Investigation and Optimization of Hybrid Organic/Inorganic Heterojunction Solar Cells

Von der Fakultät für Elektrotechnik und Informationstechnik der Rheinisch-Westfälischen Technischen Hochschule Aachen zur Erlangung des akademischen Grades eines Doktors der Naturwissenschaften genehmigte Dissertation

vorgelegt von

Martin Weingarten, M.Sc.
aus Köln

Berichter: Univ.-Prof. Dr.-Ing. Andrei Vescan
Univ.-Prof. Dr. rer. nat. Uwe Rau


Diese Dissertation ist auf den Internetseiten der Universitätsbibliothek online verfügbar.
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<tbody>
<tr>
<td>$A$</td>
<td>solar cell area</td>
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<tr>
<td>$A^*$</td>
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<td>$c$</td>
<td>concentration</td>
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<tr>
<td>$c_L$</td>
<td>speed of light</td>
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<tr>
<td>$C$</td>
<td>light concentration factor</td>
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<tr>
<td>$D_h$</td>
<td>diffusion coefficient for holes</td>
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<td>$\hbar$</td>
<td>reduced Planck constant</td>
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<td>$I_{ph}$</td>
<td>photocurrent</td>
</tr>
<tr>
<td>$J$</td>
<td>current density</td>
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<td>$J_0$</td>
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<td>$J_{ph}$</td>
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<td>short-circuit current density</td>
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<tr>
<td>$k$</td>
<td>extinction coefficient</td>
</tr>
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<td>$k_B$</td>
<td>Boltzmann constant</td>
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$L_D$ exciton diffusion length
$m_e$ effective electron mass
$M_n$ number average molecular weight
$n$ real refractive index
$n_i$ intrinsic charge carrier density
$N$ complex refractive index
$N_C$ effective density of conduction band states
$N_D$ donor atom concentration
$N_V$ effective density of valence band states
$P_{in}$ incident light power density
$P_{\text{max}}$ maximum power density
$q$ elementary charge
$R$ reflectance
$R_{sh}$ sheet resistance
$R_C$ contact resistance
$R_{CT}$ series resistance of the contact
$R_L$ load resistance
$R_P$ parallel resistance
$R_S$ series resistance
$R_{SC}$ series resistance of the semiconductor
$T$ temperature
$U_{NR}$ non-radiative recombination rate
$U_{RR}$ radiative recombination rate
$V_{OC}$ open-circuit voltage
$\alpha$ absorption coefficient
$\epsilon_r$ dielectric constant
$\eta$ diode ideality factor
$\eta_{fex}$ external fluorescence efficiency
$\lambda$ wavelength
$\mu$ charge carrier mobility
$\mu_e$ electron mobility
$\mu_h$ hole mobility
$\mu_m$ relative permeability
$\sigma$ electrical conductivity
<table>
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<tr>
<td>$\tau$</td>
<td>transmittance</td>
</tr>
<tr>
<td>$\tau_r$</td>
<td>minority carrier lifetime</td>
</tr>
<tr>
<td>$\chi$</td>
<td>electron affinity</td>
</tr>
<tr>
<td>AFM</td>
<td>atomic force microscope</td>
</tr>
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<td>Ag</td>
<td>silver</td>
</tr>
<tr>
<td>Al</td>
<td>aluminum</td>
</tr>
<tr>
<td>AO</td>
<td>atomic orbital</td>
</tr>
<tr>
<td>ARC</td>
<td>antireflection coating</td>
</tr>
<tr>
<td>Au</td>
<td>gold</td>
</tr>
<tr>
<td>AWR</td>
<td>average weighted reflectance</td>
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<tr>
<td>BOE</td>
<td>buffered oxide etch</td>
</tr>
<tr>
<td>CT</td>
<td>charge transfer</td>
</tr>
<tr>
<td>DI water</td>
<td>deionized water</td>
</tr>
<tr>
<td>DMSO</td>
<td>dimethyl sulfoxide</td>
</tr>
<tr>
<td>DOS</td>
<td>density of states</td>
</tr>
<tr>
<td>e-beam</td>
<td>electron beam</td>
</tr>
<tr>
<td>e-h pair</td>
<td>electron-hole pair</td>
</tr>
<tr>
<td>EQE</td>
<td>external quantum efficiency</td>
</tr>
<tr>
<td>FF</td>
<td>fill factor</td>
</tr>
<tr>
<td>FOM</td>
<td>figure of merit</td>
</tr>
<tr>
<td>GaN</td>
<td>gallium nitride</td>
</tr>
<tr>
<td>HCl</td>
<td>hydrochloric acid</td>
</tr>
<tr>
<td>HF</td>
<td>hydrofluoric acid</td>
</tr>
<tr>
<td>HLG</td>
<td>HOMO-LUMO gap</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>IPA</td>
<td>isopropyl alcohol</td>
</tr>
<tr>
<td>IQE</td>
<td>internal quantum efficiency</td>
</tr>
<tr>
<td>J-V</td>
<td>current density-voltage</td>
</tr>
<tr>
<td>KOH</td>
<td>potassium hydroxide</td>
</tr>
<tr>
<td>LCAO</td>
<td>linear combination of atomic orbitals</td>
</tr>
<tr>
<td>Li</td>
<td>lithium</td>
</tr>
<tr>
<td>LiF</td>
<td>lithium fluoride</td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>Symbol</td>
<td>Abbreviation</td>
</tr>
<tr>
<td>--------</td>
<td>--------------</td>
</tr>
<tr>
<td>MIS</td>
<td>metal-insulator-semiconductor</td>
</tr>
<tr>
<td>MO</td>
<td>molecular orbital</td>
</tr>
<tr>
<td>MOVPE</td>
<td>metalorganic vapor phase epitaxy</td>
</tr>
<tr>
<td>MPP</td>
<td>maximum power point</td>
</tr>
<tr>
<td>OLED</td>
<td>organic light-emitting diode</td>
</tr>
<tr>
<td>OPV</td>
<td>organic photovoltaics</td>
</tr>
<tr>
<td>OVPD</td>
<td>organic vapor phase deposition</td>
</tr>
<tr>
<td>P3HT</td>
<td>poly(3-hexylthiophene-2,5-diyl)</td>
</tr>
<tr>
<td>PCE</td>
<td>power conversion efficiency</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)</td>
</tr>
<tr>
<td>PEN</td>
<td>pentacene</td>
</tr>
<tr>
<td>PFN</td>
<td>poly[(9,9-bis(3’-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)]</td>
</tr>
<tr>
<td>PV</td>
<td>photovoltaic</td>
</tr>
<tr>
<td>RMS</td>
<td>root mean square</td>
</tr>
<tr>
<td>RPM</td>
<td>rotations per minute</td>
</tr>
<tr>
<td>RT</td>
<td>room temperature</td>
</tr>
<tr>
<td>SCR</td>
<td>space charge region</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
</tr>
<tr>
<td>Si</td>
<td>silicon</td>
</tr>
<tr>
<td>Spiro-MeOTAD</td>
<td>2,2',7,7'-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9’-spirobifluorene</td>
</tr>
<tr>
<td>SRH</td>
<td>Shockley-Read-Hall</td>
</tr>
<tr>
<td>Ti</td>
<td>titanium</td>
</tr>
<tr>
<td>TiO₂</td>
<td>titanium dioxide</td>
</tr>
<tr>
<td>TMAH</td>
<td>tetramethylammonium hydroxide</td>
</tr>
<tr>
<td>WF</td>
<td>work function</td>
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</table>
Chapter 1

Introduction

1.1 Motivation

The continuously increasing global population and the constant improvement of their living standards cause a significantly increasing global energy demand. Due to the finite supply of fossil fuels and their environmental impact especially related to massive CO$_2$ emissions, there is an emerging need to shift to renewable, non-polluting energy sources (e.g. photovoltaics (PV), wind energy). Although the share of renewable energy sources has continuously increased in the last years, in 2015, the non-renewable energy sources still had a contribution of 76.3% to the global electricity production (cf. Fig. 1.1).

Fig. 1.1: Estimated renewable energy share of global electricity production for the end of 2015 (CSP: concentrating solar thermal power) [1].

According to [2], the potential of solar energy which could be harvested by humans is 1575–49837 EJ per year. This is 286 – 9061 times the global energy consumption in
INTRODUCTION

1.2 This Work

2015 (5.5 EJ [3]). Therefore, using PV for the generation of electricity is one of the most promising alternatives to burning fossil fuels. However, in 2015, the share of PV to the global electricity production was only 1.2%. The main reason for the low market penetration is its high cost per kWh of 10–30 cent (for Germany, coal: ~5 cent/kWh, gas: <10 cent/kWh [4]). As a consequence, reducing the cost of solar energy generation is essential.

In 2015, silicon (Si) wafer based PV technology accounted for more than 90% of the total solar cell production [5]. Si-based solar cells are efficient (17–21% in average [5]), but they are rather expensive. To a non-negligible extent, this is related to the high-temperature, and thus cost-intensive, doping process which furthermore requires complicated, high-priced equipment (e.g. ultra-clean high-temperature furnaces) [6, 7]. As a consequence, the elimination of the cost-intensive doping process step is a promising strategy to reduce the manufacturing cost of Si solar cells.

In this context, one promising approach are hybrid organic/Si solar cells. In these devices, a usually hole-conducting organic semiconductor is deposited on crystalline n-doped Si. The hybrid heterojunction is used to replace the functionality of the pn-junction of conventional Si solar cells. The major advantages of organic semiconductors are their very simple processability and the tuneability of their opto-electrical properties in a wide range. Thin films of organic semiconductors can be deposited using low-cost and high-throughput techniques, such as spray-coating, inkjet printing or lamination [8]. Furthermore, the tuneability allows for the production of tailor-made, application-specific materials. Since the photocurrent ($I_{ph}$) generation in Si-based hybrid solar cells predominantly takes place in Si, theoretically, for the hybrid organic/Si solar cells, efficiencies comparable to those of conventional crystalline Si solar cells are attainable [9].

1.2 This Work

In this work, hybrid organic/inorganic solar cells are studied. First, devices based on different combinations of organic and inorganic semiconductors are characterized to demonstrate the functional principles of this type of solar cells (additional $I_{ph}$ generation, blocking of the reverse electron current, antireflection coating (ARC), (cf. Sec. 1.6)).

To demonstrate the additional $I_{ph}$ generation within the organic semiconductor, hybrid solar cells based on the wide-bandgap semiconductor gallium nitride (GaN) are
investigated. In contrast to Si, the bandgap ($E_G$) of GaN is larger than the HOMO-LUMO gap (HLG, HOMO: highest occupied molecular orbital, LUMO: lowest unoccupied molecular orbital) of the investigated organic semiconductor. This makes it especially favorable to investigate the $I_{ph}$ generation in the organic semiconductor since there is a wavelength range in which only the organic semiconductor can contribute to $I_{ph}$. As organic part of the hybrid solar cell, the small molecule pentacene (PEN) is employed.

To demonstrate the blocking of the reverse electron current and the function as an antireflection coating of the organic film, devices based on Si as inorganic part of the hybrid solar cell are studied. As electron blocking organic materials, the polymers poly(3-hexylthiophene-2,5-diyl) (P3HT) and poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) are used and for the ARC, the small molecule 2,2',7,7'-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (Spiro-MeOTAD) is employed.

After the demonstration of the functional principles, the device structure of the Si-based hybrid solar cells is optimized to improve their efficiency and explore the potential of this hybrid approach.

The top contact layout and composition are optimized to improve its transmittance ($\tau$) and thus the short-circuit current density ($J_{SC}$) of the solar cells. An anisotropic etching step is introduced to reduce the reflection losses at the organic/Si interface and in turn further improve $J_{SC}$. Furthermore, different backside contact interlayers are investigated to reduce the contact resistance and hence improve the fill factor (FF) of the solar cells.

1.3 Semiconductor Basics

In this section, the fundamentals of the substantially different properties of inorganic and organic semiconductors are discussed. Particular attention is paid to the energetics of both material classes and the different $I_{ph}$ generation mechanisms. These are fundamental to comprehend the functional principle of the hybrid organic/inorganic solar cells. A detailed description of this topic can be found e.g. in [10, 11, 12, 13, 14, 15, 16].
1.3.1 Inorganic Semiconductors

Most commonly, inorganic semiconductors exhibit a crystalline structure which is comprised of one (elemental semiconductor, e.g. Si) or more (compound semiconductor, e.g. GaN) chemical elements covalently bound to each other.

Due to the interaction of the periodically arranged atoms, the energy states of the single atoms are broadened and bands are formed [10]. The most relevant energy bands are the valence band (highest occupied band) and the conduction band (lowest unoccupied band) with their corresponding band edge energies $E_V$ and $E_C$. For the graphical representation of the energetics, band diagrams are used in which all energy levels are plotted in reference to the vacuum level energy ($E_{\text{vac}}$). Other relevant parameters which can be derived from the band diagram are:

- the bandgap $E_G = E_C - E_V$
- the Fermi level energy ($E_F$)
- the work function $WF = E_{\text{vac}} - E_F$ which is the minimum work needed to extract an electron from the solid to the vacuum
- the electron affinity $\chi = E_C - E_{\text{vac}}$ which is the amount of energy released when an electron is inserted to a neutral atom out of the vacuum

An exemplary band diagram of an inorganic semiconductor is shown in Fig. 1.2 (a).

![Exemplary band diagram of an undoped (a) and n- and p-type doped (b) inorganic semiconductors.](image)

**Fig. 1.2:** Exemplary band diagram of an undoped (a) and n- and p-type doped (b) inorganic semiconductors.
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The electrical conductivity ($\sigma$) of inorganic semiconductors is directly dependent on its concentration of mobile charge carriers ($n$: electrons, $p$: holes) and the respective mobilities $\mu_n$ and $\mu_p$ [10]:

$$\sigma = q (n\mu_n + p\mu_p)$$  \hspace{1cm} (1.1)

$q$: elementary charge

For an intrinsic semiconductor under thermal equilibrium [10]:

$$n = p = n_i$$  \hspace{1cm} (1.2)

with:  \hspace{1cm} \[ n_i = \sqrt{N_C N_V \exp \left( -\frac{E_G}{2k_BT} \right)} \]  \hspace{1cm} (1.3)

$n_i$: intrinsic charge carrier density, $N_C$: effective density of conduction band states, $N_V$: effective density of valence band states, $k_B$: Boltzmann constant, $T$: temperature

In a perfectly crystalline inorganic semiconductor, the energy bands are extended over the entire volume and the transport of mobile charge carriers within these bands is only limited by scattering mechanisms, e.g. impurity or phonon scattering [10]. As a consequence, high charge carrier mobilities ($\mu$) are achieved (e.g. Si: electron mobility $\mu_e \sim 1500 \text{ cm}^2/\text{Vs}$, hole mobility $\mu_h \sim 450 \text{ cm}^2/\text{Vs}$ for room temperature (RT) [17]).

The concentration of mobile charge carriers and thus $\sigma$ of the semiconductor can be varied by doping. Here, dopant atoms with a different number of valence electrons from that of the host material are introduced into the crystal. If the dopant has an additional valence electron, it is called donor (n-type dopant) and if it exhibits one less, its called acceptor (p-type dopant). The additional electron can be transferred into the conduction band with low energy input and the acceptor trap state can be easily filled by a valence band electron from the semiconductor [10]. This is represented in the band diagram by the donor level energy ($E_D$) close to $E_C$ or the acceptor level energy ($E_A$) close to $E_V$, and as a result a corresponding shift of $E_F$ (cf. Fig. 1.2 (b)). As a consequence, usually already for RT, a significant number of free conduction band electrons or valence band holes are generated out of the donor or acceptor states, respectively [10]. The electron and hole concentrations
of a doped semiconductor in thermal equilibrium can be determined as follows:

\[ n \cdot p = n_i^2 \]  \hspace{1cm} (1.4)

with:
\[ n = N_C \exp \left( - \frac{E_C - E_F}{k_B T} \right) \]  \hspace{1cm} (1.5)
\[ p = N_V \exp \left( - \frac{E_F - E_V}{k_B T} \right) \]  \hspace{1cm} (1.6)

By appropriate doping, the type of free charge carriers (electrons or holes) as well as their concentration can be varied. By this, \( \sigma \) of the semiconductor can be tuned in a wide range.

