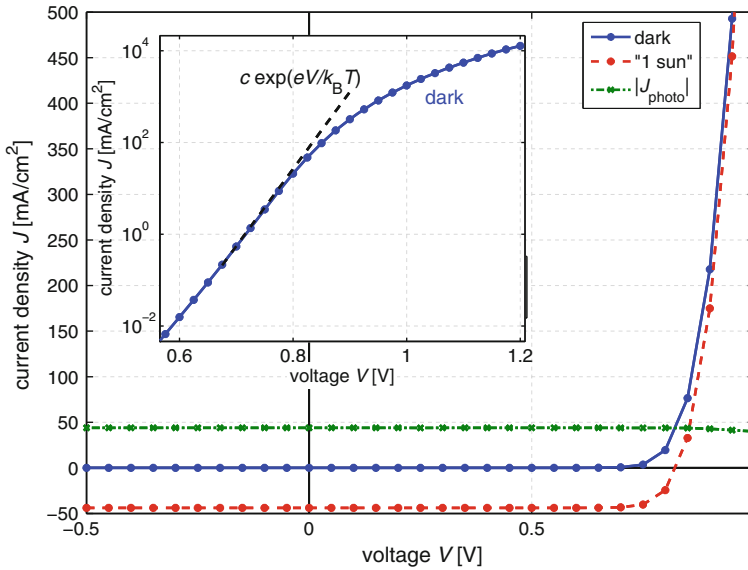


Fig. 4.19 Simulated J - V curves of a p-n junction in the dark and under illumination. The photocurrent J_{photo} as difference between the current under illumination and in the dark is mainly independent of the applied voltage. The *inset* shows a logarithmic plot of the dark curve, visualizing the slope expected from the Shockley equation before entering the regime limited by the series resistance

4.9 Experimental Determination of Material Properties

Several material properties were discussed during the last chapters. They are required to properly describe charge transport, generation, recombination, charge carrier injection, etc. Some of these input parameters of the simulation can be chosen as fitting parameters. However, most of the parameters should be known. This section gives a very brief summary on experimental techniques to measure several material properties.

Layer Thickness d

Layer thicknesses can indirectly be determined during (vacuum-based) solar-cell processing via *quartz crystal monitors* (QCM) which detect the amount of evaporated material. Since these devices measure the mass, the density of the material has to be known to calculate the thickness. Additional inaccuracies result from the fact that the monitor is not located directly at the position of the substrate. This error can be corrected for by tooling the sources. An additional source of errors are differences in the sticking coefficients of substrate and QCM.

Profilometer measurements, where a tip touches the surface of a sample which is laterally moved during a measurement, give information on the topology. For this

measurement the organic layer should be covered by metal to achieve acceptable results. The layer thickness is then measured at an edge of the film. Alternatively, a scratch in a soft film on a scratch-proof substrate can be used. Note that the results can be influenced by the pressure applied to the tip during measuring.

Further, more indirect, methods can be used for a determination of film thicknesses. These methods require a specific model for the extraction of layer thicknesses in a material stack. They cover for example ellipsometry, X-ray diffraction, or other spectroscopic methods [71].

Constants n and κ

The optical constants can be determined by measuring reflection and transmission of a series of samples with different layer thicknesses. These data can be used to calculate n and κ under the assumption of a model [72]. Optical *ellipsometry* data is even suited to reveal information on anisotropic n and κ , as it measures the reflection of polarized light under variable angles of incidence.

Optical Gap E_g^{opt}

The optical gap E_g^{opt} can be determined by the onset of absorption deduced from spectrally resolved reflectance and transmittance measurements of an organic film.

Exciton Diffusion Length L_D

The standard method of investigating exciton diffusion lengths is measuring photoluminescence quenching [73] of layers with different layer thicknesses (or absorption profiles) and a quencher located at a defined position in the sample. Alternatively, the quencher can be realized by a heterojunction and the photocurrent can be detected as a function of layer thicknesses [29] or illumination wavelength [27]. In both cases the diffusion equation is applied to extract L_D .

Energy Levels E_{ht} , E_{et} , Transport Gap E_g^{DA} , and Dipoles

Measuring molecular energy levels of a film is very difficult due to two reasons: On the one hand they change with the surrounding of the molecule (polarization) and on the other hand they are a distributions (DOS) rather than discrete values. *Cyclic voltammetry* gives values for oxidation and reduction potentials of a molecule measured in solution or solid state with reference to a known potential (e.g. silver electrode) [74]. We call these values HOMO_{CV} and LUMO_{CV}. Since the signal shows broad peaks, it is urgently required to state whether the peak or the (somehow determined) onset of the signal is chosen as HOMO or LUMO.

In the following, we prefer, as already mentioned, data from *ultraviolet photoelectron spectroscopy* (UPS) [75, 76]. This measurement is performed at a thin film in vacuum. Therefore, the determined energy levels are as close as possible to the values of the film itself, including polarization effects. The idea of this method is the utilization of the outer photoelectric effect, which describes electron ejection induced

by UV light. Detecting the velocity distribution of the emitted electrons yields the value for the ionization potential (IP), which is $-\text{HOMO}_{\text{UPS}}$. The error of such a measurement is in the range of 0.05 to 0.1 eV [77]. The much more complicated inverse photoemission spectroscopy experiment gives the electron affinity (EA) or $-\text{LUMO}_{\text{IPES}}$ [78, 79]. For these measurements it has to be clarified as well, whether the HOMO/LUMO values refer to the onset or the maximum of the (first peak of the) DOS. Unless stated otherwise, we use the onset because most of the mobile charge carriers are found at the onset of the DOS close to the band edge. We also call these values transport levels E_{ht} and E_{et} . Their difference is the transport gap $E_{\text{g}}^{\text{trans}}$. The exciton binding energy can then be estimated as $E_{\text{g}}^{\text{trans}} - E_{\text{g}}^{\text{opt}}$. The UPS signal is also capable of revealing information on the relative shape of the DOS. When investigating interfaces, UPS can be applied to detect interface dipoles (cf. Sect. 6.5).

Another method of monitoring surface potentials is *Kelvin Probe Force Microscopy* (KPFM) [80–83]. During this measurement a metal tip mounted on a cantilever scans over the specimen surface. The work function difference of specimen surface and tip creates an electrostatic potential and charge transfer. This potential is compensated by an applied voltage. Adjusting and monitoring the voltage allows to track potentials at the surface. The signal contains also the topology of the surface like a conventional atomic force microscopy measurement. An alternating current signal applied to the tip introduces oscillations of the tip. Their evaluation provides a higher sensitivity and allows for a separate monitoring of topology and potential.

Doping Concentrations N_{A}^{-} , N_{D}^{+} and Fermi Level E_{F}

Although the amount of doping molecules co-evaporated with the matrix in a doped film is roughly known, not all dopants are active. Consequently, only a fraction of molecules contributes to the doping effect by delivering one free charge carrier.

UPS can determine the position of E_{F} relative to the HOMO and, thus, give an idea of the doping efficiency. Thickness resolved UPS measurements are capable of monitoring the region of energy level bending starting at an interface [77]. Several subsequent measurements between breaks in the evaporation process are necessary because UPS is only surface sensitive. The result is a width of the space-charge layer which is used to calculate an effective doping concentration. A measurement based on the Seebeck effect is another method for determining the difference between transport and Fermi level [84]. Impedance measurements (see following paragraph) are capable of indirectly giving doping concentrations by measuring the capacity of space-charge (i.e. depletion) layers.

Dielectric Constant ϵ

The dielectric constant can be determined by measuring the geometric (plate capacitor) capacitance of a series of MIM devices with different thicknesses by means of *impedance spectroscopy* [85]. This method works as follows: A small sinusoidal voltage signal is applied to the sample at a given DC bias. Measured is the AC current

response. A variation of the frequency of the AC voltage gives the complex resistance (impedance) as a function of frequency. When knowing the thickness of the layer, ϵ can be calculated from the capacitance. Additionally, impedance spectra allow for the identification of processes at different time scales.

Traps

Trap distributions and response times can be measured by impedance spectroscopy as well. However, equivalent circuit models are mostly applied to fit measurement data. Another method would be *thermally stimulated current* (TSC) spectroscopy, which works as follows. Initially, trap states are filled by optical excitations or electrical injection at low temperatures [86, 87]. Then, the temperature is slowly increased. While increasing the temperature, trapped charges are thermally released and contribute to a current signal, which is detected. The temperatures at which current peaks occur are related to the energetic positions of traps within the gap.

Charge Carrier Mobility μ and Lifetimes τ

Measuring the conductivity of a film delivers the product of charge carrier density and mobility. The conductivity is easily accessible if the current-voltage relation is linear (2.34). As the conductivity contains the product of charge carrier density and mobility, it is not sufficient to state the separate values of both. In inorganics, Hall measurements are usually applied to separately measure the mobility. This technique is not applicable to organic materials due to their low mobility.

Time of flight (TOF) measurements provide estimations for μ [88]. In this measurement charge carriers are optically generated close to the surface of a film and the transient current response is measured under an applied field. From these data the transit time can be extracted and μ can be calculated by (2.33) with the knowledge of the layer thickness and the assumption of a constant electric field. Drawbacks of this method are the required thicknesses ($> 1 \mu\text{m}$) of samples and the difficulty of defining μ in case of dispersive charge transport.

Another method consists of measuring *space-charge-limited currents* (cf. Sect. 4.8.1). A fit of (4.99) to the measured J - V curve directly provides μ . A thickness series increases the reliability of this method, which requires ohmic contacts and high current flows. An experimental realization of these conditions is not easy.

From the experimental point of view, measuring the mobility in an *organic field-effect transistor* (OFET) is easy to realize. Commonly prepatterned substrates are used containing a gate metal (or highly doped silicon), a gate dielectrics (often silicon oxide), and source and drain contacts. The organic film is simply deposited on those structures. Upon biasing the gate electrode, charges accumulate in the organic layer close to the insulating gate dielectrics. These charges provide the flow of electric current between source and drain, when applying a bias to those contacts. Equations for the current in a field-effect transistor contain only the mobility as material parameter, which is easy to extract. However, the mobility is measured at a lateral current in a narrow channel near the interface to the gate dielectrics and containing high charge carrier densities. As these conditions are far from a solar cell under operation, the

OFET mobility cannot be transferred directly to photogenerated charges in a solar cell.

Impedance spectroscopy is also capable of delivering values for mobilities [89, 90].

A further variety of transient measurements exists to extract the mobility. They have to be applied with caution due to RC limitations resulting from a delay time due to charging/discharging the electrodes of the solar cell, which behaves like a capacitance. The required current cannot be provided instantaneously due to the series resistance of the electrodes and the input resistance of the measurement equipment. These constraints lead to a delay time of the current for e.g. a step in the applied voltage. The *photoinduced charge extraction in linearly increasing voltage* technique (Photo-CELIV) [91] is suited to extract commonly one effective value for the mobility, where it remains unclear whether the mobility of the hole, the electron, or the sum of both is measured. In this method a voltage ramp characterized by $dV/dt = 0$ is applied after a short light pulse provided by a laser. The capacitive response of the device and circuitry is seen in a constant displacement current due to a constant $J_{\text{displ}} = C \cdot dV/dt$. The additionally measured current is then due to extracted (photogenerated) charge. The mobility can be derived from the delay and height of the peak representing the extraction current. Varying the delay between illumination pulse and the extraction ramp allows to extract also parameters regarding the lifetime/recombination. One drawback of this method is that an injection and/or an early extraction of charge carriers is detrimental. This disadvantage is minimized by applying a forward voltage to the solar cell. The voltage is selected to operate the solar cell close to field-free conditions (“flat band”). Another option is to disconnect the solar cell from the measurement circuit during the delay time. An elegant improvement of CELIV is a technique called open-circuit corrected charge-carrier extraction (OTRACE) [92]. There, the voltage applied during the delay time is the one previously measured from a photovoltage decay experiment. This means that charges are not injected or extracted during the delay time. The only drain for charge carriers is recombination. Due to the reduced loss of charge carriers, an LED can be used as light source instead of a laser. However, relating measurement data to physical parameters is not straight forward due to non homogeneous distributions of charges carriers.

The Built-In Potential V_{bi}

The built-in potential V_{bi} is a device property. In theory, it is defined as the difference between the work functions of the two contacts, either metal or doped charge transport layers. However, unpredictable interface dipoles change the vacuum level alignment and thus V_{bi} . Consequently, a direct measurement of V_{bi} is desirable. *Electro-absorption* is an applicable method where the Stark effect is exploited. Here, the change of absorption is measured under an applied small AC-signal under a constant, however adjustable, background DC bias voltage [93]. The signal vanishes as soon as the DC bias compensates for V_{bi} . Mostly, a quantitative interpretation with the desired accuracy is difficult due to non-linearities in the bias dependence

of the electro-absorption signal resulting, e.g., from different components contributing to the signal [94]. On the other hand, a careful analysis allows for a reliable determination of V_{bi} [95].

Another method could be electron holography where the phase shift between electrons passing through a thin specimen cross section and through vacuum gives information about the potential within the specimen [96]. This method, however, requires the knowledge of the inner potential of the investigated material itself. Furthermore, it demands for a complicated preparation of cross sections of samples via the focused ion beam milling of a lamella [97]. The measurement itself is performed in a transmission electron microscope (TEM). The advantage of this method lies in its capability of resolving the potential distribution within a (working) device.

CT-State Energy E_{CT} and Lifetime $1/k_{relax}$

A characterization of the CT state is difficult due to its low absorption cross section. Only highly sensitive methods give information about it. Most common is a Fourier transform spectroscopy method [98], showing the EQE caused by absorption of CT states. Also electro- and photoluminescence can be measured. Time resolved spectroscopy reveals lifetimes. We discussed those approaches in detail in Sect. 3.4.

Properties of Blends

Since mixed layers are treated as a new effective material in the simulation, it is most straight-forward to perform the mentioned measurements on blend layers as well and determine the parameters of a specific blend deposited under defined conditions, e.g. with a given mixing ratio and at a specified temperature. Deriving properties of blends from the single components is difficult. Only some values such as energy levels come close to those of the single materials, whereas mobilities are totally different and dependent on the morphology of the blend.

4.10 Summary of the Main Input Parameters for a Drift-Diffusion Model

In summary, the presented approach for a device simulation covers the processes discussed in Sect. 3.3.1 in the following way:

- Light absorption and exciton generation are modeled by a transfer matrix algorithm treating the solar-cell stack coherently, except the first glass slide.
- Exciton diffusion is modeled by a diffusion equation according to Fick's law. It is skipped for blend layers, where photogenerated excitons lead to free charge carriers at the location of photon absorption.
- The exciton dissociation mechanism at a D/A interface is, as mentioned, highly debated. Without doubt it constitutes a drain for excitons and a source of electron/

hole pairs at the heterointerface. If considered, charge transfer (CT) state dissociation can be modeled with Onsager-Braun theory.

- Charge carrier transport and extraction/injection at the electrodes are described by a drift-diffusion model, containing all relevant electrical processes like charge transport and recombination. The interplay between both is the most important mechanism determining the current-voltage characteristics. Thus, they are the focus of this book.

Both, the optical and electrical model are one-dimensional. Hence, the main conditions are flat layers with small plane roughness to exclude scattering and allow a definition of a precise layer thickness. The simulation assumes homogeneity within the surface plane and has to be fed by the following main input parameters, where in the case of blend layers effective parameters are chosen:

- layer thicknesses,
- optical constants n & κ and illumination spectrum for the optical simulation,
- energy levels: E_{ht} , E_{et} (E_{g}), relative positions and offsets and in some cases σ ,
- density of charge transport states/sites N_{C} and N_{V} ,
- doping concentrations of charge transport layers and/or work functions of metal electrodes,
- charge carrier mobilities μ_n , μ_p ,
- recombination models and constants: direct/bimolecular recombination coefficient β , CT state parameters (a , k_{relax}), SRH-constant, and
- temperature T .

4.11 Answers to the Initial Questions and Further Reading

- *Which approaches exist to model organic solar cells?*

Organic solar cells can be modeled in various ways from equivalent circuits, to drift-diffusion models, to more microscopic approaches like Monte-Carlo simulations of hopping transport. Quantum-chemical methods are used to calculate the energetics of molecules and transfer integrals for charge transport. Molecular dynamics is applied to simulate the molecular structure and arrangement in a film.

- *What are the main assumptions for a drift-diffusion model? Where are difficulties in applying it to organic solar cells?*

The drift-diffusion model is based on differential equations describing a system with continuous variables of state like electric field and charge carrier densities. Commonly, latter are assumed to be relaxed in their density of states following Fermi-Dirac statistics. Therefore, the (microscopic) nature of hopping transport including the localization of charge carriers is not well represented in this model.

- *What are the basic equations and input parameters?*

Main equations are the continuity and charge-transport equations for electrons and holes and Poisson's equation relating the electrical potential to space charge. Main input parameters are the mobility, recombination constants, and energy levels.

- *Charge carrier mobility and recombination in organic semiconductors: How can they be described? Are they interrelated?*

The mobility defines the drift velocity of charge carriers at a given electric field. However, the classical derivation of the mobility does not hold for disordered organic semiconductors. In fact, hopping is responsible for a mobility that is activated with temperature and increases with the electric field. Recombination can be of bimolecular type. One model called Langevin recombination describes a recombination limited by the movement of charges to each other. Thus, recombination scales with charge carrier mobilities.

- *What is the role of the contacts—mathematically and physically?*

The contacts define the boundary conditions in the simulation. They are a reservoir for charge carriers and with their work functions they define the built-in potential. A surface recombination velocity allows to define the selectivity of the contacts.

- *Why is the Lambert-Beer law incapable of describing absorption in organic solar cells? What is coherence?*

The Lambert-Beer law is based on the assumption of optical energy incident from one side and an absorption proportional to the intensity. This situation results in an exponentially decaying absorption profile. Organic solar cells, however, are so thin that light is transmitted through the absorber and reflected at the back electrode. This effect gives rise to interference and, therefore, a changed intensity profile. To interfere, the light has to be coherent, which is the case even for sunlight in a sub-wavelength length scale. Here, coherence means a defined relation between phases at different locations in the solar cell, which is a condition for interference.

- *What is the basic idea of the transfer-matrix model?*

Imagine a thin-film stack with several interfaces. Light incident from one side faces multiple reflections and bounces back and forth in the stack. Calculating the intensity at a position within the stack is not straight-forward. The transfer-matrix approach offers a method, where the relation between forward- and backward-flowing intensity is expressed by matrices for interfaces and bulk layers. The matrices contain only optical constants and the geometry. Multiplying these matrices allows to analytically calculate the overall reflection or transmission of a stack including multiple reflections.

- *What are the different working regimes of a single-carrier device?*

A single-carrier device can work in the ohmic regime ($I \propto V$) if the layer provides sufficient charges (e.g. by doping). If this is not the case, it works in the space-charge-limited regime ($I \propto V^2$). If traps are present, they cause an additional immobile space-charge resulting in $I \propto V^n$ with $n > 2$. In all these cases the I - V curve is symmetric in V . However, the current might be limited by injection, giving a current-voltage relation that depends on the injection mechanism (e.g. $I \propto \sqrt{V}$). The device behaves more and more like a capacitor when the injection barrier is increased.

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Chapter 5

Simulation Study on Single-Layer Bulk-Heterojunction Solar Cells

Abstract This chapter contains a detailed simulation study on a single-layer bulk heterojunction sandwiched between two metal contacts. We apply the simulation approach discussed in the previous chapter and compare the results to the predictions of approximated analytical solutions introduced in Chap. 3. In particular we investigate the interplay between mobilities and different recombination mechanisms and their effect on the fill factor and the open-circuit voltage. In the calculations we combine various properties of the bulk heterojunction with characteristics of the contacts. We point out the role of injection barriers, built-in potential, bending of energy levels, and contact selectivity. The quest for an optimum mobility will be discussed as well. In the final part of the chapter we analyze the photocurrent (dark current subtracted from current under illumination) as a function of voltage to identify processes that limit the photocurrent. In particular, we want to clarify the following points: (a) Is there an optimum mobility for charge carriers in the active layers of an organic solar cell? (b) What order of magnitude for the mobility is required for a high-performance solar cell? (c) Does the mobility influence the open-circuit voltage? (d) What does selectivity of the contacts mean and why is it important? (e) What is the role of injection barriers at the electrodes? (f) Which processes reduce the open-circuit voltage and which do not? (g) What governs the temperature dependence of the open-circuit voltage? (h) What can be learned from the intensity dependence of the photocurrent-voltage relation? (i) What is the meaning of a point of intersection between the J - V curves in dark and under illumination? (j) What does the fill factor as a function of device thickness tell?

5.1 Device Structure and Definitions

To keep the study as simple as possible, we investigate a device which consists of a bulk heterojunction (BHJ) sandwiched between two metal contacts, as depicted energetically in Fig. 5.1. In Sect. 3.3.1 it was discussed that such a BHJ “layer” consists of a blend of two materials, donor and acceptor. Light absorption takes

The content of Sects. 5.2 and 5.3 is published in [1].

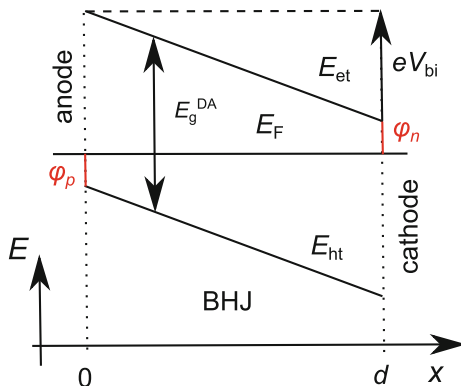


Fig. 5.1 Energy diagram of a bulk heterojunction (BHJ) as an effective medium with thickness d located between two metal contacts, which determine the built-in potential V_{bi} . Offsets between charge-carrier transport levels and the metal work function (including potentially present dipoles) give rise to injection barriers φ . The effective gap E_g^{DA} is the difference between the hole transport level of the donor (E_{ht}) and the electron transport level of the acceptor (E_{et}) in the blend

place on one or ideally on both components where an absorbed photon creates a molecular excited state, known as an exciton. This exciton migrates diffusively and is separated into a charge-carrier pair at a heterojunction. In this chapter we start our descriptions of photocurrent generation at this point. Hence, the processes treated are dissociation of the electron-hole pair, transport of the electron located on an acceptor domain and the hole located on a donor phase, and their collection at the electrodes.

As stated in Sect. 4.2.4, in a one-dimensional simulation a BHJ is modeled as a single layer between metal contacts, which define the boundary conditions. This single layer is described as an effective medium. The energy levels that charges are transported on are defined by the energy levels measured on a film consisting of the pristine materials. This approach is sufficient, as long as screening effects do not significantly change upon blending of the donor and the acceptor. Otherwise, the energy levels of the blend have to be measured separately. Using experimental data we will discuss in Sect. 8.1 that energy levels can indeed change when mixing two materials. Nevertheless, the ionization potential (IP), defining the hole transport level E_{ht} of the film, is (roughly) determined by the donor. The electron affinity (EA), which is the electron transport level E_{et} , is given by the acceptor. The energy gap, relevant for charge carrier transport, is then an effective gap E_g^{DA} , measured between these two levels.

During the following discussions the terms “majority” and “minority” charge carriers will be used. Commonly, these terms are defined for doped layers (cf. Sect. 2.2.1). Here, we relate them to the concentrations in an intrinsic BHJ close to the contacts. These concentrations are determined by an exchange of charge with the electrode as discussed in Fig. 3.34. Therefore, electrons are the majority at the cathode and holes are the majority at the anode as long as the injection barriers $\varphi_{n,p}$ are smaller than $E_g^{DA}/2$ (cf. Fig. 5.1).

The charge carrier densities at the contacts are set according to a thermal injection model (cf. Sect. 4.5). The injection barrier φ is defined as the difference between the charge transport level and the metal work function. Thus, φ_n at the cathode is given by $\text{WF}_{\text{cathode}} + E_{\text{et}} = \text{WF}_{\text{cathode}} - E_{\text{A}}$ and φ_p at the anode by $-E_{\text{ht}} - \text{WF}_{\text{anode}} = \text{IP} - \text{WF}_{\text{anode}}$. All relevant energy levels are depicted in Fig. 5.1.

As one focus of the study is on a differentiation between selective and non-selective contacts, we use (4.63) for the surface current (here shown for electrons at the cathode at position d):

$$(n(d) - n_0) s_n \stackrel{4.64}{=} \left(n(d) - N_C e^{-\frac{\varphi_n}{k_B T}} \right) s_n. \quad (5.1)$$

Here, s_n is the surface recombination velocity, and n_0 is the electron density at the cathode in equilibrium, which is replaced using (4.64). In the following, we consider a sufficient extraction of majority charge carriers. This condition is fulfilled for a metal/organic contact of working solar cells. Therefore, we can assume $s_{\text{majority}} \rightarrow \infty$, which means that the charge carrier density at the contact is fixed to $n(d) = n_0(d)$ and $p(0) = p_0(0)$. A reduced velocity or probability for the extraction of majority carriers [2] is not discussed in this chapter. In experiment such an effect can result from a thin insulating layer between metal and active material. We will focus on a reduced extraction of majority carriers due to energy barriers at the contacts in Chap. 6.

Selectivity of a contact is determined by the extraction velocity of (minority) charge carriers, i.e. charges reaching the “wrong” contact (electrons the anode and holes the cathode). For non-selective contacts, we set $s \rightarrow \infty$ and thus $p(d) = p_0(d)$, $n(0) = n_0(0)$. Selective contacts mean a perfect blocking of holes at the cathode ($s_p(d) = 0$) and electrons at the anode ($s_n(0) = 0$). Usually, metal contacts are non-selective, because both types of charge carriers are extracted. In real devices selective contacts are achieved by introducing passivation or blocking layers between metal and active material. Recalling the ideal solar-cell structure in Fig. 2.17, we recognize that any conductive material which provides one adjusted energy level (e.g. E_{et}) and a high offset in the other one (e.g. E_{ht}) should be capable of making the contact selective (e.g. blocking holes). In experiment, often very thin (order of 1 nm) low-conductivity layers are inserted, which are only partially selective and loose selectivity in case of larger forward bias, where charges might tunnel through the thin energy barrier. Nevertheless, the selectivity for voltages below V_{oc} is still beneficial for device performance [3].

Apart from charge carrier densities, the contacts also define the built-in potential V_{bi} , which is given by the difference between the work functions of anode and cathode. It can equivalently be expressed using E_{g}^{DA} and the injection barriers:

$$eV_{\text{bi}} = E_{\text{g}}^{\text{DA}} - \varphi_n^{\text{cathode}} - \varphi_p^{\text{anode}}. \quad (5.2)$$

In the following sections, we examine variations of the charge carrier mobilities and recombination parameters to investigate the interplay between generation

Table 5.1 Standard input parameters for the simulations

Parameter	Name	Value
E_g^{DA}	Donor-acceptor transport gap	1.2 eV
$N_C = N_V$	Effective density of states	10^{21} cm^{-3}
ϵ_r	Dielectric constant	5
d	Device thickness	50 nm
G	Optical generation rate	$1.5 \times 10^{22} \text{ cm}^{-3} \text{ s}^{-1}$
$c_t N_t$	SRH recombination constant	$0/10^8 \text{ s}^{-1}$
$\varphi_n = \varphi_p$	Injection barriers	0.1/0.3 eV
T	Temperature	300 K

The values might represent a typical ZnPc:C₆₀ bulk heterojunction solar cell

and recombination processes and the relation between the current in the dark and under illumination. Recalling the previous chapter, we know that a drift-diffusion simulation requires several input parameters, which are set to values representing an ordinary solar cell and are given in Table 5.1.

Note that the qualitative conclusions of the following investigations are not sensitive to these fixed parameters. In contrast to the discussed trends, absolute values might shift, e.g., photocurrents depend linearly on Gd . The absolute values of the open-circuit voltage V_{oc} change with E_g^{DA} and N_C/v . A variation of ± 2 in ϵ is not significant. Solar cells based on thicker layers (larger d) generally require a higher μ to reach the same fill factor as thinner solar cells. However, d does not significantly change the presented results as all plots show μ in a logarithmic scale. A subsequent Sect. (5.5) will deal with variations of d as well.

5.2 On the Optimum Mobility, Contact Properties, and the Open-Circuit Voltage

5.2.1 Investigated Mobility and Recombination Models

One major material property with significant influence on organic BHJ solar-cell efficiency is the charge carrier mobility μ . The electron (hole) mobility is a function of the hopping rates between acceptor (donor) molecules and depends strongly on the morphology of the intermixed layer. In the effective medium approach of a one-dimensional simulation, all these effects are included in μ , which therefore has to be seen as an effective parameter. For simplicity, we assume μ to be independent of the electric field and charge carrier densities. We defined μ as the proportionality factor relating the effective drift velocity v of an electron to the electric field F via $v = -\mu F$ (2.33). The diffusion current is also proportional to μ assuming the validity of the Einstein relation (4.14).

According to its definition, the mobility determines how fast electrons respond to an applied electric field. Therefore, one might conclude that the mobility is not

important for a solar cell under operation, which is a point of steady state. However, the extraction of photogenerated charges is in competition with recombination, which is a loss mechanism. This means, the longer the charges remain in the device, the higher is the probability for a recombination event. As the field in the device decreases with applied forward bias, the drift velocity becomes smaller and recombination more likely. This interplay commonly limits the fill factor (FF) of organic solar cells and eventually the short-circuit current density (J_{sc}) as well. Thus, a high mobility is expected to be beneficial for a high device performance.

However, there is one peculiarity regarding disordered low-mobility semiconductors. The recombination itself can linearly scale with the mobility as described by Langevin theory (4.46). Thus, a high mobility also increases the detrimental process of recombination. Furthermore, organic solar cells are very thin. Photogenerated charge carriers can reach the wrong electrode, where they are extracted as well. This process is a source of surface recombination enabled by non-selective contacts. As it requires a (diffusive) transport of the charge carriers towards the electrodes, surface recombination is expected to be influenced by the mobility as well. The importance of Langevin and surface recombination triggered several theoretical studies on the role of the mobility [4–8]. Some of those lead to claims of an optimum mobility, which has not yet been experimentally verified.

In the following, we will systematically investigate the interplay between charge extraction and recombination. The latter can be described with the models presented in Sect. 4.4.2 in detail. For the sake of comprehensibility the main equations are rewritten here:

- Direct (bimolecular) recombination, where a free electron recombines with a free hole (4.46):

$$R_0 = \beta \cdot (np - n_i^2). \quad (5.3)$$

The recombination constant β can be assumed to be independent of the mobility or it may follow Langevin theory according to (4.46):

$$\beta_L = \frac{e \cdot (\mu_n + \mu_p)}{\epsilon_0 \epsilon_r}. \quad (5.4)$$

Furthermore, a modification of β_L according to Koster et al. [9] can be applied, replacing the sum of the mobilities in (5.4) by the minimum of the two mobilities:

$$\tilde{\beta}_L = \frac{e \min(\mu_n, \mu_p)}{\epsilon_0 \epsilon_r}. \quad (5.5)$$

- Recombination via CT states including geminate recombination. Here, on the one hand, a photogenerated bound electron-hole pair recombines before the charges have completely separated. On the other hand, a free electron-hole pair does not instantaneously vanish after recombination, as electron and hole first form

(“recombine” into) a CT state. This state either dissociates again or relaxes with the rates k_{diss} and k_{relax} , respectively. According to (4.52) and (4.53) this process can be summarized in modified rates for the generation G and recombination R of free charge carriers considering a certain (dissociation) probability P :

$$G = G_0 P; \quad R = R_0 \cdot (1 - P); \quad P = \frac{k_{\text{diss}}}{k_{\text{diss}} + k_{\text{relax}}} \quad (5.6)$$

with

$$k_{\text{diss}} = \beta e^{-\frac{E_B}{k_B T}} \cdot f(F, E_B), \quad (5.7)$$

where $f(F, E_B)$ summarizes the further dependence of k_{diss} on the binding energy E_B of the CT state and on the electric field F . An exact expression of f is not required at this stage.

- Trap-assisted recombination, where a simplified (midgap traps and same capture coefficients for electrons and holes) SRH expression (4.50) is used:

$$R_{\text{SRH}} = c_t N_t \frac{np - n_i^2}{n + p + n_1 + p_1}. \quad (5.8)$$

5.2.2 Recombination only in the BHJ Guaranteed by Selective Contacts

In this section we investigate different recombination mechanisms within the BHJ. Hence, we have to assume selective contacts, where a loss of charge carriers via surface recombination is excluded.

Figure 5.2 shows the power-conversion efficiency η as a function of electron and hole mobility for the different recombination models. In case of direct recombination with a constant recombination coefficient β (Fig. 5.2a), the efficiency increases with mobility of each charge carrier type independently of the mobility of the other one. The reason is an enhanced efficiency for the collection of charge carriers if the mobility of one charge carrier is increased. An optimum extraction efficiency is obtained for $\mu \approx 10^{-2} \text{ cm}^2/\text{V s}$, where η reaches saturation. The absolute value of η depends on the choice of β (here $7.23 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$) and obviously on G and E_g^{DA} .

In case of Langevin recombination (Fig. 5.2b), η can be negatively affected by a too high mobility of one charge carrier. The optimum efficiency is found for balanced mobilities, as proposed in another modeling study [10]. The reason is that the recombination constant in (5.4) is dominated by the faster charge carrier, whereas the collection of charge carriers requires the extraction of both types of charge carriers, i.e. electron and hole. Consequently, the slower charge carrier limits the extraction

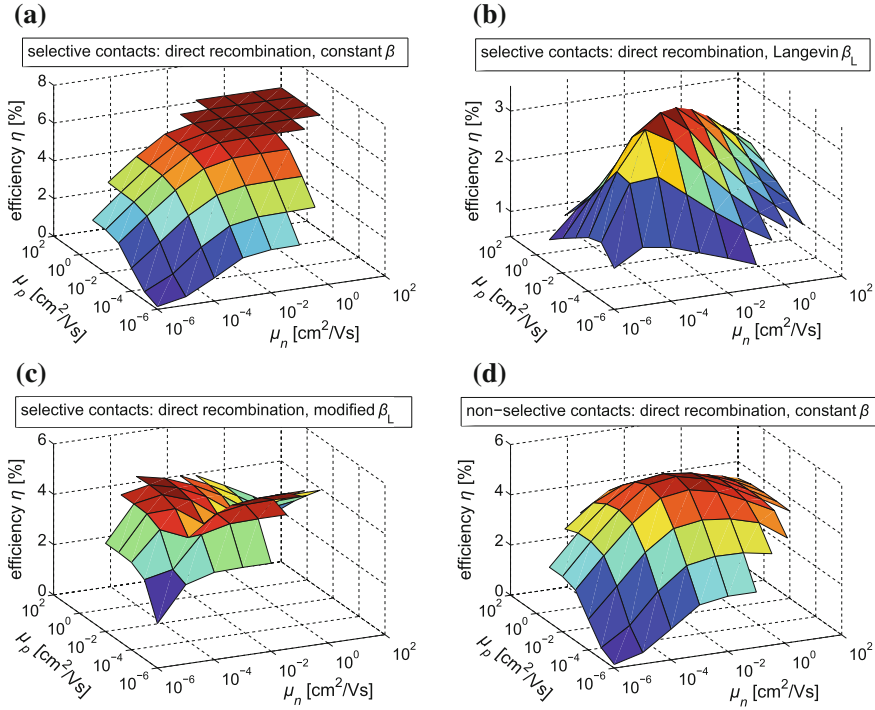


Fig. 5.2 Efficiency η as a function of electron and hole mobility μ_n and μ_p for different recombination models and contact properties: **a–c** Selective contacts with **a** constant β (qualitatively similar to Langevin recombination via a distinct CT state); **b** direct Langevin recombination; **c** same as case (b), but with a modified Langevin β_L according to (5.5). **d** Non-selective contacts and a constant β

efficiency, although the faster charge carrier can compensate for the slower one to some extent. The imbalance in transport causes a pile-up of the faster charge carriers close to their electrode. They cannot be collected in a sufficient way, because in steady state the same amount of positive and negative charge has to be extracted. Otherwise the device would continuously charge itself. However, the piled up charges create a space-charge [11] which increases the electric field close to the electrode where the slower charge carrier is extracted (cf. inset of Fig. 5.17). Therefore, the extraction of the slower charge carrier is enhanced. However, the FF is lower in case of imbalanced mobilities compared to the case of balanced high mobilities.

Interestingly, Fig. 5.2b predicts an optimum value for η even in case of balanced mobilities ($\mu_n = \mu_p = 10^{-3}$ cm²/V s). Although being balanced, higher mobilities lead to a decrease in efficiency. This will be explained subsequently, when we differentiate between the influences of recombination on FF and V_{oc} .

Figure 5.2c displays η as a function of mobilities under the assumption of a modified β according to (5.5). This case results in the opposite conclusion compared to the case of classical Langevin recombination. Balanced mobilities are detrimental,

because recombination is dominated by the slower charge carrier, whereas extraction can be enhanced by increasing μ of the faster one. Overall, higher mobilities are better than lower ones. However, just as for Langevin recombination, η drops for too high values ($>10^{-3} \text{ cm}^2/\text{V s}$) of the mobilities, independent of their (im)balance.

In the following, we explain the observed trends in η by separately examining the effect of the mobility on V_{oc} and the FF , which codetermine η [cf. (3.70)]. For simplicity we select the case, where $\mu_n = \mu_p$. We do not explicitly discuss the short-circuit current density, as it does not give any additional insights. Its maximum is given by the device thickness multiplied with eG_0 . For very low probabilities of charge carrier extraction it will follow the trends seen in the FF .

Direct/Bimolecular Recombination

Figure 5.3 displays (a) V_{oc} and (b) the FF as a function of $\mu_n = \mu_p$ for different recombination models. We discuss direct recombination first, where we observe a different trend in V_{oc} when comparing the case of a constant β (black crosses) with the case of Langevin recombination (β_L) (red diamonds). In the case of Langevin recombination V_{oc} decreases monotonically with μ . As η scales with V_{oc} (3.70), this decay is responsible for the observed decrease in η for high (even balanced) μ (Fig. 5.2b). The effect of a decreasing V_{oc} with μ governs η as soon as the increasing charge extraction properties seen in a rise in FF cannot over-compensate the loss in V_{oc} . This tradeoff results in an optimum mobility of $\approx 10^{-3} \text{ cm}^2/\text{V s}$.

Interchanging β_L with a constant β , results in a V_{oc} which is independent of μ . Therefore, the monotonous gain with μ in efficiency is due to an increase in FF only. Note that the two curves in Fig. 5.3 for a constant β and a β_L intersect for $\mu_n = \mu_p = 10^{-4} \text{ cm}^2/\text{V s}$. The reason is that the constant β was set to the value that Langevin recombination predicts for this mobility. Another constant value of β would simply result in a horizontal shift of V_{oc} where an increase of one order of magnitude in β results in a decrease of $\approx 60 \text{ meV}$ for $T = 300 \text{ K}$ [cf. (5.12)]. To explain the dependence of V_{oc} on μ in the case of Langevin recombination, we shortly review the origin of V_{oc} .

From Sect. 3.3.2 we know that a photovoltage is generated by an excess charge-carrier density in a device which is non-symmetric regarding positive and negative charges. Under the assumption of quasi-equilibrium, V_{oc} can be expressed by the maximum splitting of the quasi-Fermi levels, the solar cell can reach under illumination without load (3.26):

$$eV_{\text{oc}} = E_{\text{g}}^{\text{DA}} - k_{\text{B}}T \ln \frac{N_{\text{C}}N_{\text{V}}}{np}. \quad (5.9)$$

Although this equation is only valid for Boltzmann approximation with effective densities of states (N_{C} and N_{V}), we have discussed in Sect. 3.3.2 that comparable equations with possibly modified E_{g}^{DA} and $N_{\text{C}}/N_{\text{V}}$ describe a similar dependence of V_{oc} on np for a real organic solar cell as well.

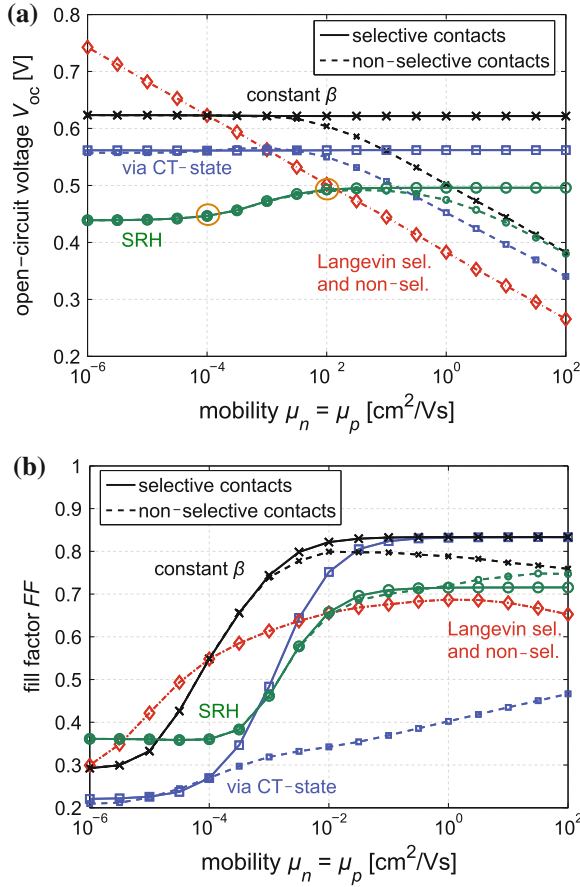


Fig. 5.3 **a** V_{oc} and **b** FF as a function of the mobility $\mu_n = \mu_p$ for different recombination models (symbols) and selective (solid lines) and non-selective contacts (dashed lines). When assuming a constant β , it is chosen to 7.23×10^{-11} cm³ s⁻¹, which equals β_L for $\mu = 10^{-4}$ cm²/V s. V_{oc} depends strongly on μ for direct Langevin recombination without CT states or in the case of non-selective contacts, where losses increase with μ due to diffusion towards the contacts. In case of Langevin recombination, V_{oc} is limited by bulk recombination for all μ as V_{oc} and FF are independent of the selectivity of the contacts. The orange circles in (a) indicate two points that are further examined in Fig. 5.5

The key point of (5.9) is a V_{oc} which increases logarithmically with the product of electron and hole density. Therefore, one might conclude [6] that a high μ reduces V_{oc} due to a more efficient charge extraction giving rise to a reduction of the charge carrier density within the device. It is correct that a higher μ results in a lower np as long as (drift) current flows ($J = en\mu F$). However, it does not hold at V_{oc} , where current does not flow by definition. Hence, no net-charge extraction occurs. Thus, μ itself cannot change V_{oc} in this case. As the data for a constant β (black crosses

in Fig. 5.3) show, V_{oc} is independent of μ despite a strongly enhanced extraction of charges (at $V < V_{oc}$).

To understand V_{oc} we need to know np in the case where current does not flow. In general, np cannot easily be calculated. However, under some assumptions we can find analytical equations describing np . For this purpose we solve the continuity equation containing the condition that charge carrier densities can only be changed upon generation, recombination, and/or a spatial gradient in particle current. This equation is the basis for the numerical simulation [cf. (4.17) and (4.18)]. It is formulated for electrons and holes:

$$\frac{\partial p, n}{\partial t} = G_{p, n} - R_{p, n} - \frac{1}{\pm e} \frac{\partial J_{p, n}}{\partial x} \stackrel{\text{steady state}}{=} 0 \quad (5.10)$$

Here, G is the optical generation rate of free charge carriers upon exciton dissociation, R the recombination rate, and J the current density. Integrating this equation over the total device thickness d gives for holes and electrons:

$$\begin{aligned} Gd &= \int_0^d \beta n(x) p(x) dx - (J_p(d) - J_p(0))/e, \\ Gd &= \int_0^d \beta n(x) p(x) dx + (J_n(d) - J_n(0))/e. \end{aligned} \quad (5.11)$$

Here, $G_n = G_p = G$ is assumed to be independent of x . R is replaced by the expression for bimolecular recombination according to (5.3), where the intrinsic charge carrier density is neglected as it is much smaller than the photogenerated one.

Net-current does not flow at V_{oc} . Thus, the overall current density $J = J_n + J_p$ has to be zero at each x , and in turn $J_p(x) = -J_n(x)$. This means that a flow of electrons into one direction has to be compensated by an equal current of holes in the same direction. In steady state, J has to be independent of x to avoid infinite charging of some regions in the device. For selective contacts the minority currents $J_n(0)$ ($J_p(d)$) towards the electrodes are zero. As the overall current has to be zero as well, $J_p(0)$ equals 0 ($J_n(d) = 0$). This situation represents V_{oc} in case of selective contacts where all charges photogenerated in the device recombine within the device. Consequently, there is no reason for large gradients in the hole or electron current. With $dJ_{p, n}/dx \approx 0$ in (5.10) it follows $G \approx \beta np$ for each x . This approximation allows us to replace np in (5.9):

$$eV_{oc} = E_g^{DA} - k_B T \ln \frac{N_C N_V}{G/\beta}. \quad (5.12)$$

Note that this equation (and its derivation) is identical to (3.29), which we used when discussing the dependence of V_{oc} on illumination intensity. V_{oc} is influenced by β and decreases with an increased β . The higher β , i.e. the “stronger” the recombination, the faster charge carriers recombine. For a given illumination intensity

represented by G , an increase of β implies a lower np ($G = \beta np$) and thus a lower V_{oc} .

The mobility is not contained in (5.12) in the case of a constant β . Therefore, μ does not change V_{oc} . This conclusion is consistent with the data (black crosses) in Fig. 5.3a. However, μ enters (5.12) in the case of Langevin recombination, where $\beta = \beta_L(\mu)$. Therefore, V_{oc} is expected to decrease logarithmically with β and consequently with $\mu_n + \mu_p$. This trend is observed at the data (red diamonds) in Fig. 5.3a.

Recombination via CT States

Now we want to investigate whether a modified recombination path via CT states influences V_{oc} in a characteristic way. The blue squares in Fig. 5.3 show that V_{oc} follows a similar behavior with μ as in the case of a constant β , despite the application of (5.4) for β . A high FF requires higher mobilities because charge extraction competes with geminate recombination. The absolute values of V_{oc} and in particular the FF depend on the choice of the model and its parameters describing the CT state. Here, Onsager-Braun theory is applied assuming a geminate pair with a binding energy E_B of 350 meV [cf. (3.89)] and a relaxation rate k_{relax} of $10^6 s^{-1}$. These values result in a V_{oc} of around 0.57 V, which is independent of μ and β_L [4]. This is not surprising when we recall the discussion in Sect. 3.3.2, which lead to (3.39). That equation was derived assuming $dJ_{p,n}/dx \approx 0$ in (5.10) as previously and applying (5.6) and (5.7):

$$\begin{aligned} G &= G_0 P = R = R_0 \cdot (1 - P) \\ \Rightarrow G_0 &= R_0 \cdot \frac{1 - P}{P} = R_0 \cdot \frac{k_{relax}}{k_{diss}} = R_0 \cdot \frac{k_{relax}}{\beta e^{-\frac{E_B}{k_B T}} f(F, E_B)}, \end{aligned} \quad (5.13)$$

where R_0 is bimolecular recombination between free charge carriers according to (5.3).

Replacing np in (5.9) by (5.3) and (5.13) yields:

$$eV_{oc} = E_g^{DA} - E_B - k_B T \ln \left(\frac{N_C N_V k_{relax}}{G_0 f(F, E_B)} \right). \quad (5.14)$$

The step-by-step derivation of this equation can be found in Sect. 3.3.2. Equation (5.14) shows that the equilibrium between generation and recombination becomes independent of β . V_{oc} is determined by the lifetime $1/k_{relax}$, the dissociation probability, and the energy of the CT state.

Comparing (5.14) with (5.12) reveals a significant difference in the temperature dependence of V_{oc} which was already sketched in Fig. 4.7b. Equation (5.12) predicts a maximum value for $V_{oc}(T = 0 \text{ K})$ of E_g^{DA}/e . For a β which is independent of temperature V_{oc} scales linearly with $-T$. The slope of $V_{oc}(T)$ is governed by β and G , where the latter scales with illumination intensity. This is illustrated in Fig. 5.4 showing two curves for different values of β (marker x), where the (negative) slope is lower for a reduced β .

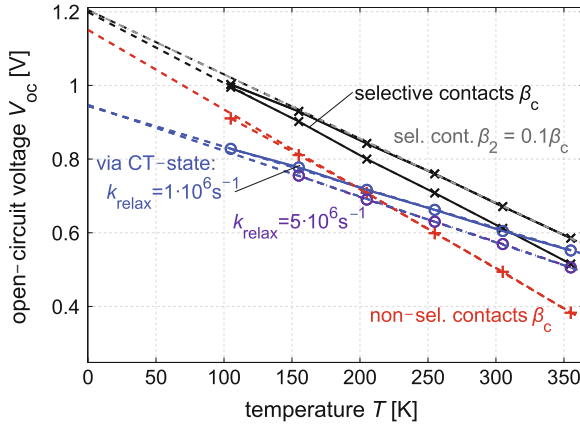


Fig. 5.4 Dependence of V_{oc} on temperature for different recombination constants β ($\beta_c = 7.23 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$), CT-state lifetimes $1/k_{\text{relax}}$ ($E_B = 290 \text{ meV}$), and non-selective contacts (+) ($\mu = 1 \text{ cm}^2/\text{V s}$). The slope is determined by β for direct recombination without CT state and by k_{relax} for recombination via CT states. In the simulation Onsager-Braun theory is assumed, demanding for very high lifetimes of CT states to result in a realistic dissociation probability for the selected E_B . Dashed lines are linear extrapolations of $V_{oc}(T = 250 \dots 350 \text{ K})$, reaching E_g^{DA}/e for direct recombination and the CT state energy for a recombination via CT states. Surface recombination due to non-selective contacts changes $V_{oc}(T)$

In the case of recombination via a CT state (5.14), $V_{oc}(T = 0)$ is reduced to $E_g^{\text{DA}} - E_B$, which is the energy of the CT state E_{CT} . The slope of $V_{oc}(T)$ is then, according to (5.14), determined by the parameters describing the CT state (circles in Fig. 5.4).

Extrapolations of $V_{oc}(T \rightarrow 0)$ yielding either E_g^{DA}/e [12] or E_{CT}/e [13] were proven valid in experimental studies.

It is worth mentioning that in the case of a distribution of CT states, the independence of V_{oc} of β does not hold any more. This was theoretically elaborated for a two-level system in [4].

Trap-Assisted Recombination

Trap-assisted recombination is governed by a capture coefficient c_t (5.8). If c_t increases with μ , a qualitatively similar behavior of η with μ is expected when comparing trap-assisted and Langevin recombination without CT state: V_{oc} decreases with c_t and μ . However, assuming that c_t is independent of μ , V_{oc} is expected to be independent of μ as well. Figure 5.3 shows that V_{oc} is roughly constant, but increases slightly with μ (green circles, $N_t c_t = 10^8 \text{ s}^{-1}$). The absolute value of V_{oc} depends on the choice of $N_t c_t$. This slight increase can be explained with the aid of charge carrier density and recombination profiles at V_{oc} shown in Fig. 5.5. These profiles give information on spatial distributions between the two electrodes. We recognize a large gradient in the charge carrier densities comparable to the data in Fig. 3.34.

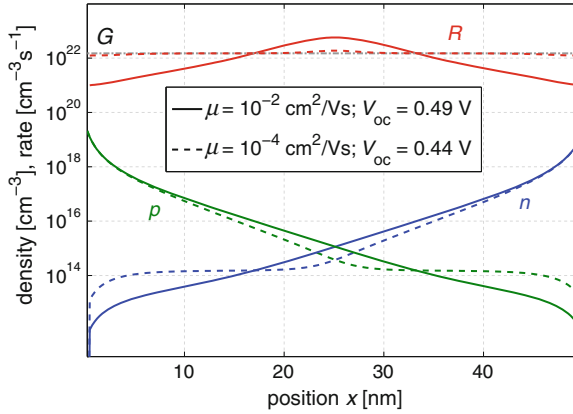


Fig. 5.5 Electron (n) and hole (p) density and the recombination rate (R) within a device, where trap-assisted (SRH) recombination dominates. The data are obtained at V_{oc} , i.e. 0.49 V for $\mu = 10^{-2} \text{ cm}^2/\text{V s}$ and 0.44 V for $\mu = 10^{-4} \text{ cm}^2/\text{V s}$ (points marked in Fig. 5.3a). Recombination close to the contacts is higher for a lower value of μ , which reduces V_{oc}

The gradient is due to high concentrations of majorities close to their contacts. These equilibrium or (dark) background charge carriers result from low injection barriers at the contacts according to (5.1).

We compare data obtained for two different values of μ ($10^{-2} \text{ cm}^2/\text{V s}$, $10^{-4} \text{ cm}^2/\text{V s}$). In case of a high mobility (solid lines), photogenerated charge carriers tend to move towards the center of the device. Consequently, the minority carriers approach their low dark (equilibrium) densities closer to the contact. Thus, the recombination maximum is found in the center of the device, where electron and hole densities are both moderate. For low mobilities (dashed), charge carrier transport is slower than the recombination process. Therefore, charge carriers recombine mainly where they are created. This situation leads to an increased minority carrier density close to the contacts and consequently an increased recombination there, where the (dark) majority concentration is large. The result is a lower V_{oc} .

We can conclude that the presence of background charge carriers and a redistribution of photogenerated charges results in a V_{oc} that depends slightly on μ . The condition for such a redistribution to change V_{oc} is that R is not simply proportional to np . In case of trap-assisted recombination (5.8), recombination close to the contacts is approximately proportional to the minority charge carrier density. We will see later that the effect of μ on V_{oc} becomes even weaker if we reduce the majority carriers by introducing higher injection barriers. This proves that the majority carriers are responsible for a $V_{oc}(\mu)$. Whether such an effect is relevant in experiment remains undetermined.

5.2.3 Recombination (also) at Electrodes Due to Non-selective Contacts

So far, the device performance was mainly governed by the properties of the bulk heterojunction itself, as we assumed ideal, i.e. energetically well-adjusted and selective, contacts. Now, we allow for non-selective contacts, i.e. a surface recombination velocity of infinity in (5.1) also for minority carriers. This case is expected in experiment for a metal-organic interface without any blocking layers.

We select a constant β to investigate the influence of non-selective contacts on η . For this case, η as a function of μ_n and μ_p is shown in Fig. 5.2d. Compared to the case of selective contacts (Fig. 5.2a), η follows the same trend for low mobilities. However, it does not reach a plateau but starts to decrease for $\mu \gtrsim 10^{-2} \text{ cm}^2/\text{V s}$. This behavior is relatively independent of the model assumed for recombination of charge carriers within the bulk heterojunction. That is why we do not explicitly show the other plots here.

The reason for this universal decrease of η with high mobilities is, again, a decrease of V_{oc} , which is shown as dashed lines in Fig. 5.3a. There, V_{oc} becomes limited by the contacts independent of the bulk recombination model. Only for Langevin recombination, a difference in V_{oc} between selective and non-selective contacts cannot be observed. This is due to bulk recombination (scaling with μ) dominating over surface recombination for all μ .

To understand the effect of surface recombination on V_{oc} , we can come back to (5.10). Now, we cannot neglect the last term, which is the gradient in currents $J_{n,p}$. This gradient causes a contribution to the continuity equation which results in a decrease in R as G is constant. A decrease in R implies a decrease in charge carrier densities, as all equations for recombination scale with the charge carrier densities, cf. (5.3) and (5.8); for bimolecular recombination: $R = \beta np$. As we assumed β to be a material constant, np has to decrease for larger gradients in current. Consequently, V_{oc} is reduced according to (5.9).

We illustrate this effect by comparing the results of the numerical simulation for selective and non-selective contacts at the extreme case of a very high μ . Recombination and charge carrier density profiles are shown in Fig. 5.6a. The solid lines illustrate the case of selective contacts. As already anticipated in the previous discussions, it holds $G = R$ for each x . However, this is not valid in the case of non-selective contacts (and a high μ) as visualized by the dashed lines. R is much smaller and in particular reduced close to the contacts, where the minority carrier densities are lower compared to the case of selective contacts. Note that both recombination profiles describe the situation at V_{oc} (0.62 V for selective and 0.5 V for non-selective contacts) where the overall current is zero. However, the source term G is unmodified. Therefore, another drain than R is required.

The current profiles (Fig. 5.6b) illustrate the additional drain. They show the flow of electrons and holes, where a positive value for the holes (electrons) means a flux towards the right (left). In the case of selective contacts, charges do not move (in average in x -direction), as they effectively recombine where they are generated.

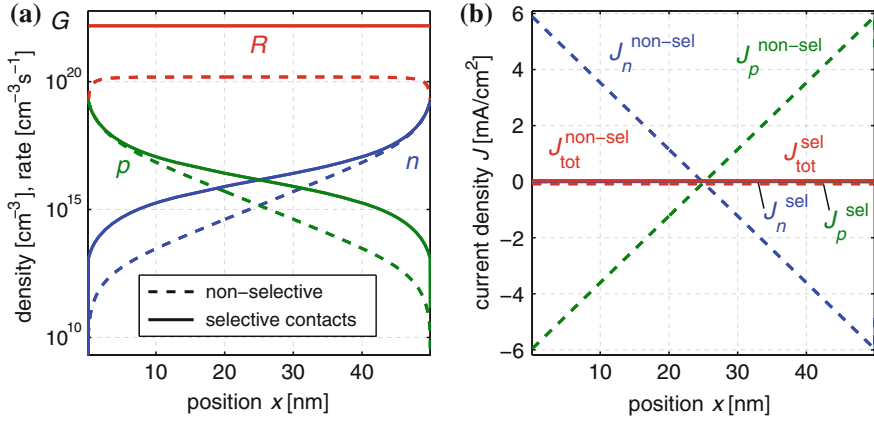


Fig. 5.6 **a** Spatial profiles of charge carrier and **b** current densities at V_{oc} for selective (solid lines, $V_{oc} = 0.62$ V) and non-selective contacts (dashed lines, $V_{oc} = 0.50$ V). Here, $\beta = 7.23 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ and $\mu = 1 \text{ cm}^2/\text{V s}$. For selective contacts, generation G equals recombination R for all x , whereas for non-selective contacts charge carriers are lost due to diffusion towards both contacts

However, in case of non-selective contacts there are equal particle currents of electrons and holes ($J_p = -J_n$, $J_{tot} = 0$ at every x) towards the electrodes. A collection of almost all charge carriers, which are homogeneously generated by absorption, gives rise to linearly increasing fluxes of electrons and holes towards the electrodes. This current of electrons and holes in the same direction is driven by diffusion due to a drain at the contacts. The diffusion current at a given particle gradient increases linearly with μ according to the Einstein relation (4.14). Consequently, with a larger μ more minority charges reach the “wrong” electrode, where they are extracted. As this extraction happens at the wrong electrode, the charge carriers do not contribute to V_{oc} but are lost due to what we called surface recombination. Comparing Figs. 5.6b to 3.40b we notice some similarities. That figure was obtained using the analytical equation by Sokel and Hughes [14] (3.86), which is often used to describe experimental photocurrents [15, 16]. We recall that this equation can be applied if bulk recombination is negligible and the solar cell works in a completely diffusion limited mode, where all charge carrier losses are due to diffusion to the “wrong” contact. It is obvious that this equation cannot be applied to devices with selective contacts. We will focus on further conditions for an applicability of this equation in Sect. 5.4.

How can we distinguish surface from bulk recombination limiting V_{oc} ? Measurements of V_{oc} as a function of intensity are capable of pointing out differences in recombination mechanisms. We have shown the effect of intensity on V_{oc} in Fig. 3.25 and will exploit it in Sect. 8.4.2. Here, we focus on the effect of temperature and device thickness.

We expect a stronger effect of the temperature T on diffusion as diffusion is activated by temperature [cf. (2.36) and (4.14)]. To prove this, $V_{oc}(T)$ for non-selective contacts is added as a red dashed line (+) to Fig. 5.4. V_{oc} decreases more

rapidly with T compared to the reference with selective contacts (solid black line, x). This curve with a higher (negative) slope can be extrapolated linearly towards $T \rightarrow 0$ K. However, $V_{oc}(T \rightarrow 0 \text{ K})$ does not result in E_g^{DA}/e , but in a lower value. If E_g^{DA} is precisely known, the discrepancy between E_g^{DA}/e and $V_{oc}(T \rightarrow 0 \text{ K})$ can be used as an indication for a scenario limited by surface recombination. For a low V_{bi} , $V_{oc}(T)$ tends to saturate due to surface recombination (cf. Fig. 3.30a).

