Impact of Charge Carrier Density and Trap States on the Open Circuit Voltage and the Polaron Recombination in Organic Solar Cells

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1. Introduction

At the 30th of June, 2011, the German Bundestag voted to accept a change in the atomic energy act, resulting in a stop of all German nuclear power plants until 2022. The impact of this decision becomes obvious when one takes into account that nuclear power provided 108 billion kWh of electrical energy in 2011, which is 17.6 % of the gross electric power generation in Germany, and 39 % of the base load power supply [46]. To provide a stable electricity supply the capacities have to be replaced by other types of energy generation since the tendency of the total electrical energy consumption did not significantly decrease in the last years. As nuclear power has a relative low carbon dioxide emission per kWh, the power stations that will replace these nuclear power plants have to be low CO₂ emissive, too, in order to not further accelerate the climate change. This excludes conventional energy sources like coal or gas as long as no working carbon capture and storage methods are developed, to reduce CO₂ emission. All these points lead inevitably to the expansion of the so-called renewable energy, with the most important types for electricity production being water, wind, sun and biomass beside others.

The expansion of the usage of water power is limited, at least in Germany, since most interesting spots are already occupied and the fabrication of new plants is not easy because it often has a high impact on nature and countryside. In the case of the usage of biomass, the limitation could be given by an ethnic conflict: how much of the limited area can we supply for production of biomass instead of food. Nevertheless, those two types are important for the future energy mix because they are base loadable instead of sun and wind energy, where energy storage systems and smarter electricity grids have to be designed before they can be connected to the grid in great number. Wind energy is the renewable energy with the highest actual percentage at all being 7.6 % of the German gross electric power generation 2011 [46], with growing tendency and the potential to even reach 25 % in 2025 [45]. These values are already impressive, nevertheless the fraction in the gross electric power generation (3.1 %) is still low, which is why electric energy from the sun with its high potential is also an important candidate for near future clean energy generation. This gets obvious by just taking into account that the sun delivers around 1.08×10¹⁸ kWh per year to the earth, which is 7000 times the global primary energy consumption [86]. Up to now the market for photovoltaics is dominated by conventional silicon solar cells (SC) (crystalline and amorphous) with only a small but growing fraction of thin film solar cells (CIS, CIGS, CdTe). The reason why photovoltaics are not more important at present are the relative high costs of the produced energy in comparison with other technologies and the commercialization is highly depending on governmental subsidies. This disadvantage of inorganic solar cells can be the starting point for new photovoltaic concepts like dye sensitized solar cells (DSSC) or organic solar cells (OSC) (small molecules or polymeric) that can be processed from solution or by evaporation in a roll-to-roll process which promises to have a high throughput and low cost. Up to now the efficiencies are still too low to compete with inorganic solar cells, 11.9 % for DSSC and 11.1 % for OSC in lab scale with growing tendency [38], anyhow the chance for commercialization is present especially because of their other beneficial
1. Introduction

properties like being lightweight or the ability to produce the cells in various colors. To further increase the performance of those solar cells, more investigations about the working principles and the testing of new materials are inevitable.

In this thesis the focus is set on one special type of organic solar cell concepts, the so-called organic bulk heterojunction (BHJ) solar cells. In the second chapter, a brief overview is given on what organic semiconductors are and of which materials organic BHJ SCs consist of. Then the general working principles of organic BHJ SCs starting from the absorption of light to the final extraction of the generated charge carriers at the electrodes into the external circuit is explained. Afterwards the correct measurement of the three important characteristics determining the performance of the SC, the open circuit voltage $V_{oc}$, the short circuit current density $j_{sc}$ and the fill factor $FF$ is presented. The performance is not only influenced by external parameters like light intensity or temperature, but also by microscopic properties, where one of the most important is the recombination of generated charge carriers within the active layer of the SC, which was investigated in this thesis under open circuit conditions. Therefore, the different recombination mechanisms as well as $V_{oc}$ are discussed in more detail in separate subchapters.

After the theory part, chapter 3 will be more technical. First the charge extraction (CE) experiment, which is not a common technique, is introduced as this measurement provides the basis of many investigations described in the experimental results chapters later on. The measurement principle, the used setup and important points that have to be considered when evaluating the CE signals will be explained. Up to that point, the working principles and the measurement technique is presented, but one important part is missing: the object under investigation itself. Therefore, a short prescription of how the standard solar cell preparation takes place is given. The chapter is closed by a detailed description of the specific single materials used in the framework of the thesis.

In chapter 4 the first experimental results are presented. Here the relation of the open circuit voltage to the charge carrier density $n$ under open circuit conditions in the active layer of BHJ SC is discussed. Therefore, $V_{oc}$ and $n$ were measured under different light intensities and temperatures in standard P3HT:PC$_{61}$BM solar cells. Additionally, the influence of non-ohmic contacts as well as an electron acceptor with different LUMO energy level were investigated.

Chapter 5 focuses on recombination of charge carriers, which is an intensively discussed topic in organic photovoltaics. By determination of the charge carrier density under open circuit and short circuit conditions in combination with $j_{sc}$ and $V_{oc}$ it was shown that the recombination rate can not be explained by known recombination paths alone but an additional effect has to be taken into account to explain the experimental results. This recombination mechanism is based on the existence of trap states, which is an inherent property of organic semiconductors. The measurements confirming the extended theory were not only performed for the standard material system but also on a material system which shows the highest efficiency of all commercially available materials.

Whereas in chapter 5 only intrinsic trap states caused by e.g. disorder of the organic semiconductors were investigated, in chapter 6 additional extrinsic trap states were introduced into the active material system. This was done by controlled oxygen exposure of the active material as well as the incorporation of small amounts of an additional material into the absorber layer. By

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1 poly(3-hexylthiophene-2,5-diyl)
2 [6,6]-phenyl C61 butyric acid methyl ester
3 Lowest Unoccupied Molecular Orbital
performing various measurement techniques for characterization of the solar cells a qualitative
dependence of the recombination rate, the dominant recombination process and the overall solar
cell efficiency on the amount of extrinsic trap states could be established.

Chapter 7 differs from the other experimental chapters 4-6, as here the focus is not set on
$V_{oc}$, $n$ and recombination processes. An effect is discussed that can take place in organic pho-
tovoltaics (OPV), when the electrode and the active material do not fit together energetically
as perfectly as in the material systems presented in the foregoing chapters. In special cases
the current voltage characteristics under illumination do not show the typical behavior, but an
s-shape, which significantly reduces the solar cell efficiency, especially at higher illumination
levels. In this work, such s-shaped solar cells could be reproducibly fabricated, characterized
and the physical background of the s-shape could be identified.

The results of the complete thesis are summarized in chapter 8 and chapter 9. The list of used
abbreviations and symbols can be found in appendix A and B.
1. Introduction
2. Bulk Heterojunction Solar Cells

This chapter is a brief introduction into the physics of organic solar cells. At first, the term "organic" is described and why these materials can act as semiconductors. The second part will go directly in media res summarizing the fundamental physical processes occurring in organic solar cells, describing their operation principles and showing their limitations. The recombination of charge carriers, that is the annihilation of two oppositely charged charge carriers, and one of the important parameters determining the efficiency of a SC – the open circuit voltage is discussed in more details. Finally, it is explained how to measure the efficiency of a working solar cell correctly and why it is more difficult than just to use a solar simulator and measure a current–voltage curve.

2.1. Organic Semiconductors

Organic matter is commonly known as material that is produced by living organisms or decay products of those. In chemistry and physics another definition is used: Organic materials are carbon-based compounds, hydrocarbons, and their derivatives. In the field of organic photovoltaics, small molecules (e.g. fullerenes) and polymers are used. The large number of different organic materials and their properties have their origin in the special electronic configuration of the carbon, namely \([\text{He}]\ 2s^2\ 2p^2\). This configuration is the basis of the ability of carbon to hybridize to special orbitals. In materials used for organic electronics the \(sp^2\) orbitals are essential. In this case one \(2s\) electron and two \(2p\) electrons form three \(sp^2\) orbitals, oriented \(120^\circ\) relative to each other, forming \(\sigma\)-bonds and hence the planar sigma framework of the molecule. The residual electron occupies the \(p_z\) orbital perpendicular to the molecular plane in which the \(\sigma\)-bonds lie.

The crossover from an isolated carbon atom via a small molecule to a polymer formed with many carbon atoms and the accompanying evolution of the electronic properties is shown schematically in Fig. 2.1. In a single carbon atom the electron in the \(p_z\) orbital (\(\pi\)) has one specific energy. When a second carbon atom is added to build a covalent \(\sigma\)-bond to the first atom, the \(p_z\) energy level splits into two molecular orbitals. The one that lies lower in energy is populated by both \(\pi\) electrons, which form the binding \(\pi\)-bond, and is called HOMO (Highest Occupied Molecular Orbital). The unpopulated one is called LUMO, which has an antibinding character. Adding more carbon atoms to the carbon chain leads to additional splitting until the energy states can be seen as continuous and a \(\pi\)-band is formed in which the \(\pi\) electrons are delocalized over the whole carbon chain. In such a system no band gap would exist and the material would have metal rather than semiconductor properties. The reason for the opening of the band gap is the Peierls distortion, which is that the atomic positions are not perfectly ordered as in a crystal but rather oscillate in space.

Organic semiconductors as commonly used for bulk heterojunction solar cells exhibit band gaps in the range of \(1–3\ \text{eV}\) and mobilities in the range of \(10^{-5}–10^{-3}\ \text{cm}^2/(\text{Vs})\) \([64, 115]\).
2. Bulk Heterojunction Solar Cells

Figure 2.1.: Evolution of the electronic levels from a single carbon atom to a very long conjugated carbon chain resulting in energy band, which is the basis of organic semiconductors. In this case the material would show metallic character, the reason for the molecule to be a semiconductor is the Peierls distortion which causes the opening of a band gap (not shown). (After [4])

Details about the specific organic semiconductors used in this thesis are given in section 3.3.

2.2. Operating Principles

2.2.1. Fundamentals

The motivation to build solar cells is to convert photon energy into electric energy. In the case of SC using organic semiconductors as photo active layer the fundamental processes for the energy conversion differ from the commonly known inorganic semiconductor solar cells such as silicon SC. In Fig. 2.2 the main fundamental steps that have to take place for a working solar cell are illustrated and can be summed up as:

(I) Photon Absorption and Exciton Generation
(II) Exciton Diffusion and Dissociation to Polaron Pairs
(III) Polaron Pair Dissociation
(IV) Charge Carrier Transport to the Electrodes
(V) Charge Carrier Extraction at the Respective Electrodes

In the following all steps concerning the device operation and their influence on the solar cell behavior are discussed in detail. Since in this work polymeric organic bulk heterojunction solar cells were investigated, the main focus is set on this type, whereas the differences to other OSCs types, like e.g. planar heterojunction solar cells consisting of small molecules will be referred to in special cases. Many high quality overview articles about the fundamentals of
**2.2. Operating Principles**

Figure 2.2.: Energetic scheme to describe the fundamental steps occurring in a working solar cell, starting from the absorption of a photon (I) to the final extraction of free charge carriers (V). The intermediate steps are: exciton diffusion and dissociation (II), polaron pair dissociation (III) and charge transport (IV). Details about all processes are given in the text.

OSC were published for example by Deibel et al. [26] and Bredas et al. [18], for more detail it is recommended to have a closer look at these.

(I) Photon Absorption and Exciton Generation

The first step to create electrical energy from photons is their absorption. In organic materials the absorption band is intense because of the overlap between the wave functions of the electronic ground state and the lowest excited state [18]. The large extinction coefficient in the range of $10^{-5} \text{ cm}^{-1}$ ensures that film thicknesses of only 80 to several hundred nm are sufficient to absorb most of the incident photons in the material.

If a photon is absorbed, an electron from the HOMO will be excited into the LUMO. Together with the remaining hole on the HOMO the electron on the LUMO forms instantly an excited singlet exciton which exhibits a high binding energy and is therefore called a Frenkel exciton. Because of the strong electron–vibration coupling in π-conjugated systems the excitation relaxes into the lowest excited state $S_1$, whereby this thermalization process is a first energy loss. The reason for the high binding energy of the $S_1$ is the small relative dielectric constant $\varepsilon_r$ of organic molecules or polymers in the range of 3-4. Assuming a distance of 1 nm between hole and electron together with $\varepsilon_r = 3$ would result in a rough estimation of the binding energy $E_B$ of around 0.5 eV. In regioregular P3HT, $E_B$ was determined to be 0.7 eV by a combination of (inverse) photoemission spectroscopy, absorption and external quantum efficiency measurements [27]. This strongly bound exciton can not be dissociated into free charge carriers by thermal energy ($\sim 25 \text{ meV at room temperature}$) and will decay radiatively within its lifetime ($\tau = 400 \text{ ps for P3HT [97]}$) which can be detected by photoluminescence (PL) measurements. To dissociate the exciton effectively, a second material with a higher electron affinity (imply-
2. Bulk Heterojunction Solar Cells

ing a lower LUMO level) acting as electron acceptor has to be introduced. In this work the
used electron donating materials (from now on called donors) are polymers but also the use of
small molecules as donors is possible. The electron accepting materials (acceptors) used here
are fullerene derivates. In this definition of donors and acceptors, the exciton generation takes
place in the donor material, which is not generally the case. Even if in the commonly used
donor-acceptor (DA) systems most of the photons are absorbed by the donor material, also ex-
citons in the acceptor can be generated. However, since most fullerene acceptors exhibit only
low absorption coefficients this process is less probable, but many efforts are made to develop
polymeric acceptors to increase the absorption width of the complete system.

(II) Exciton Diffusion and Dissociation to Polaron Pairs

In organic photovoltaics two different device configurations are often used: the bilayer and the
bulk heterojunction solar cell. In a bilayer solar cell an acceptor layer is applied on top of a
donor layer and in a bulk heterojunction solar cell the donor and acceptor are mixed within one
single layer. Both approaches yield advantages and disadvantages but have in common that
the exciton has to reach the DA interface within its diffusion length $L_D$ to get dissociated. In
bilayer solar cells the DA interface is planar and therefore smaller than in BHJ solar cells and
only excitons generated in the volume within the distance of the exciton diffusion length to this
interface can be separated. In contrast, in BHJ cells the area of the interface is large because of
the fine intermixing of donor and acceptor. This disadvantage of bilayer SC can be compensated
by higher diffusion lengths of the excitons, since in this approach the donor consists almost
always on evaporated small molecules, which are highly ordered yielding reported diffusions
lengths of e.g. 62 nm in Cu-phthalocyanine \[106\]. $L_D$ values in polymeric systems are smaller,
likely caused by the higher disorder. For example in P3HT, values of 2.6 to 8.5 nm \[57, 69, 97\]
have been reported. The diffusion of the exciton itself is often described by a Förster resonant
energy-transfer.

If the exciton, e.g. located on the donor, reaches the donor–acceptor interface, the electron
is transferred from the donor to the acceptor. This process appears to be very efficient since it
takes place on the fs time scale and is therefore much faster than any other competing process as
for instance the before described exciton lifetime which is in the range of ns. In P3HT:PC$_{61}$BM
blend charge separation times <120 fs have been reported \[48\]. After the splitting of the exciton
the electron on the acceptor and the hole on the polymer may still be Coulomb bound and
have to be further dissociated. This state is called polaron pair or charge transfer (CT) state in
literature.

In recent publications by Banerji et al. \[5, 6\] it was claimed that the above stated process of
photoinduced charge separation after diffusion of excitons to the DA interface is not consistent
with the measured time scale of exciton formation and migration and the ultrafast photoinduced
electron transfer time. It was shown that the exciton migration is too slow to explain the mea-
sured electron transfer rate. Therefore they propose, that “the excitation (from a $\pi-\pi$ interband
transition) reaches the polymer:fullerene interface for charge separation before it becomes spa-
tially self-localized and bound within an exciton” \[5\]. In this picture the exciton diffusion and
binding energy become irrelevant to the charge transfer. The measurements on P3HT:PC$_{61}$BM
and PCDTBT\textsuperscript{1}\textsuperscript{-}\textsuperscript{-}\textsuperscript{1}PC\textsubscript{71}BM\textsuperscript{2} blends show that even in these well investigated systems it is not clearly understood how exciton formation and dissociation work.

Concerning excitons a second loss mechanism beside the exciton recombination has to be mentioned. In molecules with heavy atoms or spherical shape, as for instance in fullerenes, an intersystem crossing from a singlet exciton to a triplet exciton is allowed. If the intersystem crossing is faster than the charge transfer, a triplet exciton can be formed which decays by phosphorescence and the excitation is lost for the photocurrent. Another possibility to create an undesired triplet is by an electron back transfer from the CT state to the triplet state, if the triplet state lies lower in energy than the CT state, which was already observed experimentally \cite{65}.

### (III) Polaron Pair Dissociation

After dissociation of the exciton, the resulting bound polaron pair has to be further separated to gain free charge carriers which can contribute to the photocurrent. Beside many models, the most used one to describe this process is the Onsager–Braun theory. Already 1934 Onsager calculated the dissociation probability for an ion pair with a primary distance with the help of an external field \cite{82}. Braun expanded the theory to the dissociation of polaron pairs in DA systems and included their finite lifetime \cite{17}. Fig. 2.3 visualizes this process. $k_d$ is the dissociation rate of bound polaron pairs into free charge carriers, $k_f$ is the rate given for the competing process of the polaron pair decay back into the ground state. The dissociation probability $P$ can than be calculated by

$$P(T,F) = \frac{k_d(F,T)}{k_d(F,T)+k_f},$$  \hspace{1cm} (2.1)

where $k_d(F,T)$ is a complex term dependent on the temperature $T$ as well as the electric field $F$. The free charge carriers can now be transported to the respective electrodes leading to the desired photocurrent or meet again and recombine to polaron pairs with the rate $k_r$.

![Figure 2.3: Schematic description of the possible processes determining the dissociation probability $P$ of polaron pairs (see Eq. (2.1)). The desired dissociation takes place with the dissociation rate $k_d$. These free charge carriers can recombine again with a certain rate $k_r$ into the bound polaron pair state, which can once more be dissolved or decays with the rate $k_f$.]

\textsuperscript{1}Poly[9-(1-octylnonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl]

\textsuperscript{2}[6,6]-phenyl C71 butyric acid methyl ester
2. Bulk Heterojunction Solar Cells

An often addressed issue is the question of the driving force leading to the polaron generation which was investigated by Ohkita et al. [81] for eight different polymers. As result it was shown that the generation of long-living polarons, which was measured by transient absorption, depends exponentially on the free energy difference for charge separation $\Delta G$. In a simple picture $\Delta G$ is the offset between the LUMO levels of donor and acceptor ($\Delta G = E_{LUMO}^{donor} - E_{LUMO}^{acceptor}$). This finding has a high impact for the optimization of solar cells because a high $\Delta G$, which is preferable for the photocurrent generation, always limits the open circuit voltage that is among other things given by the effective band gap $E_g$ ($E_g = E_{HOMO}^{donor} - E_{LUMO}^{acceptor}$).

(IV) Charge Transport

After the polaron pairs are dissociated into free charge carriers, these have to move to the respective electrodes. For organic semiconductors several theories about charge transport exist which can mainly be classified in two different mechanisms. One is the description by a hopping transport in a percolating network and the other is a band like transport in the presence of trap states. Both theories will be briefly explained in the following, for more details review articles specified for charge transport are recommended [26, 103, 108].

The principle of the hopping transport mechanism is shown in Fig. 2.4, where the transport is achieved by a hopping of charge carriers from one localized state to another. Localized states in disordered organic materials occur from the lack of high range order in contrast to inorganic semiconductor crystals where a band structure is formed leading to a delocalization over the whole crystal. Even one single long polymer chain consists of many different localized states which are extended in space over several monomers. This is called conjugation length, which is typically around 20 monomers long, for example in PPV[1] 9-12 nm [85]. The energy levels of the localized states are distributed in a density of states (DOS) which is assumed to have an exponential or a Gaussian shape. For polymers a Gaussian shape is often used, explained by randomly distributed conjugation lengths forming one localized state or polarization effects between neighboring polymers. The hopping process itself is a statistic process, given by the rate $W_{ij}$ with which a charge carrier located in state $i$ with energy $\epsilon_i$ hops into a state $j$ with energy $\epsilon_j$. There exist many expressions for $W_{ij}$ where the most popular is known as Miller–Abrahams equation [76]

$$W_{ij} = v_0 \exp(-2\gamma_0|R_{ij}|) \left\{ \begin{array}{ll} \exp\left(-\frac{(\epsilon_j-\epsilon_i)}{k_B T}\right) & \epsilon_j > \epsilon_i \\ 1 & \text{otherwise} \end{array} \right.. \tag{2.2}$$

$v_0$ is the phonon vibration frequency, also often called the "attempt to escape frequency" and $k_B$ the Boltzmann constant. The first exponential factor $\exp(-2\gamma_0|R_{ij}|)$ describes the tunneling of charge carriers to overcome the spatial distance $R_{ij}$ between site $i$ and $j$. $\gamma_0$ is the inverse localization radius given by the overlap integral of the wavefunctions of both states. The second factor describes the process of overcoming the energetic distance. In the case of a hop into a higher energy state a phonon has to be absorbed and the hopping probability is handicapped which is taken into account by a Boltzmann factor. For a hop into deeper lying energy states it is assumed that a phonon can always be emitted. It is obvious from Eq. (2.2) that hopping into deeper states is always more probable as into higher states, assuming the spatial distance

$^1$poly(p-phenylenevinylene)
Figure 2.4.: Schematic description of the microscopic hopping transport in disordered organic semiconductors in the case of electrons. The electrons are randomly generated (by light or injection) in the electron density of states (stated as LUMO$_{\text{acceptor}}$), that consist of many localized states that are distributed in space and in a gaussian manner in energy forming the Gaussian density of states (DOS). As given by the Miller–Abrahams equation (Eq. (2.2)), downhops in energy are more probable resulting first of all in a thermalization of the electrons until most lower lying energy states are occupied. Then the equilibrium charge transport takes place around a specific energy – called transport energy – by downhops and uphops. To fulfill the energy conservation, a phonon has to be rather emitted (downhop) or absorbed (uphop), the spatial distance is overcome by tunneling.
$R_{ij}$ is equal. This leads to an effect that is called relaxation. When a free polaron is formed after dissociation of a polaron pair or by injection into the device via contacts, these are located in most cases in relative high lying states (in terms of energy). Therefore, they will first of all perform a number of downhops until they arrive at energies where charge carriers, that are already relaxed, occup most sites. For a further transport uphops have to be executed as well as downhops. The energy where the probability for hops (downwards and upwards) is maximized is called transport energy $E_{tr}$. This is one definition of the transport energy and can differ in details from other reported models.

The second way to interpret the charge transport in a disordered system is the trap controlled band transport adopted from amorphous inorganic semiconductors - often referred to as multiple trapping and release model (MTR). The principle of the model is depicted in Fig. 2.5 and can be summarized as follows: Above a certain energy — in inorganic semiconductors named mobility edge, here transport energy — the charge carriers move quasi-freely in a band like in crystalline semiconductors. The transport is hindered by unoccupied states below $E_{tr}$ in which charge carriers can be trapped. These trapped polarons can be detrapped after a certain time, depending on the depth of the trap state, and participate in the transport again until they are retrapped.

Both presented models are microscopic models. In measurements only macroscopic physical values are accessible. The most important physical value concerning charge transport is the mobility $\mu$ which is defined as proportionality factor between the drift velocity $v_d$ and the electric field $F$:

$$v_d = \mu F$$  \hspace{1cm} (2.3)

In organic solar cells the mobility has to fulfill two major requirements: Firstly, the mobilities of electrons in the acceptor phase $\mu_n$ and holes in the donor phase $\mu_p$ need to be balanced. Otherwise a space charge would form up limiting the solar cell performance. Secondly, the mobility values have to be in a special range. At a first glance one might think that higher mobilities would lead to a more efficient charge extraction and therefore a better performance of the solar cell. Nevertheless, if the mobility is too high, the fast charge extraction leads to a low charge carrier density in the device decreasing the open circuit voltage. More details
about the open circuit voltage will be given in section 2.2.3. Macroscopic simulations using typical P3HT:PC\textsubscript{61}BM parameters with balanced mobilities varied from $10^{-14}$ to $10^6 \text{ m}^2/\text{Vs}$ showed that the best solar cells would be obtained for mobilities of $10^{-6} \text{ m}^2/\text{Vs}$\cite{30}. In real P3HT:PC\textsubscript{61}BM devices, a balanced transport is e.g. achieved in an annealed sample with a donor:acceptor weight ratio of 1:1 yielding mobilities of $10^{-8} \text{ m}^2/\text{Vs}$\cite{9}.

The mobility itself is dependent on a number of parameters. The most intuitive is the dependence on the temperature that can be explained best by the above introduced microscopic models. At lower temperatures the probability to perform a hop into a higher lying state decreases which directly lowers the mobility. Also the disorder influences the mobility in that way that a higher disorder means lower mobility. The disorder can be parametrized for instance by the width of the Gaussian DOS \(\sigma\) in the Gaussian disorder model (GDM). Monte-Carlo simulations using the GDM and Eq. (2.2) gave\cite{8}

\[
\mu(T, \sigma, F) \propto \exp\left[-\left(\frac{2\sigma}{3k_B T}\right)^2\sqrt{F}\right],
\]

which includes even a square root dependence on the electric field. Additionally, the charge carrier density in the device can have an impact on the mobility which will be discussed in more detail in chapter\cite{5}

During the transport of the polarons to the respective electrodes recombination can take place, that has a high impact on the functionality of organic solar cells. If a free polaron meets a free polaron of opposite charge, they can annihilate and will be lost for the photocurrent. This process is named bimolecular recombination and will be explained in more detail in section 2.2.2.

(V) Charge Extraction

Finally, after the charge carriers have been transported to the electrodes, they have to leave the device via the contacts to the external circuit to generate power. Therefore, the contacts have to be chosen carefully, otherwise two main problems can occur:

If the charge carriers can only be extracted with a lower rate than they are generated, they will accumulate at the contact and form a space charge. This would result in an s-shaped current–voltage (IV) behavior and low solar cell efficiencies as often reported in literature. In the framework of this thesis solar cells with adjustable s-shaped IV-characteristics could be fabricated. These cells could be modeled using the parameter of a finite surface recombination velocity by Wagenpfahl et al.\cite{117}.

The second problem is the extraction of charge carriers at the wrong electrode, meaning electrons (holes) at the anode (cathode) which are then lost for the photocurrent. This effect was recently investigated by Monte Carlo simulations\cite{105}, where the importance of selective electrodes was highlighted. Selective electrodes can experimentally be achieved by (electron / hole) blocking layers between the active material and the respective electrode.

2.2.2. Recombination Processes

Already mentioned in section 2.2.1 several loss mechanisms occur in working OSC devices. Fig 2.6 illustrates the main recombination processes in inorganic semiconductors: band-to-band
2. Bulk Heterojunction Solar Cells

and trap assisted recombination as well as recombination via interface states. In the band-to-band recombination the free electron in the conduction band (CB) drops back into the valence band (VB), annihilating the electron hole pair. Energy conservation is fulfilled by either emission of a photon or by energy transfer to another electron in the CB (named Auger recombination). In the trap-assisted recombination an electron (hole) is firstly captured by a trap state in the band gap of the semiconductor, in the second step a hole (electron) is captured in the same already occupied trap state leading to recombination of both charge carriers. This mechanism is called Shockley-Read-Hall (SRH) recombination. At the interface of two materials, which can stand for semiconductor–semiconductor as well as semiconductor–metal interfaces, additional energy states can be formed inside the band gap over which the recombination can occur in successive small steps.