If an energy quantum larger than \( E_G \) is added to the semiconductor, e.g. by illumination, an electron is transferred from the valence band into the conduction band by leaving a hole in the valence band. The quasiparticle formed by the interacting electron-hole pair (e-h pair) is named exciton. Due to the generally large dielectric constant (\( \epsilon_r \)) of inorganic semiconductors, the interaction of the electron and the hole and in turn the absolute exciton binding energy (\( E_{ex} \)) are very small, usually below the thermal energy at RT of \( \sim 25 \text{ meV} \) \([10]\). As a consequence, the excitons instantly dissociate at RT and free mobile charge carriers are generated. In contrast to doping the semiconductor, this is a non-equilibrium process and thus \( n \cdot p \neq n_i^2 \).

### 1.3.2 Organic Semiconductors

By definition, organic compounds are carbon-containing molecules. To enable semiconducting characteristics, they have to exhibit a conjugated system of \( \pi \) bonds with delocalized electrons \([14]\). A conjugated system consists of an alternation of single and double bonds between consecutive carbon atoms \([18]\). In this configuration, the carbon atoms exhibit a sp\(^2\) hybridization. In the ground state, a carbon atom has an electron configuration of \( 1s^2 \ 2s^2 \ 2p^2 \) \([14]\). For the sp\(^2\) hybridization, three symmetric in-plane hybrid atomic orbitals (AO) with an angle of 120° in between are formed by a linear combination of the 2s AO and two out of three 2p AO of the carbon atom \([19]\) (cf. Fig. 1.3).

The sp\(^2\) hybrid orbitals can form \( \sigma \) bonds to adjacent atoms. The remaining 2p orbital is used two form a \( \pi \) bond to an adjacent sp\(^2\)-hybridized carbon atom \([21]\). For illustration purposes, Fig. 1.4 shows the structural formula and a schematic drawing of the molecular orbitals of the most simple double-bonded hydrocarbon ethene.
1.3 Semiconductor Basics

**Fig. 1.3:** Ground state and $sp^2$ hybrid AO of a carbon atom [20].

In an alternating chain of single and double bonds, the remaining $2p$ AO and in turn the contained electrons are delocalized over the entire conjugated system [23]. According to the LCAO (linear combination of atomic orbitals) theory, the orbitals of a molecule (MO) can be approximated by a linear combination of the participating AO [24]. The AO can be combined either in-phase or out-of-phase resulting in bonding or antibonding MO, respectively [25] (cf. Fig. 1.5 (a)).

In the context of organic semiconductors, the most important MO are the highest occupied MO (HOMO) and the lowest unoccupied MO (LUMO). When comparing with inorganic semiconductors, HOMO and LUMO in principle correspond to the valence and conduction band edges. As for the inorganic semiconductors, an exciton is formed by transferring an electron from the HOMO into the LUMO if an appropriate energy quantum is introduced to the organic semiconductor. As a consequence, the HLG forms the counterpart to $E_G$ in the inorganic semiconductors. In contrast to the excitons in inorganic semiconductors, here, strongly bound excitons ($E_{ex} \sim 0.3–1$ eV [27]) are formed due to the low $\epsilon_r$ of the organic semiconductors and the confinement of the e-h pair to the size of a molecule. As
a consequence, the excitons in organic semiconductors do not dissociate instantaneously at RT. Actually, an additional energy input is necessary for their dissociation otherwise they recombine (radiatively or non-radiatively). This leads to fundamentally different characteristics regarding the application of organic semiconductors in PV devices. This will be discussed in more detail in Sec. 1.6.

The structure of organic semiconductors can vary from totally amorphous to that of molecular crystals. For molecular crystals, the \( \pi \) electron systems of the single molecules are coupled via hydrogen bonds and/or van der Waals interaction [28, 29]. As a consequence, in analogy with inorganic crystals, the energy levels are broadened and energy bands are formed [15]. However, compared to inorganic semiconductors, the interaction and in turn the delocalization of the electrons are weak. Hence, they exhibit significantly lower charge carrier mobilities \( \mu \) (0.1–20 cm\(^2\)/Vs [30]). Furthermore, due to this weak interaction, moderate temperatures are sufficient to disturb the order and in turn the band structure [15, 31].

With increasing disorder, the energy levels are becoming discrete again. For the extreme of a totally amorphous structure, the molecules are randomly arranged and thus the interaction of adjacent molecules varies. As a result, the discrete energy states of the single molecules are statistically (Gaussian) distributed with maximum DOS values at the positions of the band edges of the molecular crystal [15] (cf. Fig. 1.5 (b)). Therefore, the
charge carriers have to overcome a spatial and an energetic barrier to be transferred to an adjacent molecule [14]. This transport mechanism is named hopping transport since the charge carriers have to “hop” from molecule to molecule (cf. Fig. 1.5 (c)). Each “hop” can be considered as a thermally activated tunneling process [32]. As a result, amorphous organic semiconductors usually exhibit a significantly lower $\mu$ ($<0.1 \text{cm}^2/\text{Vs}$ [30]) compared to their crystalline counterparts and especially compared to inorganic semiconductors [15].

In analogy with inorganic semiconductors, the energetics and in turn the electrical properties of organic semiconductors can be altered by electrical doping. However, the doping mechanism in organic semiconductors differs from that of inorganic semiconductors. Whereas in inorganic semiconductors, doping is based on the ionization of dopant atoms, in organic semiconductors, electrons have to be introduced to the LUMO (n-type) or removed from the HOMO (p-type) of a molecule [33]. As a result, the dopant has to exhibit appropriate energy levels: For n-type doping, the valence band/HOMO of the dopant must be above the LUMO of the matrix material and for p-type doping, the conduction band/LUMO has to be below the HOMO of the matrix material [34] (cf. Fig. 1.6). As a consequence of carrier localization and hopping transport, the doping efficiency in organic semiconductors is much lower compared to that of their inorganic counterparts. As a result, significantly higher doping concentrations in the order of percent are necessary [35].

Fig. 1.6: Schematic illustration of the doping mechanism in organic semiconductors [27].

### 1.4 Solar Cell Basics

Solar cells are electronic devices which convert solar radiation into electrical power. In principle, solar cells are diodes which comprise a photoactive layer for light absorption.
Nevertheless, they have special characteristics and requirements which will be discussed in this section.

First, the fundamental operation principle of inorganic and organic solar cells is discussed. Subsequently, the equivalent circuit and the corresponding equations to describe the current density-voltage (J-V) characteristics of a solar cell are depicted. Finally, common figures of merit of solar cells are introduced.

### 1.4.1 Fundamental Operation Principle

A solar cell utilizes the photovoltaic effect to convert the energy of the incident light into electric energy. Basically, this process can be divided into three fundamental steps which are schematically depicted in Fig. 1.7 for an inorganic (Schottky type) and an organic bilayer (donor/acceptor) type solar cell, respectively.

1. absorption of light $\Rightarrow$ generation of e-h pairs/excitons
2. separation of electrons and holes
   a) exciton diffusion
   b) exciton dissociation \{ only for organic solar cells \}
3. extraction of electrons and holes at the opposing contacts

**Fig. 1.7:** Schematic demonstration of the operation principle of inorganic and organic solar cells exemplified by a Schottky type solar cell (a) and a bilayer organic solar cell (b).
Absorption and generation of e-h pairs

The first step of the energy conversion process is the absorption of the incident light. Basically, there are two requirements for a photon to be absorbed in the solar cell. First, the photon has to reach the active region of the device and second, its energy $E_{\text{photon}}$ has to be large enough to overcome $E_G$ (for inorganic materials) or $\text{HLG}^*$ (for organic materials) of the solar cell material.

The first process is limited by the absorption losses in the layers which are on top of the active region (e.g. contacts, extraction layers) on the one hand and by reflection losses at the interfaces on the other hand. As a consequence, to reduce the absorption losses, the on-top layers have to be as transparent as possible. Furthermore, the reflection losses can be reduced by the utilization of an antireflection coating (ARC) or by a texturing of the interface (cf. Sec. 1.5).

For an efficient utilization of the solar spectrum, $E_G/\text{HLG}$ of the active material should be as small as possible. However, if $E_{\text{photon}}$ is larger than $E_G/\text{HLG}$, the excess energy is lost due to thermalization [36]. As a consequence, with decreasing $E_G/\text{HLG}$, the number of generated e-h pairs increases, but on the other hand, the thermalization losses increase as well. According to the calculations of Shockley and Queisser [37, 38], the optimal $E_G$ of a material used in a p-n junction based solar cell is $\sim 1.3$ eV. An option to overcome this limitation are stacked solar cells which employ more than one absorber material with different $E_G/\text{HLG}$. Hereby, a larger fraction of the solar spectrum can be utilized without significantly increasing the thermalization losses [39].

Charge carrier separation

In the next step, the generated e-h pairs have to be separated. This step is fundamentally different for solar cells based on inorganic or organic semiconductors, respectively.

In inorganic semiconductors, as described in Sec. 1.3, $E_{\text{ex}}$ normally is below the thermal energy at RT and therefore free e-h pairs are generated. To separate them, only an internal electrical field, e.g. in the space charge region (SCR) of a Schottky contact (cf. Fig. 1.7 (a)), is necessary in which the electrons and holes drift in opposite directions.

*In organic semiconductors, the optical bandgap can differ from HLG due to the direct excitation of the first singlet excitonic state $S_1$. For simplification, here, HLG is used as equivalent for the optical bandgap.
In contrast, in organic semiconductors, strongly bound excitons \((E_{ex} \sim 0.3–1 \text{eV})\) are generated which do not instantaneously dissociate at RT (cf. Sec. 1.3). Here, additional energy or a heterojunction is necessary to split the exciton. In organic photovoltaics (OPV), commonly, a donor/acceptor heterojunction is used to separate the excitons. The LUMO of the acceptor (for electron transfer) or the HOMO of the donor (for hole transfer) must be appropriate to facilitate either the electron or the hole transfer into the adjacent material. Thus, an energetically favorable charge transfer (CT) exciton is formed whose electron and hole are located at two different molecules. Subsequently, the CT exciton, which exhibits a lower binding energy, dissociates into a free e-h pair \([40, 41]\). Since the exciton is electrically neutral, it is not affected by an electric field. Therefore, the movement of the exciton is a statistical diffusion process. As a consequence, only excitons which reach the heterojunction interface within their diffusion length \(L_D\) are dissociated. All other excitons recombine and thus cannot contribute to \(I_{ph}\). Once the exciton is dissociated into free charge carriers, the electron and hole can be separated by an internal electric field again.

**Charge carrier transport and extraction**

In the last step of the \(I_{ph}\) generation, the separated charge carriers have to be transferred to and extracted at the respective contacts without recombining. The dominant loss mechanisms are different for inorganic and organic solar cells.

For inorganic solar cells, the dominant recombination mechanism are (radiative) band-to-band recombination, Shockley-Read-Hall (SRH) recombination and Auger recombination \([42]\) (cf. Fig. 1.8). For direct-bandgap materials, e.g. GaN, the radiative band-to-band recombination dominates. However, for indirect-bandgap materials, such as the most commonly used Si, this mechanism usually can be neglected. Here, the SRH recombination, which is a recombination process via deep levels formed by impurities or defects, is more important. The deeper the trap, the higher the recombination probability. The traps can be either located in the bulk or at the surface/interface. Auger recombination is most significant for high charge carrier concentrations as they occur at high doping levels or for concentrated illumination \([43]\).

For conventional organic solar cells, which are comprised of a donor and an acceptor material, the main difference compared to inorganic solar cells is that the transport of electrons and holes takes place in different materials. Electrons are transported in the acceptor and holes in the donor material. As a consequence, the recombination of separated
charge carriers is a bimolecular process and thus is limited to the donor/acceptor interfaces. The main recombination mechanisms are Langevin and SRH recombination [44]. The Langevin theory describes a band-to-band recombination process whose effective rate is limited by the finding of electron and hole (diffusion-limited). Thus, this recombination mechanism is dominant in materials with low charge carrier mobilities such as organic semiconductors. In analogy with the inorganic semiconductors, the SRH recombination is dominant if a significant number of trap states are present in the device.

Finally, to ensure an efficient charge carrier extraction, the energy levels of the contact materials have to match those of the charge-transporting layers. The aim is to prevent the formation of an energetic barrier which hinders the charge extraction and thus would enhance the recombination losses.

### 1.4.2 Equivalent Circuit

An ideal solar cell can be described by a rectifying diode which is parallel-connected to a current source. Here, the current source represents the photocurrent which is generated in the solar cell under illumination. The photocurrent is a reverse current. As a consequence, the J-V characteristics of the ideal solar cell can be described by the Shockley diode equation superposed with a constant photocurrent density $J_{ph}$ [45, 46]:

$$J = J_0 \left[ \exp \left( \frac{qV}{\eta k_B T} \right) - 1 \right] - J_{ph}$$

(1.7)

$J_0$: dark saturation current density, $\eta$: diode ideality factor
In this simplified model, for defined measurement conditions \((T\) constant), the J-V characteristics are predominantly determined by \(J_{ph}\) and \(J_0\). While the first is directly related to the charge generation efficiency of the solar cell, the second can be considered as a measure of the detrimental recombination current of the device [47]. The diode ideality factor \(\eta\) describes the difference between a practical and an ideal diode which is attributed to intrinsic loss mechanisms. Normally, \(\eta\) has a value in the range of 1 – 2. In inorganic diodes, \(\eta\) is mainly determined by the dominant recombination and transport mechanisms [48]. However, for organic semiconductors, the circumstances affecting \(\eta\) are not completely comprehended [49, 46].

To better fit the characteristics of a real solar cell, a parallel \((R_P)\) and a series resistance \((R_S)\) are added to the equivalent circuit (cf. Fig. 1.9). In \(R_S\), all serial resistances (e.g. contact resistances, lead resistances, etc.) are summarized. On the other hand, all shunting phenomena are consolidated in a finite \(R_P\).

![Fig. 1.9: Common equivalent circuit of a solar cell (\(J_{ph}\): photocurrent density, \(R_P\): parallel resistance, \(R_S\): series resistance, \(R_L\): load resistance) [42].](image)

According to this modified equivalent circuit, the current density of the solar cell can be described as follows:

\[
J = J_0 \left[ \exp \left( \frac{q (V - JAR_S)}{\eta k_B T} \right) - 1 \right] + \frac{V - JAR_S}{R_P} - J_{ph} \tag{1.8}
\]

\(A\): solar cell area

### 1.4.3 Figures of Merit

The most important figures of merit (FOM) of a solar cell are extracted from its illuminated J-V characteristics and are introduced in this section. Exemplary J-V characteristics of a solar cell with and without illumination are shown in Fig. 1.10.
Fig. 1.10: Typical J-V characteristics (illuminated and dark) of a solar cell ($J_{SC}$: short-circuit current density, $V_{OC}$: open-circuit voltage, MPP: maximum power point.

**$J_{SC}$: short-circuit current density**

$J_{SC}$ is defined as the current density measured at short-circuit conditions ($V = 0$). For an ideal solar cell, according to equation Eqn. 1.7, $J_{SC}$ can be determined as follows:

$$J_{SC} = -J_{ph} \quad (1.9)$$

As a consequence, for a defined illumination intensity, $J_{SC}$ is determined by the charge generation and separation efficiency of the solar cell. Furthermore, for a non-ideal solar cell, $J_{SC}$ can differ from $J_{ph}$ due to $R_S$ and $R_P$ (cf. Eqn. 1.8).

**$V_{OC}$: open-circuit voltage**

$V_{OC}$ is specified as the voltage measured at open-circuit conditions ($J = 0$). According to equation Eqn. 1.7, $V_{OC}$ of an ideal solar cell can be determined as:

$$V_{OC} = \frac{\eta k_B T}{q} \ln \left( \frac{J_{ph}}{J_0} + 1 \right) \quad (1.10)$$

The cell temperature $T$ and the photocurrent density $J_{ph}$ (depended on the illumination intensity) are defined by the measurement or application conditions. Furthermore, a higher $\eta$ would deteriorate the device performance (lower FF, see below). Thus, the only way to optimize $V_{OC}$ is by reducing $J_0$ and as a result the recombination losses of the solar cell.
**$P_{\text{max}}$: maximum power density**

The generated power of a solar cell strongly depends on the employed operation point. $P_{\text{max}}$ is the maximum power density which can be delivered by a solar cell. The corresponding operation point is denoted maximum power point (MPP). $P_{\text{max}}$ is specified as:

$$P_{\text{max}} = -V_{\text{MPP}} \cdot J_{\text{MPP}}$$ (1.11)

**FF: fill factor**

The FF is a measure of the quality of the solar cell and is defined as:

$$\text{FF} = \frac{P_{\text{max}}}{V_{\text{OC}} \cdot J_{\text{SC}}}$$ (1.12)

In Fig. 1.10, the FF is depicted as the ratio of the blue to the red area. The higher the FF, the closer are the characteristics to that of an ideal solar cell ($R_S = 0, R_P = \infty$, idealized diode with a threshold voltage of $V_{\text{OC}}$). The FF is mainly influenced by $R_S$ and $R_P$ of the device. The larger $R_S$ and the lower $R_P$, the lower is the FF of the solar cell. Additionally, the FF decreases with increasing diode ideality factor $\eta$.