The second approach for identifying surface recombination is a study of V_{oc} as a function of the layer thickness. Figure 5.7 shows the dependence of V_{oc} on the BHJ thickness d for a device with selective contacts and non-selective contacts. In the first case, V_{oc} is independent of d , as it simply follows (5.9). In the latter case, V_{oc} increases logarithmically with device thickness as visualized in the inset. This trend can be explained by the fact that the electric field F in the device decreases approximately linearly with device thickness ($F \approx V/d$). Thus, the drift current ($J \propto F$), which has to be balanced by a diffusion current at V_{oc} , decreases linearly with d if V is kept constant. Or in other words, as the diffusion current is proportional to the diffusion gradient, the overall diffusion gradient decreases linearly with d . A decreased diffusion gradient corresponds to a decreased gradient in the quasi-Fermi levels, which are logarithmically related to charge carrier densities. Thus, a diffusion current creates a voltage which scales logarithmically with the current. This is known, e.g., from the ideal diode (2.49). Therefore, this diffusion voltage, which is reverse to V_{oc} , decreases logarithmically with d and leads to the observed increase of V_{oc} .

When experimentally exploiting the dependence of V_{oc} on d , it is essential to adjust the light intensity to achieve a constant averaged generation rate G for all devices with different d . It can be verified at a constant ratio between photocurrent

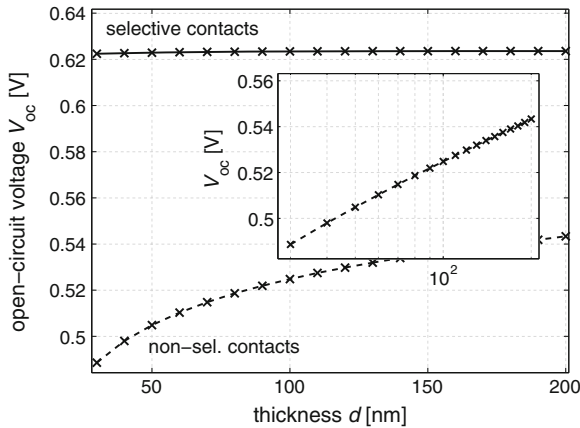


Fig. 5.7 Dependence of V_{oc} on device thickness d in case of selective (*solid line*) and non-selective (*dashed*) contacts, constant G , $\mu = 1 \text{ cm}^2/\text{V s}$, and bimolecular recombination with $\beta = \beta_L$ ($\mu = 10^{-4} \text{ cm}^2/\text{V s}$) $= 7.23 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. The distinct behavior of $V_{oc}(d)$ can be used to identify the selectivity of the contacts

and d . Observed deviations in V_{oc} for different thicknesses are then due to charge carrier losses at the “wrong” contact.

The dashed lines in Fig. 5.3a show a logarithmic decrease of V_{oc} with μ in the case of surface recombination (large μ). This can be explained analogously to the dependence of V_{oc} on d : For a constant d the total diffusion gradient is fixed by the charge carrier densities at the contacts according to (5.1). Then, the diffusion losses are directly proportional to μ and, therefore, cause a loss in voltage which depends logarithmically on μ .

To summarize this section, we can state that also in the case of non-selective contacts, it is not the increase of the transport parameter μ that decreases V_{oc} . In fact it is the indirect effect of μ being an enhancement factor for surface recombination. The qualitative difference between selective and non-selective contacts is often observed in experiment. That is one reason for interlayers at the electrodes as mentioned in Sect. 3.62 when introducing common solar-cell stacks (cf. Fig. 3.48). The highest values of V_{oc} for a ZnPc:C₆₀ BHJ are reported for devices where the blend is sandwiched between wide-gap transport layers (cf. Sect. 8.1) in a p-i-n architecture [17]. For the ideal p-i-n structure minority charge carriers cannot penetrate the charge transport layers. However, the doped charge transport layers cannot prevent the recombination of minority with majority carriers at the interface between the transport layer and the BHJ. Thus, interface recombination decreases the selectivity of the electrode. We will experimentally and theoretically elaborate on this effect in Chap. 6, where it is also shown that a planar heterojunction contains the selectivity already as a built-in property.

5.2.4 Injection Barriers

So far we discussed the situation of low injection barriers, giving rise to a $V_{bi} = 1 \text{ V} > V_{oc}$ (5.2). Now we perform the same study for higher injection barriers ($\phi = 0.3 \text{ eV}$), i.e. metal work functions that are less adjusted to the charge transport levels. Higher injection barriers result in two effects: First, according to (5.1) the majority charge carrier densities at the contacts are reduced. Second, according to (5.2) the built-in potential is reduced as well (here to $V_{bi} = 0.6 \text{ V}$). The latter is expected to be detrimental for a guided flow of charge carriers to the “correct” electrodes. In this section, we investigate the role of contact selectivity with regard to the correlation of V_{bi} and V_{oc} .

Selective Contacts

Equations (5.9) and 5.10 predict a V_{oc} that is independent of the properties of the contact, as long as contacts do not introduce a drain term for minority charges. When discussing the ideal solar-cell structure in Sect. 2.4, we have claimed that selective contacts are sufficient to obtain the V_{oc} that is intrinsic to the absorber. That is why an injection barrier does not change V_{oc} (cf. solid lines in Figs. 5.3a and 5.8a) in

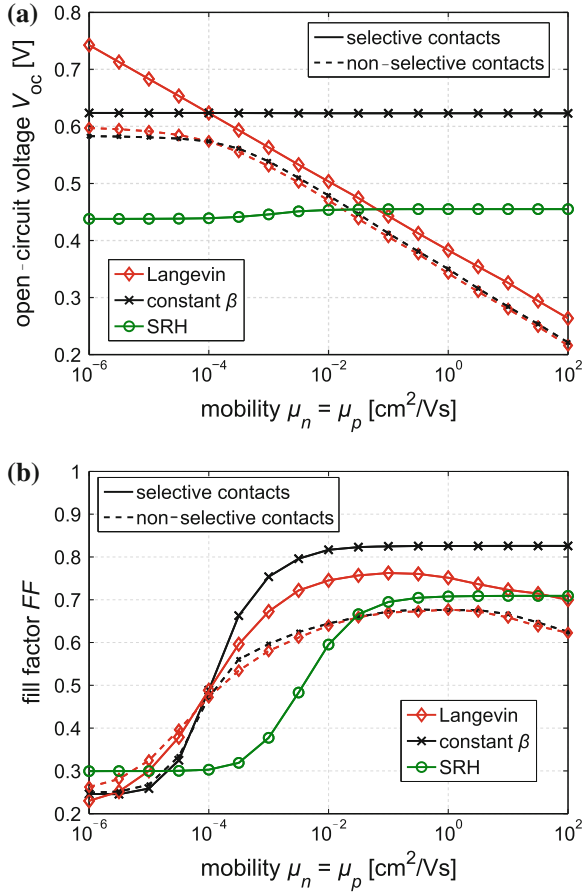


Fig. 5.8 **a** V_{oc} and **b** FF as a function of the mobility $\mu_n = \mu_p$ assuming injection barriers of 0.3 eV. V_{oc} remains unchanged compared to Fig. 5.3 for selective contacts (solid lines), whereas it decreases due to the higher injection barrier for non-selective contacts (dashed lines). The FF is affected by the injection barrier as well

the case of bimolecular recombination. V_{oc} can even exceed V_{bi} (0.6 V) as already visualized in Fig. 3.29.

The solid lines in Figs. 5.3b and 5.8b indicate that the trend of the FF with mobility is not significantly changed when introducing an injection barrier. However, there is an interesting peculiarity in case of Langevin recombination, which is shown in the inset of Fig. 5.9. Interestingly, a high injection barrier turns out to be beneficial for charge carrier extraction in case of high mobilities. Although this effect is expected to be rather unlikely in experiment, we want to understand its origin in the simulation to learn more about the role of dark carriers in the device.

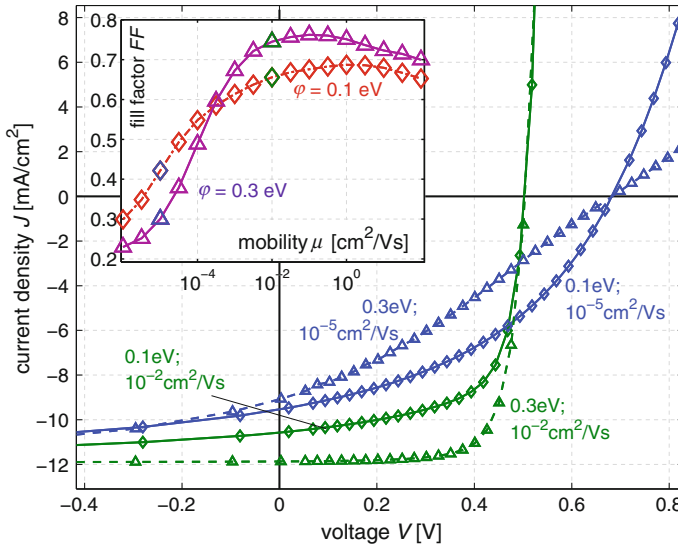


Fig. 5.9 J - V curves of devices with two different mobilities (10^{-2} and $10^{-5} \text{ cm}^2/\text{Vs}$) paired with injection barriers of 0.1 eV (solid lines, diamonds) and 0.3 eV (dashed, triangles). Recombination follows Langevin theory and contacts are selective. The *inset* compares the dependence of the FF on μ for the two barrier heights. Interestingly, the FF is higher for the device with a higher barrier in case of high mobilities. The reason is pointed out with the aid of the subsequent figure

The reduction of the FF for a low μ paired with a large φ is easy to understand. A decreased built-in field (Fig. 5.10a) and a high V_{oc} lead to a stronger dependence of charge carrier collection on the applied bias. Therefore, recombination is enhanced at the center of the device (dashed in Fig. 5.10b). The J - V curve for the large φ shows an S-kink (Fig. 5.9) because the current is mainly driven by diffusion. We will discuss this effect in Sect. 6.3.1 in detail.

More difficult to understand is the higher FF for a larger φ paired with a high μ . A high μ and therefore (Langevin) low V_{oc} provide a sufficient extraction of charge carriers also for the lower built-in field. However, the overall recombination at a given $V < V_{oc}$ is higher for a lower φ . The increase in R is due to higher densities of majority charge carriers close to the contacts as shown in Fig. 5.10c, d. These background charges increase the probability for recombination of photogenerated minority carriers close to the contacts. Note that this difference in recombination does not influence V_{oc} as it is only present as long as charge carriers are extracted. Summarizing, this example shows that background (equilibrium) charge carriers, originating from well-aligned electrodes, can be detrimental. However, in experiment, it is usually a too low mobility that limits the FF .

For completeness data for SRH recombination is also shown in Fig. 5.8. As already anticipated, V_{oc} is less dependent on μ compared to the case of a lower φ (Fig. 5.3), where more background carriers are present close to the contacts.

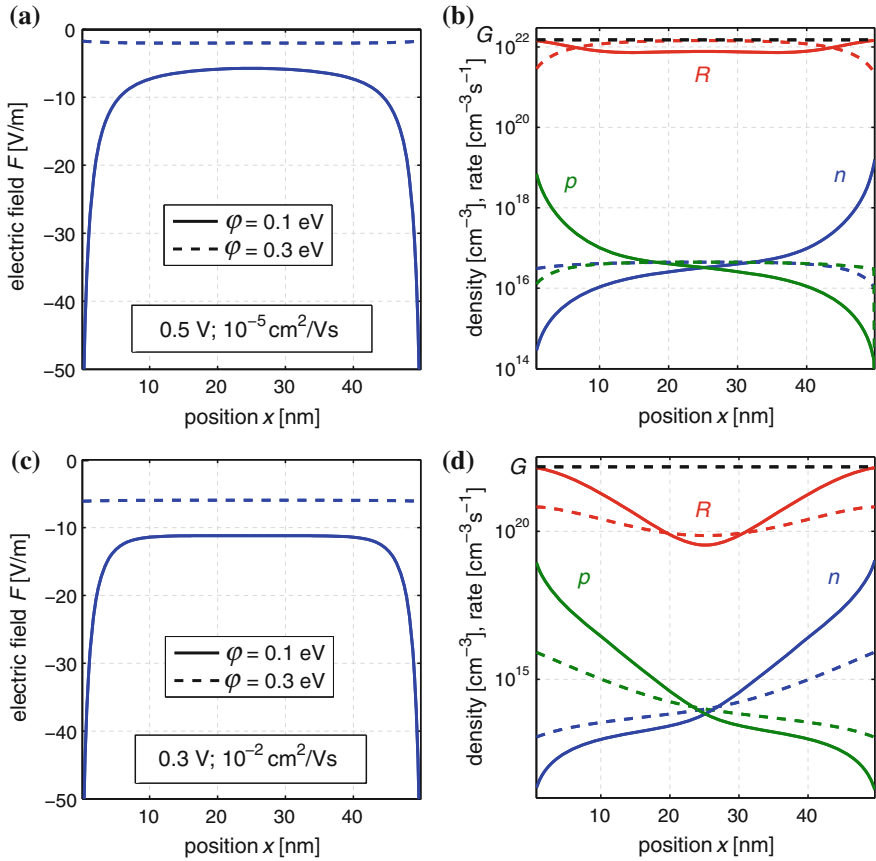


Fig. 5.10 Profiles of electric field and charge carrier densities for selected voltages of the J - V curves shown in Fig. 5.9, where Langevin recombination, selective contacts, and a varied ϕ are assumed: **a** and **b** $V = 0.5$ V and $\mu = 10^{-5}$ cm²/V s, **c** and **d** $V = 0.3$ V and $\mu = 10^{-2}$ cm²/V s. In case of a low μ and a high barrier, the overall recombination is high [dashed in (b)], whereas for a high μ (d) recombination dominates close to the contacts. For a lower ϕ , the densities of majority charge carriers close to the contacts are higher and that is why the FF is lower for low barriers and a high μ .

Non-selective Contacts

In case of non-selective contacts, η is generally lower for a higher ϕ . That is due to a lower FF and a reduced V_{oc} for an increased ϕ (dashed lines in Fig. 5.8). The reason is that diffusion to the “wrong” electrode becomes relevant at lower positive applied voltages because of the lower V_{bi} . Then, one observes two regimes in $V_{oc}(\mu)$:

On the one hand, the difference in contact work functions (i.e. V_{bi}) can directly limit V_{oc} , which happens if eV_{bi} is lower than the maximum possible quasi-Fermi level splitting in the material. In this case, there is no directive driving force at

$V_{oc} = V_{bi}$. Therefore, V_{oc} becomes independent of μ as seen for low mobilities (up to $10^{-4} \text{ cm}^2/\text{V s}$) in Fig. 5.8.

On the other hand, for higher μ ($> 10^{-4} \text{ cm}^2/\text{V s}$) the diffusion or in the case of Langevin recombination possibly bulk recombination limits V_{oc} . This is the same effect as discussed for a low φ . The larger φ , the more pronounced is the limit by the low V_{bi} compared to the bulk recombination limit. In our study, surface recombination dominates for both Langevin theory and a constant β as visualized by the roughly coinciding curves in Fig. 5.8.

5.3 Bending of Energy Levels and the Open-Circuit Voltage

In Sect. 3.3.2 we have already mentioned the role of a bending of energy levels close to the contacts. Now we can use numerical simulation as a tool to investigate the effect of bending of energy levels on V_{oc} . The inset of Fig. 5.11 shows what is meant with the bending $\Delta\phi_B$. An investigation of this bending is interesting as it reduces the field in the central part of the device to $(V_{bi} - \Delta\phi_B/e)/d$, which is below V_{oc}/d [18]. The reason for this bending is a high concentration of majority charge carriers close to the contact (low φ in 5.1), as the Fermi level approaches the charge-transport levels. The majority concentration constitutes a space charge, which gives rise to a change in the electric potential according to Poisson's equation (4.16).

From (5.1) we see that we can reduce the space charge at the electrodes by either increasing φ or decreasing the effective densities of states $N_{C,V}$. We follow the latter

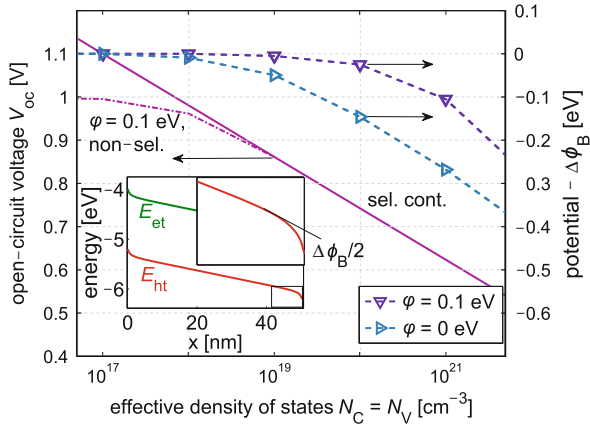


Fig. 5.11 The open-circuit voltage and the potential drop $\Delta\phi_B$ as a function of the effective densities of states $N_C = N_V$ for two values of the injection barrier φ . $\Delta\phi_B$ is due to bending of the energy levels at the contacts as depicted in the *inset*. V_{oc} is a function of N_C/V ($\beta = 7.23 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$), independent of φ , and does not directly correlate with $\Delta\phi_B$. For non-selective contacts V_{oc} is limited to a value below $V_{bi} = 1 \text{ V}$

as it does not come along with a change in V_{bi} . Figure 5.11 shows that $\Delta\phi_B$ becomes significant for $N_{C,V} > 10^{19} \text{ cm}^{-3}$ (10^{20} cm^{-3}) dependent on φ . V_{oc} is also plotted in the figure. Despite showing the same trend, the change of V_{oc} is independent of φ and does not correlate with $\Delta\phi_B$. The decrease of V_{oc} with $N_{C,V}$ is due to a completely different origin. $N_{C,V}$ represent the amount of states that can be filled not only by injected charges, but by photogenerated ones as well. Therefore, the same charge carrier density np gives rise to a lower splitting of quasi-Fermi levels and therefore a lower V_{oc} with larger $N_{C,V}$. This effect is predicted by (5.9).

The figure shows the case of non-selective contacts as well, where V_{oc} is not reduced by $\Delta\phi_B$ either. Therefore, we confirmed the statement of Sect. 2.4 saying that an ohmic and selective contact is perfect also with respect to a simulated MIM type solar cell. Note that it is not excluded that the FF might be negatively affected if the electric field in the bulk of the absorber is lower due to strong fields close to the contacts.

5.4 Photocurrent and Characteristic Points of the J - V Curve

In Sect. 3.3.5 we discussed analytical models for the photocurrent J_{photo} . It is a common approach to evaluate $J_{photo}(V)$ instead of the overall current of the J - V curve. For this purpose, $J_{photo}(V)$ is obtained by subtracting the $J_{dark}(V)$ from the one measured under illumination $J_{illu}(V)$. From the experimental point of view, one might use a pulsed photocurrent measurement to increase the reproducibility of the obtained results [19]. The reason is that the forward current is commonly very sensitive to small changes in the environment or sample, e.g. due to heating-up of the device under illumination.

The motivation for analyzing $J_{photo}(V)$ instead of $J_{illu}(V)$ is to correct for effects resulting from (dark) charge carrier injection. Considering J_{photo} allows the definition of additional characteristic points in the J - V curve. In this section, it is shown to which extent drift-diffusion simulation can contribute in describing the physical origin of these points which are:

- The open-circuit voltage V_{oc} as the point where the overall current under illumination becomes zero;
- The compensation voltage V_0 as the point where the J - V curve measured in the dark and under illumination cross each other, i.e. $J_{illu}(V_0) = J_{dark}(V_0) \Rightarrow J_{photo}(V_0) = 0$;
- The built-in potential V_{bi} as the point where the mean field within the device becomes zero.

A further point, called point of optimal symmetry $V_{POS} \neq V_0$, introduced as the voltage where most of the bulk becomes field free and to which J_{photo} is symmetrical [16, 19], did not turn out to be meaningful [20–22].

V_{oc} was already discussed in the previous section where it became clear that the processes dominating at V_{oc} depend on the properties of the contacts. If the contacts

are selective, V_{oc} is the point where all charge carriers recombine within the device. In case of non-selective contacts, bulk recombination competes with the diffusion and subsequent extraction/recombination of charge carriers at the “wrong” electrode. Thus, in the extreme case, there is no recombination of (separated) charges in the bulk. For selective contacts, V_{oc} is independent of V_{bi} whereas for non-selective contacts V_{oc} scales with V_{bi} as long as V_{bi} limits V_{oc} . In the following, we discuss $J_{photo}(V)$ as a function of illumination intensity, distinguishing between these two extreme cases of recombination.

5.4.1 Negligible Recombination in the Bulk

We want to understand the meaning of V_0 and first study the case of recombination occurring mainly at the contacts. For this purpose we select a high $\mu = 1 \text{ cm}^2/\text{V s}$, a moderate $\beta = 7.23 \times 10^{-11} \text{ cm}^3/\text{s}$, and non-selective contacts (cf. Fig. 5.6).

Figure 5.12 shows simulated J - V curves at different illumination intensities for a device with a low concentration of dark charge carriers due to high injection barriers (0.3 eV) at the contacts. All J - V curves cross at $V_0 = 0.6 \text{ V}$ which equals V_{bi} . This can be seen at the photocurrents, all reaching zero at 0.6 V. The reason is that the homogeneous field in the device changes its sign at V_{bi} . Because of the

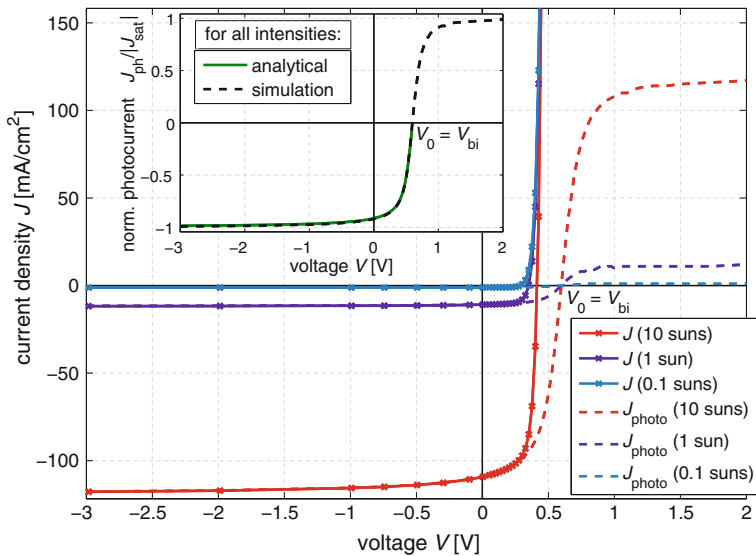


Fig. 5.12 Diffusion limit ($\varphi_{injec} = 0.3 \text{ eV}$): J - V curves and photocurrent $J_{photo} = J_{illu} - J_{dark}$ as a function of voltage for different illumination intensities. All J - V curves cross at V_0 . The *inset* shows that J_{photo} normalized to the saturated photocurrent is independent of light intensity and follows the analytical expression given by (3.86)

non-selectivity of the contacts, the net-extracted photocurrent is driven only by the electric field. Therefore, extraction works in both directions and is symmetric to V_0 . Plotting the normalized photocurrent shows that the curves coincide for all intensities and can be described by 3.86, introduced as diffusion-limited case in Sect. 5.2.3. This result means that charge carrier extraction is completely independent of μ . The consequence is an increase in FF with intensity from 62 % at 0.01 suns to 67 % at 1 and 10 suns in the case of $V_0 = 0.6$ V. The reason is that the relative photocurrent extracted at each voltage is independent of intensity. However, the FF is evaluated at the J - V curve under illumination and not at J_{photo} only. Thus, the relative effect of the injected dark forward current, which also affects the FF , becomes more important for low illumination intensities. That is why the FF decreases for lower illumination intensities relative to 1 sun, which is in contradiction to most experimental data. This result also shows that a FF larger than ≈ 67 % cannot be obtained for non-selective contacts and a $V_{\text{bi}} = 0.6$ V. Note that a larger V_{bi} shifts the photocurrent-voltage curve towards higher voltages, which results in a higher FF .

However, the FF of common BHJ is mostly lower than 67 %. If (3.86) is applied to such experimental data, additional losses are introduced and assigned to geminate recombination. In that case, the effective generation rate usually is modified according to Onsager-Braun theory (cf. Sects. 3.35 and 4.4.2) [15, 16]. Nevertheless, the photocurrent is expected to scale linearly with illumination intensity giving rise to a very weak dependence of the FF on intensity.

However, the situation of recombination only at the electrodes is not very realistic for solar cells with an optimized V_{oc} and high forward currents. Such cells comprise selective contacts (cf. p-i-n concept). Simulations of a device with selective contacts are shown in Fig. 5.13a. The dashed line shows J_{photo} normalized to its saturation

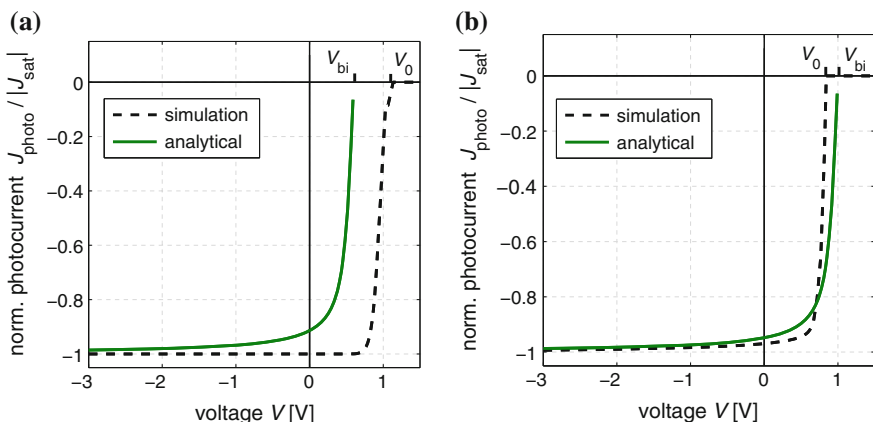


Fig. 5.13 **a** J_{photo} under the same conditions (injection barrier $\varphi_{\text{injec}} = 0.3$ eV) as in Fig. 5.12, but now for selective contacts. **b** J_{photo} for $\varphi_{\text{injec}} = 0.1$ eV. In both cases $V_0 \neq V_{\text{bi}}$ and (3.86) is not applicable. In **(a)** the selectivity increases V_0 and in **(b)** higher charge carrier densities due to a lower φ_{injec} increase bulk recombination and decrease V_0

value, as J_{photo} and V_0 are found to be independent of light intensity (curves coincide). Photocurrent cannot be observed in forward direction due to the selectivity of the contacts. However, V_0 is larger than V_{bi} and (3.86) does not describe the shape of the negative photocurrent. The reason is that the selectivity of the contacts introduces a diffusion force which increases the values of V_{oc} , V_0 , and the value of J_{photo} at a certain voltage compared to the results of (3.86).

Efficient solar cells employ ohmic contacts which imply low values of φ (here we select 0.1 eV) and, thus, high charge carrier densities at the contacts. As discussed previously (Sect. 5.3), space charge causes a bending of the energy levels $\Delta\phi_{\text{B}}$ at the contacts accompanied by a reduced field in the central region of the device. The shape of $J_{\text{photo}}(V)$ is influenced by dark carrier concentrations which are, especially close to the contacts, in the range or even larger than the photogenerated charge densities (cf. profiles in Fig. 5.10). From Fig. 5.13b, V_0 might be close to $V_{\text{bi}} - \Delta\phi_{\text{B}}/e$. However, J_{photo} is suppressed in forward direction, although non-selective contacts are assumed. The strong energy level bending close to the contacts (cf. Fig. 5.11) means a large field, which increases the selectivity of the contacts. This effect is comparable to the back-surface field applied in silicon solar cells, which was mentioned in Sect. 2.5.1.

5.4.2 Photocurrent Limited by Recombination in the Bulk

To study the effect of recombination within the device, we select a relatively low mobility ($\mu = 10^{-5} \text{ cm}^2/\text{V s}$), selective contacts, and direct recombination ($\beta = 7.23 \times 10^{-11} \text{ cm}^3/\text{s}$) as dominating recombination mechanism.

Figure 5.14 shows that the shape of $J_{\text{photo}}(V)$ is significantly influenced by the illumination intensity. This effect is independent of the value for the injection barrier, which is 0.1 eV in (a) and 0.3 eV in (b). The probability of bimolecular recombination is enhanced for higher intensities as it scales quadratically with the charge carrier density (5.3). This results in a larger dependence of J_{photo} on the voltage and, therefore, a lower FF of the J - V curve. Alternatively, we can say that J_{photo} at a given voltage is non-linear (which means sublinear here) in intensity. A decrease of FF with intensity is usually observed in experiment as well (cf. Fig. 8.20). In such a situation, obviously (3.86) is not applicable at all, as it does not contain any dependence on intensity. Observing this behavior means that the photocurrent is most likely limited by bimolecular recombination.

The most interesting result is a positive photocurrent although the selective contacts do not allow an extraction of photocurrent in forward direction. Thus, the current has to be an enhanced forward current driven by injected charge carriers. This effect can be explained by examining current and charge carrier density profiles shown in Fig. 5.15. For stronger illumination, charge carrier densities are increased within the device, especially minority densities (holes at the cathode, electrons at the anode). This leads to a higher recombination probability and a higher recombination current closer to the contacts which increases the overall forward current. In case of high

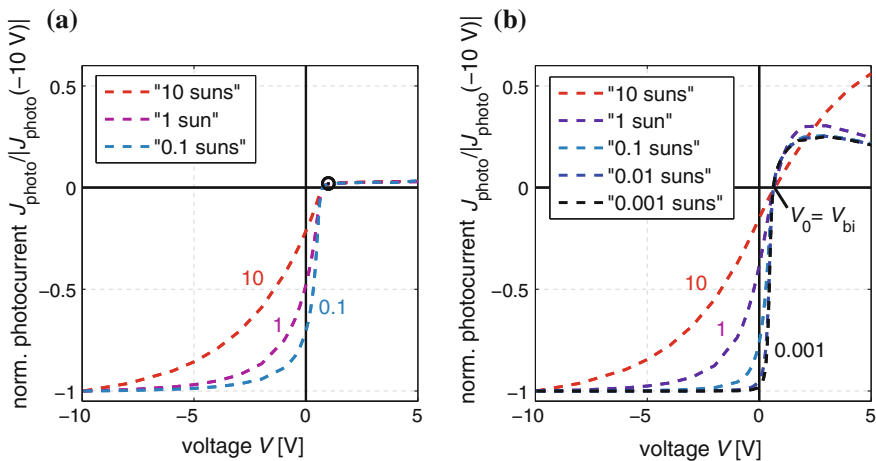


Fig. 5.14 Normalized photocurrent $J_{\text{photo}}/|J_{\text{photo}}(-10 \text{ V})|$ for different intensities and selective contacts for **a** an insignificant barrier ($\varphi_{\text{injec}} = 0.1 \text{ eV}$) and for **b** $\varphi_{\text{injec}} = 0.3 \text{ eV}$. The dependence of the normalized photocurrent on intensity is due to a high bimolecular recombination ($\beta = 7.23 \times 10^{-11} \text{ cm}^3/\text{s}$) and a low mobility ($\mu = 10^{-5} \text{ cm}^2/\text{V s}$). Positive values of J_{photo} are due to an enhanced dark injection current. This effect is examined in Fig. 5.15 at the point (1 V) marked in (a)

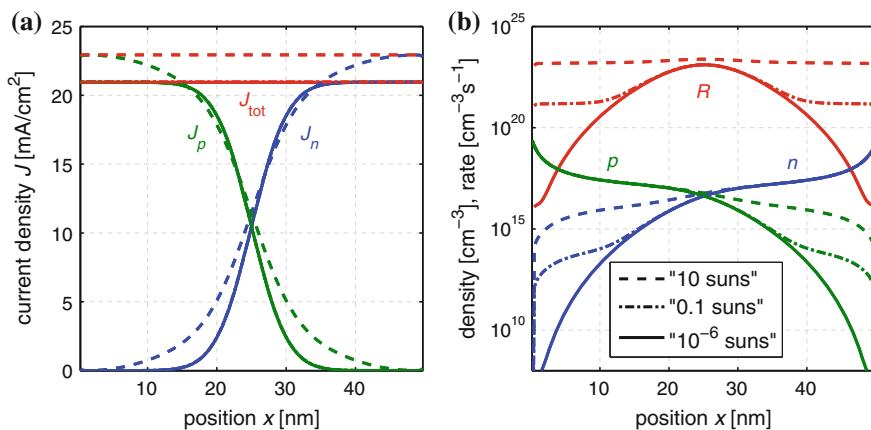


Fig. 5.15 Spatial profiles for the device of Fig. 5.14a at 1 V: **a** currents and **b** charge carrier densities and recombination rates. The charge carriers additionally present by photogeneration increase the recombination probability also further away from the center of the device. This leads to a higher overall forward current under illumination

injection barriers, even a significant change of the electric field can be present (not shown), increasing the probability for the injection of charge carriers. Consequently, a point of intersection between J - V curves in the dark and under illumination can be observed despite selective contacts. We can call the current in forward direction photoenhanced injection current, which is also discussed in [22].

There is an additional reason for a crossing between J - V curves in the dark and under illumination. This is photoconductivity, in particular of adjacent layers, e.g. electron or hole transport layers. Then, illumination simply reduces the series resistance of the solar cell. This effect can be seen in experiment if the difference between forward current in the dark and under illumination significantly exceeds the photocurrent. In this case, the shape of the J - V curve in forward is mostly close to linear.

The case studied so far was characterized by a very high bimolecular recombination rate. If we consider devices with a FF in the range of 60–70 % (at 1 sun), the non-linearity with intensity introduced by bimolecular recombination becomes less visible [23, 24]. This is shown in Fig. 5.16a, where $\beta = 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ and $\mu = 10^{-4} \text{ cm}^2/\text{V s}$. We have already mentioned the reasons for a linear scaling of the photocurrent with intensity despite bimolecular recombination (cf. Sect. 3.3.5): The J - V curve and changes in FF with illumination intensity can be dominated by injected charges if recombination is weak. That happens in the simulation of the data shown in Fig. 5.16a. For low voltages recombination appears mainly close to the electrodes where a large background charge density is located (cf. Fig. 5.10b, d). For larger voltages ($>0.5 \text{ V}$), injection of charges increases. This gives rise to an injected charge carrier density within the device that is higher than the one photogenerated for intensities smaller than 1 sun. At higher intensities (here 10 suns) recombination between photogenerated charge carriers starts to dominate leading to a reduction of J_{photo} in the fourth quadrant.

Comparing bimolecular recombination of that case (Fig. 5.16a) to trap-assisted recombination (Fig. 5.16b) does not reveal a significant qualitative difference in the

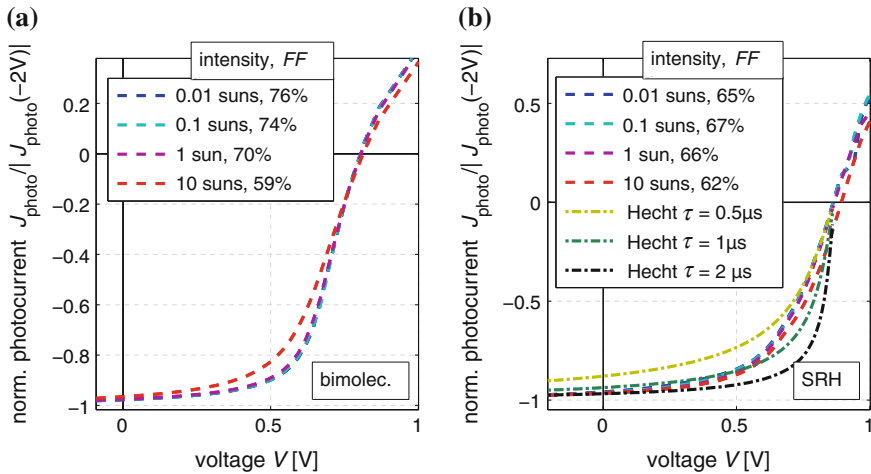


Fig. 5.16 Normalized photocurrent for devices with a high fill factor ($\mu = 10^{-4} \text{ cm}^2/\text{V s}$). **a** Bimolecular recombination with $\beta = 7.23 \times 10^{-12} \text{ cm}^3/\text{s}$ and **b** trap-assisted recombination with $c_t N_t = 10^6 \text{ s}^{-1}$. The photocurrent is almost linear in intensity at all voltages for both, bimolecular and SRH recombination. In **b** analytical results are added obtained using the Hecht equation (3.83)

behavior of the photocurrent with intensity. Consequently, a qualitative investigation of the intensity dependence of the photocurrent does not allow for unambiguous conclusions.

In Sect. 3.3.5 we introduced the $\mu\tau$ product and the Hecht equation (3.83) describing an extraction of charge carriers that is limited by the drift length. Then we expect the photocurrent to originate from regions close to the electrodes as visualized in Fig. 3.38. Charge carriers generated in the center of the device are predominantly lost as their distance to the electrodes is larger than the drift length at a given applied voltage. Simulations show that such a situation is not very likely for a well-working solar cell, as the dark charge carrier densities are very high at the electrodes and therefore increase the probability for recombination there. The high charge carrier densities also lead to a $V_0 = 0.86$ V that is smaller than $V_{bi} = 1$ V. Applying a Hecht fit using V_0 does not describe the voltage dependence of the photocurrent very well (dash-dotted lines in Fig. 5.16b). However, the lifetime extracted from the Hecht equation (μ is known) is close to the value expected from a SRH recombination constant of 10^6 s $^{-1}$, which was assumed for the simulations.

We mentioned the alignment of energy levels to the electrodes as a source of a high dark charge carrier density close to the electrodes. Another source of charges can be an (unintentional) doping of the active layer. In the extreme case, the photocurrent scales perfectly linearly with intensity, as shown in Fig. 5.17, where the curves

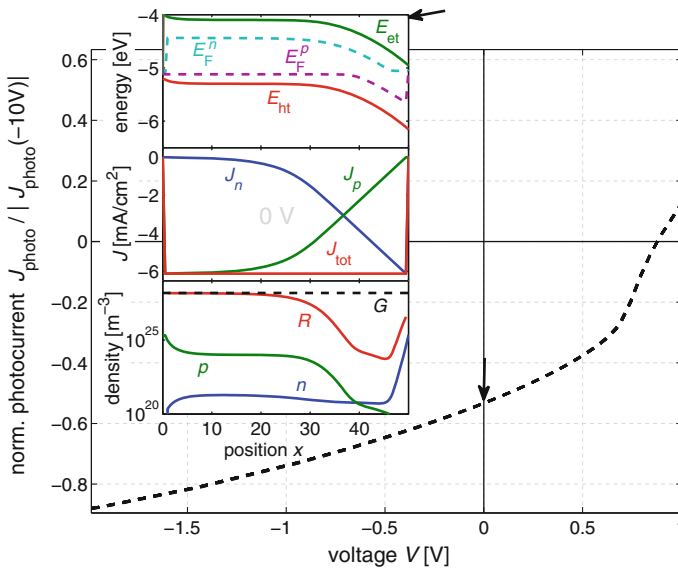


Fig. 5.17 Normalized photocurrent for bimolecular recombination ($\beta = 10^{-12}$ cm ^{3} s $^{-1}$, $\mu = 10^{-4}$ cm ^{2} /V s) and a high p-type doping $N_A^- = 10^{18}$ cm $^{-3}$. The normalized photocurrent is independent of illumination intensity (0.01 ... 10 suns). The reason is recombination of electrons with the high background density of holes as visualized in the inset (at 0 V). Photocurrent is only collected from the depletion region close to the cathode (right side). This region increases with reversed bias

for all intensities coincide. The inset visualizes that the high amount of charges screens the built-in potential. There is only a field in the depletion region close to the electrode comparable to a metal/semiconductor junction with a Schottky barrier (cf. Fig. 3.45b). Photocurrent is only harvested in this region as there is no force for charge extraction in the field-free region. There, recombination equals generation. An increased negative bias enhances the photocurrent by increasing this depletion region. Here, we assumed a very high value for the doping concentration, but lower (more realistic) values become important for thicker devices as demonstrated for the most common polymer:fullerene system P3HT:PCBM [25].

A high imbalance in mobilities can cause a similar situation characterized by significant space charge as well. In both cases, doping and high imbalance in mobility, the collection efficiency of charges depends strongly on the location of their generation. We will probe and exploit this effect in Sect. 8.3 where we systematically vary the generation profile.

We can conclude that subtracting the dark curve from the one under illumination does not always result in the photocurrent, i.e. the amount of extracted photogenerated electron-hole pairs. The presence of photogenerated carriers influences the forward current driven by injected charge carriers. Vice versa, the presence of dark carriers modifies the photocurrent in reverse. Thus, a careful analysis of the dominating mechanisms is essential including further experiments in addition to J - V measurements. Then, using the intensity dependence of the photocurrent can be a powerful approach to understand the dominating recombination mechanism.

5.4.3 Photocurrent Transients

Photocurrent transients can be used to determine whether the bending of energy levels close to the contacts or the selectivity of the contacts plays an important role. The term “photocurrent transient” refers to the time response of the solar cell upon toggling the illumination intensity. Transient signals can give information on the processes that lead to the establishment of steady state. Among those are the build-up of space charge or diffusion gradients, which are expected to result in a prominent feature of the photocurrent response. For a demonstration we choose a device with the parameters given in Table 5.1, however using a modified thickness $d = 100$ nm, generation rate $G = 10^{22} \text{ cm}^{-3} \text{ s}^{-1}$, and recombination constant $\beta = 7.34 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$.

We start with a device comprising selective contacts and high injection barriers of 0.3 eV, which limit V_{bi} to 0.6 V. Figure 5.18 shows the results of simulated transients at different applied voltages and for $\mu_n = \mu_p = 10^{-4} \text{ cm}^2/\text{V s}$. Here, the light is switched on at time 0 and switched off after 30 μs . Interestingly, close to open circuit ($V_{\text{oc}} = 0.73$ V) overshoots are observed in the signal. Other simulations (data not shown) verify that this is not the case for devices without selective contacts and a relatively homogeneous field within the layer. In Fig. 5.18 the overshoots become obvious as soon as the applied bias exceeds V_{bi} . Then, the electric field in the device operated in the dark (rough approximation: $F \approx (V - V_{\text{bi}})/d$) has changed sign and

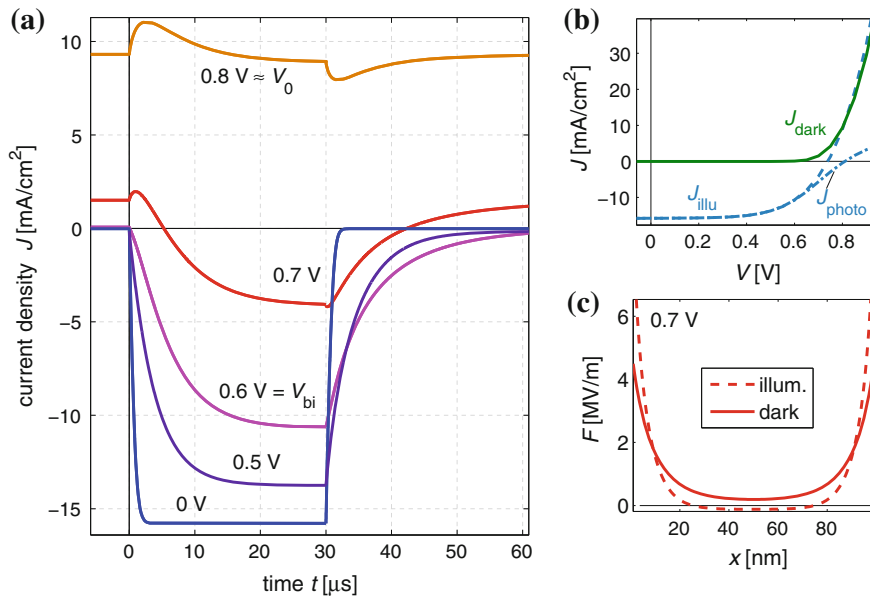


Fig. 5.18 **a** Simulated photocurrent transients upon switching on the illumination at 0 s and switching it off after 30 μs . **b** J - V curves in the *dark* (solid line), under illumination (dashed), and the difference between both (dash-dotted). **c** The electric field F within the device in the *dark* (solid lines) and under illumination (dashed lines)

photogenerated charges are driven towards the opposite electrode compared to the current flow at short circuit. This can be seen in Fig. 5.18c, showing that the field within the whole device is positive in the dark (solid line). Driven by the positive field, the current rises directly after switching on the illumination. However, the electrodes are selective, which means that they prohibit this current flow. Instead, charges pile up close to the electrode and, thereby, change the electric field with time, which is equivalent to a displacement current (cf. Sect. 4.3.5) close to the electrodes. This displacement current guarantees that the overall current is constant [cf. (4.40)]. As soon as sufficient charge has piled up, the current is reduced and can even change sign as it is the case at 0.7 V. The piled up charge has two effects: First, it causes a diffusion gradient for electrons towards the cathode and holes towards the anode, which are the designated electrodes. Second, it constitutes a space charge, which changes the electric field in the center of the device. At 0.7 V, the field (dashed line in the inset) can even reach negative values which allows for a drift current towards the correct contacts. When switching off the light, this concentration and field profile can yield a negative overshoot (here for 0.8 V), before charges have been displaced and recombined to reach steady state.

For a voltage larger than V_{oc} , J - V curves in the dark and under illumination intersect (in Fig. 5.18b for $V_0 = 0.81$ V) which is due to a photoenhanced injection current as discussed previously. Recall that in case of non-selective and poorly-injecting

contacts, it holds $V_0 = V_{bi}$ (Fig. 5.12). Obviously, in that case V_0 is independent of the illumination intensity. For photoenhanced injection currents, however, V_0 is a function of illumination intensity and increases with higher intensity (data not shown). This observation might be useful when interpreting experimental data, where this trend can also be observed.

Now we investigate a device with very high charge carrier densities at the electrodes ($\varphi = 0.1 \text{ eV} \Rightarrow V_{bi} = 1 \text{ V}$), giving rise to a strong bending of the energy levels close to the contacts. Simulation results are shown in Fig. 5.19, where we assumed $\mu_n = \mu_p = 10^{-5} \text{ cm}^2/\text{V s}$. Again, we observe overshoots close to $V_{oc} \approx 0.71 \text{ V}$. However, they are much smaller in amplitude and show the opposite direction compared to the data of the previous case. How can these features be explained? We already mentioned that V_0 (here 0.75 V) is commonly lower than V_{bi} as the electric field in the bulk changes sign before the applied voltage reaches V_{bi} due to the high field close to the contacts (cf. solid lines in Fig. 5.10). As previously, the overshoots are a result of a redistribution of charges. Photogenerated charge carriers close to the electrodes tend to drift against the injection current. Upon switching off the light, the driving force for this current is gone. Consequently the injection current rises until the displaced charge reduces the field close to the electrodes. Then the injection current decreases again. Also here, V_0 increases with illumination intensity.

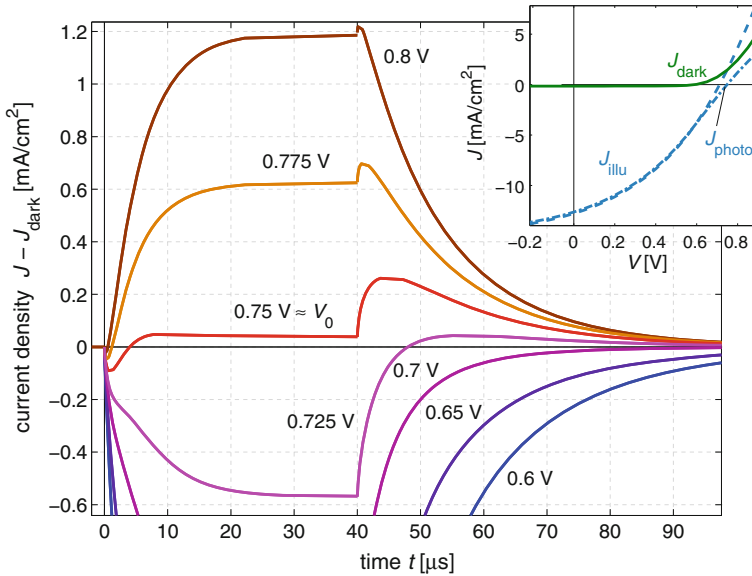


Fig. 5.19 Simulated photocurrent transients upon switching on the illumination at 0 s and switching it off after $40 \mu\text{s}$. Dark current is subtracted to better visualize the overshoots. The *inset* shows the J - V curves in the dark (solid line), under illumination (dashed), and the difference between both (dash-dotted)

An experimental observation of these overshoots depends on many factors including mobilities, recombination constant, generation profile, thickness etc. Therefore, lacking overshoots do not necessarily exclude high charge carrier densities at the electrodes. However, if the characteristic overshoots are observed, they indicate inhomogeneous field profiles within the layer and might be employed for (the so far missing) experimental verification of very high charge carrier densities and bending of the energy levels at ohmic contacts. Note that for all transient current responses the time needed to reach steady state depends mainly on charge carrier mobilities. Here, mobilities in the range of $10^{-5} \dots 10^{-4} \text{ cm}^2/\text{V s}$ result in response times in the range of μs .

Further analyses of transient photocurrents are performed when analyzing experimental data of devices with injection and extraction barriers in Sect. 6.6.3.

5.5 Fill Factor, Absorber Thickness, and Mobility Imbalance

So far we selected a constant thickness of the BHJ which we set to either 50 or 100 nm. A value of 50 nm was chosen as it is a common upper limit for state-of-the-art small-molecule solar cells. Thicknesses of efficient polymer-based devices are commonly in the range of 100 nm. Thicker active layers would allow for an increased absorption but reduce the probability for the extraction of charge carriers. Figure 5.2 already visualized that η is strongly limited by mobilities, before it saturates for sufficiently high mobilities. In the saturation regime, increasing the layer thickness enhances η further, as long as more photons can be absorbed. We will show in Sect. 10.1.2 a realistic example how an increased mobility will allow for significantly thicker layers and therefore higher power-conversion efficiencies. There we assume a calculated generation rate using the optical parameters of an absorber material as an input for the simulations. Now we want to investigate only the FF as a function of the layer thickness to draw conclusions on the role of mobilities and recombination. The FF is of particular importance here, as the decrease of η for reduced mobilities in Fig. 5.2 is due to a low FF (3.70).

Figure 5.20 shows the FF as a function of the layer thickness for different values of the mobility and the recombination constant. Examining the data one can distinguish two regimes: A thickness range where the FF strongly depends on d and a saturation regime. In the first regime, the FF drops almost exponentially with layer thickness if recombination constants are high and mobilities low. For higher mobilities the FF becomes less sensitive to the device thickness in this regime.

The second regime is interesting. For large thicknesses, the FF converges to a value of 25 % representing a straight line of the J - V curve in the fourth quadrant. This value is reached very quickly for balanced mobilities. However, in case of imbalanced mobilities, the FF becomes very weakly dependent on d starting at 150–250 nm. The reason for this behavior is the formation of a space charge due to uneven distributions of electrons and holes. As previously mentioned, this space charge screens the field. In steady state, the faster charge carrier has to wait until a slower one reaches its

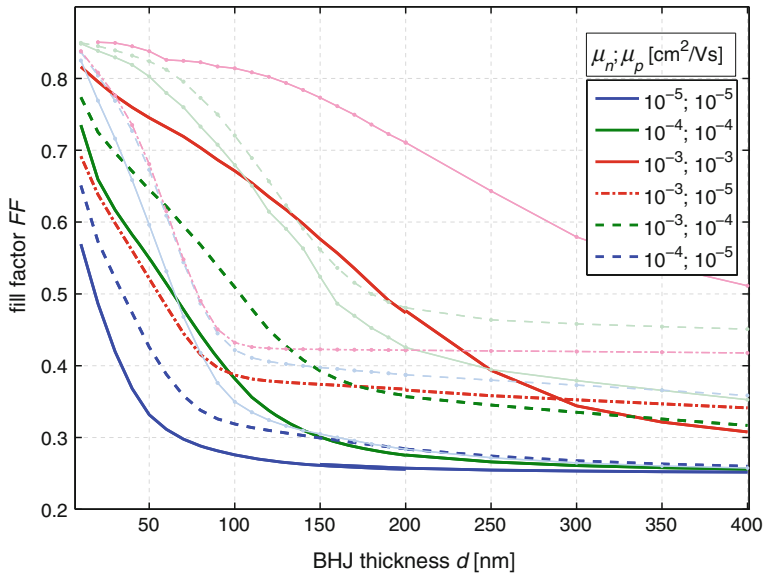


Fig. 5.20 The fill factor as a function of the active layer thickness d for different values of charge carrier mobilities μ . *Thick lines* show data for $\beta = 7.23 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ and *thin lines* for $\beta = 7.23 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$. Generally, for higher thicknesses the FF tends towards 25 % representing a straight line of the J - V curve in the fourth quadrant. In case of highly imbalanced mobilities, the FF saturates at values larger than 25 % due to space-charge effects making the region where photocurrent is collected independent of d . Therefore, such a plot is capable of giving information on the (im)balance of charge carrier mobilities

electrode. That is why faster charge carriers pile up and alter the electric field in a way that the slower ones are extracted more efficiently close to their electrode (which is a region depleted of the fast charge carriers). This means that the spatial region where photocurrent is collected for voltages between 0 V and open circuit (which is important for the FF) is significantly smaller than d and independent of d . That is why the FF saturates at a higher value as long as the fast charge carrier does not limit charge extraction through the whole d . This effect of space-charge is similar to the case of doping discussed in the preceding section. The inset of Fig. 5.17 demonstrates that photocurrent is only collected from a limited region of the device (there for $x \gtrsim 25 \text{ nm}$).

Experimental studies addressing the dependence of the photocurrent on thickness are not very common because it is difficult to only change the thickness without modifying other properties of the film related to its morphology. That holds in particular for solution-processed films. A changed morphology comes along with varied values for mobilities and eventually parameters characterizing generation and recombination.

5.6 Summary

This chapter addressed fundamental properties of the active layer and the contacts. The conclusions drawn are based on drift-diffusion modeling of the active layer as one effective medium sandwiched between metal electrodes.

The main conclusion is that V_{oc} is determined by recombination, either in the active layer or at the contacts. The latter can be avoided with selective contacts, only collecting one charge carrier type. Recombination in the active layer can be of bimolecular type, via a CT state, or trap-assisted. The recombination parameters of the dominating process determine V_{oc} . This implies that the mobility itself does not change V_{oc} , but can give rise to modified recombination rates applying Langevin theory or an increased surface recombination for higher mobilities and non-selective contacts.

The fill factor in typical bulk heterojunctions was found to be a result of the competition between charge carrier extraction and recombination. It therefore increases with increased charge carrier mobilities.

The investigation of the photocurrent-voltage relation demonstrated that even the photocurrent can reflect a superposition of dark and photogenerated charge carriers, although the dark current is subtracted. Recombination of photogenerated charge carriers with present dark carriers complicates an identification of the dominating recombination process.

We can summarize the main points of this chapter along the initial questions:

- *Is there an optimum mobility for charge carriers in the active layers of an organic solar cell?*

The answer depends on two conditions: If the recombination follows Langevin theory, there is indeed an optimum mobility because too high mobilities give rise to too high recombination constants which reduce the open-circuit voltage. There is an optimum mobility also for surface recombination. There, a too high mobility increases diffusion losses to the wrong contact. For common thicknesses the optimum mobility is in the range of $10^{-2} \text{ cm}^2/\text{V s}$. However, for non-Langevin type recombination and selective contacts, the efficiency monotonically increases with mobilities.

- *What order of magnitude for the mobility is required for a high-performance solar cell?*

A mobility of 10^{-3} – $10^{-2} \text{ cm}^2/\text{V s}$ is sufficient assuming realistic recombination parameters and layers in the 100 nm range.

- *Does the mobility influence the open-circuit voltage?*

In general, it does not. However, when it is related to recombination it does. This is the case for Langevin theory and surface recombination.

- *What does selectivity of the contacts mean and why is it important?*

Selectivity means that one electrode accepts only one type of charge carriers and blocks the other one, e.g. the cathode only extracts electrons and reflects holes. If contacts are not selective, they constitute a drain for the wrong charge carrier. This loss called surface recombination can reduce the open-circuit voltage.

- *What is the role of injection barriers at the electrodes?*
Injection barriers obviously decrease forward current. They also imply a low built-in potential compared to the donor-acceptor gap. If contacts are not selective, the open-circuit voltage can suffer from a low built-in potential. However, for selective contacts, an injection barrier does not modify the open-circuit voltage but the low built-in potential leads to inefficient extraction of charges seen in low fill factors.
- *Which processes reduce the open-circuit voltage and which do not?*
All processes changing generation and recombination rates influence charge carrier densities at open circuit and therefore the voltage. All processes related with charge transport do not change the open-circuit voltage.
- *What governs the temperature dependence of the open-circuit voltage?*
The open-circuit voltage increases with a reduced temperature, theoretically linearly approaching the effective donor-acceptor energy gap for 0 K. The slope is defined by recombination parameters of charges (lifetime of charge-transfer state) and the incident illumination intensity.
- *What can be learned from the intensity dependence of the photocurrent-voltage relation?*
The photocurrent calculated as the difference between the J - V curves under illumination and in the dark has to be handled with care. A sublinear dependence on intensity indicates a higher-order recombination, e.g. bimolecular recombination. However, a (roughly) linear scaling does not directly imply a monomolecular recombination mechanism (trap-assisted or geminate), especially in cases of a high fill factor.
- *What is the meaning of a point of intersection between the J - V curves in dark and under illumination?*
This point of intersection means that the current in forward and under illumination is larger than the dark current. There might be several reasons like an extracted photocurrent which changes sign (for non-selective contacts), a photoenhanced injection current, or photoconductivity of adjacent layers reducing the series resistance.
- *What does the fill factor as a function of device thickness tell?*
A fill factor decreasing with device thickness indicates limitations due to charge extraction. Then, a saturation of the fill factor for thick devices at values larger than 25 % indicates space-charge effects, induced either by doping or by a strong imbalance in mobilities.

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Part II
Joint Experimental and
Simulation Studies

Chapter 6

Interplay Between Electrodes and Active Materials: The Open-Circuit Voltage and S-shaped J - V Curves

Abstract This chapter contains a detailed study on the effects of energy barriers at the electrode. To vary these barriers in a controlled and systematic way, the interface between a hole-transport layer and the donor is selected. This interface serves as a model system for a contact between active layer and electrode in general. Different values for the HOMO levels of both organic materials give rise to barriers for injection or extraction of charge carriers. We discuss through experiment and simulation how these barriers influence the current-voltage characteristics, in particular the open-circuit voltage. One main observation are S-shaped current-voltage curves, which severely limit the fill factor. Such “S-kinks” are frequently observed when characterizing organic solar cells. That is why we develop methods to identify the reasons for S-kinks. Amongst those methods are measurements as a function of temperature or light intensity. Another method is based on transient photocurrent measurements, which reveal redistributions of the electric field or a pile-up of charge carriers. The following questions are of particular relevance: (a) What are the definitions of injection and extraction barriers for charges? What causes such barriers? (b) Why, and under what conditions does an injection barrier change the open-circuit voltage? (c) Why are injection barriers detrimental for efficient extraction of charge carriers? (d) What experimental approaches exist to distinguish S-kinks introduced by extraction barriers from those caused by injection barriers? (e) In which case does the illumination intensity influence the S-kink and why? (f) What can transient photocurrent measurements close to open-circuit voltage tell about the driving forces for charge carrier extraction?

6.1 Methodological Approach

In the previous chapters we have elaborated on the factors influencing the open-circuit voltage V_{oc} . We found that the maximum V_{oc} is given by the splitting of the electrochemical potentials or quasi-Fermi levels in the absorber (3.26). This splitting represents the quasi-equilibrium between generation and recombination. It contains

The content of Sects. 6.1–6.3 of this chapter is published in [1], 6.6.3 in [2], and 6.6.4 in [3].

an entropic term which depends on the charge carrier density. This term is responsible for the dependence of V_{oc} on temperature and illumination intensity. Furthermore, it includes the potential energy of an electron-hole pair, which is related to the energy levels these charges are transported on. We defined E_g^{DA} as the difference between the electron (E_{et}) and hole (E_{ht}) transport level, which might be interchangeable with the energy of the charge-transfer state [4] (cf. discussion in Sects. 3.3.2, and 5.2.2).

We have already explained that the real V_{oc} can be limited by the contacts. We attributed this loss to a collection of charges at the “wrong” electrode, which we called surface recombination. In that case, the selectivity of the contacts and the built-in potential V_{bi} play an important role. Recall that V_{bi} according to (5.2) is given as the difference between the work functions of the electrodes including modifications by surface dipoles if present.