Figure 2.6.: Illustration of the recombination mechanisms known from inorganic semiconductors: In the case of band–to–band recombination (left) a free electron in the conduction band (CB) directly recombines with a hole in the valence band (VB). In this case two different processes can occur to fulfill the energy conservation, by emission of a photon or by transferring the energy to a second electron. The latter is a three particle process and known in literature as Auger recombination. Trap–assisted recombination (middle) occurs, when trap states are located in the band gap. This mechanism is often described by Shockley–Read–Hall recombination and tends to be the dominant recombination mechanism in inorganic semiconductors. Recombination over interface states (right) that form at the interface (grains, metal–semiconductor) is the third important mechanism.

Whereas in inorganic crystalline semiconductors the recombination mechanisms are well understood and it is known that SRH recombination is the dominating process, for organic BHJ solar cells things are more complicated. The reason therefore is the phase separation of donor and acceptor that implies that free electrons and free holes can only meet at the DA interface. If two free polarons of opposite charge - not originating from the same exciton - meet and recombine, this process is called nongeminate bimolecular recombination. Recombination of polarons which originate from the same exciton is called geminate and appears to be a monomolecular process. This process was already described above in the framework of polaron pair dissociation and is illustrated in Fig. 2.3 with the rate \( k_r \). Monomolecular means that the recombination rate is directly proportional to the charge carrier density, whereas bimolecular stands for a process where the recombination rate is proportional to the square of the charge carrier density.

Many work was carried out to find the dominating recombination process in organic BHJ SC. Until now, the discussions about this topic are still controversial. Many authors explain their
results by bimolecular recombination, whereas others state the main recombination process is monomolecular, where SRH as well as recombination over interface states is mentioned. The reason for this different opinions could lie in the various measurement conditions that are applied, i.e. temperature, light illumination level, open circuit or short circuit conditions, equilibrium or only quasi–equilibrium, different material systems, purity of the materials and so forth.

In general, without knowing the exact physical mechanism, the influence of recombination gets obvious mathematically by looking at the continuity equation

$$\frac{dn}{dt} = -\frac{1}{q} \frac{dj}{dn} + G - R$$ \tag{2.5}$$

where $q$ is the elementary charge, $dn/dt$ is the time derivative of the charge carrier density, $dj/dn$ the spatial derivative of the current density, $G$ the generation rate and $R$ the recombination rate of charge carriers. In steady–state $dn/dt$ is zero and the rate of extraction of photogenerated charge carriers, which is defined by $dj/dn$ and represents the photocurrent, is directly related to the $G - R$. For $R = 0$, the current density would be

$$j = GqL$$ \tag{2.6}$$

where $L$ is the thickness of the active layer in which the charge carriers are generated. If recombination takes place the current density decreases inevitably.

The recombination rate can be given by the empirical equation

$$R = k_{\lambda}n^{\lambda+1}$$ \tag{2.7}$$

where $k_{\lambda}$ is a constant recombination prefactor and $\lambda + 1$ is the recombination order. Assuming only monomolecular recombination would result in a recombination order of one and one obtains:

$$R = k_r n$$ \tag{2.8}$$

where $k_r$ is the monomolecular recombination rate. Bimolecular recombination with a recombination order of two is often described as Langevin recombination \[59\]. Despite the theory having been developed for ions finding each other by brownian motion in a diluted electrolyte, it has been applied to organic solar cells. The recombination rate is given as

$$R = \gamma (np - n_i^2) \approx \gamma n^2$$ \tag{2.9}$$

where $\gamma$ is the Langevin recombination prefactor, $n$ and $p$ are the electron and hole density, respectively. $n_i$ is the intrinsic charge carrier density which is very low because it is very unlikely to thermally activate charge carriers over a band gap of $\sim 1$ eV, therefore $n_i$ can be neglected. Since the dissociation of an exciton always results in one hole and one electron, it can also be assumed that $n = p$. The recombination prefactor itself is defined by:

$$\gamma = \frac{q}{\varepsilon} (\mu_n + \mu_p)$$ \tag{2.10}$$

with $\varepsilon$ the absolute permittivity of the active layer, $\mu_n$ and $\mu_p$ the mobility of electrons and holes, respectively. The mobility takes into account that the limiting process in bimolecular
recombination is not the recombination of the two free charge carriers itself but the finding of those.

Evaluation of experimental data of OSCs using Langevin theory (Eq. 2.9) showed that the theory overestimates the recombination rate by several orders of magnitude [25, 49]. This can be taken into account by implementing a reduction factor $\zeta$. The discrepancy between Langevin theory and experiment was explained by different approaches. Koster et al. [56] argued that not the fastest charge carriers dominate the recombination rate like in Eq. (2.10) but the slowest ($\gamma_K = \frac{q}{\varepsilon \min(\mu_n, \mu_p)$). Another explanation is given by Adriaenssens et al. [1]. They claim that potential fluctuations in the semiconductor lead to a thermally activated recombination resulting in a reduced recombination prefactor $\gamma_A = \gamma \exp(\Delta E/(k_B T))$, where $\Delta E$ is activation energy. Both approaches can explain a reduced Langevin recombination, unfortunately they cannot reproduce the temperature behavior correctly. To solve this problem Deibel et al. [31] gave another quite simple explanation. In experiments the extracted charge carrier density $n_{\text{extr}} = n = p$ is the average density over the whole active area. This does not take into account the spatial gradient of the electron density $n(x)$ and the hole density $p(x)$ that results from asymmetric contacts. The parameter $x$ is the position in an one dimensional model, where position $x = 0$ is the anode and $x = L$ the cathode. For example, the density of electrons at the anode $n(0)$ is orders of magnitudes lower than at the cathode $n(L)$. This results in the recombination prefactor

$$\gamma_D = \frac{\frac{1}{L} \int_0^L n(x)p(x)dx}{n(x) \cdot p(x)},$$

where the denominator is the spatial average of the charge carrier density and corresponds to measured values from charge extraction experiments. This model can describe the temperature behavior of the recombination prefactor correctly, nevertheless it needs a second factor that is temperature independent to describe the absolute values which has to be investigated further.

Beside monomolecular ($\lambda + 1 = 1$) and bimolecular ($\lambda + 1 = 2$) recombination, several publications reported recombination orders even higher than two [35, 50, 73, 98, 100]. The reason for this is still not understood and will be discussed in more detail in the experimental chapter 5.

### 2.2.3. The Open Circuit Voltage

The open circuit voltage $V_{oc}$ is one of the key parameters of solar cells which directly influences their efficiency. Therefore, it is important to know the limitations and dependencies of $V_{oc}$ in order to optimize the solar cell. Beside this, there is a second aspect making the open circuit voltage interesting to investigate. As can be seen from Eq. (2.5), under open circuit conditions at steady state, i.e. $dj/dx = 0$ and $dn/dt = 0$, the generation rate equals the recombination rate, making this distinguished point in the IV-curve dedicated for recombination investigations.

For the sake of simplicity it is started again with the inorganic p-n junction solar cell where the IV-curve in forward bias is given by the ideal Shockley equation

$$j = j_0 \left[ \exp \left( \frac{V}{n_{\text{id}} k_B T} \right) - 1 \right] - j_{\text{ph}},$$

where $j_0$ is the dark saturation current density, $V$ the applied voltage, $n_{\text{id}}$ the ideality factor and $j_{\text{ph}}$ the (voltage independent) photocurrent density. From Eq. (2.12) it is easy to find a first
expression for the open circuit voltage:

\[ V_{oc} = \frac{n_i d k_B T}{q} \ln \left( \frac{j_{ph}}{j_0} \right) \]  

(2.13)

Unfortunately, Eq. (2.12) is, as the name says, only valid for an idealized system. In a real device a parallel \( R_p \) and serial \( R_s \) resistance influences the IV-behavior, leading to the not ideal Shockley equation:

\[ j = j_0 \left[ \exp \left( \frac{(V - j R_s)}{n_i d k_B T} \right) - 1 \right] - \frac{V - j R_s}{R_p} - j_{ph} \]  

(2.14)

Fig. 2.7(a) displays the dark IV-curve of an organic solar cell using P3HT:PC_{61}BM as active material together with a fit according to Eq. (2.14) \( (j_{ph} = 0) \). Since both curves show a very good accordance it can be stated that the Shockley equation can be applied also to organic solar cells even if the equation was derived for inorganic p-n junctions, at least for \( j_{ph} = 0 \).
2. Bulk Heterojunction Solar Cells

Since the validity of the Shockley equation is not proven for OSC, Koster et al. suggested an alternative approach for $V_{oc}$ [55]. Describing the semiconductors as effective medium with the LUMO of the acceptor (LUMO\text{acceptor}) as conduction band and the HOMO of the donor HOMO\text{donor} as valence band they introduced the quasi Fermi levels of electrons $\varphi_n$ as

$$n = n_i \exp \left( \frac{q (V - \varphi_n)}{k_B T} \right).$$  \hspace{1cm} (2.15)

The same applies to holes with density $p$ and the quasi Fermi level $\varphi_p$. From a drift–diffusion model and the additional assumptions that the generation and (Langevin) recombination of charge carriers takes place completely via charge transfer states, (see section 2.2.2) they found the following expression for $V_{oc}$.

$$V_{oc} = \frac{E_g}{q} - k_B T \varphi_n \ln \left( \frac{(1 - P)N_c^2}{PG} \right),$$  \hspace{1cm} (2.16)

where $E_g$ is the effective band gap ($= |E_{\text{HOMO}\text{donor}} - E_{\text{LUMO}\text{acceptor}}|$), $P$ is the dissociation probability of polaron pairs and $G$ the generation rate of these. $N_c$ is the effective density of states ($N_c^2 = N_e N_h$, $N_e$: electron density of states, $N_h$: hole density of states). Using the continuity equation in a different form than Eq. (2.5) [54]

$$\frac{1}{q} \frac{d}{dx} j_n(x) = PG - (1 - PR) ,$$  \hspace{1cm} (2.17)

where the left side is zero under open circuit conditions, in combination with Eq. (2.9) results in

$$V_{oc} = \frac{E_g}{q} - k_B T \varphi_n \ln \left( \frac{N_c^2}{n p} \right) .$$  \hspace{1cm} (2.18)

This simple dependence of $V_{oc}$ on the charge carrier density was investigated in the framework of this thesis experimentally, where the results for different organic BHJ solar cell configurations are discussed in chapter 4. Eq. (2.18) was also derived by Cheyns et al. [20] for bilayer solar cells in an analytical approach starting from

$$q V_{oc} = |E_{\text{HOMO}\text{donor}} - E_{\text{LUMO}\text{acceptor}}| + BB_{\text{donor}} + BB_{\text{acceptor}} - \varphi_n - \varphi_p$$  \hspace{1cm} (2.19)

In this calculation the band bending of the electrostatic potential ($BB_{\text{acceptor}}, BB_{\text{donor}}$) as well as injection barriers of the contacts ($\varphi_n, \varphi_p$) were taken into account. For bulk heterojunction devices as investigated here, it was found that Eq. (2.18) is only valid for negligible injection barriers. The dependence of $V_{oc}$ on different injection barriers was firstly investigated experimentally by Mihailetchi et al. [74] where they used cathode materials with different work functions. For non-ohmic contacts, i.e. large injection barriers, they found that $V_{oc}$ is controlled by the work function difference of both electrodes in accordance to the metal–insulator–metal (MIM) model [67], whereas for ohmic contacts the open circuit voltage is governed by the effective band gap as described by the above mentioned equations. This was previously experimentally observed by Brabec et al. [15], where different acceptors with varying electron affinities (i.e. LUMO levels) were fabricated with the aim to investigate the influence on $V_{oc}$. For devices using PC$_{61}$BM as acceptor it was shown by comparing the $V_{oc}$ versus the oxidation
level (i.e. HOMO level) of the donor taken from various material systems that the open circuit voltage follows the simple relation $V_{oc} \approx E_g / q - 0.3$ V \[94\].

The main question is, which mechanisms exactly limits the open circuit voltage and if it is possible to eliminate or at least minimize these? In a thermodynamic approach, again for p-n junction solar cells, Shockley and Queisser determined the efficiency limit for a given band gap by a detailed balance approach, the famous Shockley–Queisser limit. In the framework of this calculation they showed that $V_{oc}$ is limited by recombination which they divided into two parts: radiative and non-radiative recombination. For organic solar cells Vandewal et al. \[114\] could isolate the different recombination processes from each other and quantify their influences. Therefore, they started with Eq. (2.13) and related $j_0$ to electro-optical properties \[88\]

$$j_0 = \frac{q}{E_QE_{EL}} \int E_QE_{PV}(E) \phi_{BB}^T dE \ ,$$ (2.20)

where $E_QE_{EL}$ is the external quantum efficiency of the electroluminescence (EL), i.e. the ratio between the number of emitted photons originating from radiative recombination to the number of injected charges. $E_QE_{PV}(E)$ is the photovoltaic external quantum efficiency, meaning the number of extracted charges divided by the number of incident photons, which is dependent on the energy of the incident photon $E$. $\phi_{BB}^T$ is the black body radiation at a temperature $T$, which has a strong decrease with increasing energy at NIR-VIS at room temperature. Therefore, the integral in Eq. (2.20) is mainly determined by the low energy range of the $E_QE_{PV}$, which was shown to be a direct CT state absorption by highly sensitive Fourier–transform photocurrent spectroscopy \[113\]. Using the spectral lineshape of the CT state absorption according to Marcus theory \[37, 72\] for the calculation of the spectral shape of $E_QE_{PV}$ in the CT absorption range one can calculate Eq. (2.20) in a new form which results finally in an expression for $V_{oc}$, where the losses can be parted in those occurring from radiative ($\Delta V_{rad}$) and non radiative recombination ($\Delta V_{nonrad}$):

$$V_{oc} = \frac{E_{CT}}{q} + k_BT \ln \left( \frac{J_{sc}h^3c^2}{q2\pi(E_{CT} - \lambda_0)} \right) + \frac{k_BT}{q} \ln(E_QE_{EL}) \ .$$ (2.21)

$E_{CT}$ is the energy of the charge transfer state and can be set equal to $E_g$, $\lambda_0$ is the reorganization energy as defined from Marcus theory and $f$ is a factor describing the interaction between donor and acceptor. $h$ is Planck’s constant and $c$ the speed of light in vacuum. For different material systems they could extract the parameters directly from EQE and EL measurements or the respective fits of the data and quantify $\Delta V_{rad}$ as well as $\Delta V_{nonrad}$. In a P3HT:PC$_{61}$BM device they calculated for example $\Delta V_{rad} = 0.11$ V and $\Delta V_{nonrad} = 0.42$ V. The overall loss is more than the predicted 0.3 V from Scharber et al. \[94\], nevertheless Eq. (2.21) correctly predicts the light intensity and temperature dependence of $V_{oc}$. In their conclusion Vandewal et al. \[114\] noted that the radiative losses are unavoidable, but the reduction of non-radiative decay paths are important for the development of BHJ solar cells. Unfortunately, no practical details how this can be achieved were proposed.

In recent works by Blakesley et al. \[11, 12\], the dependence of the open circuit voltage on the disorder of the device was discussed for two different density of states models: a Gaussian
2. Bulk Heterojunction Solar Cells

and an exponential distribution. In the case of the Gaussian DOS

\[ g_{h/e}(E) = \frac{N_{h/e}}{\sigma\sqrt{2\pi}} \exp \left[ -\frac{(\pm E - E_{\text{HOMO donor}}/E_{\text{LUMO acceptor}})^2}{2\sigma^2} \right] \quad , \]  

(2.22)

with width \( \sigma \), they calculated an expression similar to Eq. (2.18), in which only the band gap \( E_g \) is reduced by \( \sigma^2/(k_B T) \) to a new effective band gap \( E_{g,\text{eff}} \).

\[ V_{oc} = \frac{1}{q} \left| E_{\text{HOMO donor}} - E_{\text{LUMO acceptor}} \right| - \frac{\sigma^2}{k_B T} + \frac{k_B T}{q} \ln \left( \frac{G}{\gamma N_{h/e}} \right) \]  

(2.23)

This result can be explained by the relaxation of charge carriers in the DOS (see Fig. 2.4). In a DOS with higher \( \sigma \) the charge carriers can relax into deeper states, therefore the oppositely charged charge carriers get in average closer together in energy, leading to a smaller \( E_{g,\text{eff}} \).

\[ g_{h/e}(E) = \frac{N_{t,h/e}}{E_0} \exp \left[ \pm\left(\frac{E - E_{\text{HOMO donor}}/E_{\text{LUMO acceptor}}}{E_0}\right) \right] \]  

(2.24)

under assumption of \( E_0 \gg k_B T \) leads to

\[ V_{oc} = \frac{E_g}{q} + n_{id} \frac{k_B T}{q} \ln \left( \frac{G}{\gamma N_{t,h/e}} \right) \]  

(2.25)

where the ideality factor \( n_{id} \) (in this case \( n_{id} = E_0/(k_B T) \)) is an additional factor reducing \( V_{oc} \). \( N_{t,h/e} \) is the exponential density of states of holes/electrons. In both cases only bimolecular Langevin recombination of free charge carriers is assumed.

To take also into account a recombination process of trapped charge carriers \( n_t \) with free (conductive) charge carriers \( n_c \) \( (n = n_c + n_t) \) Blakesley et al. used the MTR model (see Fig. 2.5) [12]. The open circuit voltage in this case is determined by the effective density \( N \) of free charge carriers at energy \( E_{\text{HOMO donor}}/E_{\text{LUMO acceptor}} \) and the exponential tail of trap states with density \( N_t \) and the characteristic energy \( E_0 \).

\[ V_{oc} = \frac{E_g}{q} + n_{id} \frac{k_B T}{q} \ln \left( \frac{G}{\gamma N_t} \right) \]  

(2.26)

\( n_{id} \) in this case given by \( n_{id} = 2/(1 + (k_B T)/E_0) \).

At last the influence of contacts has to be mentioned. As stated above, injection barriers can have a significant impact on the open circuit voltage, but also the effect of the surface recombination velocity has to be taken into account. The surface recombination velocity \( S \) itself is a parameter describing the charge transfer from the blend to the metal contact and is defined as proportionality factor between the current through the interface \( J \) and the surface charge carrier density \( n \): \( J = qS(n - n_{th}) \). \( n_{th} \) is the thermally activated charge carrier density that can be calculated by thermonic emission theory. In a solar cell four different surface recombination velocities can be defined for the metal-organic interfaces, concerning the contact (anode/cathode) in combination with the charge carrier specimen (electrons/holes). It was recently shown by Wagenpfahl et al. [117] that a reduced \( S \) can cause a reduction of the open circuit voltage. Details about this effect will be given in chapter 7.
2.3. Determination of Power Conversion Efficiency

Despite the legitimate interest in all the fundamental physical processes taking place in OSCs, as described in Section 2.2.1, the most important parameter of a solar cell from a practical point of view is the efficiency $\eta$. It is defined by the ratio of maximal electrical energy taken from the cell $P_{\text{max}}$ to the incident light power $P_L$:

$$\eta = \frac{P_{\text{max}}}{P_L}.$$  \hspace{1cm} (2.27)

$P_{\text{max}}$ can be determined from the current–voltage characteristics of the illuminated solar cell, which is exemplarily shown in Fig. 2.8 for a PTB7:PC$_{71}$BM solar cell together with the power–voltage (PV) graph. At zero voltage the solar cell delivers the maximal current in the 4th quadrant, called the short circuit current $I_{\text{sc}}$, nevertheless the supplied power is zero. Increasing the voltage leads to an increase of the power that can be extracted from the cell until a maximum $P_{\text{max}}$ is reached at $V_{\text{mpp}}$. This point is named maximum power point (mpp), the corresponding current is $I_{\text{mpp}}$. Further increase of the voltage leads to a reduction of the extracted power until it drops again to zero when the current gets zero. The voltage at this point is called the open circuit voltage $V_{\text{oc}}$ as discussed above. The third important parameter beside $V_{\text{oc}}$ and $I_{\text{sc}}$ is the fill factor $FF$ which is defined as

$$FF = \frac{I_{\text{mpp}}V_{\text{mpp}}}{I_{\text{sc}}V_{\text{oc}}}.$$  \hspace{1cm} (2.28)

---

$^{1}$Poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b’]dithiophene-2,6-diy1][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediy]]
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and describes the "squareness" of the diode in the 4th quadrant. The efficiency can now be calculated by

$$\eta = \frac{I_{mpp}V_{mpp}}{P_L} = \frac{I_{sc}V_{oc}FF}{P_L}$$  \hspace{1cm} (2.29)

To account for different active areas $A$ generating $I_{sc}$, it is common to use the short circuit current density $j_{sc} = I_{sc}/A$. In this case the absolute light power $P_L$ has to be replaced in Eq. 2.29 by the light power density $\Phi_L = P_L/A$.

Making it possible to compare the efficiencies of different research groups it is important to define standard testing conditions (STC) under which the IV-characteristics are measured. These STC are defined by the International Electrochemical Commission in the norm IEC60904-4 and are listed in Table 2.1.

<table>
<thead>
<tr>
<th>criteria</th>
<th>value</th>
</tr>
</thead>
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<tr>
<td>temperature</td>
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</tr>
<tr>
<td>irradiation power density</td>
<td>100 mW/cm$^2$</td>
</tr>
<tr>
<td>irradiation spectra</td>
<td>AM1.5g after ASTM G173-03</td>
</tr>
</tbody>
</table>

Table 2.1.: The standard testing conditions as defined by the International Electrochemical Commission.

In the used setup no temperature controlling was possible which implies that all cells were measured at room temperature. The most probable reason for wrong determination of the efficiency is the AM1.5g (ASTM G173-03) standard illumination spectra, which cannot be exactly reproduced by commercial solar simulators. Fig. 2.9 displays the spectra of the used commercial solar simulator using AM1.5g filters together with the AM1.5g spectra for comparison. One can see a spectral mismatch that has to be taken into account for every measurement. This can be achieved by two different methods, which ensure that the solar simulator can be considered as equivalent to 100 mW/cm$^2$ of AM1.5g: the direct and indirect method.

The more simple method is the indirect method. Here we only need to measure the external quantum efficiency EQE over the whole wavelength range in which the solar cells absorbs and calculate the theoretical short circuit density $j_{sc}$ under any desired spectrum, in our case the AM1.5g spectrum ($\Phi_{AM1.5g}$), by

$$j_{sc,AM1.5g} = \frac{q}{hc} \int_0^\infty \lambda \Phi_{AM1.5g}(\lambda)EQE(\lambda) d\lambda,$$  \hspace{1cm} (2.30)

where $\lambda$ is the wavelength. To calibrate the solar simulator one has only to change the light intensity of the solar simulator until the measured short circuit current density matches the determined $j_{sc,AM1.5g}$. It has to be noted that the EQE has to be measured under bias light in the range of 1 sun to take into account recombination effects at short circuit conditions. For optimized solar cells, e.g. P3HT:PC$_{61}$BM, the recombination effects at short circuit are negligibly small and Eq. 2.30 can be used even for EQEs measured without bias light illumination.

The more complex method is the direct method. Here the EQE of the solar cell that has to be tested ($EQE_{tc}$) as well as from a calibrated reference cell ($EQE_{rc}$) has to be known together
2.3. Determination of Power Conversion Efficiency

Figure 2.9.: AM1.5g solar spectrum in comparison to the spectrum of the solar simulator measured with a calibrated spectrometer (getSpec 2048) ranging from 300–1100 nm. The discrepancy elucidates the importance of a correct calibration of the solar simulator.

with the spectrum of the solar simulator $\Phi_{ss}$. With all these data one can calculate the mismatch factor $M$ by

$$M = \frac{\int_0^\infty \lambda \Phi_{AM1.5g}(\lambda) EQE_{rc}(\lambda) d\lambda}{\int_0^\infty \lambda \Phi_{ss}(\lambda) EQE_{rc}(\lambda) d\lambda} \frac{\int_0^\infty \lambda \Phi_{ss}(\lambda) EQE_{tc}(\lambda) d\lambda}{\int_0^\infty \lambda \Phi_{AM1.5g}(\lambda) EQE_{tc}(\lambda) d\lambda}$$  \hspace{1cm} (2.31)

To calibrate the solar simulator, the short circuit current $I_{sc, rc, ss}$ of the reference cell under the solar simulator has to be adjusted to

$$I_{sc, rc, ss} = \frac{I_{sc, rc, AM1.5g}}{M}$$  \hspace{1cm} (2.32)

where $I_{sc, rc, AM1.5g}$ is the short circuit current of the reference cell under AM1.5g spectrum. The advantage of this method is that only the spectral shape of the EQE is important, not the absolute values, which allows to use EQE measurements without bias light even for solar cells, in which recombination does affect the short circuit current.
2. Bulk Heterojunction Solar Cells
3. Experimental

In this section the experimental technique mainly used in this thesis — a charge extraction method — will be introduced. Also, the standard sample preparation, starting from the ITO\(^1\) coated glass substrate and the raw materials to the final solar cell will be presented as well as a short description of the used materials.

3.1. Charge Extraction Measurements

To determine the charge carrier density at open circuit conditions a charge extraction (CE) method was used. Its working principle is depicted in Fig. 3.1, the scheme of the setup is shown in Fig. 3.2.

Before the charge extraction measurement can be performed, the open circuit voltage of the solar cell under a specific illumination level has to be determined. Therefore, the solar cell is illuminated constantly by a high power light emitting diode (LED) with 10 W electrical power (Seoul P7 Emitter) and the current–voltage characteristics are measured using a Keithley 2602 source–measure unit.

The actual charge extraction measurement consists of two different time periods. In the first, the LED is on and charge carriers are generated in the solar cell. At the same time a double pulse generator (Agilent 81150A) applies the previously measured $V_{oc}$ to the solar cell. In steady state conditions no current flows in the external circuit and all generated charge carriers recombine ($G = R$). At $t_0$ the LED is switched off by shorting the constant current source (Keithley 2602) with a high power transistor triggered by the double pulse generator. To synchronize the turning off of the LED with the short-circuiting of the solar cell ($V=0$ V) one has to take into account the transistor switching time of 215 ns. The resulting current is preamplified by a FEMTO DHPCA-100 current-voltage amplifier before the signal is detected with an Agilent DSO 90254A digital storage oscilloscope. To obtain the extracted charge $Q_{extr}$ one has to integrate the current signal $I(t)$ over time,

\[
Q_{extr} = \int_{t_0}^{\infty} I(t) dt \quad .
\]

(3.1)

In reality, it is not possible to integrate to infinity but to a specific time $t_{end}$ where $I(t_{end})$ is approximately zero and no difference to the signal noise can be detected, where $t_{end}$ depends on the material system and the temperature. As $Q_{extr}$ is dependent on the volume $V_s$ of the solar cell, it is preferable to calculate the extracted charge carrier density $n_{extr}=Q_{extr}/(V_s q)$, where the volume $V_s$ is given by the area of the active layer $A$ and its thickness $d$. The active layer area is defined as the overlap of both electrodes and was determined with an optical microscope (Carl Zeiss Axiotech vario 25 HD), the thickness was measured with a mechanical profilometer (Veeco Dektak 150). To calculate the real amount of photogenerated charge carriers in the device at $V_{oc}$,

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\(^{1}\)indium tin oxide
3. Experimental

Figure 3.1: Scheme of working principle of the charge extraction measurement. On the left side of the scheme ($t < t_0$) the LED is on and generates continuously charge carriers in the solar cell. Additionally, a specific voltage, the open circuit voltage $V_{oc}$, corresponding to the light intensity is applied to the solar cell. In steady state this leads to $I=0$ A implying that all generated charge carriers recombine in the device. At $t_0$ the LED is switched off and the solar cell is short-circuited ($V=0$ V) resulting in a current, which gives, when integrated over time, the number of extracted charges.
3.1. Charge Extraction Measurements

![Figure 3.2](image)

**Figure 3.2.** Setup used for charge extraction measurements. 1: double pulse generator for applying $V_{oc}$ and the triggering of the LED and the oscilloscope 2: oscilloscope to record the extraction signal 3: constant current source for LED 4: transistor to switch the LED on or off 5: current voltage preamplifier 6: LED 7: six position filter wheel 8: cryostat containing the solar cell.