**PCE: power conversion efficiency**

The power conversion efficiency (PCE) is the most common parameter in the context of solar cell efficiencies. It is a measure of how efficient the incident light power (density) $P_{\text{in}}$ is converted into electrical power (density) by the solar cell operated in its MPP. The PCE is defined as follows:

$$\text{PCE} = \frac{P_{\text{max}}}{P_{\text{in}}} = \frac{-\text{FF} \cdot V_{\text{OC}} \cdot J_{\text{SC}}}{P_{\text{in}}}$$ (1.13)
**1.5 Light Management – Suppression of Reflection Losses**

**$R_S$: series resistance**

Since a large $R_S$ deteriorates the FF of the solar cell, it has to be as low as possible. Most commonly, $R_S$ is extracted from the illuminated J-V measurement as the inverse slope at $V_{OC}$:

$$R_S = \left( A \cdot \frac{\partial J}{\partial V} \bigg|_{V=V_{OC}} \right)^{-1} \quad (1.14)$$

$A$: solar cell area

**$R_P$: parallel resistance**

Since a low $R_P$ implies parasitic shunt currents which directly reduce $J_{SC}$ and thus the efficiency of the solar cell, $R_P$ has to be as high as possible. $R_P$ is commonly extracted from the J-V measurement as the inverse slope at $V = 0$:

$$R_P = \left( A \cdot \frac{\partial J}{\partial V} \bigg|_{V=0} \right)^{-1} \quad (1.15)$$

**1.5 Light Management – Suppression of Reflection Losses**

In a first-order approximation, $I_{ph}$ of a solar cell is directly proportional to the number of photons which reach the active region of the device. As a consequence, for an efficient solar cell, it is crucial to reduce the fraction of photons which are lost before reaching the active region due to reflection either at the surface or at an interface of the solar cell.

When light passes an interface of two materials with different real parts $n$ of their refractive index $N$, a part of the light is reflected and a part is transmitted and refracted (cf. Fig. 1.11).

For non-magnetic materials (relative permeability $\mu_m = 1$), the fraction of the reflected and transmitted light depends on the polarization (perpendicular (s) or parallel (p)) and the incidence angle of the light as well as the $N$ values of both materials. The reflected intensity fraction is defined as reflectance $R$ and the transmitted fraction as transmittance $\tau$. Using
The Fresnel equations [50], for a single interface, they can be calculated as:

\[
R_s = \left| \frac{N_1 \cos \theta_1 - N_2 \cos \theta_2}{N_1 \cos \theta_1 + N_2 \cos \theta_2} \right|^2 \quad R_p = \left| \frac{N_2 \cos \theta_1 - N_1 \cos \theta_2}{N_2 \cos \theta_1 + N_1 \cos \theta_2} \right|^2
\]

\[
\tau_s = 1 - R_s \quad \tau_p = 1 - R_p
\]

with:

\[
N = n - i \cdot k
\]

\[
n: \text{real refractive index, } k: \text{extinction coefficient}
\]

The refraction angle \( \theta_2 \) (complex) depends on the ratio of \( N \) of both materials and can be determined by Snell’s law [50]:

\[
\sin \theta_2 = \frac{N_1}{N_2} \sin \theta_1
\]

For normal incidence, which is a good approximation for planar solar panels, the distinction between \( s \) and \( p \) polarization vanishes and the equation for the reflectance simplifies to:

\[
R = \left| \frac{N_1 - N_2}{N_1 + N_2} \right|^2
\]

As a consequence, at every interface of two materials, a part of the light is reflected and therefore cannot contribute to \( I_{ph} \) of the solar cell. The larger the difference in \( N \) of the materials, the more light is reflected. There are two commonly used approaches to reduce these reflection losses of a solar cell: structuring of the interface and the application of an antireflection coating (ARC). Both methods are discussed in the following subsections.
1.5 Light Management – Suppression of Reflection Losses

1.5.1 Interface Texturing

The first commonly used technique is structuring the interface. As described before, at every interface, a fraction of the light is reflected and a fraction is transmitted. For flat interfaces, the reflected light is lost since it does not reach the active region of the solar cell. However, by purposeful texturing of the interface, it is possible to guide the reflected light to another region of the interface (cf. Fig. 1.12).

![Functional principle of the transmission improvement via surface structuring.](image)

There, again, a part of the light is reflected and a part is transmitted. In a first-order approximation and neglecting interference effects, the total reflectance $R_{\text{ges}}$ is the product of all involved single-step reflectances $R_i$:

$$R_{\text{ges}} = \prod_i R_i \ll 1$$

Thus, the total fraction of the reflected light is significantly reduced compared to a non-structured surface. As a result, more light reaches the active region of the solar cell which in turn improves $J_{SC}$ of the solar cell.

**Example calculation for anisotropically etched Si and a wavelength $\lambda$ of 550 nm:**

By anisotropically etching of Si (discussed in more detail in Sec. 4.2.1), a pyramidal surface structure is generated. The pyramids exhibit an internal angle of $= 54.74^\circ$. Further given parameters are: $N_{\text{air}} = 1$ and $N_{\text{Si}}(550 \text{ nm}) = 4.077 - 0.028i$.

The reflectance of the unstructured Si surface can be determined according to Eqn. 1.19 (normal incidence):

$$R_{\text{unstructured}} \approx 36.7\%$$
Assuming non-polarized incident light and no polarization change due to the first reflection step, the reflectance of the structured Si surface can be approximated using Eqn. 1.16:

first step: \( \theta_{1,1} = 54.74^\circ \)
\[ \Rightarrow R_1 = \frac{R_{s,1} + R_{p,1}}{2} \approx 36.4\% \]

second step: \( \theta_{1,2} = 15.78^\circ \)
\[ \Rightarrow R_2 = \frac{R_{s,2} + R_{p,2}}{2} \approx 36.7\% \]

\[ \Rightarrow R_{\text{structured}} = R_1 \cdot R_2 \approx 13.4\% \ll R_{\text{unstructured}} \approx 36.7\% \]

1.5.2 Antireflection Coating

Another option to reduce the reflection losses is to employ an antireflection coating (ARC). The functional principle of the ARC relies on the destructive interference of the light reflected at both interfaces of the coating (cf. Fig. 1.13).

\[ R_{\text{structured}} = R_1 \cdot R_2 \approx 13.4\% \ll R_{\text{unstructured}} \approx 36.7\% \]

Assuming normal incidence, to achieve completely destructive interference between the reflected light rays \( R_1 \) and \( R_2 \), the real refractive index \( n_{\text{ARC}} \) and the thickness \( t_{\text{ARC}} \) of
the ARC have to fulfill the following requirements:

\[ n_{ARC} = \sqrt{n_1n_2} \]  \hspace{1cm} (1.20)

\[ t_{ARC} = \frac{c \cdot \lambda}{4n_{ARC}} \quad \text{with: } c = 1, 3, 5, ... \]  \hspace{1cm} (1.21)

As a consequence of Eqn. 1.21, completely destructive interference can only be achieved for specific wavelengths \( \frac{4n_{ARC}}{c} \cdot \lambda \). However, partially destructive interference is achieved for a broader wavelength range around these peak wavelengths. A more detailed discussion of this topic can be found in [51, 52].

To demonstrate the impact of an ARC, optical simulations of a silicon substrate with a titanium dioxide (TiO\(_2\)) ARC are performed using the freeware tool FreeSnell [53]. TiO\(_2\) is a widely used ARC for Si-based solar cells [54] since its \( n \) fits well to the requirement of Eqn. 1.20 for the air/Si interface. The simulation results for different TiO\(_2\) thicknesses, including a reference without TiO\(_2\) (0 nm), are shown in Fig. 1.14. The corresponding average weighted (AM1.5 solar spectrum) reflectance (AWR) values are summarized in Tab. 1.1.

![Simulated reflected light intensity of a Si wafer covered with a TiO\(_2\) ARC with different thicknesses.](image-url)

**Fig. 1.14:** Simulated reflected light intensity of a Si wafer covered with a TiO\(_2\) ARC with different thicknesses.
1.6 Operation Principles of Hybrid Solar Cells

In this section, the operation principles of the hybrid solar cells which are investigated in this work are described. First, the energetics of the hybrid solar cell are discussed. Depending on the combination of organic and inorganic semiconductors, the organic material can function either as an additional $I_{ph}$ source or as a blocking layer for the detrimental reverse electron current. The two different mechanisms are discussed in the second and third subsection, respectively.

Furthermore, due to its $n$ in the range of 1.5–2.0, the organic material can function as an ARC for most inorganic semiconductors which normally exhibit larger $n$ values (e.g. $n$(Si) $\sim$3.5). As described in Sec. 1.5.2, this reduces the reflection losses which results in an increase of $J_{SC}$.

1.6.1 Energetics

Since the intrinsic charge carrier concentration in organic semiconductors is commonly very low [15], in a static first-order approximation, they can be considered as insulators.
As a result, it is feasible to describe the hybrid organic/inorganic solar cells as metal-insulator-semiconductor (MIS) structures. In this work, only combinations of hole conducting (p-type) organic semiconductors and n-type doped inorganic semiconductors are investigated. An exemplary energy level diagram is shown in Fig. 1.15.

![Energy Level Diagram of Hybrid Solar Cell](image)

**Fig. 1.15:** Schematic energy level diagram of a hybrid organic/inorganic solar cell.

As mentioned before, besides functioning as an ARC, the organic interlayer can fulfill two different functions: either as an additional $I_{ph}$ source or as an electron blocking layer. Independently of its function, the energy levels of the organic semiconductor, especially the HOMO, have to be aligned to that of the inorganic semiconductor and the top contact material. To ensure an efficient extraction of all generated holes, from the organic as well as from the inorganic semiconductor, the HOMO of the organic material has to be located between $E_V$ of the inorganic semiconductor and the WF of the anode contact material.

Since $I_{ph}$ generation in inorganic semiconductors normally is more efficient compared to that in organic semiconductors, the HLG of the organic semiconductor has to be smaller than $E_G$ of the inorganic semiconductor to enable the utilization of photons with a lower energy and thus allow for additional $I_{ph}$ generation in the organic film.

In contrast, for an efficient blocking of the reverse electron current, the LUMO of the organic semiconductors has to be as high as possible (low $\chi$). Combined with the alignment of the HOMO, this makes a large HLG of the organic material necessary.
1.6.2 Additional Photocurrent Generation

As described in Sec. 1.4.1, the mechanisms of $I_{ph}$ generation in organic and inorganic solar cells are fundamentally different. The distinct generation processes for photons absorbed in the organic and in the inorganic part of the hybrid solar cell are depicted in Fig. 1.16.

![Fig. 1.16: Schematic demonstration of the $I_{ph}$ generation mechanisms in hybrid solar cells (the contacts are omitted for the sake of clarity).]

Photons which are absorbed in the organic semiconductor generate strongly bound excitons. To become dissociated, these excitons have to diffuse to the hybrid interface. Here, the electron is transferred to the energetically favorable conduction band of the inorganic semiconductor. For an efficient dissociation, the energy difference between the LUMO of the organic semiconductor and $E_C$ of the inorganic semiconductor has to be large enough to overcome $E_{ex}$. Furthermore, a transfer of the complete exciton into the inorganic semiconductor is possible. Here, due to $E_{ex} < k_B T$ for RT (cf. Sec. 1.3.1), the exciton instantaneously dissociates into an free e-h pair. The dissociated charge carriers are separated by the internal electric field. The holes are transported in the organic semiconductor to the anode and the electrons in the inorganic semiconductor to the cathode.

As a consequence, only excitons which reach the hybrid interface within their exciton diffusion length ($L_D$) can contribute to $I_{ph}$. All other excitons are lost to recombination. Since the hybrid solar cell has no bulk heterojunction structure as commonly used in classical organic solar cells [44], $L_D$ of the organic material is a very crucial parameter in context of $I_{ph}$ generation. The higher $L_D$, the larger the contributing volume and as a result, the generated $I_{ph}$. Furthermore, to minimize the recombination losses, the thickness
of the organic layer should be comparable to its $L_D$, which is mainly determined by the structure of the organic semiconductor. For polymers, which commonly form amorphous films, normally $L_D$ is less than 10 nm (e.g. ∼8 nm for P3HT [55]). In contrast, for small molecules, which can exhibit a crystalline structure, $L_D$ can reach values above 50 nm (e.g. 50–65 nm for PEN [56, 57]).

On the other hand, photons which are absorbed in the inorganic semiconductor directly generate free e-h pairs which again are separated to the opposing contacts by the internal electric field. Here, it is essential to ensure an unhindered transfer of the hole into the organic semiconductor. As a consequence, the HOMO of the organic semiconductor must not be lower than $E_V$ of the inorganic semiconductor.

### 1.6.3 Blocking of the Reverse Electron Current

The second function of the organic interlayer is to block the detrimental electron dark current of the solar cell (forward current of the non-illuminated diode) which flows in the opposite direction compared to $I_{ph}$ (cf. Fig. 1.17).

According to Eqn. 1.10, $V_{OC}$ of the solar cell is dependent on the ratio $J_{ph}/J_0$, with $J_0$ being a measure for the dark current of the device. As a consequence, a reduction of the electron dark current would directly improve $V_{OC}$ of the solar cell. For a Schottky diode, $J_0$ is determined by the Richardson equation [58]:

$$J_{0,\text{Schottky}} = A^* T^2 \exp \left( -\frac{\varphi_{b,\text{Schottky}}}{k_B T} \right)$$  \hspace{1cm} (1.22)

$A^*$: Richardson constant

By introducing a predominantly hole-conducting organic semiconductor with an energy difference $\Delta E$ between its LUMO and $E_C$ of the inorganic semiconductor, an additional electron barrier is formed which reduces the electron dark current into the anode (cf. Fig. 1.18).
INTRODUCTION

1.6 Operation Principles of Hybrid Solar Cells

Fig. 1.17: Schematic demonstration of the different currents in a Schottky junction solar cell ($\phi_{b,\text{Schottky}}$: barrier height of the Schottky junction).

Fig. 1.18: Schematic demonstration of the different currents in a hybrid organic/inorganic solar cell ($\phi_{b,\text{hybrid}} = \phi_{b,\text{Schottky}} + \Delta E$: barrier height with organic interlayer, $\Delta E = E_{\text{LUMO}} - E_{C}$: additional electron barrier).