With the following experimental study we want to verify several of those predictions. We use flat heterojunction (FHJ) and bulk heterojunction (BHJ) solar cells realized in the p-i-metal architecture (cf. Sect. 3.6.2). We systematically vary the energy levels of the donor and the hole transport layer (HTL). This approach enables us to change the properties of the interface between active layer and charge transport layer in a controlled way. The interface can be seen as a model for an interface between electrode and active material, avoiding the issues of metal-organic interfaces. The employment of different metal(-like) electrode materials of varying nominal work function usually does not result in the simple predictions discussed in Sect. 3.5.1. It is known that the properties of metal-organic interfaces depend strongly on an (unintentional) pretreatment of the metal surface, which can give rise to unknown surface dipoles. The work function can change with time after a treatment, e.g. as reported for indium-tin-oxide (ITO) treated by an oxygen plasma and afterwards illuminated with UV light [5]. The sequence of deposition, i.e. organic material deposited on metal or metal evaporated on an organic layer, changes the interface and most likely the film beneath it. We mentioned in Sect. 3.5.2 that the push-back effect or polaron states additionally influence the alignment of energy levels [6, 7]. Furthermore, unavoidable oxide layers can lead to (thin) insulating interlayers between the metal and the organics.

Obviously, the HTL has to be contacted by an electrode, which is ITO in this case. The HTL close to ITO is electrically p-doped as discussed in Sect. 3.6.2. Doping guarantees hole injection, extraction, and hence a solar-cell performance independent of the work function of the ITO anode and HOMO of the HTL [8] by shifting the Fermi level in the doped HTL close to the HOMO level of the donor material [9–11]. Consequently, we can assume that the contact ITO/p-HTL is ohmic and does not limit the current.

The solar-cell stacks under investigation are sketched in Fig. 6.1a, visualizing the combination of different HTLs and donors. Figure 6.1b shows energy level diagrams in the case of FHJ devices. Offsets in the hole-transport level of HTL and donor give rise to barriers for the transport of holes. We recognize an injection barrier (on the right), when the HOMO of the HTL lies higher than the HOMO of the donor. In the MIM picture this relates to the case of an electrode with too low of a work function

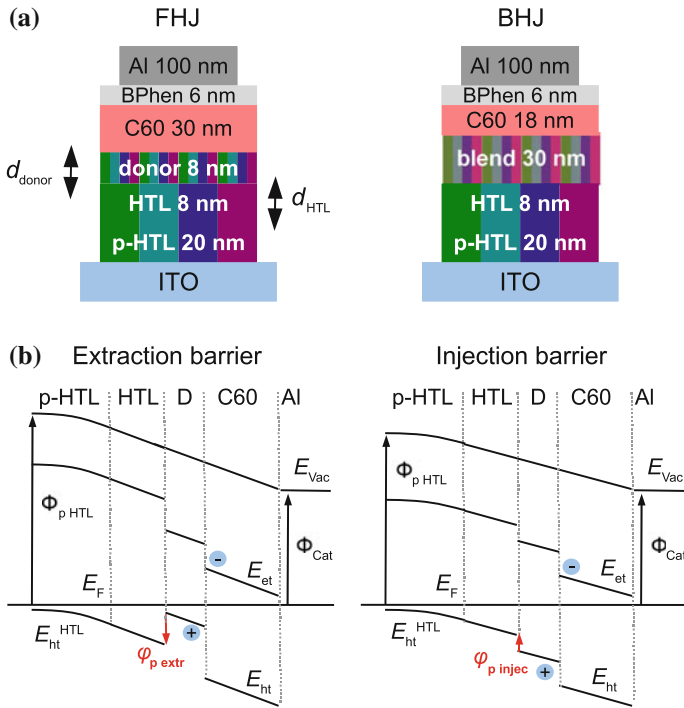


Fig. 6.1 **a** Solar-cell stack with p-doped hole transport layer (HTL) providing ohmic contact to the ITO, intrinsic HTL, the active material stack, and BPhen/Al contact. The active material stack consists in the case of a flat heterojunction (FHJ) of a bilayer donor/C₆₀ or in the case of a bulk heterojunction (BHJ) of a blend layer of donor:C₆₀ with a mixing ratio of 1:1, followed by 18 nm C₆₀. **b** Schematic energy-level diagrams of a FHJ with ϕ_p as hole extraction (left) or injection barrier (right). The type of ϕ (injection or extraction) depends on the hole transport levels $E_{\text{ht}} \approx \text{HOMO}$ of the HTL and donor materials combined

(cf. Fig. 5.1). In contrast to a metal-organic interface, the HTL-donor interface can show well-defined barriers also with a reversed sign, which we call extraction barriers. As shown on the left of Fig. 6.1b, an extraction barrier is formed if the HOMO of the HTL lies deeper than the HOMO of the donor. Note that the nomenclature of the barrier is referring to the working regime of the solar cell: An injection barrier means that there is a barrier for the injection of charges (here holes) into the device, i.e. from HTL to donor. Consequently, an extraction barrier denotes a barrier for the extraction of charges, i.e. holes photogenerated at the donor-acceptor (D-A) interface flowing towards the HTL.

Extraction barriers are also relevant for absorbers sandwiched between metal electrodes. As already mentioned, the metal surfaces might be covered by a high-bandgap and therefore very low-conductive oxide layer. This layer can behave like a barrier for charge carrier extraction and possibly injection.

In this study, nominal barrier heights between 0 and 0.6 eV are realized using HTL and donor materials with different HOMO values. Recall the ambiguity of the term “HOMO level”, which can change considerably depending on how it is measured and which type of sample it is (in solution, on films with different morphology). The energy level we are interested in here is the charge transport level E_{ht} in a thin film as denoted in Fig. 6.1b. That is why we use the (negative) ionization potential for E_{ht} . It is obtained from ultraviolet photoelectron spectroscopy (UPS onset) measured on a thin film. According to the convention of this book (cf. Sect. 4.9) it is also regarded as HOMO_{UPS} . The height of the barrier is the difference between the values for HOMO_{UPS} of HTL and donor under the assumption of vacuum level alignment at the HTL-donor interface. Commonly, vacuum level alignment is observed by UPS measurements between these kinds of intrinsic materials [12]. We will perform a detailed investigation of one of the HTL-donor interfaces in Sect. 6.5.

The experimental realization of the p-i-metal geometry follows the layer sequence ITO/p-HTL (20 nm)/HTL (8 nm)/active layer stack (48 nm)/BPhen (6 nm)/Al (Fig. 6.1a). In the FHJ devices the active layer stack consists of a bilayer donor (8 nm)/C₆₀ (40 nm) and in the BHJ devices it consists of a blend donor:C₆₀ (30 nm, 1:1) followed by C₆₀ (18 nm). The materials used as HTL and donor are ZnPc (HOMO −5.0 eV), MeO-TPD (−5.1 eV), α -NPD (−5.5 eV), and BPAPF (−5.6 eV). Their structures can be found in Figs. 3.51 and 3.54. These molecules are commonly applied as hole transporting materials, showing reasonable mobilities. Although the materials are transparent (except ZnPc) in the visible spectral range, they work as donors (in the sense of hole acceptors) in a solar cell with a photocurrent resulting from the absorption on the acceptor, C₆₀. To avoid any influence of the dopant on the charge transport over the HTL-donor interface, the HTL (8 nm) adjacent to the donor is intrinsic, i.e. undoped. All combinations of the four hole-conductive materials as donor and HTL result in 16 FHJ and 16 BHJ solar cells with nominal barrier heights ranging from 0 eV to injection or extraction barriers of 0.6 eV.

In the following, the experimental data is compared to simulation data generated by the drift-diffusion simulation described in Chap. 4. The experimental stack of Fig. 6.1 is modeled as a four-layer stack p-HTL/HTL/donor/acceptor. The thin BPhen interlayer is not explicitly considered, but is modeled via thermionic injection (4.64). The boundary condition at the p-side is obtained by assuming that the p-doped layer reaches its equilibrium concentration of charge carriers far from interfaces. Therefore, the hole density is set to an effective doping concentration of $5 \times 10^{18} \text{ cm}^{-3}$. The exact value is not crucial, but the number chosen guarantees an ohmic contact, which does not limit the current in the working regime of the device. This assumption is justified as shown by J - V measurements of samples with variable layer thicknesses that indicate a good (tunneling) contact to the metal, and the conductivity of the doped layer is high compared to the other layers in the devices. UPS measurements show that bending of energy levels at the interface of metal and highly-doped HTL is indeed restricted to 2–5 nm. At this distance, the charge carrier density adjusted by doping is reached [9, 10]. Hence, the device characteristics are ruled by the properties of the bulk layers themselves and the organic–organic interfaces for both simulation and experiment.

For simplicity, we assume a constant charge carrier mobility in the layers of our devices, where the electron mobility is pre-supposed to be roughly one order of magnitude larger than the hole mobility. The details are found in [1]. This assumption is sufficient to qualitatively describe the effect of energy barriers. We account for disorder at the interfaces. Motivated by the Gaussian disorder model, (cf. Sect. 3.2.3) we assume a Gaussian density of states (DOS) with a width σ for HOMO and LUMO, and Fermi-Dirac statistics to describe the occupation probability. As elaborated in the section on modeling (Sect. 4.6.1), the rates for charge transport at the interface are modified by a probability, which ensures a constant Fermi level in equilibrium.

The width σ of the Gaussian DOS is set to 0.1 eV and the hopping distance a to 1 nm. Similar values are generally reported for organic materials [13]. However, these parameters only change the quantity of the observed features, not the quality, and exact values are therefore not significant for the main conclusions of the following sections.

6.2 Current-Voltage Data

6.2.1 Characteristic Parameters

Before discussing complete J - V curves, we focus on the characteristic parameters of the solar cells summarized in Table 6.1. We start with V_{oc} , whose dependence on the HOMO levels of donor and HTL is additionally visualized in the sub-figures of Fig. 6.2, which show a significant difference between FHJ and BHJ solar cells.

Table 6.1 V_{oc} , FF , and the slope of the J - V curve at V_{oc} of all 32 devices under investigation

Donor		ZnPc		MeO-TPD		α -NPD		BPAPF	
HTL		FHJ	BHJ	FHJ	BHJ	FHJ	BHJ	FHJ	BHJ
ZnPc −5.0 eV*	V_{oc} (V)	0.38	0.49	0.56	0.55	0.68	0.54	0.82	0.56
	FF (%)	55	50	37	48	37	44	29	49
	$\frac{dJ}{dV} _{V_{oc}}$ (mA V ^{−1} cm ^{−2})	60	70	20	20	10	30	2	40
MeO-TPD −5.1 eV*	V_{oc} (V)	0.42	0.57	0.56	0.58	0.85	0.64	1.0	0.69
	FF (%)	51	42	44	23	35	22	28	23
	$\frac{dJ}{dV} _{V_{oc}}$ (mA V ^{−1} cm ^{−2})	50	40	30	2	8	3	0.2	10
α -NPD −5.5 eV*	V_{oc} (V)	0.41	0.55	0.56	0.58	0.83	0.83	0.95	0.93
	FF (%)	9	22	38	32	51	31	45	28
	$\frac{dJ}{dV} _{V_{oc}}$ (mA V ^{−1} cm ^{−2})	0.4	3	10	5	30	3	20	9
BPAPF −5.6 eV*	V_{oc} (V)	0.39	0.55	0.54	0.58	0.84	0.84	0.95	1.0
	FF (%)	10	7.7	10	21	46	33	49	25
*HOMO _{UPS}	$\frac{dJ}{dV} _{V_{oc}}$ (mA V ^{−1} cm ^{−2})	0.02	0.1	0.2	0.6	10	4	20	2

Four different p-type materials are employed in different combinations as a hole transport layer (rows) and/or as a donor (columns) in FHJ and BHJ solar cells

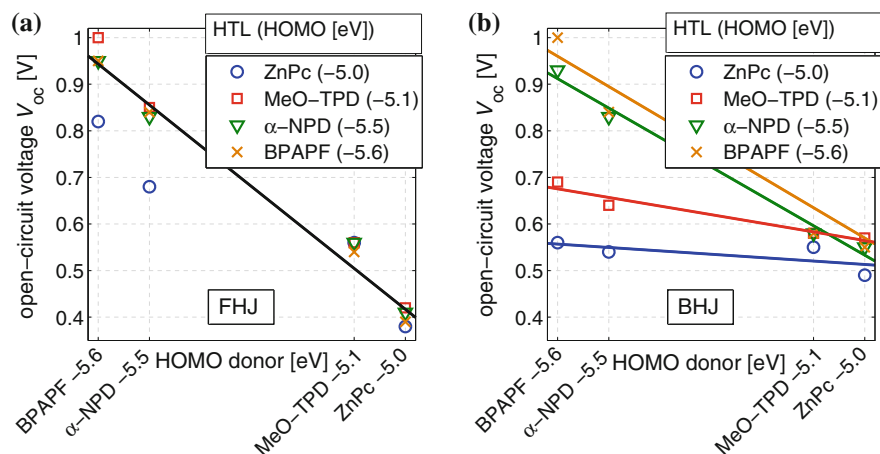


Fig. 6.2 The open-circuit voltage V_{oc} as a function of the $HOMO_{UPS}$ of the donor material in devices with different HTLs. The data shown is for **a** flat heterojunction (FHJ) and **b** bulk heterojunction (BHJ) solar cells. V_{oc} is limited by the HTL only in case of a BHJ

In the FHJ (Fig. 6.2a), V_{oc} is mostly independent of the choice of the HTL and determined by the HOMO of the donor (combined with C_{60}). V_{oc} increases when using donors with a lower lying HOMO level. The line in Fig. 6.2a indicates that V_{oc} scales almost linearly with the HOMO level and therefore with the effective gap E_g^{DA} since the acceptor is not changed. This trend is expected according to (3.26) and is commonly observed, e.g. in [14, 15]. Assuming a LUMO of -4.0 eV for the acceptor C_{60} [16], we find a difference of around 0.6 eV between E_g^{DA} and eV_{oc} . This value, which is in a common range for organic solar cells (cf. Fig. 3.33), can mainly be explained by two mechanisms. One is that a relatively high recombination rate at the D–A interface leads to low charge carrier densities (cf. Sect. 5.2.2). Another being that holes (electrons) can be located in (disorder-induced) tail states of the HOMO (LUMO) (cf. Sect. 3.3.2), effectively reducing E_g^{DA} . Both of these effects decrease the splitting of the quasi-Fermi levels and hence V_{oc} as demonstrated in previous chapters.

There is one slight exception in the experimental data, solar cells with ZnPc, which is an HTL that reduces V_{oc} of the FHJ devices with α -NPD and BPAPF as donors. In contrast to the other HTL materials, ZnPc grows in (nano)crystalline domains, which give rise to a higher surface roughness of the layer when compared to other HTL materials. Most likely this increased roughness in HTL leads to non-closed donor layers which have a nominal thickness of 8 nm. Consequently, direct contact between ZnPc and C_{60} is present, where the HTL ZnPc partly acts as a donor and slightly shunts the designated donor.

V_{oc} of the BHJ solar cells is strongly influenced by the HOMO of the HTL (Fig. 6.2b). When it is lying higher than the HOMO of the donor, i.e. causing an injection barrier, the HOMO of the HTL (roughly) limits V_{oc} . This leads, in case of ZnPc as an HTL, to a V_{oc} of around 0.55 V, which is almost independent of the donor.

Coming back to Table 6.1, we recognize that the FF of the FHJ is reduced for a mismatch of donor and HTL material (the entries beside the principle diagonal). Hence, barriers reduce the FF . Another measure for the significance of barriers apart from the FF , is the slope at V_{oc} . It is also given in the table and decreases for higher injection and extraction barriers.

6.2.2 Current-Voltage Characteristics Under Illumination

Having discussed the fingerprints of the solar cells, we now study the complete J - V curves of selected devices. We start with solar cells showing injection barriers. There, we found differences between the qualitative behavior of FF and V_{oc} for FHJ and BHJ devices. These differences become obvious from the J - V curves in Fig. 6.3,

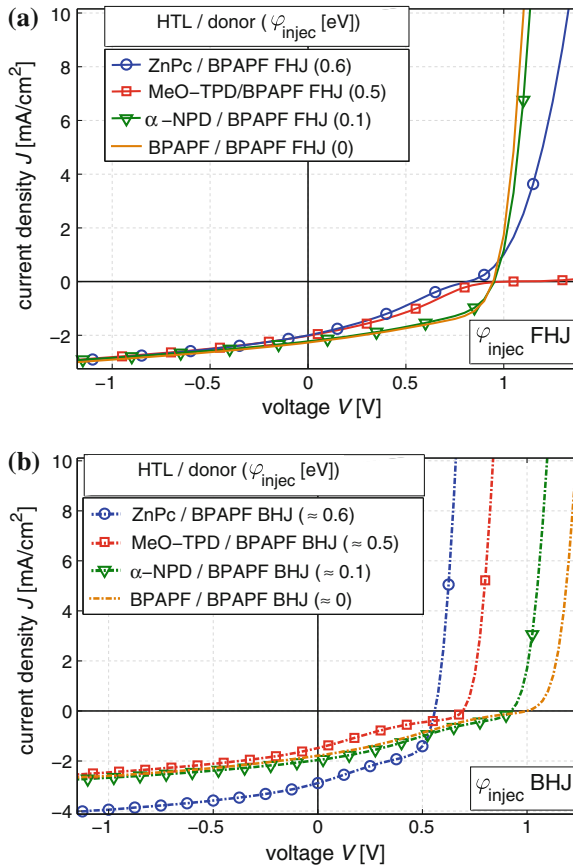


Fig. 6.3 Experimental J - V curves for devices with injection barriers (φ_{injec}) where the donor BPAPF is maintained and the HTL is varied for **a** FHJs and **b** BHJs. An S-kink occurs in case of FHJs with φ_{injec} , whereas V_{oc} is only affected by φ_{injec} in case of BHJs

where BPAPF is selected as a donor and the HTL material is varied. The forward current of the FHJ is affected by a low injection rate for holes caused by the injection barrier. As a result, the FF decreases due to a kink in the J - V curve. However, a decreased injection of forward current cannot be observed for the BHJ (Fig. 6.3b) despite an injection barrier. Instead, V_{oc} decreases with increasing injection barrier as already visualized in Fig. 6.2, when looking at a fixed donor material.

With Fig. 6.4, we turn our focus onto extraction barriers. In the case of FHJs (Fig. 6.4a), where the donor (shown is ZnPc) is held constant and the HTL is varied, V_{oc} remains independent of the HTL. However, the shape of the J - V curve changes tremendously with an increased barrier height. An S-kink emerges in the fourth

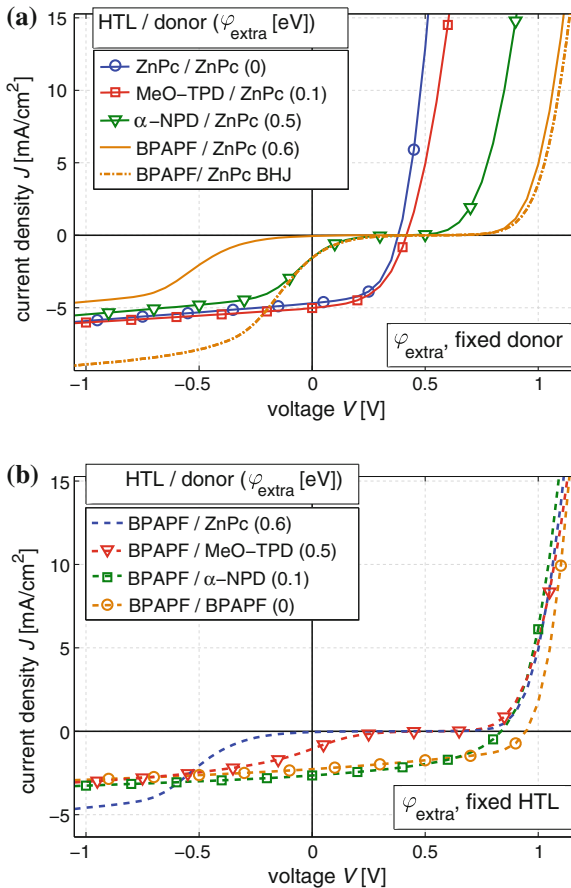


Fig. 6.4 Experimental J - V curves for FHJ devices with extraction barriers (φ_{extra}) where in **a** the HTL is varied and the donor held constant as ZnPc and in **b** the donor is varied and the HTL held constant as BPAPF. In **a** data of one BHJ (dash-dotted) is also shown. The open-circuit voltage is determined by the donor-acceptor combination and the onset in forward by the HTL. Thus extraction barriers can lead to S-kinks for FHJ and BHJ solar cells

quadrant, explaining the low FF seen in Table 6.1. The onset of forward current is shifted to a higher bias voltage, which is defined by the HTL. This can be seen in the J - V curves where the HTL (BPAPF) is held constant and the donor is varied (Fig. 6.4b). In contrast to the case of injection barriers, for extraction barriers the qualitative behavior between FHJ and BHJ is the same. As an example, the experimentally measured combination BPAPF/ZnPc is shown as the dash-dotted line in Fig. 6.4a.

The S-kink is a qualitative difference to the J - V curves discussed so far in this book. As it is relevant for many material systems [17–32], we will explain its origin in the next section and discuss further sources of S-shaped J - V curves in Chap. 7.

6.3 Detailed Microscopic Explanations

The experimental results are discussed using the simulated J - V curves shown in Fig. 6.5. The simulations reproduce the characteristic shape of the measured J - V curves (Figs. 6.3 and 6.4) over the entire voltage range. The absolute value of V_{oc} is difficult to predict with a drift-diffusion model, because it depends on several mostly unknown parameters, including the choice of recombination model, which is still under debate (see previous chapter and Sect. 8.4.2) [33, 34]. However, once having fixed these parameters, the position and eventual shifts in V_{oc} result only from the combination of HTL and donor.

In addition to the trends, the strength of the S-shape as a function of the energetic barrier ϕ is reproduced very well, though with a slight overestimation in the case of extraction barriers (Fig. 6.5b). Here, allowing for energetic disorder (represented in σ), is important and not negligible to reach a realistic probability for charge carriers to overcome the barrier. Adjusting σ , the jump distance, along with the hole mobilities provides a way to fine-tune the modeling of the S-shape. However, it is not the scope of the elaboration here, where we focus on a qualitative understanding. Deviations between simulation and experimental data can be seen for negative applied voltages. The simulated curves show a much better saturation of the photocurrent than the experimental ones. One reason for this discrepancy can be a photoshunt [35], which is a parasitic effect that is not considered in the simulation.

The good overall qualitative fit of simulation to experimental data confirms that the results of the model can be used to explain the experimental J - V curves. In the following, we focus on V_{oc} as a function of the barrier type (injection or extraction) and the difference between FHJ and BHJ.

6.3.1 Injection Barriers

Recall that we observed a qualitative difference between FHJ and BHJ in the case of injection barriers [22], which became obvious with the J - V curves shown in Figs. 6.3 and 6.5a. In the FHJ, the barrier affects the shape of the J - V curve and hence the FF ,

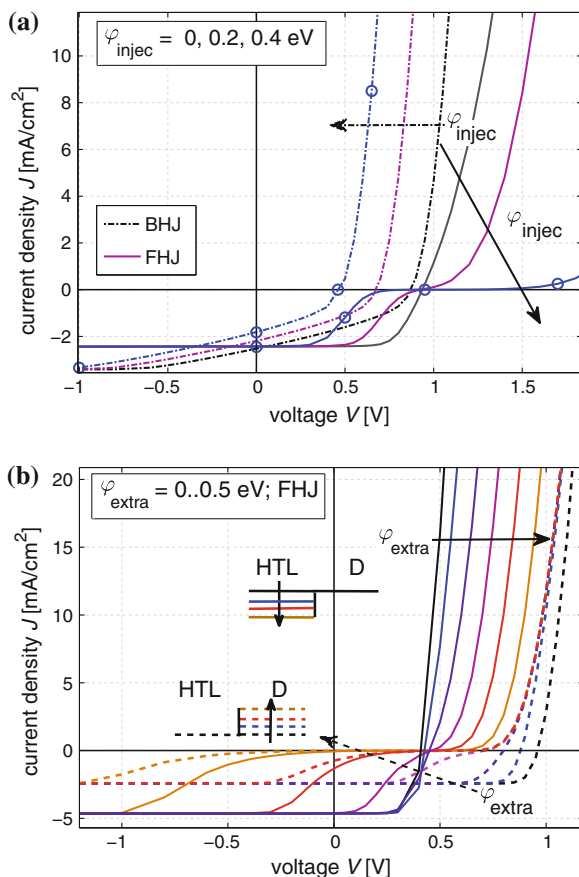


Fig. 6.5 Simulated J - V curves for **a** injection barriers (0, 0.2, 0.4 eV) at $\text{HOMO}_{\text{donor}} = -5.6$ eV for FHJs (solid lines) and BHJs (dash-dotted). **b** Extraction barriers for FHJs with varied HOMO_{HTL} and a $\text{HOMO}_{\text{donor}}$ fixed to -5.1 eV (solid lines); and varied donor and a HOMO_{HTL} fixed to -5.6 eV (dashed). The curves show good qualitative agreement with the experimental data of Figs. 6.3 and 6.4. The circles in **a** denote the points which are examined in more detail in Fig. 6.6

whereas in the BHJ it instead affects V_{oc} . FHJ devices show S-shaped J - V curves and low forward (injection) currents. In contrast, the J - V curves of the BHJ solar cells is basically shifted in voltage. Most likely poor charge transport properties in the BPAPF:C₆₀ blend results in the two inflection points in the fourth quadrant, which cause a slight kink also for BHJs independent of the HTL (Fig. 6.3b). This kink is not affected by the injection barrier and it is qualitatively different to the one discussed here, where one inflection point is located at V_{oc} .

The different behavior between the FHJ and BHJ devices is explained with the aid of spatial profiles of simulated charge carrier densities and distributions of the electric field in the device shown in Fig. 6.6.

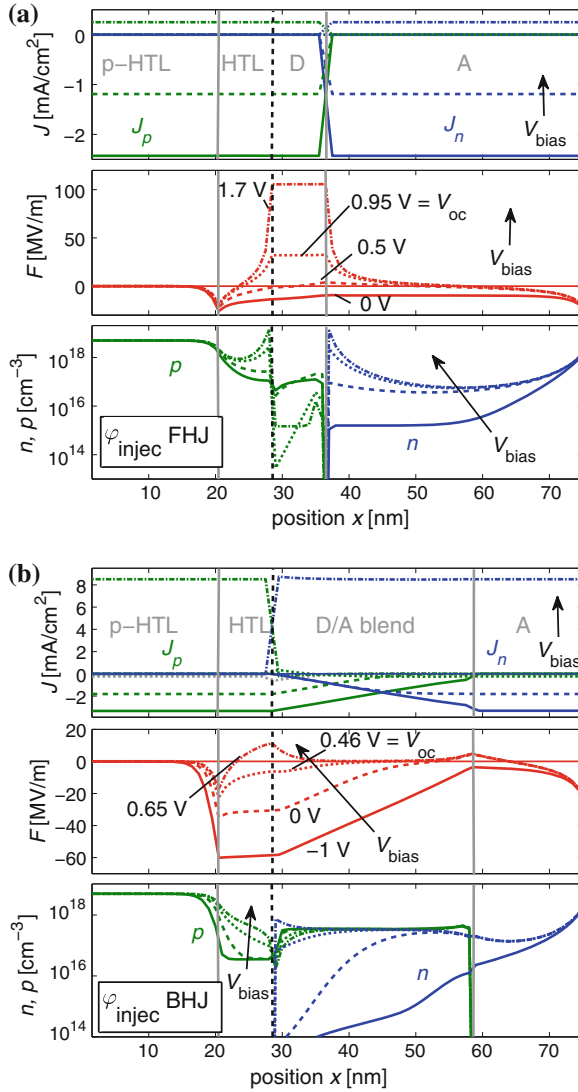


Fig. 6.6 Simulation data for a device with an *injection barrier* of 0.4 eV: Profiles of current density (J), electric field (F) and charge carrier densities (n, p) with applied bias (V_{bias}) as a parameter. The coordinate x denotes the distance from the anode, *green lines* (high values on p-side) show hole values and *blue lines* [high values in acceptor (A)] show values for electrons. The profiles for electric field and charge carrier densities indicate the applied boundary conditions: constant doping concentration on p-side, thermal injection on n-side with a work function of the cathode of 4.2 eV. **a** FHJ ($V_{bias} = 0, 0.5, 0.95, 1.7$ V); **b** BHJ ($V_{bias} = -1, 0, 0.46, 0.65$ V). These values correspond to the points marked in the J - V curves shown in Fig. 6.5

For the FHJ, V_{oc} is independent of the HTL used, although an upward shift of the HOMO of the doped HTL causes an injection barrier [36]. This barrier decreases the built-in potential V_{bi} of the device if the doping concentration in the different HTLs is comparable. In this case, the distance between Fermi level and HOMO level in each HTL is maintained [cf. (2.15)], which leads to a shift of the Fermi level of the HTL, which follows the shift of the HOMO level. V_{bi} is given by the difference between the Fermi level (= work function) of the doped HTL and the work function of the cathode. Therefore V_{bi} is reduced for a higher lying HOMO. If V_{bi} does not change significantly for a higher injection barrier, the charge carrier density in the HTL is strongly increased. However, V_{oc} remains unchanged. Figure 6.6a illustrates the reason for this. In the S-kink region (starting at 0.5 V), the electric field in the donor becomes positive, although the current is still negative. This means that photocurrent is extracted against the electric field. The photogenerated charge carriers are driven by diffusion, as can be deduced from the charge carrier density profiles, exhibiting a diffusion gradient pointing away from the D–A interface for voltages larger than 0.5 V. This process leads to an inefficient extraction of charges which is observed as an S-kink in the J - V curve.

We mentioned that for higher injection barriers, V_{bi} is lower. Simultaneously, the charge carrier concentration in the donor close to the HTL-donor interface is reduced due to the barrier [cf. (4.64) for a metal-organic interface]. This results in a larger diffusion gradient that points away from the D–A interface towards the electrode. An essential factor for the establishment of the diffusion gradient towards the electrodes is that generation of free charge carriers from excitons happens at a D–A interface, which is spatially localized in the stack. After exciton dissociation, the generated holes are located on the donor and the electrons on the acceptor. Due to the high HOMO (LUMO) offsets at the D–A interface, holes (electrons) cannot penetrate the acceptor (donor) and are inhibited from flowing to the Al cathode (ITO-anode). That is an important property of an excitonic FHJ solar cell [37].

Another useful means of illustration is the energy diagram at V_{oc} shown in Fig. 6.7a. The positive field in the donor and acceptor close to the D–A interface is represented by a tilt of the energy levels, which indicates an electric force towards the D–A interface, for both holes in the donor and electrons in the acceptor.

Quasi-Fermi levels are shown in the energy-level diagrams as well. From Sect. 2.2.2 we know that they equal the electrochemical potential of electrons and holes. The chemical energy of an electron-hole pair is represented by the splitting of the quasi-Fermi levels. Recall that it is this energy which is free of entropy that can be measured as a maximum open-circuit voltage. In Fig. 6.7a the quasi-Fermi levels of the majority carriers (electrons in the acceptor, holes in the donor and HTL) are almost constant. Therefore, the splitting of the quasi-Fermi levels at the D–A interface equals the difference at the electrodes and hence eV_{oc} . The reason is that the D–A interface is the only position where (photogenerated and injected) holes and electrons are able to recombine. Thus, the chemical energy of the electron-hole pair at the D–A interface can be converted by almost 100 % to electrical energy at open circuit.

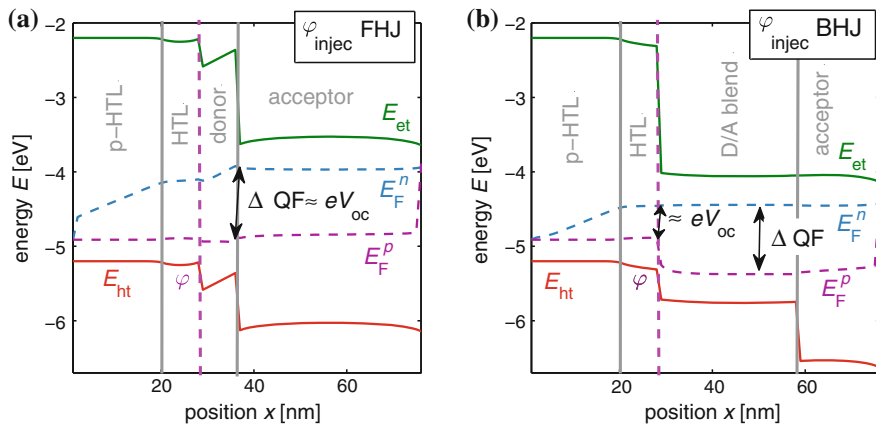


Fig. 6.7 Calculated energy-level diagrams close to V_{oc} for a FHJ (a, $V_{bias} = 0.95$ V) and a BHJ (b, $V_{bias} = 0.46$ V). The injection barrier is 0.4 eV. The charge transport levels HOMO/ E_{ht} , LUMO/ E_{et} (lines), and the quasi-Fermi levels (dashed) for electrons and holes are shown. For the BHJ device, V_{oc} does not reach the maximum quasi-Fermi level splitting (ΔQF) due to recombination of photogenerated electrons at the HTL-blend interface

In forward bias (1.7 V in Fig. 6.6a) the current is strongly limited, because holes have to pass the barrier, where they pile up, and travel through the donor to the D–A interface to recombine with injected electrons accumulating on the acceptor at the D–A interface.

The situation in a BHJ is completely different, because electrons and holes are not spatially separated in the active materials as is the case in a FHJ. Consequently, a diffusion gradient does not exist to push photogenerated holes towards the anode and electrons towards the cathode. Figure 6.6b demonstrates that the photocurrent is collected over the entire blend layer at -1 and 0 V. As soon as the field reaches positive values (0.65 V), charges injected from the electrodes cause a large positive, i.e. forward current. The profiles of electron and hole currents show that an injection of holes overcoming the barrier is not required. The current through the blend is completely driven by electrons which recombine with holes on the HTL at the HTL-blend interface.

Due to the lower built-in field, the directive electric force promoting the extraction of photogenerated charge carriers is lower compared to a device without a barrier and the same HOMO of the donor. As soon as the applied bias approaches the built-in potential, there is no directive driving force for charges of different polarity. That is why V_{oc} is reduced with an increased injection barrier, and the onset of forward current shifts to lower voltages. Consequently, the HOMO level of the donor becomes unimportant and the J - V curve mainly follows the curve of an HTL-acceptor solar cell. This is in contrast to the FHJ, where the diffusion gradient compensates for the low V_{bi} and counteracts the field close to V_{oc} .

An energy diagram for a BHJ with an injection barrier at open circuit is depicted in Fig. 6.7b. The splitting of the quasi-Fermi levels in the blend is reduced towards the HTL-blend interface due to a high probability for recombination of electrons with holes at the HTL-blend interface. These holes are delivered from the anode and are easily transported through the doped HTL. The recombination of holes with electrons at the HTL-blend interface is comparable to the high surface recombination (Fig. 2.13) situation discussed in Sects. 2.4 and 5.2.3. Thus, eV_{oc} as the difference between the quasi-Fermi level for holes at the anode and the quasi-Fermi level for electrons at the cathode does not reach the maximum splitting of the quasi-Fermi levels in the absorber. In terms of the definitions in Sect. 2.4, chemical energy is lost during the conversion to electrical energy.

From the explanations presented here, it is obvious that the observed difference in V_{oc} between FHJ and BHJ is not caused by the active layer itself. Hence, it is not a property of the blend compared to a planar heterojunction. The key point is the device structure. As long as it allows contact of electrons and holes only at the D–A interface, the J - V curve for a BHJ will show the same qualitative characteristics as the one for a FHJ. Avoiding contact of electrons and holes at the electrodes can be achieved by choosing selective contacts, which allow only one species of charge carriers to pass. The theoretical role of selectivity was extensively discussed in the previous chapter. There, the V_{oc} of a BHJ with selective contacts was independent of φ and showed an S-kink (cf. Fig. 5.9), whereas a BHJ without selective contacts suffered from a decrease in V_{oc} . Selectivity can experimentally be realized by a combination of FHJ and BHJ, where the BHJ is sandwiched between neat layers of donor and acceptor [38, 39]. This “hybrid” structure avoids direct contact of the acceptor with a misaligned HTL or metal electrode and profits from the higher photocurrent of a BHJ compared to a FHJ. If the energy levels (HOMO of HTL to donor, LUMO of electron transport layer to acceptor) are well aligned, the p-i-n structure with wide-gap transport layers guarantees selective contacts as well. Details on this structure were addressed in the theory chapter (Sect. 2.5.3) and the experimental section (Sect. 3.6.2).

6.3.2 Extraction Barriers

In the case of extraction barriers, there is no qualitative difference between BHJ and FHJ. As an extraction barrier does not provide an additional path of recombination (in contrast to an injection barrier in a BHJ), V_{oc} is independent of the HTL. It is defined by the splitting of quasi-Fermi levels at the D–A interface, independent of whether the absorber is as a blend or bilayer. The strong kink in the curves of Figs. 6.4 and 6.5b is due to the hindered extraction of photogenerated holes at the HTL-donor interface. The holes pile up in front of the barrier and require a high reverse voltage to be extracted. The piled-up holes constitute a space charge which partially screens the field present in donor and acceptor. The reduced field gives rise to an increased recombination which is seen as the S-kink in the J - V curve. We will discuss the role

of the piled-up charge in Sects. 6.6.3 and 6.6.4, where transient currents and J - V data, as a function of illumination intensity, are investigated.

The onset of forward current was found to depend on the HOMO of the HTL only (Fig. 6.4b). This observation is explained as follows: When discussing the MIM picture in Sect. 3.3.4, we found that forward current flows as soon as the applied bias reaches a certain value, where the diffusion current significantly exceeds the negative drift current resulting from V_{bi} . The bias at which this point is reached depends only on the charge carrier concentrations in the organic layers adjacent to the electrodes, and on V_{bi} . When shifting the HOMO of the HTL downwards, V_{bi} increases if the doping concentration (and hence the distance between the Fermi level and the HOMO) remains the same, or the charge carrier density decreases if the work function remains constant. Both effects lead to the same shift of the onset of forward current to higher voltages. Thus, only the position of the HOMO of the HTL defines the current onset independent of the actual position of E_F . This allows reliable calculations without precisely knowing V_{bi} and the amount of active dopants in the HTL.

Using the p-i-n approach, it is possible to reduce the negative effect of an extraction barrier. If the intrinsic HTL is replaced by a doped HTL, the S-kink can vanish despite the extraction barrier [40]. The reason is that heavily doping the HTL gives rise to a strong bending of the energy levels close to the donor. This increases the probability for tunneling of charges through the barrier, which is comparable to a highly doped metal-organic contact as described in Sect. 3.5.1.

6.3.3 Comparison Between Flat and Bulk Heterojunction

Sometimes it is stated that V_{oc} of a blend is lower than V_{oc} of a flat heterojunction comprising of the same materials [41]. As can be seen from Table 6.1, this is not necessarily the case. It holds for injection barriers, which indicates that injection barriers are a common phenomenon. However, V_{oc} in a BHJ can even be higher than in the respective FHJ. This might be due to the effect that the HOMO of the donor can shift upon blending it with an acceptor. The shift in HOMO would change the height of a barrier towards a specific HTL which is expected to be seen in a change in the strength of the S-kink, which can indeed be observed. Figure 6.4a shows the example with the donor ZnPc, where the current in the S-kink region of the BHJ with BPAPF (HOMO -5.6 eV) as a HTL follows the curve of the FHJ with α -NPD (HOMO -5.5 eV) as a HTL, implying a comparable extraction barrier. Consequently, the HOMO of ZnPc in the BHJ is supposed to be shifted downwards by 0.1 eV compared to its value in ZnPc as a neat layer. The shift fits roughly to a V_{oc} of the BHJ that is 150 mV higher than V_{oc} of the FHJ. Certainly, other parameters influencing V_{oc} change in the blend as well, such as recombination probabilities (in Langevin theory e.g. by modified mobilities). Therefore, further investigations of this effect will be undertaken in Sect. 8.1, where the effect of the mixing ratio on V_{oc} is examined when blending ZnPc with C₆₀.

The low FF in BHJs compared to FHJs can be attributed to two effects: first, to a lower mobility in the blend due to an unfavorable morphology, and second, to the fact that even if the HTL consists of the same material as the donor in the blend, the HOMO of the HTL and donor may not be completely adjusted. This restricts the statement of the previous section that a BHJ sandwiched in between neat donor and acceptor layers is *a priori* the optimum structure. According to Table 6.1, other experiments with high performance solar cells, and from simulations, a small extraction barrier of around 0.1 eV seems to be the optimum case. Under this condition, extraction still works well, and recombination between holes on the HTL and electrons on the acceptor is hindered from a high V_{bi} .

6.4 Current-Voltage Curves on a Logarithmic Current Scale

To further discuss the effect of barriers on the J - V curve, the absolute value of the current is plotted on a logarithmic scale. Figure 6.8 shows curves measured under illumination and in the dark to visualize the effect of barriers also on dark J - V curves. BHJs (Fig. 6.8b) with injection barriers show similar slopes (referring to a logarithmic current scale) in forward bias and confirm the idea of simply shifted J - V curves due to the higher lying HOMO of the HTL. This slope is governed by the recombination processes within the blend (discussed in Chap. 8) and is not influenced by the HTL. Injection barriers for FHJ solar cells (Fig. 6.8a) reveal that the slope of the exponential region in forward bias is strongly influenced by the barrier. Consequently, the ideality factor n_D is affected, which is obtained if the curves are fitted by the Shockley equation (2.49). This implies that n_D does not reveal any information about recombination at the D–A interface. Its value is governed by the barrier and can exceed the physical range between 1 and 2 given by the mechanism for charge recombination [cf. (3.72)].

For extraction barriers (Fig. 6.8c, d) the slope in the exponential region of the J - V curve and hence the n_D values are modified by barriers as well. Consequently, stating ideality factors for organic solar cells is very questionable, as barriers at the electrodes can hardly be avoided. Barriers might be an explanation for the reported values of n_D larger than 2. Several curves show additional features between 0 and 0.5 V, which are partly due to a parallel resistance, if they are characterized by a comparable current at the same reverse voltage. Others probably show the overlap of several effects related to overcoming the barrier and to the usual diffusion against the built-in field. In the case of extraction barriers, the photocurrent in reverse bias shows a dependence on voltage which is close to exponential (straight lines in Fig. 6.8c, d). This relation reveals an exponential field dependence of the probability for photogenerated charge carriers to overcome the extraction barrier.

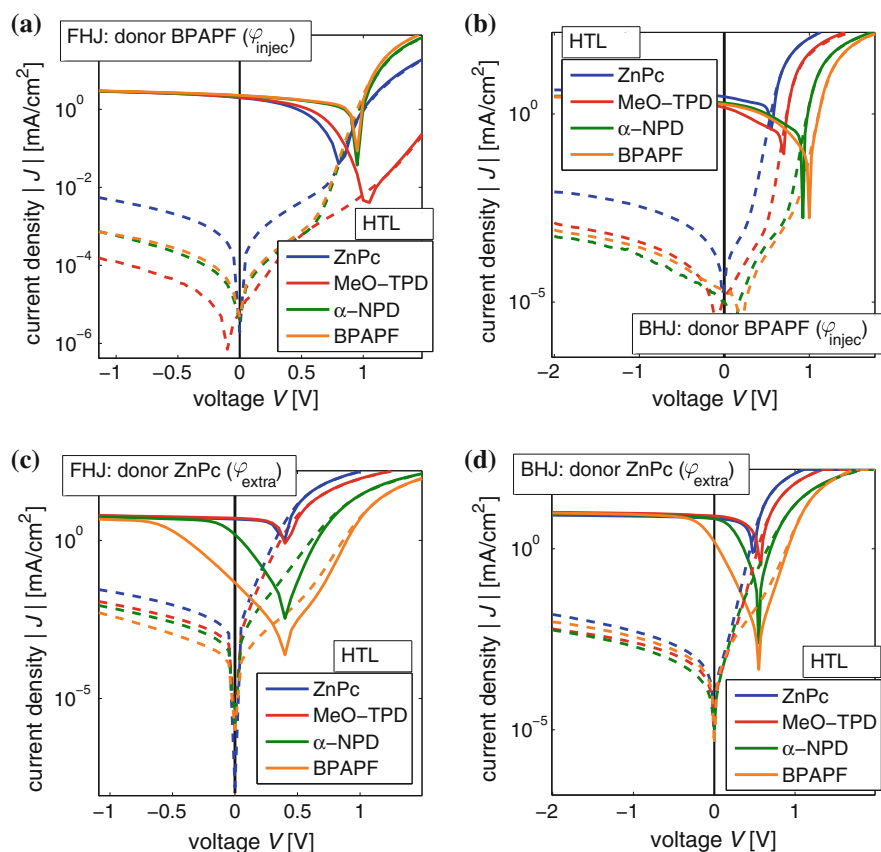


Fig. 6.8 Experimental J - V curves on a logarithmic current scale. Dark curves are *dashed*. (a and b) *Injection barrier* (φ_{injec}) devices with the donor fixed to BPAPF and varied HTLs for (a) FHJ and (b) BHJ. (c and d) *Extraction barrier* (φ_{extra}) devices with varied HTLs and the donor fixed to ZnPc in c FHJ and d BHJ. In some cases, the dark current at 0 V is not 0 due to measurement inaccuracies for current densities lower than $\approx 10^{-5} \text{ mA}/\text{cm}^2$. Both injection and extraction barriers change forward and reverse currents and make the application of a diode ideality factor difficult

6.5 Characterizing an Organic–Organic Interface with Photoelectron Spectroscopy

For a detailed analysis of organic–organic interfaces, the rough estimation of vacuum level alignment may not be sufficient, and a knowledge of exact (within an experimental error of $\pm 0.05 \text{ eV}$) barrier heights is desired. Ultraviolet photoelectron spectroscopy (UPS) is a method capable of yielding information on the energy-level alignment at interfaces. These measurements should be done at samples with an architecture as close as possible to the solar cells. The reason is that the barrier φ can

be modified by interface dipoles, pinning effects, the choice of substrate, and the sequence of layer deposition.

When performing a UPS measurement, the sample is illuminated with UV photons. Based on the outer photoelectric effect, electrons are ejected with a kinetic energy that is detected. The release of electrons requires a supply of electrons to avoid charging of the sample. That is why low-conductivity layers have to be thin and a conductive substrate has to be used.

For the UPS study, we selected the two materials MeO-TPD and BPAPF with a nominal HOMO offset of 0.5 eV. They form amorphous and closed layers even for thicknesses in the range of few nm. Both layer sequences, MeO-TPD/BPAPF (injection barrier) and BPAPF/MeO-TPD (extraction barrier), are investigated.

The sample with the injection barrier consists of Ag/p-MeO-TPD(7 nm)/MeO-TPD(5 nm)/BPAPF(3 nm). Figure 6.9 shows four UPS spectra measured subsequently during breaks in the evaporation procedure of the stack. As UPS is a surface sensitive method (maximum penetration depth of a few monolayers), it probes the density of occupied valence states of the top most layer(s). The fastest electrons show the lowest binding energy (E_B), which means that they are ejected from the highest occupied states (Fig. 6.9b). The energy scale is referenced to the work function of the substrate, which here is silver. In metals the work function, i.e. Fermi level coincides with the energy of the highest occupied states in a partially filled band. Hence, a metal substrate allows a calibration of the measurement regarding E_F .

Organic materials (here MeO-TPD and BPAPF) show several peaks representing molecular orbitals (Fig. 6.9b). The peak with the lowest E_B describes the HOMO.

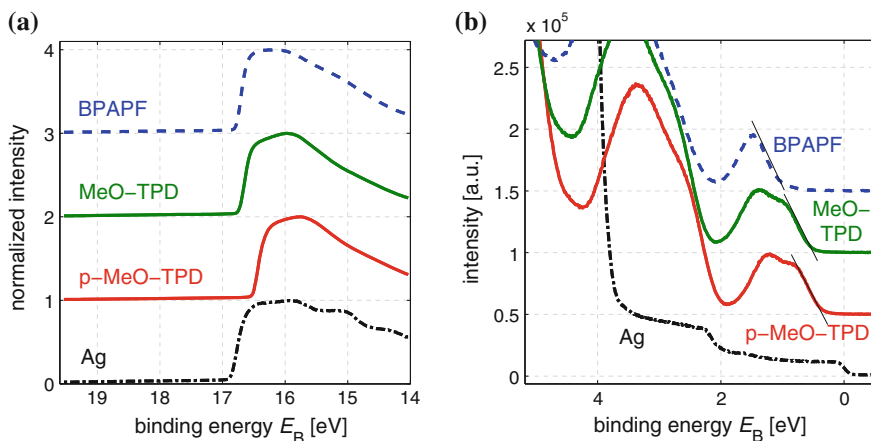


Fig. 6.9 Subsequently measured UPS spectra of the sample Ag/p-MeO-TPD(7)/MeO-TPD(5)/BPAPF(3 nm). **a** High-binding-energy cutoff, defining the vacuum level and **b** low binding energy region giving the HOMO. The lines at the HOMO onset visualize the determination of the IP as an intersection of these lines with the base line. The reference energy ($E_B = 0$) is the Fermi energy of the silver substrate. The data of this figure is used to draw the energy-level diagram in the next figure

Its value relative to E_F can be directly derived from the spectrum. As the HOMO is broad, one has to specify how a value, which is later given as a single number, is deduced from the spectrum. Most common is to use the onset of the intensity, as this is the region where holes are supposed to be located. One definition of the onset is the point of intersection between the base line and a tangent which is attached to the turning point of the spectrum. This point is then defined as E_{onset} , which describes E_{ht} relative to E_F .

Together with the high binding energy cutoff (Fig. 6.9a), one can draw the complete energy diagram. The high binding energy cutoff E_{HBEC} describes the electrons with highest binding energies, i.e. the slowest electrons. Actually, in this case the energy is not really a binding energy as this signal results from so-called secondary electrons. These electrons have already undergone inelastic scattering in the film. However, the difference between E_{HBEC} and the energy of the UV excitation (commonly He I line with 21.22 eV) gives the minimum energy needed to extract an electron from the sample. Thus, we can write for the work function WF:

$$\text{WF} = h\nu_{\text{UV}} - E_{\text{HBEC}}. \quad (6.1)$$

Knowing the WF and the difference between HOMO onset and Fermi level, we can calculate the ionization potential IP:

$$\text{IP} = \text{WF} + E_{\text{onset}} = h\nu_{\text{UV}} - (E_{\text{HBEC}} - E_{\text{onset}}). \quad (6.2)$$

A shift in E_{HBEC} upon deposition of an additional layer represents a shift of the vacuum level E_{vac} relative to the Fermi level, which is supposed to be constant. If this shift is abrupt (i.e. it occurs roughly within a monolayer) at an interface, we relate it to an interface dipole (cf. Fig. 3.44). If it changes gradually with the thickness of the deposited layer, we attribute it to a bending of energy levels due to space charge.

Extracting E_{vac} and the IP from Fig. 6.9 allows us to draw the energy diagram shown in Fig. 6.10a. It has to be noted that this energy diagram with the spatial coordinate as abscissa does not represent the distribution of the potential within the layer(s). It is the potential at the surface when the layer (stack) was x nm thick. The Fermi level is close to the HOMO in the p-doped MeO-TPD layer due to the high doping concentration. The values of the IPs of MeO-TPD and BPAPF reproduce the known values of 5.1 and 5.6 eV. The injection barrier is 0.5 eV as expected.

The same investigation is done for a sample with an extraction barrier, i.e. the layer stack Ag/p-BPAPF(7)/BPAPF(5)/MeO-TPD. The alignment of the energy levels is shown in Fig. 6.10b. The estimated value of 0.3 eV for the extraction barrier is significantly lower than expected. It is accompanied by a dipole at the BPAPF/MeO-TPD interface. Interestingly, the distance between Fermi level and IP changes with layer thickness. The shift causes an uncertainty in the value of the extraction barrier, as the first measurement is performed at a MeO-TPD thickness of 3 nm. Using thinner layers is experimentally difficult, because the measured spectrum would consist of an overlap between the HOMO of MeO-TPD and the subjacent BPAPF. Therefore, an accurate determination of the extraction barrier is hardly possible.

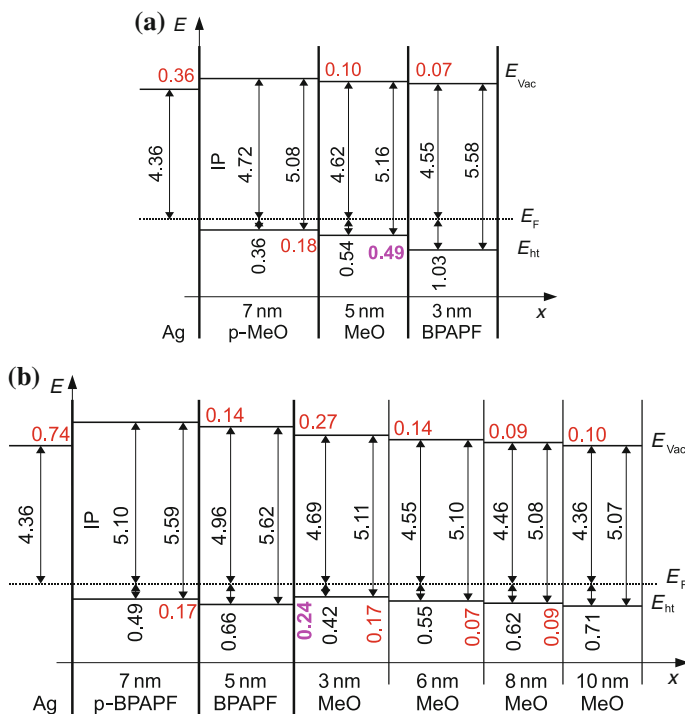


Fig. 6.10 Energy level alignment extracted from UPS data. **a** *Injection barrier* sample with $\varphi_{injec} \approx 0.5$ eV. **b** *Extraction barrier* sample with $\varphi_{extra} \approx 0.3$ eV. This value is estimated since the distance between IP and E_F increases for an increased MeO-TPD thickness and tends towards its value for intrinsic MeO-TPD. The lower value of φ_{extra} is due to the interface dipole (0.27 eV) seen in the shift of the vacuum level. Depositing only 1 nm might give a more precise value of φ_{extra} , but is experimentally difficult. Data analysis and sketch by M. Tietze, IAPP

However, it is known that the Fermi-level in a MeO-TPD film cannot come closer to the IP than 0.35 eV [9], which limits φ_{extra} to 0.31 eV based on the values shown in Fig. 6.10. Such a pinning of E_F at a certain distance to the HOMO is commonly observed at metal-organic contacts and is attributed either to tail states or to polaronic levels as discussed in Sect. 3.5.2. The data of Fig. 6.10b and of doped MeO-TPD [9] indicate that the latter can be excluded because the pinning occurs at an intrinsic organic-organic interface. Screening is not expected to be altered as the dielectric constants of two organic materials are in the same range in contrast to the dielectric constants of metal and organics. Chemical reactions at the interface can be excluded as well because the reversed stack sequence (Fig. 6.10a) does not show a significant dipole at the MeO-TPD/BPAPF interface. In conclusion, the pinning is most likely due to a significant amount of (trap) states within the energy gap. These traps can also explain the increased distance between IP and E_F for an increased thickness of the MeO-TPD layer. If the layer was totally intrinsic, a shift of energy levels would

not be expected. A shift, i.e. bending of energy levels, can only be caused by space charge, which could be provided by trapped holes in this case.

What we called HOMO in Fig. 6.9 can be more precisely named density of states (DOS) as a function of energy (cf. Sect. 2.2.1). Logarithmic plots of the DOS for MeO-TPD and BPAPF are shown in Fig. 6.11 and visualize tail states at energies above the IP. The reference energy (abscissa 0) is the value of the IP obtained for MeO-TPD and BPAPF, respectively, from the onset in the linear plot (Fig. 6.9b). Thus, the energy scale for each curve is individually set relative to the IP of MeO-TPD and BPAPF, respectively. The DOS is normalized by fitting a Gaussian to the BPAPF peak and setting the area of this Gaussian to 1. If one assumes that the area is equal to the density of molecules, it represents a total amount of states on the order of 10^{21} cm^{-3} . The tails indicate the possibility for a significant amount of charge carriers being located at energies between 0 and 0.5 eV above the hole transport level. The signal at larger energies is limited by the resolution of UPS. The tails can be fitted by exponential functions. According to these fits, there are states on the order of 10^{17} cm^{-3} at an energy of 1 eV above the HOMO onset. These tail states are broader for the BPAPF and could be the reason for the larger distance between the IP and E_F for the p-doped BPAPF compared to the p-doped MeO-TPD (Fig. 6.10).

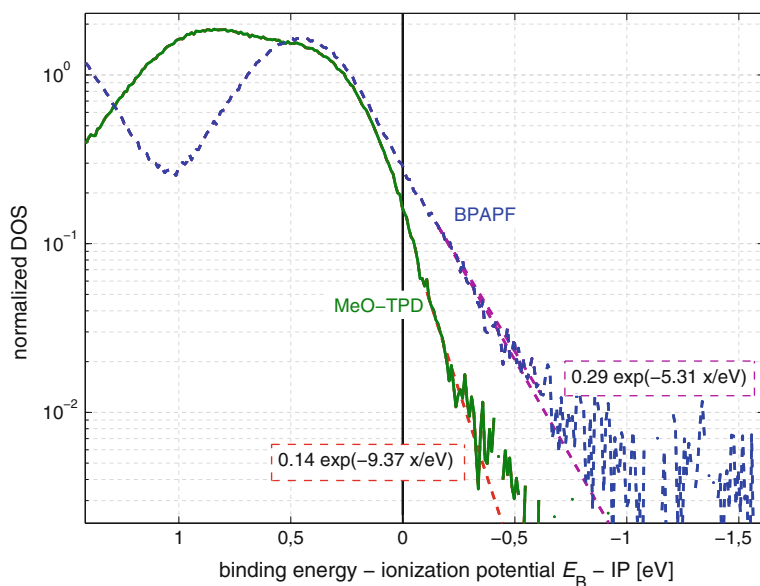


Fig. 6.11 UPS measurement data of the normalized HOMO density of states (DOS) with the IP of the respective material as reference for the energy ($E_B - \text{IP}$ as abscissa). The DOS tails below the energy gap are fitted by an exponential function (red dashed lines). BPAPF shows a broader distribution of tail states, which might explain the larger distance between the Fermi and HOMO level of the doped layers, as shown on the left in the previous figure (0.49 vs. 0.36 eV)

Instead of using a (narrow) Gaussian DOS in the simulation, one might directly apply the DOS measured by UPS. However, one major problem arises, these tail states are very unlikely to describe the energetic position of free charge carriers for two reasons. First, the large number of these tail states for low energies would lead to a very low V_{oc} in a solar cell, under the assumption of realistic recombination constants and charge carrier densities within the device. Second, the charges in the tail are less mobile than those close to the IP. Consequently, a mobility model is required that describes the dependence of the mobility on charge carrier densities in an exponential DOS comparably to the Pasveer model [13] for a Gaussian DOS. Another option would be the definition of a mobility edge.

Due to these reasons the previously sketched approach of the simulation is most reasonable. There, the IP is selected as the transport level for free charges, which is broadened by a Gaussian with a small σ representing the effect of disorder on charge transport, but not the real DOS.

6.6 Ways to Distinguish Between Extraction and Injection Barriers

We found that both injection and extraction barriers can cause S-shaped J - V curves, which look relatively similar, as a comparison between Figs. 6.3a and 6.4 reveals. In our study, we knew based on the design of the experiment which barrier was present. However, this is not the usual case. Commonly, unwanted S-kinks are observed while fabricating solar cells with an energy level alignment at the electrodes that is not completely known. In this case it is desired to find the reason for the S-kink. Knowing the origin, targeted measures can be undertaken to solve the issue. In the case of an injection barrier, the work function of the electrode has to be modified, e.g. by a dipole layer. In the case of an extraction barrier, the electrode has to be treated more carefully or a high-conductive and protective interlayer inserted to avoid the formation of an insulating oxide film.

In the following, several approaches are presented to distinguish between extraction and injection barriers. Some of them are rather theoretically important, which means that it is not easily possible to follow them in each case. Other methods require only simple measurements. Therefore, they are easy to apply experimentally.

6.6.1 Dependence of the J - V Curve Shape on Layer Thicknesses

A variation of donor and HTL thickness in a p-i-n stack allows a discrimination between injection and extraction barriers. Furthermore, the dependence of the strength of the S-kink on layer thickness can address the role of the electric field in considering the probability for charge carriers to cross the barrier. The thicker the layers,

the lower is the electric field at a given applied voltage. Additionally, the state of relaxation of photogenerated charge carriers can be probed. If the probability for crossing an extraction barrier depends on the distance between the D–A interface and the HTL, the charge carriers might have further relaxed during hopping in the donor.

Donor Thickness

We start with a variation of the donor thickness. J - V data of devices with the donor BPAPF are shown in Fig. 6.12a and MeO-TPD in Fig. 6.12b.