By varying the illumination intensity and temperature of the solar cell, it was possible to influence $V_{oc}$ and the corresponding charge carrier density. To control the temperature, all charge extraction measurements were performed in a closed cycle cryostat (Janis CCS 550) with He as contact gas. Inside the cryostat the temperature was checked with two sensors and two heaters working against the permanent cooling of the compressor. One heater-sensor pair was located near the device, the other near the coldhead, both were controlled by a Lakeshore 332 cryogenic temperature controller.

The calibration of the light intensity is a complicated issue since the LED provides a heavily mismatched spectrum to the AM1.5g spectrum ranging only from 400 to 700 nm, with a sharp peak in the blue at 450 nm, resulting in a cold white color with a correlated temperature color of 6300 K. With respect to this high spectral mismatch, the light intensity was defined as $P_L=1$ sun when the solar cell supplies the same short circuit current as obtained from the efficiency determination under the mismatch corrected spectra delivered by a solar simulator. To illuminate the test cell with lower light intensities it is necessary to correlate the constant current driving the LED $I_{LED}$ with the supplied light intensity $P_x$. The calibration was performed with a silicon solar cell (Hamamatsu S1133) which exhibits a linear response of the short circuit current $I_{sc,S1133}$ on the incident light intensity $P_x$. The measured $I_{sc,S1133}(I_{LED})$ dependence together with $P_x \propto I_{sc,S1133}^x$ ($x=1$) results in $P_x(I_{LED})$. Using the fixed current defining $P_L=1$ sun now allows to illuminate the test solar cell with various intensities in fractions of suns. To reach low...
intensities it is not possible to just reduce the current to any desired $I_{LED}$ because at low currents the LED starts to jitter. Therefore, neutral density filters (Thorlabs ND) in a six position filter wheel (Thorlabs FW102C) were used to reduce the light intensity. This complicates the calibration because the given values of the optical densities of the filters are only mean values over a special wavelength range and their transmission is again wavelength dependent. Therefore, it is not correct to supply for instance a special $I_{LED}$ to illuminate the cell with $P_L=1$ sun and to use filter with an optical density of 1 and define the light intensity on the solar cell as $P_L=0.1$ sun. To calibrate the light intensity as exactly as possible, the following procedure was performed for every solar cell before it was measured:

1. Find $I_{LED}$ to match the short circuit current $I_{sc}$ of the cell to the measured value under the calibrated solar simulator without using a neutral density filter and define the light intensity as $P_L=1$ sun.

2. Calculate $I_{LED}$ that is necessary to obtain $P_L=0.3$ suns from the calibration curve.

3. Measure $I_{sc}$ under $P_L=0.3$ suns.

4. Turn the filter wheel to the position with the next lowest optical density.

5. Find $I_{LED}$ to match the short circuit current $I_{sc}$ of the cell to the measured value under $P_L=0.3$ sun, to get a calibration for this filter.

6. Calculate $I_{LED}$ necessary for $P_L=0.3 \times 0.3$ suns.

7. Repeat steps 3. to 6. to get a $P_L(I_{LED})$ calibration for every single filter position.

After this more technical part of the section, the focus will now be set on the two physical effects which have to be taken into account when calculating the (real) charge carrier density stored in the device at open circuit conditions in steady state: the above mentioned capacitance effect and the recombination of charge carriers during the extraction.

**Capacitance Effect**

A solar cell can not only be considered as a diode but also as a parallel-plate capacitor with the two electrodes as plates and the active material as dielectric. Since the relative dielectric constant ($\varepsilon_r \sim 3-4$) of organic materials is small and the active material is thin ($d \sim 100-300$ nm), the capacitance $C$ of the device is relatively high and can be calculated by

$$C = \varepsilon_r \varepsilon_0 \frac{A}{d}. \quad (3.2)$$

Before the solar cell is short circuited in the charge extraction measurement it can be described as a loaded capacitor where the charge stored on the plates $Q_{plates}$ is given by $C$ and the applied $V_{oc}$,

$$Q_{plates} = C \cdot V_{oc}. \quad (3.3)$$

This charge contributes additively to the charge extraction signal when the capacitor is discharged at $t_0$ and must therefore be subtracted from $Q_{extr}$. In principle it is possible to calculate $Q_{plates} = \varepsilon_r \varepsilon_0 \frac{A}{d} V_{oc}$ using literature values of $\varepsilon_r$ and the measured $A$ and $d$, but all these values
3.1. Charge Extraction Measurements

can be imprecise and for some material systems no literature values of $\varepsilon_r$ are available. Fortunately, the above described setup allows to measure the capacitance. This can be achieved by performing a charge extraction measurement by applying a small voltage in reverse bias ($V_{appl} < 0$ V) in the dark without using a LED. At $t_0$ the solar cell is short-circuited ($V=0$ V). The obtained signals for different voltages ranging from $V_{appl}=-0.05$ to $-0.25$ V can be seen in Fig. 3.3 (a).

Figure 3.3.: Charge extraction signals, when applying only small voltages $V_{appl}$ to the test cell in reverse bias in the dark without using the LED (a). Here the solar cell acts as a capacitor. At this voltages only a negligible amount of charge carriers is injected into the solar cell which can be seen in the dark IV–curve, the triangles indicate the used voltages (b). The amount of charges stored on the plates as result of the integration of the CE signals shown in (a) as function of $V_{appl}$ shows a linear dependency of $Q_{plates}$ on $V_{appl}$, where the slope yields directly the capacitance (c).
In this voltage range the diode is reversed-biased and only a negligible current is flowing as can be seen from the dark IV curve (Fig. 3.3b)). This implies that only an insignificant amount of charge carriers is injected into the active material and the number of charges stored on the electrodes $Q_{plates}$ can be obtained by integrating the signal over time. Plotting $Q_{plates}$ over the applied absolute voltage (Fig. 3.3c)) results in a linear dependence as predicted by Eq. (3.3). From the fit one can determine $C$ of the solar cell.

Another issue, which will be important when calculating the recombination of charge carriers during the extraction, is that the transients of the different signals for the capacitance determination only vary in height. In Fig. 3.3(a) the signal of $V_{appl}$=−0.15 V was multiplied by a factor of 4/3 and matches perfectly the signal of $V_{appl}$=−0.2 V. This implies the possibility to scale the capacitance signal to every applied voltage.

Recombination during Extraction

The first step to calculate the recombination losses during the charge extraction is to subtract the part of the signal originating from the capacitance from the charge extraction signal. This is for example done in Fig. 3.4(a) for a P3HT:PC$_{61}$BM cell under $P_L$=1, 0.1 and 0.017 suns illumination at 300 K. It becomes obvious from the graph that the influence of the capacitance is higher for lower light intensities. Integration of the obtained signal leads to the charge carrier density stored in the device at any time $n_{dev,0}(t)$, which is given by:

$$n_{dev,0}(t) = n_{extr,0} - n_{extr,0}(t) \tag{3.4}$$

$n_{extr,0}$ is equal to $(Q_{extr} - Q_{plates})/V$ as described above. $n_{extr,0}(t)$ and $n_{dev,0}(t)$ are shown in Fig. 3.4(b) for $P_L$=1 sun.

The next step is to discretize the time $t$ to $t_i$, here a step size of $\Delta t = t_{i+1} - t_i$=1 ns was used. The recombination losses $n_{loss}(t_i)$ in the time interval from $t_i$ to $t_{i+1}$ is then given by:

$$n_{loss}(t_i) = R(n_{dev,0}(t_i)) \cdot n_{dev,0}(t_i) \cdot \Delta t \tag{3.5}$$

where $R$ is the recombination rate, which was determined by transient photovoltage / transient photocurrent measurements performed on the same device. It has to be noted that Eq. (3.5) is only valid when the difference between $n_{dev}(t_i)$ and $n_{dev}(t_{i+1})$ is small, which was ensured by using a narrow discretization. To calculate the whole recombination losses one has to sum up all $n_{loss}(t_i)$,

$$n_{loss,j+1}(t) = \sum_{t_i=0}^{t} R(n_{dev,j}(t_i)) \cdot n_{dev,j}(t_i) \cdot \Delta t \tag{3.6}$$

Together with

$$n_{dev,j+1}(t) = (n_{dev,0}(t) + n_{loss,j+1}(t)) \tag{3.7}$$

one can calculate the real $n_{dev}(t)$ by applying Eq. (3.6) and (3.7) iteratively, where $j$ is the iteration step. The routine has to be continued until $n_{dev,j+1} - n_{dev,j} \to 0$. This is achieved in most cases after 4-5 iteration steps, nevertheless 10 steps were routinely performed.

The results for $n_{loss,10}$ as well as $n_{dev,10}$ are shown in Fig. 3.4(b). The recombination losses in this case ($P_L$=1sun, $T$=300 K) were 6.1 %. For lower light intensities the losses decrease to
3.1. Charge Extraction Measurements

Figure 3.4.: Charge extraction measurements for different illumination levels. The raw signals (dashed lines) were corrected (solid lines) by their capacitive contribution (dotted lines). The black line is a capacitance signal measured at V=-0.15 V (a). The influence of recombination during a charge extraction measurement is shown exemplary for 1 sun illumination. The red dashed line shows the integral charge density extracted from the device where no recombination was taken into account, the red solid line is the corresponding stored charge carrier density. The black lines are corresponding data, where recombination during extraction was taken into account using the iteration described in the text. The blue line shows the recombination losses (b).

1.1 % for $P_L=0.1$ suns and 0.3 % for $P_L=0.017$ suns. At lower temperatures the recombination rate drops which implies that the recombination losses at lower temperature will decrease even if the extraction time increases.

Since most measurements were performed in the range of illumination intensities of 1 sun or only a bit higher, recombination losses can be neglected. Therefore, all data shown in the results are not corrected for recombination losses: their calculation is very time consuming and do not change the main statements of this work. Thus, all presented charge carrier densities were calculated by $(Q_{extr} - Q_{plates})/(V_s q)$. 

---

1.0
0.8
0.6
0.4
0.2
0.0
charge carrier density $[x \times 10^{17} \text{cm}^{-3}]$

10^{-7} 2 4 6
10^{-6} 2 4 6
10^{-5} 2 4 6
10^{-4}
time [s]

ndev,0    
nextr,0    
ndev,10
nextr,10
nloss,10
3. Experimental

3.2. Sample Preparation

The working principles of organic BHJ solar cells were discussed in chapter 2 from a physical point of view. In this part, the preparation of solar cells like those used in this work is described from a technical aspect. Deviations from the here presented standard routine will be given in the respective sections.

The standard organic BHJ SC device configuration is shown schematically in Fig. 3.5. As a transparent electrode indium tin oxide (ITO) coated on glass is used, which is the most important transparent conductive oxide (TCO) in the field of organic SCs or LEDs. ITO was purchased from PGO (Präzisions Glas & Optik GmbH, CEC010S) with a sheet resistance lower than $10 \ \Omega / \square$). The ITO layer is around 180 nm thick, the substrate consists of 1.1 mm thick HQ–float glass and a 25 nm thick SiO$_2$ passivation layer to prevent Na to diffuse into the ITO. In order to process more than one solar cell per substrate and to be able to define the area of a solar cell, a lithography based on wet chemical etching was performed to achieve two separate 3 mm thick ITO stripes.

Before starting with the lithography, the ITO coated glass substrates were cleaned by

- mechanical cleaning with soap water
- at least 10 min in soap water in an ultrasonic bath (USB)
- thoroughly rinsing under deionized water and drying
- at least 10 min in acetone in an USB
- at least 10 min in isopropyl alcohol in an USB
- drying by a nitrogen gas flow

![Figure 3.5.](image-url) Scheme of an organic solar cell as used in this work.
The lithography itself was done by the following steps:

- 10 min heating of the substrates at 120 °C on a hot plate
- spin coating of the photoresist (AZ 1518, MicroChemicals) with 3000 rpm, 1 s acceleration for 60 s
- annealing for 50 s at 100 °C
- UV illumination through a shadow mask for 59 s
- developing of the photoresist (AZ 351B, MicroChemicals): $2 \times$ AZ 351B:H$_2$O=1:3 for 30 s
- removing of developer with deionized water
- annealing for 2 min at 120 °C
- etching of the ITO with H$_2$O:HCl:HNO$_3$=12:12:1 for 13 min in an USB
- removing of acid residues with deionized water
- removing of photoresist with acetone

After the lithography was finished, the substrates were treated by another cleaning run as described above.

On top, a thin layer (~40 nm) of PEDOT:PSS\textsuperscript{1} (Heraeus CLEVIOS\textsuperscript{TM} P VP Al 4083) was spin coated (3000 rpm, 1 s acceleration, 60 s) as a hole transport layer (HTL). Afterwards the substrates were transferred into a nitrogen filled glovebox to avoid contact of the solar cells with oxygen. Here the PEDOT:PSS coated substrates were first heated at 130 °C for 10 min to remove residual water.

The active layer was spin coated from a solution of the donor–acceptor blend. To obtain a blend solution the respective materials were dissolved in an organic solvent such as chlorobenzene in a specific concentration. In most cases the single materials were dissolved in separate solutions for several hours and blended before application, in some cases the donor–acceptor blend was dissolved in one solution. The material concentration as well as the spin speed were used as parameters to obtain the favored film thickness. After spin coating of the active layer an optional annealing step was applied. This temperature treatment can beneficially influence the morphology and enhance the performance of the solar cells, especially of those consisting of P3HT as donor material. In contrast, in other material systems the heating can influence the solar cell performance negatively. Wether or not a heating step was applied will be stated in the specific sections.

Without breaking the nitrogen atmosphere the substrates were transferred into an evaporation chamber where the metal contacts were thermally evaporated on top of the active layer through a shadow mask. The base pressure was lower than $1 \times 10^{-6}$ mbar. The contacts consisted of a 3 nm thin calcium (Ca) interlayer and a 100-120 nm thick aluminum (Al) layer.

The finished solar cells were directly measured under a solar simulator to determine their efficiencies before they were transferred into the cryostat to perform the charge extraction measurements.

\textsuperscript{1}poly(3,4-ethylenedioxythiophene):(polystyrenesulfonate)
3. Experimental

3.3. Materials

In the field of OPV a vast range of different donor and acceptor materials with different physical and chemical properties exists. In the following the relevant properties of the materials used in this work are described, starting with the donor materials before going on to the acceptors.

Donor Materials

In the framework of this thesis many materials were utilized as donors, but only two polymers are mentioned in the experimental part: P3HT and PTB7. Their structural formulas are illustrated in Fig. 3.6. These two materials are polymers, as most donors in OPV are, but also different solution processable molecules such as cyanine salts can be used. The structural formulas of two cyanine salts which act as donors in combination with PC\textsubscript{61}BM are shown in Fig. 3.7 [13].

![Structural formulas of the donors used in this work, P3HT (a) and PTB7 (b).](image)

**Figure 3.6.** Structural formulas of the donors used in this work, P3HT (a) and PTB7 (b).

![Cyanine salts used as donors, which were characterized in BHJ SC in combination with PC\textsubscript{61}BM as acceptor. Not discussed in this thesis, but published in cooperation with N. Martin et al. [13].](image)

**Figure 3.7.** Cyanine salts used as donors, which were characterized in BHJ SC in combination with PC\textsubscript{61}BM as acceptor. Not discussed in this thesis, but published in cooperation with N. Martin et al. [13].
P3HT is the best investigated donor material since it was holding the efficiency record in OPV for a long time in combination with PC$_{61}$BM as acceptor (see below). Performing an internet search on web of knowledge.com with the keyword "P3HT" results in approximately 4,364 publications (as of 14. October 2011). Together with PC$_{61}$BM 1033 articles were published in the time range from 2002 to 2010 [24]. As a result many fundamental properties of this polymer are known, e.g. the energetics [27] and transport properties. The mobility is in the range of $10^{-4}$ cm$^2$/Vs in diode configuration measured by time of flight measurements [21] and can reach values of up to 0.1 cm$^2$/Vs in a field effect transistor [102]. The reason for these relatively high mobilities is that P3HT can form crystalline phases, as found by X-ray diffraction (XRD) (see Fig.3.8(a)). Also the density and energetic depth of trap states, which have a high impact on the transport of charge carriers, is known [91]. The major drawback of P3HT with respect to solar cells is the limited absorption in the visible range with an absorption edge at $\sim 650$ nm which allows to harvest only around 20% of the solar photons. P3HT used in this work was purchased from Rieke Metals, Inc. (BASF Sepiolid P200) and was used without further purification. The average molecular weight was 20-40 kDa, the regioregularity, which describes the head to tail configuration, was higher than 95% [47].

PTB7, in contrast to P3HT, is a very new material which was presented 2010 and was the first material reaching power conversion efficiencies higher than 7% in combination with PC$_{71}$BM as acceptor [63]. Optimization of the device preparation yielded even 8.37% [43], which makes it the best commercially available donor material. Up to date, only few publications about the properties of this material exist. The advantage in the view of solar cell performance in contrast to P3HT is the higher absorption range of up to 750 nm. Remarkable is the fact that the material is completely amorphous and does not show any crystallinity in the XRD spectrum (Fig. 3.8). PTB7 was purchased from 1–material.

**Acceptor Materials**

Fullerene derivates are commonly used in OPV as acceptor molecules due to various advantageous properties. The most important is the relative high electron affinity in comparison to the donors, which is responsible for the effective dissociation of excitons and the separation of the polaron pairs. Another beneficial property is the transport of the charge carriers, since the fullerene derivatives show mobility values in the same range as the donor materials which prevent that space charges build up in the active layer. A more practical property is the solubility in common organic solvents such as chlorobenzene to fabricate the solar cells from solution which is achieved by the side chain of the fullerene. All these three main requirements are fulfilled by the most famous acceptor material PC$_{61}$BM (Fig. 3.9(a)), which was used in most solar cells discussed in this thesis. It has a LUMO level of -3.72 eV [36], a solubility level in chlorobenzene of 25 mg/ml at room temperature [14] and relative high mobility values of $2 \times 10^{-3}$ cm$^2$/Vs measured in diode configuration [75].

To improve the solar cell efficiency a lot of research is focused on the synthesis of new acceptors. PC$_{61}$BM for example exhibits only a low absorption of photons in the solar spectrum and therefore contributes only very little to the photocurrent of the solar cells. So one important research topic is the creation of new acceptors which absorb in a supplementary spectral range to the donor material to increase $j_{sc}$. PC$_{71}$BM (Fig. 3.9(b)) for example shows similar properties (LUMO, mobility) to PC$_{61}$BM, but additionally absorbs photons in the visible spectra [14], which supports the generation of excitons and therefore increases the photocurrent.
3. Experimental

Figure 3.8: XRD spectra of pure P3HT and PTB7 films (a) as well as P3HT:PC_{61}BM and PTB7:PC_{71}BM blends (b). The signature at \( \sim 5.4^\circ \) in the P3HT and P3HT:PC_{61}BM spectra indicates the crystallinity of the P3HT phase, whereas no signature in the PTB7 and PTB7:PC_{71}BM spectra shows that these films are completely amorphous. The broad peak in the range 15-40\(^\circ\) results from the glass substrate.

It is often used in low bandgap materials such as PTB7. The second hot topic is shifting the LUMO level to higher values to increase the open circuit voltage of the system, which reduces the driving force \( \Delta G \) for the charge carrier generation and can again have a negative impact (see section 2.2.1(III)). Here a trade-off between \( V_{oc} \) and \( j_{sc} \) has to be found. In this work bisPC_{61}BM (Fig. 3.9(c)), a fullerene derivative which consists of two side chains instead of one as in PC_{61}BM, having a considerably higher LUMO level of -3.56 eV [36] was used. A new class of fullerene derivates are the Indene-C_{60} adducts [42]. Thereby, the bisadduct ICBA\(^I\) (Fig. 3.9(d)) fulfills the endeavor for high open circuit voltages and provided an efficiency record for P3HT based solar cells [119] and was also used in this work.

Not only the side chains of the fullerenes can be varied to change the acceptor properties, but also two fullerenes can be linked together. To investigate such acceptors, C_{60}–C_{60}, C_{60}–C_{70} and C_{70}–C_{70} homo- and heterodimers (Fig. 3.10) were characterized in solar cells in combination with P3HT as donor in collaboration with the work group of N. Martin [32]. The results are not discussed in this thesis, but mentioned here for the sake of completeness. For details, see Ref. [32].

\(^I\)Indene-C_{60} Bisadduct
3.3. Materials

Figure 3.9.: Structural formulas of the acceptors used in this work: PC$_{61}$BM (a), PC$_{71}$BM (b), bisPC$_{61}$BM(c) and ICBA (d).

Figure 3.10.: Fullerene homo- and heterodimers (C$_{60}$–C$_{60}$ (a), C$_{60}$–C$_{70}$ (b) and C$_{70}$–C$_{70}$ (c)) used as acceptors, which were characterized in BHJ SC in combination with P3HT as donor. Not discussed in this thesis, but published in cooperation with N. Martin et al. [32].
4. Relation of Open Circuit Voltage to Charge Carrier Density in Organic Bulk Heterojunction Solar Cells

4.1. Introduction

The open circuit voltage is one of the key parameters to optimize organic bulk heterojunction solar cells as already mentioned in section 2.3. A linear dependence of $V_{oc}$ on the energy difference $E_g$ between the acceptor LUMO$_{acceptor}$ and polymer HOMO$_{donor}$ was already shown in various publications [15]. This effective band gap $E_g$ was later attributed to the energy of the charge transfer state [29, 114] and is determining the maximum value of the magnitude $qV_{oc}$ that can be achieved in a particular system. This upper limit is reduced by surface [87] and bulk recombination [114] by 0.3 to 0.5 eV [94, 113]. Choosing the right electrode materials can minimize the influence of the surface losses.

As already described in section 2.2.3 Koster et al. derived an analytical equation for $V_{oc}$ based on Shockley, drift and continuity equation under assumption of Langevin recombination resulting in Eq. (2.16). Transforming this equation to Eq. (2.18) yields a direct connection of the open circuit voltage to the inherent charge carrier density in the device at open circuit conditions. Under assumption of a constant effective density of states $N_c$ for a specific donor–acceptor blend, a higher steady-state charge carrier concentration leads to an increase of $V_{oc}$. In principle, there are two ways to get a higher equilibrium charge carrier density in the device at open circuit conditions: a higher generation rate of polarons and/or a lower recombination rate. Internal quantum efficiency values close to 100% were reported for P3HT:PC$_{61}$BM [95] at short circuit conditions. In addition, photocurrent measurements on the same material system showed, that the polaron pair dissociation yield $P$ at room temperature has only a weak voltage dependence in the range between short circuit and open circuit [28, 66]. Therefore, the gain in carrier concentration at a constant light illumination by increasing the generation rate and thus $V_{oc}$ is very limited. This leads to the second and more promising point: the influence of nongeminate recombination. Reducing the recombination rate will increase the steady state polaron concentration and thus the open circuit voltage.

In this section the open circuit voltage is investigated temperature and illumination dependent together with the corresponding charge carrier density $n$ in the device. It is shown that, depending on temperature, the $V_{oc}$ is mainly determined either by the effective bandgap of the donor–acceptor blend or by the metal–insulator–metal model.

1Parts of this chapter have been published in Rauh et al. Appl. Phys. Lett., 98, 133301 (2011) [90]
4.2. Experimental

In this investigation three different types of solar cells were processed as described in section 3.2. Two devices had an active layer consisting of P3HT as donor blended with PC$_{61}$BM as acceptor in the ratio of 1:0.8. For one solar cell a Ca (3 nm) / Al (100 nm) cathode was used, for the other a Cr (3 nm) / Al (100 nm) cathode, known to form an injection barrier. For the third solar cell bisPC$_{61}$BM was used as acceptor in a ratio of 1:1 with P3HT and a Ca (3 nm) / Al (100 nm) contact. The active layers were spin coated from chlorobenzene solutions to gain an active layer thickness for all three cells of about 200 nm. All samples were annealed for 10 min at 130 °C before the metal contacts were thermally evaporated.

All temperature dependent current–voltage characteristics and charge extraction measurements were performed in a cryostat as described in section 3.1.

4.3. Results and Discussion

The IV–characteristics in dark as well as under 1 sun illumination using the solar simulator for all three devices measured in a nitrogen filled glovebox are shown in Fig. 4.1. The extracted parameters $j_{sc}$, $V_{oc}$, FF together with the overall efficiency are summarized in table 4.1.

![Figure 4.1. IV–characteristics of all three devices in dark (dotted lines) and under 1 sun illumination (solid lines). The respective parameters are given in table 4.1.](image)

<table>
<thead>
<tr>
<th></th>
<th>$j_{sc}$ [mA/cm$^2$]</th>
<th>$V_{oc}$ [V]</th>
<th>FF [%]</th>
<th>η [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC$_{61}$BM (Ca/Al)</td>
<td>8.4</td>
<td>565</td>
<td>61</td>
<td>2.9</td>
</tr>
<tr>
<td>PC$_{61}$BM (Cr/Al)</td>
<td>7.6</td>
<td>430</td>
<td>63</td>
<td>2.1</td>
</tr>
<tr>
<td>bisPC$_{61}$BM (Ca/Al)</td>
<td>5.2</td>
<td>690</td>
<td>64</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Table 4.1.: Parameters extracted from the IV–characteristic (Fig. 4.1)
4.3. Results and Discussion

In Fig. 4.2, temperature and illumination dependent $V_{oc}$ and the corresponding charge carrier densities $n$ are shown for the P3HT:PC$_{61}$BM solar cell with Ca/Al contacts. Similar dependencies of $V_{oc}$ have been previously reported for MDMO-PPV:PC$_{61}$BM [33]. Two different temperature ranges can be observed. In the high temperature regime (HTR) between around 150 to 300 K, the open circuit voltage is decreasing with increasing temperature as well as the extracted charge carrier density. The low temperature regime (LTR), ranging from 50 to 150 K, shows an increase of $n$ stored in the device with raising temperature and a saturation effect for the $V_{oc}$ at high light intensities. For lower light intensities an increase of open circuit voltage with increasing temperature is observed. The illumination level was varied more than two orders of magnitude from 0.01 to 3.2 suns leading to an increase of both $n$ and $V_{oc}$. At 300 K the extracted charge carrier density increases only by a factor of $\sim 10$ despite the more than 300-fold increase in illumination. This nonlinear behavior can be explained by the dependence of the recombination rate on the charge carrier density $R = k_{\lambda} n^{\lambda+1}$, where $\lambda$ was shown to be in the range of 1.3 to 1.75 for P3HT:PC$_{61}$BM solar cells at room temperature (see chapters 5, 6 or Ref. [35]).