The additional energy barrier can be either overcome by thermionic emission or by quantum tunneling through the organic interlayer [59, 60]. As a result, $J_0$ of the hybrid solar cell can be described as:

$$J_{0,\text{hybrid}} = A^*T^2 \exp \left(-\frac{\phi_{b,\text{Schottky}}}{k_B T}\right) \left[ \exp \left(-\frac{\Delta E}{k_B T}\right) + \exp \left(-\frac{2t_{\text{org}} \sqrt{2m_e \Delta E}}{\hbar}\right) \right]$$  \hspace{1cm} (1.23)

$t_{\text{org}}$: thickness of the organic interlayer, $m_e$: effective electron mass of the organic, $\hbar$: reduced Planck constant
The $V_{OC}$ change which results from the introduction of the organic interlayer (assuming no change of $J_{ph}$ and $\eta$) can be estimated according to Eqn. 1.10:

$$\Delta V_{OC} = \frac{\eta k_B T}{q} \left[ \ln \left( \frac{J_{ph}}{J_{0, hybrid}} + 1 \right) - \ln \left( \frac{J_{ph}}{J_{0, Schottky}} + 1 \right) \right]$$

$$\approx \frac{\eta k_B T}{q} \left[ \ln \left( \frac{J_{ph}}{J_{0, hybrid}} \right) - \ln \left( \frac{J_{ph}}{J_{0, Schottky}} \right) \right] = \frac{\eta k_B T}{q} \ln \left( \frac{J_{0, Schottky}}{J_{0, hybrid}} \right)$$

(1.24)

(1.25)

The $J_0$ ratio can be determined from Eqn. 1.22 & 1.23:

$$\frac{J_{0, Schottky}}{J_{0, hybrid}} = \exp \left( -\frac{\Delta E}{k_B T} \right) + \exp \left( -\frac{2t_{org}\sqrt{2m_e\Delta E}}{h} \right)$$

(1.26)

Inserting into Eqn. 1.25 leads to:

$$\Delta V_{OC} = \frac{\eta k_B T}{q} \ln \left( \frac{1}{\exp \left( -\frac{\Delta E}{k_B T} \right) + \exp \left( -\frac{2t_{org}\sqrt{2m_e\Delta E}}{h} \right)} \right)$$

(1.27)

For the extreme cases that either the contribution of thermionic emission or quantum tunneling dominates $J_{0, hybrid}$, the equation can be simplified as follows:

thermionic emission dominant: \[ \Delta V_{OC} \approx \frac{\eta \Delta E}{q} \] (1.28)

quantum tunneling dominant: \[ \Delta V_{OC} \approx \frac{2\sqrt{2m_e\eta k_B T}t_{org}\sqrt{\Delta E}}{qh} \] (1.29)

For the first extreme, the expected $V_{OC}$ change related to the organic interlayer is directly proportional to the energy difference $\Delta E$ between the LUMO of the organic interlayer and $E_C$ of the inorganic semiconductor. For the second extreme, $\Delta V_{OC}$ is proportional to $\sqrt{\Delta E}$ and the thickness of the organic interlayer $t_{org}$ (But: for larger $t_{org}$, thermionic emission gets dominant again). Independently of the dominant mechanism, the insertion of an organic semiconductor with a high LUMO significantly improves the performance of the solar cell.
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However, this improvement is limited by the contribution of the minority carriers (here holes) to $J_0$. According to [61], this hole saturation current density $J_{0,h}$ can be estimated as:

$$J_{0,h} = \frac{q n_i^2}{N_D} \sqrt{\frac{D_h}{\tau_r}} \quad (1.30)$$

$N_D$: donor atom concentration, $D_h$: diffusion coefficient for holes, $	au_r$: minority carrier lifetime, $N_V$: effective density of valence band states

The hole saturation current density $J_{0,h}$ can be considered as a measure for the electron-hole recombination within the solar cell, i.e. recombination at interfaces or in the bulk material, which strongly depends on the minority carrier concentration.

Example calculation for the utilized Si-wafers (cf. Sec. 2.1.1):

In this work, two types of Si wafers with different resistivities $\rho$ of 1–5 Ω cm and 10–20 Ω cm, respectively, are utilized (cf. Sec. 2.1.1). The corresponding $N_D$, $D_h$ [62] and $\tau_r$ [63] values as well as the resulting $J_{0,h}$ for both wafer types are shown in Tab. 1.2. $n_i$ for RT can be calculated according to Eqn. 1.3 as $n_i \approx 8 \cdot 10^9$ cm$^{-3}$.

<table>
<thead>
<tr>
<th>type</th>
<th>$\rho$ [Ω cm]</th>
<th>$N_D$ [$10^{14}$ cm$^{-3}$]</th>
<th>$D_h$ [cm$^2$/s]</th>
<th>$\tau_r$ [μs]</th>
<th>$J_{0,h}$ [$10^{-9}$ mA/cm$^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1–5</td>
<td>9–50</td>
<td>12</td>
<td>55–172</td>
<td>0.5–5.3</td>
</tr>
<tr>
<td>2</td>
<td>10–20</td>
<td>2–5</td>
<td>12</td>
<td>28–40</td>
<td>11.2–33.6</td>
</tr>
</tbody>
</table>

Tab. 1.2: Characteristics of the different employed Si wafers.

According to Eqn. 1.10 (assuming $\eta = 1$), for typical $J_{SC}$ ($\approx J_{ph}$) of 15–35 mA/cm$^2$ this limits $V_{OC}$ to $\sim$0.55–0.63 V for wafer type 1 and $\sim$0.51–0.56 V for wafer type 2. However, the exact values depend on the respective $J_{SC}$ of the solar cells.

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To increase the efficiency of a solar cell, at least one of its FOM ($J_{SC}$, $V_{OC}$, FF) has to be improved. In this section, the main loss mechanisms for each FOM and concepts for improvement are discussed.
1.7.1 Short-Circuit Current Density $J_{SC}$

$J_{SC}$ of a solar cell is mainly determined by two factors:

1. How much light reaches the active region of the solar cell?
2. Which fraction of this light can be utilized for $I_{ph}$ generation?

To increase the quantity of light in the active region, the absorption losses in the layers above the active region and the reflection losses at the corresponding interfaces have to be reduced. This can be realized by improving the transmittance $\tau$ of the top contact and by implementing interface structuring or an ARC to reduce the reflection losses (cf. Sec. 1.5).

The fraction of light which can be utilized is directly dependent on $E_G$ or HLG of the absorber material. The lower $E_G$/HLG, the more light can be harvested (cf. Fig. 1.19). However, as described in Sec. 1.4.1, a lower $E_G$ reduces the attainable $V_{OC}$ of the solar cell due to thermalization losses. An approach to overcome this conflict is to employ multiple photoactive materials with different $E_G$ (stacked solar cells). In this way, the usable fraction of the solar spectrum can be increased without additional thermalization losses [64].

![Fig. 1.19: Maximum attainable $J_{SC}$ of a solar cell (AM1.5 illumination) as a function of the band gap $E_G$ of the photoactive material.](image-url)
1.7 Guidelines for Efficient Solar Cells

1.7.2 Open-Circuit Voltage $V_{OC}$

$V_{OC}$ is fundamentally limited to the energy of a generated e-h pair and therefore by $E_G/\text{HLG}$ of the photoactive material for homojunction devices or by the energy difference between $E_V/E_{HOMO}$ of the donor material and $E_C/E_{LUMO}$ of the acceptor material for heterojunction devices. According to [65], for a homojunction solar cell, this dependence of $V_{OC}$ on $E_G$ can be estimated by the following equation:

$$V_{OC} = \frac{E_G}{q} - \frac{k_B T}{q} \ln \left( \frac{C_{\text{max}}}{C} \right) - \frac{k_B T}{q} \ln \left( \frac{1}{f_{RR} \eta_{fex}} \right)$$

(1.31)

with:

$$f_{RR} = \frac{U_{RR}}{U_{RR} + U_{NR}}$$

(1.32)

$C$: light concentration factor, $f_{RR}$: radiative recombination efficiency

$\eta_{fex}$: external fluorescence efficiency, $U_{RR}$: radiative recombination rate,

$U_{NR}$: non-radiative recombination rate

There are several effects which reduce $V_{OC}$ under non-ideal conditions. To achieve the maximum $V_{OC}$ of $\frac{E_G}{q}$, the following requirements have to be fulfilled:

- optimal light concentration: $C = C_{\text{max}} \approx 46200$

  According to thermodynamics, the maximum $V_{OC}$ can only be reached if the solar cell is able to utilize incident photons within the same solid angle in which photons generated within the solar cell (due to radiative recombination) are emitted into. Thus, for maximum $V_{OC}$, a solid angle of $\pi$ has to be utilized (representing $C = C_{\text{max}}$). To increase the utilized solid angle, optical lenses must be employed to concentrate the incident light onto the active area of the solar cell. However, this effect is not investigated in this work.

- no non-radiative recombination losses: $U_{NR} = 0 \Rightarrow f_{RR} = 1$

  At open-circuit conditions, the generated charge carriers cannot be extracted and thus they build up in density and recombine, ideally radiative. Any non-radiative recombination impairs the carrier density build-up and hence limits $V_{OC}$ of the solar cell [66].

- perfect external fluorescence: $\eta_{fex} = 1$

  $\eta_{fex}$ is a measure for how efficient photons, which are generated within the solar cell due to radiative recombination, can be emitted from the device. Since at open-circuit conditions, radiative recombination is desired, a high $\eta_{fex}$ is an indicator for low...
internal optical losses. Therefore, counter-intuitively, $\eta_{fex}$ close to 1 is necessary for an efficient solar cell [66].

As a consequence, to achieve high $V_{OC}$, besides the concentration of the incident light (not investigated in this work), the optical losses ($\eta_{fex} \Rightarrow 1$) and the non-radiative recombination ($U_{NR} \Rightarrow 0$) have to be minimized. In the context of Eqn. 1.10, minimizing the optical losses improves $J_{ph}$ while a reduction of the non-radiative recombination decreases $J_0$.

The optical losses can be reduced by an efficient light management (cf. Sec. 1.5). An effective approach to reduce $J_0$ is to block the detrimental reverse dark current by implementing an interlayer. The energy levels of this interlayer have to be appropriate to block the unfavored charge carrier type while non-hindering the transport of the desired type of charge carriers. In Sec. 1.6.3, this mechanism is discussed in more detail for an interlayer comprised of an organic semiconductor.

### 1.7.3 Fill Factor FF

The FF of a solar cell is mainly influenced by $R_S$ and $R_P$. For an optimal FF, $R_S$ has to be as low and $R_P$ as high as possible.

In $R_S$, all series resistances for the generated e-h pairs are summarized. The most important ones are the transport resistance within the semiconductors $R_{SC}$, the contact resistances $R_C$ and the transport resistance of the contacts $R_{CT}$. To improve $R_{SC}$, the semiconductors have to be either very thin or exhibit a high conductivity. The second can be tuned e.g. by electrical doping. $R_C$ can be improved e.g. by interface doping or with interlayers to support the charge carrier extraction. For low $R_{CT}$, highly conductive materials have to be utilized for the contacts. For the transparent contact of the solar cell, this is not trivial since high electrical conductivity and high optical transparency are competing demands [67].

To achieve a high $R_P$, parasitic current paths which shunt the diode have to be prevented. Possible reasons for those shunts are e.g. surface/interface currents between the anode and the cathode and non-coalesced or punctured layers within the solar cell.
Chapter 2

Experimental

2.1 Materials

In this section, the materials which are utilized in this work are introduced. The materials are categorized into inorganic and organic materials.

2.1.1 Inorganic Materials

**Gallium Nitride (GaN)**

GaN is a compound semiconductor with a wurtzite crystal structure. It exhibits an electron affinity $\chi$ of 4.1 eV and a direct bandgap $E_G$ of 3.4 eV \cite{68}. The absorption spectrum is depicted in Fig. 2.1 (a). In this work, we employ an $n$-type doped GaN template (Si as dopant) which is grown by metalorganic vapor phase epitaxy (MOVPE) on a 2 in sapphire substrate. The layer stack of the GaN template is shown in Fig. 2.1 (b). It consists of a 2 $\mu$m thick nucleation layer, a 2 $\mu$m thick highly $n$-doped ($n^+$, $N_D \sim 10^{18}$ cm$^{-3}$) and a 1 $\mu$m thick moderately $n$-doped ($n^-$, $N_D \sim 10^{17}$ cm$^{-3}$) region. The functional principle of the hybrid solar cells is mainly determined by the organic/inorganic interface. Thus, only the topmost $n^-$-GaN layer, which is in contact to the organic semiconductor, is relevant. The measured sheet resistance ($R_{sh}$) of the template is 65 $\Omega$/sq.
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2.1 Materials

(a) sapphire substrate
2 µm n+-GaN
2 µm GaN nucleation
1 µm n–-GaN

(b) Fig. 2.1: (a): Absorption spectrum of GaN (at 293 K) [69]. (b): Cross-section of the employed n-GaN template. Doping levels of $n^-$-GaN and $n^+$-GaN layer are $\sim 10^{17}$ cm$^{-3}$ and $\sim 10^{18}$ cm$^{-3}$, respectively.

Silicon (Si)

Si is the most common material in PV technology and besides oxygen, the most abundant element in the crust of the earth [70]. Si crystallizes in a diamond structure and exhibits an indirect band gap with $E_G$ of 1.1 eV and $\chi$ of 4.1 eV [71]. The absorption spectrum of Si is shown in Fig. 2.2. In this work, we use two types of n-doped (phosphorous as dopant) Si wafers with different resistivities (cf. Tab. 2.1) which were obtained from Siegert Wafer. All employed wafers are grown via the Czochralski process [72].

Fig. 2.2: (a): Absorption spectrum of Si [73].
<table>
<thead>
<tr>
<th>type</th>
<th>diameter [mm]</th>
<th>orientation</th>
<th>resistivity [Ω cm]</th>
<th>thickness [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>(100)</td>
<td>1–5</td>
<td>525</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>(100)</td>
<td>10–20</td>
<td>525</td>
</tr>
</tbody>
</table>

**Tab. 2.1: Characteristic values of the employed Si wafers.**

**Lithium Fluoride (LiF)**

Lithium fluoride (LiF) is an insulator \(E_G = 13.6\text{eV} [74]\) with \(\chi \text{ of 1.0eV} [75]\). It is often used as interlayer (~1nm) in organic light-emitting diodes (OLED) [76, 77] and in OPV [78, 79] to improve the electron injection/extraction at the aluminum (Al) cathode/anode contact.

**2.1.2 Organic Materials**

**Pentacene (PEN)**

PEN is a predominantly hole-conducting organic semiconductor. It is a planar small molecule which is comprised of five linearly fused benzene rings and tends to crystallize in the so-called ‘herringbone pattern’ (cf. Fig. 2.3).

Under illumination, Frenkel excitons with a binding energy \(E_{ex}\) of 0.5–0.6eV are generated [83]. The PEN absorption spectrum is depicted in Fig. 2.3 (c). Due to the crystallinity of PEN, large exciton diffusion lengths \(L_D\) in the range of 50–65 nm [56, 57] and \(\mu_h\) in the range of 0.01–10 cm²/Vs [84, 85] are reached. Its LUMO and HOMO energy levels are given as \(-3.0\text{eV}\) and \(-5.0\text{eV}\), respectively [80]. Furthermore, PEN shows a high absorption coefficient \((\alpha)\) in the order of \(10^4\text{cm}^{-1}\) for the visible wavelength range, which is why it is often used as a donor material in organic solar cells [86]. In this work, PEN is deposited from the vapor phase using an organic vapor phase deposition (OVPD) system resulting in a polycrystalline material with grain sizes in the order of 0.1–2µm in diameter.
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2.1 Materials

Fig. 2.3: (a): Structural formula of PEN [80]. (b): Schematic of the herringbone crystal structure (benzene rings are oriented out of plane) [81]. (c): Absorption spectrum of PEN (at RT) and the position of the photoluminescence peaks [82].

2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9’-spirobifluorene (Spiro-MeOTAD)

Spiro-MeOTAD is a small-molecule organic semiconductor which is widely used as hole transport material in perovskite and dye-sensitized solar cells [87, 88]. The structural formula and the absorption spectrum of Spiro-MeOTAD are depicted in Fig. 2.4. For undoped Spiro-MeOTAD, $\mu_h$ in the order of $\sim 10^{-5} \text{cm}^2/\text{Vs}$ is reported [89]. Here, Spiro-MeOTAD powder is obtained from Sigma-Aldrich. The energy levels are given as $-2.1 \text{eV}$ and $-5.0 \text{eV}$ for the LUMO and HOMO, respectively [90]. In this work, Spiro-MeOTAD is processed by spin-coating from a chlorobenzene solution in a nitrogen-filled glove box.
2.1 Materials

Poly(3-hexylthiophene-2,5-diyl) (P3HT)

P3HT is a predominantly hole-conducting conjugated polymer which, due to its high $\alpha \sim 2.5 \cdot 10^5 \text{ cm}^{-1}$ [93], is widely used as donor material in OPV applications [94, 95, 96]. Its structural formula and absorption spectrum are displayed in Fig. 2.5. In P3HT, excitons with $E_{ex} \sim 0.7 \text{ eV}$ [97] and $L_D \sim 8 \text{ nm}$ [55] are generated under illumination. P3HT exhibits $\mu_h$ of $\sim 10^{-4}–10^{-3} \text{ cm}^2/\text{Vs}$ [98]. For P3HT, the morphology strongly depends on the regioregularity. Whereas regiorandom P3HT normally forms amorphous layers, regioregular P3HT tends to be highly crystalline [99]. In this work, regioregular powdery P3HT with number average molecular weight ($M_n$) of 54 000–75 000 g/mol is obtained from Sigma-Aldrich. LUMO and HOMO are specified as $-3.0 \text{ eV}$ and $-5.0 \text{ eV}$, respectively [100]. P3HT is deposited via spin-coating from a toluene solution under ambient conditions.
Poly(3,4-ethylenedioxythiophene):Poly(styrenesulfonate) (PEDOT:PSS)

PEDOT:PSS is the most common transparent conductive polymer and is widely used in electroluminescent and OPV devices [102]. To be precise, PEDOT:PSS is an acidic complex of the conjugated polymer poly(3,4-ethylenedioxythiophene) (PEDOT) and the polyelectrolyte poly(styrene sulfonic acid) (PSS) (cf. Fig. 2.6), forming a stable dispersion in water [102, 103]. PEDOT:PSS is an ionically doped predominantly hole-conducting organic semiconductor [104] with a LUMO of $-3.4 \text{ eV}$ and a HOMO of $-5.1 \text{ eV}$ [105]. Here, a 1.1 wt% solution (pH $< 2.5$) is purchased from Sigma-Aldrich. To enhance the electrical conductivity ($\sigma$) of PEDOT:PSS and to enable the deposition onto the hydrophobic Si surface, 8 wt% dimethyl sulfoxide (DMSO) (Sigma-Aldrich) and 0.5 wt% of the surfactant Capstone FS-3100 (DuPont) are added to the solution [106, 107].