An increased thickness of the donor layer should predominantly influence two processes: one, charge transport in the donor and two, crossing the barrier. For the first process, increasing the donor thickness results in a higher series resistance effect due to a low hole mobility. This effect is present independent of the barrier. It can be seen for both materials in the dashed J - V curves, where the HTL is equal to the donor. In this case, the FF and the forward current decrease with increased donor layer thickness. The second effect implies that increasing the thickness of an intrinsic layer reduces the field within the device at a given value of the applied voltage. Therefore, it gives information on the field-dependence of the barrier crossing. In the case of injection barriers (Fig. 6.12a), a scaling of the strength of the S-kink with donor thickness is observed. This effect is also reproduced by simulation data shown in Fig. 6.13a. The reason is an increase in recombination at the D–A interface due to a lower field and lower diffusion gradient there caused by a thicker intrinsic donor

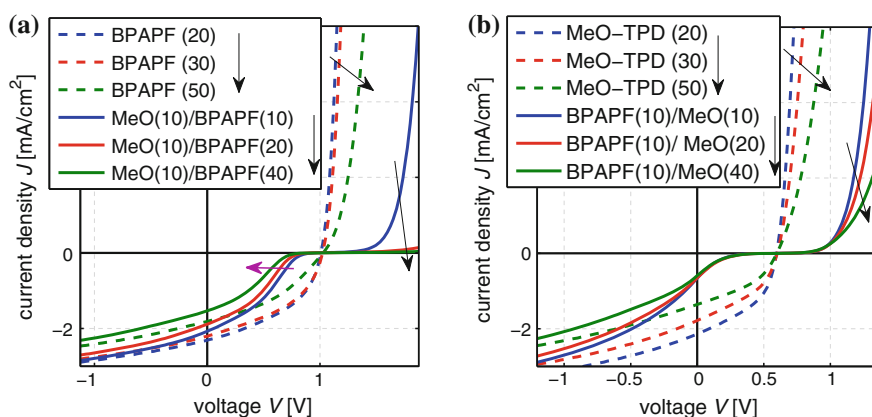


Fig. 6.12 Experimental J - V data Variation of the donor thickness (given in nm by the numbers in parenthesis) for a device with p-HTL (20 nm)/i-HTL (10 nm)/donor (d)/C₆₀ (40 nm)/BPhen/Al. Dashed lines show the case where HTL material = donor material and solid lines the case of an energetic barrier: **a** Injection barrier with HTL MeO-TPD and donor BPAPF. **b** Extraction barrier with HTL BPAPF and donor MeO-TPD. The S-kink is affected by d only for devices with injection barriers

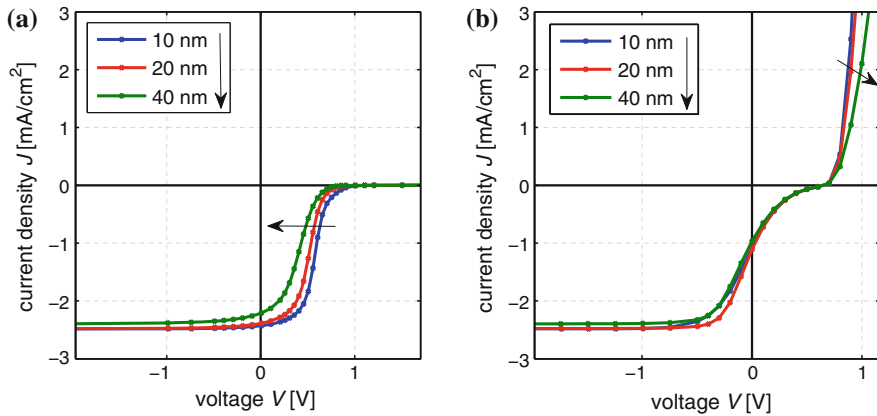


Fig. 6.13 Simulated J - V data Variation of the donor layer thickness for **a** an injection barrier of 0.5 eV and **b** an extraction barrier of 0.3 eV. As in experiment, the S-kink is only affected for devices with injection barriers

layer. Additionally, forward current, which requires an injection of charges over the barrier, is strongly affected by thicker donor layers.

However, the strength of the S-kink is independent of the donor thickness in the case of an extraction barrier. This holds for experiment (Fig. 6.12b) and simulation (Fig. 6.13b) and can be explained as follows. We have stated and will further discuss in a subsequent Sect. 6.6.4 that photogenerated holes pile up in front of an extraction barrier. Consequently, the electric potential mainly drops over the intrinsic HTL because the piled-up charges screen the field in the donor. Thus, the field at the interface of HTL and donor, which determines the extraction current, is mainly independent of donor layer thickness.

For the device with an extraction barrier, the independence of the S-shape with donor layer thickness reveals another important finding that excess energy of photogenerated holes does not play a role in charge extraction. One might have assumed that free charge carriers generated at the D–A interface are injected into the (Gaussian) DOS at elevated energies [42] and relax according to the Bässler model after several hops, until they reach the transport energy. Bässler [43] showed that the relaxation time for a charge carrier in a Gaussian DOS with σ in the range of several $k_B T$ is in the order of 10–1,000 times the dwell time of a charge carrier on a site. Therefore, a complete relaxation of charge carriers requires many hops. This implies that photogenerated holes possess a relatively large energy when they reach the extraction barrier in the case of thin donors. This should result in an increased probability for overcoming the barrier and consequently in a reduction of the S-kink for lower thicknesses. As it is not observed, one could come to several conclusions: σ is negligibly small, or the relaxation time is much shorter, or the charge carriers are already generated at the lowest energy possible because they result from split (non-hot) CT states. Although this question cannot be completely answered here, we can be sure that

the assumption of a relaxed distribution at the HTL-donor interface in the model is valid. Most likely these small-molecule systems do not show a significant relaxation of photogenerated charges on the length scale of several nm.

Intrinsic HTL Thickness

In the previous section, we stated that for a device with an extraction barrier operating in the S-kink region that the electric field at the donor-HTL interface is not significantly changed by a varied thickness of the donor layer. However, a variation of the thickness of the intrinsic HTL is expected to influence the field. J - V data of such a variation are shown in Fig. 6.14a, which demonstrate that the strength of the S-kink increases significantly with the thickness of the intrinsic HTL. This effect is compatible with the fact that the forward current in the case of an injection barrier scales with the thickness of the donor layer. It is always the thickness of the layer behind the barrier (referring to the direction of the charge-carrier current flow), which defines the field. There, the voltage drops because charge carriers pile-up in front of a barrier forming a space charge which screens the field in the layer in front of the barrier.

The simulation data in Fig. 6.14b shows excellent agreement with experiment. It is not even necessary to assume a broadening of the DOS. However, a hopping distance of $a = 1$ nm is selected, which increases the probability for barrier crossing compared to the Boltzmann factor [cf. (4.72)]. Note that a σ in the range of several 10s of meV leads to comparable results. Consequently, charges are located at a relatively discrete transport level if the value of $\varphi_{\text{extra}} = 0.3$ eV that we determined from UPS measurements is correct. Whether a or σ is dominating the probability

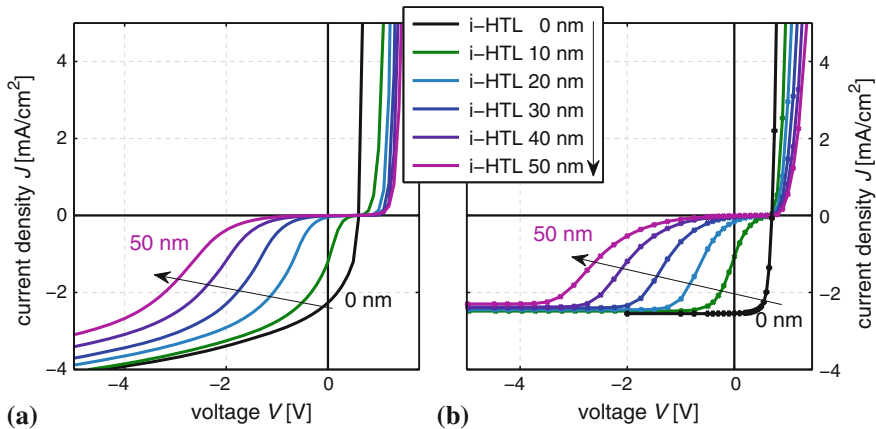


Fig. 6.14 Variation of the HTL thickness for devices with an *extraction barrier* and the stack p-BPAPF (20 nm)/BPAPF (d)/MeO-TPD (10 nm)/C₆₀ (40 nm)/BPhen/Al. **a** *Experimental data* and **b** *simulation data* with a discrete φ_{extra} of 0.3 eV and a hopping distance $a = 1$ nm. Both examples show a significant influence of the HTL thickness on the S-kink

for overcoming the barrier could not be clarified despite the variation of the HTL thickness. A clarification would require further investigations in comparison with temperature-dependent data which would allow a discrimination between processes that are based on tunneling or thermally activated jumps. Further knowledge of the interactions and transfer integrals between the two molecules would be essential for a detailed quantitative discussion, as it is not only the energetic barrier, but the overlap integral that determines the hopping rate [cf. (3.15) and (3.17)].

The drawback of varying layer thicknesses is that many devices have to be fabricated. Especially when doing solution processing, variations in thickness without changing other properties are not very easy. Furthermore, the thickness of an unintentional interlayer can hardly be varied. That is why approaches are desired that allow determination of the origin of the S-kink in a single sample. The following proposals fulfill this criterion.

6.6.2 Temperature Dependent Measurements

According to (4.68), overcoming a barrier is activated with temperature. Thus, an investigation of the temperature dependence of the current is supposed to give further insights into the prevailing mechanisms. Temperature dependent J - V data of a device with an injection barrier and a device with an extraction barrier are shown in Fig. 6.15. The temperature covers a range of 220–340 K.

The main difference between an (a) injection and (b) extraction barrier is that the S-shape of the J - V curve for the device with an injection barrier is not affected by the temperature T whereas the S-kink for the device with an extraction barrier becomes

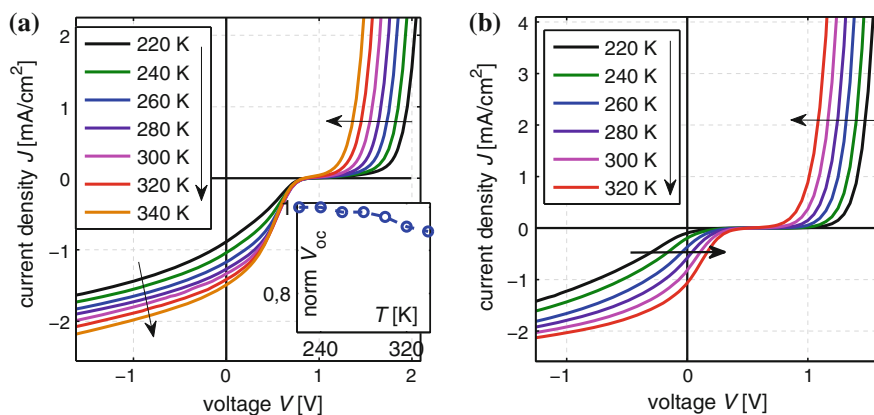


Fig. 6.15 Experimental data: Temperature dependence of the J - V curve for a device with **a** an injection (.../MeO-TPD(10)/BPAPF(10)/...) and **b** an extraction barrier (.../BPAPF(10)/MeO-TPD(10)/...). In case (a) the S-kink is relatively independent of temperature whereas it is shifted in case (b)

more pronounced with lower T . The inset shows that V_{oc} increases sublinearly with decreased temperature, which might be caused by a broad DOS (cf. Fig. 3.23). The photocurrent decreases with lower temperatures independent of applied bias voltage (the curves are parallel in the third quadrant). This trend is an indication for an exciton diffusion length L_D which depends on temperature. If L_D increases with temperature, the saturated photocurrent will show the same trend. Changes in charge carrier mobilities do not seem to dominate for these devices within the measured temperature range.

The experimental curves are compared to simulation data where T is varied. The results are shown in Fig. 6.16. First, we discuss the case of an injection barrier (Fig. 6.16a). It is observed that the S-kink does not significantly change its shape and is shifted to higher voltages with decreased T . At first glance, this contradicts the experimental data, where the S-kink is independent of T . The reason for this discrepancy is the strong increase in V_{oc} with decreased T in the simulation according to (3.26). However, V_{oc} is only slightly changed in the experimental data of Fig. 6.15. This weak temperature dependence of V_{oc} for a FHJ is not yet well-understood. It implies that (3.26) requires some modifications due to the fact that electrons and holes are located on different sides of an interface. However, (3.26) shows validity for BHJs [44], which is a clear indication that the assumption of a BHJ as a new effective medium describes the physics better than the idea of a BHJ as a folded FHJ. This means that in a FHJ other processes are dominating, which are less understood.

To be able to visually compare the effect of T on the strength of the S-kink, we change the point of reference on the voltage scale. The correct point of reference to evaluate the strength of an S-kink is V_{oc} . Therefore, the simulated J - V curves are shifted by the offset in V_{oc} caused by the temperature. The dashed lines in Fig. 6.16a

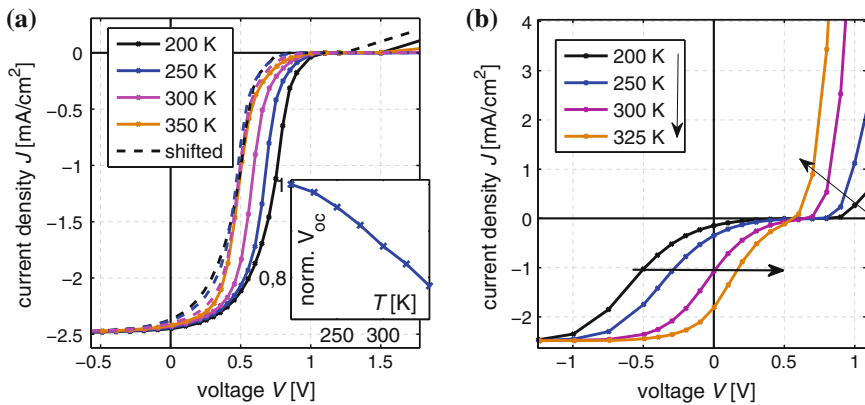


Fig. 6.16 Simulation data: **a** Injection barrier: The S-kink is shifted to lower voltages for higher temperatures due to a decrease of V_{oc} with T (inset). Dashed lines show the J - V curves, where the voltage is corrected for the difference in V_{oc} compared to V_{oc} at 350 K. These curves coincide, like in experiment where V_{oc} barely changes with T . **b** Extraction barrier: The S-kink depends strongly on T and is less pronounced for higher T as that observed in experiment (Fig. 6.15)

show shifted J - V curves with respect to V_{oc} of the J - V curve for $T = 350$ K. The S-kinks coincide, which is in agreement with the experimental data, where a correction for the offset in V_{oc} is not necessary due to the weak dependence of V_{oc} on T . The reason for the independence of the S-kink with temperature is found in the role of diffusion. As a higher T increases diffusivity, the diffusion current, which is dominant in the S-kink region, is larger. However, a higher T also increases charge carrier injection over the injection barrier and thus the hole concentration in the donor at the HTL-donor interface. This higher concentration means a decreased concentration gradient from the D-A interface to the HTL-donor interface and thus a decreased diffusion force. In total the effects cancel each other so that the overall diffusion force remains unmodified.

In the case of an extraction barrier (Fig. 6.16b), the simulation data shows an increase in the strength of the S-kink with decreased T . This trend is comparable to the experimental data. The reason for this is that the probability for crossing a barrier and consequently the probability for extraction of charge carriers is enhanced by a higher temperature. This correlation is obvious from (4.68), which shows a thermal activation.

To gain a deeper insight, more studies as a function of temperature will need to be done. However, the effect of temperature is complex and opens a broad field, which we cannot discuss entirely in this book.

6.6.3 Transient Photocurrent Measurements

We found that barriers lead to a redistribution of charge carriers within the device. To probe this effect experimentally, transient photocurrent measurements are carried out, where the current response on square pulses of light is monitored. This method described in Sect. 3.7.3 can in principle be used to determine mobilities [45] and also to describe the trapping of charge carriers [46]. Here, these measurements are performed under an applied bias voltage to monitor the photocurrent response of the solar cell for voltages in the S-kink region. This approach, in comparison to simulation data, allows the characterization of different working regimes of a device showing an S-shape in the J - V curve. Again, data of MeO-TPD/BPAPF samples are shown only. We start with a .../MeO-TPD(8)/MeO-TPD(8)/...sample, followed by a sample with an extraction barrier .../BPAPF(10)/MeO-TPD(20)/..., and conclude with a sample with an injection barrier .../MeO-TPD(8)/BPAPF(8)/....

A Solar Cell Without Barriers

Figure 6.17 shows measured transient currents for the device ITO/p-MeO-TPD(20)/MeO-TPD(16)/C₆₀(40)/BPhen(6)/Al. This solar cell does not contain any significant energetic barriers because the HTL and donor consist of the same material. The current signal follows the illumination pulse (switched on at 0 s and turned off after 50 μ s), and reaches steady state within several μ s, which is a commonly observed

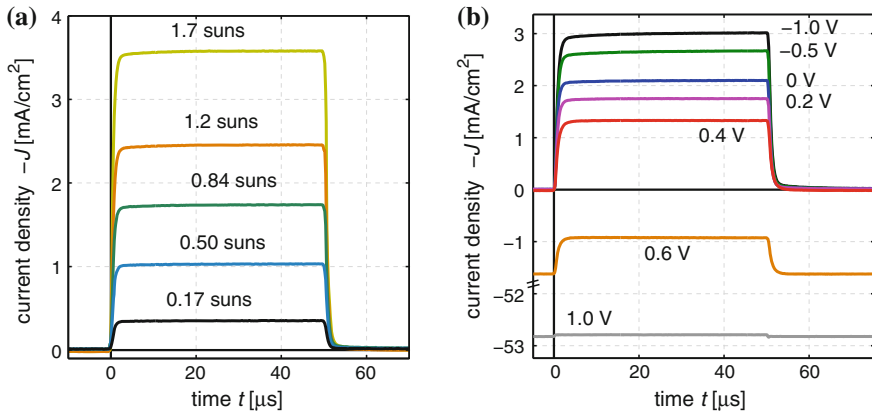


Fig. 6.17 *Experimental data* Transient current response of a sample with HTL = donor = MeO-TPD (8 nm). The illumination pulse has a length of 50 μs . The data represents the qualitative response of a well-working solar cell. As convention, positive values of the ordinate mean extracted photocurrent. Thus, the current axis is inverted compared to J - V plots. **a** Intensity dependence. **b** Dependence on the applied bias. Injection current is visible from 0.6 V. The photocurrent approaches 0 for higher voltages and does not change sign. This indicates the selectivity of the FHJ device

feature [46]. The response time can be used to characterize the charge transport properties of the intrinsic organic layers. However, dynamics with time constants in the range of 1 μs and lower can already be limited by the macroscopic series resistance and capacitance, rather than by charge transport processes in the device itself. The series resistance results from the lateral current through the ITO (30...40 Ω) and the measurement resistor (50 Ω). The assumption of the intrinsic layers with a total thickness of 56 nm behaving as one planar capacitor gives a capacitance C of:

$$C = \epsilon_r \epsilon_0 \frac{\text{area}}{\text{thickness}} = 5\epsilon_0 \times 6.4 \text{ mm}^2 / 56 \text{ nm} \approx 5 \text{ nF}. \quad (6.3)$$

Consequently, the time constant $\tau = RC$ is $\approx 0.5 \mu\text{s}$ and describes the time to (dis)charge (by $\exp(-1) \approx 0.37$) the electrodes of the device as a planar capacitor. This time might limit the rise time after toggling the illumination, but does not dominate the overall shape of the current response to illumination pulses with widths in the range of 100 μs . Therefore, regarding our investigations, the RC time is not significant as long as we do not extract quantitative data from the decay time.

The photocurrent in Fig. 6.17a increases with light intensity, whereas the shape of the response does not change. This indicates that the hole mobility is not significantly changed in the investigated intensity range. A dependence of the mobility on illumination intensity might be observable in cases of large trap densities or a broad DOS where deeper states in the HOMO are filled first.

Figure 6.17b shows transient current responses for different applied voltages. The steady-state currents in the dark and under illumination follow the respective J - V curves, whereas the characteristic shape of the response remains unchanged with voltage. The current signal, for voltages larger than the open-circuit voltage, does not change sign, but does approach 0. That proves the selectivity of the planar heterojunction, which does not allow photogenerated charges to be extracted at the other electrode (electrons at the anode and holes at the cathode).

A Solar Cell with an Extraction Barrier

In Fig. 6.18a light-intensity dependent transient photocurrents at 0 V for the device ITO/p-BPAPF(20)/BPAPF(10)/MeO-TPD(20)/C₆₀(40)/BPhen(6 nm)/Al with an extraction barrier of ≈ 0.3 eV are plotted. Compared to the previous device without a barrier, the photocurrent in steady-state ($t > 200$ μ s) is reduced to values < 1 mA/cm². This is expected when taking into account the short-circuit current that is extracted from the J - V curve (cf. Fig. 6.12). However, the most significant differences between a device with and without an extraction barrier are the overshoots observed in Fig. 6.18a, which depend on the light intensity. Small overshoots when switching on the light have already been observed and attributed to traps in the active layer [46]. In the case of traps governing the transient current curve, an overshoot is not expected when switching off the light. The current decay is then qualitatively comparable to the data of Fig. 6.17, and showing a larger decay time. This larger decay time means a slower response and is due to the contribution from trapped charges, which are extracted after a certain detrapping time (distribution).

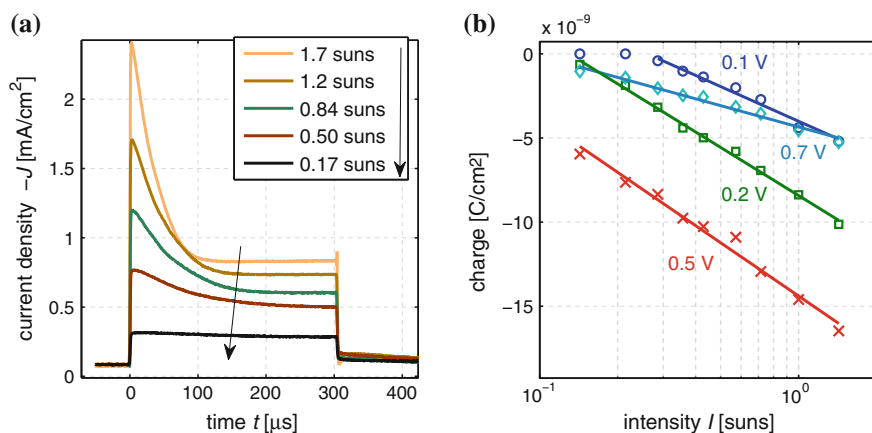


Fig. 6.18 **a** Experimental transient photocurrent of a device with extraction barrier (.../BPAPF(10)/MeO-TPD(20)/...) measured under varied intensities of the illumination pulse. **b** Piled-up charge obtained by an integration of the area below the negative overshoot-peak (cf. Fig. 6.19) for several applied bias voltages

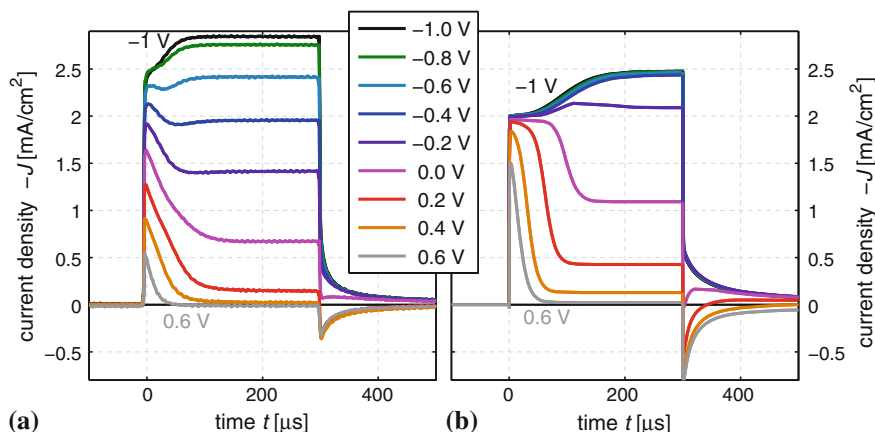


Fig. 6.19 Transient photocurrent response of a device with an *extraction barrier* (.../BPAPF(10)/MeO-TPD(20)/...) for different applied bias voltages: **(a)** *experiment* and **(b)** *simulation*. The characteristic overshoots are observed when toggling the illumination on at 0 and off at 300 μ s

The device with an extraction barrier, however, shows current in the reverse direction upon switching off the light. This effect occurs at a certain applied voltage, as can be seen in Fig. 6.19a, which shows the photocurrent responses of a complete voltage sweep. The negative current represents charges that enter the device after switching off the light. For a normal device (Fig. 6.17a) one expects that the remaining photogenerated charge carriers slowly leave the device and the current approaches 0 without changing sign. The characteristic shape of the photocurrent response in Fig. 6.19 is observed for several devices with an extraction barrier. Thus, it is concluded that this kind of double-overshoot in the transient response is a fingerprint of an extraction barrier.

The data of Fig. 6.19a map the voltage range of the entire S-kink region. It can be seen that under an increased reverse bias, the steady-state current rises, which is in accordance with the J - V curve (cf. Fig. 6.12). When leaving the S-kink region ($V < -0.5$ V) the positive and negative overshoots vanish, because the blocking effect of the barrier is overcompensated by the field-driven current over the barrier. The simulation data of Fig. 6.19b shows this transition as well. Therefore, simulation data are employed to explain the overshoots by investigating time evolutions for distributions of charge carrier densities within the device.

The overshoot, when switching on the light, is attributed to photogenerated charge carriers moving away from the D-A interface. The fast electrons in the acceptor leave the device quickly. Their extraction from the acceptor leads to a high displacement current over the intrinsic HTL due to the fact that there are no free charge carriers. Photogenerated holes drift and diffuse away from the D-A interface to the donor-HTL interface, where they pile up at the extraction barrier. This current causes the observed overshoot and stops as soon as the device is in steady state, where most of the potential drops over the intrinsic HTL.

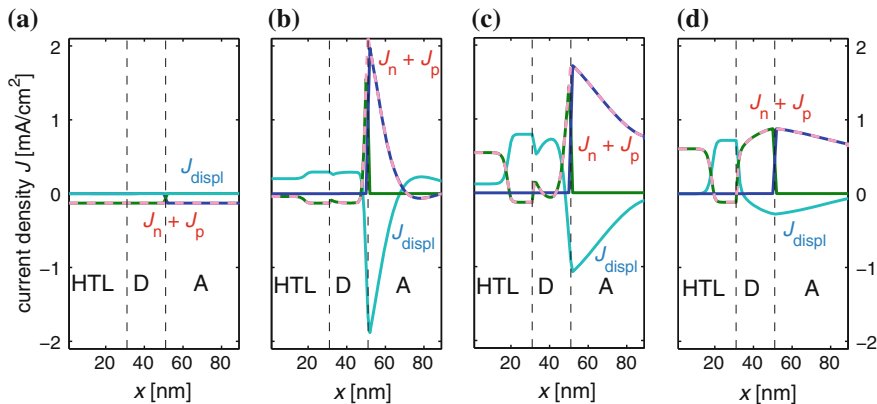


Fig. 6.20 Evolution of the spatial current distribution with time at 0.4 V after switching off the illumination of a device with an extraction barrier: **a** 0 s, **b** 30 ns, **c** 0.2 μ s, **d** 5 μ s. Positive current means current towards the D–A interface and negative current means extraction current. Shown are electron current (in acceptor A) J_n , hole current J_p , total charge current $J_n + J_p$, and the displacement current J_{displ} . After switching off the light, electrons flow to the D–A interface (b+c), followed by the slower holes, which have been piled-up at the HTL-donor interface. The intrinsic HTL ($20 \text{ nm} < x < 30 \text{ nm}$) mostly shows displacement current

Figure 6.20 shows simulated current profiles (J vs. x) to illustrate what happens when switching off the illumination. These current profiles are plotted for several time intervals after the light was switched off. The electric particle current $J_n + J_p$ is constant and negative at $t = 0$ (a). It represents the steady-state photocurrent provided by the holes (J_p) in the donor and HTL, and by the electrons (J_n) in the acceptor.

The current $J_n + J_p$ is no longer constant during the transient. The current measurable from externally is the sum of the particle and the displacement currents, where the latter guarantees that the sum is independent of x (cf. Sect. 4.3.5). Directly after switching off the light, the electron-hole source at the donor-acceptor interface vanishes, which leads to a strong diffusion gradient for electrons and holes toward the D–A interface. The faster electrons respond first and the electron current J_n changes its sign (b). This means that electrons are flowing towards the D–A interface. In (c) they are entering the device at the acceptor/cathode contact (on the right). The injected hole current in the doped HTL (on the left side) is equivalent to an extracted negative current. Thus, negative charge is transferred over the external contacts from the left to the right. Finally (d), the piled-up holes in the donor respond. The holes diffuse away from the HTL-donor interface back to the D–A interface and recombine with electrons. This process leads to an effective injection current when switching off the light. Such a current response to switching the light on and off exists if the holes are stored away from their location of generation. This proves the predictions of the simulations that holes are stored close to the extraction barrier and also shows the importance of charge diffusion. The height of the simulated overshoots is strongly

dependent on the electron and hole mobilities of the acceptor and donor, respectively, and can be significantly suppressed by a high series resistance.

Another approach to explain these overshoots is an analysis of the device using an equivalent-circuit model. The intrinsic HTL is then represented by a capacitance, which results from a planar capacitor approximation. This capacitor consists of the 10 nm intrinsic HTL as a dielectric, and the doped HTL and the interface HTL-donor as “electrodes”. The overshoot in the current response when switching on the light, is the current that charges this capacitor. The charging procedure takes some time, which is represented by the slow decay and limited by hole transport in the donor and the external resistance.

If we consider the device under short circuit conditions, the D–A interface should be capable of delivering the short-circuit current of the device without an extraction barrier. However, the photocurrent of the device with an extraction barrier is reduced compared to the short-circuit current of the device without an S-kink (cf. J - V curves in Fig. 6.12). Consequently, the D–A heterojunction is not operating at short-circuit, but is generating a photovoltage. This voltage drops over the charged capacitance, resulting in a voltage drop of 0 V measured externally. When switching off the light, the charging current source, and hence the voltage at the capacitor vanish and the capacitor is discharged with a current in the reverse direction.

The extraction of physical parameters from the rise and decay of the curves in Fig. 6.19 is difficult, because charge transport and recombination mechanisms are supposed to happen at sub-microsecond time scales. Therefore, the response is either limited by a trapping processes or by the RC -time of the setup itself. A reduction of the RC -constant would mean another solar-cell layout with smaller areas to reduce the capacitance. However, at the same time the reduced area decreases the photocurrent signal. The same holds for a lower measurement resistor, which reduces the series resistance, but decreases the quantity to measure, which is the photocurrent detected as a voltage drop over the input resistance of the oscilloscope.

Nevertheless, an integration in time of the current overshoot upon switching off the illumination gives an estimate of the amount of charges stored in the device. This number gives an idea of the expected charge carrier density close to the barrier. As most of the stored holes cannot overcome the barrier, there is no other way out of the device for them than flowing back to the D–A interface, where they recombine with electrons. Thus, in contrast to a charge extraction measurement of a blend [47], where charge collection after switching off the light is in competition with recombination, this is not the case here, because only the recombining charge carriers are measured. The charge (injected electrons) as a function of light intensity is shown in Fig. 6.18b for several applied voltages. The accumulated charge is highest at 0.5 V and decreases with higher applied bias, because the electric field in the device, which pushes the charges away from the D–A interface, becomes lower. The current is then mainly driven by diffusion. This weak driving force does not deliver much charge to be stored at the donor-HTL interface. Under decreased applied bias, the charge decreases as well, because the probability for overcoming the extraction barrier increases.

The accumulated charge shows a logarithmic dependence on light intensity for all voltages. This trend is expected, as the stored charge on a capacitor is proportional to the voltage applied to the capacitor. The voltage results from the illumination and scales with the photovoltage of the device, which is known to depend logarithmically on light intensity (cf. Fig. 3.25 in Sect. 3.3.2). The logarithmic dependence of the stored charges on intensity indicates that the probability of a charge carrier to overcome the barrier is not increased by a higher charge carrier density. Thus, there is no evidence for a filling-up of a possibly existent broad DOS in the intensity range discussed.

A Solar Cell with an Injection Barrier

Voltage dependent transient current data for the device with injection barrier ITO/p-MeO-TPD(20 nm)/MeO-TPD(8)/BPAPF(8)/C₆₀(40)/BPhen(6)/Al are plotted in Fig. 6.21a. The curves show mainly a shape which is comparable to the device without a barrier because charge extraction works well. However, there is a difference for voltages >0.4 V, where the S-kink is present. There, a small positive overshoot after switching on the illumination and a negative overshoot after switching off the illumination is observed. A simulation of a device with an injection barrier, shown in Fig. 6.21b, reproduces this effect.

Analogous to the extraction barrier situation, we explain the negative overshoot by a time evolution of current distributions within the device, starting from the situation of a steady state photocurrent (Fig. 6.22a). We discussed in Sect. 6.3.1 that this current is mainly driven by diffusion. When switching off the light, the source of electron-hole pairs rapidly vanishes and the diffusion current stops. However, there are many charge carriers in the donor, which constituted the diffusion gradient. These holes

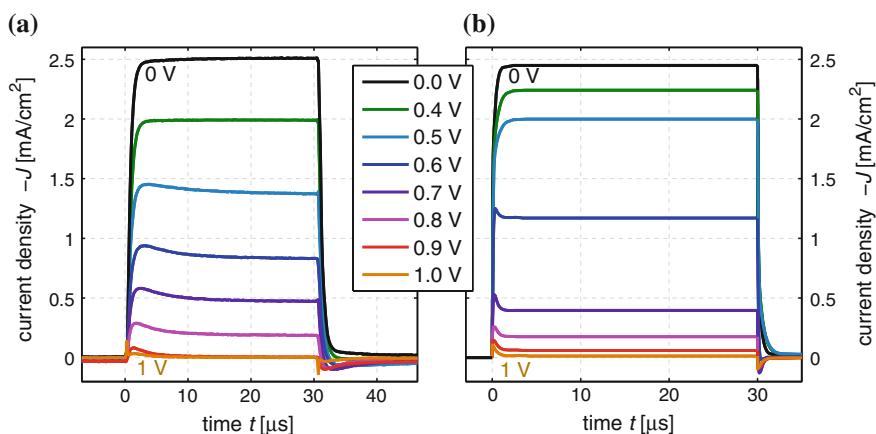


Fig. 6.21 Transient photocurrent of a device with an *injection barrier* (.../MeO-TPD(8)/BPAPF(8)/...) for different applied bias voltages: **a** *experiment* and **b** *simulation*. The small overshoots are due to current driven by diffusion

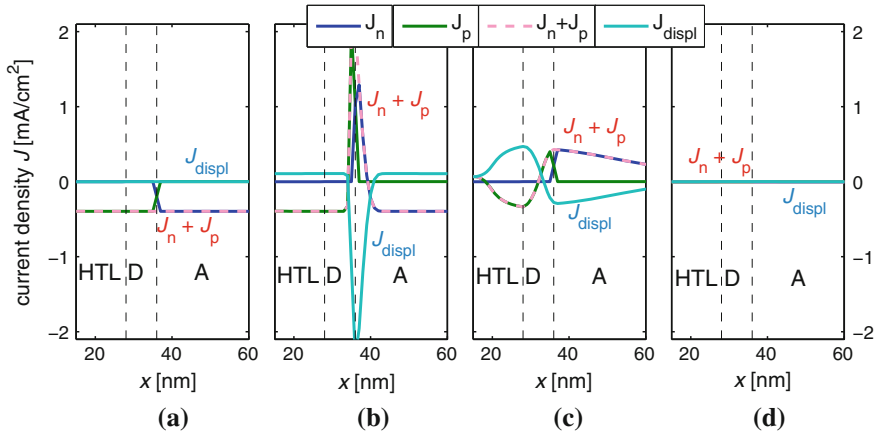


Fig. 6.22 Evolution of the spatial current distribution with time at 0.7 V after switching off the illumination of a device with an *injection barrier*: **a** 0 s, **b** 1.3 ns, **c** 0.19 μ s, **d** steady state. Shown are the electron current J_n in the acceptor A, hole current J_p , total charge current $J_n + J_p$, and the displacement current J_{displ} . A recombination current occurs at the D–A interface (positive) due to the reversed electric field (cf. Figs. 6.6a and 6.7a)

then face the reverse field (cf. Fig. 6.6a) and flow back to the D–A interface, instead of being extracted. This leads to a short, reversed current flow, which is seen in an overall positive current in Fig. 6.22c, which results the negative overshoot in the transient photocurrent. This overshoot is much less pronounced than in the case of the extraction barrier and does not show a distinct narrow peak. Therefore, the shape of the overshoot allows for a differentiation between the two types of barriers. Whereas all of the investigated samples with an extraction barrier showed overshoots, this feature is not observed for every sample with an injection barrier.

6.6.4 Intensity Dependent Measurements

The final method proposed to distinguish between an extraction and an injection barrier is the simplest. The reader is asked to reflect upon the following question for a second. Do we expect a different trend in the S-kink when performing J - V measurements at different illumination intensities? Think about the microscopic origins of the S-kink in relation to space charge.

The solution is found in Fig. 6.23, where normalized J - V curves measured at different illumination intensities are plotted. The normalization is done at a point of negative applied bias where the photocurrent is roughly saturated. This normalization allows for an easy comparison of the strength of the S-kink. Figure 6.23a shows data for a device with an extraction barrier. This time, we select α -NPB as the HTL combined with ZnPc as the donor. The nominal extraction barrier is then 0.5 eV maximum. The curves show that the higher the intensity, the more pronounced is the

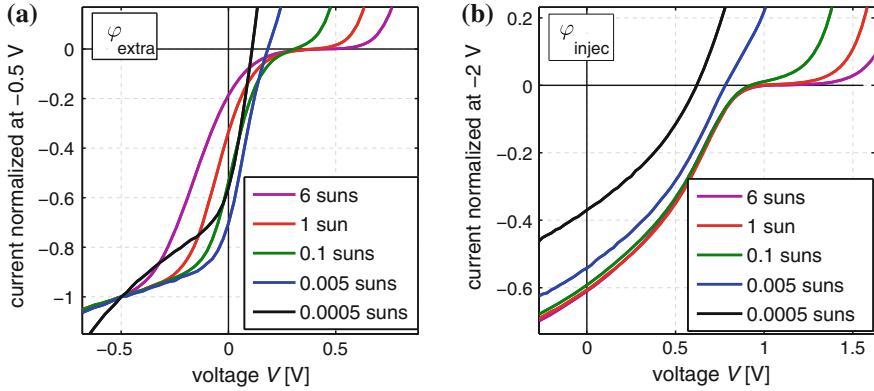


Fig. 6.23 *Experimental data* Normalized J - V curves measured at different illumination intensities. The normalization is done at a voltage in reverse bias, where saturation has been reached. **a** Device with an *extraction barrier* for holes: ITO/p-doped α -NPB (20 nm)/ α -NPB (8 nm, $\text{HOMO}_{\text{UPS}} \approx -5.5$ eV)/ZnPc (8 nm, $\text{HOMO}_{\text{UPS}} \approx -5.0$ eV)/C₆₀ (40 nm)/BPhen(6 nm)/Al (100 nm). **b** Device with an *injection barrier* for holes: ITO/p-doped MeO-TPD (20 nm)/MeO-TPD (8 nm, $\text{HOMO}_{\text{UPS}} \approx -5.1$ eV)/BPAPF (8 nm, $\text{HOMO}_{\text{UPS}} \approx -5.6$ eV)/C₆₀ (40 nm)/BPhen(6 nm)/Al (100 nm)

S-kink. Together with an increased V_{oc} for higher intensities, points of intersection for all normalized J - V curves emerge. These points are located in the fourth quadrant. The scaling of the S-kink with intensity is reproduced by the simulation data shown in Fig. 6.24a.

In contrast, the J - V curves in the case of an injection barrier do not show points of intersection (Fig. 6.23b). The curves mainly coincide for intensities larger than 0.1 suns. Deviations are only observed close to V_{oc} , due to an increased V_{oc} for higher intensities. At very low light intensities, the S-kink completely vanishes. When

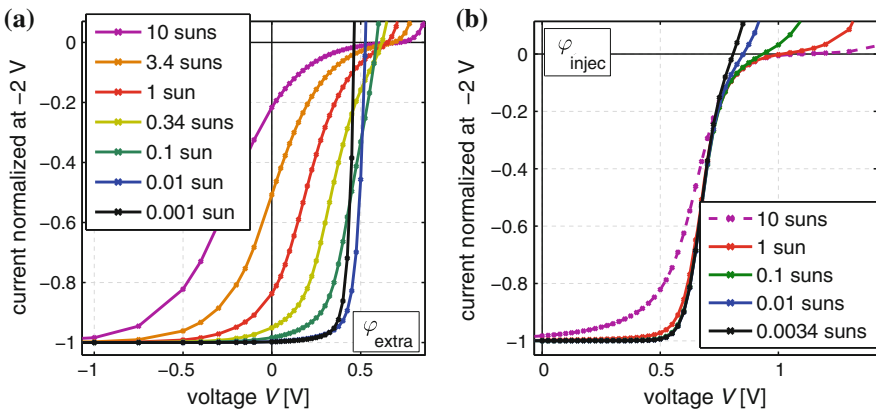


Fig. 6.24 *Simulated J - V curves* for devices with **a** an *extraction barrier* and **b** an *injection barrier* of 0.3 eV. The current is normalized at -2 V. The probability for overcoming the barrier is modeled according to Sect. 4.6 with a jump distance of 1 nm

comparing the experimental data to the simulated data in Fig. 6.24b, we recognize a similar behavior, which is characteristic for devices with an injection barrier. The curve at 10 suns is an exception, as bimolecular recombination sets in and reduces the FF due to an assumed bimolecular recombination in the simulation.

We want to explain the observed systematic differences using simulated profiles of charge densities and of the electric field within the device. We begin with the case of an extraction barrier. Figure 6.25a displays the simulated charge density and electric field for different illumination intensities and at 0 V. The positive charge at the donor-HTL interface shows that photogenerated holes pile-up in front of the barrier at this interface. This charge has to be compensated by a negative charge because the device

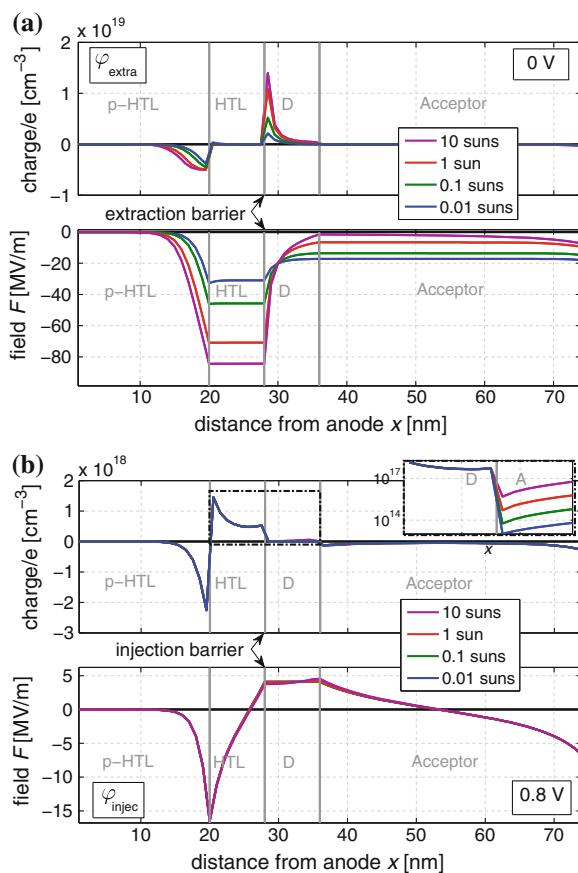


Fig. 6.25 Simulated spatial profiles of charge density and the electric field for a device with **a** an *extraction barrier* and **b** an *injection barrier*. For the device with an extraction barrier, the field at the donor-acceptor interface depends on the amount of piled-up charge, which is a function of the illumination intensity. For the device with an injection barrier, the field is not significantly modified under varied illumination intensities

was neutral before illumination. As the acceptor shows a sufficiently high electron mobility and the p-HTL is highly p-conductive, electrons and holes can provide the current in these regions. One can imagine that the electrons, being extracted at the right side, enter the device at the left side as the device is in short-circuit. Thus, the equal amount of electrons and holes neutralize each other. What remains is a negative space charge at the p-HTL/HTL interface. This is due to ionized dopants and is comparable to the space charge region in a p-n junction (cf. Sect. 2.5.1).

The key point of this figure is the increase of the piled-up charge with light intensity. This behavior is expected because the more charge generated provides more charge that piles up as determined by the transient measurements in the preceding section (Fig. 6.18). This charge influences the distribution of the electric field in the device. We have mentioned this effect several times during this chapter. The profiles of the electric field shown in the bottom part of Fig. 6.25a visualize this effect. The higher the intensity, i.e. the more charge that piles-up, the higher is the (negative) field in the HTL and consequently the lower is the (negative) field in donor and acceptor layers. In other words, the electric field in the donor and acceptor layers is partially screened by the piled-up charges, and the intrinsic HTL behaves like a dielectric of a capacitor. The lower electric field at the D–A interface means that the D–A interface works at a reduced field with higher light intensity. For instance, if the solar cell operates at 0 V applied bias, the working point of the D–A interface shifts with intensity towards lower electric fields, i.e. a higher forward bias voltage. Consequently, the share of the provided current for higher intensities is reduced due to the lower field at the D–A interface. This is exactly what the normalized J - V curves show. The S-kink becomes more prominent for higher intensities, because the piled-up charge screens the field at the D–A interface more efficiently. The screening is detrimental for photocurrent generation at the D–A interface and for transport of charges through the donor (and acceptor) layer.

Profiles for a device with an injection barrier operating in the S-kink regime (0.8 V) are shown in Fig. 6.25b. Recall that similar data was presented in Fig. 6.6a. Neither space charge nor the electric field are significantly changed upon a variation of the illumination intensity. The space charge is generated by the holes diffusing from the p-HTL into the i-HTL, leaving the (negative) ionized dopants in the p-HTL. The holes are stuck in the HTL due to the injection barrier towards the donor. The electric field in p- and i-HTL is caused by this space charge, which is comparable to the depletion region in a p-n junction. Recall that the S-kink for devices with an injection barrier was due to a V_{oc} which is larger than V_{bi} and a diffusion current against the electric field. This is seen here as well as the field at the D–A interface is positive. A higher illumination intensity simply increases the diffusion component (inset) and therefore V_{oc} . For low intensities, V_{oc} becomes smaller than V_{bi} and the S-kink vanishes. A redistribution of the electric field due to photogenerated charge carriers does not take place. The field distribution is basically given by the electrodes and the background charge.

In this section, we employed flat heterojunctions solar cells with known barrier types to demonstrate the technique of analyzing the light intensity dependence of the S-kink. However, an application of this approach to polymer:PCBM bulk-heterojunction solar cells was successfully demonstrated as well [3].

6.7 Summary

This chapter contained a study of the influence of the energy levels of the donor and HTL on the V_{oc} and the shape of the J - V curve. Thereby, it was possible to experimentally prove several predictions of the previous chapter considering the effect of contact properties. It was found that V_{oc} is decreased by injection barriers in the case of BHJs because the contacts are not selective and electrons can directly recombine with holes at the HTL-blend interface. However, V_{oc} is independent of the HTL and scales with the effective gap in the case of FHJs. The reason is the built-in selectivity of a FHJ due to the localized donor-acceptor interface, which keeps electrons away from the HTL. Considering extraction barriers, it was found that they do not significantly change the V_{oc} .

However, injection and extraction barriers can lead to S-kinks in the J - V curve. In the case of an extraction barrier, charge extraction requires higher negative applied voltages. That is why an S-kink is seen. Injection barriers cause S-kinks only in the case of selective contacts, here realized by FHJs. The reason is that photocurrent is driven by diffusion against the electric field, because V_{oc} exceeds V_{bi} .

Ideas were demonstrated on how to identify the type of barrier. The S-shapes caused by injection and extraction barriers show a qualitatively different behavior with temperature. Furthermore, the strength of the S-kink is affected by the thickness of the donor in the case of injection barriers and by the thickness of the HTL in the case of extraction barriers. The reason is that the thickness of the layer “behind” the barrier determines the electric field and therefore the current at the interface with the barrier. Transient photocurrent measurements were applied to visualize a pile-up of charge carriers in front of an extraction barrier, which causes characteristic overshoots in the current response. Injection barriers may also show small overshoots due to the drift current opposing the diffusion current. Studies on the dependence of the S-kink on the illumination intensity turned out to be a simple measure of discrimination between injection and extraction barriers.

All the experimental findings were explained by the aid of simulations, which were capable of reproducing the trends qualitatively and in the correct quantitative range. A more quantitative analysis, if desired, remains for further studies. This will require a more detailed knowledge of the charge transfer processes between different molecules.

Brief answers to the initial questions are:

- *What are the definitions of injection and extraction barriers for charges? What causes such barriers?*

The barriers are related to the interface between the active layer and the electrode or charge-transport layer. An injection barrier means an energetic barrier for the injection of charges when the device is operated in the forward direction. An extraction barrier means a barrier for extraction of photogenerated charges. Injection barriers can be caused by mis-aligned electrode work functions, whereas extraction barriers can result from thin insulating interlayers between the electrode and active material.

- *Why, and under what conditions does an injection barrier change the open-circuit voltage?*

An injection barrier can only change the open-circuit voltage, if the contact is not selective. In this case, the low built-in potential facilitates charges reaching the wrong electrode where they recombine. For a bilayer device, the selectivity is intrinsically given.

- *Why are injection barriers detrimental for efficient extraction of charge carriers?*

Injection barriers support the extraction of photogenerated charges that are close to the electrode. However, injection barriers imply a low built-in potential. In low-mobility materials, efficient extraction relies on drift currents supported by a high built-in potential. If extraction is only driven by diffusion against the electric field (as possible for selective contacts), the extraction efficiency will be low. In the extreme case, the current-voltage curve shows an S-kink.

- *What experimental approaches exist to distinguish S-kinks introduced by extraction barriers from those caused by injection barriers?*

Transient photocurrents and current-voltage data as a function of illumination intensity, temperature and layer thicknesses can be used.

- *In which case does the illumination intensity influence the S-kink and why?*

The illumination intensity influences the S-kink only in the case of extraction barriers, because the S-kink is due to a pile-up of charges at the barrier. The higher the intensity, the more charges pile-up. As these charges screen the electric field in the active layers, the efficiency for charge extraction is reduced.

- *What can transient photocurrent measurements close to open-circuit voltage tell about the driving forces for charge carrier extraction?*

Overshoots in transient current generation close to open-circuit conditions indicate that charges are displaced in the device. Consequently, these overshoots tell something about the pile-up of charges and the existence of diffusion gradients.

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Chapter 7

Further Origins of S-shaped J - V Curves

Abstract This chapter is dedicated to S-kinks in the J - V curve of organic solar cells. They are very interesting because they represent a pronounced feature in the J - V curve, which is related to a change in the working regime of the device. Often, they are manifest with decreased solar-cell performance. Consequently, it is desired to remove them based on the knowledge of their origin. In the previous chapter, barriers at electrodes have been discussed as possible reasons for S-kinks. In this chapter further sources of S-kinks are presented. We describe how a strong imbalance in mobilities (hole mobility in donor, electron mobility in acceptor) in flat heterojunction devices or a field-dependent dissociation of geminate pairs at the donor/acceptor interface causes S-kinks. In the final parts of this chapter “unconventional” kinks with turning points at voltages higher or lower than the open-circuit voltage are discussed. The following questions cover the content of this chapter: (a) Under what conditions can imbalanced mobilities cause S-shaped J - V curves? (b) What is the mechanism in which imbalanced mobilities cause S-shaped J - V curves? (c) How can this effect be identified and distinguished from others? (d) How can kinks in the forward current be explained? (e) What might be the reason for “unconventional” distortions of the J - V curve?

7.1 Imbalanced Mobilities in Planar Heterojunction Solar Cells

We start with an investigation of imbalanced mobilities in planar heterojunctions, i.e. bilayers of donor and acceptor. Note that imbalanced mobilities cannot cause S-kinks in a homogeneous bulk heterojunction. However, inhomogeneities in bulk heterojunctions, for instance due to a vertical phase separation, could create similar conditions as discussed here.

The content of Sect. 7.1 is partly published in [1].

Table 7.1 Fixed values for the modeled bilayer device

Structure		Donor	Acceptor
Thickness	d	30 nm	30 nm
HOMO	E_{ht}	−5.2 eV	−6.4 eV
Electrical gap	E_{g}	2.1 eV	2.3 eV
LUMO density of states	N_{C}	$2.4 \times 10^{19} \text{ cm}^{-3}$	$4.2 \times 10^{21} \text{ cm}^{-3}$
HOMO density of states	N_{V}	$2.4 \times 10^{19} \text{ cm}^{-3}$	$7 \times 10^{21} \text{ cm}^{-3}$
Dielectric constant	ϵ_{r}	3.4	3.4
Exciton diffusion length	L_{D}	7 nm	35 nm

The work function of the anode is chosen to 5.2 eV and of the cathode to 4.2 eV. The injection mechanism is thermionic with a backward flowing recombination current (4.67). The lifetime of excitons within the layer is much higher than at the D-A interface. Recombination of free charges at the D-A interface is assumed to happen within the Coulomb radius. The temperature is 300 K, and the discretization is 0.5 nm. A homogeneous exciton generation rate of $1.5 \times 10^{22} \text{ cm}^{-3} \text{ s}^{-1}$ is assumed. This assumption does not influence any statement of this chapter, as the exciton generation rate and the values for L_{D} determine the saturated photocurrent. This photocurrent is wanted to be constant for a good comparability of the J - V curves

7.1.1 Imbalanced Mobilities in Simulation

To gain insight into the interplay between electron and hole mobilities in flat heterojunction solar cells, we study simulation data of model devices according to the methods detailed in Chap. 4. They consist of a donor-acceptor bilayer with thermionic contacts. The injection barriers at the contacts are assumed to be low (≤ 0.1 eV) showing a negligible effect on the J - V curve (cf. Chap. 5). In this case, the charge carrier densities obtained according to (4.64) may be realistic. We start with a thickness of 30 nm for both donor and acceptor, which is a common value for small-molecule organic solar cells. The other input parameters used for the simulations can be found in Table 7.1.

Figure 7.1 shows simulation results for a large variation of hole mobility in the donor ($\mu_{\text{p}}^{\text{D}}$) and electron mobility in the acceptor ($\mu_{\text{n}}^{\text{A}}$). For better comparability of the J - V curves, the recombination constant for bimolecular recombination is set independently of mobility to a value of $5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, which is expected for Langevin theory at a mobility of $\approx 10^{-3} \text{ cm}^2/\text{V s}$. Using the Langevin expression (4.46) has a minor effect on the qualitative shape of the J - V curve. However, we know from Chap. 5 that a varied recombination constant changes V_{oc} , but that would make a graphical comparison of the J - V curves here more difficult.

The simulated J - V curves of Fig. 7.1 show that high mobilities lead to high FF , whereas low mobilities decrease the FF strongly, comparable to the results of a bulk heterojunction (BHJ) in Chap. 5. The lower the mobility, the higher the electric field needs to be to extract a certain amount of charge carriers before they recombine at the heterointerface. Specific to the flat heterojunction is the emergence of an S-kink in case of imbalanced mobilities. The S-kink becomes obvious for a mobility mismatch $\mu_{\text{n}}^{\text{A}}/\mu_{\text{p}}^{\text{D}}$ (or $\mu_{\text{p}}^{\text{D}}/\mu_{\text{n}}^{\text{A}}$, respectively) of ≈ 100 or greater. The S-kink does not appear

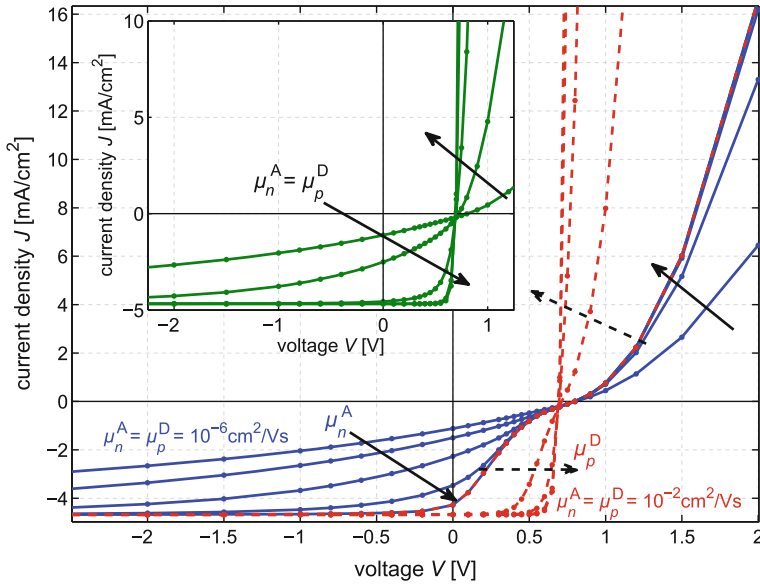


Fig. 7.1 Simulation data of a bilayer device with varied mobilities. *Solid lines* The hole mobility in the donor μ_p^D is fixed to $10^{-6} \text{ cm}^2/\text{V s}$, whereas the electron mobility in the acceptor μ_n^A is varied ($10^{-6}, 10^{-5}, 10^{-4}, 10^{-3}, 10^{-2} \text{ cm}^2/\text{V s}$). *Dashed lines* μ_n^A is fixed to $10^{-2} \text{ cm}^2/\text{V s}$ and μ_p^D is varied $10^{-6} \dots 10^{-2} \text{ cm}^2/\text{V s}$. *Inset* Balanced mobilities $\mu_n^A = \mu_p^D = 10^{-6} \dots 10^{-2} \text{ cm}^2/\text{V s}$. An imbalance in mobilities larger than a factor of 100 results in S-kinks

when both mobilities are balanced independent of whether they are high or low. This situation is demonstrated in the inset of Fig. 7.1 where J - V curves for balanced mobilities are shown.

Calculations with other mobility pairs reveal that the relative imbalance factor μ_p/μ_n governs the strength of the S-kink. Furthermore, the strength of the S-kink scales with the thickness ratio of low-mobility to high-mobility layer and is less influenced by the total device thickness. This is visualized by the series of J - V curves in Fig. 7.2, where $\mu_n^A/\mu_p^D = 1,000$ is assumed. There, for each ratio between donor and acceptor thicknesses (different colors) the total device thickness is also varied. The S-kink is more severely affected by the thickness of the layer showing the low mobility. J - V curves within the same ratio of donor to acceptor thickness almost coincide in the S-kink region in the fourth quadrant independent of the total thickness of the device. The effect of the overall thickness is seen in forward direction where in particular a thicker layer showing low mobility decreases the slope. This trend might be regarded as an increased (non-constant, but rather space-charge limited) series resistance caused by the low-mobility layer.