The temperature dependent open circuit voltages for all investigated solar cells at 1 sun are

---

Figure 4.2: Temperature dependent $V_{oc}$ (a) and corresponding charge carrier density (b) for different illumination levels ranging from 0.01 to 3.16 suns of an annealed P3HT:PC$_{61}$BM solar cell. The dotted lines in (a) indicate the fit using Eq. (2.18) as fit function.
Figure 4.3.: Temperature dependent $V_{oc}$ behavior for three different solar cells. PC$_{61}$BM and bisPC$_{61}$BM were used as acceptor in blends with P3HT, the cathodes used are indicated in brackets.

shown in Fig. 4.3. The P3HT:bisPC$_{61}$BM SC has an overall higher $V_{oc}$ than the P3HT:PC$_{61}$BM solar cell with the same Ca/Al contact, which is due to the higher LUMO level of bisPC$_{61}$BM compared to PC$_{61}$BM [60]. The saturation effect in the LTR is also visible, although it is not as pronounced. The P3HT:PC$_{61}$BM solar cell with Cr/Al contact has a lower open circuit voltage than the cell with the Ca/Al contact, indicating that in this case the contact is limiting, since the bulk properties have not changed. The temperature dependence of $n$ for the P3HT:bisPC$_{61}$BM and the Cr/Al P3HT:PC$_{61}$BM cell show the same behavior as the Ca/Al P3HT:PC$_{61}$BM cell, but with slightly lower values (not shown).

Investigating the influence of the charge carrier density generated in the solar cell on the open circuit voltage, the $V_{oc}(T)$ was fitted using Eq. (4.1) under the assumption of $n = p$. $n(T)$ obtained from CE measurements provides $E_g$ and $N_c$ as fitting parameters. For the fits shown in Fig. 4.2 (a) (dotted lines) only the HTR was used, where Eq. (4.1) describes the $V_{oc}$ behavior very well. Expanding the fit using $E_g$ and $N_c$ from the HTR to the LTR shows a clear discrepancy between the fit and the measured voltage. This implies that the polaron concentration is not responsible for the saturation of $V_{oc}$ at low temperatures, although it can explain the HTR range well. Hence, it can be proposed that the saturation effect at low temperatures is not caused by bulk properties but by the contacts, limiting the maximum achievable voltage.

To support this proposition macroscopic simulations of temperature dependent IV-characteristics were performed. There, Poisson, continuity and drift–diffusion equations were solved simultaneously by an iterative approach explained in Ref. [30] [116] in more details. The mobilities of electrons and holes were assumed to be balanced, their temperature dependencies were calculated by the Gaussian disorder model [8] by $\mu(T) = \mu_0 \exp(-2\sigma/(3k_BT)^2)$, with $\mu_0 = 1.1 \times 10^{-7} \text{m}^2\text{V}^{-1}\text{s}^{-1}$ and $\sigma = 0.06 \text{ eV}$ as width of the Gaussian density of states. Recombination was considered by the reduced Langevin model, whereas field and temperature dependent polaron pair dissociation was not taken into account. The other parameters used are summarized in table 4.2.

In addition, different energy barrier heights for charge injection into the blend for electrons
4.3. Results and Discussion

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Table 4.2.: Parameters used for simulation.

$\Phi_n$ and holes $\Phi_p$ were considered in order to investigate their influence on the temperature dependence of the simulated open circuit voltage.

The results are depicted in Fig. 4.4(a). Without an injection barrier, implying perfect ohmic contacts at both electrodes, a linear temperature dependence of $V_{oc}$ over the whole temperature range from 100 to 400 K is determined. A linear fit of this data leads to an intersection at $T=0$ K about 1.2 eV which is above the given $E_g$ of 1.1 eV. Based on the square root shaped density of states as necessary approximation for the numerical calculations, this effect originates from the fixed boundary conditions of thermionic emission at the contacts and charge carrier densities above the effective density of states in the bulk (see Fig. 4.4(b)). Including a barrier for electrons of 0.1 eV and holes of 0.2 eV already shows a saturation effect of $V_{oc}$ at lower temperatures at 0.8 V. For higher temperatures these relatively low barrier heights can still be considered as ohmic contacts, reducing the open circuit voltage only slightly. Raising the sum of the electron and hole injection barrier to 0.8 eV shows a high impact on $V_{oc}$ even at high temperatures. The difference in $V_{oc}$ compared to the cell with ohmic contacts of 0.53 V at 300 K implies that non-ohmic contacts limit the open circuit voltage at room temperature. Furthermore, it can be seen that it is not appropriate to extrapolate the linear $V_{oc}$ range to $T=0$ K and use this intersection point as $E_g/q$, as long as the contacts barriers are not zero. The simulation explains the saturation behavior of $V_{oc}$ at low temperatures and can also predict the value at which it occurs, namely $qV_{oc} = E_g - (\Phi_n + \Phi_p)$. For example in the simulation with an injection barrier for the electrons of 0.1 eV and for the holes of 0.7 eV, together with $E_g=1.1$ eV, the saturated $V_{oc}$ is 0.3 V. This makes it possible to determine the sum of the barriers by temperature dependent IV measurements and determine the built in voltage $V_{bi}$, which is the value at which $V_{oc}$ saturates.

The simulated charge carrier density $n$ under open circuit conditions is given in Fig. 4.4(b) in dependence of the temperature and for all three injection barrier variations. Here $n = \sqrt{\int_0^L p(x)n(x)dx}$, with $p(x)$ and $n(x)$ the spatial profile of the hole and electron density and $L$ the thickness of the cell. This charge carrier density is different from that one measured experimentally, nevertheless, $n$ taken from the simulation decreases with increasing temperature in the HTR similar to the experimental results shown in Fig. 4.2(b). In the LTR of the simulated solar cells, this trend is continued, whereas in the experiment $n$ is decreasing with decreasing temperature, which can be an indication for a hindered extraction of the generated charge carriers at lower temperatures resulting in an underestimation of the experimental $n$. Anyhow, even the low experimental charge carrier densities in the LTR would result in a higher $V_{oc}$ in terms of Eq. (2.18) than the measured values which can be seen by the fits in Fig. 4.2(a). Inserting the
4. Relation of Open Circuit Voltage to Charge Carrier Density in Organic Bulk Heterojunction Solar Cells

Figure 4.4: Temperature dependent open circuit voltage (a, solid line) and respective charge carrier densities $\sqrt{np}$ under open circuit conditions (b) obtained from macroscopic simulations with varying electron $\Phi_n$ and hole $\Phi_p$ injection barriers at the contacts. Applying the simulated charge carrier densities to Eq. (2.18) results in calculated $V_{oc}$ values (a, symbols) higher than the simulated ones.

Comparing the experimental results in terms of $V_{oc}$ with the simulated ones shows qualitatively good agreement. In both solar cells with Ca/Al contact the saturation of the open circuit voltage can be observed at low temperatures. If the work function of the Ca/Al cathode was the same for these two cells, implying the same $V_{bi}$, both cells should saturate at the same voltage. It is proposed that the difference of $\sim 0.1$ V in the saturation voltage can be explained by different interface dipoles between the PC$_{61}$BM/Ca and bisPC$_{61}$BM/Ca interface, thus changing the corresponding work functions. Indeed, interface dipoles have often been observed for interfaces of evaporated small molecules to metals [44] and polymer:fullerene blends to metals [41], and it is a credible assumption that different material combinations will influence the magnitude of the dipole. Thus, within this scenario, $V_{oc}$ in the LTR is limited by the contacts and only slightly influenced by bulk effects such as the charge generation (see light intensity dependence in Fig. 4.2 (a)).

The difference of $V_{oc}$ in the HTR is mainly caused by the difference of the LUMO levels of PC$_{61}$BM (-3.7 eV [71]) and bisPC$_{61}$BM (-3.56 eV) [34, 36], as the charge density is in the same range. This indicates that in this temperature range the open circuit voltage is mainly affected by bulk properties such as the photogeneration and recombination of polarons. Thus, the equation given by Brabec et al. [15], $V_{oc} \approx |E_{HOMO_{donor}} - E_{LUMO_{acceptor}}| / q - 0.3$ V, can be used as a rule of thumb.

Simulation and experiment are also consistent for the solar cells with a limiting contact, as experimentally demonstrated by using a Cr/Al cathode, because of the low workfunction of Cr creating a non-ohmic contact. In this case, the open circuit voltage is limited even in the HTR.
in contrast to the P3HT:PC$_{61}$BM solar cell with the Ca/Al cathode, although the bulk properties are the same. Such a device is completely contact limited, despite the $V_{oc}$ slightly increases with lower temperature. Thus, it can be concluded, that in the case of limiting contacts, $V_{oc}$ is determined by the MIM model [74].

In the description of Fig. 4.3 it was already mentioned that for lower light intensities in the LTR the open circuit voltage is lower than $(E_g - (\Phi_n + \Phi_p))/q$. To find the origin of this effect, temperature dependent simulations using fixed injection barriers of $\Phi_n=0.1$ eV and $\Phi_p=0.2$ eV, but varying generation rates to account for different light intensities were performed. Fig. 4.5(a) shows the results, where no decrease of $V_{oc}$ below $E_g - \Phi_n - \Phi_p$ for low generation rates in the LTR can be observed. This is a first evidence that the nature of this effect is not lying in the elementary bulk properties or the contacts. A reasonable explanation for the measured behavior could be, that $V_{oc}$ is suppressed by a too low parallel resistance, an effect which is more pronounced for lower photocurrents (see section 2.2.3 Fig. 2.7(b)) which are generated at low illumination levels and temperatures. Since the experimentally obtained light intensity dependence of $V_{oc}$ for the P3HT:PC$_{61}$BM (Ca/Al) solar cell (see Fig. 4.5(b)) shows a similar curve like $V_{oc}(j_{ph})$ in the case of low $R_p$ as calculated by the Shockley equation (Fig. 2.7(b)), this proposition can be seen as very probable.

![Figure 4.5:](image-url) Simulated $V_{oc}$ in dependence of the temperature using fixed injection barriers for electrons and holes ($\Phi_n=0.1$ eV, $\Phi_p=0.2$ eV) with varying generation rates, representing varying illumination levels (a). No decrease of $V_{oc}$ below $E_g - \Phi_n - \Phi_p$ for low generation rates in the LTR can be observed. Plotting the $V_{oc}$ data of the P3HT:PC$_{61}$BM (Ca/Al) solar cell (Fig. 4.2(a)) versus the light intensity results in a similar curve as given in section 2.2.3 Fig. 2.7(b), where it was shown that the parallel resistance of the solar cell can limit the open circuit voltage with a higher influence at lower photocurrents.
4.4. Conclusion

In conclusion, IV and CE measurements of organic BHJ solar cells were performed at various temperatures and illumination intensities to investigate the relation between the open circuit voltage and corresponding charge carrier density. At HTR a linear increase of $V_{oc}$ with decreasing temperature was observed. The saturation at LTR was identified to be caused by injection barriers for charge carriers at the contact, as verified by macroscopic simulations. If these barriers are high and lead to non ohmic contacts, they can reduce $V_{oc}$ and therefore the solar cell efficiency at device operation conditions.
5. Charge Density Dependent Nongeminate Recombination in Organic Bulk Heterojunction Solar Cells

5.1. Introduction

One of the unresolved issues in OSC concerns the exact loss mechanism limiting the device performance. Therefore, the recombination of charge carriers will be discussed in this section in more details. The different recombination processes that can occur in OSC were already introduced in section 2.2.2, nevertheless they will be summarized once again here. The recombination rate $R$ can be expressed empirically as $R = k_\lambda n^{\lambda+1}$ (see Eq. (2.7)), where $\lambda + 1$ means the order of decay and $k_\lambda$ the recombination prefactor, here defined to be independent of the charge carrier density $n$. In this simple equation, the concentration of electrons $n$ and holes $p$ is not distinguished, as this is usually not possible by experiment. Many authors explain their experimental results by Langevin recombination [25, 59], in which the annihilation rate of electrons with holes is determined by the mobility. For pure Langevin recombination (Eq. (2.9)), $k_\lambda$ can be described by the Langevin recombination prefactor $\gamma = (q/\varepsilon)(\mu_n + \mu_p) \approx (q/\varepsilon)\mu$ (see Eq. (2.10)). Nongeminate recombination was also reported to occur via interface states [23] or trap states [10, 52], described by Shockley–Read–Hall recombination [110]. These processes change the recombination dynamics towards first order, as electron and hole concentrations become imbalanced. For first order recombination, $1/k_\lambda$ is the lifetime. However, several studies reported recombination orders exceeding two [22, 35, 78, 100].

For apparent recombination orders between one and two, or exceeding two, the prefactor $k_\lambda$ is empirical. The former case can usually be explained by a combination of Langevin and SRH recombination rates. The origin of the higher recombination orders, however, is still under discussion [22, 35, 98].

All approaches to explain the high orders of decay have in common that the recombination process is basically of Langevin type, with the disordered nature of the organic semiconductor blend being responsible for trapping of charge carriers. The influence of energetic disorder on the charge carrier mobility is already known for decades: the thermally activated hopping process of charge carriers, which can also be described by the multiple trapping and release approach, leads to a charge carrier concentration dependent mobility [7, 77, 80]. Charge carriers located in the density of states below the transport energy are trapped and immobile (with density $n_t$) whereas charge carriers above (with density $n_c$) are free and have the mobility $\mu_0$. The overall mobility of all charge carriers (with density $n = n_c + n_t$) corresponds to the measured mobility $\mu$ defined by $\mu_0 \cdot n_c = \mu \cdot n$. Nelson [79] used one-dimensional Monte Carlo simula-

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1Parts of this chapter have been published in Rauh et. al. Adv. Funct. Mater. 22, 3371 (2012) [89]
5. Charge Density Dependent Nongeminate Recombination in Organic Bulk Heterojunction Solar Cells

tions to understand the stretched exponential decays of the charge carrier concentration found in transient absorption experiments. Trapping of charge carriers in the tails of the density of states distribution was found to be responsible for this finding, as it slowed down nongeminate recombination. Recently, Shuttle et al. \[98\] investigated P3HT:PC_{61}BM solar cells experimentally at 300 K. They showed that $k(n) \propto \mu(n)$ completely accounted for the charge carrier concentration of the recombination rate in excess of the expected value of two, i.e., $R = k(n)n^2$ where $k(n) \propto n^{\lambda-1}$.

In this section, experimental evidence that the observed order of decay can only partly be explained by the charge carrier concentration dependent mobility will be presented. This discrepancy will be quantified for P3HT:PC_{61}BM solar cells at temperatures below 300 K and for PTB7:PC_{71}BM cells at room temperature. Although the MTR model already includes the existence and influence of trap states it will be demonstrated that in addition to the influence on the charge carrier mobility, the donor–acceptor phase separation can protect trapped charge carriers from recombination. The spatial separation of electrons and holes implies that charge carriers trapped within the tail of the density of states distribution cannot be reached by an oppositely charged mobile charge carrier until the trapped charge carrier is emitted from the deep state and becomes mobile. Only then this charge carrier can participate in the recombination process. Thus, the emission rates from the trap states slow down the recombination rate even more than the charge carrier mobility, i.e., the impact of trapping on the recombination prefactor alone, can account for. This model is able to explain the experimentally observed high recombination orders, in contrast to earlier approaches.

5.2. Experimental

In this investigation two different active layer material systems were used: P3HT:PC_{61}BM as reference system and the new and high efficient blend PTB7:PC_{71}BM. Molecular structures and more details concerning the single materials are given in section 3.3. The general fabrication steps were similar to those described in section 3.2. In the case of the P3HT:PC_{61}BM SC, the active layer was spin coated from a 30 mg/ml chlorobenzene solution with a DA weight ratio of 1:0.8, resulting in a 200 nm thick film. The PTB7:PC_{71}BM film was spin coated from a 20 mg/ml chlorobenzene solution where 3 volume % 1,8-diiodoctane was added to influence the morphology of the film. The DA blend ratio was 1:1.5 and the resulting layer thickness was 105 nm. Before the thermal evaporation of the Ca/Al metal contacts the P3HT:PC_{61}BM film was annealed at 130 °C for 10 min, the PTB7:PC_{71}BM film was left as cast.

Since the spectral mismatch $M$ for the solar simulator calibration using the direct method (see section 2.3) was close to 1 ($M=0.96$ for P3HT:PC61BM, $M=1.04$ for PTB7:PC71) the light intensity was not readjusted for exact efficiency determination because the error of spatial inhomogeneity of the light beam was in the same range.

All temperature dependent current–voltage characteristics and charge extraction measurements were performed as described in section 3.1. In this investigation it is distinguished between two different CE measurements: charge carrier generation (illumination) under open circuit and short circuit conditions to measure the respective equilibrium charge carrier density. An example for the charge extraction signal for the determination of $n$ under short circuit conditions is given in section 7 (Fig. 7.6(a)). Since the solar cell is held at $V=0$ V during the complete measurement, the current in the time range $t_0 \leq 0$ s is equal to the short circuit current.
Switching the LED off at \( t_0 \) leads to a decrease of the current, integration of the current signal from \( t_0 \) to \( t \), where the current is dropped to zero, leads to the equilibrium charge present under short circuit conditions.

5.3. Theory

As already explained in section 2.2.2 it is preferable to study recombination processes by analyzing the charge carrier density at open circuit conditions for different illumination levels and temperatures, as at \( V_{oc} \) all charge carriers generated with generation rate \( G \) have to recombine \((G = R)\). From CE measurements it is not possible to determine the recombination rate directly which is compensated by the calculation of \( G \), which can be extracted from the current–voltage characteristics under illumination. Therefore, the assumption is needed that at sufficiently high voltages in reverse direction, all generated charge carriers will contribute to the saturated photocurrent density \( j_{sat,ph} \) and will not recombine. \( G \) can then be derived by \( G = j_{sat,ph}/(qL) \) (see Eq. (2.6)), where the photocurrent density is derived by subtracting the dark IV-curve from the illuminated one. Using \( G = R \) and the charge carrier density \( n \) measured under open circuit conditions, \( R(n) \) can be obtained and from the slope \( dR/dn \) the recombination order (Eq. (2.7)).

Here, it is assumed that the polaron pair dissociation is independent of the electric field in the device, i.e., that the generated number of polarons at \( V_{oc} \) and at reverse bias, where \( j_{sat,ph} \) is calculated, is equal. This assumption is so far justified for P3HT:PC\(_{61}\)BM between short circuit and open circuit [53, 66, 104].

As the aim of the investigations in this section is to find out wether the charge carrier concentration dependent mobility alone can explain the recombination orders exceeding two, the different charge carrier concentration dependent contributions to the Langevin recombination rate were analyzed: Therefore, the prefactor

\[
k(n) = \frac{R}{n^2} \propto n^\beta ,
\]

(5.1)
determined as described in the previous paragraph was compared to the independently measured mobility \( \mu(n) \propto n^\alpha \) as outlined below. If the recombination order could be completely described by the charge carrier concentration dependent mobility (together with the order of 2 for bimolecular recombination), then \( k(n) \propto \mu(n) \), i.e., \( \alpha = \beta \) should be found.

In order to determine the charge carrier density dependence of the mobility, the short circuit current density \( j_{sc} \) was assumed to be drift-dominated [98],

\[
j_{sc} \approx j_{drift} = \mu_{drift} n F .
\]

(5.2)

Here \( n \) is the charge carrier density measured under short circuit conditions, \( F \) the electric field given by the built-in potential and \( \mu_{drift} \) the mean drift mobility. In well optimized solar cells, unbalanced electron and hole mobilities would inevitably lead to a drop of the \( FF \) and the open circuit voltage [68], which is not the case in the devices investigated here, at least at room temperature. Therefore, it is assumed that \( \mu_{drift} \) approximately equals the mobility of electrons and holes. As only the charge carrier concentration dependence, i.e. the exponent \( \alpha (\mu(n) \propto n^\alpha) \) is important in the following argumentation, it is sufficient to calculate a parameter proportional to \( \mu \),

\[
\mu \propto \frac{j_{sc}}{n} \equiv \tilde{\mu}
\]

(5.3)
for constant $F$. Thus one obtains
\[ \mu(n) \propto \bar{\mu}(n) \propto n^\alpha. \] (5.4)
The same proportionality \((j_{sc}/n)\) results assuming the current to be dominated by diffusion, only the proportionality factor is different.

In the framework of the MTR model it is possible to calculate a theoretical \(\mu(n)\) dependence for different density of states distributions when the system is in equilibrium. Although, in most cases the DOS is assumed to be of Gaussian type for organic semiconductors, the here presented calculations consider the case of an exponential DOS \(g(E)\) \((2.24)\), as the tail of a Gaussian distribution is similar to an exponential shape and the calculations using an exponential DOS is much simpler. Starting from the charge carrier trapping and release equations \([3]\) together with the density of occupied states \(\rho(E)\) being
\[ \rho(E) = \frac{g(E)}{1 + \exp \left( -\frac{E-E_F}{k_B T} \right)} , \] (5.5)
where \(E_F\) is the Fermi energy, the dependence of the free charge carrier density on the total charge carrier density can be calculated, resulting in
\[ n_c(n) = \nu_0 \tau_0 N_t \left( \frac{n}{N_t} \right)^\frac{E_0}{k_B T} - 1 . \] (5.6)
\(\tau_0\) is the lifetime of free charge carriers until they are trapped. Using \(\mu_0 \cdot n_c = \mu \cdot n\), this leads directly to the following theoretical mobility dependence on the charge carrier density
\[ \mu(n) = \mu_0 \nu_0 \tau_0 \left( \frac{n}{N_t} \right)^\frac{E_0}{k_B T} - 1 . \] (5.7)
As mentioned above, Eq. \((5.6)\) and \((5.7)\) were derived for a system in equilibrium without recombination effects being considered. Despite the charge carriers are extracted from a solar cell which is held in equilibrium, the continuous generation of charge carriers in the complete DOS will lead to a proportionally higher ratio of free to trapped charge carriers, as some charge carriers are still in the thermalization process (see section 2.2.1). Nevertheless, Eq. \((5.6)\) and \((5.7)\) can be used for first estimations.

It was already pointed out that the aim of this investigation was to show that \(\alpha\) is not always equal \(\beta\), i.e. that the high recombination orders can generally not be solely explained by the charge carrier concentration dependent mobility. Instead, a more general recombination rate based on the Langevin rate and prefactor is considered,
\[ R = \frac{q}{\varepsilon} (\mu_n + \mu_p) (n_c + n_t) (p_c + p_t) \]
\[ = \frac{q}{\varepsilon} (\mu_n + \mu_p) n_c p_c + \mu_n n_c p_t + \mu_p p_c n_t + 0 \cdot n_t p_t \] . (5.8)
With the assumptions made before, this equation can be simplified to
\[ R \propto \mu(n) (n_c p_c + n_c p_t + p_c n_t) \propto n^{\beta+2} . \] (5.9)
Here, the charge carrier mobility depends on the charge carrier concentration due to trapping and release. The first term on the right hand side of Eq. (5.9) corresponds to Langevin recombination, but only of mobile charge carriers. The second and third term are equivalent to SRH recombination, i.e., recombination of a (previously) trapped with a free charge carrier, and is proportional to the mobility of the respective mobile charge carriers. Therefore, the Langevin prefactor can be adapted for this case as well. As trapped charge carriers are immobile, the term \( n_t p_t \) does not contribute to the recombination rate. The advantage of Eq. (5.9) is its higher degree of transparency as compared to the superposition of Langevin and SRH recombination.

Bear in mind that free and trapped charge carriers are not completely separate reservoirs of charge carriers, but that free charge carriers can be trapped and trapped ones can be reemitted as described by the MTR framework. Due to Fermi–Dirac statistics, \( n_t > n_c \) in steady state. It has to be mentioned that in the case of a significant donor–acceptor phase separation, recombination can only take place at the heterointerface. Thus, only mobile charge carriers could recombine directly, as trapped charge carriers would be protected from recombination within their respective material phase. Thus, Eq. (5.9) would simplify to \( R \propto \mu(n)n_c p_c \), where the free carrier reservoirs are refilled by reemission from trapped charge carriers, this thermal activation process becomes the limiting factor for the recombination rate instead of the mobility. This case leads to a slower decay of the overall charge carrier concentration, corresponding to a higher recombination order going beyond the impact of the mobility. Fig. 5.1 summarizes schematically all possible recombination mechanisms that can occur in OSC.

5.4. Results and Discussion

5.4.1. Results

The measurements were performed on P3HT:PC_{61}BM and PTB7:PC_{71}BM solar cells showing photovoltaic behavior comparable with literature [16, 63]. The P3HT:PC_{61}BM solar cell had an efficiency of \( \eta=3.4\% \) (\( V_{oc}=570 \text{ mV}, j_{sc}=8.6 \text{ mA/cm}^2, FF=69\% \)) under 1 sun illumination, the PTB7:PC_{71}BM \( \eta=7.0\% \) (\( V_{oc}=700 \text{ mV}, j_{sc}=15.0 \text{ mA/cm}^2, FF=67\% \)). The IV curves in dark and for 1 sun illumination are shown in Fig. 5.2.

Fig. 5.3 shows \( \tilde{\mu}(n) \) and \( k(n) \) obtained from CE and IV measurements for light intensities ranging from 0.01 to 0.5 suns. For both material systems and at all temperatures the power law dependence of \( k(n) \) and \( \tilde{\mu}(n) \) as described by Eq. (5.1) and Eq. (5.4) can be observed. The slopes of \( \tilde{\mu}(n) \) and \( k(n) \) are different, implying that the charge carrier density dependence of the mobility alone cannot explain the \( k(n) \) dependence.

The recombination prefactor \( k(n) \) was calculated using Eq. (2.9) and Eq. (2.6), where for \( j_{sat,ph} \) the value at -3.5 V was used. At this negative bias the photocurrent was saturated for all temperatures which was proven by the linear dependence of the calculated generation rate vs. the light intensity \( P_L \). The exponent \( \delta \) from \( G \propto P_L^\delta \) ranged from 0.95 at 300 K to 0.92 at 150 K for P3HT:PC_{61}BM and from 0.95 to 0.94 for PTB7:PC_{71}BM. Recombination losses during the extraction in the CE measurements were in the range of only a few percent and therefore not taken into account. The steady state charge carrier density under short circuit conditions was always lower than under open circuit conditions at the same illumination level because of the continuous sweep out of charge carriers before extraction.

The \( V_{oc}(T) \) dependence for both material systems is shown in Fig. 5.4 where the linear
Figure 5.1.: The three possible recombination mechanisms that can occur in a BHJ solar cell. (I): Recombination of two oppositely charged free charge carriers. This process is called Langevin recombination. (II): Recombination of two oppositely charged free charge carriers, whereas at least one of the two charge carriers was captured for a certain time in a trap before it was emitted to participate in the recombination process. In the framework of this thesis this process is called trap limited recombination. (III): A trapped charge carrier recombines directly with an oppositely charged free carrier. Due to the DA phase separation this process can only take place when the trapped charge carrier is very close to the interface in such a way that it can overcome the spatial distance to the interface by tunneling with a reasonable probability. This type of recombination is called trap assisted recombination or SRH recombination.