![Fig. 2.6: Structural formula of PEDOT and PSS [108].](image)

![Fig. 2.7: (a): Absorption spectrum of PEDOT:PSS [109].](image)
2.2 Deposition Techniques

For the deposition of the organic materials, different deposition techniques are utilized. For the deposition of the small-molecule PEN, an OVPD system is used. All other organic materials are deposited via spin-coating. Both techniques are briefly described in this section.

2.2.1 Organic Vapor Phase Deposition (OVPD)

OVPD is a deposition technique, which is primarily developed for the fabrication of OLED. In the OVPD system, the different organic materials (most commonly powders) are stored in separate sources which are heated to sublime the organic materials. During the deposition of a material, the respective source is purged with a carrier gas. The sublimed organic material then is transported via the hot carrier gas to the cooled substrate on which it is deposited. A schematic illustration of an OVPD system is shown in Fig. 2.9.

In order to improve the homogeneity of the deposited layer, a showerhead is employed to uniformly distribute the gas flow over the entire substrate area. All lines and the
showerhead are heated to prevent unintentional deposition of the organic material. The deposition rates of the organic materials are controlled by the carrier gas flux. Furthermore, the morphology of the deposited layer can be tuned via the substrate temperature. Since polymers usually break up on sublimation [117], OVPD is only suitable for small molecules.

2.2.2 Spin-Coating

Spin-coating is a method to deposit thin films of a material from a solution onto a substrate. The method utilizes the centrifugal force occurring during the rotation of the substrate to uniformly distribute the solution on its surface. Spin-coating is commonly used to deposit polymer and small-molecule thin films in lab-scale.

For the deposition, a small amount of the solution is applied on the center of the substrate while it is rotating slowly or not rotating at all. Afterwards, the rotation speed is increased to spread the solution. The used solvent is volatile and evaporates during spin-coating. Nevertheless, often an additional drying step at elevated temperatures is applied to completely remove the solvent and to tune the morphology of the deposited layer. A schematic illustration of the spin-coating process is shown in Fig. 2.10.

The deposited film thickness can be easily tuned by the concentration \( c \) of the material in the solution as well as by the rotation speed of the substrate. In addition, the thickness depends on the viscosity of the solution and hence of the used solvent. Furthermore, the solvent (or mixtures of several solvents) can strongly influence the morphology of the deposited layer [119, 120, 121].
2.3 Device Layouts

In this section, the device layout and processing steps of the hybrid organic/inorganic solar cells which are investigated in this work are described. As inorganic part of the device, GaN and Si are utilized. For the GaN-based devices, the template described in Sec. 2.1.1 is employed, and the Si-based devices are processed on commercial Si wafers. Both device types require a different layout and process which are described in the following subsections.

2.3.1 GaN-Based Devices

Since the GaN template is processed on a non-conductive sapphire wafer, both contacts have to be formed on the topside. Schematic drawings of the cross section and the top view of the processed devices are shown in Fig. 2.11. The corresponding energy level diagram based on the literature data cited before is displayed in Fig. 2.12.

Under illumination, light is coupled into the device via the semitransparent gold (Au) top contact (15 nm) and is absorbed either in the organic semiconductor or in GaN. The GaN layer is contacted via an ohmic topside contact which consists of 15 nm titanium.

---

**Fig. 2.10:** Schematic illustration of the spin-coating process [118].

**Fig. 2.11:** Schematic cross section (a) and top view (b) of the processed hybrid organic/GaN solar cells.
2.3 Device Layouts

**Fig. 2.12:** Energy level diagram of the materials of the hybrid organic/GaN solar cells (Au: [122]).

(Ti), 100 nm Al an 50 nm Au. The detailed functional principle of this metal stack is explained in [123]. During the evaporation of the top contact, the bottom right active area (cf. Fig. 2.11 (b)) is covered to keep it metal-free. This area can be used for the characterization of the (unmetallized) deposited organic layer. The template is structured by photolithography to obtain six active areas of $5 \times 5 \text{mm}^2$ each, in which the organic semiconductor is in contact with GaN.

The processing of the devices (process parameters in appendix A.1) can be divided into the following steps which are illustrated in Fig. 2.13 and will be discussed successively:

1. Formation of the ohmic contact
2. Definition of active areas via photolithography
3. Deposition of the organic semiconductor
4. Deposition of the semitransparent top contact

**Fig. 2.13:** Schematic process diagram for the GaN-based hybrid solar cells.

**Formation of the ohmic contact**

All metals (Ti, Al, Au) are deposited on the GaN template via electron beam (e-beam) evaporation through a shadow mask. Afterwards, the metals are annealed in nitrogen atmosphere.
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**2.3 Device Layouts**

**Definition of active areas via photolithography**
To define the active area of the devices and to prevent electrical short circuits between the top contact and GaN, a photoresist layer is deposited on the template and structured via photolithography. The photoresist is deposited by spin-coating (cf. Sec. 2.2.2) and structured via photolithography. The resulting resist layer has a thickness of \(\sim 2.7 \mu m\).

**Deposition of the organic semiconductor**
PEN is deposited via a gas phase process in an OVPD system [124] (cf. Sec. 2.2.1). In the OVPD tool, the PEN powder can be processed as obtained. The thickness controllability of the OVPD tool is significantly better compared to that of the spin-coating process. PEN thicknesses of 60–80 nm have been deposited.

**Deposition of the semitransparent top contact**
Finally, the semitransparent (15 nm) Au top contact is deposited onto the active areas by a thermal evaporation tool within the OVPD system using a shadow mask. This thickness was found to be the best compromise between a low \(R_{sh}\) (4 \(\Omega/\text{sq}\)) on the one hand and a high transmittance \(\tau\) (cf. Fig. 2.16) on the other hand.

**2.3.2 Silicon-Based Devices**
For the Si-based hybrid solar cells, two different reference device layouts are utilized. Schematic drawings of both layouts (cross section + top view) are shown in Fig. 2.14. The corresponding energy level diagram is displayed in Fig. 2.15. Layout #1 exhibits a semitransparent Au top contact whereas layout #2 has a top contact based on a combination of PEDOT:PSS and a Au grid. One difference of both top contacts is their transmittance \(\tau\) (cf. Fig. 2.16). Furthermore, since PEDOT:PSS is a predominantly hole conducting polymer, it functions as a hole selective top contact (cf. Sec. 3.2.2) rendering the organic interlayer optional in this device layout. The different top contacts and their impact on the device performance are discussed in Sec. 4.1 in more detail. Deviations from these reference layouts are described in the relevant sections.
Before processing, the 100 mm Si wafers are divided into quarters. Then, the quarter wafers are structured via photolithography to form six areas of $5 \times 5 \text{mm}^2$ (marked by the blue squares in Fig. 2.14 (b,d)) and three areas of $4 \times 8 \text{mm}^2$ (marked by the red rectangles in Fig. 2.14 (b,d)), in which the organic interlayer is in direct contact with Si. For layout #1, the organic interlayer is covered at the $5 \times 5 \text{mm}^2$ areas by a semitransparent (15 nm) Au top contact. For layout #2, PEDOT:PSS is deposited onto the organic interlayer and the $5 \times 5 \text{mm}^2$ areas are covered with a Au grid. The $4 \times 8 \text{mm}^2$ areas are kept metal-free to characterize the uncoated organic layer. Si is contacted via an evaporated Al backside contact. To prevent electrical short circuits, in layout #2, the six devices are electrically insulated from each other by mechanically scratching PEDOT:PSS in the resist-coated areas. For layout #1, this is not necessary due to the very low conductivity of the thin undoped organic interlayer.
Fig. 2.15: Energy level diagram of the materials of the hybrid organic/Si solar cells. PEDOT:PSS is used as transparent contact material. As organic interlayer, either P3HT or Spiro-MeOTAD is employed.

Fig. 2.16: Transmittances of a 15 nm Au layer and a 65 nm PEDOT:PSS layer (both normalized to the transmittance of the glass substrate). For the PEDOT:PSS-based top contact, the effective transmittance is lower than depicted due to the coverage of the additional Au grid.

The processing of the devices (process parameters in appendix A.2) can be divided into the following steps which are illustrated in Fig. 2.17 and will be discussed successively:

1. Wafer cleaning
2. Removal of the silicon oxide
3. Structuring via photolithography
4. Removal of the newly formed silicon oxide
5. Deposition of the organic semiconductors
6. Deposition of the Au top contact
7. Deposition of the Al backside contact

**Fig. 2.17:** Schematic process diagram for both types of Si-based hybrid solar cells (BOE: oxide removal).

**Wafer cleaning**

To remove organic and inorganic residues from the quartered wafers, they are cleaned using a standard cleaning procedure.

**Removal of the silicon oxide**

The natively formed silicon oxide is removed by a buffered oxide etch (BOE) dip. BOE is an etching solution for silicon oxide and silicon nitride.

**Structuring via photolithography**

As for the GaN-based devices, the quarter wafers are structured via photolithography. Six active areas of $5 \times 5 \text{mm}^2$ and three of $4 \times 8 \text{mm}^2$ for the characterization of the organic layers are formed.

**Removal of the newly formed silicon oxide**

To remove the silicon oxide which is formed during the structuring of the wafers, a second short BOE dip (1 min) is applied.

**Deposition of the organic semiconductors**

All organic semiconductors which are employed in the Si-based hybrid solar cells (P3HT, Spiro-MeOTAD, PEDOT:PSS) are deposited via spin-coating. For P3HT and Spiro-MeOTAD, first, the obtained powder has to be dissolved in an appropriate solvent. P3HT is dissolved in toluene and Spiro-MeOTAD in chlorobenzene. PEDOT:PSS is
obtained as an aqueous solution. To improve the wettability of PEDOT:PSS onto Si and the electrical conductivity $\sigma$ of the deposited layer, Capstone and DMSO are added. The composition of the solutions as well as the rotation speed are varied. After deposition, the organic layers are dried.

**Deposition of the Au top contact**

The Au top contact (semitransparent or grid) is deposited onto the six active areas via e-beam evaporation employing a shadow mask. For layout #1, a Au thickness of 15 nm is employed to form a semitransparent top contact which covers the entire active area. For layout #2, a Au grid contact (150 or 300 nm) is deposited onto PEDOT:PSS at the active areas.

**Deposition of the Al backside contact**

Finally, 200 nm Al are deposited onto the entire backside of the Si wafer by e-beam evaporation to form the substrate contact.

### 2.4 Measurement Techniques

In this section, the measurement techniques and setups which are utilized to characterize the processed solar cells are described.

#### 2.4.1 Illuminated J-V Measurement

In the context of solar cell characterization, the most important measurement technique is the illuminated J-V measurement. As described in Sec. 1.4.3, all characteristic parameters of a solar cell ($J_{SC}$, $V_{OC}$, FF, PCE, $R_S$, $R_P$) can be extracted from this measurement.

For the illumination, an ABET technologies solar simulator is employed which simulates AM1.5 conditions. It is calibrated to a radiant power density of 1000 W/m² using a silicon reference solar cell. The J-V measurements are performed utilizing a Hewlet-Packard 4155A semiconductor analyzer.
2.4.2 External Quantum Efficiency Measurement

The external quantum efficiency (EQE) of a solar cell is defined as:

\[
\text{EQE} = \frac{\text{rate of generated electrons}}{\text{rate of incident photons}} = \frac{\text{photocurrent / charge of an electron}}{\text{incident light power / energy of a photon}}
\]

\[
\Rightarrow \text{EQE}(\lambda) = \frac{I_{ph}}{P_{in} \frac{\lambda}{hcL}} = \frac{I_{ph}hcL}{qP_{in}\lambda}
\]

\[\text{EQE}(\lambda) = \frac{I_{ph}}{P_{in} \frac{\lambda}{hcL}} = \frac{I_{ph}hcL}{qP_{in}\lambda}\] (2.1)

\[I_{ph}: \text{photocurrent; } \lambda: \text{wavelength; } h: \text{Planck constant; } c_L: \text{speed of light}\]

The EQE measurement returns the wavelength-dependent EQE (\(\lambda\)) and therefore shows in which wavelength range and how efficient \(I_{ph}\) is generated in the solar cell.

The EQE measurements are performed using a \(pv\)-\(tools\) LOANA Solar Cell Analysis Tool.

2.4.3 Representation of Measurement Data

Unless otherwise noted, all shown measurement results represent the average data of all functional devices (up to the total of six) on each processed quarter wafer, and the extracted parameters have to be considered as the mean value of these devices.
Chapter 3

Investigation of the Different Functional Principles of Hybrid Solar Cells

As described in Sec. 1.6, dependent on the employed combination of organic and inorganic materials, the organic material can fulfill the following functions in the hybrid organic/inorganic solar cells:

- Additional $I_{ph}$ source
- Blocking of the reverse electron current
- Antireflection coating

In this chapter, hybrid solar cells with different combinations of organic (PEN, P3HT, PEDOT:PSS, Spiro-MeOTAD) and inorganic (GaN, Si) semiconductors are investigated to demonstrate and study the different functional principles.

The results of this chapter have been published in [125], [126], [127] and [128] and were presented at the International Conference on Hybrid and Organic Photovoltaics (HOPV) in Sevilla in 2013, at the 2015 MRS Spring Meeting in San Francisco and the winterschool “Organic Photovoltaics: from materials to modules” at Hasselt University in 2015.

3.1 Additional Photocurrent Generation

Due to the very efficient $I_{ph}$ generation for photons with $E_{photon} > E_G$ of inorganic semiconductors, the only way to achieve an additional $I_{ph}$ generation from the organic semiconductor is to reap additional photons by choosing a material combination in which
the HLG of the organic is smaller than $E_G$ of the inorganic semiconductor. For this case, the organic material allows for the utilization of a larger fraction of the solar spectrum which in turn increases $I_{ph}$ of the solar cell. Furthermore, the employed organic semiconductor has to have a large $L_D$ since the hybrid solar cells are based on a flat heterojunction (in contrast to the bulk heterojunction which is commonly used in OPV devices [44]). As a consequence, $L_D$ of the organic material directly determines the maximum volume which can contribute to the $I_{ph}$ generation.

Thus, to demonstrate this effect, the wide-bandgap ($E_G = 3.4$ eV) semiconductor GaN is employed as inorganic part of the device, and PEN with a HLG of 2 eV and a large $L_D$ of 50–65 nm as organic part. The device layout and the corresponding energy level diagram are shown in Sec. 2.3.1.

**Expectations**

The theoretical maxima of $V_{OC}$ for a pn-junction solar cell with AM1.5 illumination can be determined by the detailed balance theory of Shockley and Queisser [37]. In analogy with a pn-junction solar cell, the Schottky junction solar cell is based on a single junction. Thus, in a first order approximation, both device types should have the same theoretical maxima of $V_{OC}$. According to [38] (corresponding to the detailed balance theory), $V_{OC}$ is limited to 3.0 V for a GaN-based solar cell ($E_G = 3.4$ eV).

The theoretical limit for $J_{SC}$ can be determined by integration of the AM1.5 solar spectrum up to $E_G$ of the absorber material. For GaN-based devices this results in a maximum $J_{SC}$ of 0.6 mA/cm$^2$.

Due to the limited transmittance $\tau$ of the semitransparent Au top contact (average $\tau$ of 40% for $E_{photon} > E_G$ of GaN), a significantly lower $J_{SC}$ of 0.25 mA/cm$^2$ is expected*.