Although an S-kink is detrimental as it implies a low FF , imbalanced mobilities are still preferred to balanced low mobilities. The J - V curves of Fig. 7.1 show that the power-conversion efficiencies of devices with S-shaped J - V curves are higher

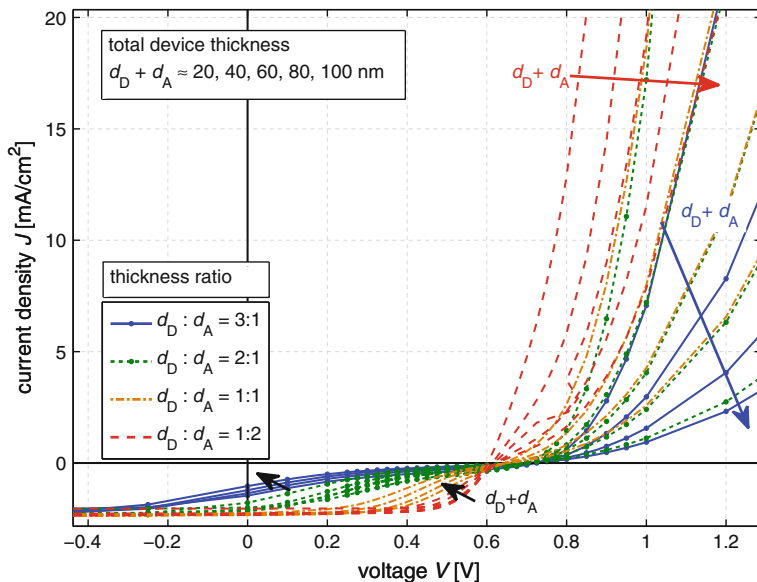


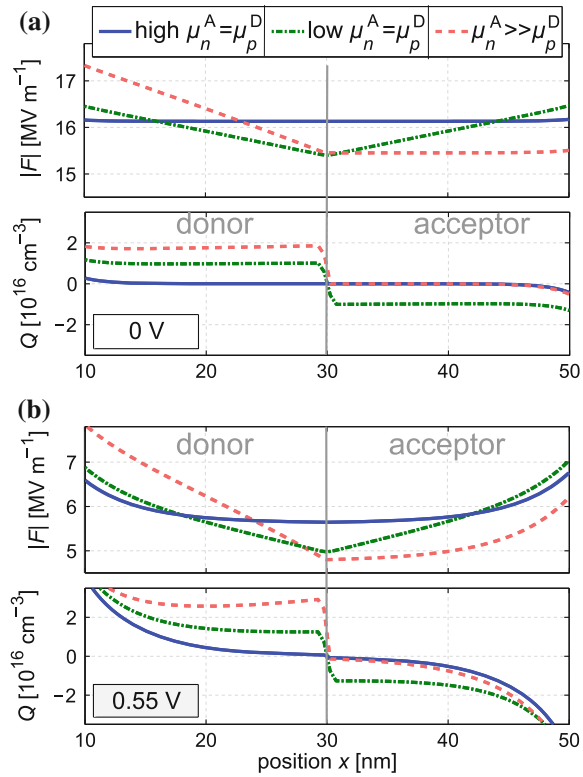
Fig. 7.2 Simulation data for a variation of donor and acceptor thicknesses, using $\mu_n^A = 10^{-2} \text{ cm}^2/\text{V s}$ and $\mu_p^D = 10^{-5} \text{ cm}^2/\text{V s}$. A variation of the total device thickness and the ratio between donor and acceptor thickness shows that the S-kink is dominated mainly by the ratio

compared to the case of low mobilities, where short circuit current density and sometimes FF are even lower.

To explain the observations we refer to simulated profiles of the electric field and of charge carrier densities within the layers. Figure 7.3 shows data of three mobility pairs at two different applied voltages, 0 and 0.55 V, which sample the S-kink region. For balanced high mobilities (solid line), the electric field (at zero bias originating from the built-in voltage) in the device is constant except at the contacts due to the high density of dark/background charge carriers there (cf. Sect. 5.3). For both voltages, all charge carriers are extracted due to their high mobilities. The driving force is mainly drift due to the built-in field assisted by diffusion away from the interface. The situation is different for very low mobilities (dash-dotted). In this case, a space charge is built up in the complete device, because electrons and holes cannot be extracted sufficiently fast. Their concentration at the D-A interface is increased and hence recombination probability as well, which leads to a lower FF . The effect of the space charge is also seen in the electric field which is not constant.

In the case of imbalanced mobilities (dashed), the field distribution is asymmetric, because only the less mobile holes give rise to an extended space charge. The space charge reduces the drop of the electric potential in the acceptor and increases the magnitude of the field in the donor. This adjustment assures that for every extracted electron (with high mobility), a hole is extracted in steady state, which is a requirement to not steadily charge the device. The rearrangement of the field guarantees the

Fig. 7.3 Electric field F and charge density Q per elementary charge as a function of distance x from the anode. **a** at 0 V, **b** at 0.55 V applied bias for a device with high mobilities $\mu_n^A = \mu_p^D = 10^{-2} \text{ cm}^2/\text{V s}$ (solid), low mobilities $\mu_n^A = \mu_p^D = 10^{-5} \text{ cm}^2/\text{V s}$ (dash-dotted), and highly imbalanced mobilities $\mu_n^A = 10^{-2} \text{ cm}^2/\text{V s}$, $\mu_p^D = 10^{-5} \text{ cm}^2/\text{V s}$ (dashed). Latter results in asymmetric profiles giving rise to S-shaped J - V curves



extraction of every photogenerated charge carrier at 0 V. However, with decreasing field, resulting from positive applied bias (Fig. 7.3b), electrons pile up at the D-A interface as well. Consequently, recombination is increased and in turn the current is decreased. The J - V curve approaches the curve for low mobilities, which results in an S-kink. For applied bias voltages larger than V_{oc} , the J - V curve for imbalanced mobilities follows mainly the J - V curve for balanced low mobilities. The reason is that forward current in this voltage range is driven by diffusion and hence mainly limited by the charge carrier with the low mobility.

As the S-kink results from the spatial separation of electrons and holes in combination with a redistribution of the electric field, an S-kink is not expected in a bulk heterojunction with imbalanced mobilities. The reason is that in the case of a BHJ, the field-free region (resulting from the μ -imbalance) close to the contact of the more mobile charge carrier decreases continuously with negative applied bias. As recombination roughly equals generation in this region, where the driving force for extraction of charge carriers is weak, photocurrent is not collected there. The decrease of this region with enhanced applied negative bias leads to a smooth increase of photocurrent. In the extreme case it scales with the square root of the applied bias and with the intensity to the power of $3/4$ [2]. This effect was discussed with the aid of

analytical equations in Sect. 3.3.5 and with numerical simulations in Sect. 5.5 (energy diagram comparable to the one in Fig. 5.17). Note that a non-homogeneous bulk heterojunction, where gradients in material concentrations might introduce gradients in mobility, lead to a similar situation as for a flat heterojunction. Thus, the J - V curve of such a bulk heterojunction device might show an S-kink [3].

7.1.2 Experimental Verification

To demonstrate the relevance of the simulation data, experimental data is shown in this section. One should check in particular the following points to discriminate the case of imbalanced mobilities from the case of barriers discussed in the previous chapter:

- The I - V curve of a flat heterojunction (FHJ) comprising a D-A combination with a high mobility mismatch and with ohmic contacts shows an S-kink.
- The thickness dependence of the S-kink matches the predictions from simulations.
- The S-kink disappears with a decreased imbalance in mobility.
- The S-kink vanishes in a blend while V_{oc} does not change significantly.
- Photocurrent transients do not show overshoots.

Solar cells of p-i-n type (cf. Sect. 3.6.2) and comprising the donor material Ph4-Ph4-DIP [4] (cf. Fig. 3.51) are chosen to prove these points. The stack consists of ITO/p-doped BPAPF (25 nm, 10 wt%)/Ph4-Ph4-DIP (10, 20, 40, 60 nm)/[C₆₀ or Me-PTCDI (30 nm)]/n-C₆₀ (10 nm, 3 wt%)/Al.

Ph4-Ph4-DIP is synthesized as a substitute for the commonly used ZnPc with the aim of shifting the absorption from the red into the green spectral range accompanied by a higher V_{oc} . Thus, additional photons can be harvested which are not accessible by ZnPc/C₆₀ solar cells (cf. Fig. 3.53). Both goals are realized. However, the photocurrent in a FHJ with C₆₀ is low due to a low exciton diffusion length. This can be seen when comparing the absorption data with EQE data shown in Fig. 7.4a, b. As mobility and exciton diffusion length are expected to follow the same trend (for Dexter transfer, cf. Sect. 3.2.1), a low μ_p can be anticipated.

J - V data from single-carrier devices (p-i-p) with layer thicknesses between 10 and 60 nm suggest a mobility which is strongly dependent on the electric field (F) and the illumination intensity, probably due to trapping effects. The J - V curves shown in Fig. 7.5 are measured under simulated solar illumination to represent a situation as close as possible to the working conditions of solar cells. Dashed lines show simulation data where a Poole-Frenkel mobility, $\mu(F) = \mu_0 \exp(\gamma\sqrt{|F|})$ (4.42), is assumed. The parameters given in the figure result in a satisfactory reproduction of the experimental data. The values of μ_0 and γ for the four devices with different thicknesses describe a mobility of the same order of magnitude. This rough estimation results in a very low value and is sufficient for the discussions here. The reason for such a low value could be the phenyl end groups of the molecule (cf. Fig. 3.51), which are free to rotate out of plane, hindering close stacking and hence π -electron

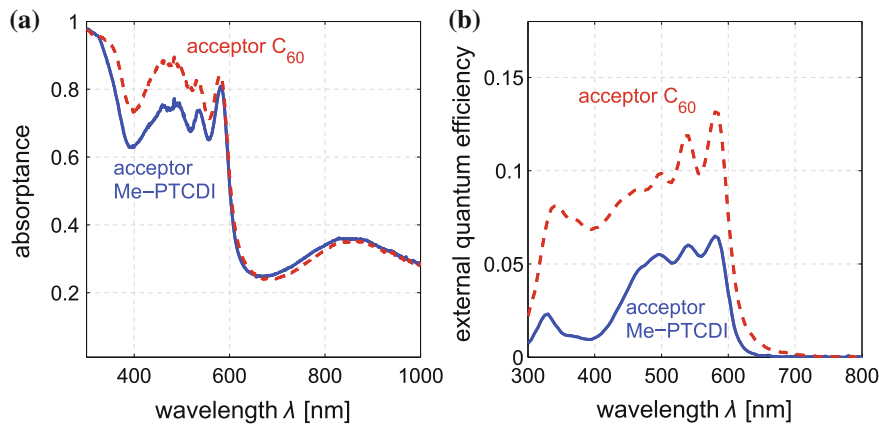


Fig. 7.4 **a** Absorbance and **b** external quantum efficiency of a complete solar cell. The stack is ITO/p-doped BPAPF (25 nm)/Ph4-Ph4-DIP (15 nm)/[C₆₀ or Me-PTCDI (20 nm)]/n-doped C₆₀(20 nm)/Al (100 nm)

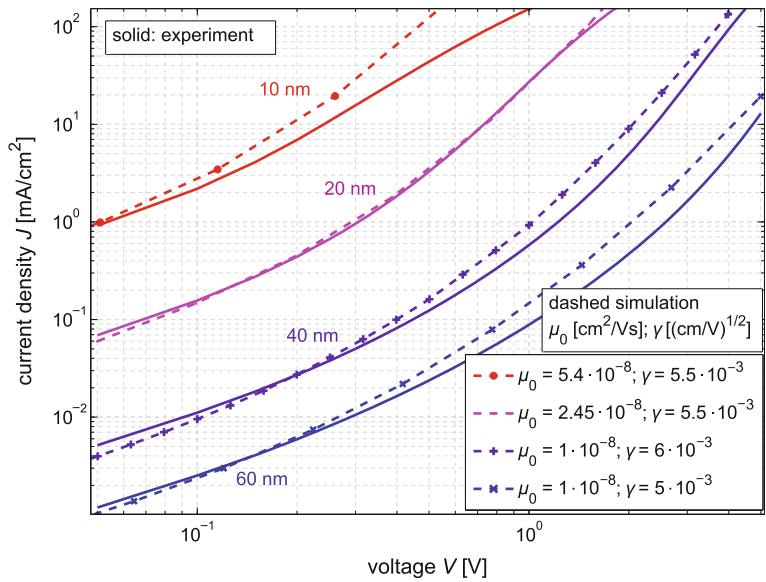


Fig. 7.5 Experimental (*solid lines*) and simulation (*dashed*) data of single-carrier devices with the structure ITO/NDP9 (1)/BPAPF:NDP9(25, 10 wt%)/Ph4-Ph4-DIP(10; 20; 40; 60)/BPAPF:NDP9 (25, 10 wt%)/NDP9 (1)/Au (9)/ Al (100). The ITO series resistance becomes visible at high currents. Its influence can be seen in the sample with a Ph4-Ph4-DIP layer thickness of 10 nm

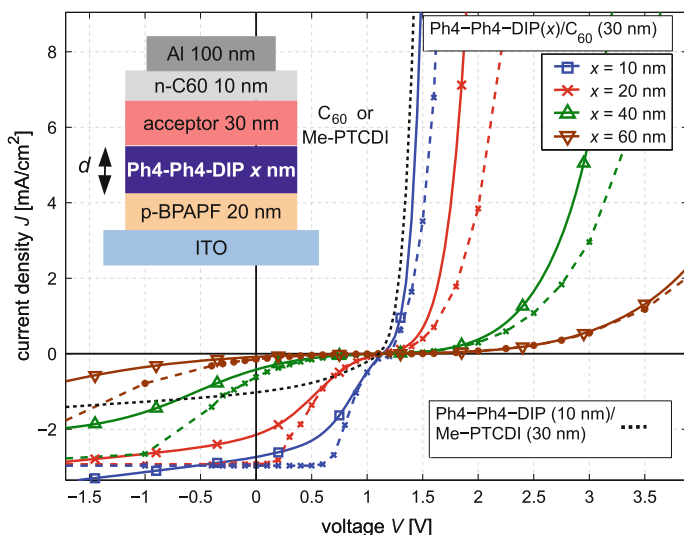


Fig. 7.6 Solid lines Experimental data of devices ITO/p-BPAPF/Ph4-Ph4-DIP/(C₆₀ or Me-PTCDI)/n-C₆₀/Al. The FF is 41 % for 10 nm Ph4-Ph4-DIP/C₆₀ and 37 % for 10 nm Ph4-Ph4-DIP/Me-PTCDI. The J - V curves are measured under illumination of simulated sunlight with an intensity of 100... 110 mW/cm² monitored by a calibrated silicon photodiode and roughly corrected for spectral mismatch. Dashed simulation data

wave-function overlap between molecules. In contrast, the mobility of the acceptor C₆₀ in a thin film is reported to be in the range of 10⁻² cm²/V s [5]. Comparing these mobility data to the predictions of simulation (Fig. 7.1), an S-kink is anticipated for a FHJ consisting of Ph4-Ph4-DIP/C₆₀.

Current-Voltage Characteristics

Figure 7.6 shows J - V curves of Ph4-Ph4-DIP/C₆₀ solar cells with different Ph4-Ph4-DIP layer thicknesses measured at a mismatch-corrected intensity of 100–110 mW/cm². The respective solar-cell parameters are found in Table 7.2. A simulation (dashed lines) of the complete solar-cell stack with the mentioned mobilities and without any parameter optimization describes the shape of the S-kink around V_{oc} well, including the strong dependence on the thickness of the donor layer. This fact and the good alignment of the hole transport levels of BPAPF and Ph4-Ph4-DIP, which is indicated by a similar V_{oc} of 1–1.1 V in a FHJ with acceptor C₆₀ (for BPAPF/C₆₀ solar cell, see data of previous chapter, p. 304), exclude large barriers at the contacts as the reason for the S-kink.

In the following the effect of a decrease in mobility imbalance is investigated: Increasing μ_p^D by replacing Ph4-Ph4-DIP with ZnPc leads to well-known ZnPc/C₆₀ solar cells without S-shapes (cf. previous chapter). Thus, it is more interesting to maintain the donor material Ph4-Ph4-DIP and investigate a decrease of μ_n^A . To do so, Me-PTCDI, a material with a comparable electron affinity to C₆₀ is employed to

Table 7.2 Solar-cell parameters of devices consisting of ITO/p-doped BPAPF (25 nm, 10 wt %)/Ph4-Ph4-DIP (10, 20, 40, 60 nm)/C₆₀ (30 nm)/n-C₆₀ (10 nm, 3 wt %)/Al

Thickness (nm)	V_{oc} (V)	FF (%)	J_{sc} (mA/cm ²)	J_{sat} (mA/cm ²)
10	1.1	41	2.7	2.8
20	1.1	24	2.2	2.4
40	1.1	14	0.4	1.5
60	1.1	15	0.08	1.3

The saturated photocurrent J_{sat} is estimated by correcting the J - V curve in reverse bias for a photoshunt [6]

replace the acceptor C₆₀. OFET measurements are used to determine the mobility of the materials. They deliver an electron mobility of Me-PTCDI which is significantly lower than the one in C₆₀ (C₆₀: 7×10^{-3} , Me-PTCDI: 2×10^{-4} , Ph4-Ph4-DIP: 2×10^{-6} cm²/V s). Although the OFET mobility is determined under different measurement conditions (lateral surface current and high charge carrier densities, cf. Sect. 4.9) than relevant for charge transport in organic solar cells, rough trends can be transferred to layers in solar cell geometry.

The dotted J - V curve in Fig. 7.6 representing a Ph4-Ph4-DIP (10 nm)/Me-PTCDI device indeed does not show an S-kink. This behavior is expected from the simulation data displayed in Fig. 7.1. The FF is lower than in the solar cell with C₆₀ caused by the lower mobility of Me-PTCDI. The photocurrent is decreased mainly due to a smaller contribution from Me-PTCDI compared to C₆₀ and possibly a decreased charge carrier separation efficiency, because the EQE (Fig. 7.4) drops over the entire spectral range. However, the lower photocurrent cannot explain the difference in the shape of the J - V curves between C₆₀ and Me-PTCDI as acceptor, because a varied illumination intensity does not significantly influence the S-kink. Me-PTCDI solar cells also show an S-kink for thicker Ph4-Ph4-DIP layers, which qualitatively fits to the predicted thickness dependence (data not plotted).

To further confirm our hypothesis that imbalanced mobilities is the primary cause of the S-kinks in these systems, inverted solar cells are made. Their J - V curves are plotted in Fig. 7.7. They show the same trends, which means that the observed features do not depend on the stack order. The open-circuit voltage of the Me-PTCDI samples is reduced which might be due to the inverted stack. Previously for all solar cells, an n-doped C₆₀/Al contact was used, whereas here an ITO/C₆₀ or ITO/Me-PTCDI contact is used as electron collecting electrode. Furthermore, the material batch was changed. However, the S-kink is significantly present in the FHJ with C₆₀, whereas the FHJ with Me-PTCDI shows a reasonable FF . This is in accordance with the discussions so far. Now the FHJ data is compared to bulk heterojunction (BHJ) data, displayed in Fig. 7.7 as well. The BHJ solar cells (dashed) do not show S-kinks for both acceptors. The FF of the C₆₀ BHJ device is significantly increased compared to the FHJ. The reason is that charge transport is mainly provided by electrons. This can also be seen in the higher forward currents for the BHJ. Here, the electrons are capable of driving the complete current through the bulk, in contrast to current for FHJ where a flow of holes in the pristine donor layer is required as well.

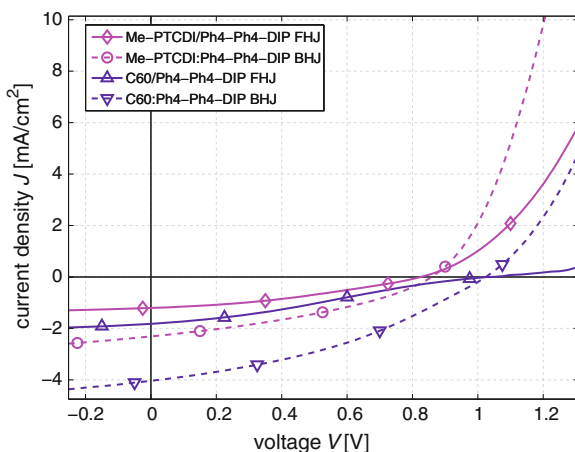


Fig. 7.7 Comparison between flat (FHJ) and bulk heterojunction (BHJ) solar cells in inverted architecture: ITO/ETL (20 nm)/active layer /Ph4-Ph4-DIP (5 nm)/p-BPAPF (40 nm)/p-ZnPc (10 nm)/Au (40 nm) with active layer acceptor (5 nm)/Ph4-Ph4-DIP (25 nm) for FHJ and acceptor:Ph4-Ph4-DIP (25 nm; 3:2) for BHJ. Either C₆₀ or Me-PTCDI is used as acceptor and electron transport layer (ETL). The S-kink is only observed for the FHJ with C₆₀

In Chap. 6, we found differences between FHJ and BHJ depended on the type of contact barrier. There, it was shown that in the case of extraction barriers, the S-kink remains for both FHJ and BHJ, whereas in the case of an injection barrier the S-kink of a FHJ vanishes when the same materials are employed in a BHJ. The latter result is comparable to the observation here. However, in Chap. 6 the removal of the S-kink was accompanied by a significant reduction of V_{oc} . This is not the case here. V_{oc} is almost independent of whether the solar cell consists a BHJ or a FHJ. Thus, an injection barrier as the main source of the S-kink is excluded and the S-kink is attributed to the low mobility of Ph4-Ph4-DIP which shows a high imbalance with the electron mobility of C₆₀.

Transient Photocurrents

A further proof of the significance of the low-mobility donor is revealed by performing a photocurrent transient measurement. In the previous chapter (Sect. 6.6.3), this method has already been used to identify the existence of barriers at overshoots in the current signal. There, transient photocurrent measurements were proposed as means of discriminating different reasons for an S-kink.

A voltage sweep of transient current data for the device with 20 nm Ph4-Ph4-DIP/30 nm C₆₀ is shown in Fig. 7.8. Although the shape of the J - V curves of a mobility-mismatch and barrier-induced S-shape look similar (cf. Figs. 7.6 and 6.4), the transients behave differently. In Fig. 7.8 the transients for the mobility-mismatch solar cell are characterized by a very slow response due to the low mobility (time range is milliseconds). A small overshoot is visible when switching on the light,

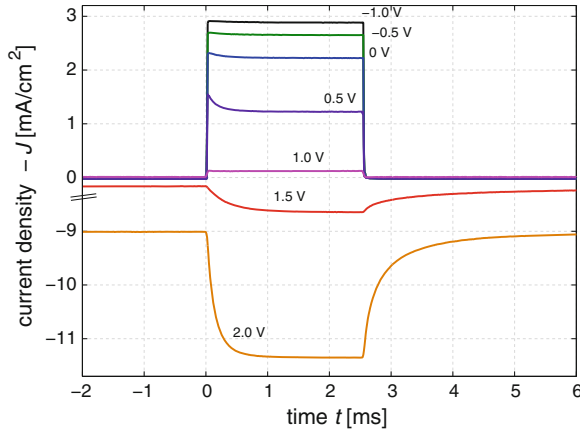


Fig. 7.8 Transient current response of a FHJ sample containing 20 nm Ph4-Ph4-DIP / 30 nm C₆₀. The response time is in the range of milliseconds. In forward bias (>1.5 V), a photoconductivity effect is seen

but not when switching it off. At V_{oc} transient current is not measurable at all. This means that a redistribution of charges within the device cannot be observed. Most likely the hole transport in the donor away from the donor-acceptor interface limits the response time.

The transients at voltages larger than V_{oc} show that illumination results in an increase of forward currents. Possible reasons for this phenomenon were discussed in Sect. 5.4. The absolute value of this current reaches values larger than the photocurrent extracted in reverse direction. This observation and the increased time constant compared to current extraction clearly indicate that the reason for this increased current is an increase in the conductivity of Ph4-Ph4-DIP upon illumination. Thus, this current does not originate from photocurrent, extracted in forward direction, but from a photoconductivity effect which decreases the series resistance of the device under illumination. As already mentioned in Sect. 5.4, a decreased series resistance can be responsible for an intersection of J - V curves measured in the dark and under illumination. In the transient photocurrent measurement this effect appears as additional photocurrent.

7.2 Field-Dependent Exciton Dissociation

Thus far, the S-kink in the simulated J - V curves was due to transport properties of free charge carriers only. A field-dependent exciton dissociation was not considered. Now, we investigate this effect using Onsager-Braun theory (Sect. 4.4.2). Although this theory is highly-debated, it is applicable to qualitatively investigate the role of a field-dependent dissociation of geminate pairs. It turns out that this process can be a source of S-kinks as well, even for other dissociation models [7]. The

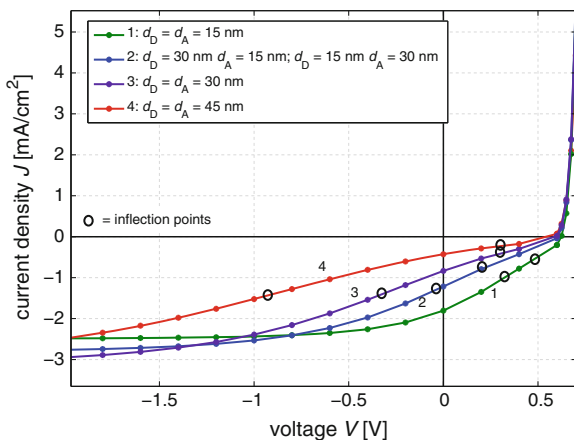


Fig. 7.9 S-kink caused by field-dependent exciton dissociation according to Onsager-Braun theory with $a = 1.2$ nm and $k_{\text{relax}} = 5 \times 10^6$ s $^{-1}$ (cf. Sect. 4.4.2). Other parameter pairs, where this process is significant, show a qualitatively similar behavior. In comparison to the case of imbalanced mobilities (Fig. 7.2), only the overall device thickness is important for the strength of the S-kink (as long as donor and acceptor show the same dielectric constant and charge transport is not limiting). Forward current is relatively unaffected compared to the data of Fig. 7.1. The inflection points of the J - V curve are marked with circles

simulation data shown in Fig. 7.9 demonstrate that the curvature of such an S-kink is lower than in the case of imbalanced mobilities or barriers. Therefore, the S-kink covers a larger voltage range. In some cases, the complete S-kink cannot be observed in an experimental measurement, where high negative voltages might not be accessible.

The S-kinks in Fig. 7.9 show some qualitative differences compared to those previously discussed: The strength of the S-kink scales with the overall device thickness and is independent of the ratio between the thickness of the donor layer and the acceptor layer, as long as their dielectric constants are similar. Previously, one of the two turning points was located at V_{oc} , which is not the case here. Therefore, the forward current is not affected when the strength of the S-kink changes. This is the most important characteristic to discriminate field-dependent exciton dissociation effects from the other sources of S-kinks. A field-dependent dissociation is not expected to change the (forward) injection current. This kind of S-kink has been reported for both polymer [8] and small molecule [9] solar cells.

7.3 Kinks in Forward Direction

Apart from kinks with turning point close to V_{oc} , J - V curves can exhibit kinks in forward direction as well. An example is displayed in Fig. 7.10. This J - V curve shows besides the known kink with the second turning point at V_{oc} an additional

kink at around 0.7 V. The device under investigation consists of a TQ1:PC71BM blend sandwiched between two PEDOT:PSS electrodes, where the bottom electrode is modified by an interface material PFPA1 which is capable of reducing the work function of PEDOT, (partially) converting it to a cathode [10, 11] (for materials, cf. Figs. 3.55 and 3.61). Employing this design strategy is interesting because a device based on two PEDOT electrodes allows for the production of a potentially low-cost semitransparent solar cell. Although other experiments have shown better performing devices, the example here demonstrates that the conversion of PEDOT into a cathode does not completely work. Otherwise, we would not expect S-shaped J - V curves.

We use simulation data to suggest an explanation for the behavior of this PEDOT-based device, in particular addressing the second kink occurring at a voltage larger than V_{oc} . Simulation data are shown as lines in Fig. 7.10. They are obtained by assuming experimentally determined values of mobilities and recombination parameters in the blend. Furthermore, a hole injection barrier at the anode and a thin widegap layer at the cathode representing the PFPA1 are introduced. The fit to both current under illumination and in the dark is excellent. Additionally, transient current responses

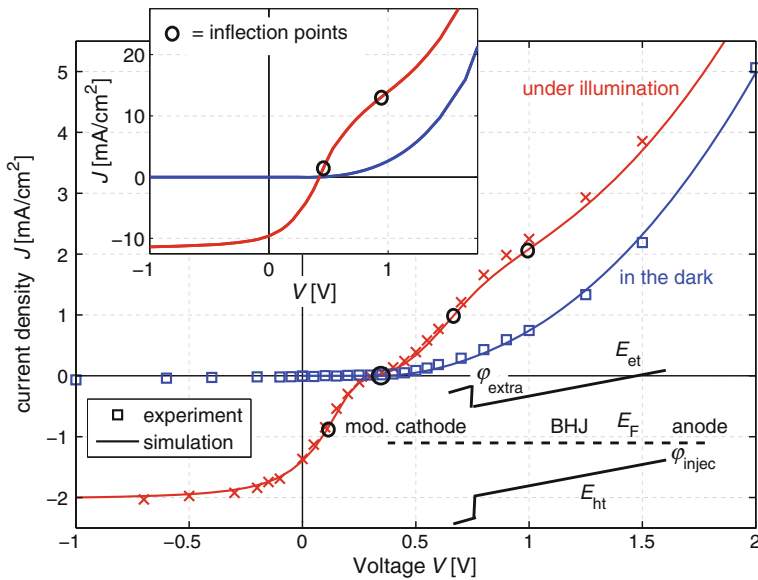


Fig. 7.10 Experimental (symbols) and simulation (lines) data for a semitransparent device ITO/PEDOT:PSS/PFPA1 (a few nm)/TQ1:PC71BM (≈ 90 nm)/PH1000. The PFPA1 interlayer is used to decrease the work function of PEDOT converting PEDOT into a cathode. In the case shown here, the conversion worked only partially. In the simulation, the PFPA1 layer is considered as a barrier layer causing the kink at V_{oc} . The kink at 0.8 V is due to an (additional) injection barrier at the anode side (0.35 eV). The inset shows a simulation of a single-layer BHJ (50 nm, $E_g^{DA} = 1.2$ eV, $\beta = 7.23 \times 10^{-12} \text{ cm}^{-3} \text{ s}^{-1}$) device with high (0.4 eV) injection barriers at both contacts assuming thermionic injection. A hindered injection paired with a non-selective extraction of photocurrent gives rise to a kink at a voltage larger than V_{oc}

are reproduced as well (not shown). However, we do not want to claim that the effect of the modified interface is completely understood, reproducibly realized, and the simulation parameters are unambiguously defined. Nevertheless, the prevailing experimental J - V curves and their theoretical counterparts are well suited to explain some effects that can occur when fabricating organic solar cells in general:

- The low V_{oc} (the active material combination can deliver up to 0.9 V [12]) is attributed to a low V_{bi} .
- The S-kink in the fourth quadrant is attributed to an extraction (and injection) barrier at the modified-PEDOT interface.
- The difference between the forward current under illumination and in the dark is due to an extraction of photocurrent (with changed sign) also in forward direction.
- The kink in forward direction (at ≈ 0.8 V) is caused by a weak injection of dark carriers paired with a stronger extraction of photogenerated charges. This combination gives rise to a kink when the injection current sets in, and indicates that the unmodified PEDOT electrode (anode) shows an injection barrier for holes as well (see inset). This barrier is anticipated because the work function of PEDOT is around 5.2 eV, whereas the HOMO of TQ1 is $\lesssim -5.5$ eV.

In summary, a kink in the forward direction (1st quadrant) can be due to a shifted onset of injection current compared to photocurrent extracted in the “wrong” direction. In this case, the J - V curve under illumination has already crossed the dark curve at this point and the dark curve does not show an S-kink. Note that the kink in forward can occur independently of the kink in reverse (inset of Fig. 7.10), if extraction of photogenerated charges works well at both electrodes and in both directions, however injection of charges is limited due to injection barriers at both electrodes. A photoenhanced injection current (cf. Sect. 5.4) might pronounce this feature giving rise to a larger difference in forward current under illumination and in the dark.

7.4 Kinks for Voltages Below Open Circuit

In experimental J - V curves a variety of kinks can be observed. In this last example we address a very general and important concern one should always be aware of when interpreting J - V curves. We employ J - V curves of a ZnPc:C₆₀ solar cell realized as p-i-metal stack. The J - V curves shown in Fig. 7.11a are recorded while aging the device. During degradation mainly the short-circuit current and the FF are negatively affected, whereas the open-circuit voltage and the saturated photocurrent under reverse bias remain roughly unchanged. Interestingly, an S-kink emerges that shows both turning points of the J - V curve below open circuit and extends into the third quadrant. The evolution of the J - V curves shows a clear trend during aging. The reader is invited to speculate on the reason for such an S-kink. One hint is given: It was found that the degradation is related to an oxidation of the Al electrode, starting from pinholes and increasing in area.

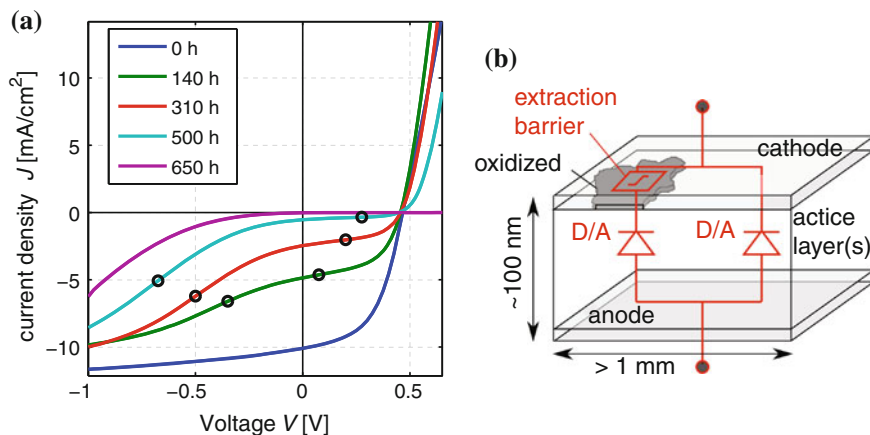


Fig. 7.11 **a** Experimental J - V curves of solar cells during aging. The stack is ITO/p-HTL (30 nm)/i-HTL (5 nm)/ZnPc:C₆₀ (30 nm)/C₆₀(30 nm)/BPhen (6 nm)/Al. An S-kink close to short circuit appears for degraded devices. The inflection points of the J - V curves are marked. **b** Sketch showing the effect of a partly oxidized electrode-organic interface in an equivalent circuit model, where a solar cell with and without barrier are connected in parallel

Yes, this J - V curve does not result from one device, but from two—a device with an extraction barrier and a well-working device. They are connected in parallel, as sketched in Fig. 7.11b. With an increase of the area of the oxidized electrode, the characteristics of a device with extraction barrier become more and more obvious. This idea is proven by a short-circuit current that scales with the oxidized area whereas the saturation current remains almost unaffected.

Figure 7.12 shows J - V curves obtained from a simulation of a device with (circles) and without (crosses) an extraction barrier. The other curves are superpositions of both curves, and the percentage in the legend denotes the contribution of the J - V curve with barrier. The characteristic shape of the experimental data showing a kink for voltages below 0 V is well reproduced.

This example is so important because it shows that a measured J - V curve of a device can represent a superposition of several I - V curves of devices connected in parallel. This issue is well-known for large-area devices. There, lateral currents in the electrode can cause a significant drop in voltage such that the electrode cannot be approximated as an equipotential surface. In this case, the (microscopic) solar cells run at different voltages, although one defined voltage is applied to the electrode (close to the connection to the outer circuit). However, superposition can also happen for small (mm²) devices (remember that the thickness is ≈ 100 nm), if part of the electrodes are modified as shown in the prevailing example. Changes in the active layer itself, which are on the length scale of μm will also show up in a superposition of several I - V curves establishing the effective J - V curve of the macroscopic device.

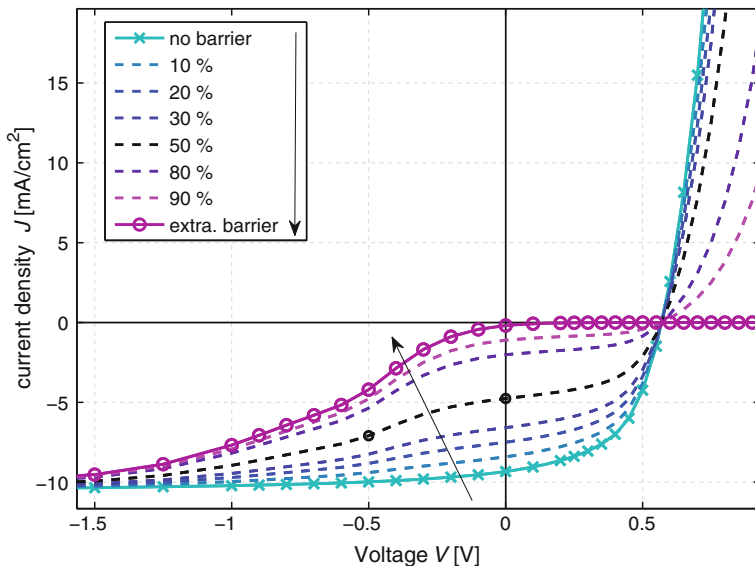


Fig. 7.12 Simulated J - V curves for conditions like in Fig. 7.11. The *solid lines* are simulations with an extraction barrier of 0.1 and 0.5 eV, respectively, towards the BPhen. The parameters of the BHJ are $\beta = 1.6 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, $E_g^{\text{DA}} = 1.08 \text{ eV}$, $\mu_n = 10^{-4} \text{ cm}^2/\text{V s}$, and $\mu_p = 2 \times 10^{-5} \text{ cm}^2/\text{V s}$, which characterize a ZnPc:C₆₀ solar cell according to Table 8.3. The *dashed lines* are obtained by a weighted addition of both curves representing a parallel connection of regions with and without the barrier. The inflection points of the J - V curve (50 %) are marked

7.5 Summary

This chapter focused on S-shaped J - V curves. Apart from barriers at the electrodes, further origins of S-kinks were presented. These include highly imbalanced mobilities in donor and acceptor layers of flat heterojunction solar cells and a field-dependence of the dissociation of a geminate electron-hole pair. A bulk heterojunction without selective contacts, but injection barriers at both electrodes can give rise to a kink in forward direction. J - V curves with unconventional kinks might be a result of an averaging over several effects when measuring a macroscopic device.

We summarize the conclusions of this chapter by answering the initial questions:

- *Under what conditions can imbalanced mobilities cause S-shaped J - V curves?*
Imbalanced mobilities can only cause S-shaped J - V curves for flat heterojunction devices or vertically inhomogeneous bulk heterojunction solar cells.
- *What is the mechanism in which imbalanced mobilities cause S-shaped J - V curves?*
The imbalance in mobilities alters the electric field due to space-charge effects. This rearrangement leads to a significant voltage dependence of the extraction probability of the slower charge carrier.

- *How can this effect be identified and distinguished from others?*

This effect strongly depends on the ratio between the thicknesses of donor and acceptor layers. It is not present for bulk heterojunction solar cells consisting of the same materials. Furthermore, affected devices show a slow transient photocurrent response.

- *How can kinks in the forward current be explained?*

An injection of charges which is weaker than the extraction of photogenerated charges in forward direction can give rise to a kink in the J - V curve for positive currents.

- *What might be the reason for “unconventional” distortions of the J - V curve?*

Here, “unconventional” means that the S-kink cannot be easily categorized into one of the previous cases suggested by simulation. One reason for such kinks is found in a superposition of I - V curves of different devices operating in a parallel connection. An example is when contact barriers are introduced in an unintentional way and therefore, might be present in sub-sections of the total electrode area. Because lateral dimensions are much larger than the thickness, lateral inhomogeneities can result in different independent microscopic devices. The superposition of their current-voltage characteristics can give rise to “unconventional” S-kinks.

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Chapter 8

The Model System ZnPc:C₆₀

Abstract The topic of this chapter will be a detailed investigation of current-voltage data of the model system ZnPc:C₆₀. We start by explaining the influence of the donor:acceptor mixing ratio on the open-circuit voltage. Then, we investigate a possible optimization of the morphology in the bulk heterojunction by using a vertical concentration gradient of donor and acceptor. The main focus of the further parts of this chapter is on the role of recombination and charge transport governing the power-conversion efficiency. By manipulating spatial absorption profiles in the bulk heterojunction we conclude that charge extraction and recombination between charges are the competing processes limiting the fill factor. An investigation of the open-circuit voltage as a function of illumination intensity allows us to discriminate between direct, indirect, and surface recombination. In particular, this chapter addresses the following questions: (a) What are possible explanations for different open-circuit voltages of devices consisting of the same active material system (e.g. when changing the mixing ratio)? (b) What are simple experiments to identify the correct reason? (c) Which explanations exist for a changed donor-acceptor gap in a bulk heterojunction based on the same materials? (d) Why is it interesting to investigate graded junctions? (e) What are possible explanations for the fill factor depending on the color of the illumination? What is the role of charge-carrier mobility? (f) Why does the internal quantum efficiency depend on the wavelength of the incident light and on the thickness of the optical spacer? What is the consequence for the spectral mismatch factor? (g) What point of the *J-V* curve is a good choice to investigate the dominating recombination mechanisms in a solar cell? How can this be done? (h) What does the diode ideality factor tell?

8.1 Open-Circuit Voltage and Mixing Ratio

In Sect. 6.3.3 we observed differences between the open-circuit voltage of a flat heterojunction and a bulk heterojunction consisting of the same material combination. These differences are the topic of this section. Compared to a flat heterojunction,

The results shown in Sect. 8.1 are published in [1] and those of Sect. 8.2 in [2]; parts of Sect. 8.3 in [3] and parts of Sect. 8.4 in [4].

a bulk heterojunction offers more degrees of freedom regarding the morphology of the blend (cf. Sect. 3.6.4). Here, one important parameter is the stoichiometry, which can be expressed as a volume mixing ratio between donor and acceptor.

To investigate the effect of the mixing ratio, we use several devices in the p-i-metal architecture known from previous chapters. The active layer is embedded between an ITO/hole-transport layer (HTL, 25 nm) and a 15 nm/6 nm C₆₀/BPhen electron transport layer, covered by an Al layer as cathode. The active layer consists of a blend of ZnPc and C₆₀ (45 nm) or a bilayer ZnPc (20 nm)/C₆₀ (25 nm) for a planar heterojunction as reference. Different HTLs are employed to separate effects that originate either from the contacts or from the bulk. The applied HTL materials are: MeO-TPD (HOMO_{UPS} −5.1 eV), Di-NPD (HOMO_{UPS} −5.35 eV), and BF-DPB (HOMO_{UPS} −5.25 eV). Their molecular structures are depicted in Fig. 3.54.

Figure 8.1 shows the V_{oc} for a series of solar cells with varied mixing ratio and different HTLs. The data illustrates that the choice of HTL has a minor influence on V_{oc} . (The HTLs do not cause injection barriers (cf. Fig. 6.2) as the HOMO levels of all HTLs are below the HOMO of ZnPc.) However, a clear trend is observed in the investigated interval of mixing ratios: V_{oc} increases with a higher concentration of C₆₀. As this increase is independent of HTL, this trend is expected to result from the blend itself. A dependence of V_{oc} on the mixing ratio is observed also for other material systems [5–8]. To explain its origin, we recall the equation for V_{oc} (3.26), showing that it is determined mainly by two properties:

$$eV_{oc} = E_F^n - E_F^p = E_g^{DA} - k_B T \ln \frac{N_C N_V}{np}. \quad (8.1)$$

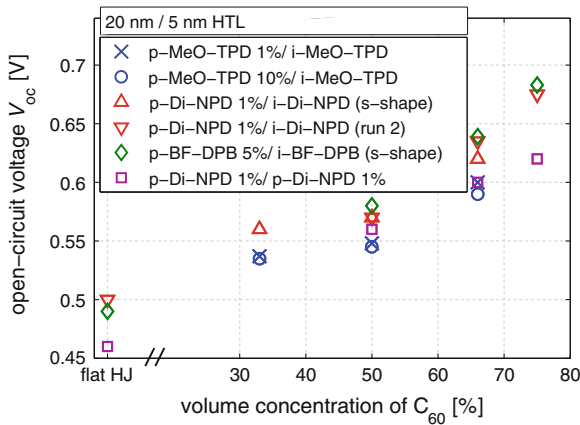


Fig. 8.1 The open-circuit voltage V_{oc} as a function of the volume mixing ratio of ZnPc:C₆₀. The symbols denote different HTLs. The increase of V_{oc} with C₆₀ content is independent of the HTL

First, V_{oc} scales with the effective energy gap E_g^{DA} . Second it depends on the charge carrier densities np in the device. The higher their concentrations the larger is the chemical potential of an electron-hole pair. This concentration is directly related to the dynamical equilibrium between generation and recombination: The higher the probability for recombination, the lower are np for a given generation rate, i.e. illumination intensity. We found equations for different recombination mechanisms in (3.29), (3.31), and (3.39), which we will reuse later in this chapter.

Consequently, either E_g^{DA} or recombination parameters change with the mixing ratio. For Langevin recombination the recombination constant changes with mobility. As we expect different mobilities for different mixing ratios (see discussion below), recombination might change as well. However, simulations with changed recombination constants do not fit the trends in the J - V curve [1]. Therefore, we follow the first idea of a changed E_g^{DA} . The most direct proof for this hypothesis is a measurement of the charge transport levels or E_g^{DA} . In doing so the main challenge is the high accuracy needed to resolve the observed changes of V_{oc} and consequently E_g^{DA} in the range of some 10s of mV (meV). Measuring E_g^{DA} is therefore very hard. However, detecting the energy of the CT state via a sensitive absorption measurement (FTPS) is possible [9, 10]. Alternatively to (8.1), V_{oc} can be expressed as a function of the energy of the CT state (3.39):

$$eV_{oc} = E_{CT} - k_B T \ln \left(\frac{N_C N_V k_{relax}}{G f(F, E_B)} \right). \quad (8.2)$$

This equation predicts a linear scaling of V_{oc} with the energy of the CT state E_{CT} . The second summand describing generation and recombination can be further developed assuming microscopic theories [cf. (3.64)]. Data obtained for E_{CT} as a function of mixing ratio is shown in Fig. 8.2. The energy of the CT state follows indeed the trends observed for V_{oc} .

In Sect. 6.3.3 we suspected that it is mainly E_{ht} , i.e. the HOMO level of ZnPc, that changes when going from a FHJ to a BHJ. In contrast to the LUMO (EA), the HOMO_{UPS} ($= -IP$) can be measured with much better accuracy using photoelectron spectroscopy as described in Sect. 6.5. The IPs of ZnPc and C₆₀ in the blends with varied mixing ratio are shown in Fig. 8.2. Assuming a constant gap of C₆₀, we can estimate E_g^{DA} , which is added to subfigure (b). It shows the same trend as V_{oc} for larger amounts of C₆₀. Details can be found in [9].

Based on the investigations on extraction barriers in Chap. 6, we expect changes in the strength of an S-shape when we attach a ZnPc:C₆₀ blend with varied mixing ratio to a given HTL with a deep HOMO. J - V data of such a study are shown in Fig. 8.3 where Di-NPD is chosen as HTL. Di-NPD has a HOMO_{UPS} of ≈ -5.35 eV, which gives rise to an extraction barrier of 0.1–0.3 eV depending on the mixing ratio (Fig. 8.2a). Therefore, the S-kink should be strongest for a FHJ and reduced for higher concentrations of C₆₀ in a blend. This effect is indeed observed when comparing the J - V curves in Fig. 8.3.

To quantify the strength of the S-kink we calculate the slope of the J - V curve at open circuit. These data are plotted in Fig. 8.4. They reproduce the effects seen

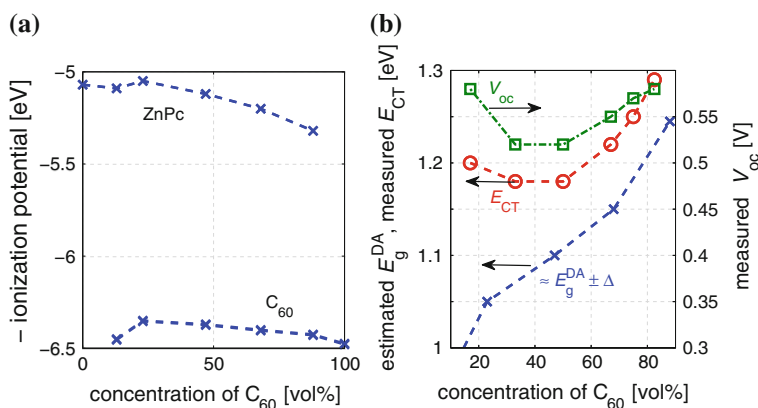


Fig. 8.2 a Ionization potential of ZnPc and C₆₀ determined by UPS of blends. Stronger shifts in the HOMO of ZnPc indicate a change in the effective donor-acceptor gap E_g^{DA} , which is roughly estimated by subtracting both values and adding 2.35 eV. This implies an unchanged gap of C₆₀. Note that this is a rough estimation, i.e. Δ in **b** might contain both a constant offset (order of 0.1 eV) and small variations (<0.1 eV) between different mixing ratios. However, the trends of E_g^{DA} , the open-circuit voltage, and the energy of the CT state coincide for larger concentrations of C₆₀. Data are from [9]

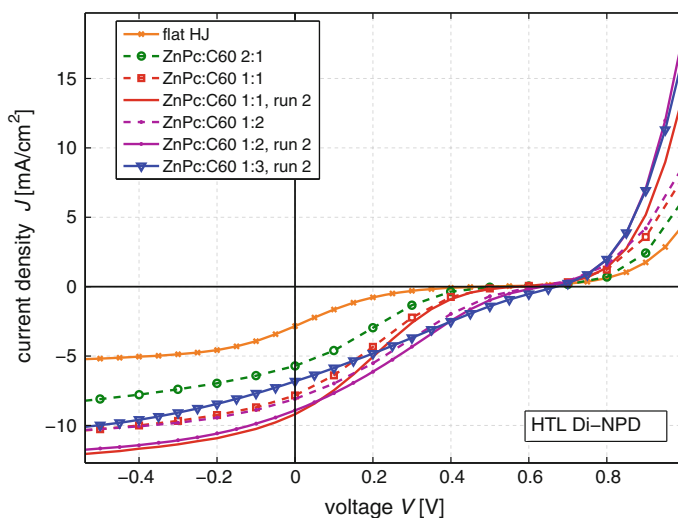


Fig. 8.3 J - V curves of devices with varied mixing ratio in the BHJ and Di-NPD as the HTL. The strength of the S-kink is a measure of the height of the extraction barrier at the interface HTL/blend. This observation indicates that the hole-transport level in the BHJ is a function of the mixing ratio

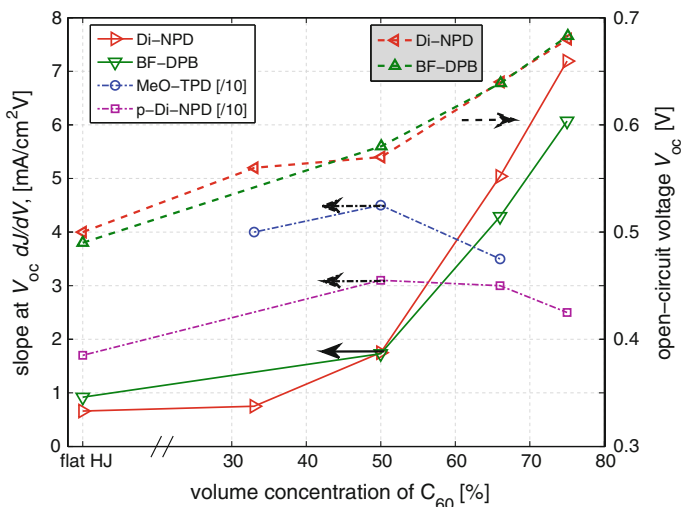


Fig. 8.4 Slope dJ/dV at V_{oc} for several HTLs as a function of the ZnPc: C_{60} mixing ratio. dJ/dV is estimated from $\Delta J/\Delta V$ at V_{oc} with $\Delta V = 0.05$ V. Lines are to be seen as guide to the eye. For the S-kink devices, also V_{oc} is shown, which correlates with the dJ/dV at V_{oc}

at the J - V curves, as the slope increases with a higher C_{60} concentration, i.e. a lower extraction barrier. To guarantee that the slope of these (extraction barrier) devices with Di-NPD or BF-DPB as HTL is not governed by the blend itself, we show the slopes for a well-adjusted HTL MeO-TPD (dash-dotted). They show an optimum value for a mixing ratio of about 1:1 and decrease for both higher ZnPc and higher C_{60} concentrations. Therefore, the charge transport properties of the active material cannot explain the changes in the slope at V_{oc} for the devices with S-kink. We conclude that indeed the barrier is changed, i.e. the HOMO is a function of the mixing ratio as measured by photoelectron spectroscopy.

What is the reason for the HOMO changing with mixing ratio? To find an answer we have to go back to the Sect. 3.1.2 where we discussed the electric processes occurring during the formation of a film out of single molecules. Energy levels shift and energy gaps become smaller. One reason is the increased polarizability of the surroundings. In case of a blend, the environment of ZnPc molecules is also determined by C_{60} . However, the macroscopic dielectric constant of C_{60} ($\epsilon_r = 5$) is similar to the one of ZnPc ($\epsilon_r = 4$) and cannot explain significant shifts of polarization energies [9]. Another effect is due to ZnPc itself. The higher the concentration of ZnPc in a blend, the more likely ZnPc forms nano-crystallites. Although a clear difference between the (nano-)crystallinity of ZnPc in a blend and in a pure film can be detected using GIXRD, significant trends in blends with different mixing ratios could not be observed [9]. In principle, larger nano-crystalline domains should give rise to a better π - π stacking and a larger overlap of electronic wave functions. This can lead to a larger delocalization of π electrons, which decreases the energy gap.

For instance, it is known from polymer solar cells that the nano-crystallinity of PCBM in blends with polymers changes energy levels [8, 11].

This study has shown that the morphology does not only influence charge transport properties but also energy levels. Here we addressed the mixing ratio as determinant altering the morphology. Similar effects are expected when changing the substrate temperature during the deposition of the blend. Commonly, higher temperatures lead to a stronger phase separation and favor agglomeration and crystallization of the components. Annealing of spin-coated films can induce such a trend as well.

8.2 Optimizing the Morphology Using Graded Junctions

In the previous section we have discussed that the mixing ratio changes the energetic properties of the blend. Therefore, the blend is best described as an effective medium in this case. Recalling that the blend consists of an interpenetrating network of donor and acceptor molecules, which are partly phase-separated, one might come up with the following idea to improve charge carrier collection: Desired is an interdigitating network between donor and acceptor (cf. Fig. 3.19a), as it is so far considered as ideal morphology with a low probability for bimolecular recombination. It might be approached using a vertical concentration gradient in the bulk heterojunction [12–15]. A higher concentration of donor material close to the anode and a higher concentration of acceptor material close to the cathode is supposed to enhance the collection of charge carriers and reduce losses due to encounters of electrons and holes during extraction. On the one hand, such a gradient can result from an unintentional vertical phase separation of spin-cast films. Therefore, it can explain differences between the performance of the same active material system in standard and inverted geometry. In the latter the direction of charge extraction is reversed referred to the substrate.

On the other hand, an intentionally generated gradient might be used to systematically improve the performance. Here, small-molecule solar cells fabricated via co-evaporation of donor and acceptor are well suited, as the ratio between the evaporation rates can be changed during the deposition of the blend. We perform such a study on the system ZnPc:C₆₀ and choose again devices in p-i-metal architecture with MeO-TPD as hole transport layer. This approach guarantees ohmic contacts between active layer and the electrodes. The complete stack is ITO/MeO-TPD:NDP2 (25 nm)/(45 nm ZnPc:C₆₀)/C₆₀(30 nm)/BPhen(6 nm)/Al (100 nm) (inset of Fig. 8.5). Different gradients ranging from 2:1...1:2, 3:1...1:3, and 4:1...1:4 are investigated.

In the prevailing case of a donor absorbing in the red and an acceptor absorbing in the blue, such gradients are beneficial for an optimized absorption at a given device thickness. The reason is that the electro-optical field distribution governed by interference shows a maximum for a selected wavelength at a certain distance from the acceptor. The larger the wavelength, the further away is this maximum from the reflective cathode. An exemplary calculation of an intensity distribution shown in Fig. 4.14 visualizes the dependence of the interference maximum on wavelength.

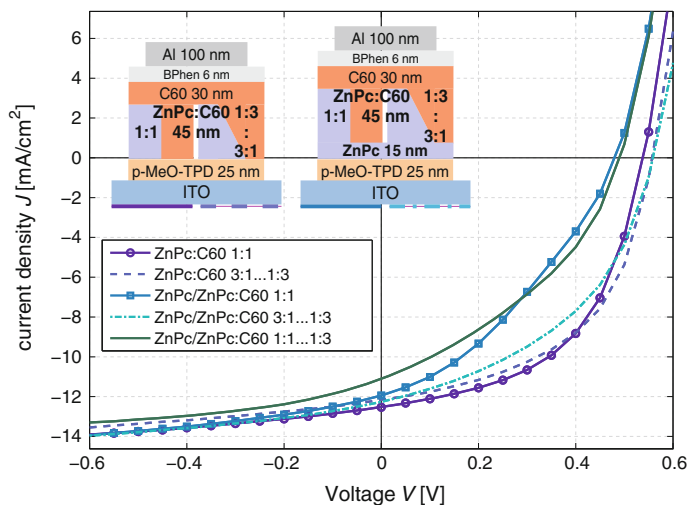


Fig. 8.5 J - V curves of devices with and without an intrinsic ZnPc interlayer and with different realizations of the blend layer. Graded junctions are fabricated by a gradual change of evaporation rates during the deposition of the blend. The *insets* show the stacks

Although the benefit of a graded junction of ZnPc:C₆₀ regarding absorption is weak, it can be observed in experiment [2].

Gradients spanning a too large variation are expected to be detrimental as they contain regions with a very low concentration of one component. Therefore, percolation paths are missing, which guarantee an efficient extraction of charges. For ZnPc:C₆₀ the photocurrent is observed to drop at a mixing ratio of 4:1 [2].

With the J - V data shown in Fig. 8.5 we arrive at the charge transport properties of the blends. Comparing the curves, we find that optimized devices with gradient do not show a significant increase in performance. For instance, the J - V curves of devices with a homogeneous 1:1 and a graded 3:1...1:3 blend are shown in Fig. 8.5. All characteristic parameters and the shape of the J - V curves are similar indicating that the gradient does not significantly change the probability for the extraction of charges.

The figure also shows J - V curves of complete hybrid planar bulk heterojunction devices, where a 15 nm thick pure ZnPc layer is inserted between HTL and blend. We mentioned when discussing injection barriers that such a structure might be beneficial for the selectivity of the contacts. However, V_{oc} is significantly reduced when adding ZnPc. Recalling the preceding discussions on the influence of the mixing ratio, this is not surprising. There, we found that the HOMO of pure ZnPc lies higher than that of the blend which implies an injection barrier from ZnPc into ZnPc in the blend. That is why V_{oc} is reduced when adding an intrinsic ZnPc layer. Interestingly, this reduction of V_{oc} can be avoided when using a graded junction with a large amount of ZnPc close to the pure ZnPc. This implies that the selectivity of the contacts is enhanced. It is less likely that photogenerated electrons on the C₆₀ reach an interface with the

pure ZnPc where they recombine. Therefore, we can conclude that one benefit of a graded junction can be found in its capability of effectively increasing the selectivity of the contacts.

8.3 Correlation of Fill Factor with Absorption Profile and Imbalance in Mobilities

8.3.1 Idea and Solar-Cell Design

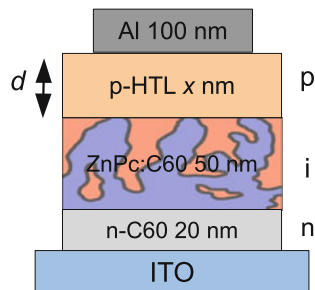
After the excursion to graded junctions we return to homogeneous blends, where we focus on the fill factor (FF). From the ideal solar cell, we know that the maximum FF is limited due to thermodynamics demanding an increased recombination in the presence of an increased potential, i.e. charge carrier density in the absorber [cf. (2.31) and Fig. 2.12]. In case of a p-n junction, an equivalent description is that the increase in current around the maximum-power point is caused by injected charges flowing in the reverse direction compared to the photocurrent. The photocurrent itself as the difference between the J - V curves under illumination and in the dark is not changed. Consequently, in these cases of the fundamental limit, the FF does not reflect the charge transport properties of the absorber but recombination within the absorber. The FF is then expected to be in the range of 80...90% dependent on the bandgap of the absorber and the concentration of the sun light.

Fill factors significantly lower than these values indicate additional losses. Fill factors of state-of-the-art organic solar cells are in the range of 50–70%. In these cases, the FF reflects the competition between the extraction of charge carriers and their recombination, as discussed in a simulation study in Chap. 5. Additionally, the FF might include a field-dependence of the dissociation of geminate pairs, which are Coulombically bound after exciton separation at a donor-acceptor interface. The consecutive geminate recombination is difficult to distinguish from recombination between charge carriers.

Recall that the order of recombination can be determined by J - V measurements as a function of intensity, where a sub-linear scaling of the current with intensity is attributed to bimolecular recombination. However, an accurate determination of non-linearities of the photocurrent with illumination intensity is difficult: Especially using a linear scaling of the short-circuit current density is often meaningless as e.g. recombination is weak at this point (cf. Sect. 5.4). Doing a study closer to V_{oc} is also problematic as the influence of the series resistance can easily result in a non-linearity of the current with intensity, which is actually due to an increased voltage drop at the series resistance. Furthermore, both geminate and trap-assisted recombination are expected to show monomolecular behavior.