Figure 5.2.: Current–voltage characteristics of P3HT:PC_{61}BM and PTB7:PC_{71}BM solar cells under 1 sun illumination conditions and in the dark.
Figure 5.3.: Charge carrier dependence of $\tilde{\mu}$ (Eq. (5.3)) (triangles, left axis) and the Langevin recombination prefactor $k$ (circles, right axis) for P3HT:PC$_{61}$BM (top) and PTB7:PC$_{71}$BM (bottom). Solid circles were used for temperatures where the contacts are ohmic, open circles where the solar cell was limited by injection barriers. Details are given in the text. The dashed–dotted lines indicate the fits to Eq. (5.4) and Eq. (5.1), respectively.
increase of the open circuit voltage with decreasing temperature in the case of P3HT:PC$_{61}$BM indicates that the contacts have an ohmic behavior with negligible injection barriers (chapter 4). Therefore, $V_{oc}$ is directly related to the charge carrier density at open circuit conditions by

$$V_{oc} = \frac{E_g}{q} + \frac{n_{id}k_B T}{q} \ln \left( \frac{np}{N_c^2} \right),$$

(5.10)

with $E_g$ the effective band gap, $n_{id}$ the ideality factor, $k_B$ Boltzmann’s constant and $N_c$ the effective density of states [20, 54]. The situation changes regarding the PTB7:PC$_{71}$BM solar cell, where a linear increase of $V_{oc}$ with decreasing temperature can only be observed in the range of around 250 to 300 K, whereas at lower temperatures the open circuit voltage is limited by injection barriers that are dominant then (chapter 4). In this regime Eq. (5.10) is not valid and the measured charge carrier density can also be affected by the barriers. Hence, no further evaluation of the $k(n)$ data in the temperature range of 150 to 250 K for PTB7:PC$_{71}$BM was performed, as indicated in Fig. 5.3 by open instead of solid circles.

![Figure 5.4](image_url)

**Figure 5.4.** The open circuit voltage versus temperature at 1 sun. For the P3HT:PC$_{61}$BM solar cell the contacts are not limiting the $V_{oc}$ justified by the linear behavior, for the PTB7:PC$_{71}$BM solar cell, the contacts influence the $V_{oc}$, especially at lower temperatures which becomes visible by a saturation of $V_{oc}$.

$\beta$ was obtained from the data presented in Fig. 5.3 by using the slope of the linear fit of $\ln(k)$ vs. $\ln(n)$ over the whole data set (Eq. (5.1)), $\alpha$ from the $\ln(\bar{\mu})$ vs. $\ln(n)$ fit (Eq. (5.4)). The fits are presented in Fig. 5.3 as dash–dotted lines. The determined values of $\beta$ and $\alpha$ are summarized in Fig. 5.5. The case of $\beta = \alpha$ would imply that the recombination orders higher than two can be explained completely by pure Langevin recombination with an additional charge carrier density dependent mobility.

### 5.4.2. Discussion

For the P3HT:PC$_{61}$BM solar cell at 300 K (Fig. 5.3), the mobility ($\alpha$) shows nearly the same carrier concentration dependence as the recombination prefactor $k$ ($\beta$), i.e. the apparent recom-
5.4. Results and Discussion

Figure 5.5.: The values of $\alpha$ and $\beta$ obtained from Fig. 5.3 using Eq. (5.4) (triangles) and Eq. (5.1) (circles) for P3HT:PC$_{61}$BM (black) and PTB7:PC$_{71}$BM (red) versus temperature. $\beta$ for PTB7:PC$_{71}$BM at lower temperatures was not evaluated because of the contact limitation of $V_{oc}$ in this temperature range.

The 275 K and 300 K data of PTB7:PC$_{71}$BM hold a clear statement. Whereas the values of $\alpha$ are similar to those of the P3HT:PC$_{61}$BM device, $\beta$ is higher. This results in a high discrepancy between $\beta$ and $\alpha$ even at room temperature for PTB7:PC$_{71}$BM in contrast to P3HT:PC$_{61}$BM.

In both material systems the charge carrier density dependence of the mobility alone cannot explain the recombination order being higher than two and a trap limited recombination mechanism has to be taken into account.

Generally, the temperature dependence of the charge carrier concentration dependent mobility (i.e., $\alpha$) is experimentally not well investigated. Tanase et al. [107] showed charge carrier dependent mobility data of P3HT diodes and field effect transistors (FET). In the regime of low charge carrier densities ($1 \times 10^{21} - 4 \times 10^{22}$ m$^{-3}$) occurring in solar cells under standard light intensities, they observed almost no $\mu(n)$ dependence by determining the mobility in the space charge limited regime. The data from the FET measurements at higher charge carrier densities ranging from $2 \times 10^{24} - 3.5 \times 10^{25}$ m$^{-3}$ showed a clear $\mu(n)$ dependence. Overall they proposed $\mu \propto n^\left( {E_0 / (k_B T)} \right)^{-1}$. This implies an increasing $\alpha$ with decreasing temperature, which is in good agreement with our measurements. The same trend for $\alpha(T)$ was predicted by Pasveer et al. from numerical simulations of the hopping transport in a master equation approach [83].

The temperature dependence of the difference between $\mu(n)$ (i.e., $\alpha$) and $k(n)$ (i.e., $\beta$) reinforces the assumption, that at lower temperatures the influence of trapping on recombination becomes more pronounced. Under these conditions the release of a trapped charge carrier into a transport state is less probable than at room temperature, as the emission is thermally activated.
5. Charge Density Dependent Nongeminate Recombination in Organic Bulk Heterojunction Solar Cells

by a Boltzmann factor. The existence of a broad distribution of traps in P3HT:PC_{61}BM ranging from 20 to 400 meV was confirmed by thermally stimulated current (TSC) technique with the distribution maximum at 105 meV [92].

Considering the contributions to the recombination rate discussed in section 5.3 in the context of Eq. (5.9), three contributions can be separated, two of them are directly apparent:

1. The recombination of mobile charge carriers, \( n_c p_c \), corresponds to the classical Langevin picture, with the difference that not all charge carriers participate. Depending on the dynamics of trapping and emission, the order of recombination in view of the overall charge carrier concentration \( n \) can exceed the value of two. An additional contribution to the charge carrier concentration dependence is due to the recombination prefactor, i.e., the mobility \( \mu(n) \), as described e.g. by Nelson [79].

2. The recombination of mobile charge carriers with trapped ones, \( n_c p_t \) and \( p_c n_t \). The prefactor is proportional to the mobility of the free charge carriers [52], leading again to a recombination rate in accordance with Langevin theory. Alternatively, this contribution can be described by SRH, although the charge carrier concentration dependence of the mobility does not automatically follow from the trap population—in contrast to MTR. Accordingly, more fit parameters are required for SRH.

3. Contributions to recombination of free with free and free with trapped charge carriers, as described in the previous two scenarios, considering (partial) phase separation. Experimentally, phase separation has been reported at least for P3HT:PC_{61}BM, see e.g. Ref. [2]. Charge carriers trapped within their respective material phase cannot be reached by their oppositely charged recombination partners residing in the other material. Only upon thermal activation of the trapped charge carriers from the deep states they are able to recombine at the heterointerface. This third contribution therefore increases the first one, \( n_c p_c \), combined with a reduced second contribution due to the phase separation. Consequently, the recombination rate is decreased due to the slow emission process, leading to high orders of decay.

It has to be pointed out that for P3HT:PC_{61}BM the impact of trapping is more pronounced for lower temperatures due to a higher effective disorder, i.e. a much slower emission rate from traps, directly influencing the third contribution. Similarly, in P3HT:bisPC_{61}BM films a significantly slower decay of the polaron signal than for P3HT:PC_{61}BM was found by transient absorption measurements [34]. This corresponds to a higher apparent recombination order and is consistent with bisPC_{61}BM exhibiting more and deeper traps than PC_{61}BM, as observed by TSC [93].

The importance of the phase separation gets also apparent, when using Eq. (5.6) and (5.7) to calculate the recombination order after Eq. (5.9) in the case of \( \mu_n = \mu_p \) and \( n = p \), which is a valid assumption for describing both material systems because of the high solar cell FF. In this approach no phase separation is integrated, which indeed results in recombination orders higher than two, but in this case the apparent recombination orders can be completely explained by the \( n \) dependence of the mobility. These calculation supports the assumption that the discrepancy between \( \alpha \) and \( \beta \) is a result of DA phase separation. Nevertheless, the calculation can be used to get an impression of the dependencies of the recombination order on the depth of the traps, which is implicitly included in the parameter \( E_0 \) or the number of trap states \( N_t \). Fig. 5.6(a)
5.5. Conclusion

displays clearly that with deeper traps (higher $E_0$), the recombination order strongly increases to values much higher than two. Increasing the number of trap states without changing the overall shape of the exponential DOS does not lead to an increase of the apparent recombination order but only to a reduction of the overall recombination rate which is shown in Fig. 5.6(b).

![Figure 5.6: The calculated Langevin recombination rate in dependence of the charge carrier density using the $\mu(n)$ dependence after Eq. (5.7) with varying $E_0$ (a) and $N_t$ (b). Both show recombination orders higher than two (numbers according to the lines). The deviation from the recombination order of two increases with increasing $E_0$.](image)

From the given experimental results as well as the theoretical calculations, it is clear that trap states have a strong impact on the apparent recombination order, in terms of the charge carrier mobility and the populations of charge carriers which are available for recombination. The impact on the device performance needs to be considered accordingly.

5.5. Conclusion

In this section the charge carrier dependence of the mobility $\mu$ and the recombination prefactor $k$ were determined for various temperatures by independent experimental techniques. For P3HT:PC$_{61}$BM solar cells at 300 K, the mobility showed nearly the same dependence as $k$ on the charge carrier density in accordance with literature [98]. At lower temperatures the discrepancy between the $\mu(n)$ and $k(n)$ increased. Investigations of a highly performing PTB7:PC$_{71}$BM solar cell showed the discrepancy between $\mu(n)$ and $k(n)$ dependency already at room temperature. These findings substantiate the proposition that not only the impact of trapping on the recombination prefactor proportional to the charge carrier mobility is responsible for increasing the order of charge carrier decay beyond the value of two expected for bimolecular recombination. Instead, for systems with (partial) phase separation, trapped charge carriers can be protected from recombination. Only after their thermally activated release from the deep states they are able to contribute to the recombination rate, leading to an additional increase of the
recombination order. This scenario implies that in PTB7:PC$_{71}$BM the influence of trapping in combination with phase separation is more significant than in P3HT:PC$_{61}$BM, lowering the charge carrier recombination rate. Therefore, the apparent recombination orders higher than two should be an inherent property of disordered organic semiconductor blends.
6. Influence of Trap States on the Open Circuit Voltage and the Recombination Dynamics in Organic Solar Cells

In this section the influence of trap states within the band gap of the active material will be discussed, where the main focus is on their influence on the solar cell parameters — especially $V_{oc}$ — and the recombination dynamics of photogenerated charge carriers. The first and easiest possibility to introduce trap states into organic solar cells is to expose them to oxygen. The results of this study are shown in section 6.1. Another possibility is to add a second acceptor material (guest molecule) to the DA blend (host molecules). When the LUMO level of the guest molecule is significantly lower than that of the host molecule, the LUMO levels of the guest molecule act as electron trap states. In the here presented study (section 6.2), TCNQ\textsuperscript{1} as guest molecule was used in a P3HT:PC\textsubscript{61}BM blend system.

6.1. Influence of Oxygen Exposure on the Open Circuit Voltage and Recombination Dynamics in P3HT:PC\textsubscript{61}BM

6.1.1. Introduction

Beside the efficiency and the costs of organic solar cells, the lifetime of these devices is crucial before they can make their way in the mass market, away from just being a niche product. Therefore, degradation measurements are important to identify the mechanisms leading to the decrease of efficiency with time. Many publications concerning the lifetime of solar cells were presented, where the measurements were performed in a variety of different conditions that are crucial for their degradation behavior: encapsulated or not, in dark or under illumination, under nitrogen, ambient or synthetic air. In this subsection the influence of synthetic air (80 % N\textsubscript{2}, 20 % O\textsubscript{2}, < 1 ppm H\textsubscript{2}O) in dark and under illumination is investigated. Thereby, the main focus is set on on the open circuit voltage, also the light intensity dependence of $V_{oc}$, as well as the recombination dynamics of charge carriers.

6.1.2. Experimental

The investigated solar cell was prepared as described in section 3.2. The 190 nm thick active layer consisted of P3HT:PC\textsubscript{61}BM blend using a weight ratio of 1:0.8. As cathode a Ca (3 nm)/Al (90 nm) electrode was used, the active area of the complete solar cell was 9.32 mm\textsuperscript{2}. After IV-characterization under AM1.5g simulated illumination the solar cell was

\textsuperscript{1}7,7,8,8-Tetracyanoquinodimethane
6. Influence of Trap States on the Open Circuit Voltage and the Recombination Dynamics in Organic Solar Cells

directly transferred to the cryostate, where the degradation measurements were performed. During the transfer, the solar cell was exposed to ambient air for a few minutes. During the measurements the solar cell was stored in He atmosphere, during the degradation steps the cryostat was filled with synthetic air. The calibration of the illumination level was performed as described in section 5.1. At every degradation step the light intensity was varied from 0.001 to 3.98 suns and at every single illumination level an IV-curve as well as a charge extraction measurement to deduce the charge carrier density under open circuit conditions was performed. Additionally, a $V_{oc}$ transient was recorded for an initial illumination level of 1.58 suns. The measurement cycle was performed before starting the degradation, and after 1, 3, 10 and 30 h in dark. Afterwards, the degradation under 1 sun illumination on the same solar cell was started and was characterized again after 1, 3, 10 and 30 h.

6.1.3. Results and Discussion

The solar cell used for the degradation study exhibited photovoltaic performance like P3HT:PC$_{61}$BM solar cells described in literature or chapter 5, e.g. $V_{oc}$ =0.57 V, $j_{sc}$ =8.2 mA/cm$^2$, $FF$ =69 % leading to $\eta$ =3.2 % under AM1.5g illumination using a solar simulator. The IV–curves measured under 1 sun LED illumination for every degradation step are depicted in Fig. 6.1(a).

![Figure 6.1](image1)

**Figure 6.1:** IV-curves of P3HT:PC$_{61}$BM under 1 sun illumination (a) and the respective parameters $V_{oc}$, $j_{sc}$, $FF$ and $\eta$ normalized to the initial values (b) extracted from these curves for different degradation steps.

The normalized respective parameters extracted from the curves are shown in Fig. 6.1(b). They show similar behavior to the already published data by Schafferhans et al. [92]. In the dark only the short circuit current drops to 71 % of the initial value after 30 h, whereas the open circuit voltage remains unaffected and the fill factor even increases slightly (103 % of the initial value after 30 h). This was explained by doping of the active material and confirmed by macroscopic simulations. For the degradation under illumination the behavior differs a bit from
where $V_{oc}$, $j_{sc}$ and $FF$ dropped all by 10% after 3h of degradation under illumination whereas in this study all parameters dropped at a much slower rate: $j_{sc}$ from 71% to 59%, $FF$ from 103% to 100% and $V_{oc}$ from 100% to 97% of the initial value after additional 30 h under illumination.

\[ \text{Figure 6.2.: The charge carrier density under open circuit conditions of P3HT:PC_61BM as obtained from charge extraction measurements for the different degradation steps.} \]

The results of the charge extraction measurements to obtain the charge carrier density $n$ under open circuit conditions is illustrated in Fig. 6.2. For the not degraded solar cell, $n$ shows the typical exponential dependence on $V_{oc}$ ($n = n_0 \exp(c_n V_{oc})$, where $c_n$ is a proportionality factor). With increasing degradation time $n_0$ increases and $c_n$ decreases, their values are summarized in table 6.1. Since for higher $V_{oc}$ values at longer degradation times the slope $c_n = d\ln(n)/dV_{oc}$ is not constant but a bending appears in the $\ln(n)(V_{oc})$ curve, the fits for the calculation of $n_0$ and $c_n$ were performed in the linear range of the logarithmic plot, namely for the values obtained for light intensities from 0.001 to 0.63 suns. For the calculation of $n$ as described in section 3.1 the capacitance of the fresh solar cell was used for all degradation steps, since it is very unrealistic that the geometric capacitance changes from 2.20 nF to 6.62 nF (see also table 6.1).

Fig. 6.3 shows the decay of the open circuit voltage after switching of the light with an illumination level of 1.58 suns. It can clearly be seen that in the time range of $\sim 10^{-6}$ s to $5 \times 10^{-4}$ s the decay is similar for all degradation steps, whereas for longer times the decay is slower for the more degraded solar cells. It has to be noted, that the open circuit voltage at $5 \times 10^{-4}$ s of around 0.36 V is the same as $V_{oc}$ achieved in steady-state IV-measurement using 0.001 suns background illumination.

To ensure that the measured voltage is correct one has to keep in mind that in this case, the solar cell at open circuit conditions (which acts here as voltage source) must have a low resistance in comparison to the input resistance of the oscilloscope, which is 1.5 GΩ in this case. To prove if this prerequisite is fulfilled over the whole time range the resistance at $V_{oc}$ ($R_{Voc}$) was first calculated for every IV-curve measured. Therefore, the IV-curve was fitted around $V_{oc}$ using three measurement points below and above $V_{oc}$ with a 4th order polynomial function and taking the inverse of the slope of this fit at $V_{oc}$ as resistance. Fig. 6.4(a) depicts...
6. Influence of Trap States on the Open Circuit Voltage and the Recombination Dynamics in Organic Solar Cells

<table>
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<th>$C$ [nF]</th>
<th>$R_p$ [k$\Omega$]</th>
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Table 6.1.: The slope $c_n$ of the semilogarithmic plot $\ln(n)$ vs $V_{oc}$ as well as $n_0$ as obtained from Fig 6.2 using the expression $n = n_0 \exp(c_n V_{oc})$ for all degradation steps. The fits were performed in the linear range of $\ln(n)$ vs $V_{oc}$ where the light intensity was varied from 0.001–0.63 suns. $C$ is the measured capacitance as described in section 3.1 by charge extraction measurements in the dark for small bias voltages in reverse direction. $R_p$ is the parallel resistance obtained from the respective dark IV-curves.

Figure 6.3.: Time evolution of the open circuit voltage for every degradation step after switching off the background light ($P_L = 1.58$ suns). In the time range up to $5 \times 10^{-4}$ s (dash-dotted line) the decay is similar for all degradation steps, whereas for longer times the decay is slower for the more degraded solar cells. At $5 \times 10^{-4}$ s $V_{oc}$ is around 0.36 V, which is the same as $V_{oc}$ achieved in steady-state IV-measurement using 0.001 suns background illumination.
that this procedure works well for IV-curves under low light intensities (0.001 suns) as well as under higher illumination levels (1 sun). Since the open circuit voltage from the illuminated IV-curves only reached 0.35 V for the lowest measured light intensity of 0.001 sun, whereas in the $V_{oc}$ transients values down to 0.12 V were measured in the detected time scale, one can not say for sure if $R_{Voc}$ at these voltages is low enough for a correct measurement in basis of this data. To substantiate the assumption of a correct $V_{oc}(t)$ measurement $R_{Voc}$ was plotted semilogarithmic against $V_{oc}$ (Fig. 6.4(b)), where an exponential behavior $R_{Voc} \propto \exp(V_{oc})$ can be observed in the range of lower $V_{oc}$. However, without the justification of any physical theory, since to best of my knowledge no theory concerning $R_{Voc}$ in organic BHJ solar cells exists, one can extrapolate the exponential behavior to even lower $V_{oc}$ values, which is marked in Fig. 6.4(b) as "guide to the eye". With the assumptions that the extrapolation is valid and the oscilloscope measures $V_{oc}$ with only negligible errors as long as $R_{Voc}$ is lower than 1 % of the input resistance of the oscilloscope, which is marked as line in Fig. 6.4(b), the lower limit for the $V_{oc}$ transient is $\sim 0.18$ V. Since in the $V_{oc}$ transient, as already mentioned above, the lowest $V_{oc}$ value is 0.12 V, at least the lowest $V_{oc}$ have to be treated with special care.

For an identical fabricated P3HT:PC$_{61}$BM solar cell IV-measurements were performed with illumination intensities down to $10^{-6}$ suns in a different setup. Evaluation of $R_{Voc}$ showed that in this device at $10^{-6}$ suns, which resulted in a $V_{oc}$ of around 0.23 V, $R_{Voc}$ was low enough that $V_{oc}$ could be correctly measured with the 1.5 GΩ input resistance of the oscilloscope.

---

**Figure 6.4.** Illuminated IV-curves ($P_L=0.001$ suns and $P_L=1$ sun) with the respective fits using a 4th order polynomial function to obtain the resistance at open circuit conditions $R_{Voc}$ (a). Variation of $R_{Voc}$ in dependence of the open circuit voltage for all degradation steps. By extrapolating the exponential part of the curve to lower $V_{oc}$ values it is possible to estimate the limits of the $V_{oc}(t)$, that is when the resistance at $V_{oc}$ is not negligibly small compared to the input resistance of the used oscilloscope (1.5 GΩ) (b).
Together with the $n(V_{oc})$ data as shown in Fig. 6.2, it is possible to calculate a $n(t)$ dependence to investigate the change of the recombination order with degradation time. Therefore, to reduce the amount of data points, corresponding $V_{oc}$ and $t$ data pairs were created in steps of 1 mV over the whole voltage range of the transients by interpolation of the raw data. The corresponding $n$ values were obtained by $n = n_0 \exp(c_n V_{oc})$ using the fit parameters given in Table 6.1. The results are shown in Fig. 6.5 for every degradation step.

![Figure 6.5](image)

**Figure 6.5:** Time evolution of the charge carrier density under open circuit conditions after switching the illumination off for all degradation levels. The data were obtained by a combination of $V_{oc}(t)$ (Fig. 6.3) and $n(V_{oc})$ (Fig. 6.2). The dash-dotted lines indicate the fits to Eq. (6.1) for times up to 500 µs to obtain the recombination order $\lambda + 1$. The dotted lines show linear fits in the double logarithmic plot starting from 800 µs, used to calculate $\lambda_l + 1$.

With degradation time, the decay of the charge carrier density is slowed down, which indicates a change in the dominating recombination mechanisms. The recombination order $\lambda + 1$ can be obtained by fitting the $n(t)$ curve using

$$n(t) = \left(n_{t=0}^{-\lambda} + k\lambda t\right)^{-1/\lambda},$$

(6.1)

which directly follows from the integration of $dn/dt = k\lambda n^{\lambda+1}$. Here $n_{t=0}$ is the charge carrier density at $t = 0$. However, because of the two different regimes in the $n(t)$ behavior, the fits using Eq. (6.1) were only performed in the time range up to 500 µs, indicated in Fig. 6.5 as dash-dotted lines. The fit parameters $n_{t=0}, k\lambda$ and the recombination order $\lambda + 1$ are summarized in Table 6.2. In the second regime at longer times, where the decay is slower, the recombination order, in this case called $\lambda_l + 1$, was determined using the negative inverse of the slope of the linear fit of $\ln(n)$ vs $\ln(t)$.

The observation of two different time regimes of recombination can be explained as follows: At first mainly two types of charge carriers recombine: free charge carriers of opposite sign with each other (Langevin) and/or a free charge carrier with a second one just emitted from a shallow trap (delayed Langevin). Deeper trapped charge carriers do not significantly contribute.
6.1. Influence of Oxygen Exposure on the Open Circuit Voltage and Recombination Dynamics in P3HT:PC<sub>61</sub>BM

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</tbody>
</table>

**Table 6.2.** The recombination orders for all different degradation times as obtained from the fitted (Eq. (6.1)) \(n(t)\) data (Fig. 6.5) up to 500 \(\mu s\) together with the two other fit parameters \(n_0\) and \(k_\lambda\). \(\lambda_l + 1\) is the recombination order extracted also from \(n(t)\) but at longer times (>800 \(\mu s\)), whereas \(\lambda_G + 1\) was derived by calculating the generation rate under illumination as described in chapter 5.

To the recombination process in this time regime. The delayed recombination mechanism is the reason for the apparent recombination orders higher than two as already discussed in chapter 5. The ratio between trapped and free charge carriers increases and the apparent recombination order \(\lambda + 1\) is further raised with increasing time. Additionally, charges are emitted from deeper trap states causing a longer delay of the recombination, which leads to higher apparent recombination orders in the second time regime at longer times. The appearance of two different time regimes was recently shown in high sensitive charge extraction measurements under short circuit conditions [101]. In PBDTTTPD<sub>1</sub>PC<sub>61</sub>BM devices, a material system exhibiting deep trap states, both regimes were obtained, where the first was attributed to charge carriers in mobile states and/or shallow traps and the second to charge carriers in deep traps. In P3HT:PC<sub>61</sub>BM devices the second regime was not visible, which is in accordance to the interpretation of the \(n(t)\) transient of the not degraded solar cell, where the difference between \(\lambda + 1 = 2.40\) and \(\lambda_l + 1 = 2.68\) is very small and no second regime is visible.

With increasing degradation time in the dark, the recombination order increases only to \(\lambda_l + 1 = 3.12\) and \(\lambda_G + 1 = 3.63\) after 30 h of degradation. This is only a small change indicating that the incorporation of additional traps is negligible which was experimentally proven by thermally stimulated currents (TSC), where the lower limit of the density of trapped charges increased only a bit [92]. Since the increase of \(\lambda + 1\) (\(\Delta(\lambda + 1) = 0.95\) from 0 h to 30 h dark degradation) was stronger than for \(\lambda_l + 1\) (\(\Delta(\lambda_l + 1) = 0.72\)), one can conclude that proportionally more deeper trap states are introduced than shallow ones. This is again in accordance with TSC measurements where an increase of the density of deeper trap states was detected [92].

In the case of light induced degradation the recombination rate increases stronger on shorter time scale. After 3 h of illumination in synthetic air, \(\lambda + 1\) increased further to 3.81, which is a similar increase (0.69) as the in the dark degradation case in the tenfold time. After 30 h \(\lambda + 1\) even shows values of 5.19. Additionally, in the longer time range recombination orders up to

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<sup>1</sup>poly(di(2-ethylhexyloxy)benzo[1,2-b:4,5-b’]dithiophene-co-octylthieno[3,4-c]pyrrole-4,6-dione)
6. Influence of Trap States on the Open Circuit Voltage and the Recombination Dynamics
in Organic Solar Cells

6.73 are reached.

To substantiate the recombination order data obtained from the open circuit voltage transients, \( \lambda + 1 \) was additionally evaluated using the approach presented in chapter 5. Here again, the generation rate \( G \) was determined by the photocurrent at \( V = -3.5 \) V for every illumination level, which was assumed to be saturated at this negative bias. The slope of \( \ln(G) \) vs. \( \ln(n) \) is equal to the recombination order and was determined for the data obtained from illumination levels ranging from 0.001 to 0.63 suns. The values are summarized in table 6.2, where they are named \( \lambda_G + 1 \), to distinguish them from the two other recombination order values obtained from the transient \( V_{oc} \) approach. For the not degraded solar cell \( \lambda_G + 1 \) equals the values of \( \lambda + 1 \). With increasing degradation, when the influence of deep traps gets more pronounced resulting in an increasing difference between \( \lambda + 1 \) and \( \lambda_G + 1 \), \( \lambda_G + 1 \) is always between both recombination order values but slightly closer to \( \lambda + 1 \). The reason therefore is, that \( \lambda_G + 1 \) was calculated for illumination levels down to 0.001 suns, the same range which was evaluated in the \( n(t) \) plot for the calculation of \( \lambda + 1 \).