To achieve the maximum $V_{OC}$ of 3.0 V, according to Eqn. 1.10, $J_0$ as low as $5 \cdot 10^{-52}$ mA/cm$^2$ would be necessary. However, Schottky junction solar cells normally show a significantly larger $J_0$. Assuming $J_0$ in the order of $10^{-12}$ mA/cm$^2$, which is determined in [129] for a Au/n-GaN Schottky diode, $V_{OC}$ of $\sim$0.67 V is predicted.

By implementing the PEN interlayer, the theoretical limit for $J_{SC}$ is increased to 15.5 mA/cm$^2$ assuming that all photons with $E_{photon} >$ HLG of PEN contribute to $J_{SC}$. Due to the limitation of the active PEN thickness to $L_D$ of 50–65 nm and its $\alpha$ of $\sim 10^4$ cm$^{-1}$,

*denoted by multiplication of the average $\tau$ and the theoretical $J_{SC}$ limit
only $1 - e^{-\alpha L_D} \approx 6\%$ of the relevant photons can be utilized in PEN. However, the remaining $94\%$ can generate $I_{ph}$ within GaN if their energy is larger than $E_G$ of GaN ($3.4\,eV$). Hence, in combination with the limited transmittance $\tau$ of the top contact (average $\tau$ of $52\%$ for $E_{photon} > HLG$ of PEN and $40\%$ for $E_{photon} > E_G$ of GaN), the expected $J_{SC}$ can be calculated as follows:

$$J_{SC} = \tau_{contact,PEN} \cdot 0.06 \cdot J_{SC,max,PEN} + \tau_{contact,GaN} \cdot 0.94 \cdot J_{SC,max,GaN}$$

$$\approx 0.71\,mA/cm^2$$

This is almost threefold the expected $J_{SC}$ of the reference device without PEN interlayer.

For $I_{ph}$ generation in both parts of the hybrid solar cell, $V_{OC}$ should have a value between $V_{OC,PEN}$ and $V_{OC,GaN}$ which correspond to $I_{ph}$ generation only within GaN or PEN, respectively. As discussed before, $V_{OC,GaN}$ is expected as $1.0\,V$. On the other hand, $V_{OC,PEN}$ is determined by the energy difference between the HOMO of PEN ($5.0\,eV$) and $E_C$ of GaN ($4.1\,eV$). However, for all-organic solar cells, the measured $V_{OC}$ normally differs from this value by $0.3\,V$ [130]. This is attributed to the reverse dark current and the non-ideality ($\eta \neq 1$) of the solar cells [130]. Assuming comparable characteristics for the hybrid solar cells, $V_{OC,PEN}$ of $\sim0.6\,V$ is expected. As a consequence, for the hybrid PEN/GaN solar cell, $V_{OC}$ in the range of $\sim0.6$–$1.0\,V$ is anticipated.

Summarized, by introducing a PEN interlayer and assuming no change of the FF, a relative PCE improvement in the order of $84\%$ is expected due to the additional $I_{ph}$ generation within PEN.

**Morphological characterization**

PEN layers with different thicknesses of 60, 70 and 80 nm are processed on GaN templates (cf. Fig. 2.1 (b)). To investigate the surface morphology of the deposited PEN films, atomic force microscope (AFM) pictures of all three layers are taken (cf. Fig. 3.1).

With increasing layer thickness, the crystallites grow and coalesce. For the sample with $t = 60\,nm$, circular crystallites with diameters of $0.1$–$0.2\,\mu m$ can be identified, which do not cover the whole surface. For the $70\,nm$-sample, the crystallites have a size of $0.5$–$1\,\mu m$ and are almost completely coalesced. However, at some grain boundaries, non-covered areas remain. By further increasing the thickness to $80\,nm$, dendritic crystallites, which
3.1 Additional Photocurrent Generation

*Fig. 3.1:* AFM images (5 × 5 µm²) of PEN layers with different thicknesses \( t \) deposited on GaN templates by OVPD.

are typical for PEN [131], are formed. Here, the crystallites are expected to be completely coalesced\(^4\) and have a size of 1.3–1.8 µm.

Since the metal contact is evaporated on top of the PEN, a completely coalesced layer is required for the functionality of the solar cell. Otherwise, the metal would directly contact the GaN and thus electrically short-circuit the PEN layer and adversely affect the solar cell performance. Therefore, only the PEN layer with a thickness of 80 nm is regarded suitable to be used in hybrid solar cells.

**PV characteristics**

Subsequently, a hybrid PEN/GaN solar cell with a PEN thickness of 80 nm as well as a Schottky junction reference device without PEN are processed (cf. Sec. 2.3.1) and characterized by illuminated J-V measurements. The results are displayed in Fig. 3.2 and summarized in Tab. 3.1.

<table>
<thead>
<tr>
<th></th>
<th>( J_{sc} ) [mA/cm²]</th>
<th>( V_{oc} ) [V]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schottky</td>
<td>0.253 (0.25)</td>
<td>0.669 (0.67)</td>
<td>65.0</td>
<td>0.11</td>
</tr>
<tr>
<td>hybrid</td>
<td>0.753 (0.71)</td>
<td>0.574 (0.6–1.0)</td>
<td>48.6</td>
<td>0.21</td>
</tr>
</tbody>
</table>

*Tab. 3.1:* PV characteristics of hybrid PEN/GaN solar cells with a PEN thickness of 80 nm as well as reference devices without PEN. The values in parentheses represent the theoretically predicted values.

\(^4\)cannot be guaranteed due to the limited height control of the AFM
The Schottky junction reference shows $J_{SC}$ of 0.253 mA/cm$^2$ and $V_{OC}$ of 0.669 V. This perfectly correlates with the expected values of 0.25 mA/cm$^2$ and 0.67 V, respectively.

For the hybrid solar cell, $J_{SC}$ of 0.753 mA/cm$^2$ is measured. This well fits to the expected $J_{SC}$ of 0.71 mA/cm$^2$. Furthermore, the measured $V_{OC}$ of 0.574 V well correlates with the lower limit of the expected $V_{OC}$ range ($\sim$0.6 V). However, the FF of the hybrid solar cell is significantly lower (-25%) compared to that of the Schottky reference. This is mainly related to a smaller $R_P$ (11 k$\Omega$ compared to 87 k$\Omega$) which may be due to still not completely coalesced PEN regions resulting in parasitic currents bypassing the PEN layer. Nevertheless, in summary, the hybrid solar cell shows a significant relative PCE improvement of 91%.

**Conclusion**

In this section, a hybrid PEN/GaN solar cell is investigated to demonstrate the $I_{ph}$ generation in the organic interlayer. Since the HLG of PEN is lower compared to $E_G$ of GaN, additional $I_{ph}$ generation within PEN and thus a higher $J_{SC}$ were expected. On the other hand, a lower $V_{OC}$ of the hybrid solar cells was presumed due to the limitation by the energy difference $\Delta E = 0.9$ eV between the HOMO of PEN and $E_C$ of GaN and the additional $V_{OC}$ penalty of $\sim$0.3 V which is commonly observed in OPV.
The measured PV characteristics of the hybrid solar cell as well as of the Schottky junction reference device are in good agreement with the expected values. This clearly confirms the assumed model of additional $I_{ph}$ generation within the PEN layer.

### 3.2 Blocking of the Reverse Electron Current

According to Eqn. 1.10, a reduction of $J_0$ improves $V_{OC}$ and thereby the efficiency of a solar cell. As described in Sec. 1.6.3, a predominantly hole-conducting organic interlayer should be able to reduce the reverse electron current into the anode and thereby $J_0$ of the solar cell. The expected $V_{OC}$ improvement is directly dependent on the energy difference $\Delta E$ between the LUMO of the organic semiconductor and $E_C$ of the inorganic semiconductor. The larger $\Delta E$, the larger is the $V_{OC}$ improvement. As a consequence, for efficient electron blocking, the organic interlayer has to possess a high LUMO.

On the other hand, the organic interlayer must not hinder the intended hole transfer into the anode. Hence, the HOMO of the organic interlayer has to be between $E_V$ of the inorganic semiconductor and the WF of the anode contact.

In this section, two different types of hybrid solar cells are investigated to demonstrate the electron blocking characteristics of the organic material. Both utilize Si as inorganic part of the solar cell. The corresponding device layouts are discussed in Sec. 2.3.2. The first type is based on device layout #1 (semitransparent Au top contact) and utilizes P3HT as organic interlayer. The second type is based on device layout #2 (PEDOT:PSS + Au grid). Here, the predominantly hole conducting polymer PEDOT:PSS combines the functions of a top contact material and an electron blocking layer.

#### 3.2.1 P3HT-Based Hybrid Solar Cells

As described in Sec. 2.1.2, P3HT is a predominantly hole-conducting polymer with a LUMO of $-3.0 \text{ eV}$ and a HOMO of $-5.0 \text{ eV}$. Its HOMO fits well to $E_V$ of Si ($-5.2 \text{ eV}$) and the WF of Au ($-5.1 \text{ eV}$). Hence, no significant suppression of the hole transport is expected. On the other hand, the LUMO of P3HT forms an additional energy barrier $\Delta E = 0.9 \text{ eV}$ for electrons generated in Si (cf. Fig. 3.3). This should result in a higher $V_{OC}$ compared to a Schottky junction reference device without P3HT interlayer.
Expectations

The maximum $V_{OC}$ and $J_{SC}$ of the Si-based solar cells can be calculated in analogy with the GaN-based solar cells. The theoretical maxima of $V_{OC}$ and $J_{SC}$ are 0.85 V and 44.1 mA/cm$^2$.

Due to the limited transmittance $\tau$ of the semitransparent Au top contact (average $\tau$ of 41% for $E_{photon} > E_G$ of Si), a $J_{SC}$ in the order of 18.1 mA/cm$^2$ is expected for the Schottky junction reference device. Furthermore, due to the moderate electron blocking properties of a Schottky junction, a significantly lower $V_{OC}$ is expected. In [132], $J_0$ of 3.48 \cdot 10^{-4}$ mA/cm$^2$ is determined for a Au/n-Si Schottky diode. As a result, a $V_{OC}$ of 0.28 V is expected.

For the hybrid P3HT/Si solar cell, a slightly lower $J_{SC}$ is predicted due to the absorption in P3HT. With $\alpha_{P3HT}$ of $\sim 2.5 \cdot 10^5$ cm$^{-1}$ (absorption edge at 650 nm) and the employed P3HT thickness $t_{P3HT}$ of $\sim 4$ nm the expected $J_{SC}$ can be calculated as:

$$J_{SC} = \tau_{contact} [\exp(-\alpha_{P3HT}t_{P3HT}) \cdot J_{SC,max,\lambda<650\text{nm}} + J_{SC,max,\lambda>650\text{nm}}]$$

$$\approx 17.4 \text{ mA/cm}^2$$

The expected $V_{OC}$ improvement related to the additional energy barrier $\Delta E$ can be estimated according to Eqn. 1.27 (assuming $\eta = 1$ and $m_e =$ electron rest mass):

$$\Delta V_{OC} = \frac{\eta k_B T}{q} \ln \left( \frac{1}{\exp \left( \frac{-\Delta E}{k_B T} \right) + \exp \left( -\frac{2\hbar q \sqrt{2m_e \Delta E}}{h} \right) } \right)$$

$$\approx 0.87 \text{ V}$$
This would result in a $V_{OC}$ of 1.15 V. However, as described in Sec. 1.6.3, the $J_0$ reduction and, as a result, the $V_{OC}$ improvement are limited by the minority-carrier-related recombination within the solar cell. Using $J_{0,h}$ of the utilized Si wafer type 2 (cf. Tab. 1.2) and $J_{SC}$ of 17.4 mA/cm$^2$ calculated above, a maximum $V_{OC}$ in the range of 0.51–0.54 V is estimated for the hybrid P3HT/Si solar cell using Eqn. 1.10. This is almost twice the $V_{OC}$ of the reference device without organic interlayer.

In summary, assuming no change of the FF, a relative PCE improvement in the range of 75–85% is expected for the hybrid solar cell compared to the reference device.

**P3HT film characterization**

The $\sim$4 nm thick P3HT layer is deposited using a solution with a $c$ of 1.25 mg/ml and a rotation speed of 2000 RPM. With these parameters, the thinnest coalesced P3HT film is achieved. The P3HT layer has to be as thin as possible due to its limited electrical conductivity $\sigma$ and its quite high absorption coefficient $\alpha$. As a consequence, the thicker the P3HT layer, the larger is $R_S$ and the lower is $J_{SC}$ of the hybrid solar cell. An AFM image of the deposited layer is shown in Fig. 3.4. The P3HT layer has a quite bumpy surface with a root mean square (RMS) of 0.5 nm and a peak-to-valley height of $\sim$5 nm. The layer thickness of $\sim$4 nm is determined by scratching through the P3HT down to the Si and measuring the depth of the scratch by AFM.

![AFM image (5 × 5 μm²) of a $\sim$4 nm thick P3HT layer (c = 1.25 mg/ml, 2000 RPM).](image)

In addition, a P3HT film is deposited on a glass substrate (same deposition parameters) to characterize its transmittance. The measured transmittance (normalized to the transmittance of the glass substrate) and the corresponding $\alpha$ are shown in Fig. 3.5.
The shape of the absorption spectrum as well as the peak $\alpha$ well correlate to those published in [93]. The larger $\alpha$ ($3.6 \cdot 10^5 \text{cm}^{-1}$ instead of $2.5 \cdot 10^5 \text{cm}^{-1}$) slightly reduces the expected $J_{SC}$ value from 17.4 mA/cm$^2$ to 17.1 mA/cm$^2$.

**PV characteristics**

To demonstrate the electron blocking properties of the P3HT interlayer, a hybrid P3HT/Si solar cell as well as a Schottky junction reference device without P3HT interlayer are processed according to Sec. 2.3.2 and using device layout #1. The devices are characterized by illuminated J-V measurements. The results are shown in Fig. 3.6 and Tab. 3.2.

The Schottky junction reference exhibits $J_{SC}$ of 16.8 mA/cm$^2$ which is close to the expected value ($-7\%$). This slight deviation is probably related to reflection losses at the Au/Si interface and a non-ideal internal quantum efficiency (IQE). The measured $V_{OC}$ of 0.292 V for the reference is in a good agreement with the expected value of 0.28 V.

On the other hand, the PV characteristics of the hybrid solar cell strongly deviate from the expectations. $J_{SC}$ ($-13\%$) and especially $V_{OC}$ ($-17\%$) are significantly lower than anticipated. Furthermore, the J-V measurement of the hybrid solar cell shows a pronounced hysteresis. Hysteresis effects are normally related to trap states, which are filled/emptied during the measurement. Since the Schottky reference shows no hysteresis, it has to be related to the P3HT interlayer or its interfaces. Interestingly, as can be seen in Fig. 3.7 which shows the J-V and PCE measurements of the P3HT/Si solar cell at...
Functional Principles

3.2 Blocking of the Reverse Electron Current

Fig. 3.6: J-V (a) and PCE (b) measurements of Schottky diode reference devices and hybrid P3HT/Si solar cells (PCE data refer to the reverse J-V measurement direction).

![J-V and PCE plots](image)

Tab. 3.2: PV characteristics of Schottky diode reference devices and hybrid P3HT/Si solar cells. Data of the hybrid solar cells are for the reverse measurement direction (hysteresis effect). The values in parentheses represent the theoretically predicted values.

<table>
<thead>
<tr>
<th></th>
<th>J_{SC} [mA/cm²]</th>
<th>V_{OC} [V]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schottky</td>
<td>16.8 ± 0.3 (18.1)</td>
<td>0.292 ± 0.002 (0.28)</td>
<td>51.9 ± 0.8</td>
<td>2.6 ± 0.1</td>
</tr>
<tr>
<td>hybrid</td>
<td>14.8 ± 0.7 (17.1)</td>
<td>0.426 ± 0.021 (0.51 – 0.54)</td>
<td>47.4 ± 2.4</td>
<td>3.0 ± 0.4</td>
</tr>
</tbody>
</table>

different times after fabrication (stored in ambient environment), the hysteresis vanishes over time. After one week, only a small hysteresis is left and after one month, it disappears completely. Furthermore, the PV characteristics of the hybrid solar cell significantly improve (cf. Tab. 3.3). After three month, J_{SC}, V_{OC}, FF and PCE are improved by 2, 18, 40 and 67%, respectively. In contrast, the PV characteristics of the Schottky diode reference do not improve with time.