Usually, analytical analyses of the measurement results are based on the assumption of homogeneities in the absorber, e.g. regarding charge carrier densities or generation profiles. In the following we show how inhomogeneities in charge carrier

Fig. 8.6 Solar-cell stack in n-i-p architecture with varied thickness d of the hole transport layer (HTL). Here, the HTL acts as an optical spacer in the stack ITO/C₆₀:NDN1 (20 nm, 3 wt%)/ZnPc:C₆₀(50, $x:y$)/Di-NPD(1)/Di-NPD:NDP9 (d , 5 wt%)/NDP9(2)/Al(100). Di-NPD is one choice for the HTL



generation can be exploited to get insights into the mechanisms limiting the FF . For this purpose, solar cells are designed to achieve highly asymmetric absorption profiles with a distinct position of the maximum absorption within the blend. If the FF of such a solar cell depends on the location of maximum charge carrier generation, charge transport limits the FF instead of geminate recombination. In this case charges with the lower mobility are expected to be predominantly harvested when created close to the collecting electrode. Thus, this effect is expected to be more pronounced with an increased imbalance in electron and hole mobility.

The main advantage of manipulating the generation profile in contrast to, e.g., a variation of the absorber thickness is the fact that the electric field within the device (in the dark) is not changed. In cases where the electric field is changed, both charge carrier extraction and field-dependent exciton dissociation (geminate recombination) are affected and it is difficult to distinguish between the two.

For an experimental realization of the outlined idea, a stack based on the p-i-n concept is employed. The generation profile is tuned by the thickness of the transparent doped charge-transport layer between reflecting contact and blend (Fig. 8.6). Due to the availability of several hole-transporting materials (cf. Chap. 6), hole transport layers are used as optical spacers in a then inverted (n-i-p) stack. The active layer consists of a 50 nm thick ZnPc:C₆₀ bulk heterojunction (BHJ) with mixing ratios of 2:1, 1:1, 1:2, and 1:3.

In contrast to the thickness values reported in previous chapters, here the thickness of the blend is not estimated using the densities of the single materials, but determined based on reflectance and transmittance data of a thickness series of samples consisting of single layers. These data give very accurate values for the thicknesses, which are essential for a quantitative evaluation of the measurement data. The BHJ is embedded between an n-doped C₆₀ layer deposited on ITO and a p-doped hole transport layer (HTL) consisting of Di-NPD or MeO-TPD and covered by 100 nm Al. Any pristine (HTL, donor, or acceptor) layer is avoided to reach ideal conditions for extraction and injection of charge carriers and to omit photocurrent from other sources except the BHJ. The stacks read in detail ITO/C₆₀:NDN1(20 nm, 3 wt%)/ZnPc:C₆₀(50, varied ratios)/Di-NPD(1)/Di-NPD:NDP9(d_{HTL} , 5 wt%)/NDP9(2)/Al(100). In

some samples, Di-NPD is replaced by MeO-TPD, doped with 2 wt% NDP9 (Fig. 8.6).

The thicknesses of the HTLs ($d_{\text{HTL}} = 25, 45, 90, 180 \text{ nm}$) are selected based on optical simulations to reach extreme cases of the absorption profiles. The mobility imbalance is manipulated applying four different mixing ratios in the blend. Data evaluation is done employing absorption measurements in comparison to optical simulations, monochromatic J - V curves to enforce the effect of a narrow generation profile, and EQE data dependent on applied voltage.

8.3.2 Absorption Data

Optical simulation according to the transfer-matrix approach (cf. Sect. 4.7) is applied to predict the absorption profile, which is the absorbed photon flux density per unit length in photons $\text{m}^{-2}\text{s}^{-1}\text{m}^{-1}$. As described in Sects. 4.2.4 and 4.7, this profile roughly equals the charge carrier generation profile. This approximation implies that every absorbed photon (in the UV-vis spectral range) creates one exciton, which is subsequently split and forms an electron-hole pair. Furthermore, the exciton dissociation is assumed to occur close to the location of its generation, i.e. absorption. In doing so, a modification of the profile (in vertical direction x) caused by significant exciton diffusion is supposed to be negligible. This condition is fulfilled for a bulk heterojunction with intimate intermixing, which is given for ZnPc:C₆₀ solar cells prepared at room temperature. Several morphology studies using grazing incidence X-ray diffraction or AFM indeed show very small or no crystalline grains in such ZnPc:C₆₀ BHJs [16]. Therefore, it is justified to set the spatial photon absorption profile directly equal to the charge carrier generation profile. Thus, in the following, the expressions absorption, exciton generation, and charge carrier generation profile are used interchangeably.

Before discussing the simulated absorption profile, we need to find experiments to verify the simulation data. The reason is that the simulated absorption profile cannot be directly monitored by a measurement method. However, it can be indirectly verified by a comparison of measured and simulated absorption spectra. The reason is that a particular absorption spectrum is connected to a respective absorption profile under a known illumination spectrum.

Measured (solid) and simulated (dashed) absorption data for selected devices are shown in Figs. 8.7 and 8.8. The fit of simulation to experimental data is good and proves that the nominal thicknesses of the layers are reasonable (nominal HTL thickness of 190 nm was changed to 180 nm). Figure 8.7 illustrates that the absolute values of the absorption peaks for ZnPc (between 600 and 700 nm) and C₆₀ (around 450 nm) (cf. Fig. 3.53) change dependent on the amount of ZnPc and C₆₀ in the blend. According to Fig. 8.8 the thickness of the HTL as optical spacer significantly influences the shape of the absorption spectrum. The reason is the relatively thin absorber layer (50 nm) compared to the distribution of the electro-optical interference maxima for wavelengths between 400 and 800 nm. Here, the sample with an HTL thickness of

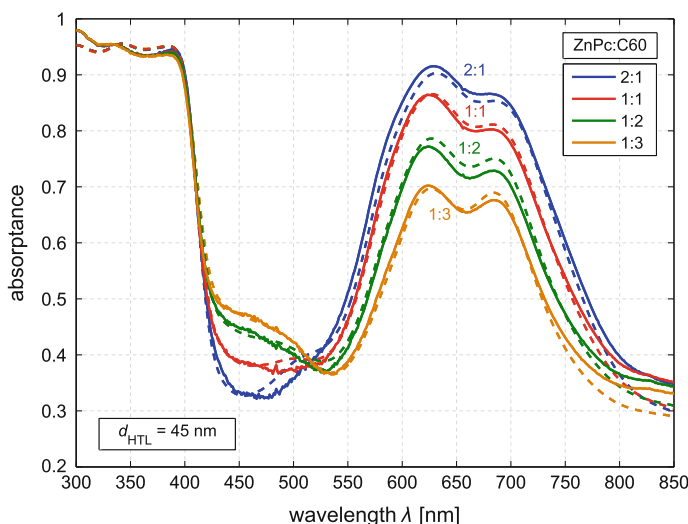


Fig. 8.7 Measured (*solid lines*) and simulated (*dashed lines*) absorption data of solar cells with different blend mixing ratios and an HTL thickness of 45 nm. With increased ZnPc content, the absorbance increases in the range between 600 and 750 nm and decreases at around 450 nm. This is expected from the absorption spectra of the respective molecules (cf. Fig. 3.53). The simulation data fit well

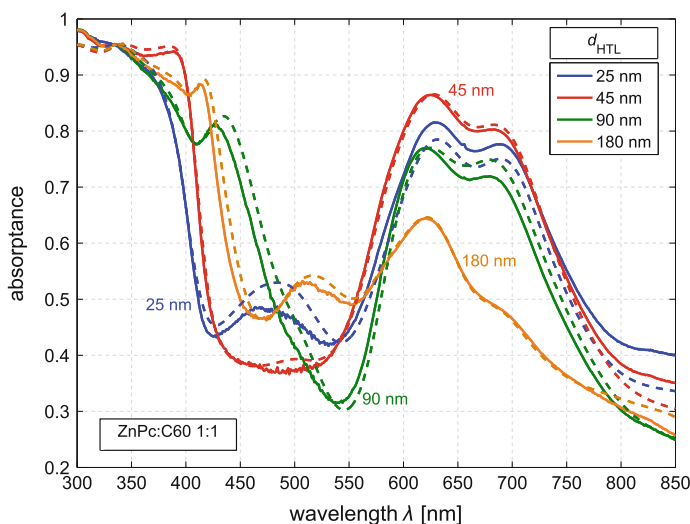


Fig. 8.8 Measured (*solid lines*) and simulated (*dashed lines*) absorption data of solar cells with blend mixing ratio 1:1 and different thicknesses of the HTL. The samples with a 25 and 180 nm thick HTL show a pronounced absorbance in C₆₀ due to constructive interference, which for these devices enhances the intensity in the blend for wavelengths ≈ 500 nm

180 nm represents an extreme case where the electro-optical field intensities at 630 and 680 nm differ so significantly that the characteristic double peak of absorption on ZnPc is heavily distorted.

8.3.3 Simulated Generation Profiles

Having verified the results of the optical simulation, we discuss the generation profiles, which are obtained according to the equations in Sect. 4.7. Here we use the spectrum of the solar simulator as input because all J - V measurements are done under simulated sunlight. For a comparison of its spectrum to AM1.5g, see Fig. 3.64.

Simulated generation profiles for different HTL thicknesses and blend mixing ratios are shown in Fig. 8.9. Their shapes rationalize the HTL thicknesses which are chosen in a way to create an absorption profile with a maximum close to the HTL (a, d), close to the ETL (c), and a relatively balanced profile (b). Case (a) is a tradeoff

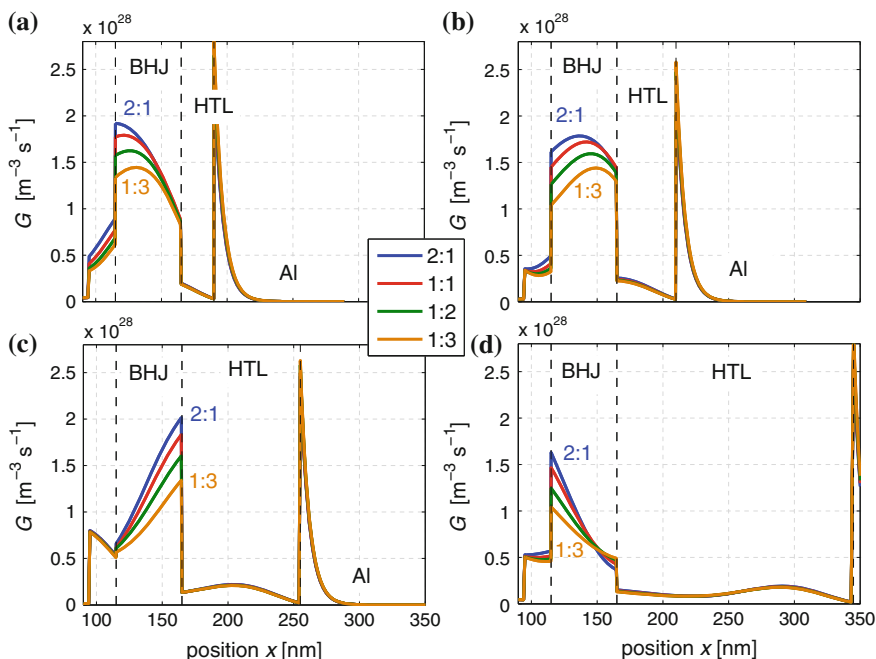


Fig. 8.9 Simulated absorption, i.e. exciton-generation profiles $G(x)$ for different ZnPc:C₆₀ volume mixing ratios (*colors*) and different HTL thicknesses **a** 25 nm, **b** 45 nm, **c** 90 nm, **d** 180 nm. The stack consists of glass (1 μ m)/ITO (95 nm)/n-doped C₆₀(20)/BHJ (50)/HTL (d_{HTL})/Al (100). The abscissa x denotes the distance from the interface glass/ITO. The spectrum of the solar simulator (cf. Fig. 3.64) is used as illumination spectrum. The shape of the absorption profile within the BHJ is governed by interference effects, which are tuned by the HTL thickness

between tuning the generation profile and guaranteeing a certain HTL thickness to protect the blend during evaporation of aluminum. The motivation for the two similar shapes of the profiles of cases (a) and (d) is an exclusion of any effect of the HTL thickness itself. In all four cases the qualitative shape of the absorption profile is maintained for all mixing ratios. The overall absorption is highest for the 2:1 blend, which can be directly deduced from the absorption spectra (Fig. 8.7) and the spectrum of the sun (Fig. 2.2) or solar simulator (Fig. 3.64) in this case. With larger C_{60} content the absorption maxima for a fixed HTL thickness are shifted to the right, because the interference maxima for lower wavelengths where C_{60} absorbs are localized closer to the reflecting contact.

8.3.4 Current-Voltage Data

Now we investigate the effect of the generation profile on the electrical performance of the devices under illumination. For this purpose we compare the characteristic parameters of the solar cells. Those are shown in Table 8.1 presenting data for all combinations of HTL thickness and mixing ratio. V_{oc} turns out to be almost independent of the HTL thickness. It is defined by the mixing ratio as expected based on the results of Sect. 8.1. Irrespective of mixing ratio, V_{oc} decreases for all solar cells with the thickest HTL due to a lower overall absorption as evident from a low short-circuit current density (J_{sc}). This reduction is due to the operation of the solar cells at the onset of the second interference maximum.

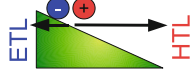
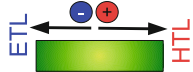
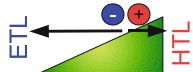
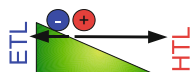
The short-circuit current density is maximum for samples with an HTL thickness of 45 nm, as these devices yield the largest integrated generation profile (cf. Fig. 8.9). Comparing J_{sc} of devices with different mixing ratios and a fixed HTL, J_{sc} is largest for the 1:1 blend. It decreases with larger C_{60} content due to the lower overall absorption in the spectral range where most photons arrive (cf. Fig. 8.9). The decrease in J_{sc} of the 2:1 samples cannot be explained by a decreased absorption. One reason for the lower J_{sc} is that the photocurrent is further away from being saturated at J_{sc} . An indication for this is the low FF (43...44 %). The other reason might be an internal quantum efficiency which is lower independent of applied voltage. This loss is indicated by J_{sat} in the table, which is lower for the 2:1 blend than for the 1:1 blend. Details are given later on when we discuss simulations of the J - V curves.

This study focuses on changes of the FF with varied generation profile paired with differences in electron and hole mobility. Here, the mobilities shown in Table 8.2 are obtained by OFET measurements. Recall the discussions in Sect. 4.9, where we noted that OFET measurements are conducted under different conditions compared to the working point of a solar cell. Commonly, measured OFET mobilities of organic semiconductors are one or two orders of magnitude higher than the mobilities observed in a working solar cell [18]. The reason is the dependence of the mobility on charge carrier density which is very high in the channel of an OFET. Nevertheless, the OFET mobility is applicable to show trends in the mobility. According to the table, the hole mobility of the blend increases with a higher ZnPc content by two orders of

magnitude, whereas the electron mobility decreases significantly. This trend is expected because the mobilities are values of the effective medium blend, where holes are transported on ZnPc and electrons on C₆₀. As the electron mobility of C₆₀ is much higher than the hole mobility of ZnPc, a 2:1 blend shows almost balanced transport, whereas the imbalance increases with mixing ratios from 1:1 to 1:3.

The trends in the *FF* shown in Table 8.1 can be explained considering the ratio between electron and hole mobility. The *FF* does not depend on the HTL thickness and thus on the generation profile for balanced mobilities (ZnPc:C₆₀ 2:1). However, for the devices with different donor:acceptor mixing ratios, the *FF* is highest for the 90 nm thick HTL. This thickness represents the case where the absorption maximum is close to the electrode collecting the (slower) holes. The dependence of the *FF* on the generation profile becomes more pronounced for an increased imbalance (47...50 % (1 : 1) → 43...49 % (1 : 3)). Thus, it is favorable for a high *FF* if the generation is close to the contact collecting the slow holes. Although the absolute

Table 8.1 Characteristic parameters of solar cells with different mixing ratio and different HTL thicknesses

Generation profile ↓	<i>d</i> _{HTL} ↓	Mixing ratio → <i>μ_n</i> / <i>μ_p</i> →	2:1 2.5	1:1 93	1:2 1300	1:3 > 3000
	25 nm	FF (%)	43.2	47.0	45.3	43.4
		<i>J</i> _{sc} (mA/cm ²)	8.7	9.9	8.8	7.9
		<i>J</i> _{sat} (mA/cm ²)	10.8	11.6	10.3	9.2
		<i>V</i> _{oc} (V)	0.54	0.55	0.60	0.63
		<i>η</i> (%)	2.0	2.6	2.4	2.2
	45 nm	FF (%)	43.4	47.9	46.8	45.1
		<i>J</i> _{sc} (mA/cm ²)	9.0	10.5	9.4	8.2
		<i>J</i> _{sat} (mA/cm ²)	11.3	12.3	10.8	9.4
		<i>V</i> _{oc} (V)	0.54	0.55	0.60	0.63
		<i>η</i> (%)	2.1	2.8	2.6	2.3
	90 nm	FF (%)	43.9	50.1	50.0	48.6
		<i>J</i> _{sc} (mA/cm ²)	7.5	8.4	7.4	6.4
		<i>J</i> _{sat} (mA/cm ²)	9.4	9.6	8.1	7.2
		<i>V</i> _{oc} (V)	0.53	0.55	0.60	0.63
		<i>η</i> (%)	1.7	2.3	2.2	2.0
	180 nm	FF (%)	43.7	46.6	45.4	43.9
		<i>J</i> _{sc} (mA/cm ²)	4.4	4.9	4.2	3.8
		<i>J</i> _{sat} (mA/cm ²)	5.4	5.6	5.0	4.4
		<i>V</i> _{oc} (V)	0.51	0.52	0.57	0.60
		<i>η</i> (%)	1.0	1.2	1.1	1.0

The first column shows schematic representations of the generation profiles from Fig. 8.9. The saturated photocurrent density *J*_{sat} is estimated correcting the *J-V* curves for a photoshunt [17]. The ratio between electron and hole mobility *μ_n*/*μ_p* is obtained from OFET measurements (Table 8.2). The dependence of the *FF* on the generation profile increases with a higher imbalance in mobilities

Table 8.2 Charge carrier mobilities in ZnPc:C₆₀ blends with different mixing ratios obtained from OFET measurements

Mixing ratio	ZnPc	2:1	1:1	1:2	1:3	C ₆₀
$\mu_n(\text{cm}^2/\text{V s})$	–	1.3×10^{-3}	1.4×10^{-2}	3.9×10^{-2}	9.1×10^{-2}	0.2
$\mu_p(\text{cm}^2/\text{V s})$	1.9×10^{-3}	5.2×10^{-4}	1.5×10^{-4}	2.9×10^{-5}	–	–

changes in *FF* may appear small, the relative changes are 15 %. Concluding, we can state that the *FF* is limited by charge transport.

8.3.5 Monochromatic *J-V* Curves

In the previous section, the *FF* of samples with the same architecture and the same BHJ thickness have been compared. However, the analysis was based on different samples with varied HTL thickness. This approach was selected to show the importance of the generation profile for devices working under solar illumination. A more strict analysis requires a comparable study based on data which are acquired from one sample only. In this case, any effects arising from a comparison between different samples are excluded. Thus, it is necessary to manipulate the generation profile within the blend of one sample. This can be achieved by a comparison of monochromatic illumination of different wavelengths. Monochromatic illumination yields narrower absorption profiles than illumination with a broad spectrum and allows for shifted profiles with illumination color.

To experimentally probe the effect of the illumination spectrum on the *FF*, *J-V* curves are recorded while illuminating the sample with high-power blue and red LEDs. Figure 8.10 exemplary shows data of two samples comprising a 1:2 blend and the HTL BF-DPB (30 and 150 nm). The illumination intensity is set to reach the same short-circuit current. This condition suggests a comparable overall charge carrier generation rate within the blend, although it would be more correct to take the reverse saturation current. However, as these samples do not show a clear saturation, *J_{sc}* is the most pragmatic choice. A comparison of the *J-V* curve of one sample under red and blue illumination shows that *FF* and *V_{oc}* differ significantly. The difference is not caused by the illumination color or the molecule that is excited (donor or acceptor). This is proven by the control experiment with the second sample, which shows a reversed trend in *V_{oc}* and *FF*. The reason is an inverted shape of the monochromatic generation profiles in the second sample compared to the first one. Therefore, the difference between red and blue illumination of each sample is due to a changed generation profile when illuminating the sample with light of varied wavelengths.

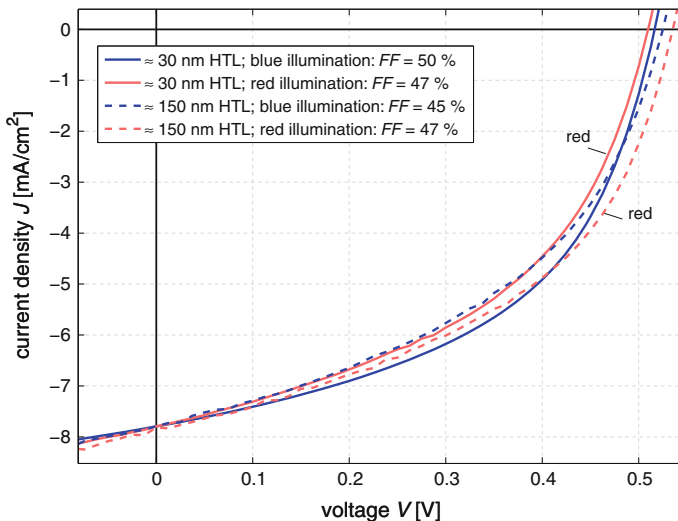


Fig. 8.10 “Monochromatic” J - V curves of samples with .../ZnPc:C₆₀(1:2)/BF-DPB/.... The illumination was provided by high-power LEDs. The intensity was adjusted to obtain the same J_{sc} for all four measurements. FF and V_{oc} depend on the illumination color due to changed generation profiles

8.3.6 External Quantum Efficiency as a Function of Voltage

The logical further step following quasi-monochromatic blue and red excitation is a measurement of the external quantum efficiency over the whole spectral range as a function of the applied voltage. This method is directly capable of visualizing the effect of the location of free charge carrier generation by using measurements on a single sample. Here, the role of tuning the generation profile is passed from the spacer layer thickness in Table 8.1 to the wavelength like in the previous case of monochromatic J - V curves.

We select three samples: a 2:1 blend with a 45 nm thick HTL and two 1:2 blends, one with an HTL thickness of 25 nm, and the other one with an HTL thickness of 90 nm. Figure 8.11a shows the EQE spectra of the first sample for bias voltages between -1 and 0.5 V. The shapes roughly resemble the absorption spectra of ZnPc and C₆₀ (cf. Fig. 3.53). The absolute signal decreases with increased applied bias. This behavior reflects a reduced photocurrent with increased bias, i.e. a FF that is limited by recombination of photogenerated charges. In Fig. 8.11b the EQE is normalized to the ZnPc peak at 630 nm to visualize the effect of the wavelength on the dependence of charge carrier extraction on voltage. All curves coincide in the whole spectral range. Consequently, the collection of charge carriers does not depend on the wavelength and, thus, not on the generation profile, which differs for each wavelength. This holds for all 2:1 samples independent of the HTL thickness

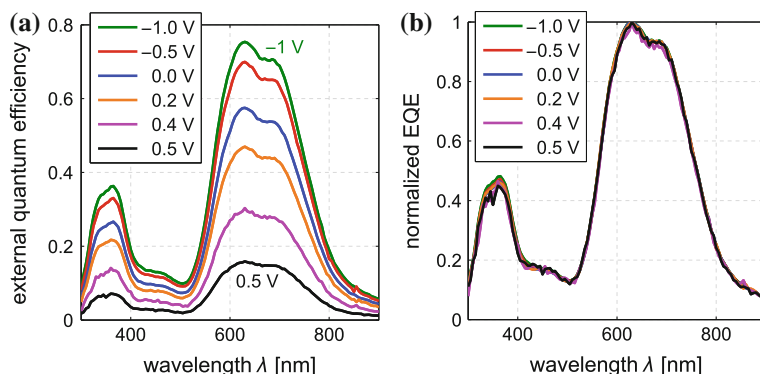


Fig. 8.11 **a** External quantum efficiency of sample .../ZnPc:C₆₀(2:1)/Di-NPD(45 nm)/... measured at different applied voltages. **b** Data normalized at 630 nm. The shapes of the spectra do not change with applied voltage

(not shown) and is in agreement with the data of Table 8.1, which does not show any influence of the generation profile on *FF*.

Absolute and normalized EQE spectra of the ZnPc:C₆₀ samples with a mixing ratio of 1:2 are shown in Figs. 8.12 and 8.13. The absolute spectra decrease with voltage comparable to the sample with a mixing ratio of 2:1. However, the relative dependence on the voltage is different for different spectral regions as evident from the normalized EQE. The sample with a 25 nm HTL (Fig. 8.12b) exhibits a weaker decrease of the EQE in the blue compared to the EQE in the red spectral range. The simulated monochromatic generation profiles in the inset prove that this effect is due to different generation profiles. The maximum generation rate in case of blue

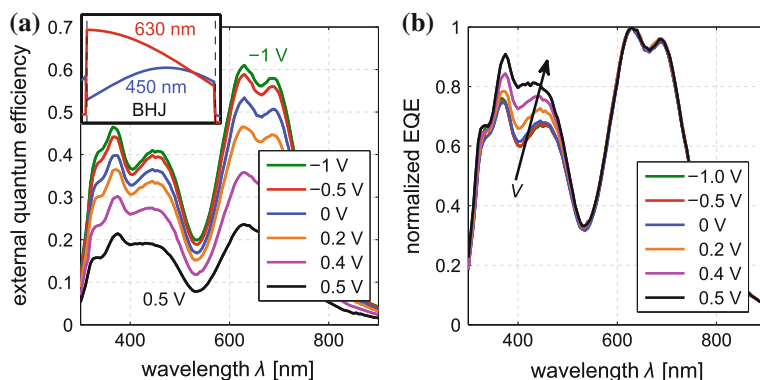


Fig. 8.12 **a** External quantum efficiency of sample .../ZnPc:C₆₀(1:2)/Di-NPD(25 nm)/... measured at different applied voltages. The *inset* shows the shape of the simulated generation profile within the BHJ for monochromatic red and blue illumination. **b** Data normalized at 630 nm. The decrease of the EQE with increasing bias is less pronounced for shorter wavelengths

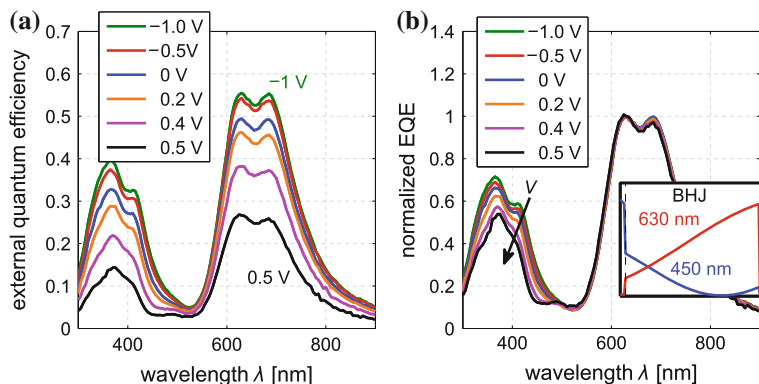


Fig. 8.13 **a** External quantum efficiency of sample .../ZnPc:C₆₀(1:2)/Di-NPD(90 nm)/... measured at different applied voltages. The *inset* shows the shape of the simulated generation profile within the BHJ for monochromatic red and blue illumination. **b** Data normalized at 630 nm. The relative decrease of the EQE with increased voltage is more significant for shorter wavelengths

illumination is closer to the right contact collecting the slower holes. The data of Fig. 8.13 show an inverted generation profile accompanied by a reverse trend in the EQE, where the signal in the blue decreases more strongly than in the red spectral range.

Altogether the experiments support the hypothesis of the generation profile dominating the voltage dependence of the photocurrent and consequently the *FF*. EQE spectra that depend on the applied voltage have practical consequences for a proper characterization of solar cells under simulated sunlight. It was discussed in Sect. 3.7 that the photocurrent calculated from EQE (0 V) and AM1.5g spectrum is used to set the accurate intensity of the solar simulator. The reason is a spectral mismatch (MM) between the spectra of simulator and the sun. Here, we introduce a new complexity. The mismatch factor depends on the applied voltage if the spectral shape of the EQE is a function of the applied voltage. To correct for this effect, the intensity of the solar simulator has to be set individually not only for each sample but for each voltage point of the *J-V* curve. Regarding the investigated samples and the used solar simulator (spectrum in Fig. 3.64), the MM factor changes from 0.76 (−1 V) to 0.75 (0.5 V) (from 0.78 to 0.79). These values yield a relative deviation of around 1 % which is acceptable for a reliable characterization. However, a voltage dependent MM may not be negligible for other devices and/or very precise measurements of the power-conversion efficiency.

8.4 Recombination

Although it was shown that the probability for recombination depends on the spatial generation profile of charge carriers and the (im)balance of mobilities, we have so far not identified the dominating recombination mechanism. From the previous sections,

we can only conclude that charge transport limits the FF , because the slower charge carriers generated further away from their electrode are predominantly lost. This effect implies that some space charge builds up within the layer (cf. Sect. 3.3.5) which changes the electric field. Recombination is then dominant in the region with a low field close to the contact collecting the faster charge carrier type. However, we cannot distinguish whether this recombination is geminate, direct/bimolecular, or indirect/trap-assisted. Therefore, the J - V data is further analyzed and measurements under varied illumination intensity are performed.

8.4.1 Exponential Region of Dark J - V Curves

The diode ideality factor n_D has been mentioned several times in this book. When introducing the MIM picture (Sects. 3.3.4 and 3.3.5) we stated that such a structure shows an exponential J - V curve in the dark. The injected current is driven by diffusion against the built-in potential V_{bi} and can in principle be described by the Shockley equation. However, in Sect. 6.4 it was demonstrated that the “slope” of the dark curve of a real organic solar cell is influenced by additional layers. Transport layers without aligned charge transport levels decrease the slope in forward, which results in large values of n_D or an n_D that cannot be correctly determined (cf. Fig. 6.8). In such a case, an application of the one-diode Shockley equation (2.49) is not justified. Only if the ideality factor is determined by the active material system itself, it may be capable of giving information about dominating recombination processes.

A brief simulation study demonstrates the effect of several material and device parameters on the slope of the exponential region of the J - V curve in the dark. The parameters for the simulations are those of the model device presented in Table 5.1. Figure 8.14 shows J - V curves for direct (bimolecular) recombination. The slope in the exponential region of the curves is independent of the recombination constant β and independent of charge carrier mobilities. A fit with the Shockley diode equation (3.72) yields a value of 1 for n_D . A higher recombination constant or a lower effective gap E_g shifts the onset to lower voltages, which is equivalent to a higher reverse saturation current in the Shockley equation (2.49). The high-mobility ($\mu = 1 \text{ cm}^2/\text{V s}$) curve represents a case where charge carriers pass through the whole device and recombine at non-selective contacts. This case is comparable to an ideal diode where recombination does not happen in the space charge region, which corresponds to the intrinsic layer in a MIM device. If recombination happens within the layer, the exponential region of the J - V curve is independent of mobility. The mobilities determine the current at higher voltages. The J - V curve bends due to limitations in charge transport (e.g. space-charge-limited currents), which give rise to a phenomenological series resistance. Recombination via a charge-transfer state does not change the slope either. It effectively changes E_g and the recombination properties, as elaborated in detail in (5.14).

The inset of Fig. 8.14 visualizes the effect of a changed recombination mechanism. In case of indirect (Shockley-Read-Hall) recombination, n_D approaches 2. That is

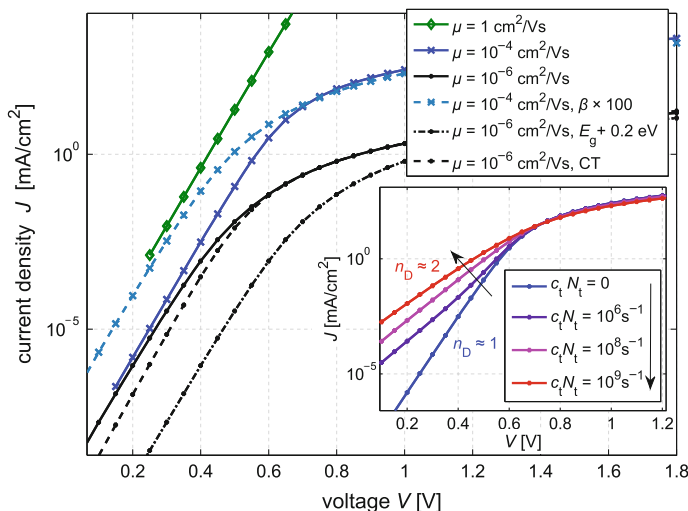


Fig. 8.14 Simulation data of a MIM device in the dark assuming different values of μ , β , E_g , and considering recombination via CT states (initial distance $a = 1.2$ nm and $k_{\text{relax}} = 10^6 \text{ s}^{-1}$), which do not influence the slope in the exponential region. The *inset* shows additional SRH recombination characterized by the effective recombination constant $c_t N_t$

known from inorganics where n_D was originally introduced to account for (trap-assisted) recombination in the space charge region of a p-n junction. In the presence of direct and indirect recombination, n_D is found in between 1 and 2.

In the following we analyze J - V curves of the devices from Table 8.1 considering the discussed simulation data. Figure 8.15 shows J - V curves of all devices measured in the dark. Curves for devices with the same mixing ratio and a varied HTL thickness coincide as the doped HTL is a highly conductive layer, whose thickness does not influence the device performance in the dark. All curves show an exponential region between 0.4 and 0.6 V. For higher voltages the ITO series resistance dominates the current and all curves coincide. A shunt resistance is responsible for currents at voltages smaller than 0.2 V. The shifted onsets of forward current for devices with different mixing ratios can be attributed to the dependence of the effective gap on mixing ratio (cf. Sect. 8.1). An exponential fit of the region between 0.4 and 0.6 V delivers a slope of around 20 V^{-1} . This value corresponds to $n_D \approx 1.9$, which is independent of mixing ratio. Therefore, recombination via traps is supposed to be the mechanism dominating the forward current in the dark.

The data discussed so far (Fig. 8.15) have been measured at room temperature. According to the Shockley equation and simulations of the MIM device, the slope is expected to decrease with increased temperature T as long as n_D remains constant. Figure 8.16 shows data of a temperature dependent J - V measurement performed on a p-i-n sample ITO/MeO-TPD:NDP2(20 nm, 10 wt%)/MeO-TPD(5)/ZnPc:C₆₀(45, 1:2)/C₆₀(15)/BPhen(6)/Al(100). The ideality factor at room

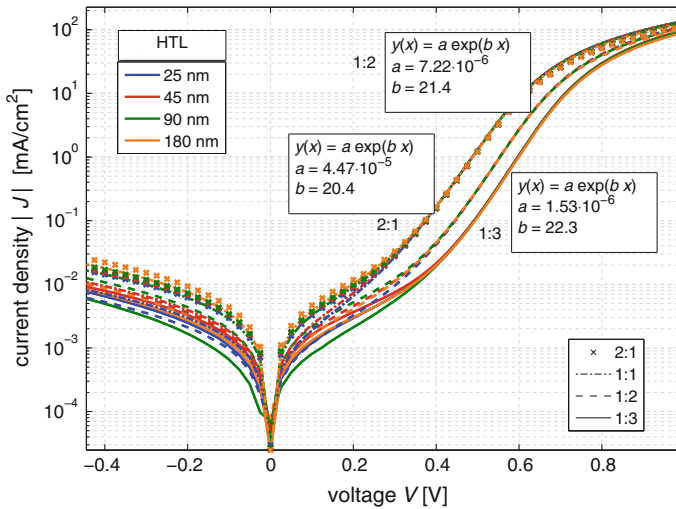


Fig. 8.15 Dark J - V curves of devices with different HTL thickness and mixing ratio, displayed in a logarithmic plot of the current. They are independent of HTL thickness and show an onset shifted with mixing ratio due to a changed effective donor-acceptor gap. The recombination mechanism is not changed as the slopes of the curves are comparable for all mixing ratios. They correspond to a diode ideality factor of 1.9, which is a hint for indirect recombination

temperature is comparable to the one of the devices discussed previously. The slope of the exponential region decreases with T , however not that significantly to result in a constant n_D . Consequently, n_D decreases from values above 2 at 200 K to 1.5 at 350 K. On the one hand, this shows that the ideality factor is a questionable measure. On the other hand, a physical explanation may be provided: An $n_D > 2$ for low T might be due to barriers or a strong localization of charge carriers becoming visible at low temperatures only. The decrease of n_D with T may be explained by the dominating mechanism shifting from indirect to direct recombination. A possible reason for this effect is the broad DOS resulting from disorder. The fraction of more mobile, quasi-free charge carriers increases with T giving rise for more direct recombination. Harada et al. [19] explained high values of n_D by the generalized Einstein relation that is also addressed in other studies on n_D [20, 21], showing that the interpretation of n_D is not completely settled yet.

8.4.2 J - V Data Dependent on Illumination Intensity

After having discussed the charge carriers injected in the dark and under forward bias, we turn focus on those that are photogenerated. J - V data dependent on light intensity are commonly used to distinguish between recombination mechanisms. As already discussed, a sublinear dependence of J_{sc} on intensity is attributed to

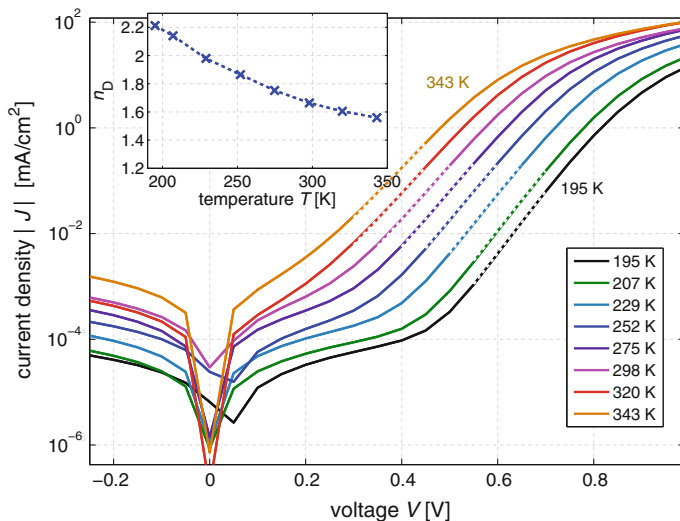


Fig. 8.16 Dark J - V curves of a p-i-n sample ITO/MeO-TPD:NDP2(20 nm, 10 wt%)/MeO-TPD(5)/ZnPc:C₆₀(45, 1:2)/C₆₀(15)/BPhen(6)/Al(100) measured at several temperatures. The *dashed regions* are used to fit an exponential function to the J - V curve. The slope increases with decreased temperature. However, the decrease is too low to result in a constant diode ideality factor n_D (*inset*)

bimolecular recombination, whereas a linear correlation indicates a monomolecular (geminate or trap-assisted) recombination mechanism. The reason is that charge carrier losses increase superlinearly with light intensity for direct recombination, where two charges have to meet (5.3). In case of geminate recombination the losses are proportional to the amount of CT states which scales linearly with light intensity. Trap-assisted recombination losses are only proportional to illumination intensity if the amount of trapped charges is assumed to be mainly independent of the amount of photogenerated charges.

However, investigating J_{sc} has several disadvantages. Especially for high- FF solar cells, there is almost no recombination in the device at this working point (IQE close to 1), because all charges are collected. Therefore, the current scales linearly with light intensity independent of the recombination mechanism limiting the FF . Second, recombination via dark carriers at the contacts may lead to a case, where the majority charge carrier density is hardly affected by illumination. Thus, even in the case of bimolecular recombination, a linear J_{sc} can be observed (cf. discussions in Sect. 5.4).

Nevertheless, J_{sc} is shown for four selected samples in Fig. 8.17. There, J_{sc} scales linearly with illumination intensity for intensities in the range of 1–200 mW/cm². The linear plot in the inset visualizes that J_{sc} increases sublinearly for higher light intensities. Due to the high values of J_{sc} a correction of the J - V data for the electrode series resistance (R_S) becomes necessary. The series resistance is obtained for each sample by correcting the logarithmic J - V data to compensate for the bending at high

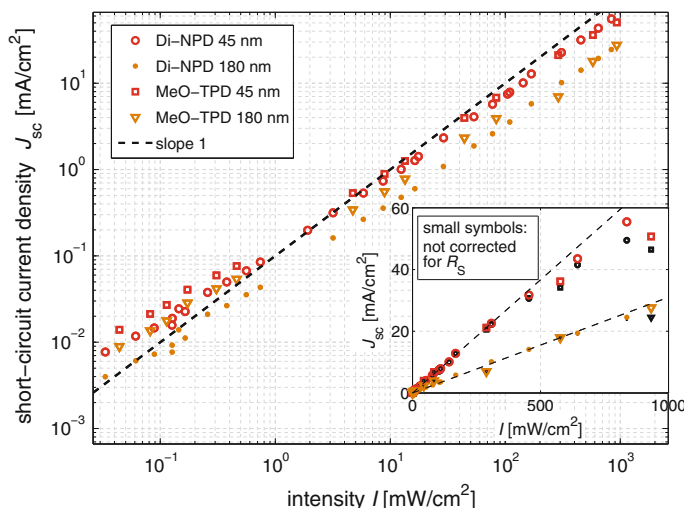


Fig. 8.17 J_{sc} as a function of illumination intensity for four different samples comprising a ZnPc:C₆₀ 1:3 blend. The light intensity is measured by a silicon reference diode where 128 mW/cm² represent 1 sun, corrected for spectral mismatch. The data are corrected for a series resistance whose influence can be seen at the linear plot shown in the *inset*

applied bias voltages (>0.6 V in Fig. 8.15). R_S is in the range of $2 \Omega \text{ cm}^2$ (30Ω), which is basically the ITO series resistance. The coincidence of all J - V curves in Fig. 8.15 indicates that it is indeed the resistance of the ITO which limits the forward current. Thus, the correction is meaningful, although it includes a correction for the resistance of the blend as well. The lateral resistance of the ITO stripes is not exactly known as their dimensions differ from sample to sample probably due to small changes in the alignment of the masks during evaporation. That is why it is preferred to always show the unmodified measurement data together with the data corrected for R_S , which is most likely overestimated.

Even after the correction for R_S , J_{sc} scales sublinearly with the intensity as visible in the inset of Fig. 8.17. This can be seen as an indication for bimolecular recombination becoming important for high light intensities even at short circuit. The slightly higher currents for intensities smaller than 1 mW/cm^2 do not result from the physics of the device itself but are rather related to the measurement conditions. For instance, using an aperture reduces this effect, indicating that parasitic currents make a definition of the active area more difficult.

As anticipated, it is difficult to use J_{sc} to learn much about recombination. It makes more sense to select a point on the J - V curve, where recombination dominates. One option is open-circuit characterized by an effective recombination of all photogenerated charge carriers. V_{oc} is shown as a function of illumination intensity for eight different samples in Fig. 8.18. Due to the lower overall absorption, V_{oc} is slightly lower for all samples with a 180 nm thick HTL (cf. Table 8.1 and Fig. 8.9). Additionally, V_{oc} is lower for the MeO-TPD samples in the case of higher light

intensities. Before coming to this phenomenon, the two dashed lines are discussed which show theoretical slopes of V_{oc} .

We derived these slopes in Fig. 3.25 where we studied the effect of different recombination mechanisms on V_{oc} . Starting with (3.26) expressing V_{oc} by the splitting of the quasi-Fermi levels, we found for bimolecular recombination [$R = \beta np$, (3.28): (3.29)]:

$$eV_{oc} = E_g^{DA} - k_B T \ln \frac{N_C N_V}{np} \stackrel{R=\beta np}{=} E_g^{DA} - k_B T \ln \frac{N_C N_V}{G/\beta} \quad (8.3)$$

and for trap-assisted recombination (3.31):

$$eV_{oc} \stackrel{R \approx c_t N_t \frac{np}{n+p}}{=} E_g^{DA} - k_B T \ln \frac{N_C N_V}{G^2 C}. \quad (8.4)$$

Here, we assume that the generation rate G is spatially constant, although we know that this is not completely true, but the order of magnitude at a given intensity is constant. Both equations predict that V_{oc} scales logarithmically with light intensity because the generation rate G is proportional to the incoming intensity. The slope in a graph, where the illumination intensity is plotted in the logarithm to the base 10, is $k_B T / \log e^1 \approx 2.3 \cdot k_B T \approx 59 \text{ mV/decade}$ ($T = 300 \text{ K}$) for bimolecular recombination. In contrast, trap-assisted recombination results in the double value due to the G^2 in the argument of the logarithm.

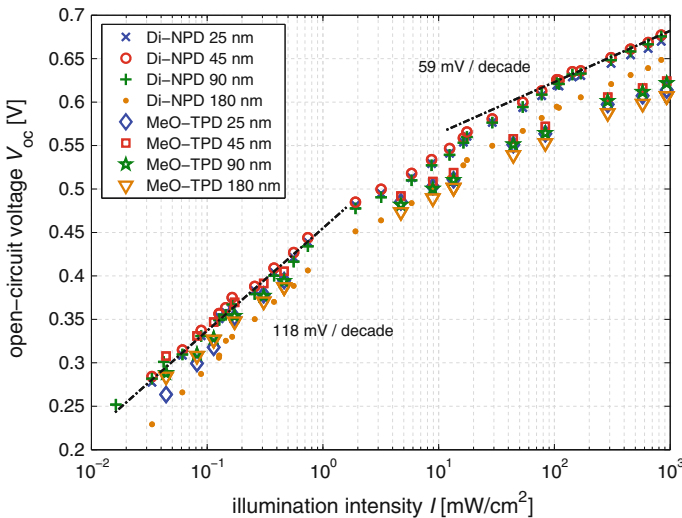


Fig. 8.18 V_{oc} as a function of the light intensity I for ZnPc:C₆₀(1:3) samples with different HTL materials and thicknesses. Dashed lines visualize the theoretical slope of V_{oc} for SRH recombination at low intensities and for direct recombination at higher intensities

The two dashed lines in Fig. 8.18 visualize these two slopes, where the offsets are arbitrarily selected. The experimental data follow the line with the high slope for intensities lower than 1 mW/cm^2 and the one with the lower slope for intensities larger than 10 mW/cm^2 . This trend is a clear indication that the dominating recombination mechanism switches from SRH to bimolecular type with increased intensity. Such a behavior is reasonable as the probability for bimolecular recombination scales with the square of the charge carrier density and therefore superlinearly with intensity. Thus, it superimposes trap-assisted recombination at higher intensities. As already mentioned, the slope of the experimental data is further decreased for intensities larger than 100 mW/cm^2 , especially for MeO-TPD as HTL.

To further clarify the dependence of V_{oc} on light intensity and HTL material, data of samples with different mixing ratios are examined in Fig. 8.19 where several trends are observed: First, the postulated transition from SRH to bimolecular recombination is present for all mixing ratios. Second, the absolute difference between V_{oc} of samples with different mixing ratios does not change with intensity indicating that indeed not recombination, but a changed effective gap causes the different values of V_{oc} (cf. Sect. 8.1). This is further proven by photovoltage decay times (inset) that are independent of mixing ratio. They are extracted from transient photovoltage experiments where a small perturbation light pulse is applied to the sample illuminated with a certain background intensity (cf. Sect. 3.7.3). The decay time is supposed to be correlated with the lifetime of charge carriers at that intensity [22–24].

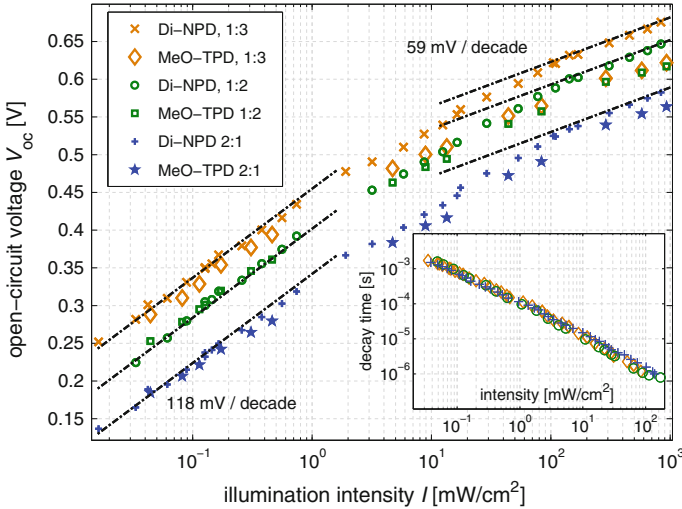


Fig. 8.19 V_{oc} as a function of illumination intensity I for devices with an HTL thickness of 90 nm. For higher intensities V_{oc} is limited by the HTL MeO-TPD. The *dashed lines* show the theoretically expected slope for SRH (118 mV/decade) and direct (59 mV/decade) recombination. The *inset* shows decay times extracted from transient photovoltage measurements. They coincide for all mixing ratios indicating that the lifetime of charge carriers does not depend on the mixing ratio

Third, the difference in V_{oc} of otherwise identical samples comprising the two different HTLs increases with intensity. On the one hand, this difference remains relatively low for the 2:1 sample, where V_{oc} is lowest. On the other hand, the open-circuit voltages of the 1:2 and 1:3 samples with HTL MeO-TPD are significantly reduced and even coincide for high intensities. The reason is that the HTL limits V_{oc} for voltages larger than around 0.6 V. The HOMO of MeO-TPD lies higher than the HOMO of Di-NPD (-5.1 eV vs. -5.35 eV). Therefore, samples with MeO-TPD suffer from a lower built-in potential and even a slight hole injection barrier into the 1:3 blend, whose HOMO is expected at $\lesssim -5.2$ eV according to the discussions in Sect. 8.1. This limit becomes more relevant for elevated values of V_{oc} which are present at higher light intensities. Therefore, it is concluded that the dominating recombination mechanism changes from indirect/SRH to direct/bimolecular to contact-limited (“surface”) recombination with increased intensity. This observation proves the proposed picture in Fig. 3.25b and agrees with the idea of different HOMO levels for different mixing ratios.

In case of direct recombination we cannot say whether this recombination happens via a bound CT state, because the characteristic behavior of V_{oc} is the same as for direct recombination between charges. According to Sect. 5.2.2, only the effective recombination constants are changed, and the dependence on illumination intensity remains unmodified. However, the previous section showed that the solar cells are mainly limited by charges recombining with each other.

In Chap. 5 we have studied the influence of recombination on the FF . It was found that the FF suffers from too strong recombination. Figure 8.20 shows the FF as a function of light intensity. Going from high light intensities towards lower ones, the FF increases. This trend is typical for bimolecular recombination, where the probability for recombination scales with the product of electron and hole densities. Consequently, recombination decreases superlinearly with a reduced light intensity, resulting in a higher FF . However, the FF drops at a certain point.

There are several possible reasons for a reduction of the FF with illumination intensity: First, the reduced charge carrier density for lower intensities might shift the ratio between free and trapped charges towards more trapped charges or charges in the tail of a Gaussian density of states. This shift would reduce the mean mobility of photogenerated charges and therefore the FF . Second, the influence of the shunt resistance might become visible for lower light intensities where photocurrents are low. The shunt induces a slope in the dark J - V curve of the solar cell which effectively reduces the FF under illumination, if shunt currents are in the order of photocurrents at low intensities. Third, even the FF of an ideal solar cell decreases with intensity. The reason is simply the definition of the FF according to (3.70): Considering the J - V curve in Fig. 3.32 and the fact that V_{oc} decreases with illumination intensity, we see that the FF has to decrease as well as the “bended region” of the J - V curve in the fourth quadrant is shifted towards lower voltages for reduced intensities. The shift increases the relative loss introduced by $V_{MPP} < V_{oc}$.

In Fig. 8.20, additionally data corrected for R_S are shown to visualize the two extrema of the FF within which the real value is expected. R_S becomes significant

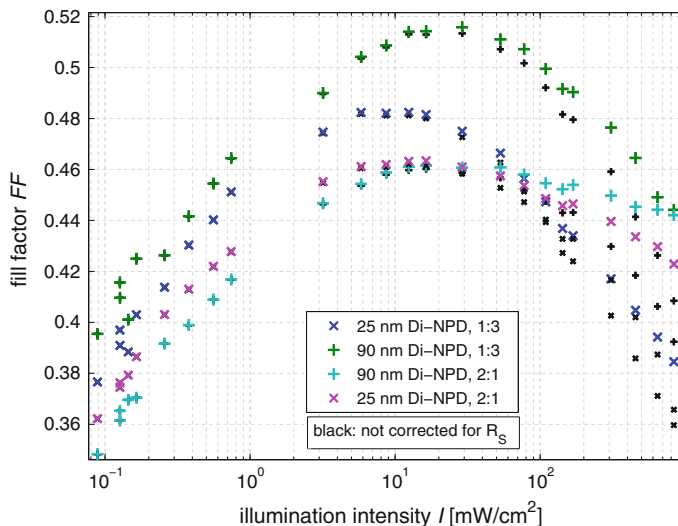


Fig. 8.20 Fill factor FF as a function of illumination intensity I for devices with different HTL thicknesses and mixing ratios. Maxima are observed at an intensity of $\approx 10 \text{ mW/cm}^2$

for intensities larger than 100 mW/cm^2 , where the real FF is expected to be closer to the corrected data.

8.5 Comparison with Simulations

So far the discussion focused on a qualitative interpretation of the measurement results. In this section, simulation data are presented which allow for more quantitative statements. However, it is emphasized that the amount of parameters makes an automated fitting difficult. Therefore, the selected parameters represent one possible combination which fits the experimental data relatively well. Different parameters have to be selected subsequently and in an iterative loop. The strategy applied here to find reasonable parameters for each mixing ratio, which are summarized in Table 8.3, is as follows:

1. The effective gap E_g^{DA} is selected in the following way: A constant electron affinity ($-E_{\text{et}}$) of 4.03 eV is chosen for C_{60} , which is a reasonable value (cf. Sect. 3.6.3). It is assumed to be independent of the mixing ratio, which is an acceptable approximation, but not completely true [9]. The hole transport level is taken from the ionization potential measured by UPS for blends with different mixing ratios, where a fine-tuning in the range of $\pm 20 \text{ meV}$ was allowed. This approach leads directly to a very good reproduction of the different values of V_{oc} which are mainly due to the changed effective gap, as the lifetimes of charge carriers do not change much with mixing ratio [4].

Table 8.3 Main parameters for the simulation of the ZnPc:C₆₀ BHJ

Parameter	2:1	1:1	1:2	1:3
E_{ht} (eV)	-5.08	-5.11	-5.16	-5.19
E_{g}^{DA} (eV)	1.05	1.08	1.13	1.17
β (cm ³ s ⁻¹)	8×10^{-12}	8×10^{-12}	8×10^{-12}	8×10^{-12}
μ_n (cm ² /V s)	4×10^{-5}	1×10^{-4}	2×10^{-4}	3×10^{-4}
μ_p (cm ² /V s)	2.25×10^{-5}	2.25×10^{-5}	8×10^{-6}	4×10^{-6}
k_{SRH} (s ⁻¹)	10 ⁶	10 ⁶	10 ⁶	10 ⁶
d_{BLEND} (nm)	48	54	50	50
d_{HTL} (nm)	25	45	86	170

2. The dependence of V_{oc} on the illumination intensity is used to set the two recombination constants β and $c_t N_t$. They are chosen to reproduce the absolute values of V_{oc} and the change in the slope of V_{oc} as a function of intensity. The latter requires including a trap-assisted recombination process.
3. Compared to their nominal values, thicknesses are slightly modified to optimize the fit between experimental and optically simulated saturated photocurrent. The experimental saturation current is obtained by correcting the J - V curves for a photoshunt [17].
4. Mobilities are determined by a comparison of fill factors obtained from simulation and experiment dependent on HTL thickness as shown in Table 8.1. For simplicity, μ is assumed to be independent of the electric field.
5. E_{ht} of the HTLs is set to -5.3 and -5.1 eV, respectively, according to UPS data and without further fitting.
6. For a comparison also dark curves are modeled with the chosen parameters and without changing any parameter or doing any fitting.

Figure 8.21 shows J - V curves of devices with mixing ratio 1:2 and different HTL thicknesses to visualize the agreement between experiment and simulation. Measured (dashed lines) and J - V curves corrected for a photoshunt (solid lines) are plotted. Without correction, the J - V curves do not saturate and reach currents that are larger than those predicted by optical simulations. Therefore, the correction is essential and can be justified by the presence of a photoshunt. This photoshunt is supposed to be caused by additionally injected charges [17].

The simulated data (symbols) follow the experimental curves relatively well. For a better fit, an optimization of the saturation current by changing layer thicknesses or introducing a maximum IQE (<1) that is independent of voltage could be done. Also a fine-tuning of mobilities and recombination constants could be performed to further increase the fitting. However, one should keep in mind that we describe a bulk heterojunction as one effective medium using a very rough model. Thus, even perfect fits will not improve the understanding of the physics of these devices.

In Sect. 8.3 we discussed the correlation between generation profile and imbalance in charge carrier mobility. For this purpose, we summarize experimentally obtained

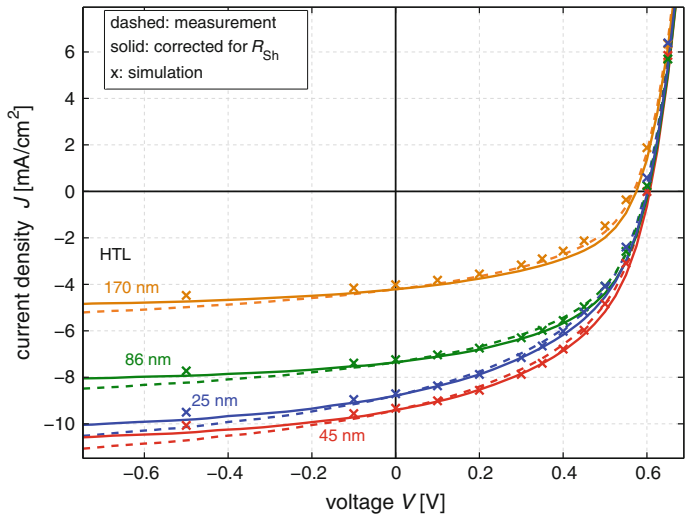


Fig. 8.21 *J-V* curves of ZnPc:C₆₀(1:2) devices with different HTL thicknesses. *Dashed lines* represent measured data, *solid lines* are experimental *J-V* curves corrected for a photoshunt [17], and *crosses* denote simulation data

and simulated values of the *FF* dependent on mixing ratio and HTL thickness in Table 8.4. The mobilities found by the simulation are lower than those measured using an OFET (cf. Table 8.2 with Table 8.3). This discrepancy is expected due to the high charge carrier densities in the channel of an OFET. Additionally, the measurement of a blend complicates the application of the simple transistor equations used to extract mobility values, as the geometry of the channel in a blend is not well-defined. The trend in the imbalance, however, follows the OFET measurements. The good agreement of simulation and experiment without considering geminate

Table 8.4 Experimental and simulated values for the *FF*

ZnPc:C ₆₀	μ_n/μ_p	HTL thickness (nm) →	25	45	90	180
2:1	1.8	<i>FF</i> , exp. (%)	46	46	47	47.5
		<i>FF</i> , sim. (%)	46	46	47	46.5
1:1	4.4	<i>FF</i> , exp. (%)	49	49.5	52	49
		<i>FF</i> , sim. (%)	49	49.5	52	47.5
1:2	25	<i>FF</i> , exp. (%)	47	48.5	52	48
		<i>FF</i> , sim. (%)	47	48.5	52	46
1:3	75	<i>FF</i> , exp. (%)	45.5	47	51	47.5
		<i>FF</i> , sim. (%)	44.5	47	51	44.5

The experimental data are taken from Table 8.1, performing a recalculation after a correction of the *J-V* curve for a photoshunt [17]. The simulation data are obtained using the mobility ratio shown in the second column. Absolute values of the hole mobilities are (2.25; 2.25; 0.8; 0.4) × 10⁻⁵ cm²/V s

recombination together with a field-dependent exciton dissociation, implies that this process is not significant here.

Figure 8.22 shows simulated EQE spectra for the devices whose experimental spectra were discussed with Figs. 8.12 and 8.13. The simulated data are obtained by considering a monochromatic illumination spectrum at a low intensity that matches the one used for EQE measurements. Comparing simulation and experiment it turns out that trends are reproduced in both a qualitative and a quantitative way.

Figure 8.23 displays the dependence of V_{oc} on light intensity for bulk heterojunctions with different mixing ratios. This data was already shown in Fig. 8.19. Now, simulated data are added and show excellent agreement with the experimental data over the whole intensity range. The simulation confirms that trap-assisted recombination becomes important for lower light intensities. Thus, this recombination mechanism is important in ZnPc:C₆₀ solar cells. As the SRH recombination constant does not change between different mixing ratios, it seems to be dominated rather by the heterojunction itself than by the morphology of the film.