A more qualitative approach to investigate the dominating recombination process is the evaluation of light intensity dependent \( V_{oc} \) data. The origin of this method is again the Shockley equation for \( \text{pn–junctions} \) as described in section 2.2.3. If the parallel resistance \( R_p \) is satisfyingly high and the serial resistance low — which is the case for this device — one can use the expression for \( V_{oc} \) derived from the ideal Shockley equation (see Eq. (2.13)) with making only a negligible error. The derivation of \( V_{oc} \) with respect to the logarithm of the photocurrent \( \ln(j_{ph}) \) is then given by

\[
\frac{dV_{oc}}{d\ln(j_{ph})} = n_{id} \frac{k_B T}{q}.
\]

(6.2)

In inorganic semiconductors, pure band-to-band (Langevin) recombination results in an ideality factor \( n_{id} \) of one, whereas for pure trap-assisted recombination (SRH recombination) \( n_{id} \) is two. A combination of both recombination types results in \( n_{id} \) between one and two. In many articles, and also in this thesis, not \( V_{oc} \) vs. \( \ln(j_{ph}) \) is evaluated but \( V_{oc} \) vs. \( \ln(P_L) \). In an ideal system with \( I_{ph} \propto P_L^\kappa \) with \( \kappa = 1 \), both methods are equal, however, in the here measured solar cell \( \kappa \) is in the range of 0.95 for all degradation steps.

The light intensity dependent \( V_{oc} \) data for every degradation step are shown in Fig. 6.6. The fits for the extraction of \( n_{id} \) were performed in the range from 0.001 to 1.58 suns. As expected, \( n_{id} \) increases continuously with degradation time, the values are displayed in Fig. 6.7. In the case of the not degraded solar cell \( n_{id}=1.18 \) increases to \( n_{id}=1.20 \) after 30 h of dark degradation and \( n_{id}=1.23 \) after additional 30 h degradation under illumination. This shows that the influence of recombination via trap states in comparison to Langevin recombination gets more pronounced with degradation time. This is accompanied by an increase of trap states at the DA interfaces, as recombination via trap states can only occur at the interface or at least in the vicinity of the interface as it is schematically sketched in Fig. 5.1. Charge carriers captured in trap states inside their specific phases, with a too large distance to DA interfaces and thus their recombination partners, do not increase trap assisted recombination but can only delay the recombination dynamics. This is due to the strong localization of the wave functions of both recombination partners, giving a negligible wave function overlap and therefore a not existing probability for tunneling of the trapped charge carrier directly to the partner, as can be seen by the Miller–Abrahams hopping rate (Eq. (2.2)).

The last point of this section is the question, why the open circuit voltage, as already men-
6.1. Influence of Oxygen Exposure on the Open Circuit Voltage and Recombination Dynamics in P3HT:PC$_{61}$BM

Figure 6.6.: Light intensity dependence of the open circuit voltage for all degradation steps.

Figure 6.7.: Change of $n_{id}$ with degradation time in comparison with the recombination order $\lambda + 1$. The increase of both parameters indicates the formation of trap states by oxygen induced degradation.
6. Influence of Trap States on the Open Circuit Voltage and the Recombination Dynamics in Organic Solar Cells

mentioned above, is stable against oxygen degradation in the dark and decreases under simultaneous oxygen and light exposure. The most probable reasons therefor, that are discussed in literature are: a change in the effective band gap or a change of the metal work function due to oxidation of the contact [39]. The change of the charge carrier density stored in the device under open circuit conditions can be excluded to be the reason for the $V_{oc}$ decrease as $n$ at 1 sun is nearly constant for every degradation step and at 0.001 suns the charge carrier density even increases from $2.6 \times 10^{21} \text{m}^{-3}$ for the not degraded cell by a factor of 4.6 to $1.2 \times 10^{22} \text{m}^{-3}$ after 30 h of dark and illuminated oxygen degradation. For a constant $E_g$ and $N_c$, when applying Eq. (2.18), the open circuit voltage should increase with an increasing charge carrier density, while in the performed investigations $V_{oc}$ decreased at the same time from 0.36 to 0.34 V at 0.001 suns.

To distinguish, if a degradation of the metal electrode or the active layer is responsible for the $V_{oc}$ decrease under illumination, temperature dependent measurements of $V_{oc}$ for different illumination levels were performed on another solar cell, for the not degraded solar cell as well as after 39 h of synthetic air exposure under simultaneous illumination ($P_L = 1$ sun). The results for $P_L=1$ and 0.01 suns is shown in Fig. 6.8(a). The solar cell was prepared the same way as the above discussed one, except for the ITO, which was treated with an oxygen plasma before spin coating the PEDOT:PSS on top of it. Nevertheless, the solar cell parameters were similar to the solar cell without plasma treatment. Despite the saturation regime of $V_{oc}$ is not completely reached for the investigated temperature range from 300 to 50 K, the measurements are important and useful since the focus of the further discussion is set on the temperature dependent difference $\Delta V_{oc}$ between the not degraded and degraded solar cell, which is displayed in Fig. 6.8(b). At 300 K, $\Delta V_{oc}$ is 49 mV for $P_L=1$ sun illumination and decreases to 41 mV at 250 K and increases again to 69 mV at 50 K. The same trend can be observed at 0.01 suns illumination level with only slightly different values. This result can be explained by at least

![Figure 6.8](image_url)

**Figure 6.8.** The temperature dependence of the open circuit voltage for not degraded (0 h) and 39 h oxygen (plus simultaneous illumination) degraded P3HT:PC$_{61}$BM solar cells under 1 and 0.01 suns illumination (a). The difference between $V_{oc}$ of the degraded and not degraded solar cells for the respective illumination levels (b).
two different mechanisms influencing the open circuit voltage, one that increases and one that decreases $V_{oc}$, both with different temperature dependencies.

In the following a possible explanation is presented, where only a degradation of the active layer has to be taken into account, whereas the electrode is not influenced by the oxygen degradation. For a better understanding Fig. 6.9 shows on the left side schematically the Gaussian DOS of the HOMO level of the donor in the not degraded case, illustrated by the small number of intrinsic trap states. The effective band $E_{g,eff,nd}$ gap is given by the difference of the transport energies of the LUMO ($E_{tr,LUMO}$) and the HOMO ($E_{tr,nd}$). The effective energy barrier between HOMO and the metal work function is $\Phi_{nd}$. After degradation, the disorder $\sigma_d$ in the HOMO level increases because of an increase of trap states, leading to a different transport energy $E_{tr,d}$, which finally results in a decrease of the effective band gap $E_{g,eff,d}$ as well as the effective energy barrier $\Phi_d$. For the sake of simplicity $E_{tr,LUMO}$ was assumed to be not influenced by degradation. Since at higher temperatures the influence of the energy barrier in P3HT:PC$_{61}$BM is almost negligible as shown in chapter 4, the effect of the reduction of the effective band gap is dominant which leads to the decrease of $\Delta V_{oc}$. Reaching even lower temperatures, the effect of the effective energy barrier gets more important, which then leads to the increase of $\Delta V_{oc}$. Whether or not this mechanism alone can explain completely the experimental behavior is not clarified. Maybe, with the aid of macroscopic simulations, the suggested theory can be confirmed. Additionally, a change of dipoles at the interface between active layer and contact, as it was mentioned shortly in chapter 4, has to be taken into account, to completely resolve the question what exactly leads to the change of $V_{oc}$ after oxygen degradation under simultaneous illumination.
6. Influence of Trap States on the Open Circuit Voltage and the Recombination Dynamics in Organic Solar Cells

Figure 6.9.: Scheme to depict the possible mechanism explaining the $V_{oc}$ behavior after degradation. Therefore, the Gaussian DOS of the HOMO level in a not degraded cell (left side, index nd) is compared with a degraded cell (right side, index d). The degradation is illustrated by the increased number of trap states on the right side, leading to an increase of the disorder ($\sigma_{nd} < \sigma_d$) and a shift of the transport energy $E_{tr}$ in the HOMO level. This has a direct impact on the effective band gap as well as the effective energy barrier, which both influence the open circuit voltage.
6.2. Influence of Extrinsic Trap States on the Performance of Organic Solar Cells

6.2.1. Introduction

The second possibility to introduce trap states into the blend system is to add a second acceptor molecule with a significantly lower lying LUMO level. The influence of extrinsic traps on the solar cell performance was already investigated in MDMO–PPV:PC$_{61}$BM using TCNQ as additional traps [71]. Here, the authors showed that $n_{id}$ increases with the incorporation of TCNQ, indicating an increase of the influence of trap assisted recombination (SRH). A similar study was performed on PCDTBT:PC$_{61}$BM blends by adding PC$_{84}$BM, where also a shift of $n_{id}$ to higher values for the PCDTBT:PC$_{61}$BM:PC$_{84}$BM was observed. Additionally, the recombination order was obtained by differential resistance analysis, that provided an evolution from bimolecular to trap assisted recombination by incorporation of additional traps [61].

In the presented work, the well known P3HT:PC$_{61}$BM blend system was used together with TCNQ as guest molecule. As the LUMO level of TCNQ (-4.5 eV) is significantly lower than of PC$_{61}$BM (-3.7 eV), TCNQ should act as an extrinsic electron trap [71]. The results will substantiate the statements of chapter 5 and section 6.1, where the apparent recombination order was attributed to trap states.

6.2.2. Experimental

The solar cells were prepared in principle as described in section 3.2, namely: a reference solar cell P3HT:PC$_{61}$BM = 1:0.8 without any TCNQ (PC$_{61}$BM:TCNQ=1:0), one with one weight percent (wt%) TCNQ with respect to the PC$_{61}$BM content (PC$_{61}$BM:TCNQ=0.99:0.01) and one with 5 wt% TCNQ (PC$_{61}$BM:TCNQ=0.95:0.05). TCNQ was dissolved in chlorobenzene (3 mg/ml) at 80°C. The active layer thicknesses were in the range of 230-260 nm. After a thermal annealing of the active layer of 10 min at 130°C the final Ca/Al electrode was thermally evaporated.

The charge extraction measurements were performed in the cryostate as described in section 3.1, the light intensity was varied from 0.001 to 2.51 suns. The open circuit voltage transient was recorded using an illumination level of 1 sun.

6.2.3. Results and Discussion

To check if the TCNQ molecules were successfully incorporated into the P3HT:PC$_{61}$BM matrix, AFM measurements were performed to examine if TCNQ forms large crystals and therefore doesn’t act as trap. In some regions of the substrates, crystals were visible on the film containing 5 wt% TCNQ, but not throughout the complete device. Fig. 6.10(d) displays the surface of such a spot over an area of 90 × 90 μm. In most regions of the substrate no such crystals were visible. The surface of the blend without (Fig. 6.10(a)) and with 1 wt% (Fig. 6.10(b)) TCNQ showed the same structure and roughness (RMS=11-13 nm). The surface of the film containing 5 wt% TCNQ but no visible crystals (Fig. 6.10(c)) showed a much smaller RMS

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1 Atomic Force Microscope, Veeco Dimension Icon, tapping mode
2 root mean squared
roughness of 6 nm, which could be an indication that TCNQ disturbs the annealing process leading to a different morphology in the blend influencing in consequence the solar cell parameters. It was reported for P3HT:PC61BM solar cells that annealing at 110 °C leads to an increased roughness of the active layer, an improved $j_{sc}$ and $FF$, a decreased $V_{oc}$ but overall higher efficiency in comparison to the untreated solar cell [62].

![Surface (AFM) images](image_url)

Figure 6.10.: Surface (AFM) images ($10 \times 10 \mu m$) of P3HT:acceptor=1:0.8 films with the acceptor being (a) only PC61BM (b) a PC61BM:TCNQ=0.99:0.01 blend and (c) a PC61BM:TCNQ=0.95:0.05 blend, at which small crystals were visible at some spots on the substrate, shown by a $90 \times 90 \mu m$ 3d plot (d).

As a second method to find out if TCNQ crystals are existent in the active layer, which are not visible under the AFM, as it is not possible to scan the hole macroscopic sample by AFM, additional X-ray diffraction (XRD) measurements were performed for both films containing TCNQ. The results of the scans are shown in Fig. 6.11 where for the PC61BM:TCNQ=0.99:0.01 solar cell, only the signature indicating a crystalline phase of P3HT (compare to Fig. 3.8) can be observed. No additional signatures indicating TCNQ crystals are visible, whereas for the PC61BM:TCNQ=0.95:0.05 additional signatures show up. This por-

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1GE Sensing & Inspection Technologies, XRD 3003 TT
tends, that in the case of the 1 wt%, the TCNQ seems to be incorporated as single molecules in the active layer, whereas in the 5 wt% TCNQ solar cell, parts of the TCNQ already form crystals, which do not act as trap states. Thus, the following study of the influence of extrinsic trap states on the solar cell characteristics and the recombination dynamics is of a qualitative nature, not quantitative.

The results of representative IV-curves in the dark and under 1 sun illumination using the solar simulator are shown in Fig. 6.12(a). The incorporation of extrinsic traps affect all photovoltaic parameters $j_{sc}$, $V_{oc}$ and $FF$, listed in table 6.3. The most influenced parameter is the short-circuit current density, which decreases from 8.5 mA/cm$^2$ to 91 % (PC$_{61}$BM:TCNQ=0.99:0.01) and 64 % (PC$_{61}$BM:TCNQ=0.95:0.05), whereas the $V_{oc}/FF$ decreases only to 98/93 % (PC$_{61}$BM:TCNQ=0.99:0.01) and 93/86 % (PC$_{61}$BM:TCNQ=0.95:0.05) in respect to the P3HT:PC$_{61}$BM device. This behavior is similar to the above mentioned studies [61, 71] and also to the degradation mechanism under illumination (section 6.1). A part of the behavior of the 5 wt% TCNQ solar cell (decrease of $j_{sc}$ and $FF$ compared to the reference P3HT:PC$_{61}$BM SC) could originate from the unfavorable morphology as mentioned above. Nevertheless, the decrease of $V_{oc}$ can not be caused by this effect, but by the incorporation of additional extrinsic trap states.

<table>
<thead>
<tr>
<th>PC$_{61}$BM:TCNQ</th>
<th>$j_{sc}$ [mA/cm$^2$]</th>
<th>$V_{oc}$ [V]</th>
<th>$FF$ [%]</th>
<th>$\eta$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:0</td>
<td>8.5</td>
<td>570</td>
<td>73</td>
<td>3.5</td>
</tr>
<tr>
<td>0.99:0.01</td>
<td>7.7</td>
<td>560</td>
<td>67</td>
<td>2.9</td>
</tr>
<tr>
<td>0.95:0.05</td>
<td>5.4</td>
<td>535</td>
<td>62</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Table 6.3.: Parameters extracted from the IV-characteristics (Fig. 6.12(a)).
6. Influence of Trap States on the Open Circuit Voltage and the Recombination Dynamics in Organic Solar Cells

Beside the AFM/XRD measurements, external quantum efficiency (EQE) measurements of all three devices (Fig. 6.12(b)) showed that at least in the PC_{61}BM:TCNQ=0.95:0.05 device TCNQ does not only act as trap states, but do also actively contribute to the photocurrent generation by absorption of photons and creation of excitons in the TCNQ, leading to charge carriers that can be transported to the electrodes. To emphasize this additional absorption the EQE was normalized to 520 nm, where P3HT:PC_{61}BM SC have their maximum EQE.

![Figure 6.12: IV-curves under 1 sun illumination for different concentrations of TCNQ (a) and the corresponding measurements of the external quantum efficiency (b).](image)

As the device without TCNQ shows nearly the same IV–characteristics than the not degraded solar cell in section 6.1, the following measurements of the charge carrier density under open circuit conditions, as well as the open circuit transients and the light intensity dependence of the open circuit voltage were only measured for the two solar cells with extrinsic traps. The obtained data will be compared to the results of the not degraded cell in section 6.1.

Fig. 6.13 shows the charge carrier density under open circuit conditions for different open circuit voltages as obtained from charge extraction measurements under various light intensities. For the solar cell with a higher TCNQ content, the overall charge carrier density is slightly higher as for the one with PC_{61}BM:TCNQ=0.99:0.01 but still lower than for the P3HT:PC_{61}BM device (Fig. 6.2). Both curves do not show a power law behavior $n = n_0 \exp(c_n V_{oc})$ over the complete measured range, but mainly two different slopes $c_n$ in the range of low and high open circuit voltages and a range of transition between them. For the further investigation of the recombination order, only the range of low charge carrier densities was analyzed. The respective fits are displayed in Fig. 6.13 as dash-dotted lines.

1The EQE was measured in a self made setup consisting of a Xe lamp as a white light source which was spectrally split up by a monochromator and chopped by an optical chopper. The monochromatic light was then divided by a two branch fiber bundle, where one part of the light was focussed on a calibrated reference Si solar cell and the other focussed on test solar cell, located inside the glovebox system. The short circuit currents of both solar cells were measured with lock in amplifiers.
6.2. Influence of Extrinsic Trap States on the Performance of Organic Solar Cells

The open circuit voltage transients (Fig. 6.14(a)) were recorded after switching off the background light simulating 1 sun. Similar to Fig. 6.4(b) it was ensured that over the complete recorded time the \( V_{oc} \) values were measured correctly and were not influenced by a voltage drop at the internal resistance \( R_{Voc} \). In the transients two different time ranges can be observed for both solar cells with TCNQ molecules, as described for the degraded solar cell. As the \( n(V_{oc}) \) fit (Fig. 6.13) can only be performed for low open circuit voltages, just the decay of the charge carriers \( n(t) \) in the longer time range can be reconstructed from \( n(V_{oc}) \) in combination with \( V_{oc}(t) \). Therefore, only \( \lambda_l + 1 \) can be calculated from \( n(t) \) (graph not shown). In the case of 1 wt% TCNQ \( \lambda_l + 1 \) is 3.07 and for the solar cell with 5 wt% TCNQ, the recombination order is even higher with a value of 3.65. In comparison with the \( \lambda_l + 1 \) value of 2.68 for the not degraded reference P3HT:PC61BM solar cell (Tab. 6.2), the recombination order increases with a higher amount of extrinsic trap states.

To investigate the dominating recombination process of both solar cells with TCNQ, the light intensity dependence of the open circuit voltage (Fig. 6.14(b)) was used to calculate the ideality factor. It has to be mentioned first, that the solar cell with 5 wt% TCNQ exhibits a high parallel resistance \( R_p \) — higher than for the 1 wt% solar cell — implying that the single TCNQ crystals do not shorten the solar cell, which would result in low \( R_p \) and therefore a high influence on \( V_{oc} \) as explained in section 2.2.1. For the solar cell with 1 wt% TCNQ the ideality factor is 1.23 and 1.25 for the 5 wt% solar cell. For comparison, the P3HT:PC61BM reference solar cell has a \( n_{id} \) of 1.18. This increase of the ideality factor with increasing TCNQ content implies that SRH recombination gets more important for higher trap contents in accordance to the results of degradation measurements.

In all these considerations, also in the degradation study, it is important that the investigated solar cells have no \( V_{oc} \) limitation by contact barriers since all measurements were performed under open circuit conditions. This implies that Eq. (2.18) as a link between \( V_{oc} \) and the polaron density has always to be valid. To confirm the importance of this statement, contact limited solar

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**Figure 6.13.** The charge carrier density under open circuit conditions as obtained from charge extraction measurements under various illumination levels for the two solar cells with incorporated extrinsic trap states.
6. Influence of Trap States on the Open Circuit Voltage and the Recombination Dynamics in Organic Solar Cells

Figure 6.14.: Time evolution of the open circuit voltage for both solar cells with TCNQ traps after switching off the background light ($P_L=1$ sun) (a) as well as the light intensity dependence of the open circuit voltage (b).

Figure 6.15.: (a) IV-curves under 1 sun illumination for different concentrations of PC$_{61}$BM acting as extrinsic traps in P3HT:ICBA solar cells and (b) the corresponding fill factors.
cells (P3HT:ICBA) with small contents of PC_{61}BM acting as extrinsic traps were fabricated
and the same measurements were performed as shown above. As ICBA has a 0.17 eV higher
LUMO level than PC_{61}BM [42][119], this will inevitably result to a higher energy barrier \( \Delta_e \) at
the Ca/Al contact. Fig. 6.15(a) displays the IV-characteristics of the solar cells with different
PC_{61}BM content, where a clear trend between solar cell performance and amount of trap states
is visible, similar to the behavior of the solar cells with TCNQ as extrinsic traps.

All solar cells parameters — \( V_{oc} \), \( j_{sc} \) and \( FF \) — are decreasing with increasing extrinsic trap
content, which is shown in Fig. 6.15(b) for the \( FF \) in more detail. The fill factor was chosen,
as it shows an interesting effect: for very high PC_{61}BM contents, here 50 % in comparison to
ICBA, the PC_{61}BM molecules are not acting as trap anymore, but form their own percolating
network which leads to a complete recovery of the \( FF \). Beside the clear trend of the IV-curves,
the recombination investigations didn’t show a trend as for example the devices with TCNQ.
Neither the recombination order determined from \( n(t) \), taken from the combination of \( n(V_{oc}) \)
and \( V_{oc}(t) \), nor the ideality factor behaved as expected from theory explained in the chapters be-
fore. The reason is that limited contacts distort recombination measurements that are performed
under open circuit conditions.

### 6.3. Conclusion

A strong influence of trap states on the performance of the solar cells and the recombination
mechanisms was demonstrated if the solar cells were either exposed to oxygen or doped with
TCNQ. All solar cell parameters decreased with an increasing amount of trap states, where
the effect on the short circuit current density was the strongest. The existence of these addi-
tional trap states was confirmed by open circuit voltage transients in combination with charge
carrier density measurements at open circuit voltage conditions, making it possible to receive
information on the polaron decay in the solar cells. Both investigations showed that for longer
degradation times or a higher TCNQ amount, the decay — especially for times longer than sev-
eral hundred microseconds — is much slower. This effect is explained by a delayed release of
charge carriers from trap states before they can recombine, as at least one charge carrier has to
be mobile before the recombination process can take place (see chapter 5, Eq. (5.9), expressed
by the terms \( n_c p_t \) and \( n_t p_c \)). From these constructed \( n(t) \) curves the apparent recombination
order was determined to strengthen the assumption presented in chapter 5 that one reason for
recombination orders higher than two is caused by trap states.

The increase of the ideality factor determined by the light intensity dependence of the open
circuit voltage with increasing degradation time or TCNQ content is an additional indicator
for the existence of trap states. Pure SRH recombination results in \( n_{id} = 2 \) and pure Langevin
recombination in \( n_{id} = 1 \). The increase of \( n_{id} \) from 1.18 (not degraded P3HT:PC_{61}BM without
TCNQ) to 1.23 (after 30 h of dark and additional 30 h of illuminated oxygen degradation) or
1.25 (5 % TCNQ) is caused by an increased influence of SRH recombination on the overall
recombination, which is always a mixture of both recombination processes.
6. Influence of Trap States on the Open Circuit Voltage and the Recombination Dynamics in Organic Solar Cells
7. S-shaped IV-Characteristics as Result of a Reduced Surface Recombination Velocity and its Influence on the Open Circuit Voltage

7.1. Introduction

When one fabricates organic solar cells using new process parameters or materials (active material, electron/hole transport layer or metal contact) the resulting IV-curve under illumination does not always look like e.g. in Fig. 2.8, instead an s-shaped IV-characteristic can occur. Such a behavior was often described in literature [58, 96, 109, 111, 112] and was attributed to surface dipoles, unbalanced mobilities, traps or defects that create energy barriers and negatively influence the extraction of the photogenerated charge carriers. In this section a way to experimentally create s-shapes with varying strengths by an extended oxygen plasma treatment of the ITO glass substrate is shown. With the help of macroscopic simulations the origin of the s-shapes was investigated. Energy barriers as described in chapter 4 did not yield s-shaped IV-characteristics. Another parameter describing the quality of the interface, here the semiconductor/metal interface, is the surface recombination velocity. This mechanism can not only be used in the determination of recombination processes in semiconductors but can also describe the extraction (recombination) of charge carriers out of the active material into the metal. Assuming a reduced surface recombination velocity of holes at the anode could reproduce the experimentally obtained s-shaped curve with excellent agreement. To validate this approach, several experiments, namely light intensity dependent IV, transient photocurrent and open circuit voltage measurements were performed.

7.2. Experimental

All solar cells were prepared as described in section 3.2 with only small changes to create s-shapes in the IV-characteristics. After the cleaning procedure the ITO coated glass substrates were treated with atmosphere plasma, where it was important that the gas contained moisture. It has to be mentioned, that with dry air, as it was used for the degradation measurements in section 6.1, no s-shapes could be observed. To influence the strength of the s-shape, the plasma application time was varied. Furthermore, two different sets of plasma treated solar

1Similar experimentally observed IV-curves under 1 sun illumination and corresponding macroscopic simulations are published by Wagenpfahl et al. [117], where the experimental work was done by myself and the theoretical and simulation part was performed by A. Wagenpfahl.
cells were prepared: solar cells with and without PEDOT:PSS as interlayer between ITO and the active layer, a blend of P3HT:PC$_{61}$BM=1:0.8. The plasma treatment times for the solar cells with PEDOT:PSS were 2, 60, 300, 900, 1800 and 3600 s. The untreated cell was used as a reference. In the set without PEDOT:PSS, 0, 60, 300, 900, 1800 and 3600 s atmosphere plasma treatment time was used. Additionally a solar cell treated with 10 s of pure oxygen plasma was prepared for comparison. The thicknesses of the active layers were all in the range of 200 nm. As cathode, a Ca/Al electrode was thermally evaporated. The IV-curves under 1 sun AM1.5g spectrum were detected under the calibrated solar simulator in a nitrogen filled glovebox, the light intensity dependent IV-curves, as well as short circuit current and open circuit voltage transients were measured in the cryostate as described in section 3.1.

![IV-curves with and without PEDOT:PSS](image)

Figure 7.1.: IV-characteristics of s-shaped solar cells induced by an atmosphere plasma treatment of the ITO substrate for different times. Two different types of P3HT:PC$_{61}$BM solar cells were fabricated: with (a) and without (b) a PEDOT:PSS interlayer between ITO and the active layer. Additionally, in (b) an IV-characteristic is shown for a solar cell, where pure oxygen plasma was used for 10 s (black line).

### 7.3. Results and Discussion

Representative IV-characteristics of the prepared solar cells are shown in Fig. 7.1 ((a): with PEDOT:PSS, (b): without PEDOT:PSS). In both cases s-shapes were created with atmosphere plasma with increasing s-shape strength by increasing plasma time. The relevant solar cell parameters are summarized in Fig. 7.2 ((a): $V_{oc}$, (b): $FF$, (c): $j_{sc}$ and (d): efficiency).