A possible explanation for the vanishing hysteresis may be residues of the P3HT solvent toluene which generate trap states within P3HT and evaporate slowly during storage. Besides the hysteresis, the trap states can be the reason for the initially very low V_{OC} of the hybrid solar cell. They might form a parasitics current path for the electrons through the P3HT which causes a lower V_{OC} improvement than expected.
**FUNCTIONAL PRINCIPLES**

### 3.2 Blocking of the Reverse Electron Current

![Graph](image)

**Fig. 3.7:** J-V (a) and PCE (b) measurements of hybrid P3HT/Si solar cells at different times after fabrication (PCE data refer to the reverse J-V measurement direction).

<table>
<thead>
<tr>
<th></th>
<th>$J_{SC}$ [mA/cm$^2$]</th>
<th>$V_{OC}$ [V]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>after fabrication</td>
<td>14.8 ± 0.7</td>
<td>0.426 ± 0.021</td>
<td>47.4 ± 2.4</td>
<td>3.0 ± 0.4</td>
</tr>
<tr>
<td>after 1 week</td>
<td>14.8 ± 0.2</td>
<td>0.485 ± 0.020</td>
<td>64.2 ± 1.9</td>
<td>4.6 ± 0.4</td>
</tr>
<tr>
<td>after 1 month</td>
<td>15.0 ± 0.3</td>
<td>0.493 ± 0.015</td>
<td>67.0 ± 1.3</td>
<td>5.0 ± 0.3</td>
</tr>
<tr>
<td>after 3 months</td>
<td>15.1 ± 0.2</td>
<td>0.504 ± 0.001</td>
<td>66.5 ± 2.1</td>
<td>5.0 ± 0.1</td>
</tr>
</tbody>
</table>

**Tab. 3.3:** PV characteristics of hybrid P3HT/Si solar cells at different times after fabrication. Data are for the reverse measurement direction (hysteresis effect).

The remarkably improved FF of the hybrid solar cell after three months might be related to the doping of P3HT by the oxygen in the air as reported in [133]. The authors discuss an auto-doping process of P3HT during the storage in an oxygen-containing atmosphere which improves especially the electrical conductivity ($\sigma$) of P3HT and thereby $R_S$ of the device. Directly after fabrication, the hybrid solar cell exhibits an $R_S$ of 57.4\,\Omega which decreases to 27.0\,\Omega after three months.

While $V_{OC} = 0.504$\,V of the aged device is close to the expected value of 0.51–0.54\,V, $J_{SC} = 15.1$\,mA/cm$^2$ is still lower than expected ($-12\%$). As for the Schottky junction reference, the lower $J_{SC}$ is probably attributed to reflection losses and an IQE $<1$ which presumably is even lower for the hybrid solar cell due to a smaller width of the SCR.
The significantly larger (+73%) $V_{OC}$ compared to the reference device clearly proves the expected function of the organic interlayer as a blocking layer for the reverse electron current.

Besides the expected $V_{OC}$ improvement, the hybrid solar cell possesses a significantly larger FF compared to the reference device (hybrid: 66.5%, Schottky: 51.9%) which is attributed to a higher $R_P$ of 10 kΩ for the hybrid solar cell compared to 1.5 kΩ for the Schottky reference. This may be related to the suppression of leakage current paths, which are present in the Schottky reference, by the introduced P3HT layer.

Due to the significantly improved $V_{OC}$ and FF, the hybrid P3HT/Si solar cell exhibits a PCE which is almost twice (+92%) that of the reference device without P3HT interlayer.

**Conclusion**

In this subsection, hybrid P3HT/Si solar cells are investigated to demonstrate the function of the organic interlayer as a blocking layer for the reverse electron current into the anode contact. Due to the additional energy barrier $\Delta E$ for the electrons formed by the LUMO of P3HT, a significantly lower $J_0$ and as a result a improved $V_{OC}$ was predicted.

The measured $V_{OC}$ of the hybrid solar cells matches with the theoretically predicted values and is significantly higher compared to $V_{OC}$ of the Schottky junction reference device without P3HT. This clearly demonstrates the function of the organic interlayer as a blocking layer for the reverse electron current.

**3.2.2 PEDOT:PSS-Based Hybrid Solar Cells**

As described in Sec. 2.3.2, the second device layout of the Si-based hybrid solar cells employs a combination of PEDOT:PSS and a Au grid as semitransparent top contact. Since PEDOT:PSS is a predominantly hole conducting doped polymer with a LUMO of −3.4 eV (cf. Sec. 2.1.2), it furthermore functions as a blocking layer for the reverse electron current. As a consequence, for this device layout, no additional electron blocking interlayer is necessary. In this subsection, solar cells with a hybrid PEDOT:PSS-based top contact are investigated to demonstrate the function of the hole selective (electron blocking) top contact.
Expectations

For the hybrid solar cells with top contacts based on highly (ionically) p-type doped PEDOT:PSS, $I_{ph}$ generation takes places in Si. Although the high doping of PEDOT:PSS should affect the SCR in Si, its impact on the IQE should be negligible. Thus, the theoretical limits for $V_{OC}$ and $J_{SC}$ are the same as for the P3HT-based devices ($V_{OC}$: 0.85 V, $J_{SC}$: 44.1 mA/cm$^2$).

Compared to the semitransparent Au top contact which was used before, the Au/PEDOT:PSS top contact has a considerably higher transmittance $\tau$ (average $\tau$ of 83 % for $E_{photon} > E_G$ of Si, $\sim$10 % surface coverage of the Au grid included). As a consequence, a significantly higher $J_{SC}$ is expected. Assuming the same reflection and IQE losses as for the P3HT-based hybrid solar cells (14 %), a $J_{SC}$ in the order of 31.5 mA/cm$^2$ is estimated.

In analogy with the P3HT-based hybrid solar cells, the PEDOT:PSS-based devices are expected to be limited by the minority-carrier related $J_0$. Thus, for the employed Si wafer type 1 (1–5 $\Omega$ cm) and the presumed $J_{SC}$ of 31.5 mA/cm$^2$, the maximum reachable $V_{OC}$ is estimated as 0.57–0.63 V.

PEDOT:PSS film characterization

The 65 nm thick PEDOT:PSS layer is deposited by spin-coating at 4000 RPM. Its transmittance spectrum (on glass substrate, w/o Au grid) is shown in Fig. 3.8.

![Transmittance spectrum of 65 nm PEDOT:PSS layer](image)

**Fig. 3.8:** Transmittances of a 65 nm PEDOT:PSS layer (normalized to the transmittance of the glass substrate).
The PEDOT:PSS film exhibits an average $\tau$ of 93%, and $R_{sh}$ is measured as 307 $\Omega$/sq. These values well correlate with literature [134, 135].

**PV characteristics**

To demonstrate the electron blocking by the Au/PEDOT:PSS top contact, a device with this contact layout (350 nm Au grid) is processed. The results of the illuminated J-V measurement are shown in Fig. 3.9, and the PV characteristics are summarized in Tab. 3.4. For comparison, the characteristics of a device with semitransparent Au top contact (cf. Sec. 3.2.1 Schottky reference) are added.

![J-V and PCE measurements of solar cells](image)

**Fig. 3.9**: J-V (a) and PCE (b) measurements of solar cells with a hybrid Au/PEDOT:PSS and a semitransparent Au top contact.

<table>
<thead>
<tr>
<th>contact type</th>
<th>$J_{SC}$ [mA/cm²]</th>
<th>$V_{OC}$ [V]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>semitransparent Au</td>
<td>16.8 ± 0.3</td>
<td>0.292 ± 0.002</td>
<td>51.9 ± 0.8</td>
<td>2.6 ± 0.1</td>
</tr>
<tr>
<td>Au/PEDOT:PSS</td>
<td>30.1 ± 1.6 (31.5)</td>
<td>0.576 ± 0.002 (0.57 – 0.63)</td>
<td>65.4 ± 1.8</td>
<td>11.3 ± 0.4</td>
</tr>
</tbody>
</table>

**Tab. 3.4**: PV characteristics of solar cells with a hybrid Au/PEDOT:PSS and a semitransparent Au top contact. The values in parentheses represent the theoretically predicted values.

The device with the Au/PEDOT:PSS top contact shows a $J_{SC}$ of 30.1 mA/cm² which is in good agreement with the expected value of 31.5 mA/cm². The measured $V_{OC}$ of 0.576 V is within the predicted $V_{OC}$ range of 0.57–0.63 V. Compared to the reference device with
the semitransparent Au top contact, this is an improvement of 97% and clearly proves the hole selectivity (electron blocking properties) of the Au/PEDOT:PSS top contact.

Besides the improved $V_{OC}$, all other PV characteristics are improved as well. The larger $J_{SC}$ (+79%) is attributed to the higher transmittance and the greater FF (+26%) is due to a larger $R_P$ and a smaller $R_S$. The differences between both contact layouts are discussed in more detail in Sec. 4.1.

**Conclusion**

In this subsection, a solar cell with a hybrid Au/PEDOT:PSS top contact is investigated to show its functions as a hole-selective (electron blocking) top contact. Due to the predominantly hole-conducting PEDOT:PSS and its LUMO of $-3.4$ eV, electrons are blocked by the energy barrier of $0.7$ eV at the Si/PEDOT:PSS interface. As a consequence, in analogy with the hybrid solar cells with P3HT interlayer, an improved $V_{OC}$ compared to a reference device with semitransparent Au top contact was expected.

The measured $V_{OC}$ of the device with Au/PEDOT:PSS top contact matches with the expected value. Furthermore, it is significantly higher compared to the reference device with semitransparent Au top contact. In summary, this clearly shows the hole selectivity of the hybrid Au/PEDOT:PSS top contact.

**3.3 Antireflection Coating**

As described in Sec. 1.5.2, if the real part $n$ of the refractive index of the organic interlayer is between those of the top contact and the inorganic semiconductor, it can function as an antireflection coating (ARC). For this case, the reflection losses are decreased and as a result, $J_{SC}$ of the solar cell is improved.

To demonstrate this effect of the organic interlayer, the small-molecule organic semiconductor Spiro-MeOTAD is used in a Si-based solar cell with a Au/PEDOT:PSS top contact. The spectral $n$ and $k$ values of Spiro-MeOTAD, PEDOT:PSS and Si are shown in Fig. 3.10 [136, 109].

As can be seen in the figure, $n$ of Spiro-MeOTAD is between the values of PEDOT:PSS and Si in the entire wavelength range. As a consequence, Spiro-MeOTAD should be suitable as ARC in the Si-based solar cell with a Au/PEDOT:PSS top contact. Hence, for the device
with Spiro-MeOTAD interlayer, an improved $J_{SC}$ compared to a reference device without Spiro-MeOTAD is expected.

**Optical simulations**

First, to predict the impact of the Spiro-MeOTAD interlayer and to find an optimal Spiro-MeOTAD thickness $t_{spiro}$, optical simulations utilizing the freeware tool FreeSnell [53] are performed. For $I_{ph}$ generation, the light intensity which is coupled into Si is crucial. To determine this intensity, the transmission of the layer stack shown in Fig. 3.11 is simulated with $k$ of Si being set to zero. The boundary media air and Si are assumed to have an infinite thickness.

![Layer stack employed for the optical simulations.](image)

Simulations are performed with different $t_{spiro}$, including a reference without Spiro-MeOTAD interlayer. The results are shown in Fig. 3.12.
Fig. 3.12: Simulated light intensity transmitted into Si for different Spiro-MeOTAD thicknesses $t_{spiro}$ including a reference without Spiro-MeOTAD interlayer.

For wavelengths below $\sim 410$ nm, the devices with Spiro-MeOTAD interlayer reveal a reduced transmittance compared to the reference device without Spiro-MeOTAD interlayer. The higher the Spiro-MeOTAD thickness, the lower is the transmittance. Referring to the $k$ of Spiro-MeOTAD (cf. Fig. 3.10 (b)), this is attributed to absorption in the Spiro-MeOTAD interlayer in this wavelength range.

In contrast, but as expected due to the $n$ values of Si, Spiro-MeOTAD and PEDOT:PSS, the devices with Spiro-MeOTAD interlayer show an improved transmittance for larger wavelengths. As described in Sec. 1.5.2, this is attributed to the reduced reflection losses compared to the reference without Spiro-MeOTAD. Due to the thickness dependence of the interference of the incident and reflected waves, the wavelength of the maximum transmittance and as a consequence, the point after which the devices with Spiro-MeOTAD possess a higher transmittance shift to larger values with increasing Spiro-MeOTAD thickness.

Due to increasing absorption losses and the shifting wavelength of maximum transmittance with increasing Spiro-MeOTAD thickness, the average transmittance decreases for larger Spiro-MeOTAD thicknesses. Hence, there is an optimal Spiro-MeOTAD thickness at which the average transmittance is maximized. The average transmittance for the different Spiro-MeOTAD thicknesses is shown Tab. 3.5.

It can be seen that the average $T_{Si}$ has a maximum of 78.8 % for a Spiro-MeOTAD thickness of 30 nm. This is a relative improvement of only 1 % compared to the reference without
3.3 Antireflection Coating

<table>
<thead>
<tr>
<th>$t_{\text{spiro}}$ [nm]</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
</tr>
</thead>
<tbody>
<tr>
<td>avg. $T_{Si}$ [%]</td>
<td>77.7</td>
<td>78.3</td>
<td>78.7</td>
<td>78.8</td>
<td>78.7</td>
<td>78.3</td>
<td>77.7</td>
<td>76.9</td>
</tr>
</tbody>
</table>

**Tab. 3.5:** Average transmitted light intensity into Si ($T_{Si}$) for PEDOT:PSS/Spiro-MeOTAD/Si devices with different Sio-MeOTAD thicknesses.

Spiro-MeOTAD interlayer. However, to investigate the impact on $I_{ph}$ generation within Si, the number of photons in Si is crucial. Hence, the transmittance spectrum has to be multiplied with the AM1.5 solar spectrum (photon flux, Fig. 3.13). The integral of the resulting spectrum yields the expected $J_{ph}$ of the device. The results are shown in Tab. 3.6.

\[ \text{Fig. 3.13: AM1.5 solar spectrum.} \]

<table>
<thead>
<tr>
<th>$t_{\text{spiro}}$ [nm]</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
</tr>
</thead>
<tbody>
<tr>
<td>expected $I_{ph}$ [mA/cm²]</td>
<td>33.8</td>
<td>34.9</td>
<td>35.7</td>
<td>36.3</td>
<td>36.6</td>
<td>36.6</td>
<td>36.5</td>
<td>36.1</td>
</tr>
</tbody>
</table>

**Tab. 3.6:** Expected $I_{ph}$ for PEDOT:PSS/Spiro-MeOTAD/Si devices with different Spiro-MeOTAD thicknesses.

Due to the low intensity of the AM1.5 spectrum in the absorption range of Spiro-MeOTAD, the impact of its absorption is reduced. Hence, the optimum is shifted to larger Spiro-MeOTAD thicknesses. The maximum $I_{ph}$ of 36.6 mA/cm² is expected for Spiro-MeOTAD thicknesses of 40 and 50 nm. This now is an improvement of 8% compared to the reference. The larger improvement as well is attributed to the reduced impact of the absorption losses. To determine the optimal thickness more precisely, $t_{\text{spiro}}$ of 45 nm is investigated in addition. Here, even a slightly higher expected $I_{ph}$ of 36.7 mA/cm² is
determined. As a consequence, this Spiro-MeOTAD thickness is used for the fabrication of a test device to verify the results of the simulation.

**Expectations**

Assuming a relatively constant IQE of Si in the considered wavelength range of 350–1000 nm, the simulated transmittance into Si should well correlate to the EQE of the solar cell.

According to the simulation, the maximum $J_{\text{SC}}$ of the solar cell with Spiro-MeOTAD interlayer and of the reference device are 36.7 and 33.8 mA/cm$^2$, respectively. Due to the coverage of the metal grid, these values are reduced by $\sim10\%$ resulting in $J_{\text{SC}}$ of 33.0 and 30.4 mA/cm$^2$, respectively. As shown in Tab. 3.4, the reference with Au/PEDOT:PSS top contact and no Spiro-MeOTAD interlayer exhibits $J_{\text{SC}}$ of 30.1 mA/cm$^2$ which well correlates with the result of the simulation. As a consequence, for the hybrid solar cell with Spiro-MeOTAD interlayer a $J_{\text{SC}}$ of $\sim33.0$ mA/cm$^2$ is expected.