It was mentioned earlier that V_{oc} is limited by the contacts at higher light intensities, especially for the HTL MeO-TPD with a high HOMO level of -5.1 eV. If this value is used in the simulation, this limit seen in experiment can be reproduced very well (dashed lines).

As final point, experimental and simulated dark J - V curves are compared in Fig. 8.24, which shows that the region of the onset and the slope (ideality factor) fit very well. This coincidence is another indication that the chosen parameters for the simulation are reasonable. It shows in particular that the balance between direct and SRH recombination deduced from V_{oc} is also capable of describing injected (dark) carriers. The simulation data is corrected for the ITO series resistance, which is assumed to be $1.6 \Omega \text{ cm}^2$. Furthermore, a shunt is considered which dominates the current for voltages lower than 0.3 V. This (dark) shunt resistance is deduced from

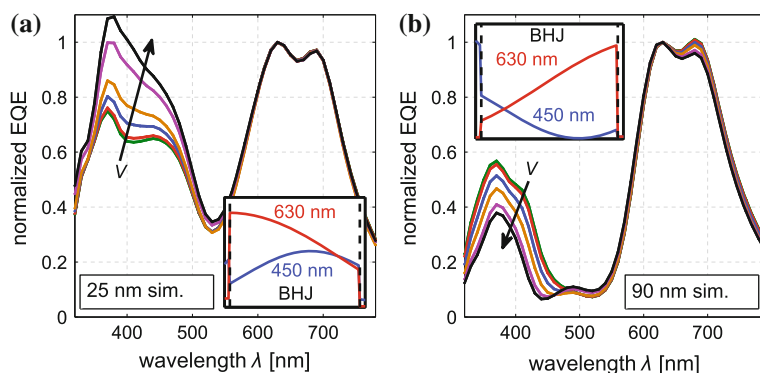


Fig. 8.22 Simulated external quantum efficiency spectra related to the experimental data shown in Fig. 8.12 for (a) and in Fig. 8.13 for (b). The trends of simulation and experimental data fit well, proving that an imbalance in mobilities can result in an internal quantum efficiency that depends on the wavelength at a given applied voltage

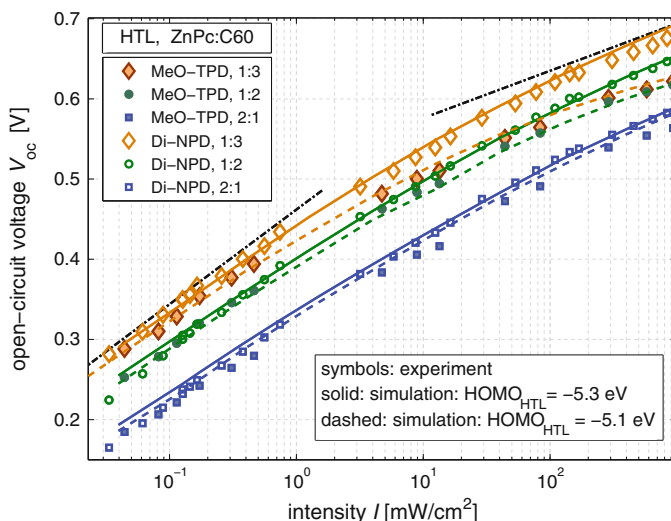


Fig. 8.23 *Simulation and experiment* The open-circuit voltage as a function of illumination intensity. The simulation data (solid and dashed lines) show good agreement with experiment and reproduce the three limits, which are SRH recombination (low intensities), direct recombination (high intensities), and recombination at the HTL-blend interface (for MeO-TPD at high intensities)

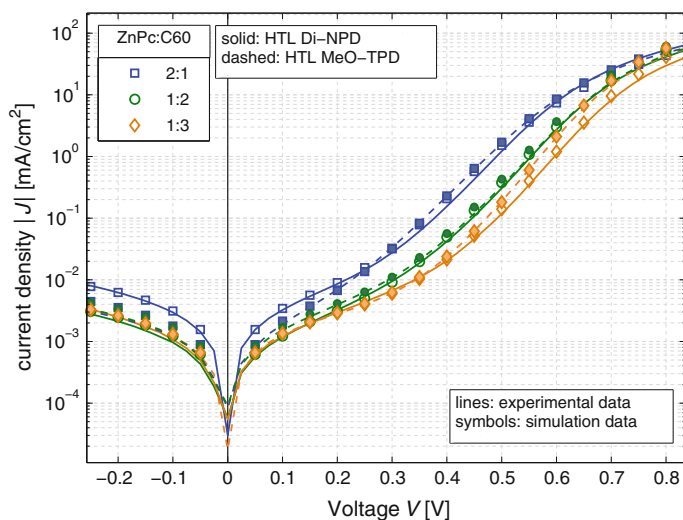


Fig. 8.24 *Simulation and experiment* Dark J - V curves of devices with different mixing ratios and an HTL thickness of 25 nm. The simulation data include the ITO series resistance of $1.6 \Omega \text{ cm}^2$ and a shunt resistance obtained from the experimental data, which dominates the current close to 0 V

the slope of the experimental J - V curves measured in the dark between -0.05 and $+0.05$ V where the current-voltage relation is indeed linear.

We can conclude that recombination via traps dominates the dark current and V_{oc} at low illumination intensities. However, at higher intensities direct/bimolecular and surface recombination become important. Thus, the ideality factors determined from a J - V curve measured in the dark and from V_{oc} under illumination can be different.

8.6 Summary

This chapter addressed the current-voltage relation of ZnPc:C₆₀ solar cells with different mixing ratios and different generation profiles in the active layer. The effect of the mixing ratio on V_{oc} was attributed to changes of the donor-acceptor gap. The dependence of V_{oc} on illumination intensity revealed that direct and indirect recombination take place in these devices. The fill factor was found to depend on the absorption profile and the illumination wavelength for samples with a high imbalance of mobilities. A comparison with simulation data allowed for a quantification of those effects.

We conclude by answering the introductory questions of this chapter:

- *What are possible explanations for different open-circuit voltages of devices consisting of the same active material system (e.g. when changing the mixing ratio)?*
Either the effective energy gap or charge carrier densities are changed. The energy gap is a function of polarization energies and changes, e.g., with the (nano-) crystallinity of phases. Charge carrier densities at open circuit are influenced by recombination rate constants and mechanisms.
- *What are simple experiments to identify the correct reason?*
A changed gap can be measured using spectroscopic methods: UPS and IPES to determine charge transport levels or FTPS and electroluminescence to detect the energy of the CT state. Changes in charge transport levels can also be probed indirectly by investigating the role of modified extraction barriers. Changed recombination conditions can be identified by transient photovoltage decay and charge extraction measurements.
- *Which explanations exist for a changed donor-acceptor gap in a bulk heterojunction based on the same materials?*
The donor-acceptor gap can change upon modifications of the surroundings of one molecule changing polarization energies. Different (nano)crystalline phases allow for a different amount of interactions between molecules, changing energy levels in a characteristic way.
- *Why is it interesting to investigate graded junctions?*
A graded junction contains a higher concentration of donor (acceptor) material close to the anode (cathode). This structure is thought to be beneficial for the extraction of charges, as it decreases the probability for direct encounters of charge carriers.

- *What are possible explanations for the fill factor depending on the color of the illumination? What is the role of charge-carrier mobility?*

One reason might be that the internal quantum efficiency directly depends on the wavelength of light. This, however, is commonly not the case. However, the collection efficiency of charge carriers can depend on the location of generation within the bulk heterojunction. As the absorption profile is a function of wavelength, it can cause different fill factors for different illumination colors. This effect is particularly important for imbalanced mobilities.

- *Why does the internal quantum efficiency depend on the wavelength of the incident light and on the thickness of the optical spacer? What is the consequence for the spectral mismatch factor?*

Both, optical spacer and the illumination color allow a tuning of the absorption profile, which modifies the internal quantum efficiency. The spectral mismatch is calculated using the external quantum efficiency containing the internal one. If this quantum efficiency depends on the applied voltage, the mismatch factor will change with applied voltage as well.

- *What point of the J-V curve is a good choice to investigate the dominating recombination mechanisms in a solar cell? How can this be done?*

Open circuit is a good choice, because every charge carrier photogenerated has to recombine at open circuit. Different recombination mechanisms show a characteristic dependence of the open-circuit voltage on the illumination intensity, which can be exploited to study recombination.

- *What does the diode ideality factor tell?*

The ideality factor characterizes the slope of (dark) J-V curves, where the current is plotted in a logarithmic scale. It was introduced to allow for recombination in the space-charge layer of a diode, which is supposed to be a non-ideal case. If it can be determined accurately, it contains information on the dominating recombination mechanism.

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Part III

Summary and Outlook

Chapter 9

Device Physics in a Nutshell

Abstract This chapter summarizes the main effects and parameters influencing the performance of organic solar cells in very brief statements. On the one hand, this is done by comparing J - V data of a fictitious device X with its reference device. On the other hand, the influence of changes in specific properties of the device is visualized by a series of calculated J - V curves. These two approaches contain a high risk for an oversimplification. For this reason, the given references pointing back to the main chapters of this book should be consulted for a detailed understanding. However, used in the right way, this chapter offers a very compressed set of guidelines on how to interpret J - V curves of organic solar cells from a drift-diffusion point of view. Simple experimental methods are suggested to distinguish several reasons for detrimental device properties such as a low V_{oc} , low FF s from S-shapes, and low photocurrents. The chapter closes with concluding thoughts about the applicability of drift-diffusion simulations to solar cells based on disordered organic thin films.

9.1 Brief Guidelines for Understanding Trends in Current-Voltage Curves

Commonly, a discussion of J - V data focuses on an analysis of the main parameters: short-circuit current density J_{sc} , open-circuit voltage V_{oc} , and fill factor FF . We will see in the following that these parameters are not sufficient for a detailed analysis. Especially, J_{sc} and FF are relatively arbitrary values, which do not simply reflect a distinct device property. Only if the photocurrent is already saturated at short circuit, a comparative interpretation of J_{sc} obtained from different solar cells is meaningful.

During the following discussions, we imagine one or several devices X that contain specific modifications compared to a well-working reference device. A comparison of reference and device(s) X is a common approach of experimental work. Usually, either one processing condition or material(-combination) is exchanged and the results for the new device X are compared to the known reference device. Although we stated that the device performance “fingerprints” alone have to be handled with care, we arrange the subsequent discussion along these values, but including further parameters. Keep in mind that it is difficult or nearly impossible to

draw resilient conclusions based on few J - V curves only. That is why suggestions are given for further experimental characterizations to complement the J - V data.

Changes in J_{sc} and J_{sat}

A change in J_{sc} itself can have several reasons, as long as the photocurrent is not saturated at this point. That is why additionally the saturated photocurrent J_{sat} should be examined. Its investigation requires a measurement of the J - V curve in reverse voltage direction. If a saturation of the current is not observed and the relation between current and voltage is linear, the best approximation for J_{sat} is found by a correction of the J - V curve for the photoshunt. If the blocking behavior of the diode is not sufficient (i.e. there is a significant reverse current in the dark), the dark current can in many cases be subtracted to obtain the current under illumination, which is saturated or can be interpreted by means of a photoshunt.

A change in the saturated photocurrent of our device X compared to the reference device results from a changed maximum generation rate of charge carriers and can be due to the following reasons:

- *A changed absorption (η_{PA})*, which can be identified by performing absorption measurements on the solar cells. The reasons might be a different absorber, a changed morphology or crystallinity of the absorber, changed layer thicknesses, or a changed stack design, giving rise to a different distribution of the electro-optical field. The latter can be examined by means of optical simulations (cf. Sect. 4.7).
- *A changed exciton-diffusion efficiency (η_{ED})*, caused by a replacement of a material or a modified morphology/crystallinity of the same material. This modification can give rise to a changed exciton diffusion length, a changed layer thickness, or a changed stack design, causing a different distribution of the electro-optical field, especially for flat heterojunctions (FHJ). In a BHJ a changed phase separation and thus grain size may lead to similar effects. They can be distinguished from the previous one (η_{PA}) by comparing absorption and EQE measurements at a reverse bias voltage where the photocurrent is saturated. In this case a changed η_{ED} is seen in a changed IQE (cf. 3.24). An increased radiative singlet emission of the absorber in a photoluminescence measurement is also an indication for a lower η_{ED} .
- *Introduction of an (additional) exciton quenching interface or species*: This effect can be distinguished from the previous case by an examination of J_{sat} as a function of layer thickness and a comparison with modeling data describing exciton diffusion. Here, photoluminescence measurements might be helpful as well.

All these effects have in common that they do not depend on voltage. Thus, if clearly present, they result in a vertical shift of the J - V curve in first approximation.

Changes in V_{oc}

V_{oc} is a very important and meaningful parameter together with J_{sat} . Although the external current is zero, the microscopic conditions within the device at this point are

not *a priori* defined. This was discussed in the context of contact properties in Chaps. 5 and 6. The main result is that in the case of selective contacts, all photogenerated charge carriers recombine within the bulk, whereas in the case of non-selective contacts, there may be a significant diffusion of (minority) charges to the “wrong” contact. The latter is an additional loss mechanism for V_{oc} .

The most important factors that can cause a change in V_{oc} of device X compared to the reference are summarized in the following:

- *A changed generation rate* due to reasons discussed in the previous section. A higher generation rate leads to a higher charge carrier density in the device and thus a higher V_{oc} . The change in V_{oc} is then accompanied by a change in J_{sat} or J_{sc} . This effect simply reflects the dependence of V_{oc} on illumination intensity. For changes of J_{sat} by, e.g., a factor of 2, some tens of mV changes in V_{oc} are expected (cf. first and last row of Table 8.1).
- *A changed effective donor-acceptor gap (E_g^{DA})* due to a different donor (acceptor) material with a different IP (EA). A change in E_g^{DA} can also result from changed polarization energies due to a modified environment or crystallinity of a molecular film. Consequently, a change in V_{oc} can originate from different mixing ratios of a donor-acceptor blend (Sect. 8.1). One approach to identify a changed E_g^{DA} is a characterization of the blend by UPS and IPES. Another option is to carry out temperature dependent measurements of V_{oc} , allowing for a determination of E_g^{DA} by an extrapolation of $V_{oc} \rightarrow 0$ K (cf. Fig. 5.4). A further approach is to investigate the energy of the CT state, which, if present, replaces the effective gap (Sect. 5.2.2). This can be done by sensitive absorption, EQE, and electroluminescence measurements.
- *Changed recombination dynamics at the heterointerface*: At a given generation rate, a higher recombination rate constant decreases the amount of charge carriers, thus the quasi-Fermi level splitting, and consequently V_{oc} (Sect. 5.2.2). It may result from impurities, acting as recombination centers, or a modified recombination cross section or wave-function overlap between orbitals at a heterojunction. A modified recombination results in a changed lifetime of charge carriers that can be detected, e.g., by transient photovoltage measurements.
- *Changed contact properties modifying the charge-collection efficiency (η_{CC})*: As long as recombination does not take place at the interface between active and adjacent transport materials, the work function and thus the built-in potential do not modify V_{oc} (cf. Chap. 5). In that case also the doping concentration and IP/EA of doped charge transport layers are irrelevant for V_{oc} . V_{oc} can only be reduced by additional recombination. This recombination can result from contacts if they are non-selective. In this case, energetically misaligned contacts that form injection barriers reduce V_{oc} of a bulk heterojunction (Chap. 6). The reason is a decreased built-in potential, increasing extraction/recombination of charge carriers at the “wrong” electrode.
- *Local shunts* due to non-continuous layers and high surface plane roughness, possibly caused by substrate heating or a highly crystalline material. In this case the blocking behavior of the diode and thus saturation and FF will be negatively

affected as well. A strong shunt (i.e. low shunt resistance) can be identified as a linear current-voltage relation close to short circuit.

Emergence of a Low Saturation in Reverse Bias

Low saturation means a strong dependence of current on applied negative bias. Here, the dark and illuminated case have to be distinguished. If the dark current is affected as well, one of the following suggestions for changes in device X compared to the reference device might be valid:

- *Shunting*: This results in an approximately linear J - V curve in reverse bias and is most likely due to some local shunts originating from processing errors or local inhomogeneities within the layers.
- *Diode breakdown*: This can be identified as a reverse current showing an exponential dependence on voltage. This effect is observed for all solar cells operated at high negative bias voltages. It often results in an irreversible effect on the device. The breakdown is field-induced and shifts towards 0 V for thin donor and/or acceptor layers (cf. Sect. 10.1.1).
- *Poor rectification behavior* due to a lack of selectivity of the device structure, which can be caused by non-selective contacts and a low built-in potential.

If only the photocurrent of device X compared to the reference device is affected by a low saturation, other effects may play an important role:

- *An increased photoshunt effect*: This can be deduced from a linear J - V curve in reverse and, in the extreme case, by the IQE appearing larger than unity for negative bias voltages. It is more pronounced for thinner and non-blended donor and/or acceptor layers, especially for pure C_{60} layers. The microscopic reasons are not yet completely understood.
- *The presence of a field-assisted exciton dissociation process* decreasing the charge dissociation efficiency η_{CD} . Such a process is difficult to identify from the J - V curve alone, but should result in a final saturation of photocurrent at reverse bias when η_{CD} becomes constant. It should also show a characteristic temperature dependence [cf., e.g., (4.53)]. Furthermore, the voltage-dependence of the photocurrent should be more pronounced for devices with larger layer thicknesses.

If the trend in saturation follows the trend in FF , the content of the following section may be relevant for the saturation as well.

Changes in FF

The FF reflects the dependence of current under illumination on voltage in the power-generating quadrant. Thus, it is related to electrical losses. A change in FF of device X compared to the reference can be caused by the following modifications:

- *Changed charge carrier mobilities*: Higher charge carrier mobilities increase the probability for the collection of charge carriers at a certain applied voltage. This results directly in a higher FF (cf. Chap. 5). The reasons for a change in mobilities

can originate from a different morphology or (nano-)crystallinity of the blend, which in turn might be due to some treatment/annealing/heating or further process parameters during fabrication or post-treatment. Increased mobilities should also affect the forward current as long as the forward current is not limited by a macroscopic (electrode-)series resistance. Consequently, a decrease of forward current and a lower FF indicate reduced charge carrier mobilities. In the case of imbalanced mobilities in a BHJ, the forward current can be driven by one charge carrier alone. If the mobility of the slower charge carrier is changed, it will only affect the FF and not the forward current.

- *Changed recombination*: As discussed in Chap. 5, the mobility (or more broadly the net charge extraction rate) has to be seen in comparison to recombination. An increased recombination probability decreases the FF . In contrast to a change in mobility, V_{oc} is also decreased, and the rise of forward current is increased if forward current is recombination limited. Thus, the effect of a change in recombination can be distinguished from mobility effects.
- *An increased active layer thickness*: If the FF is limited by charge extraction or field-dependent exciton dissociation, a larger thickness leads to higher recombination losses and therefore a lower FF .
- *A changed optical generation profile in a bulk heterojunction*, especially in the case of imbalanced mobilities. Due to an inversion of the solar-cell stack or a change of the thickness of the spacer layer(s), the location of maximum charge carrier generation may be shifted within the blend. This shift can result in significant changes in FF (cf. Table 8.1).
- *A changed probability for the dissociation of excitons*, which was already discussed in the section on the reasons for a low saturation of the photocurrent.
- *A changed overall absorption*: As the FF depends also on illumination intensity (cf. Fig. 8.20), it is affected by a changed overall absorption which can be identified by changes in J_{sat} or J_{sc} .
- *Changes in macroscopic parallel or series resistances* seen in the dark curve as well (cf. Fig. 3.37b).

Furthermore, the FF can be strongly affected in case of an S-shaped J - V curve, which is discussed in the following.

Emergence of an S-Kink

An S-kink is characterized by two inflection points in the J - V curve, the first at negative current and the second commonly around V_{oc} . Possible reasons for S-kinks are:

- *Insufficient extraction of charge carriers* due to energetic extraction barriers at the contacts or insufficient charge transport in charge transport layers giving rise to the pile-up of photogenerated charge carriers (Sect. 6.3.2). The reasons for the first are misaligned charge transport levels (EA, IP) between active material and charge transport layers/metal electrodes. Charge transport layers with very low conductivity are responsible for the second effect.

- *Extraction of charge carriers driven by diffusion against the electric field* due to injection barriers decreasing the built-in potential. Selective contacts or a flat heterojunction (or a hybrid flat-bulk heterojunction) are essential to establish the required diffusion gradient (cf. Sect. 6.3.1).
- *Largely imbalanced mobilities* in flat heterojunctions, where the slower charge carrier causes a space charge. As the space charge is only located on either the donor or acceptor layer (dependent on the mobilities), it modifies the probability for charge carrier extraction in a characteristic way giving rise to an S-shaped J - V curve (cf. Sect. 7.1).
- *Dependence of the (CT) exciton dissociation on the electric field* (cf. Sect. 7.2).

There are several approaches to identify the origin of an S-kink. Each type of S-kink shows a specific dependence on layer thicknesses and temperature (cf. Sects. 6.6.1 and 6.6.2). Transient photocurrent measurements deliver a distinct result for each origin (cf. Sect. 6.6.3). Extraction barriers can be identified by overshoots in the transient photocurrent signal showing a pile-up of charge carriers, whereas devices containing a low-mobility material show a slow response. J - V measurements as a function of the illumination intensity are a simple approach to discriminate between injection and extraction barriers (cf. Sect. 6.6.4). For the former the shape of the S-kink does not depend on illumination intensity, whereas for the latter it is a function of the illumination intensity because more photogenerated charges pile up for larger intensities.

The impact of extraction barriers can be reduced by increasing the doping concentration in the charge transport layer. This modification results in a high field at the extraction barrier, which increases the probability for an extraction of charge carriers.

Inflection points can also be observed in the forward-current regime of a solar cell. One reason for this effect is an extraction of photocurrent in forward direction but an injection of dark current that is delayed in voltage (cf. Sect. 7.3).

9.2 Which Property Influences the J - V Curve in What Way?

The following series of simulated J - V curves are supposed to give the reader an understanding on two points: First, how does a variation of a specific parameter influence the J - V curve? Second, how sensitive is the J - V curve to a single parameter?

The results will not be very surprising to the ambitious reader who carefully dealt with all the preceding chapters. The following plots offer a very compact graphical summary of the main conclusions.

To generate these graphs, we select a reference device and systematically vary one (or two) parameters. For simplicity we assume a single-layer bulk heterojunction sandwiched between metal electrodes, i.e. a MIM device. The charge carrier densities at the contacts are set according to (4.64). All relevant parameters used

Table 9.1 Default input parameters for the simulations applied to show trends in the J - V curve upon varying one selected parameter

Parameter	Name	Value
E_g^{DA}	Donor-acceptor transport gap	1.5 eV
$N_C = N_V$	Effective density of states	10^{21} cm^{-3}
ϵ_r	Dielectric constant	5
$\mu_n = \mu_p$	Electron and hole mobility	$10^{-4} \text{ cm}^2/\text{V s}$
β	Bimolecular recombination constant	$7.23 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$
d	Device thickness	100 nm
G	Optical generation rate	$10^{22} \text{ cm}^{-3} \text{ s}^{-1}$
$\varphi_n = \varphi_p$	Injection barriers	0.2 eV
T	Temperature	300 K

for modeling the reference device are found in Table 9.1. For each plot, the varied parameter is displayed in the title (Figs. 9.1, 9.2, 9.3, 9.4, 9.5 and 9.6). The observations are discussed in the respective captions. Note that the graphs are not suitable to draw quantitative conclusions, as they cannot be completely generalized. The effect of a variation of one parameter always depends (to some extent) on the unmodified values of the other parameters as well. An example for a strong interplay

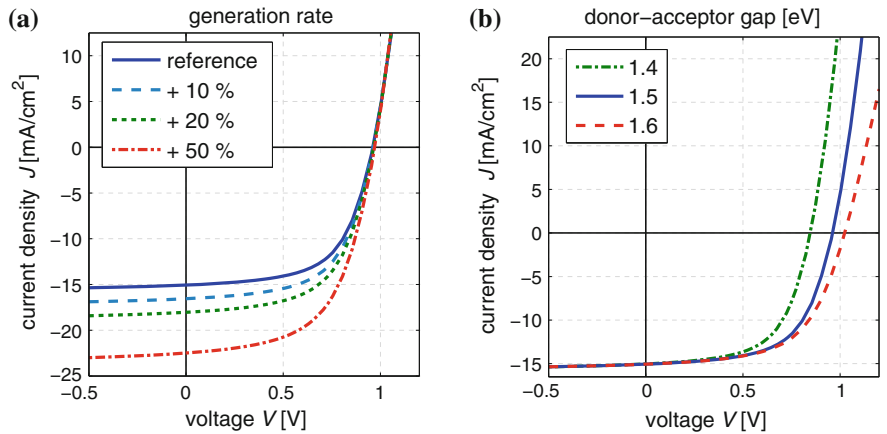


Fig. 9.1 Simulated J - V curves: **a** Changes in the generation rate (absorption or exciton diffusion efficiency) shift the J - V curve *vertically*. The offset in current is independent of voltage for negative bias, and V_{oc} slightly increases with a larger generation rate of charge carriers. The FF is slightly affected and ranges from 61, 60, 59, to 58 %. **b** Changes in the donor-acceptor gap E_g^{DA} shift the J - V curve *horizontally* with V_{oc} linearly scaling with E_g^{DA} as expected from (3.26). For too large gaps, limitations of V_{oc} due to the work functions of electrodes (which are assumed to be constant here) become visible. They give rise to surface recombination in case of poor selectivity (cf. Chap. 5). The FF is 60, 61, and 59 %

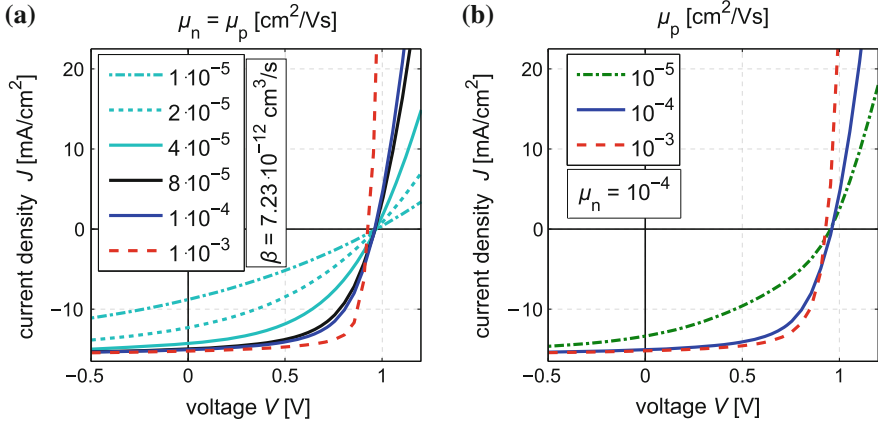


Fig. 9.2 **a** Changes in the electron and hole mobility are mainly seen in the FF (30, 36, 46, 57, 61, and 75 %) and for a very low FF in J_{sc} as well. V_{oc} decreases with too high μ due to surface recombination. **b** If the mobility of one type of charge carrier is fixed, a variation of μ of the other is less severe. The FF is 40, 61, and 69 %

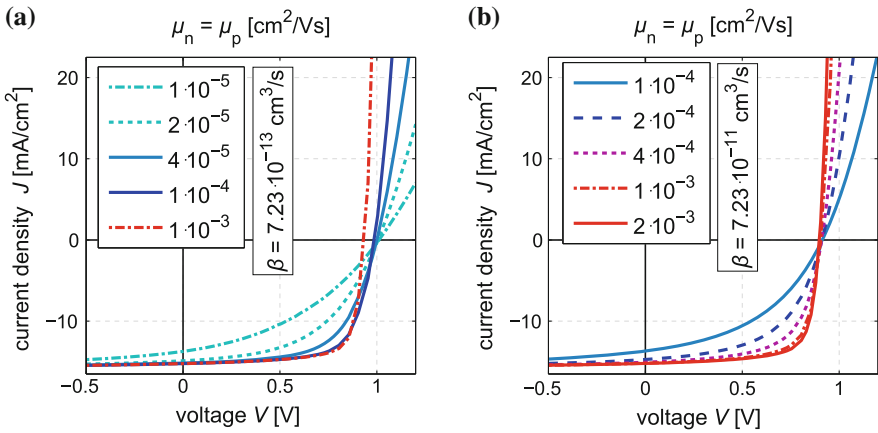


Fig. 9.3 Comparing these plots with Fig. 9.2 shows that the ratio between mobility and recombination constant determines the FF , which is in **a** 40, 51, 61, 70, and 76 %. In **b** larger mobilities are required to reach similar values of the FF (44, 55, 63, 71, and 74 %). For a high recombination constant β (**b**) surface recombination is not relevant, as V_{oc} does not change with μ

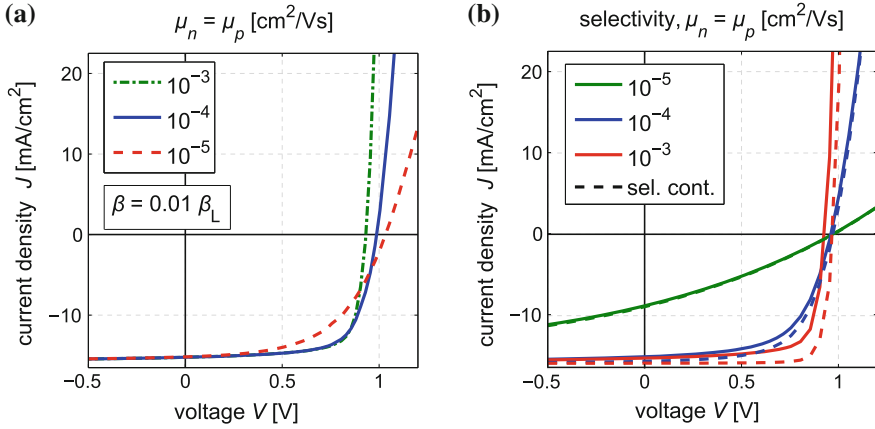


Fig. 9.4 **a** Mobility μ and bimolecular recombination constant β are related according to Langevin theory (4.46, here with prefactor 0.01). In this case, lower mobilities also decrease the probability for recombination. The FF is less affected by a decrease in μ (75, 70, 54 %), which comes along with an increased V_{oc} due to a reduced recombination. **b** Selective contacts can slightly increase FF (30, 61, 75 % reach 30, 62, and 83 %, respectively) and V_{oc} if surface recombination is relevant (here for higher μ due to significant diffusion to the “wrong” electrode)

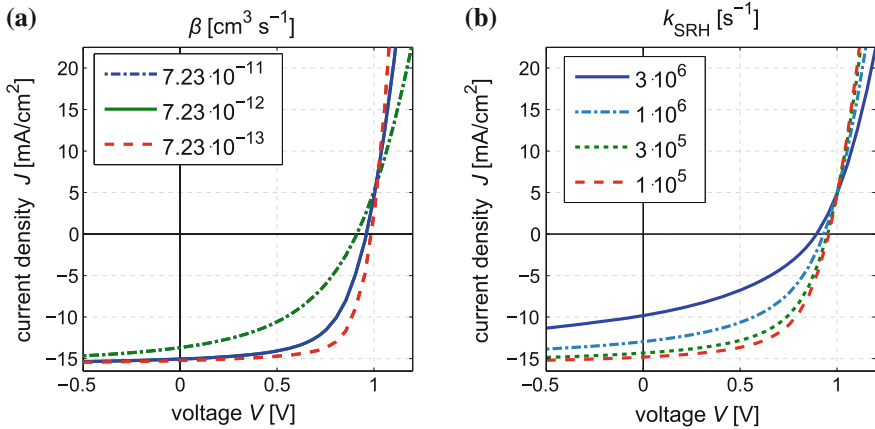


Fig. 9.5 An increase of the recombination parameters decreases FF , V_{oc} , and finally J_{sc} , for both direct and trap-assisted (SRH) recombination. The effect of the absolute numbers of the recombination parameters depends on the used values of the charge carrier mobilities. The FF increases with reduced recombination constants from 44 to 61 to 70% in (a) and from 39, 48, 55 to 59 % in (b)

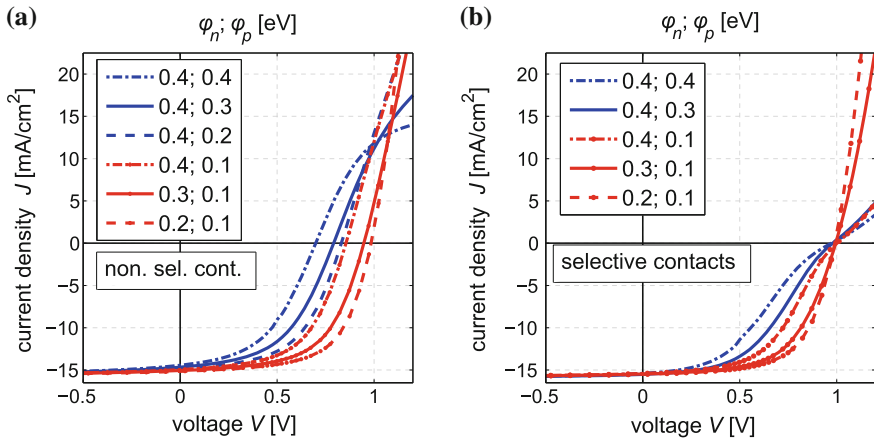


Fig. 9.6 Changes in work functions of the electrodes give rise to injection barriers. In the case of non-selective contacts (a), injection barriers mainly decrease V_{oc} due to an increased surface recombination (low V_{bi}). The FF is 47, 50, 54, 56, 58, and 62 %. For selective contacts (b), V_{oc} is independent of the barrier. However, an S-kink emerges for larger barriers. In experiment, selective contacts can be realized employing an interlayer between active layer and electrode, which blocks one type of charge carriers, e.g., due to an offset in energy levels for charge transport. The FF is 39, 46, 51, 59, and 63 %

between parameters is the combination of mobility and recombination constants (Fig. 9.3). Nevertheless, trends in certain working regimes can be helpful to identify or at least narrow down the origin of an observed difference between measured J - V curves.

9.3 Organic Solar Cells and Drift-Diffusion Simulation: Final Remarks

Throughout this book, a drift-diffusion model was extensively employed to describe organic solar cells. Here we briefly conclude on the applicability of this approach and its limits. The fundamentals of drift-diffusion modeling were introduced in Sect. 4.2. There, we found that the basic equations result from the Boltzmann equation, which can be derived if a distribution function for particles can be defined. This function describes the amount of particles as a function of their location and velocity at a given time. For a proper definition, it should describe sufficient particles in a macroscopically small volume. In inorganic semiconductors, the transport equations contain the effective mass approximation, summarizing the effect of the lattice potential in a modified mass of the electron. Its velocity is then given by accelerating forces acting on this mass and scattering events leading to a retardation. The scattering times are assumed to be much shorter than the time of free propagation. For organic semiconductors, one does not explicitly refer to the effective mass, but still uses the charge

carrier mobility as parameter to relate the current to the electric field and the charge carrier density. The differential (transport and continuity) equations are solved based on a continuum approach.

Charge transport in disordered organic materials follows a hopping mechanism, which is characterized by a charge carrier localized on a hopping site and jumping from site to site. This microscopic process cannot be described by drift-diffusion simulation. However, as long as the device thickness is much larger than a single hopping distance, the transport of a charge is characterized by a large number of hopping processes. Furthermore, regarding macroscopic device areas, the number of charge carriers is large. Many charge carriers performing many hopping steps can be well described by an averaging approach, using macroscopic material properties like for example the mobility. Thus, a description of overall charge-carrier transport in the framework of a drift-diffusion model based on a continuum approach is a valid approximation.

The good agreement between simulation and experimental data illustrated that drift-diffusion simulation is capable of describing many commonly observed effects. That is why we can conclude that this kind of simulation is a very well suitable approach to describe complex shapes of J - V curves of multilayer solar cells, as it provides sets of J - V curves within moderate computational time. The correct quantitative description of the dependence of J - V characteristics on layer thickness and illumination intensity is another strong confirmation for the applicability of this kind of simulation. The simulation results are not limited to steady-state data but can reproduce transient data as well. Calculated distributions of charge carrier densities and profiles of electric fields within devices turned out to be very helpful to understand the working principle of specific devices.

We have demonstrated this for several cases:

- Injection and extraction barriers that can cause S-kinks (Chap. 6 and Sect. 8.1).
- Imbalanced mobilities in a flat heterojunction (bilayer) as an additional source of S-kinks (Sect. 7.1).
- Transient photocurrents that can be employed to discriminate between different reasons for S-kinks (Sect. 6.6.3).
- The effect of the generation profile within a ZnPc:C₆₀ BHJ on FF in combination with (im)balanced mobilities (Sect. 8.3).
- The influence of trap-assisted and direct recombination in ZnPc:C₆₀ bulk heterojunctions investigated at the dependence of V_{oc} on the illumination intensity and at the dark J - V curves (Sect. 8.4).

In Chap. 4 we introduced several models to describe charge transport, generation, and recombination. Considering ZnPc:C₆₀ bulk heterojunction solar cells, we conclude:

- Onsager-Braun theory could not be identified as a process responsible for photocurrent generation, although geminate recombination cannot be excluded completely.

- The Langevin expression for recombination does not seem to be applicable to ZnPc:C₆₀ solar cells with different mixing ratios. The recombination constant is mainly independent of the mobility. Therefore, recombination is not diffusion-limited, but is more deeply determined by the recombination process itself. A possible reason may be a large lifetime of the charge-transfer state that is formed as an intermediate state during the recombination process, owing to local polarization of the donor-acceptor pair and their local environment.
- Both direct and trap-assisted recombination are found to be important. For high light intensities, direct (bimolecular) recombination limits the performance whereas trap-assisted recombination governs V_{oc} at low intensities and the slope of J - V curves in the dark (cf. Sect. 8.4).
- Sophisticated mobility models including the nature of disorder were not intensively applied as their applicability has not yet been proven. They introduce several unknown parameters regarding the dependence of the mobility on the electric field and on charge carrier densities. Their influence on the mobility is regarded as less critical, as long as the typical working regime of a solar cell (power-generating quadrant, 1 sun illumination, room temperature) is described. However, when investigating other types of devices or temperature variations, field- or temperature-induced changes in mobility have to be considered. As long as fundamental questions, for instance on the nature of recombination, are not settled, charge transport remains the second step of a refinement of solar-cell simulations.

Despite this success it is important to remember that the employed model is a one-dimensional approach. We called it a rather macroscopic model, where the bulk heterojunction is represented by an effective medium. This approach works very well, for instance regarding shifts of energy levels upon blending two materials, which indicates that the localization of charges is not as strong as one might anticipate when thinking of electrons hopping from site to site. However, it is obvious that a one-dimensional simulation cannot provide a direct, predictive link between morphology and device performance. It is not capable of explaining why different molecules, molecular arrangements, etc. result in different opto-electronic properties. Three-dimensional drift-diffusion approaches could better deal with the nanomorphology of the bulk heterojunction. However, it is very questionable whether it is meaningful to apply a drift-diffusion simulation with the limitations mentioned above to structures with feature sizes in the nanometer range. Explicitly considering the morphology might be preferably done using hopping models that require Monte Carlo simulations. However, also these models need input parameters, which are difficult to measure, but might be provided by quantum chemical methods. Monte Carlo simulations might overestimate the role of localization of charge. Microscopic and macroscopic models should not be regarded as competing methods to describe experimental observations. They should rather be judged as complementary approaches. Microscopic models and drift-diffusion simulations can form a symbiosis, where the former provide input parameters for the latter, which is used to describe characteristics on the device level.

In conclusion, drift-diffusion simulations are valuable to understand physical processes on the device level and to a certain extent to make predictions about the influence of small variations. It is also possible to qualitatively and partly quantitatively describe experimental data. The main challenge in modeling organic photovoltaic devices remains in the search for appropriate models with as many simplifications as possible, but without neglecting relevant features. Predictive simulations remain challenging because finding a common parameter set that can be applied to a large amount of different organic molecules is very hard, as electronic processes in a film strongly depend on the configuration and interaction between single adjacent molecules.

Chapter 10

Organic Photovoltaics—Quo Vadis?

Abstract In the preface of this book I brought up the issue of sustainability. In the long run this will determine the fate of organic photovoltaics. Sustainability is a complicated function of physical and technological factors like device efficiency and lifetime. For photovoltaics as a technology, which is supposed to be scaled up to the terawatt, i.e. square kilometer range, sustainability contains questions on the abundance of the required materials, energy input, and the feasibility of closed life cycles. Those define a technological potential of a given system. Finally, social and economic constraints are of significance as well. This chapter tries to touch upon those questions. Some of them might be formulated in the following way: (a) Why will organic solar cells with a low power-conversion efficiency not be successful, even if they are very cheap? (b) What are conventional approaches to increase the power-conversion efficiency? (c) What are the main challenges in material design to reach a new working and efficiency regime of organic solar cells? (d) Nominal power-conversion efficiency does not tell the complete story. What is the main figure of merit? Why and under which conditions can organic solar cells benefit from it? (e) What are major technological challenges? (f) What are estimated values for energy payback times, material and manufacturing costs, and lifetimes?

10.1 Towards Higher Efficiencies

This chapter deals with the future of organic photovoltaics (for further reading: [1]). The main factor determining this future is the power-conversion efficiency, although one initial concept of organic photovoltaics was the idea of low-efficient but cheap solar cells. This thinking is outdated due to several reasons:

- Costs of competing technologies dropped significantly. Organic photovoltaics will have difficulties in entering a market dominated by a technology (silicon) having profited from decades of academic and industrial development and the economy of scale.
- Low efficiency means a larger material input, long production times, larger facilities etc. These factors indicate intrinsically high costs as the figure of merit is costs per Watt peak (or per kWh, see Sect. 10.2).

- Furthermore, a low efficiency conflicts with a cheap module, as costs for substrates and encapsulation materials (e.g. PET foils, barrier foils) are accounted for by unit area.
- Low efficiency means higher costs for the balance of system: transport and installation including wiring and mounting of many low-efficient modules is more expensive.
- Finally, low efficiency demands for large areas and therefore a high land consumption. In particular for applications in industrialized countries, area is an issue and a cost factor. When targeting applications, where organic solar cells can outcompete other technologies due to their specific properties (mobile applications, mounting at facades) area is even more an issue, as it is limited and the conditions (like alignment to the sun) are worse.

In the history of photovoltaics, one example for the relevance of efficiency are solar cells based on amorphous silicon, which are supposed to be cheaper in production and in particular per area. However, they are not able to compete with (mono and multi) crystalline silicon modules which provide a doubled power-conversion efficiency.

Consequently, achieving efficiencies in the range of 15 % in the lab and around 10 % on a module is indispensable, also for organic based photovoltaics. (Maybe 5 % are sufficient for an introduction into niche markets.) These numbers include the condition of not introducing expensive production steps. Some ways and ideas towards higher efficiencies are depicted in the following sections.

10.1.1 Tandem Solar Cells

When having discussed the ultimate limits for the power-conversion efficiency, we mentioned that tandem or multi-junction solar cells are one way to go beyond the Shockley-Queisser limit of 33 % (cf. Sect. 2.7). Naturally, this approach can already be applied to increase the efficiency of a solar cell which is far below that limit. In particular for organic solar cells, the tandem concept is interesting due to two reasons:

First, there is a variety of absorbers with absorption coefficients that are large, but restricted to narrow absorption bands. Such materials provide the opportunity to produce subcells with selective absorption. They can have a separately optimized open-circuit voltage allowing for a reduction of thermalization losses. Second, the weak charge transport properties pointed out in several parts of this book restrict the optimum thickness of the absorber commonly to values below a thickness required for a high absorption efficiency. Stacking two cells with optimized thickness increases absorption whereas electrical losses are maintained at a low value.

Tandem solar cells can either be realized by mechanically stacking two independently fabricated solar cells or by a monolithic approach. The first has the advantage that the solar cells can be fabricated independently and without influencing the performance of each other. On the one hand, stacking increases the energy harvested per

unit area, but on the other hand, it requires the fabrication of two separate devices instead of one. The main drawback of two devices is that three transparent electrodes are required, as the top cell should be semitransparent and the top contact of the bottom cell should be transparent as well. That is why the second approach is more interesting and so far industrially applied for inorganic and organic solar cells. A monolithic realization shows two major requirements: First, the photocurrents of the two subcells have to be matched because the same current flows through the two subcells connected in series; Second, an efficient recombination contact is required between the two subcells to guarantee an iso-energetic recombination of electrons and holes and a high built-in potential for both subcells.

The first issue can be solved by an optical optimization of the stack which can be addressed (predominantly) by optical simulations. There, the overall absorbed photon flux of the two subcells is compared and matched by adjusting thicknesses of absorber and spacer layers [2, 3]. Commonly, current matching is sufficient for an optimization of the stack. Only subcells that show a low FF and thus a high dependence of the photocurrent on voltage close to J_{sc} require further optimization taking into account the whole J - V curve [4, 5].

The recombination contact can be realized by a thin layer of metal clusters [6] or highly doped charge transport layers forming a p-n tunnel junction [7]. We perform a brief modeling study to understand the requirements for an ideal recombination contact where electron and hole recombine without any loss in free energy.

Properties of the Recombination Contact

Modeling of a “tunneling-like” junction is complicated as it requires a theoretical description of the tunneling mechanism at the recombination contact. This mechanism is essential for modeling the forward current of a tandem cell, where the recombination contact operates in reverse direction compared to a region that generates charge carriers.

As proof of principle we do not consider complicated coherent or incoherent tunneling theories, which require effective masses and mostly a treatment in k -space [8]. We restrict ourselves to a simple description of the “tunneling” process by the introduction of a transition rate of an electron in the HOMO into the LUMO of a neighboring molecule. This approach is oversimplified, however, capable of producing a realistic current at a donor-acceptor interface under high reverse bias. The following equation is applied to describe the transition:

$$\nu_{\text{HOMO-LUMO}} = \nu_0 \exp\left(-\frac{E_g^{\text{DA}} - eFa}{k_B T}\right). \quad (10.1)$$

This equation phenomenologically follows the hopping equation (3.15): ν is the hopping rate, ν_0 a pre-factor, F describes the electric field at the interface and a the average hopping distance, which is chosen to 1 nm. The overall HOMO-LUMO transition rate is then multiplied by the amount of electrons in the HOMO and the

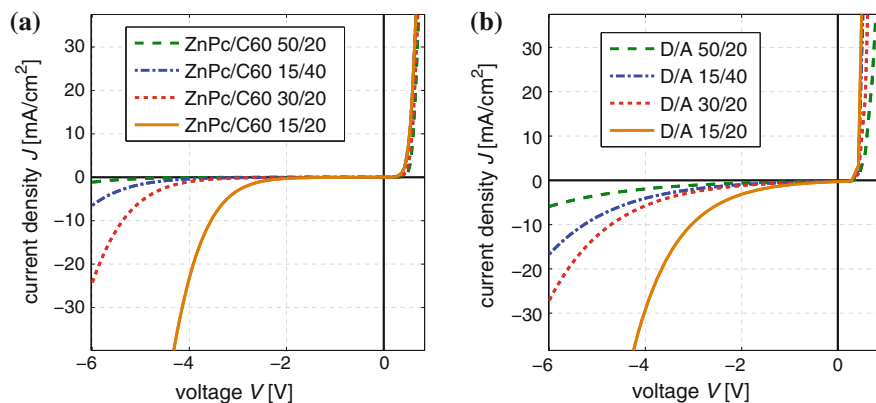


Fig. 10.1 The breakdown regime of a ZnPc/C₆₀ FHJ with different active layer thicknesses in nm. **a** Experimental dark J - V curves and **b** simulations of a bilayer, which show the same trend

probability of finding a free position in the LUMO. Note that the parameters in (10.1) might be rather empirical, as, e.g., deep states might play a role.

Nevertheless, we validate this approach using the reverse current of a single flat heterojunction solar cell (FHJ). The experimental data plotted in Fig. 10.1a are measured at devices consisting of ITO/NDP2(1 nm)/MeO-TPD:NPD2(20 nm, 2 wt%)/ZnPc(x)/C₆₀(y)/BPhen(6)/Al(100). The data show that the onset of the breakdown of the diodes is mainly defined by the overall thickness $x + y$ of the intrinsic layers ZnPc and C₆₀. The breakdown regime can be called Zener regime and is exploited in organic Zener diodes [9]. The simulation data in Fig. 10.1b reproduces the absolute values of the reverse current and the thickness dependence relatively well. The pre-factor ν_0 in (10.1) is chosen to $5 \times 10^{19} \text{ s}^{-1}$. This very large value has to be selected due to the large energy barrier on the order of 1 eV. Allowing for a broadening of the DOS, which reduces the barrier height, would lead to a reduction of ν_0 . Furthermore, trap-assisted tunneling might play a role, as evidence for trap-assisted recombination was found in Sect. 8.4.2. Tunneling through trap states might be modeled according to the Hurkx model [10, 11]. A more sophisticated study on devices based on pentacene and C₆₀ indicates that charge transport in organic tunneling junctions is based on a coherent mechanism [12].

Now we turn focus to a tandem device. The black dash-dotted line in Fig. 10.2 shows a simulated J - V curve of a solar cell in p-i-n (10/30/10 nm) geometry where the intrinsic layer is a photoactive bulk heterojunction (BHJ). The other lines are results of simulations of a tandem cell consisting of two identical BHJ with two (doped) layers in between (10/30/10 / 10/30/10). The simulation parameters are chosen according to Table 5.1 in Chap. 5. The energy levels of the interlayers are adjusted to block holes from the first BHJ and electrons from the second BHJ to increase the selectivity of the interconnector similar to experimental devices. The energy levels can be deduced from the inset, showing the energy-level diagram of the tandem cell with highly doped interlayers at short circuit.

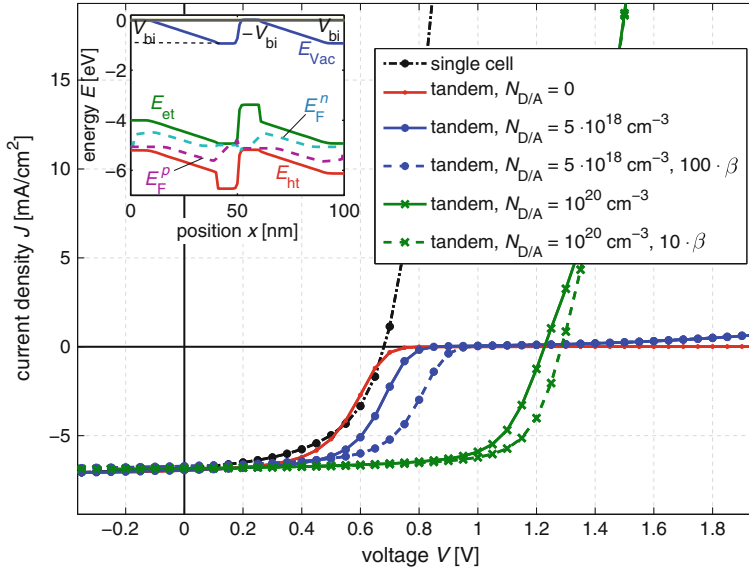


Fig. 10.2 Simulated J - V curves of a single and a tandem solar cell consisting of two identical subcells. Recombination constant β and doping concentration in the interlayers are varied. The inset shows the energy-level diagram at short circuit in the case of high doping and recombination

The simulated J - V curves in Fig. 10.2 demonstrate the crucial point of a well-working tandem solar cell, which is a highly efficient recombination contact. Its efficiency is represented in the simulation by the recombination constant β of the interlayers. Also n-doping the first and p-doping the second interlayer helps to shift recombination from the BHJ towards the recombination contact between the two interlayers.

If doping and charge carrier recombination in the interlayers are not sufficient, S-kinks emerge and V_{oc} is reduced. The reason for the S-kink is comparable to an extraction barrier S-kink (cf. Chap. 6), because a non-sufficient recombination at the junction decreases majority charge carrier extraction. The S-kink can also be explained by the injection barrier picture, because no or too low doping of the interlayers does not provide the full built-in potential (V_{bi}) for both subcells. In the case of non-doped transport layers and two identical subcells, V_{bi} in one subcell is half of the one in a single BHJ sandwiched between the doped transport layers.

In addition to the S-kink, V_{oc} is affected by an insufficient recombination contact, as it does not show the double value compared to V_{oc} of a single cell. The reason is a loss in V_{oc} at the recombination contact. If this contact is not efficient, a significant quasi-Fermi level splitting occurs, which reduces V_{oc} . Thus, one can summarize the requirements for the recombination contact in one property: selective recombination (here electrons from the left side, holes from the right side) which is highly efficient, meaning that additional (photogenerated) charge carriers do not create a quasi-Fermi

level splitting at the junction. In this case, a loss of free energy is completely avoided. The distances between E_F and the charge transport levels are irrelevant, which means that it is not necessary to fabricate a degenerate p-n junction. The p-n junction itself is also not urgently required. The best materials to guarantee a Fermi level splitting of zero are metals, which are experimentally embedded into the recombination contact as clusters [6]. In this case, it is crucial to guarantee the selectivity of the recombination contact by incorporating the metal clusters in between a p-type and n-type material.

However, doping the charge transport layers is very helpful for a high FF , because it defines the position of E_F . Thus, the two subcells each comprise the same V_{bi} as a single cell. As V_{bi} of the tandem cell is fixed by the two doped layers to the same value as in a single junction, the two V_{bi} s of the two subcells are accompanied by a voltage of $-V_{bi}$ at the p-n junction. The distribution of the potential is visible at the shape of E_{Vac} in the inset of Fig. 10.2.

When forward biasing the tandem cell, the p-n junction, which is then negatively biased, works as an electron-hole generation layer due to a transition of electrons from the HOMO of the p-doped material (leaving a hole) to the LUMO of the n-doped material. That is the reason why forward current flows through the tandem cell which incorporates a p-n junction biased in reverse.

In conclusion, there are many ways of realizing a recombination contact and several tandem and multi-junction solar cells with high (roughly 10 %) efficiency have been fabricated [13–17]. A triple junction device realized by the Heliatek GmbH currently holds the record efficiency of 12 % [18]. Realistic limits for the efficiency of organic tandem solar cells are estimated in the range of 15–20 %. Note that these values are based on empirical estimations and assumptions, however, not derived from theoretical considerations. Therefore, they can be outdated relatively quickly.

10.1.2 Optimization of the Bulk Heterojunction

It is desired to realize a highly efficient single-junction device instead of a tandem solar cell as this reduces the complexity and number of processing steps. Furthermore, every efficient tandem cell is based on two efficient sub cells. Progress in understanding the device physics has lead to relatively optimized devices regarding architectures and electrodes.

One crucial point are the energy levels at the donor-acceptor interface, in particular the offsets in the frontier orbital energies of donor and acceptor. An engineering of those energy offsets aims for achieving the highest open-circuit voltage, without losing photocurrent. A high open-circuit voltage requires low offsets, whereas efficient charge separation demands for some driving force. Consequently, the best trade-off has to be found. However, it is not completely clear what minimum energy offset is unavoidable. As discussed in Sect. 3.4 it is already difficult to define the driving force. Most likely it will not be possible to state a minimum value and predict it from the single components of the blend as the molecular orientation at the donor-acceptor

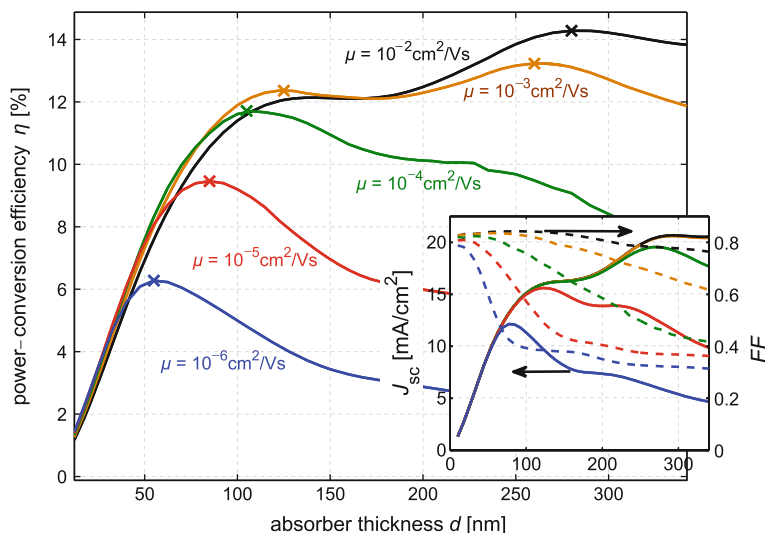


Fig. 10.3 Simulation of a variation of the absorber thickness and mobilities assuming bimolecular recombination with a reduced Langevin rate (factor 100). Higher mobilities allow for thicker layers. Efficiency and short-circuit current density at high mobilities follow the interference pattern. For low mobilities, the optimum thickness, which is marked with a cross, is limited

interface is important as well. However, the acceptor has to guarantee that the exciton binding energy in the donor (and vice versa) can be overcome upon charge transfer. Recall that in the optimum case the exciton binding energy is not an intrinsic loss to organics as this energy was never provided by the absorbed photon. The situation at the donor-acceptor interface is further complicated, e.g. by a donor triplet state whose energy can be significantly below the one of the first excited singlet state. This configuration should be avoided, as it is supposed to be a loss path (cf. discussions in Sect. 3.3.1). Examining the developments within the last decade, we can summarize that fine-tuning of the energy levels is state of the art.

Considering the electric parameters, we discussed extensively the influence of charge-carrier mobility and traps on the device performance. We found that a higher mobility in general is beneficial. Figure 10.3 shows simulation data of the power-conversion efficiency as a function of the thickness of a representative device. Here, realistic optical constants are used and recombination is assumed to follow a reduced Langevin expression (by a factor of 100). It is evident that low mobilities limit the optimum thickness and the maximum power-conversion efficiency. Mobilities should reach values of $10^{-3} \dots 10^{-2} \text{ cm}^2/\text{Vs}$ to extend the working point of the device to the second interference maximum. In this case, the efficiency completely follows the absorbed photon flux.

This example shows that optimizing the BHJ regarding charge transport is essential. Typical state-of-the-art BHJs show effective mobilities in the range of $10^{-5} \dots 10^{-4} \text{ cm}^2/\text{Vs}$. Several technological approaches for increasing the mobility

have been proposed and turned out to be successful. They include annealing steps, proper choice of solvents, the application of processing additives, or heating of the substrate during deposition. They all aim for an optimized morphology, i.e. phase separation in the bulk heterojunction in the nm length scale. A lot of research focuses on sophisticated approaches to influence the morphology, e.g., by patterning methods employing a prestructured substrate or a rod-like electrode etc. However, on this length scale only structures created by self assembly are expected to be promising for a low-cost production.

The role of traps in the bulk heterojunction is not completely clear. As discussed during this book, many experiments indicate their relevance. Some amongst those identify deep trap levels which cannot be explained by a disorder induced broadening of charge transport levels. Identifying the origins of traps will be important for a deeper understanding of the electric properties of organic semiconductors. Grain boundaries, the orientation of molecules and even specific (functional) groups are suspected to act as traps. A deep understanding of traps may provide an explanation for the large amount of non-radiative recombination usually observed in the bulk heterojunction. Reducing this recombination path might allow to (slightly) increase the open-circuit voltages for a given donor-acceptor gap.

Instead of optimizing the bulk heterojunction, it might be interesting to return to the flat heterojunction. There, the issues caused by a two-component medium would be avoided. In this case, however, materials with very large exciton diffusion lengths are required, which are more difficult to find. Looking at the state of the art, it seems easier to achieve decent mobilities and charge carrier drift lengths in a bulk heterojunction than a high exciton diffusion length in a pristine material.

10.1.3 Engineering of Interfaces

When constructing a metal-insulator-metal like device, it is obvious that the (metal) electrodes play a crucial role. Only a proper choice allows for an exploitation of the complete potential of an active material system. In particular, optimized bulk heterojunctions approach efficiency limits that are given by the electrodes which reduce the open-circuit voltage and fill factor. In this book we discussed the importance of aligned electrode work functions and the selectivity of the contacts. State-of-the-art approaches to realize these functions are the employment of electrode materials with low and high work functions, thin organic and inorganic interlayers, or doped charge-transport layers. The interlayers usually introduce a surface dipole modifying the effective work function of the electrode. Small molecules, polymers, self-assembled monolayers, and more exotic dipole layers based on ferroelectric materials have been employed [19, 20]. However, a further increase in efficiency due to interlayers is not expected, as they can only reduce losses. They are more important from a technological point of view since they increase the number of usable metal(-like) electrodes since a specific work function is not required.