In the case of solar cells with PEDOT:PSS, short plasma times up to 300 s did not lead to s-shapes but only to a slight decrease of the efficiency. Increasing the plasma exposure time to 900 s and longer, s-shapes occurred, accompanied by a drop of $FF$ and $j_{sc}$, whereas $V_{oc}$ was not influenced.
Figure 7.2.: Solar cell parameters ((a): $V_{oc}$, (b): $FF$, (c): $j_{sc}$ and (d): efficiency) extracted from the IV-curves displayed in Fig. 7.1 in dependence of the plasma treatment time for solar cells with (red) and without (purple) PEDOT:PSS. The black circles indicate the parameters obtained from the solar cell fabricated on the 10 s oxygen plasma treated ITO substrate (without PEDOT:PSS).
Solar cells without PEDOT:PSS behaved something different, as they showed already a low performance in the untreated case, where the fill factor only reached values below 40%. At short plasma treatment times (60 s), an inflection point in the IV-characteristic turned up indicating the s-shaped behavior of the curve, accompanied by a decrease of $FF$ and $j_{sc}$. The reason why $V_{oc}$ increased in the case of solar cells without PEDOT:PSS, where it should drop with an increasing s-shape behavior, is that the untreated solar cell can not be taken as a reference in that case. In principle, the used plasma treatment does not only reduce the surface recombination velocity, but can also change the work function of the ITO [51] or have a beneficial surface cleaning effect [118]. Therefore, it is more reasonable to use the solar cell as reference, where a 10 s pure oxygen plasma treatment was applied to the ITO substrate. This plasma treatment provides the same cleaning effects as the atmosphere plasma, but does not lead to a reduced surface recombination velocity, which was proven by extended O$_2$–plasma treatments up to 600 s, where no changes in the IV-curves were observed (data not shown). Taking the oxygen treated device as reference, a clear trend for the set of solar cells without PEDOT:PSS gets visible: a decrease of all parameters with increasing plasma time, which is at least for $V_{oc}$ in contrast to the data obtained from the solar cells with PEDOT:PSS.

To substantiate the claim that a reduced surface recombination velocity is the reason for the occurrence of the above described s-shaped IV-curves, macroscopic simulations were performed. To express the ability of a charge carrier to pass over from one junction to another, for example the hole on the HOMO of the donor to the electrode (PEDOT:PSS or ITO), the surface recombination rate $J$ is defined by [40]

$$J = qS(n - n_{th})$$  \hspace{1cm} (7.1)

where $S$ is the surface recombination velocity and $n_{th}$ the thermally activated charge carrier density at the respective contact. Further information about the calculation of $n_{th}$ and the background of the macroscopic simulation are given in [116,117]. Since in a solar cell two contacts (cathode, anode) are needed as well as two different charge carrier species are present (electrons, holes), four different recombination velocities are defined. In an ideal device, all surface recombination velocities should be infinity or at least be considerable high. In this case, as depicted in Fig. 7.3 schematically on the left side, the charge carriers generated in the active material can be extracted fast enough from the active layer into the electrode. On the right side of Fig. 7.3 the case of a reduced surface recombination velocity is shown. Here the generated charge carriers are transported faster to the electrode as they can be extracted, leading to a pile up of charge carriers, resulting in a local space charge and as a final consequence to an s-shaped IV-curve.

The fixed simulation parameters used here were the same as summarized in table 4.2. Additionally, the temperature $T$ was set to 300 K, the mobility $\mu_{n,p}$ of both, electrons and holes, to $10^{-8}$ m$^2$/Vs, and the injection barriers for electrons $\Phi_n$ and holes $\Phi_p$ to 0.0 and 0.1 eV, respectively. For the recombination mechanism in the bulk material pure Langevin recombination was assumed. To take into account that in the experiment only the properties of the anode were changed by the plasma treatment, the two surface recombination velocities concerning the cathode ($S_{cn}, S_{cp}$) were set to infinity, which was treated numerically with $10^{50}$ m/s. To explain both experimental data sets, with and without PEDOT:PSS, two different simulations were performed. In the first, the surface recombination velocity of electrons at the anode $S_{cn}$ was set to infinity, whereas the surface recombination velocity of holes at the anode $S_{cp}$ was varied. In the
7.3. Results and Discussion

Figure 7.3.: Visualization of the surface recombination velocity $S$. On the left side, $S$ is infinity or at least considerable high that all charge carriers can be extracted fast enough from the active layer into the electrode. On the right side the case of a reduced surface recombination velocity is depicted. Here the charge carriers can not be transferred fast enough into the electrode, leading to a pile up of charge carriers which in consequence leads to an s-shaped IV-characteristic.

The second set, $S_P^a$ was set to $10^{-9}$ m/s and $S_n^a$ was varied.

Fig. 7.4(a) shows the simulated IV-curves with the first set of parameters. As expected, with decreasing $S_P^a$, the s-shape behavior gets more pronounced, as seen in the decreasing $FF$ and $j_{sc}$, when $S_P^a$ is lower than $\sim 10^{-4}$ m/s. In the range of $10^{-2}$ m/s $< S_P^a < \infty$, the solar cell performance is not influenced by the reduced $S_P^a$, at least for the used generation rate. Not so apparent in Fig. 7.4(a) is the trend of $V_{oc}$, which also decreased with reduced $S_P^a$. Therefore, Fig. 7.4(b) displays separately the dependence of the open circuit voltage on the surface recombination velocity $S_P^a$ (red line). In the range of $10^{-2}$ m/s $< S_P^a < \infty$, $V_{oc}$ was constant, and then decreased continuously with decreasing $S_P^a$. In principle, the simulated IV-curves are in a good agreement with the experimental results obtained from the solar cells without PEDOT:PSS, as in both cases all solar cell parameters decreased with an increased plasma treatment (experiment) or decreased $S_P^a$ (simulation).

To explain the stabilization of $V_{oc}$ (Fig. 7.2(a)) for the solar cells with PEDOT:PSS as interlayer, one has first to take into account the functionality of PEDOT:PSS. In literature it is mentioned, that PEDOT:PSS improves the injection/extraction of holes at the ITO contact [19, 84], leading to an overall better solar cell performance, as it was also observed here. This allows to draw the conclusion that $S_P^a$ is higher for solar cells using a PEDOT:PSS interlayer. An additional indication therefore is, that s-shapes occur only at longer plasma treatments in the case of solar cells with PEDOT:PSS compared to solar cells without. Furthermore, PEDOT:PSS is a HTL and thus an electron blocking layer, which leads to a reduced surface recombination velocity of electrons at the anode $S_n^a$. Therefore, for the second set of macroscopic simulation parameters $S_P^a$ was set to a reduced value of $10^{-9}$ m/s to create s-shapes and $S_n^a$ was varied. Since the IV-characteristics are similar for all simulated $S_n^a$ values ($j_{sc}$ was constant for $10^{-11}$ m/s $< S_n^a < \infty$), these curves are not shown. In Fig. 7.4(b, blue line), the open circuit voltage in dependence of $S_n^a$ is depicted. For $S_n^a > 10^2$ m/s the surface recombination velocity is still too high and $V_{oc}$ is at the same level as for $S_P^a=10^{-9}$ m/s and $S_n^a = \infty$. If $S_n^a$ decreases, $V_{oc}$ is approaching the values of a solar cell with not reduced surface recombination velocities (i.e.
7. S-shaped IV-Characteristics as Result of a Reduced Surface Recombination Velocity and its Influence on the Open Circuit Voltage

\[ S_{an}^a \sim \infty \] but show an s-shaped IV-curve. Thus, the stabilization of \( V_{oc} \) for the plasma treated solar cells with PEDOT:PSS can be explained by an additionally reduced \( S_{an}^a \). The reason for the higher \( V_{oc} \) is that the reduced \( S_{an}^a \) leads to an increase of the electron density \( n \) at the anode additionally to the high hole density \( p \) caused by the reduced \( S_{ap}^a \). From the Poisson equation, the actual electrical field is proportional to the difference of \( p - n \). A higher \( n \) now reduces the difference and therefore lowers the formation of a space charge which decreases \( V_{oc} \).

To experimentally substantiate the results of the macroscopic simulations and the approach of a reduced surface recombination velocity being responsible for the occurrence of an s-shape, IV-curves for different light intensities from 0.00025 to 2.5 suns were measured. The motive behind this approach is the following: If the reduced surface recombination velocity, which figuratively speaking limits the amount of charge carriers that can be extracted into the electrode, is responsible for the s-shape, then the s-shape should vanish if less charge carriers were generated at lower light intensity. Fig. 7.5 shows the \( FF \) as well as the \( V_{oc} \), extracted from the IV-curves in dependence of the light illumination level for two solar cells (0 and 900 s plasma treatment) with a PEDOT:PSS interlayer.

First of all, the \( FF \) behavior of the 0 s plasma treated reference device has to be explained, before the solar cell with s-shaped IV-curve will be discussed. In principle, the \( FF \) is mainly influenced by the recombination of the generated charge carriers. An IV-curve in the voltage range from 0 to \( \sim 0.4 \) V, where the slope of \( dJ/dV \) is still low, is dominated by a first order

\[ \nabla E(x) = \frac{\rho(x)}{\varepsilon}, \rho \propto (p - n), \] where \( \rho \) is the charge carrier density.

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Figure 7.4.: (a) Simulated IV-characteristics showing the appearance of s-shape due to a reduced surface recombination rate for holes at the anode \( S_{ap}^a \). With decreasing \( S_{ap}^a \) the s-shape gets more pronounced. (b) Dependence of \( V_{oc} \) on the surface recombination velocity. In the case of \( S_{an}^a \to \infty \), the \( V_{oc} \) decreases with lower \( S_{ap}^a \) (red curve). Is in addition to a lowered \( S_{ap}^a (=10^{-9} \) m/s) also \( S_{an}^a \) reduced to an adequate low level (here: \( 10^{-5} \) m/s), \( V_{oc} \) reaches again the same values as for unreduced \( S_{an,p}^a \) (blue line).
7.3. Results and Discussion

![Graph showing light intensity dependence of the open circuit voltage and the fill factor for solar cells (0 and 900 s plasma treatment) with a PEDOT:PSS interlayer.]

**Figure 7.5.** Light intensity dependence of the open circuit voltage and the fill factor for solar cells (0 and 900 s plasma treatment) with a PEDOT:PSS interlayer. For high light intensities (see IV-curves Fig. 7.1(a)) the 900 s plasma treated solar cell has a low fill factor originating from the s-shape. For low light intensities, when less charge carriers are generated, the s-shape vanishes which can be seen by an increase of the FF with lower $P_L$ until it reaches the values of the not plasma treated solar cell. The reason therefore is, that the reduced surface recombination velocity is then still high enough to prevent the pile up of charges at the electrode. In the inset, the IV-curves of both solar cells under 0.001 suns illumination are displayed. $V_{oc}$ shows the same $P_L$ dependence for both solar cells, which can be explained by the reduced $S_n^r$.

recombination kinetics, whereas around $V_{oc}$ the dominating recombination process is of the second order (Langevin) \[23\]. In the range of high light intensities the $FF$ was shown to be dominated completely by Langevin recombination \[70, 99\]. This mechanism can explain the increase of $FF$ with decreasing $P_L$ down to 0.063 suns, as under lower light intensities lower charge carrier densities are present in the device, resulting in lower Langevin recombination rate. For lower light intensities, first order recombination processes get more important leading to a decrease of $FF$. In macroscopic simulations with varying generation rates the two $FF(P_L)$ ranges could be reproduced by adding a SRH (first order) recombination process to the Langevin recombination. Where in the case of pure Langevin recombination the $FF$ was continuously increasing with lower generation rate, the introduction of SRH recombination in addition to Langevin recombination led to a decrease of $FF$ for lower generation rates.

Before comparing the $P_L$ dependence of the $FF$ of the solar cells with and without s-shaped IV-curve it has to be pointed out that the active layers of both solar cells have equal properties (morphology, thickness,...) and therefore the same underlying recombination mechanisms of photogenerated charge carriers, which can be seen in the equal $V_{oc}(P_L)$ behavior. Nevertheless, a different $FF(P_L)$ trend can be observed. As explained above when discussing the IV-curves under 1 sun illumination, the reduced surface recombination rate leads to a pile up of charge carriers resulting in a space charge influencing strongly the $FF$ of the device. By reducing the
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Figure 7.6.: Photocurrent $j_{sc}$ (a) and open circuit voltage $V_{oc}$ (b) transients of 0 s (no s-shape) and 900 s (s-shape) ITO plasma treated solar cells using PEDOT:PSS as interlayer. Whereas $V_{oc}(t)$ is unaffected by the reduced surface recombination velocity, $j_{sc}(t)$ differs despite equal steady state $j_{sc}$, visible at $t = 0$ s. Details are given in the text.

light intensity and therefore the generation of charge carriers, less charge carriers are piled up, the space charge is lower and the $FF$ is increasing. This effect is still superimposed by the effects of the recombination processes, as for example the reduction of bimolecular recombination which is also partly responsible for the $FF$ increase with decreasing $P_L$ in the high light intensity range. In the case of the solar cell with s-shaped IV-curve the maximum $FF$ is reached at 0.01 suns, which is lower than for the solar cell without s-shaped IV-curve. Under this condition, the fill factor of both solar cells are nearly equal. For light intensities of 0.001 suns or lower, the $FF$ of both solar cells is the same, indicating that less charge carriers are generated than can be extracted despite the reduced surface recombination velocity without being piled. Under these conditions the fill factor is only influenced by the recombination mechanisms of charge carriers in the active layer which are equal for both devices. The inset in Fig. 7.5 shows the IV-curves of both solar cells under 0.001 suns illumination, where the s-shape has vanished in the solar cell that exhibited a s-shaped IV-curve under higher light intensities.

The similar trend was observed for the solar cells without PEDOT:PSS. Here, the reference solar cell (10 s oxygen treated), showed the same trend for $FF(P_L)$ and $V_{oc}(P_L)$ as the solar cell without s-shaped IV-curve with PEDOT:PSS. For the solar cell with a less distinct s-shape (60 s plasma treated), the $FF$ was increasing over the whole light intensity range from 2.5 suns ($FF=36\%$) to 0.00025 suns ($FF=56\%$), but did not reach completely the same $FF$ as the reference solar cell (data not shown). Since in the solar cells without PEDOT:PSS, $V_{oc}$ was not stabilized by a reduced $S_n^s$, the light intensity dependent $V_{oc}$ did not show a linear increase with increasing $P_L$ (in the $V_{oc}$ vs. $\ln(P_L)$ plot) for the solar cell exhibiting an s-shape, but a constant $V_{oc}$, whereas the reference solar cell without PEDOT:PSS showed the typical linear increase.

A last experimental hint for the applicability of the theory of a reduced surface recombination being responsible for s-shaped IV-characteristics was the measurement of the transient
photocurrent as it was performed in chapter 5 to calculate the charge carrier density under short circuit conditions. Fig. 7.6(a) shows the transients of the 0 and 900 s plasma treated solar cells with PEDOT:PSS switching off the light source with $P_L = 1$ sun. Both solar cells showed similar $j_{sc}$ under illumination, which is the value at $t=0$ s, when the light was switched off, despite the s-shaped behavior in the 900 s plasma treated solar cell. Interestingly, in the case of the solar cell with the reduced surface recombination velocity, the decrease of the photocurrent was much slower than for the solar cell without s-shaped IV-curve. As consequence, the charge carrier density under short circuit conditions was much higher for the solar cell with s-shaped IV-curve as for the 0 s plasma treated one. This can be understood referring to Eq. (7.1). In the case of a reduced surface recombination velocity $S$, the number of charges near the interface $n$ has to be increased to assure the same surface recombination rate $J$, which was equal for both solar cells due to equal short circuit currents under steady state conditions.

The identical behavior of the open circuit voltage transients (Fig. 7.6(b)) for the same two solar cells show, that under open circuit conditions no space charge is apparent in the active layer and $V_{oc}(t)$ is only determined by recombination mechanisms of the charge carriers inside the active layer. For the solar cells with s-shaped IV-curve fabricated without PEDOT:PSS, this was not the case. Here $V_{oc}$ was nearly constant in the measured time range, as $V_{oc}$ was mainly determined by the interface properties (data not shown).

### 7.4. Conclusion

In this section the experimental possibility to reproducibly create solar cells with different pronounced s-shapes was described first as a basis for various experiments and theoretical considerations. Using extended ambient air plasma treatments of the ITO/glass substrates with different treatment times led to several solar cells with s-shaped IV-curve. Two sets of solar cells were fabricated, one without using PEDOT:PSS as interlayer between the ITO and the active layer, and one using PEDOT:PSS. The first set resulted in solar cells with s-shaped IV-curve, where all solar cell parameters were decreasing with increasing plasma treatment time, which was attributed to a reduced surface recombination velocity of holes at the anode $S^p_a$. A reduced $S^p_a$ can cause a pile up of holes at the anode because they can not be extracted fast enough, leading to a space charge and as a last consequence to s-shaped IV-curves. This assumption was confirmed by macroscopic simulations. The second set of devices using PEDOT:PSS resulted also in solar cells exhibiting s-shaped IV-curves, but only for longer plasma treatment times ($t \geq 900$ s), where again the fill factor and the short circuit current decreased with increasing s-shape strength. The open circuit voltage was stabilized by the PEDOT:PSS interlayer instead. This effect was attributed to the electron blocking properties of PEDOT:PSS, which result in a reduced surface recombination velocity of electrons at the anode. This reduces the space charge at the anode at $V_{oc}$. Therefore the $V_{oc}$ in solar cells with PEDOT:PSS remains unaffected. This effect was also validated with macroscopic simulations.

To substantiate this scenario, light intensity dependent IV-curves were measured. It could be shown that under low light intensities, the reduced surface recombination velocity was still high enough to extract the photogenerated charge carriers without being piled up, resulting in not s-shaped IV-curves for solar cells that showed s-shape IV-curves under e.g. 1 sun illumination. From transient photocurrent measurements it could also be demonstrated qualitatively that in solar cells with a lower surface recombination velocity, the charge carrier density in the device
7. S-shaped IV-Characteristics as Result of a Reduced Surface Recombination Velocity and its Influence on the Open Circuit Voltage

has to be higher than in a solar cell with a higher surface recombination velocity to ensure the same surface recombination rate, meaning the same current. $V_{oc}(t)$ as well as $V_{oc}(P_L)$ measurements for solar cells with PEDOT:PSS could also solidify the assumption that PEDOT:PSS as an electron blocker eliminates the space charge under open circuit conditions and $V_{oc}$ is only dependent on the intrinsic properties of the active layer, e.g. the recombination mechanisms.

As a last point in this section a second possibility to produce solar cells with s-shaped IV-curve is briefly mentioned. Using the fact that PEDOT:PSS is an acid in water (pH=1.2–2.2 at 20 °C), PEDOT:PSS can etch the ITO. Therefore, ITO/glass substrates were spincoated with PEDOT:PSS and stored for several days in humid atmosphere before they were heated at 130 °C in the glovebox followed by the standard solar cell fabrication steps. Fig. 7.7 shows P3HT:PC$_{61}$BM solar cells where the PEDOT:PSS coated ITO/glass substrates were stored up to 30 days. For the 30 days stored device, a clear s-shape can be observed. In this case, the electron blocking properties of the PEDOT:PSS seem to be reduced, maybe by etching products of the ITO in the PEDOT:PSS layer, since $V_{oc}$ is lower than for the solar cells without s-shape.

Figure 7.7.: IV-characteristics of solar cells induced by an ITO etching process due to the acid PEDOT:PSS under humid atmosphere. The solar cell where the PEDOT:PSS/ITO/glass substrate was stored for 30 days shows a clear s-shaped IV-curve.
8. Summary

The focus of the presented work was studying recombination mechanisms occurring in organic solar cells, as well as their impact on one of their most important parameters — the open circuit voltage. Beforehand, the fundamental working principles of organic solar cells were summarized, with a special attention to the recombination mechanisms and the open circuit voltage in general. After the explanation of the measurement technique called charge extraction, which is often used in the framework of this theses, the manufacturing process of organic solar cells was briefly introduced as well as the thereby used materials.

Firstly, the relationship between open circuit voltage and the respective charge carrier density in the active layer under open circuit conditions was analyzed. Eq. 2.18 is used to describe the open circuit voltage, whose validity was proven with the aid of fits to the measured data. Thereby, it was emphasized that the equation is only valid under special conditions. In the case of the often used reference system P3HT:PC\textsubscript{61}BM, which was also used here, the fits were in agreement with the measurement data only in the range of high temperatures, i.e. 150 to 300 K, where the open circuit increased linear with decreasing temperature. At lower temperatures, the experiment showed a saturation of the open circuit voltage. Here, even under the assumption that the fit parameters effective density of states and band gap are temperature independent, a falling charge carrier density with lower temperatures, as it was observed, would result in a slower increase of the open circuit voltage with decreasing temperature according to the equation. In the temperature range from 50 to 150 K a $V_{oc}$ saturation takes place, which stands in no direct relationship to the intrinsic properties of the active layer. This effect is due to injection energy barriers at the contacts, which was ascertained by macroscopic simulations. Furthermore, it was observed that the open circuit voltage in the case of saturation is equivalent to the so called built-in potential. The difference between the saturated open circuit voltage and the voltage given by the extrapolation of the linear open circuit voltage range to 0 K, corresponds thereby to the sum of the energy barriers at both contacts.

With the knowledge that the open circuit voltage is directly related to the corresponding charge carrier density in not contact limited solar cells, it was possible to consider another hotly debated topic in OPV: the recombination of charge carriers in the active layer. It was reported in various publications that the recombination rate is proportional to the charge carrier density with an exponent higher than two, whereby the exponent is often referred to as recombination order. The recombination mechanisms Shockley-Read-Hall (SRH) or Langevin would only result in recombination orders of 1 or 2, respectively. When both take place simultaneously, a value between 1 and 2 is expected. Two main explanations exist in literature about this phenomena, where both assume that the recombination is mainly of Langevin type. One is based on the approach that there are trap states for the respective charge carriers in separated phases, i.e. electrons in the acceptor phase and holes in the donor phase, which leads to a delayed recombination of the charge carriers at the interface of both phases and finally to an apparent recombination order higher than 2. The other theory includes the higher charge carrier density
8. Summary

dependence of the recombination rate into the so called recombination prefactor. The charge carrier density dependence of this factor is then explained by the charge carrier density dependence of the mobility. To resolve which theory is to favor, the charge carrier density dependence of the mobility and the recombination prefactor were measured separately. Therefore, the reference system P3HT:PC$_{61}$BM as well as PTB7:PC$_{71}$BM, the commercially available material system reaching the highest overall efficiency, were characterized by temperature and illumination dependent current-voltage and charge extraction measurements. It was found that for the system P3HT:PC$_{61}$BM at room temperature the charge carrier density dependence of the mobility was nearly matching completely the charge carrier density dependence of the recombination prefactor. Nevertheless, at lower temperature the discrepancy between both charge carrier density dependencies became obvious, which substantiates the idea of trap states in a phase separated system. In the material system PTB7:PC$_{71}$BM the increased recombination order could not be explained by the charge carrier density dependent mobility even at room temperature. As conclusion, it can be stated that both theories have their justification and their respective impact is strongly dependent on the temperature and the material system. As the charge carrier density dependence of the mobility has its origin also in trap states, it has to be mentioned that recombination orders higher than 2 should be an inherent property of disordered semiconductors.

After making out the importance of trap states on the recombination of charge carriers in organic solar cells, additional trap states were incorporated into the solar cells to investigate their impact on the IV-characteristics as well as recombination order and type. To achieve this, a solar cell was exposed to synthetic air (in the dark and under illumination), leading to an increase of the trap state concentration. Furthermore solar cells were fabricated, in which TCNQ was added in small concentrations to the active layer consisting of P3HT:PC$_{61}$BM. This molecules act as electron traps because of their lower LUMO level. The oxygen degraded solar cell behaved similar to already reported results from literature in terms of IV-characteristics. While the open circuit voltage was not influenced in the case of degradation in the dark, the fill factor was even increasing slightly, but both decrease when it comes to oxygen degradation under simultaneous illumination. The strongest impact of degradation could be seen on the short circuit current density, which decrease in the dark as well as under illumination. The recombination order was determined by a combination of open circuit voltage transients and the dependence of the charge carrier density on the open circuit voltage. Thereby, a continuous increase of the recombination order from 2.4 to more than 5 was observed with higher degradation times. To give a statement about the dominating recombination type, the ideality factor was determined from the illumination dependence of the open circuit voltage. For pure SRH recombination, that means recombination directly through trap states, one would expect a theoretical value for the ideality factor of 1, for Langevin recombination of 2 and when both types appear at the same time, a value between 1 and 2. As with increasing degradation time, the number of traps in the active layer is increasing, it is expected that the ideality factor is also increasing, meaning a higher impact of Shockley-Read-Hall recombination in relation to Langevin recombination. This theoretical expectation was confirmed by the measurements. A similar picture was revealed for the solar cells using TCNQ molecules as extrinsic traps. In this measurement series all IV parameters were decreasing with increasing TCNQ content, whereas the strongest impact was again on the short circuit current density. The recombination investigations yielded also a consistent picture concerning the influence of trap states, as it was observed in the oxygen degradation.
degraded solar cell. The recombination order as well as the ideality factor was increasing with higher TCNQ content. Therefore, it can be finally concluded that traps have a strong impact on the IV-characteristics and thus the efficiency of organic solar cells.

Finally, a phenomenon called s-shaped IV-curves was investigated, which can occur when one for example changes the contacts of the solar cells. As such solar cells have a strongly reduced efficiency it is important to understand the underlying physical mechanism. In the framework of this thesis, a reduced surface recombination velocity was identified as origin. This initial assumption was backed up by experimental results and macroscopic simulations. To achieve this, the reproducible preparation of s–shaped solar cells was the first step. This was done by a special plasma treatment of the ITO contact. The measured IV-curves of such solar cells were then be reproduced by macroscopic simulations, where the surface recombination velocity was reduced. Hereby, it has to be distinguished between the surface recombination of majority and minority charge carriers at the respective contacts. The theory could even be experimentally confirmed by illumination level dependent IV-curves as well as short circuit current density and open circuit voltage transients.

Thus, this thesis presents a detailed study of the charge density dependence of the open circuit voltage as well as the recombination mechanisms in organic solar cells and the influence of trap states on these.
9. Zusammenfassung

Im Fokus der vorliegenden Arbeit lagen die Rekombinationsmechanismen welche in organischen Solarzellen vorkommen, sowie deren Einfluss auf eine der wichtigsten charakteristischen Kenngrößen dieser - der Leerlaufspannung. Vorab wurde die prinzipielle Funktionsweise organischer Solarzellen zusammengefasst und hierbei gesondert ein Hauptaugenmerk auf die Rekombinationsmechanismen und die Leerlaufspannung gelegt. Nach der Erläuterung der Messmethode der Ladungsträgerextraktion, welche im Rahmen der Solarzellencharakterisierung häufig angewendet wurde, wurde noch kurz auf das Standardherstellungsverfahren der Solarzellen eingegangen, sowie die dabei verwendeten Materialien vorgestellt.


Mit der Erkenntnis, das für nicht kontaktlimitierte Solarzellen ein direkter Zusammenhang zwischen der Leerlaufspannung und der zugehörigen Ladungsträgerdichte besteht war es möglich sich einem anderen heiß diskutiertem Thema der OPV zu widmen: der Rekombination von generierten Ladungsträgern in der aktiven Schicht. In mehreren Publikationen wurde berichtet, dass die Rekombinationsrate proportional zur Ladungsträgerdichte in der aktiven Schicht ist, wobei der Exponent oftmals Rekombinationsordnung genannt wird. Die Rekombinationsmechanismen nach Shockley-Read-Hall (SRH) bzw. Langevin würden allerdings nur Rekombinationsordnungen von 1 bzw. 2 oder bei einem gleichzeitigen Vorkommen beider Typen einen Wert zwischen 1 und 2 erwarten lassen. Zu diesem Phänomen existieren zwei Erklärungen in der Literatur, die darauf beruhen, dass die Rekombi-
9. Zusammenfassung


Somit behandelt diese Arbeit eine ausführliche Untersuchung über die Ladungsträgerdichte-abhängigkeit der Leerlaufspannung sowie der Rekombinationsmechanismen in organischen Solarzellen und den Einfluss von Störstellen auf diese.
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# A. List of Abbreviations

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<tbody>
<tr>
<td>AFM</td>
<td>atomic force microscope</td>
</tr>
<tr>
<td>Al</td>
<td>aluminium</td>
</tr>
<tr>
<td>AM</td>
<td>air mass</td>
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<tr>
<td>BHJ</td>
<td>bulk heterojunction solar cell</td>
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<tr>
<td>bisPC$_{61}$BM</td>
<td>bis[6,6]-phenyl C61 butyric acid methyl ester</td>
</tr>
<tr>
<td>C</td>
<td>carbon</td>
</tr>
<tr>
<td>Ca</td>
<td>calcium</td>
</tr>
<tr>
<td>CB</td>
<td>conduction band</td>
</tr>
<tr>
<td>CE</td>
<td>charge extraction</td>
</tr>
<tr>
<td>CIGS</td>
<td>copper indium gallium selenide</td>
</tr>
<tr>
<td>CIS</td>
<td>copper indium selenide</td>
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<tr>
<td>CO$_2$</td>
<td>carbon dioxide</td>
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<tr>
<td>Cr</td>
<td>chromium</td>
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<td>CT</td>
<td>charge transfer</td>
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<tr>
<td>Cu</td>
<td>copper</td>
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<tr>
<td>DA</td>
<td>donor-acceptor</td>
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<tr>
<td>DOS</td>
<td>density of states</td>
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<td>DSSC</td>
<td>dye sensitized solar cells</td>
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<tr>
<td>EL</td>
<td>electroluminescence</td>
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<tr>
<td>EQE</td>
<td>external quantum efficiency</td>
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<tr>
<td>FET</td>
<td>field effect transistor</td>
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<tr>
<td>GDM</td>
<td>Gaussian disorder model</td>
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<tr>
<td>H$_2$O</td>
<td>water</td>
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<tr>
<td>HCL</td>
<td>hydrochloric acid</td>
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<tr>
<td>He</td>
<td>helium</td>
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<tr>
<td>HNO$_3$</td>
<td>nitric acid</td>
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<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>HTL</td>
<td>hole transport layer</td>
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<tr>
<td>HTR</td>
<td>high temperature regime</td>
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### A. List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>HQ</td>
<td>high quality</td>
</tr>
<tr>
<td>ICBA</td>
<td>indene-C60 bisadduct</td>
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<tr>
<td>ITO</td>
<td>indium tin oxide</td>
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<tr>
<td>IV</td>
<td>current–voltage</td>
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<tr>
<td>LED</td>
<td>light emitting diode</td>
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<tr>
<td>LTR</td>
<td>low temperature regime</td>
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<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
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<tr>
<td>MDMO-PPV</td>
<td>poly(2-methoxy-5-(3',7'-dimethloctyloxy)-1,4-phenylenevinylene)</td>
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<tr>
<td>MIM</td>
<td>metal–insulator–metal</td>
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<tr>
<td>mpp</td>
<td>maximum power point</td>
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<tr>
<td>MTR</td>
<td>multiple trapping and release</td>
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<td>N</td>
<td>nitrogen</td>
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<tr>
<td>Na</td>
<td>sodium</td>
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<tr>
<td>O</td>
<td>oxygen</td>
</tr>
<tr>
<td>OPV</td>
<td>organic photovoltaics</td>
</tr>
<tr>
<td>OSC</td>
<td>organic solar cell</td>
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<tr>
<td>P3HT</td>
<td>poly(3-octylthiophene-2,5-diyl)</td>
</tr>
<tr>
<td>PBDTTPD</td>
<td>poly(di(2-ethylhexoxy)benzo[1,2-b:4,5-bÔ]dithiophene-co-octylthieno[3,4-c]pyrrole-4,6-dione)</td>
</tr>
<tr>
<td>PC&lt;sub&gt;61&lt;/sub&gt;BM</td>
<td>[6,6]-phenyl C61 butyric acid methyl ester</td>
</tr>
<tr>
<td>PC&lt;sub&gt;71&lt;/sub&gt;BM</td>
<td>[6,6]-phenyl C71 butyric acid methyl ester</td>
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<tr>
<td>PCDTBT</td>
<td>poly[[9-(1-octynonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl]</td>
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<tr>
<td>PEDOT:PSS</td>
<td>poly(3,4-ethylenedioxythiophene):(polystyrenesulfonate)</td>
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<td>PGO</td>
<td>Präzisions Glas &amp; Optik GmbH</td>
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<tr>
<td>PL</td>
<td>photoluminescence</td>
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<tr>
<td>PPV</td>
<td>poly(p-phenylenevinylene)</td>
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<tr>
<td>PTB7</td>
<td>poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-bÔ]dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]]</td>
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<tr>
<td>PV</td>
<td>power–voltage</td>
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<tr>
<td>RMS</td>
<td>root mean squared</td>
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<tr>
<td>rpm</td>
<td>rounds per minute</td>
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<td>SC</td>
<td>solar cell</td>
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<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>silicon dioxide</td>
</tr>
<tr>
<td>SRH</td>
<td>Shockley–Read–Hall</td>
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<tr>
<td>STC</td>
<td>standard testing conditions</td>
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<tr>
<td>TCNQ</td>
<td>7,7,8,8-tetracyanoquinodimethane</td>
</tr>
<tr>
<td>TCO</td>
<td>transparent conductive oxide</td>
</tr>
<tr>
<td>TSC</td>
<td>thermally stimulated current</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<td>--------------</td>
<td>--------------------------</td>
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<tr>
<td>USB</td>
<td>ultrasonic bath</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
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<tr>
<td>VB</td>
<td>valence band</td>
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<td>XRD</td>
<td>X–ray diffraction</td>
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## B. List of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
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<tbody>
<tr>
<td>$a$</td>
<td>exciton binding distance</td>
<td>m</td>
</tr>
<tr>
<td>$A$</td>
<td>active sample area</td>
<td>m$^2$</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>exponent of charge carrier dependence of mobility</td>
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<tr>
<td>$BB_{acceptor}$</td>
<td>band bending of the electrostatic potential in the acceptor</td>
<td>eV</td>
</tr>
<tr>
<td>$BB_{donor}$</td>
<td>band bending of the electrostatic potential in the donor</td>
<td>eV</td>
</tr>
<tr>
<td>$\beta$</td>
<td>exponent of charge carrier dependence of recombination prefactor</td>
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<tr>
<td>$c$</td>
<td>speed of light in vacuum</td>
<td>m/s</td>
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<tr>
<td>$c_n$</td>
<td>slope of $d\ln(n/dV_{oc})$</td>
<td>not defined</td>
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<tr>
<td>$C$</td>
<td>capacitance</td>
<td>F</td>
</tr>
<tr>
<td>$d$</td>
<td>active layer thickness</td>
<td>m</td>
</tr>
<tr>
<td>$\delta$</td>
<td>exponent of light intensity dependence of generation rate</td>
<td>—</td>
</tr>
<tr>
<td>$E$</td>
<td>energy</td>
<td>eV</td>
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<tr>
<td>$E_0$</td>
<td>characteristic energy (exponential density of states)</td>
<td>eV</td>
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<tr>
<td>$\Delta E$</td>
<td>activation energy</td>
<td>eV</td>
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<tr>
<td>$E_B$</td>
<td>exciton binding energy</td>
<td>eV</td>
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<tr>
<td>$E_{CT}$</td>
<td>energy of the charge transfer state</td>
<td>eV</td>
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<tr>
<td>$E_F$</td>
<td>Fermi energy</td>
<td>eV</td>
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<td>$E_g$</td>
<td>effective band gap</td>
<td>eV</td>
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<tr>
<td>$E_{g,eff}$</td>
<td>reduced effective band gap due to disorder</td>
<td>eV</td>
</tr>
<tr>
<td>$E_{g,eff,d}$</td>
<td>reduced effective band gap due to disorder in a degraded solar cell</td>
<td>eV</td>
</tr>
<tr>
<td>$E_{g,eff,nd}$</td>
<td>reduced effective band gap due to disorder in a non degraded solar cell</td>
<td>eV</td>
</tr>
<tr>
<td>$E_{HOMO}$</td>
<td>energy of highest occupied molecular orbital</td>
<td>eV</td>
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<tr>
<td>$E_{HOMO,\text{donor}}$</td>
<td>energy of highest occupied molecular orbital of the donor</td>
<td>eV</td>
</tr>
<tr>
<td>$E_{LUMO}$</td>
<td>energy of lowest unoccupied molecular orbital</td>
<td>eV</td>
</tr>
<tr>
<td>$E_{LUMO,\text{acceptor}}$</td>
<td>energy of lowest unoccupied molecular orbital of the acceptor</td>
<td>eV</td>
</tr>
<tr>
<td>$E_{LUMO,\text{donor}}$</td>
<td>energy of lowest unoccupied molecular orbital of the donor</td>
<td>eV</td>
</tr>
<tr>
<td>$E_{tr}$</td>
<td>transport energy</td>
<td>eV</td>
</tr>
<tr>
<td>$E_{tr,LUMO}$</td>
<td>transport energy in LUMO level</td>
<td>eV</td>
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</table>
## B. List of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{tr,d}$</td>
<td>transport energy in the HOMO level in a degraded solar cell</td>
<td>eV</td>
</tr>
<tr>
<td>$E_{tr,nd}$</td>
<td>transport energy in the HOMO level in a non degraded solar cell</td>
<td>eV</td>
</tr>
<tr>
<td>$EQE$</td>
<td>external quantum efficiency</td>
<td>—</td>
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<tr>
<td>$EQE_{EL}$</td>
<td>external quantum efficiency of the electroluminescence</td>
<td>—</td>
</tr>
<tr>
<td>$EQE_{PV}$</td>
<td>photovoltaic external quantum efficiency</td>
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</tr>
<tr>
<td>$EQE_{rc}$</td>
<td>external quantum efficiency of reference solar cell</td>
<td>—</td>
</tr>
<tr>
<td>$EQE_{tc}$</td>
<td>external quantum efficiency of test solar cell</td>
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<tr>
<td>$\varepsilon$</td>
<td>absolute permittivity</td>
<td>F/m</td>
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<tr>
<td>$\varepsilon_i$</td>
<td>energy of initially occupied localized state</td>
<td>eV</td>
</tr>
<tr>
<td>$\varepsilon_j$</td>
<td>energy of localized target state</td>
<td>eV</td>
</tr>
<tr>
<td>$\varepsilon_r$</td>
<td>relative dielectric constant</td>
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<tr>
<td>$\eta$</td>
<td>solar cell efficiency</td>
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<tr>
<td>$f$</td>
<td>factor describing the interaction between donor and acceptor</td>
<td>m²J²</td>
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<tr>
<td>$F$</td>
<td>electric field</td>
<td>V/m</td>
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<tr>
<td>$FF$</td>
<td>fill factor</td>
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<tr>
<td>$g(E)$</td>
<td>density of states distribution</td>
<td>m⁻³ eV⁻¹</td>
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<tr>
<td>$g_e(E)$</td>
<td>electron density of states distribution</td>
<td>m⁻³ eV⁻¹</td>
</tr>
<tr>
<td>$g_h(E)$</td>
<td>hole density of states distribution</td>
<td>m⁻³ eV⁻¹</td>
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<tr>
<td>$G$</td>
<td>generation rate</td>
<td>m⁻³ s⁻¹</td>
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<tr>
<td>$\Delta G$</td>
<td>free energy difference of charge separation</td>
<td>eV</td>
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<tr>
<td>$\gamma$</td>
<td>Langevin recombination prefactor</td>
<td>m³/s</td>
</tr>
<tr>
<td>$\gamma_0$</td>
<td>inverse localization radius (Miller–Abrahams Equation)</td>
<td>m⁻¹</td>
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<tr>
<td>$\gamma_A$</td>
<td>modified Langevin recombination prefactor (Adriaenssens et al.)</td>
<td>m³/s</td>
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<tr>
<td>$\gamma_D$</td>
<td>modified Langevin recombination prefactor (Deibel et al.)</td>
<td>m³/s</td>
</tr>
<tr>
<td>$\gamma_K$</td>
<td>modified Langevin recombination prefactor (Koster et al.)</td>
<td>m³/s</td>
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<tr>
<td>$h$</td>
<td>Planck’s constant</td>
<td>Js</td>
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<td>$I$</td>
<td>current</td>
<td>A</td>
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<tr>
<td>$I_{LED}$</td>
<td>current to drive LED</td>
<td>A</td>
</tr>
<tr>
<td>$I_{mpp}$</td>
<td>current at maximum power point</td>
<td>A</td>
</tr>
<tr>
<td>$I_{ph}$</td>
<td>photocurrent</td>
<td>A</td>
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<tr>
<td>$I_{sc}$</td>
<td>short circuit current</td>
<td>A</td>
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<tr>
<td>$I_{sc,rc,AM1.5g}$</td>
<td>short circuit current of reference solar cell under AM1.5g spectrum</td>
<td>A</td>
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<tr>
<td>$I_{sc,rc,ss}$</td>
<td>short circuit current of reference solar cell under solar simulator</td>
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<tr>
<td>$I_{sc,S1133}$</td>
<td>short circuit current of reference solar cell S1133</td>
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<tr>
<td>$j$</td>
<td>current density</td>
<td>A/m²</td>
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<tr>
<td>$j_0$</td>
<td>dark saturation current density</td>
<td>A/m²</td>
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<tr>
<td>$j_{drift}$</td>
<td>drift current density</td>
<td>A/m²</td>
</tr>
<tr>
<td>$j_{mpp}$</td>
<td>current density at maximum power point</td>
<td>A/m²</td>
</tr>
<tr>
<td>$j_n$</td>
<td>current density</td>
<td>A/m²</td>
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<tr>
<td>Symbol</td>
<td>Description</td>
<td>Unit</td>
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<tr>
<td>$j_{ph}$</td>
<td>photocurrent density</td>
<td>A/m²</td>
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<tr>
<td>$j_{sat.ph}$</td>
<td>saturated photocurrent density</td>
<td>A/m²</td>
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<tr>
<td>$j_{sc}$</td>
<td>short circuit current density</td>
<td>A/m²</td>
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<td>$j_{sc,AM1.5g}$</td>
<td>short circuit current density under AM1.5g spectrum</td>
<td>A/m²</td>
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<tr>
<td>$J$</td>
<td>surface recombination rate</td>
<td>A/m²</td>
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<td>$k$</td>
<td>recombination prefactor</td>
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<td>$k_B$</td>
<td>Boltzmann constant</td>
<td>eV/K</td>
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<td>$k_d$</td>
<td>polaron pair dissociation rate</td>
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<tr>
<td>$k_f$</td>
<td>polaron pair decay rate</td>
<td>s⁻¹</td>
</tr>
<tr>
<td>$k_r$</td>
<td>recombination rate of free charges to polaron pairs / monomolecular recombination rate</td>
<td>s⁻¹</td>
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<tr>
<td>$k_\lambda$</td>
<td>recombination prefactor</td>
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<tr>
<td>$\kappa$</td>
<td>exponent of light intensity dependence of photocurrent</td>
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</tr>
<tr>
<td>$L$</td>
<td>active layer thickness</td>
<td>m</td>
</tr>
<tr>
<td>$L_D$</td>
<td>exciton diffusion length</td>
<td>m</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>wavelength</td>
<td>m</td>
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<tr>
<td>$\lambda_0$</td>
<td>reorganization energy (Marcus theory)</td>
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<tr>
<td>$\lambda_+1$</td>
<td>recombination order</td>
<td>—</td>
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<tr>
<td>$\lambda_l+1$</td>
<td>recombination order, determined from n(t) at longer times</td>
<td>—</td>
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<tr>
<td>$\lambda_G+1$</td>
<td>recombination order, where the recombination rate was calculated</td>
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<td>$M$</td>
<td>mismatch</td>
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<td>$\mu$</td>
<td>mobility</td>
<td>m²/Vs</td>
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<tr>
<td>$\mu_0$</td>
<td>mobility of free charge carriers</td>
<td>m²/Vs</td>
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<td>$\mu_{drift}$</td>
<td>drift mobility</td>
<td>m²/Vs</td>
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<tr>
<td>$\bar{\mu}$</td>
<td>value proportional to mobility</td>
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<td>electron mobility</td>
<td>m²/Vs</td>
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<tr>
<td>$\mu_p$</td>
<td>hole mobility</td>
<td>m²/Vs</td>
</tr>
<tr>
<td>$n$</td>
<td>charge carrier density / electron density</td>
<td>m⁻³</td>
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<tr>
<td>$n_0$</td>
<td>extrapolated charge carrier density for $V_{oc}=0$ V</td>
<td>m⁻³</td>
</tr>
<tr>
<td>$n_c$</td>
<td>free (conductive) charge carrier / electron density</td>
<td>m⁻³</td>
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<tr>
<td>$n_{dev}$</td>
<td>charge carrier density stored in device</td>
<td>m⁻³</td>
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<td>$n_{extr}$</td>
<td>extracted charge carrier density</td>
<td>m⁻³</td>
</tr>
<tr>
<td>$n_i$</td>
<td>intrinsic charge carrier density</td>
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<tr>
<td>$n_{id}$</td>
<td>ideality factor</td>
<td>—</td>
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<td>$n_{loss}$</td>
<td>charge carrier density lost during extraction</td>
<td>m⁻³</td>
</tr>
<tr>
<td>$n_t$</td>
<td>trapped charge carrier / electron density</td>
<td>m⁻³</td>
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<tr>
<td>$n_{th}$</td>
<td>thermally activated charge carrier density</td>
<td>m⁻³</td>
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</table>
### B. List of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
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<tbody>
<tr>
<td>$N_c$</td>
<td>effective density of states</td>
<td>m$^{-3}$</td>
</tr>
<tr>
<td>$N_e$</td>
<td>density of states of electrons</td>
<td>m$^{-3}$</td>
</tr>
<tr>
<td>$N_h$</td>
<td>density of states of holes</td>
<td>m$^{-3}$</td>
</tr>
<tr>
<td>$N_{t,e}$</td>
<td>exponential density of states of electrons</td>
<td>m$^{-3}$</td>
</tr>
<tr>
<td>$N_{t,h}$</td>
<td>exponential density of states of holes</td>
<td>m$^{-3}$</td>
</tr>
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<td>$N_t$</td>
<td>trap density</td>
<td>m$^{-3}$</td>
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<tr>
<td>$\nu_0$</td>
<td>attempt-to-escape frequency</td>
<td>s$^{-1}$</td>
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<tr>
<td>$p$</td>
<td>hole density</td>
<td>m$^{-3}$</td>
</tr>
<tr>
<td>$p_c$</td>
<td>free (conductive) hole density</td>
<td>m$^{-3}$</td>
</tr>
<tr>
<td>$p_t$</td>
<td>trapped hole density</td>
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</tr>
<tr>
<td>$P$</td>
<td>polaron pair dissociation probability</td>
<td>—</td>
</tr>
<tr>
<td>$P_L$</td>
<td>radiant power of incident light</td>
<td>W</td>
</tr>
<tr>
<td>$P_{max}$</td>
<td>maximum electrical power of the solar cell</td>
<td>W</td>
</tr>
<tr>
<td>$P_x$</td>
<td>radiant power of incident light</td>
<td>W</td>
</tr>
<tr>
<td>$\varphi_n$</td>
<td>quasi Fermi level of electrons</td>
<td>eV</td>
</tr>
<tr>
<td>$\varphi_p$</td>
<td>quasi Fermi level of holes</td>
<td>eV</td>
</tr>
<tr>
<td>$\Phi_{AM1.5g}$</td>
<td>spectral irradiance of AM1.5g spectrum</td>
<td>Wm$^{-2}$nm$^{-1}$</td>
</tr>
<tr>
<td>$\Phi_{SS}$</td>
<td>spectral irradiance of solar simulator</td>
<td>Wm$^{-2}$nm$^{-1}$</td>
</tr>
<tr>
<td>$\Phi_d$</td>
<td>effective energy barrier in a degraded solar cell</td>
<td>eV</td>
</tr>
<tr>
<td>$\Phi_{nd}$</td>
<td>effective energy barrier in a non degraded solar cell</td>
<td>eV</td>
</tr>
<tr>
<td>$\Phi_{BB}$</td>
<td>black body radiation at a temperature $T$</td>
<td>Wm$^{-2}$s$^{-1}$</td>
</tr>
<tr>
<td>$\Phi_L$</td>
<td>radiant power density of incident light</td>
<td>W/m$^2$</td>
</tr>
<tr>
<td>$\Phi_n$</td>
<td>injection barriers of contacts for electrons</td>
<td>eV</td>
</tr>
<tr>
<td>$\Phi_p$</td>
<td>injection barriers of contacts for holes</td>
<td>eV</td>
</tr>
<tr>
<td>$q$</td>
<td>elementary charge</td>
<td>C</td>
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<tr>
<td>$Q_{extr}$</td>
<td>extracted charge</td>
<td>C</td>
</tr>
<tr>
<td>$Q_{plates}$</td>
<td>charge stored on plates (capacitor)</td>
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</tr>
<tr>
<td>$R$</td>
<td>recombination rate</td>
<td>m$^{-3}$s$^{-1}$</td>
</tr>
<tr>
<td>$R_{ij}$</td>
<td>spatial distance between initial and target state</td>
<td>m</td>
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<tr>
<td>$R_p$</td>
<td>parallel resistance</td>
<td>$\Omega$</td>
</tr>
<tr>
<td>$R_s$</td>
<td>serial resistance</td>
<td>$\Omega$</td>
</tr>
<tr>
<td>$R_{Voc}$</td>
<td>resistance at $V_{oc}$</td>
<td>$\Omega$</td>
</tr>
<tr>
<td>$\rho$</td>
<td>density of occupied states distribution</td>
<td>m$^{-3}$eV$^{-1}$</td>
</tr>
<tr>
<td>$S$</td>
<td>surface recombination velocity</td>
<td>ms$^{-1}$</td>
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<tr>
<td>$S_{n}^a$</td>
<td>surface recombination velocity of electrons at the anode</td>
<td>ms$^{-1}$</td>
</tr>
<tr>
<td>$S_{p}^a$</td>
<td>surface recombination velocity of holes at the anode</td>
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</tr>
<tr>
<td>$\sigma$</td>
<td>width of Gaussian density of states</td>
<td>eV</td>
</tr>
<tr>
<td>$\sigma_d$</td>
<td>width of Gaussian density of states in a degraded solar cell</td>
<td>eV</td>
</tr>
<tr>
<td>$\sigma_{nd}$</td>
<td>width of Gaussian density of states in a non degraded solar cell</td>
<td>eV</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td>Unit</td>
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<td>--------</td>
<td>-------------</td>
<td>------</td>
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<tr>
<td>$t$</td>
<td>time</td>
<td>s</td>
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<tr>
<td>$\Delta t$</td>
<td>time interval</td>
<td>s</td>
</tr>
<tr>
<td>$t_0$</td>
<td>lifetime of free charge carriers until they are trapped</td>
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<tr>
<td>$t_{\text{end}}$</td>
<td>specific time (charge extraction)</td>
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<tr>
<td>$T$</td>
<td>temperature</td>
<td>K</td>
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<tr>
<td>$\tau_0$</td>
<td>exciton lifetime</td>
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<td>$v_d$</td>
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<td>$V$</td>
<td>applied voltage</td>
<td>V</td>
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<tr>
<td>$V_{\text{appl}}$</td>
<td>applied voltage</td>
<td>V</td>
</tr>
<tr>
<td>$V_{\text{mpp}}$</td>
<td>voltage at maximum power point</td>
<td>V</td>
</tr>
<tr>
<td>$V_s$</td>
<td>sample volume</td>
<td>m$^3$</td>
</tr>
<tr>
<td>$V_{\text{oc}}$</td>
<td>open circuit voltage</td>
<td>V</td>
</tr>
<tr>
<td>$\Delta V_{\text{oc}}$</td>
<td>open circuit voltage difference</td>
<td>V</td>
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<tr>
<td>$\Delta V_{\text{nonrad}}$</td>
<td>loss in open circuit voltage due non radiative recombination</td>
<td>V</td>
</tr>
<tr>
<td>$\Delta V_{\text{rad}}$</td>
<td>loss in open circuit voltage due radiative recombination</td>
<td>V</td>
</tr>
<tr>
<td>$W_{ij}$</td>
<td>Miller–Abrahams hopping rate</td>
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<tr>
<td>$x$</td>
<td>spatial position</td>
<td>m</td>
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<tr>
<td>$\zeta$</td>
<td>reduction factor (Langevin recombination)</td>
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<tr>
<td>$\infty$</td>
<td>infinity</td>
<td>—</td>
</tr>
</tbody>
</table>
C. Acknowledgement

Obwohl eine Dissertation selbstständig verfasst werden muss, ist es dennoch nicht ohne Hilfe verschiedenster Personen möglich, die dahintersteckende Arbeit, die oftmals ein Vielfaches dessen beträgt, was in der tatsächlich abgegeben Schrift zum Vorzeichen kommt, zu bewältigen. Deshalb ist es mir eine Freude einigen Personen in den folgenden Zeilen meinen Dank auszusprechen.

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List of Publications

Refereed Articles


- S. Rausch, D. Rauh, C. Deibel, S. Vidi, H. P. Ebert *Thin-Film Thermal-Conductivity Measurement on Semi-Conducting Polymer Material Using the 3ω Technique*, Int. J. Thermophys. DOI: 10.1007/s10765-012-1174-4


List of Publications


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Contributed Talks


- MRS Fall Meeting 2010, Boston: **D. Rauh**, A. Wagenpfahl, C. Deibel and V. Dyakonov, *Relation of open circuit voltage to charge carrier concentration in organic bulk heterojunction solar cells*

Poster Presentations


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beruflicher Werdegang
seit 04/2012: Ingenieur Funktionsentwicklung bei Bosch Engineering GmbH

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gemäß § 5 Abs. 2 Ziff. 2 und 5
der Promotionsordnung der
Fakultät für Physik und Astronomie
der Julius-Maximilians-Universität Würzburg

Hiermit erkläre ich ehrenwörtlich, dass ich die Dissertation selbstständig und ohne Hilfe eines Promotionsberaters angefertigt und keine weiteren als die angegebenen Quellen und Hilfsmittel benutzt habe.

Die Dissertation wurde bisher weder vollständig noch teilweise einer anderen Hochschule mit dem Ziel einen akademischen Grad zu erwerben vorgelegt.


Die Dissertation wurde von Prof. Dr. Vladimir Dyakonov betreut.

Würzburg, den 05.02.2013

Daniel Rauh