10.1.4 Light Management

As an electrical optimization remains challenging, the optics could be tweaked instead to increase the absorption in a thin active layer. We have already discussed the multijunction concept which is based on the idea of stacking more thin bulk heterojunctions to profit from a larger absorption. Another proposal are V-shaped solar cells, where the optical path is enhanced independently of the electrical one, as incident light is not perpendicular to the electrode but tilted [21, 22]. Reflection of a light beam at (the back contact of) the first solar cell allows the beam to enter the second device on the other branch of the V. V-shaped solar cells can be realized by fabricating a module on a folded substrate. In contrast to the nm-scale structuring required for an optimization of the morphology, the length scales of the V-shape can be in the mm to cm range depending on the dimensions of the subcells.

Other approaches exist on how to concentrate more light into the solar cell, e.g., by light trapping through scattering structures [23]. Also near-field effects like plasmonics are investigated [24]. A dielectric scatterer as back mirror is interesting as a significant amount of photons are absorbed in the reflecting metal electrode. Figure 4.14 visualizes that 4 mA/cm^2 are lost due to absorption in the aluminum electrode. Furthermore, a Lambertian scatterer randomizes the direction of the reflected light, which increases the optical path length in the absorber.

Placing these optical (scattering or plasmonic) elements, which are metal clusters and other nano particles, within the active material is challenging. Commonly they constitute new pathways for recombination. Positioning a scatterer outside the active layer is technologically easy, however requires two transparent electrodes. Light reflected by a scatterer at the back side of the solar cell would then enter the stack again at a distribution of angles. Several light beams can bounce several times due to internal reflection. This is beneficial, however it comes along with the issue of finding good semitransparent electrodes, which is not sufficiently solved yet. In Sect. 3.6.3 we have already discussed that physical limitations make it difficult to find highly conductive and simultaneously transparent materials. Recalling Fig. 4.14 we also see that a photon flux equivalent to an electrical current of 2.5 mA/cm^2 is absorbed in the indium-tin oxide which is so far one of the best choices from the viewpoint of electro-optical properties. Consequently, a trapping of light based on total internal reflection at the ITO/glass(PET foil etc.) or glass(PET foil etc.)/air interface suffers from parasitic absorption. If the refractive index of the active layer is significantly higher than the one of the electrode, total internal reflection can happen at the electrode as well resulting in modes that are trapped in the active layer. However, the evanescent wave in the electrode suffers from absorption (an effect that is exploited at ATR (attenuated total reflection) spectroscopy). On the other hand, theoretically the absorption of an evanescent wave might be exploited in a structure, consisting of a (non-absorbing) waveguide with the active layer adjacent to it.

Although these approaches are interesting, huge boosts in power-conversion efficiency are not expected. In the ranges where the absorption coefficient of the active material is lower than the one of the electrode, parasitic absorption will dominate

effects based on the far field. For near field effects a prediction of their impact on real devices is not that obvious.

10.1.5 Material Design

The main driver for higher efficiencies in recent years was new absorber materials embedded into optimized stacks including aligned electrodes. This trend is expected to continue. Obviously, the most important property is the absorption coefficient paired with semiconducting characteristics, allowing energy and charge transport. The absorption coefficient should be large and cover a significant portion of the solar spectrum. In particular, low-bandgap polymers are required. The donor-acceptor approach lead to novel absorbers, so called push-pull molecules or polymers (Sect. 3.6.3). As the variety of organic compounds is practically infinite, better absorber molecules are expected to come out of synthesis.

Whereas optical properties are predictable to a major extent by quantum chemical calculations, the electrical characteristics of a material in a blend are hard to anticipate. Even small modifications at a side chain of a polymer or oligomer can change the electrical properties in the blend tremendously [25]. Consequently, finding good materials is not straight-forward, but requires a considerable amount of experimental screening and optimization.

Material design is not limited to the properties mentioned. To achieve a new regime of efficiencies, mainly two additional properties are discussed [26]: the dielectric constant and the reorganization energy.

The dielectric constant describes the ability of a material to screen charge (polarizability). The higher the screening, the less is the Coulomb interaction between an adjacent electron and hole. A lower attraction is beneficial for the dissociation of a geminate electron-hole pair, as its binding energy at a given distance is reduced. Furthermore, a reduction of the Coulomb radius (cf. 4.47) means less interaction of once separated charges. That is why bimolecular recombination according to Langevin theory scales inversely with the dielectric constant (cf. 4.49). It is also reported that a higher dielectric constant decreases the splitting between singlet and triplet state [43]. A low singlet-triplet splitting is supposed to avoid the loss path through a deep triplet (cf. Fig. 3.20).

Finally, a high dielectric constant reduces the exciton binding energy of the neat material. Thus, the probability increases for a direct generation of quasi-free charge carriers comparable to common inorganic semiconductors. In this case, an acceptor would not be required anymore and the issues with the bulk heterojunction are entirely avoided.

Independent of the theoretical advantages of a material with a high dielectric constant (high- k material), it has to be stressed that increasing the dielectric constant is not of first priority regarding highly efficient state-of-the-art bulk-heterojunction organic solar cells. They show high internal quantum efficiencies and fill factors which are not limited by insufficient dissociation of excitons.

Although a low dielectric constant is unpractical, it does not directly mean an unavoidable loss mechanism. A fundamental loss mechanism, intrinsic to organics, is the reorganization energy which we introduced when discussing electron transfer according to Marcus theory in Sect. 3.2.2. The reorganization energy upon optical excitations is seen in red-shifts of luminescence compared to absorption. The energy is dissipated by, e.g., vibrational modes (cf. Fig. 3.8). Heat energy with large entropy is not easily accessible for a conversion into electrical energy. The loss due to reorganization is comparable to an additional thermalization below the absorption edge. Both singlet and CT state are affected by this loss.

It is believed that reducing the reorganization energy can improve the device performance. Here, a high dielectric constant can be beneficial as well. Molecules with a high structural rigidity are supposed to show a lower reorganization energy. In particular, a torsion relaxation, as demonstrated in Fig. 3.12, should be suppressed [27].

10.2 The O-Factor

We stated that a high efficiency is required to decrease land consumption and costs per Watt peak. However, the main figure of merit is not the cost per nominal power, but per provided electrical energy, i.e. per kWh. (In the future, even time and location will be important, when and where the kWh is provided.) The first number (in euro per Watt) is easy to determine measuring the device under standard reporting conditions. The second (in euro per kWh) is more difficult as it includes the lifetime and the climatic and weather conditions at the location of installation. The lifetime is addressed in the subsequent section dealing with stability. Here, we focus on the operation conditions and define a harvesting factor:

$$\text{harvesting factor} = \frac{E_{\text{harvested}}}{\eta_{\text{SRC}} \cdot E_{\text{incident}}} = \frac{\langle \eta \rangle}{\eta_{\text{SRC}}}. \quad (10.2)$$

This equation describes the harvesting factor as the amount of electrical energy that can be produced relative to the one expected from the installed nominal power. It is unity if the efficiency $\langle \eta \rangle$ averaged over a period of time (e.g. one year) equals the efficiency at standard reporting conditions (SRC).

Climatic and weather conditions, mainly irradiance and temperature, influence the power-conversion efficiency of a solar cell. Consequently, the harvesting factor can significantly vary between different solar-cell technologies. In particular, it can deviate from what is expected considering the efficiency measured at standard reporting conditions (SRC, 25 °C and AM 1.5 g with 100 mW/cm²). During outdoor operation, module temperatures are commonly elevated and the solar radiation is less than 1 sun. These conditions of higher temperatures and low light intensities result in an advantage of organic solar cells compared to their inorganic counterparts. The efficiency of silicon solar cells decreases with illumination intensity due to a reduced V_{oc} . It also decreases with temperature, which is due to changes of V_{oc} as well (3.26).

That is why commonly the mean efficiency averaged over a year (even if the module is installed in Germany with moderate temperatures) is lower than the nominal one. Thus, the harvesting factor is smaller than unity. This effect becomes obvious when identifying the day with the highest electricity generation from solar modules installed in Germany: Usually, it is a cold and very sunny day in spring, however, not a hot and sunny day in summer.

The trends with temperature and illumination intensity are inverted for organic solar cells, as long as their performance is limited by charge transport and bimolecular recombination. A higher temperature activates charge transport, which gives rise to higher fill factors (cf. Fig. 10.6b). Lower intensities increase the fill factor as well (cf. Fig. 8.20), in particular if the solar cell is limited by bimolecular recombination or a series resistance.

Using our drift-diffusion model we perform a simulation study on the dependence of the efficiency on temperature and illumination intensity (for more details, see [28]). We are in particular interested how the harvesting factor changes when going to more efficient organic solar cells. The study is based on the data shown in Fig. 10.3. We select the optimum thickness for each mobility and assume that the mobility follows a thermal activation according to an empirical universal equation:

$$\mu(T) = 30 \text{ cm}^2/\text{V s} \cdot \exp\left(-\frac{E_a}{k_B T}\right). \quad (10.3)$$

The activation energy $E_a = 200 - 450 \text{ meV}$ is chosen to match the mobility at SRC with (10.3). This equation cannot be transferred to each organic material, but it was proven valid for a series of polymers [29]. In general, a temperature activation following $\exp(1/T^n)$ can be theoretically justified (e.g. for hopping transport).

Figure 10.4 depicts the simulated power-conversion efficiency η normalized to its value at 25°C . The devices with low mobilities show an increase of η with temperature by around 10–20 %. However, the more efficient devices with a high mobility follow a trend comparable to silicon based devices. The inset visualizes the reasons for the changes in η : V_{oc} decreases for all devices. In case of low room-temperature mobilities, its effect on η is overcompensated by the changes in fill factor for elevated temperatures.

The situation is similar for the intensity dependence of the efficiency shown in Fig. 10.5: In case of a low mobility, the increase in FF can overcompensate the decrease in V_{oc} with lower intensities.

Based on the intensity and temperature dependent data, the provided energy per year at a specific location can be calculated knowing module temperature and irradiation during the course of a year. This was done in [28] for weather data from Great Britain. Performing a simulation of many different devices with varied parameters, it turned out that the harvesting factor depends mainly on the FF at SRC. The relative enhancement of the overall efficiency compared to the one at SRC is shown in Fig. 10.6a as a function of the FF at SRC. Devices with low FF significantly benefit from what we call O-factor, whereas devices with a FF larger than 70 % do not gain efficiency as the FF can hardly be increased further.

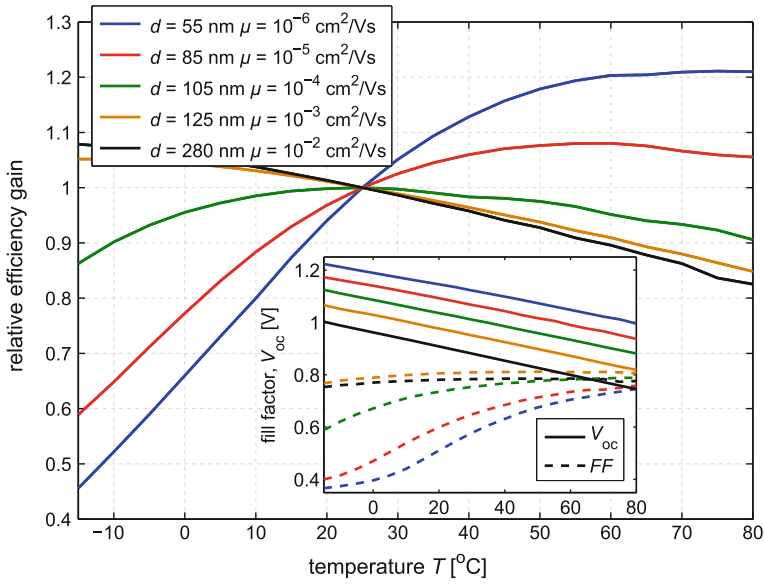


Fig. 10.4 Relative changes in efficiency as a function of temperature. The mobility values in the legend refer to the mobility at 25 °C. Its temperature dependence follows (10.3). The efficiency reflects the interplay between fill factor and V_{oc} (inset)

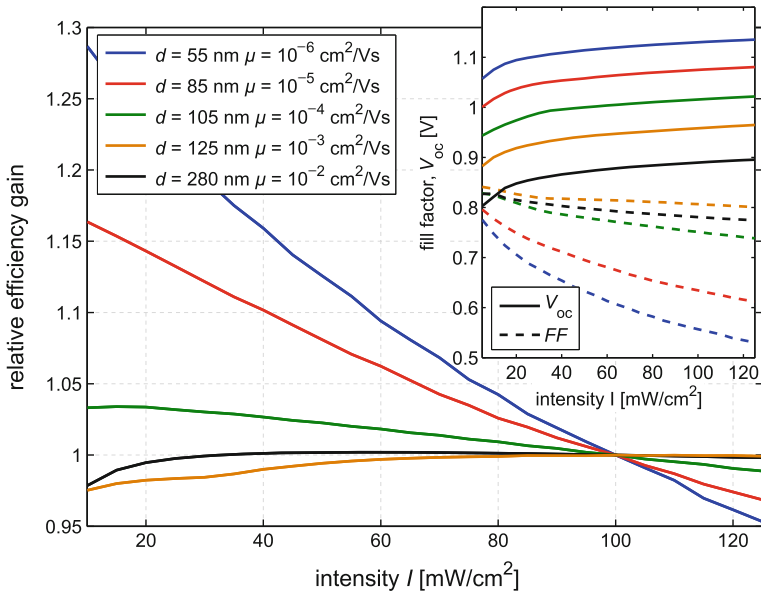


Fig. 10.5 Relative efficiency gain compared to the value at 100 mW/cm². The efficiency increases for low intensity in case of low mobilities due to reduced bimolecular recombination. This trend is inverted in case of high mobilities due to the drop in V_{oc} , which is not overcompensated by changes in FF (inset)

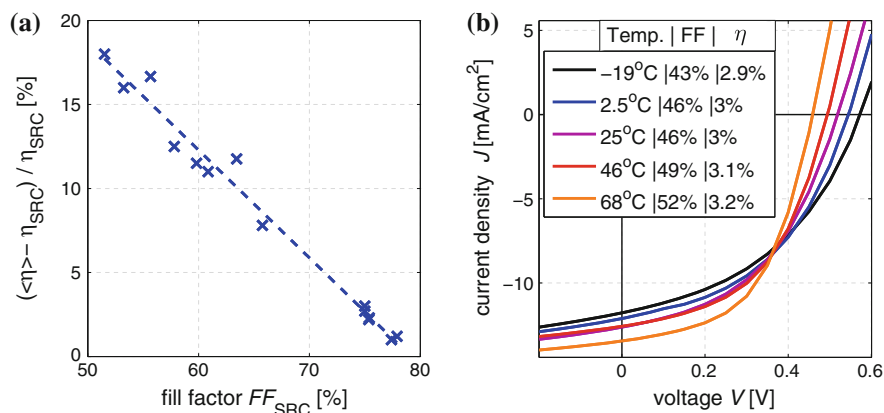


Fig. 10.6 **a** Simulation data of the year-averaged change in efficiency relative to the efficiency at standard reporting conditions (SRC). For details, see [28]. It turns out that the value can be predicted knowing the FF at SRC independent of the efficiency at SRC. **b** Experimental data: temperature dependent J - V curves of a device ITO/MeO-TPD:NDP2(20 nm, 10 wt %)/MeO-TPD(5)/ZnPc:C₆₀(1:1, 45 nm)/C₆₀(15)/BPhen(6)/Al(100). The efficiency increases slightly with temperature

Note that the significance of the O-factor depends on the location of installation. Furthermore, it depends on the loss mechanisms in the solar cell. It is less pronounced for monomolecular recombination processes and a weaker activation of mobility with temperature. The simulations are based on the extreme case of strong bimolecular recombination. Nevertheless, an increase in efficiency for lower intensities and elevated temperature is commonly observed for organic solar cells including the devices based on ZnPc:C₆₀ discussed in this book (Fig. 10.6b).

It is said that organic solar cells outperform silicon devices under diffuse light. This is supposed to be due to an increased optical path of light with non-perpendicular incidence. However, optical simulations with a transfer-matrix model (cf. Sect. 4.7) do not predict a significantly stronger absorption for light with varied angles of incidence. Oblique incidence significantly increases reflection at the glass-air interface. Consequently the better performance under diffuse light is rather due to the lower intensity of diffuse light compared to direct light of 1 sun. Thus, neither varied angles of incidence nor changed spectra during the course of a day have been considered when calculating the data of Fig. 10.6a.

In summary, the O-factor constitutes an advantage of organic solar cells compared to their inorganic counterparts. Dependent on the FF (and location), the harvesting factor is expected in the range of 1–1.2. It implies an optimization of the absorber thickness in a way that allows for a slightly reduced FF at SRC compared to a device with optimized η at SRC. Then, the solar cell benefits from a larger absorption and consequently photocurrent independent of illumination intensity. At the same time, the FF is higher under average operation conditions with low light intensity and

elevated temperatures. In that way a state-of-the-art solar cell benefits best from the O-factor. On the long run, however, it is expected that the advantages due the O-factor will vanish for efficient devices with a large FF .

10.3 Towards Large-Scale Application

Research in organic solar cells has predominantly focused on the development of the technology itself. Both academia and industry continuously improved efficiency and stability of lab-scale devices. However, for upscaling a technology, process development and quality control become important. Figure 10.7 visualizes some additional factors that have to be accounted for when converting a lab-scale device into a real-market product. The lab-scale device is mainly characterized by properties related to its working principle, let us say the power-conversion efficiency. Starting from this small-area device, the first step requires the fabrication of a solar module which has a larger size and can be produced using a dedicated industrial facility (e.g. a printing machine). This step includes upscaling of raw material production by finding suitable syntheses routes. Additionally, a module has to be designed, demanding for large-scale homogeneity of deposited layers. Series resistance and a reduced active area due to patterning and electrical connections of separate solar cells (cf. Fig. 3.60b)

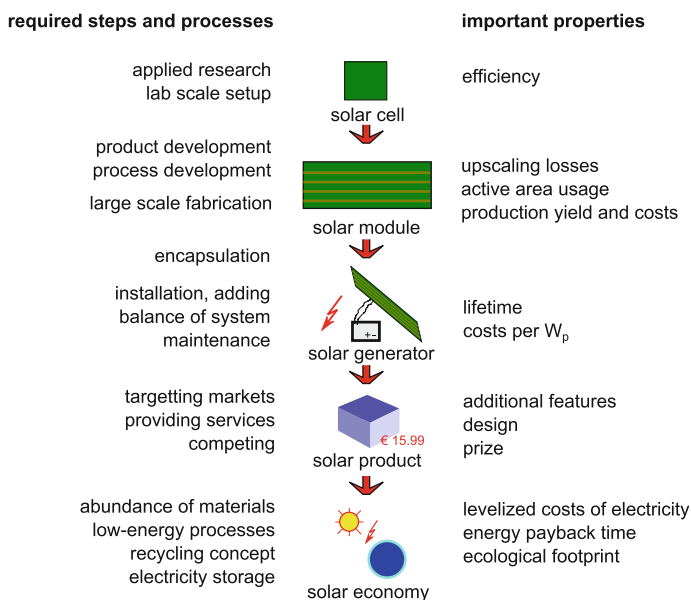


Fig. 10.7 Visualization of the steps required from a lab-scale solar cell to a system providing electrical energy. Important properties are mentioned in the right column

reduce the efficiency by a considerable amount, which is usually in the range of 10–30 %. The success and profitability of mass production is strongly influenced by the yield, i.e. the share of well-working modules achieved by the production line.

When the produced module leaves the factory, a sufficient encapsulation barrier against humidity and oxygen and a certain mechanical stability are required (cf. Sect. 3.6.5). Thus, barrier foils are laminated onto the module to avoid fast degradation. As soon as the module gets installed and used, it has to be connected to the load, requiring wiring, mechanical support, inverters, electronics, etc. These components are called balance of system (BOS). When configuring a complete photovoltaic energy converting system (power plant, roof-top, mobile charger, etc.), the lifetime of the module is particularly important.

Naturally, it will not be the producing company that mainly installs and operates its product. Consequently, the solar module faces the market. At this stage, costs, specific properties, and design of the product play an important role. In particular, the product has to compete with others providing similar functionality, i.e. other types of solar cells or even energy converters in general. Many further factors are important when launching a new product, e.g. regarding the way and the time of the integration into the market.

If the scope of the solar cell is to significantly contribute to the supply of electricity, further requirements have to be fulfilled. The materials necessary for the production should be abundant and the energy input as low as possible compared to the electricity provided during the lifetime of the module. Only in this case, ecological and economic sustainability can be reached on the long term and on a terawatt scale.

Many of the mentioned steps reduce the final efficiency and the ratio between provided electricity and required energy. Each step introduces additional costs. Consequently, the final product faces significantly more severe constraints than a lab-scale device. An optimization is necessary finding a tradeoff between efficiency, lifetime, and costs in terms of money, energy, and exploitation of resources. In the following, several individual factors are addressed in detail.

10.3.1 Stability

We have already mentioned that one major figure of merit are the costs per generated kWh electricity, where costs can be regarded as money, invested energy, or emitted carbon dioxide etc. These costs scale inversely with efficiency and lifetime of a solar module. Thus, a certain long-term stability is required to guarantee a long lifetime. Even in case of very cheap modules, BOS and maintenance costs demand for a reasonable lifetime to avoid too frequent exchange of the modules. Furthermore, producing too short-lived items promote a throw-away society with issues of waste disposal and recycling. All in all, for consumer products a module lifetime of a few years and for square-meter applications (roof tops, power plants) a lifetime of at least ten years should be targeted.

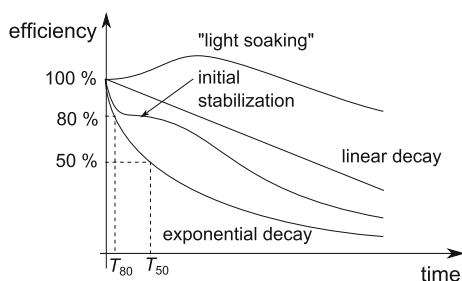
Lifetimes in the range of several years cannot be measured directly as the product development proceeds much faster. Thus, two methodological approaches are followed to state lifetimes: First, testing under real working conditions (outdoor), where the reduction of performance observed in a short time interval (e.g. some months) is used to predict a lifetime via an extrapolation according to a certain model (e.g. exponential decay with time). Obviously, such an approach can only deal with gradual aging of the device. It fails in case of an abrupt breakdown (catastrophic failure) if this breakdown is in a time span not covered by the test. If the failure is within the time under investigation, it can be included in the calculation of an expected lifetime or an uncertainty parameter by means of statistics. Reasons for an abrupt breakdown might be a failure of the encapsulation after a certain time, e.g. due to delamination.

The second approach is based on accelerated aging under harsher conditions, i.e. higher temperatures, larger humidity, and continuous illumination with high intensity (several suns). Observing the amount of degradation, a lifetime under real working conditions can be estimated, e.g. using an Arrhenius type of behavior for thermally activated processes [30].

Comparable to the efficiency, which is measured under standard reporting conditions, the lifetime requires the definition of standards to allow a comparability of different devices and measurements from different laboratories [30]. Standardization is important regarding measurement conditions, theoretical methods, and definitions of parameters. In particular, the lifetime has to be defined. Commonly, it is referred to T_{80} or T_{50} , stating a time when the performance has dropped to 80 and 50 %, respectively of the initial one. These figures still allow some ambiguity, as the initial performance can be selected directly after production, upon light soaking, which increases the performance, or following a short-term stabilization after a fast initial drop of the performance. These cases are sketched in Fig. 10.8.

To gain comparative results, conventions have been developed and Round robin studies have been performed, where different types of solar cells and modules have been measured at different labs [31, 32]. One major result is that many photoactive materials are not intrinsically unstable during illumination. The main source of degradation is related to interfaces between active layer and electrodes (cf. Sect. 3.6.5). Crucial for a high lifetime is a good encapsulation against oxygen and moisture. Finding suitable and low-cost encapsulation foils (barrier films) is one major challenge

Fig. 10.8 The power-conversion efficiency as a function of time. Exemplary curves show different degradation behaviors. The exponential decay is used to illustrate the definition of the lifetimes T_{80} and T_{50} [30]



in the field of device engineering. T_{80} lifetimes larger than 2,000 h are predicted for small-molecule solar cells with a glass encapsulation [32]. Thus, producing long-term stable organic solar modules seems to be feasible.

10.3.2 Economics

At the moment, it is too early to provide reliable and accurate numbers on midterm costs of organic solar modules due to the lack of running pilot lines in an industrially relevant size. However, it can be stated that the first commercial organic solar cells will not be capable of competing with modules of established technologies regarding retail prices. The reasons are that investments into research and development, custom-made test and production equipment, and the synthesis of small material batches give rise to high costs, which have to pay off with the first products. Thus, enterprises in this field do not address the end customer, but contract with established companies, e.g. in the automotive or building industry. Their (often anyway expensive) products like facade elements or windows gain a further functionality when combined with a (semitransparent) organic solar foil. These products service a niche market for organic photovoltaics, combining several advantages: costs are secondary (in particular regarding the produced electricity); the products demand for properties specific to organic solar cells (cf. Sect. 1.2); and rigid elements allow for a very long-term stable glass encapsulation of the solar module.

Although large-scale production has not started yet, there are first pre-industrial roll-to-roll lines in university environments such as the printing tools at Risø University (Denmark). There, different processes have been developed to fabricate solar modules in considerable number and size. Based on those processes, a cost analysis can be performed, which is as close as currently possible to an industrial manufacturing process. However, the obtained absolute numbers have to be handled with care, as in the future employed materials have to be changed, syntheses upscaled, and processes optimized. Nevertheless, these calculations are important, as they allow for an anticipation of the relations between different cost contributions. Thus, bottlenecks can be identified at an early stage.

Azzopardi et al. [36] investigated the process SolarOne [33], which is a representative process for a roll-to-roll production of inverted solar cells based at Risø University. This process uses an ITO coated PET foil as the substrate. The processing steps are visualized in Fig. 10.9a: A patterning of the ITO via etching is followed by the coating of the electron-transport layer ZnO. Then, the active layer P3HT:PCBM and the hole-transport layer PEDOT:PSS are deposited via slot die coating. Finally a silver electrode is screen printed and the module laminated.

To estimate the total costs of a produced module, they can be divided into material costs and costs related to production and processes. Performing an economic assessment from the viewpoint of the module producer, the material costs are chosen as the price, which currently has to be paid on the market. Production costs include

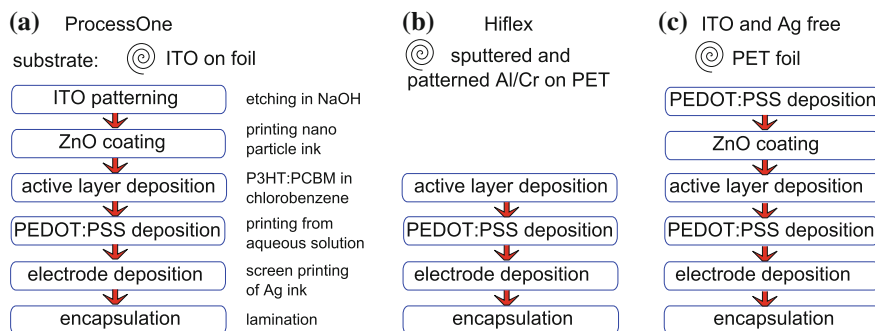


Fig. 10.9 Steps for three pre-industrial processes employed at Risø University for printing solar modules by roll-to-roll coating of square meters of foils [33–35]

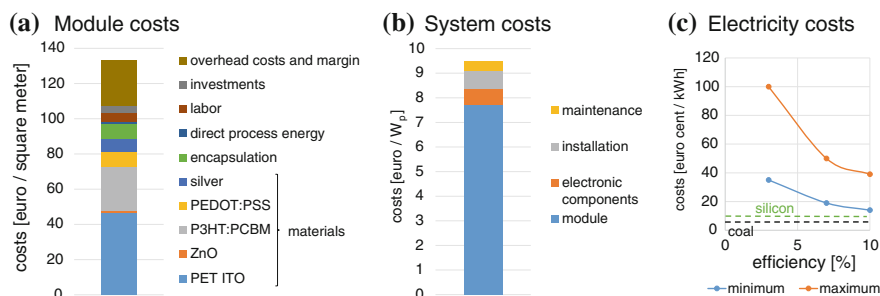


Fig. 10.10 Costs for printing process “SolarOne” according to [36]. Other studies on existing pilot lines state comparable figures, but a projection study for an ITO-free module produced on commercial scale predicts values in the range of 6 ± 2 euro/ m^2 . **a** Material and process costs per square meter; **b** costs per W_p assuming a cell efficiency of 7 % and an active area of 67 % of the module area. **c** Levelized costs of electricity for a module lifetime of 5 years and an irradiance of $1,700 \text{ kWh m}^{-2}/\text{year}$. Note that prizes for silicon modules were two orders of magnitude larger in the 1970s

costs for investments into infrastructure and equipment, process energy, labor, and overhead costs covering e.g. customer warranty etc.

Figure 10.10a shows average values for module costs in the range of 100 euro/ m^2 , which were roughly extracted from [36]. Obviously, the material costs dominate the module costs with a share of 60–80 %. Almost half of the material costs results from ITO and roughly a quarter from the active layer. Whereas economy of scale anticipates a reduction of active material costs, ITO sputtering is already a mature technology, where the scarcity of indium will increase prices. Thus, avoiding ITO is essential. Note that the discussed figures are for a pre-industrial pilot line. According to a projection study [37], commercial-scale costs for a module in standard architecture (cf. Fig. 3.48a) without ITO electrode, but with a PEDOT anode and an evaporated Al cathode are expected in the range of 6 ± 2 euro/ m^2 . Almost three quarters of

the costs are due to materials and one quarter for operating the plant. Latter rise significantly, if the production rate decreases below $1 \text{ m}^2/\text{s}$.

The costs in Fig. 10.10a are given per square meter of produced module, because material input and processing throughput scale with the area processed. More important are the costs per nominal capacity expressed in Watt peak (W_p). They can be calculated knowing the power-conversion efficiency referred to the module area A_{module} . This number can be expressed by the solar cell efficiency η considering the share of the active area:

$$\text{costs}/W_p = \text{costs}/\text{m}^2 \cdot \frac{A_{\text{module}}}{A_{\text{solar cells}}} \cdot \frac{1}{\eta_{\text{solar cells}} \cdot 100 \text{ mW}/\text{cm}^2} \quad (10.4)$$

According to this equation, the share of the active area should be maximized for low power costs. Consequently, precise patterning technologies are required to minimize the areas for interconnects and at the edges. The costs per W_p also scale with the efficiency showing that a high efficiency is a fundamental requirement for producing economic solar cells. This holds true as long as an increase in efficiency does not tremendously increase the costs per square meter. For SolarOne, the costs for the active materials, which are mainly related to efficiency, are low. The efficiency of the solar cells in produced modules is assumed to be 7 % (actually reached are rather 3 %) and the share of the active area is 67 %. Based on these numbers, module costs per W_p are in the range of 10 euros (Fig 10.10b). This value is large compared to the production costs for silicon solar cells, which are below one euro per W_p . However, they have to be seen as a starting point of the learning curve for organic photovoltaics. At the moment, the costs for the balance of system (BOS) are low compared to the module costs. However, the BOS costs become increasingly important when reducing module costs.

Motivated by the high costs for ITO, alternative processes have been developed [34], e.g. based on sputtering of a Cr/Al back electrode onto the substrate and using a front PEDOT:PSS electrode (Fig. 10.9b). However, sputtering of the metal is also expensive, leading to the conclusion by Espinosa et al. [34] that vacuum processes should be avoided completely, which might be controversially debated.

In the section dealing with the O-factor we emphasized that the costs per provided electrical energy is the number that counts. This number is called levelized cost of electricity. It is less straight-forward to calculate, as additional parameters have to be known. These are the lifetime of the module and the harvesting factor, which depend on the weather conditions and the dependence of the performance on factors like temperature T , and light intensity I (in case of gradual degradation, also on the time).

$$\text{costs}/\text{kWh} = \text{costs}/\text{m}^2 / \left(\int_{1\text{year}} \eta(T, I, \dots) I(t) dt \cdot \text{lifetime [in years]} \right) \quad (10.5)$$

The levelized costs of electricity are in the range of 20–50 cents per kWh assuming a module lifetime of five years, an irradiance of $1,700 \text{ kWh m}^{-2}/\text{year}$, a harvesting factor of 0.85, an active area efficiency of 7 %, and an active-area coverage of 65 % of the module. The maximum is obtained using a pessimistic estimation of the costs and the minimum for optimistic assumptions (for details, see [36]). Figure 10.10c compares the costs including data from silicon solar cells and a coal power plant. The numbers for organic solar cells are in a reasonable range, but relatively high. This implies two points: First, ProcessOne is intrinsically expensive and changes in technology (e.g. ITO free) are required. Second, an increase in efficiency together with an expected economy of scale will bring costs down and will make organic photovoltaics a promising technology.

In the beginning of this chapter it was mentioned that organic photovoltaics has to compete with existing technologies for energy conversion, in particular with other solar-cell technologies. This competition defines the main requirements for a successful integration into the market. It also defines a time window of opportunity, during which a successful market integration can take place. Upscaling requires heavy investments into process engineering. To further attract investors, first demonstrator products have to be realized as soon as possible, but with sufficient carefulness of a reliable product. However, investments in organic photovoltaics are risky. Decisions rely on a comparison with existing technologies and projections on the developments of all these technologies and needs of customers/markets in the future.

Additionally to the state-of-the-art, every existing and in particular every emerging and not yet established technology faces the threat of becoming overtaken by a newer, faster progressing technology. Regarding photovoltaics, solar cells based on perovskites look promising right now. The employment of these materials in efficient solar cells was recently discovered. Perovskite based devices have been developing rapidly aiming for 20 % efficiency and low-cost and low-temperature fabrication processes.

10.3.3 Sustainability

Costs in money per W_p or kWh are not sufficient to judge whether it makes sense to employ a solar-cell technology on a larger scale. One decisive figure of merit is the so-called energy return factor ERF (or EROI: energy return on investment), which describes the energy harvested $E_{\text{harvested}}$ compared to the energy used during fabrication and operation E_{in} of the energy converter:

$$\text{ERF} = \frac{E_{\text{harvested}}}{E_{\text{in}}}. \quad (10.6)$$

In case of a grid-connected solar generator, the ERF should be larger than 1. Only in cases, where the solar module is used for replacing or accompanying a battery in a remote system, an ERF smaller than unity might be tolerable. If the technology is

supposed to significantly contribute the energy supply of the society, an ERF larger than 3 [38] or even 7 is supposed to be required. One point missing when looking at the ERF only is the dynamics. For solar modules, almost the complete energy invested has to be raised during production. However, the energy return is during operation for years. If the ERF is moderate and the lifetime very long (decades), the transition towards renewable energies leads to a lag in the benefits, i.e. a short-term increase in energy demand and carbon-dioxide emission before net-saving sets in.

The ERF can alternatively be expressed as a time span, which is the energy payback time EPBT describing the time under operation required to harvest E_{in} :

$$\text{EPBT} = \frac{\text{lifetime}}{\text{ERF}} = \text{lifetime} \cdot \frac{E_{in}}{E_{\text{harvested}}}. \quad (10.7)$$

ERF and $1/\text{EPBT}$ scale with $E_{\text{harvested}}$ including the efficiency under real operation, the radiation and weather conditions at the location of installation, and the lifetime of the system. These parameters have been discussed in previous sections. Now, we focus on E_{in} . Estimations are obtained employing the methodology of life cycle assessment (LCA). It addresses the energy input from the mining of the raw materials to the end-of-life management. Besides energy, other quantities such as material usage or emissions are treated by LCA as well. Here, in particular the emission of greenhouse gases is of importance as their reduction is a major motivation for a decarbonization of the energy sector and a transformation towards “renewable energies”.

First LCA studies have been performed on organic solar cells [34, 35, 39, 40], usually ignoring questions on recycling. Some results are summarized in Fig. 10.11a. For ProcessOne the distribution of energy on the different materials and processes

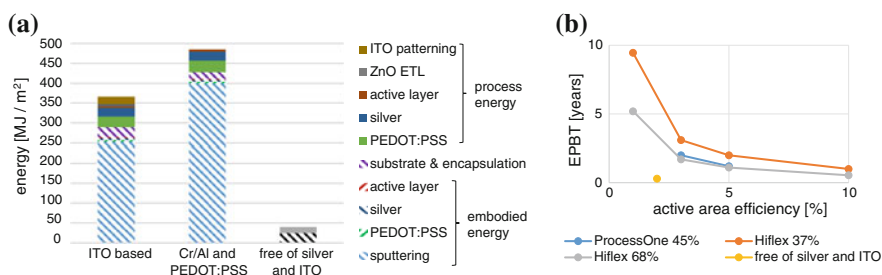


Fig. 10.11 Results from life cycle assessment according to [34, 35]. **a** Energy required per square meter for the ITO-based ProcessOne, Hiflex with sputtered Al/Cr substrate, and a silver and ITO free approach. The contribution from energy embodied to the materials is patterned. Note that the estimation for sputtered Al are at the top edge and prices from suppliers suggest significantly lower numbers for the energy input. **b** Energy payback time (EPBT) as a function of active-area efficiency. The share of the active area is given in the legend. It is 46 % for the ITO-free modules. Realized are efficiencies in the range of 2–3 % on large scale. An irradiance of $1,700 \text{ kWh m}^{-2}/\text{year}$ is assumed to calculate the EPBT

follows the trends in costs (cf. Fig. 10.10). Most of the energy is embedded in the materials, predominantly the ITO-coated substrate, where the sputtering process with Argon is very energy intensive. The direct process energy during the printing of the solar module accounts for roughly 20 %. An alternative process called Hiflex (Fig. 10.9b), which replaces the ITO electrode by aluminum/chromium, shows even a larger embodied energy due to the sputtering of the Al/Cr when fabricating the substrate [34]. A decrease of embodied energy by a factor of 10 can be obtained when avoiding all sputtering processes (ITO and metal) [35]. The back electrode of such modules consists of a high conductivity PEDOT:PSS combined with carbon graphite (Fig. 10.9c). In this process, PEDOT:PSS has the largest share in the process energy, mainly due to the drying step after the deposition of PEDOT:PSS requiring heating of the layer.

The numbers in Fig. 10.11a are expressed as a function of the produced module area as previously when we discussed costs. To calculate ERF and EPBT, efficiencies and lifetimes have to be considered. Figure 10.11b gives an overview on the estimated EPBT as a function of the efficiency of different modules. Comparing the three processes, it is obvious that the selection of a low-energy process is essential. As second step, increasing the efficiency and the active-area coverage is important. Third, active materials that are expensive and energy-intensive in their production should be replaced. Amongst those are fullerenes, in particular derivatives like PC₇₁BM. An EPBT of, e.g., 2 years means an ERF of 3–10 dependent on the lifetime of the module (6–20 years). These numbers are comparable to silicon-based photovoltaics which currently has a typical ERF between 6 and 10 [41].

Note that these studies are preliminary and the numbers might vary by factors. Consequently, they are not resilient when comparing organic solar cells with other photovoltaic technologies. However, they allow for the following conclusions:

- Overall and in particular material costs are not negligible despite a low material consumption.
- ITO and sputtering processes in general should be avoided.
- Efficiencies between 5 and 10 % and lifetimes in the order of 10 years should be aimed for. However, more important is the choice of processes, materials, and architectures to bring costs and required energy down.

Additional to the results from LCA, which are based on current markets and technologies, future developments have to be taken into consideration. As the global energy demand is huge and growing, photovoltaics can only have an impact if this technology can be scaled to terawatts of power, i.e. square kilometers of modules. Thus, the abundance of materials is crucial. Indium does not fulfill the criterion of abundance. Silver should be replaced in the long term as well.

On the edge of commercialization and broad application, process optimization has to be done. Economic constraints will define a product that shows the optimum tradeoff between performance, lifetime, additional features, and costs. Support and funding by the public has to critically judge the costs and stir the developments in photovoltaics into the right direction. This exercise of influence guarantees that

decisions do not stop at the economy, but consider impacts on the environment, energy and material input, and the complete life cycle containing disposal and recycling, where latter starts already at the choice of substrate [42].

10.4 Summary and Answers to the Initial Questions

The development of organic photovoltaics can hardly be foreseen because the progress in photovoltaics is rapid. New discoveries can lead to the emergence of novel technologies competing with organic photovoltaics. These dynamics and the demand for renewable energy make this field exciting and important.

We summarize this chapter with suggestions for possible answers to the initial questions:

- *Why will organic solar cells with a low power-conversion efficiency not be successful, even if they are very cheap?* First, most of the costs scale with the module area (substrate, amount of materials, encapsulation). Second, a low efficiency increases the share of the costs for the balance of system (wiring, mounting etc.). Third, a too low efficiency hinders applications where the size of the module is important (e.g. mobile devices). Thus, first modules should have an efficiency in the range of 5 % and the second generation should exceed 10 %.
- *What are conventional approaches to increase the power-conversion efficiency?* One approach is stacking several solar cells to reduce electrical and optical losses resulting from the tradeoff made when choosing the absorber layer thickness. Using absorber materials with different gaps, tandem (and multijunction) solar cells decrease thermalization losses. Absorption is additionally increased by applying light trapping schemes to focus more light into the thin absorber layer. Furthermore, control of the morphology and the synthesis of novel absorber materials are essential for improvements in efficiency.
- *What are the main challenges in material design to reach a new working and efficiency regime of organic solar cells?* Increasing the dielectric constant of the absorber materials is supposed to result in a higher efficiency for charge separation. Decreasing the reorganization energy might be a key to reduce energy losses.
- *Nominal power-conversion efficiency does not tell the complete story. What is the main figure of merit? Why and under which conditions can organic solar cells benefit from it?* The main figure of merit is the number of kWh generated per year and the costs per kWh. This number cannot be predicted from the efficiency measured under standard reporting conditions because the efficiency is a function of temperature and light intensity. Commonly, the fill factor of organic solar cells increases with higher temperatures and lower intensities. For most locations, low light and module temperatures significantly larger than 25 °C dominate the course of the year. Consequently, an organic solar module compared to an inorganic one, where the trends in efficiency are inverted, delivers more energy per nominal power. This advantage is called O-factor.

- *What are major technological challenges?* Processes have to be developed for upscaling to minimize losses in efficiency and active area (series resistance, interconnects). Common electrode materials (ITO, in future also silver) have to be substituted with more abundant and low-cost alternatives. Encapsulation technologies with good and low-cost barrier films have to be developed.
- *What are estimated values for energy payback times, material and manufacturing costs, and lifetimes?* It is too early to state these numbers. Estimations for a pre-industrial printing line suggest figures, which are rather high (energy payback time in the range of years, costs in the range of several 10s of euro cent per kWh). Lifetimes are supposed to be at least five years. Material costs dominate the overall costs. Upscaling of suitable syntheses, increasing efficiency and stability, and a general economy of scale will bring these numbers down.

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Part IV

Appendix

Chapter 11

References

11.1 Details on the Simulation

The discussed simulation results were obtained using a self-made drift-diffusion solver. The work by Staudigel et al. (Staudigel, J., Stössel, M., Steuber, F., Simmerer, J.: A quantitative numerical model of multilayer vapor-deposited organic light emitting diodes. *J. Appl. Phys.* **86**, 3895–3910 (1999)) served as template for the implementation of the algorithm.

While discussing simulation results in this book, it was not explicitly commented on each parameter selected as input for the respective simulations. This was done to avoid superfluous information, which was not necessary for the main messages and conclusions. More details can be found in the appendix of the author's Ph.D thesis which is freely available under

<http://nbn-resolving.de/urn:nbn:de:bsz:14-qucosa-89501>.

The source code is freely available under

<http://sourceforge.net/projects/osolsimulation/>

protected by a GNU General Public License. I am glad to receive comments. You can contact me via:

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11.2 Contributions

I want to explicitly list data that was not obtained by myself. I acknowledge all contributors arranging the following in chronological order of the appearance of the data:

- Collection of data in Fig. 3.33 was done by Koen Vandewal, Stanford University.

- Calculations of the frontier orbitals of ZnPc and C₆₀ (Fig. 3.52) were done by Beatrice Beyer, Fraunhofer COMEDD, Dresden.
- Optical constants in Fig. 3.53 were provided by André Merten, IAPP, TU Dresden.
- Optical constants in Fig. 3.56 were provided by Jonas Bergqvist, IFM, Linköping Universitet, except for PCPDTBT. This data was provided by Steve Albrecht, Universität Potsdam.
- All optical simulations according to the transfer matrix approach (displayed for instance in Figs. 4.14 and 8.7, 8.8 and 8.9) are performed using the program OSOLemio, developed by Mauro Furno, IAPP, TU Dresden.
- UPS measurements (Figs. 6.9, 6.11, and 8.2) and the data analysis and plot in Fig. 6.10 were performed by Max Tietze, IAPP, TU Dresden.
- Current–voltage measurements at different temperatures (Fig. 6.15) were performed by Johannes Widmer, IAPP, TU Dresden.
- Transient photocurrent measurements (Figs. 6.17, 6.18, 6.19, 6.20, 6.21 and 7.8) were performed by Steef Corvers, IAPP, TU Dresden.
- Solar cells for Fig. 7.7 were fabricated and characterized by Annette Petrich, IAPP, TU Dresden.
- Current–voltage data of a device during aging (Fig. 7.11a) was provided by Martin Hermenau, IAPP, TU Dresden.
- OFET mobility measurements (Table 8.2) were performed by Moritz Hein, IAPP, TU Dresden.
- The determination of the energy of the charge-transfer state in ZnPc:C₆₀ blends (Fig. 8.2) was done by Koen Vandewal, IFM, Linköping Universitet.

Index

Symbols

$\mu\tau$ product, *see also* mobility-lifetime product
 π -system, 68–72, 167, 169, 170, 172, 176, 179
2-degree-target, 3

A

Absorption, 101, 118, 414
 cross section, 122
 in a semiconductor, 30–33, 56
 of a solar cell, 57–59
 of sun light, 39
 parasitic, 59, 102, 105, 435
Absorption coefficient, 32, 80, 101, 172, 176, 177, 250
Absorption profile, 385, 386
Absorption spectrum, 76, 83, 386
Abundance of materials, 449
Active area, 189, 441
Aging, 443
 accelerated, 443
Air mass, 17
AM1.5g, 17, 54
Ampère's circuital law, 231
Aromaticity, 71
Aufbau principle, 74

B

Balance of system, 428, 442
Band diagram, 37, 43, 46
Bandgap, 23, 54, 129
 direct, 32
 indirect, 32
Bässler model, 233, 246, 338

Bending of energy levels, 125
Benzene, 71, 176
Bimolecular recombination, 281, 384, 400
 constant, 395
Black body, 18, 19, 21, 33, 54, 58, 106, 115, 119
Blend, 268
Boltzmann equation, 218, 219
Bond
 π , 70
 σ , 70
 conjugated, 72
 covalent, 68
 van der Waals, 83
Born-Oppenheimer approximation, 25, 78
Boundary condition, 241
BPAPF, 332
Breakdown of diode, 416, 430
Built-in potential, 124, 227, 242, 267, 279, 293, 295, 326, 327, 402, 415, 431
Bulk heterojunction, 102, 328, 386
 in drift-diffusion simulation, 277
 with injection barrier, 324

C

C60, 171, 378
Capacitor, 343, 347
Carnot machine, 22
Charge carrier density
 background/dark, 289, 298, 304
Charge extraction, 127
Charge transport level, 318
Charge-transfer exciton/state, 88, 102–104, 112, 236, 281, 287
 dissociation, 416
 dissociation rate, 237, 369, 384

energy, 379
 hot, 103, 154
 Chemical energy, 44
 Climate change, 1, 2
 Coherence, 251
 Compensation voltage, 298
 Concentration of sunlight, 21
 Conduction band, 23
 Conductivity, 29, 41, 266
 Contact
 non-selective, 290
 plus injection barrier, 296
 selective, 40, 45, 301, 415, 434
 plus injection barrier, 293
 Continuity equation, 220, 229, 286
 for excitons, 229
 Costs, 444
 Coulomb potential, 234, 243
 Coulomb radius, 234
 Courant-Friedrichs-Lewy condition, 230
 Current-voltage curve, 130
 in case of barriers, 321, 330
 Cyclic voltammetry, 264

D

Degradation, 187, 372
 Density of states, 26
 Gaussian, 108, 241, 336, 338, 402
 UPS, 335
 Depletion approximation, 47
 Detailed balance, 130
 Dexter transfer, 88
 Di-NPD, 402
 Dielectric constant, 265, 436
 Diffusion, 295
 of excitons, 101
 Diffusion current, 42, 46, 48, 348
 Diffusion gradient, 326
 Diffusion length
 exciton, 264
 minority carrier, 48, 261
 Diindenoperylene, 364
 Dipole, 434
 at interface, 333
 Disorder, 87, 93, 108, 216, 240, 336
 Displacement current, 230, 345
 Doping, 29, 45, 174, 244, 265, 304, 318, 352, 431
 Doublet, 74
 Drift current, 41
 Drift length, 139, 141
 Drift-diffusion

model, 217, 422
 simulation, 223
 solver, 225
 Driving force, 149

E

Economic assessment, 444
 Effective density of states, 28, 107, 297
 Effective donor-acceptor gap, 106
 Effective energy gap, 278, 320, 403, 415
 Effective mass, 26, 41, 220, 422
 Effective medium, 225, 268, 278, 390, 424
 Efficiency
 as a function of device thickness, 433
 as a function of temperature and intensity, 438
 maximum of semiconductor solar cells, 53
 organic solar cells, 130, 427
 thermodynamic maximum, 20
 Einstein coefficients, 117
 Einstein relation, 42, 221, 228
 classical, 222
 generalized, 221, 397
 Electric energy, 44, 45
 Electro-absorption, 267
 Electrochemical potential, 37, 105
 Electrode, 434
 Electron affinity, 80, 84, 101, 129
 Electron configuration, 73
 Ellipsometry, 264
 Encapsulation, 187, 443
 Energy diagram, 326, 333
 Energy dispersion, 25
 Energy dissipation, 250
 Energy payback time, 448
 Energy return factor, 447
 Entropy, 22
 Equivalent-circuit model, 137, 347
 Exciton, 32, 87, 100
 diffusion, 414
 dissociation, 113
 separation, 248
 Exciton binding energy, 265, 433, 436
 External quantum efficiency, 105, 118, 130
 as a function of voltage, 392
 Extinction coefficient, 252
 Extraction barrier, 317, 322, 328, 339, 417
 characterized by UPS, 333

F

Feed-in tariff, 3

Fermi level, 26, 30, 37, 46, 332
 Fermi's golden rule, 79, 91
 Fermi-Dirac statistics, 26, 108
 Fill factor, 130, 281, 384, 416
 as a function of layer thickness, 308
 dependence on illumination intensity, 300, 402
 limited by non-selective contacts, 300
 related to mobility, 284
 Flat heterojunction, 318, 328, 341, 434
 with injection barrier, 323
 Fluorescence, 77, 89
 Förster transfer, 88
 Forward current, 329, 369
 Franck-Condon principle, 78, 90
 Fresnel Equations, 252

G

Gaussian disorder model, 93, 233
 extended, 98
 Geminate recombination, 102, 281, 384
 Generation, 32
 Generation profile, 388
 Generation rate, 250, 400, 415
 Glass transition temperature, 185
 Global warming, 2
 Goodman and Rose photocurrent model, 140
 Graded junction, 382, 383
 Greenhouse effect, 1

H

Harvesting factor, 438
 Hecht equation, 142, 304
 Heterojunction, 51
 donor-acceptor, 100
 High binding energy cutoff, 333
 Highest occupied molecular orbital (HOMO), 71, 80, 83, 100, 318, 320, 332
 as a function of mixing ratio, 381
 Hole, 28
 Hole-transport layer, 316, 385
 Hopping, 216, 221, 241, 423, 429
 Hopping transport, 87, 93–99
 Marcus model, 95
 Miller-Abrahams rate, 94
 Hückel's rule, 71, 85
 Hund's rule, 74
 Hybrid planar bulk heterojunction, 328, 383

I

Ideality factor, 49, 128, 330, 395, 397, 408
 Image charge, 243
 Impedance spectroscopy, 265
 Index matching, 57
 Indirect recombination, 395
 Injection barrier, 242, 279, 293, 316, 321, 323, 372, 402
 characterized by UPS, 332
 Interface modeling
 barrier, 245
 organic-organic, 244
 Interference, 101
 Interlayer at electrode, 293
 Internal quantum efficiency, 105
 Intersystem crossing, 77, 103
 Intrinsic, 29
 Inverted geometry, 382
 Ionization potential, 80, 84, 101, 129, 265
 measured by UPS, 333

J

J-V curve
 and characteristic parameters, 130
 as a function of temperature, 396
 in the dark, 395
 influence of series and parallel resistance, 126
 monochromatic, 391
 Jablonski diagram, 76, 83

K

Kelvin Probe Force Microscopy, 265
 Koopmans' theorem, 80, 86

L

Lambert-Beer law, 250
 Langevin recombination, 240, 281, 379, 436
 Law of mass action, 29
 Life cycle assessment, 448
 Lifetime, 36, 443
 of module, 442, 448
 Light trapping, 57, 435
 Lorentz oscillator, 80
 Lowest unoccupied molecular orbital (LUMO), 71, 84, 100
 Luminescence, 34, 39, 58, 77
 efficiency, 118

M

Majority charge carrier, 30, 36, 48, 278, 293, 398
 Marcus theory, 89, 92, 123, 217
 Market, 442, 447
 Maximum power point, 56, 130
 Me-PTCDI, 367
 MeO-TPD, 332, 402
 MIM device, 43, 418
 Minority charge carrier, 30, 48, 278
 Mixing ratio, 378, 386, 390
 Mobility, 41, 93–99, 220, 266, 280, 360, 404, 416, 423, 433
 and layer thickness, 308
 imbalance, 283, 308, 385, 390
 models in organics, 232
 of ZnPc:C₆₀ blends, 390
 optimum, 281–284
 Pool Frenkel, 233
 Mobility edge, 96, 99, 222
 Mobility imbalance for flat heterojunctions, 360
 Mobility-lifetime product, 104
 Momentum method, 219
 Monolithic tandem, 428
 Monomolecular recombination, 384
 Monte Carlo simulation, 95, 216, 424
 Morphology, 185, 309, 382, 424, 434
 Mott-Gurney Law, 257
 Multiple-trapping and release model, 99
 Multiscale modeling, 216

O

O-factor, 437
 Octet rule, 68
 OLED, 5
 Onsager-Braun theory, 102, 236, 287
 Open-circuit voltage, 44, 50, 414, 432
 for bulk heterojunctions, 320
 for flat heterojunctions, 320
 for varied donors, 320
 for varied transport layers, 320
 comparison between flat and bulk heterojunction, 329
 dependent on illumination intensity, 399
 dependent on mixing ratio, 378
 dependent on temperature, 287
 limited by surface recombination, 290
 of organic solar cell, 105–130
 of tandem cells, 431
 related to absorber thickness, 292
 related to built-in potential, 124, 296, 326

 related to energy-level bending, 297
 related to mobility, 284
 related to recombination, 286
 related to the HOMO, 319
 Optical constants, 264
 Optical gap, 264
 Optical modeling, 250
 Optical simulation, 386
 Optical spacer, 385
 Orbital, 68
 Organic field-effect transistor (OFET), 266, 389
 Oscillator strength, 80
 OTRACE, 267

P

p-i-metal geometry, 318
 p-i-n concept, 52
 p-n junction, 45–52, 260, 432
 Pauli principle, 24
 PEDOT, 371
 Percolation paths, 383
 Phosphorescence, 77
 Photo-CELIV, 267
 Photoconductivity, 303, 369
 Photocurrent, 49, 298
 dependence on intensity, 301
 limited by bimolecular recombination, 301
 Photocurrent matching, 60, 429
 Photoenhanced injection current, 302
 Photoshunt, 323, 404
 Pile-up of charges, 345, 347, 351
 Planck's law, 19
 generalized, 34
 Plane wave, 251
 Point of intersection between *J-V* curves, 302
 Poisson's equation, 46, 223, 227
 Polarization, 84, 415
 Polaron, 85
 Polythiophene, 86
 Poole-Frenkel effect, 97
 Poole-Frenkel mobility, 364
 Potential energy surface, 90
 Power-conversion efficiency
 empirical limit, 132
 related to mobility, 282
 Predictive simulations, 424
 Profilometer, 263

Q

- Quartz crystal monitor, 191, 263
- Quasi equilibrium, 130
- Quasi-Fermi level, 31, 326
 - splitting, 44, 105, 106, 284, 296, 298, 315

R

- Radical, 74
- RC time constant, 343, 347
- Recombination, 32, 384, 395, 415
 - at contacts, 290–293, 299
 - at D/A interface, 248
 - bimolecular, 34, 110, 234
 - direct/bimolecular with constant β , 282
 - geminate, 236, 287
 - Langevin, 234, 282
 - monomolecular, 35
 - non-radiative, 34, 110
 - radiative, 32, 106
 - Shockley-Read-Hall, 34, 49, 111
 - surface, 35, 242
 - trap-assisted, 236, 282, 288
- Recombination constant, 404
- Recombination contact, 429, 431
- Reflection, 57, 251, 252, 254, 264
- Refractive index, 252
- Relaxation
 - of charge carriers, 338
- Reorganization energy, 85, 92, 95, 123, 437
- Roll-to-roll production, 444
- Round robin, 443

S

- S-shape, 295, 322, 328, 379, 417
 - dependent on illumination intensity, 349
 - dependent on temperature, 340
 - dependent on thickness, 361
 - due to degradation, 372
 - due to field-dependent exciton dissociation, 369
 - in forward direction, 370
 - in simulation, 323
 - related to layer thickness, 336
- Scatterer, 435
- Scharfetter and Gummel method, 228
- Schottky contact, 260
- Schottky-Mott theory, 157
- Screening, 352
- Secondary electrons, 333
- Selective contacts, 104, 124, 279, 328
- Selectivity, 383
- Semiconductor
 - crystalline, 23
 - organic, 5

- Semitransparent solar cell, 371
- Series resistance, 267, 343, 395, 398, 441
- Shockley diode equation, 45, 47–51, 137, 395
- Shockley-Queisser limit, 53, 56
 - and organic solar cells, 130
 - overcoming it, 60
- Short-circuit current density, 414
 - dependence on illumination intensity, 145
 - dependence on intensity, 397
- Shunt resistance, 396, 406, 415
- Silicon, 29, 32, 34, 45, 52, 56
- Simulation, 215
- Single occupied molecular orbital (SOMO), 82, 84, 129
- Single-carrier device, 257, 364
- Singlet, 74, 77, 88
- Sokol and Hughes photocurrent model, 142, 291, 300
- Solar cell
 - dye (sensitized), 51
 - heterojunction, 52
 - organic, 6
 - silicon, 4
- Solar constant, 17
- Solar module, 441
- Solar spectrum, 16
- Solvent shift, 83
- Space charge, 297, 305, 352, 362
- Space-charge-limited current, 140, 257, 266, 395
- Spectral mismatch, 192, 394
- Spin, 73, 77
 - multiplicity, 73, 77
- Stability, 442
- Standard geometry, 382
- Stefan-Boltzmann law, 20, 21
- Stokes shift, 78, 122
- Superposition
 - of I - V curves, 373
 - principle, 118
- Surface recombination
 - see also* Recombination, 316, 328

T

- Tail states, 335
- Tandem solar cell, 60, 428
 - simulation, 430
- Thermal injection, 279
- Thermalization, 30, 39, 54, 428

Thermally stimulated current spectroscopy, [266](#)
 Thermionic emission, [243](#)
 Thiophene, [85](#)
 Tight-binding approach, [24](#)
 Time of flight, [266](#)
 Time-delayed-collection-field technique, [150](#)
 Time-resolved two-photon photoemission (TR-2PPE) spectroscopy, [154](#)
 Transfer-matrix model, [224](#), [251](#), [386](#)
 Transient photocurrent, [342](#), [368](#)
 overshoots, [344](#)
 Transient photovoltage decay (TPV), [127](#), [194](#)
 Transitions
 $\pi - \pi^*$, [76](#)
 vibronic, [78](#)
 Transport energy, [86](#), [96](#), [222](#)
 Transport level, [265](#)
 Trap, [34](#), [238](#), [266](#), [334](#), [434](#)
 distribution, [240](#)
 shallow, [97](#)
 Trap-assisted recombination, [400](#)
 Triplet, [75](#), [77](#), [89](#), [433](#)
 Tunneling, [429](#)

U
 Ultraviolet photoelectron spectroscopy (UPS), [264](#), [331](#), [379](#)
 Upscaling, [441](#)

V
 Vacuum level, [37](#), [83](#)
 alignment, [157](#), [318](#)
 measured by UPS, [333](#)
 Valence band, [23](#)

W
 Work function, [43](#), [242](#), [316](#), [434](#)
 measured by UPS, [333](#)

Y
 Yablonovitch limit, [58](#)
 Yield, [442](#)

Z
 ZnPc, [168](#), [320](#), [378](#)