Due to the limitation of $V_{\text{OC}}$ by minority-carrier injection, for the device with Spiro-MeOTAD interlayer, a $V_{\text{OC}}$ comparable to that of the reference device without interlayer ($V_{\text{OC}} = 0.576$ V, cf. Tab. 3.4) is expected.

**EQE measurements**

To verify the results of the simulation, solar cells with Spiro-MeOTAD interlayer (45 nm) are processed and characterized by EQE measurements. As a reference device without Spiro-MeOTAD interlayer, the device with Au/PEDOT:PSS top contact from Sec. 3.2.2 is used. As described before, assuming a constant IQE, the EQE of the devices should correlate with the simulated light intensity which is transmitted into Si. The results of the EQE measurements as well as of the simulations are depicted in Fig. 3.14.

The EQE measurements correlate very well with the simulated light intensity. For wavelengths $\lambda$ below $\sim500$ nm, the EQE is lower for the device with Spiro-MeOTAD. This is attributed to absorption losses within Spiro-MeOTAD ($\lambda < \sim410$ nm) and interference effects ($\sim410$ nm $< \lambda < \sim500$ nm). On the other hand, due to the lower reflection losses as predicted by the optical simulations, the EQE is higher for the device with Spiro-MeOTAD for wavelengths above $\sim500$ nm. Furthermore, the relative EQE improvement of 1% matches with the simulated relative transmittance improvement. This clearly validates the results of the optical simulations.
**3.3 Antireflection Coating**

![EQE measurements](image1.png)

**Fig. 3.14:** (a): EQE measurements of hybrid solar cells w/ and w/o Spiro-MeOTAD interlayer. The curves are normalized to the maximum of the reference device. The spikes at 380 and 600 nm are measurement artifacts related to a grating change of the monochromator. (b): Corresponding simulated light intensity transmitted into Si.

**PV characteristics**

To demonstrate the impact of the Spiro-MeOTAD interlayer on the PV characteristics, the processed solar cells are characterized by illuminated J-V measurements. The result of the measurements are shown in Fig. 3.15 and Tab. 3.7.

The $J_{SC}$ values of both device types match with the predicted values of the simulations. In combination with the significant $J_{SC}$ improvement (+13%) of the device with Spiro-MeOTAD interlayer, this clearly demonstrates the function of Spiro-MeOTAD as an ARC.

Besides the expected $J_{SC}$ improvement, the device with Spiro-MeOTAD interlayer furthermore exhibits higher $V_{OC}$ (+2%) and FF (+7% relative) compared to the reference device. To a small extend (0.003 V) the $V_{OC}$ improvement is attributed to the higher $J_{SC}$. Due to the minority-carrier limitation of $V_{OC}$, the remaining $V_{OC}$ increase must be attributed to a reduced minority-carrier injection. The utilized Si wafer of type 1 are specified with a resistivity of 1–5 Ω cm, corresponding to $N_D$ of $9–50 \cdot 10^{14}$ cm$^{-3}$. For the measured $J_{SC}$ of 33.9 mA/cm$^2$, this results in a maximum $V_{OC}$ of 0.57–0.63 V (cf. 1.6.3). Since the measured $V_{OC}$ of 0.586 V is within this range, the improvement can
Antireflection Coating

The larger FF of the solar cell with Spiro-MeOTAD interlayer is attributed to a smaller $R_S$ of 11.1 Ω compared to $R_S$ of 16.5 Ω for the reference device. The Al backside contact should not be influenced by the Spiro-MeOTAD interlayer. Hence, the effect has to be attributed to the top contact. An explanation might be an improved hole extraction at the Spiro-MeOTAD/Si interface compared to the PEDOT:PSS/Si interface which might be caused by a favorable interface dipole or due to a doping of Spiro-MeOTAD by PSS. This might be investigated in subsequent experiments using for example X-ray photoelectron spectroscopy (XPS) or ultraviolet photoelectron spectroscopy (UPS).

**Conclusion**

In this section, Spiro-MeOTAD is investigated as an ARC in a hybrid solar cell with Au/PEDOT:PSS top contact. First, optical simulations were performed to predict the
impact of the Spiro-MeOTAD interlayer on the solar cell characteristics and to find an optimal Spiro-MeOTAD thickness. Subsequently, devices with this Spiro-MeOTAD thickness were processed and characterized by EQE and illuminated J-V measurements. Both, the results of the EQE as well the of the J-V measurements match with the results of the optical simulations.

As predicted by the simulations, $J_{SC}$ and as a result the PCE of the hybrid solar cells were significantly improved ($J_{SC}$: +13\%, PCE: +23\% relative) by introducing the Spiro-MeOTAD interlayer. This impressively shows the potential of Spiro-MeOTAD as an ARC in hybrid solar cells. For the best performing sample with Spiro-MeOTAD interlayer, an excellent PCE of 14.3\% is achieved.

### 3.4 Conclusion

To demonstrate the different functional principles of the organic material in hybrid organic/inorganic solar cells, devices based on different combination of organic and inorganic materials were investigated.

In the first section, to study additional $I_{ph}$ generation within the organic material, hybrid solar cells based on the small molecule PEN and GaN were analyzed. Due to the lower HLG of PEN compared to $E_G$ of GaN, the hybrid PEN/GaN solar cell is able to utilize a larger fraction of the solar spectrum compared to a Schottky junction reference device without PEN. As a result, the hybrid solar cell showed an almost threefold $J_{SC}$ compared to the Schottky reference (cf. Tab. 3.8).

<table>
<thead>
<tr>
<th></th>
<th>$J_{SC}$ [mA/cm$^2$]</th>
<th>$V_{OC}$ [V]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schottky</td>
<td>0.253</td>
<td>0.669</td>
<td>65.0</td>
<td>0.11</td>
</tr>
<tr>
<td>hybrid</td>
<td>0.753</td>
<td>0.574</td>
<td>48.6</td>
<td>0.21</td>
</tr>
</tbody>
</table>

**Tab. 3.8:** PV characteristics of hybrid PEN/GaN solar cells and a Schottky diode reference devices.

In the following section, two types of hybrid solar cells were investigated to verify the suppression of the reverse electron current into the anode contact. Both device types utilized Si as inorganic part of the hybrid solar cell. In the first device type,
the predominantly hole-conducting polymer P3HT was employed as an electron-blocking interlayer between the Au anode contact and Si. Hereby, $J_0$ of the hybrid solar was significantly decreased compared to a Schottky junction reference device without P3HT interlayer. As a consequence, the hybrid solar cell showed a notably improved $V_{OC}$ compared to the reference (cf. Tab. 3.9). In the second device type, a hybrid top contact based on the conductive (predominantly holes) doped polymer PEDOT:PSS and a Au grid was employed. Here, PEDOT:PSS functions as a hole-selective top contact material. In analogy with the P3HT interlayer, this leads to a reduced $J_0$ and a higher $V_{OC}$ compared to the Schottky diode reference device with semitransparent Au top contact (cf. Tab. 3.9).

<table>
<thead>
<tr>
<th></th>
<th>$J_{SC}$ [mA/cm$^2$]</th>
<th>$V_{OC}$ [V]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schottky</td>
<td>16.8 ± 0.3</td>
<td>0.292 ± 0.002</td>
<td>51.9 ± 0.8</td>
<td>2.6 ± 0.1</td>
</tr>
<tr>
<td>P3HT</td>
<td>15.1 ± 0.2</td>
<td>0.504 ± 0.001</td>
<td>66.5 ± 2.1</td>
<td>5.0 ± 0.1</td>
</tr>
</tbody>
</table>
| Au/PEDOT:PSS | 30.1 ± 1.6         | 0.576 ± 0.002 | 65.4 ± 1.8 | 11.3 ± 0.

Tab. 3.9: PV characteristics of hybrid solar cells with P3HT interlayer and with Au/PEDOT:PSS top contact as well as of Schottky diode reference devices.

In the last section, a Spiro-MeOTAD interlayer was investigated as an antireflection coating in a hybrid solar cell with Au/PEDOT:PSS top contact. Optical simulations were performed to predict the influence of the Spiro-MeOTAD interlayer on the characteristics of the hybrid solar cell and to find an optimal Spiro-MeOTAD thickness. Hybrid solar cells were processed with the determined Spiro-MeOTAD thickness and characterized. The results agree with the predictions of the simulations. Compared to a reference device without Spiro-MeOTAD interlayer, the devices with Spiro-MeOTAD interlayer showed an improved EQE in the predicted wavelength range and as a result a higher $J_{SC}$ (cf. Tab. 3.10). For the best performing sample, an excellent PCE of 14.3 % is achieved which is on of the highest values published for Si-based hybrid solar cells.

<table>
<thead>
<tr>
<th></th>
<th>$J_{SC}$ [mA/cm$^2$]</th>
<th>$V_{OC}$ [V]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>reference</td>
<td>30.1 ± 1.6</td>
<td>0.576 ± 0.002</td>
<td>65.4 ± 1.8</td>
<td>11.3 ± 0.4</td>
</tr>
<tr>
<td>Spiro-MeOTAD</td>
<td>33.9 ± 0.7</td>
<td>0.586 ± 0.003</td>
<td>69.7 ± 1.3</td>
<td>13.9 ± 0.6</td>
</tr>
</tbody>
</table>

Tab. 3.10: PV characteristics of hybrid solar cells w/ and w/o Spiro-MeOTAD interlayer.
In summary, this chapter shows the different functions of the organic material in hybrid organic/inorganic solar cells and the resultant improvement aspects. Especially the high efficiencies of the Spiro-MeOTAD-based hybrid solar cells clearly demonstrate the potential of this solar cell technology.
Chapter 4

Device Optimization

In this chapter, the device layout and processing of the hybrid P3HT/Si solar cell is optimized to improve the device performance. Starting point for the optimization is the device discussed in Sec. 3.2.1. The device is based on layout #1 with a semitransparent Au top contact as introduced in Sec. 2.3.2. For clarification, the device layout is shown in Fig. 4.1 once again.

![Device Layout](image)

**Fig. 4.1:** Initial device layout (cf. Sec. 2.3.2 layout #1).

The dominant loss mechanism of this device layout is the transmittance of only $\sim40\%$ of the semitransparent (15 nm) Au top contact (cf. Fig. 2.16). As a consequence, $\sim60\%$ of the incident radiant flux are already lost at the first layer of the device. Hence, in a first step, the top contact is optimized (in part already discussed in Sec. 3.2.2).

Following the path of light through the layer stack of the device, the next significant loss mechanism is reflection losses at the organic/Si interface. Therefore, an anisotropic etching
step is introduced into the process chain to structure the Si surface and thus reduce these losses (cf. Sec. 1.5.1).

Finally, two different backside interlayers (between Si and Al) are investigated to improve the electron collection/extraction at the backside contact.

The results of this chapter are published in [137].

4.1 Top Contact Optimization

As described before, due to the low transmittance \( \tau \) of the semitransparent Au layer, \( \sim 60\% \) of the incident light are lost already at the top contact. As a consequence, in this section, an alternative top contact design based on the (semi-)transparent conductive polymer PEDOT:PSS (cf. Sec. 2.1.2) is investigated.

In a second step, due to the limited conductivity of PEDOT:PSS, a supporting Au grid on top of PEDOT:PSS is employed to reduce the effective resistivity of the contact and thus improve the FF and PCE of the solar cells.

4.1.1 PEDOT:PSS-Based Top Contact

First, sole PEDOT:PSS layers are characterized to determine the thickness dependence of the transmittance \( \tau \) and \( R_{sh} \). Subsequently, solar cells with PEDOT:PSS top contacts are processed and characterized by illuminated J-V measurements.

PEDOT:PSS characteristics

For the \( \tau \) and \( R_{sh} \) characterization, PEDOT:PSS layers with different thicknesses (\( \sim 65–195 \) nm) are deposited on glass substrates. The thickness is varied by changing the rotations per minute (RPM) of the spin coater.

Subsequently, the wavelength-dependent \( \tau \) and \( R_{sh} \) of the deposited PEDOT:PSS films are measured. The results are depicted in Fig. 4.2. As reference, the transmittance and \( R_{sh} \) of the semitransparent Au film (15 nm) are added (dashed lines).

As can be seen in Fig. 4.2, all PEDOT:PSS layers show a more homogeneous and significantly higher \( \tau \) compared to the Au reference. For the thinnest PEDOT:PSS layers, average \( \tau \) above 90\% are achieved which is more than twice that of the reference (41\%) and


**Fig. 4.2:** (a): Transmittance measurements (normalized to the transmittance of the glass substrate) of PEDOT:PSS layers with different thicknesses $t$: PEDOT as well as a 15 nm Au reference. (b): Trend of the average transmittance (black) and $R_{sh}$ (red) against $t$: PEDOT. The solid lines represent mathematical fits of the measurement data according to Eqn. 4.1 and 4.2 and the dashed lines stand for the $\tau$ and $R_{sh}$ values of the Au reference.

promises a significant $J_{SC}$ improvement. On the downside, $R_{sh}$ of all PEDOT:PSS layers is larger compared to that of the Au reference. The thickest PEDOT:PSS layer exhibits $R_{sh}$ of 103 Ω/sq which is 25 times that of the reference (4 Ω/sq). As a consequence, a lower FF is expected for devices with PEDOT:PSS top contact.

As predicted by the following equations, $\tau$ as well as $R_{sh}$ decrease with increasing $t_{PEDOT}$.

$$\tau = \exp(-\alpha \cdot t_{pedot}) \quad (4.1)$$

$$R_{sh} = \frac{1}{\sigma \cdot t_{pedot}} \quad (4.2)$$

By mathematically fitting the measurement data, an average $\alpha$ of $1.4 \cdot 10^4$ cm$^{-1}$ and $\sigma$ of 470 S/cm are determined. Both values correlate well with literature [138, 135].

Since in the hybrid solar cells PEDOT:PSS is deposited onto P3HT (instead of glass), its morphology and as a result $\alpha$ and $\sigma$ might be different. Thus, the impact of $t_{PEDOT}$ on the device performance cannot be predicted quantitatively. As a consequence, the optimal PEDOT:PSS thickness is determined by characterizing completely processed solar cells.
**DEVICE OPTIMIZATION**

### 4.1 Top Contact Optimization

**PV characteristics**

To investigate the impact of the PEDOT:PSS top contact on the PV characteristics and to find an optimal PEDOT:PSS thickness, hybrid P3HT/Si solar cells with different PEDOT:PSS top contact thicknesses are processed. Since PEDOT:PSS is very soft and would be pierced by the contact needles and to achieve a more homogeneous current distribution within the active device area, supporting Au contacts (150 nm) which surround the active areas are deposited on top of the PEDOT:PSS layer. The resulting device layout is sketched in Fig. 4.3.

![Device Layout](image)

**Fig. 4.3:** Schematic cross section (a) and top view (b) of a hybrid organic/Si solar cell with PEDOT:PSS top contact.

The processed devices are characterized by illuminated J-V measurements to determine their PV characteristics. The results are shown in Fig. 4.4 and Tab. 4.1. The characteristics of a reference device with semitransparent Au top contact are added for comparison.

<table>
<thead>
<tr>
<th>t\text{PEDOT} [\text{nm}]</th>
<th>J\text{SC} [\text{mA/cm}^2]</th>
<th>V\text{OC} [\text{V}]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au reference</td>
<td>15.1 ± 0.2</td>
<td>0.504 ± 0.001</td>
<td>66.5 ± 2.1</td>
<td>5.0 ± 0.1</td>
</tr>
<tr>
<td>~65</td>
<td>30.6 ± 0.8</td>
<td>0.524 ± 0.004</td>
<td>41.3 ± 0.9</td>
<td>6.6 ± 0.3</td>
</tr>
<tr>
<td>~85</td>
<td>31.4 ± 0.3</td>
<td>0.526 ± 0.006</td>
<td>43.5 ± 3.1</td>
<td>7.2 ± 0.5</td>
</tr>
<tr>
<td>~120</td>
<td>29.0 ± 0.8</td>
<td>0.529 ± 0.004</td>
<td>46.2 ± 3.4</td>
<td>7.1 ± 0.4</td>
</tr>
<tr>
<td>~195</td>
<td>27.0 ± 0.7</td>
<td>0.527 ± 0.005</td>
<td>46.1 ± 2.6</td>
<td>6.6 ± 0.5</td>
</tr>
</tbody>
</table>

**Tab. 4.1:** PV characteristics of hybrid P3HT/Si solar cells employing PEDOT:PSS top contacts with different thicknesses t\text{PEDOT}.

As expected by the \(\tau\) and \(R_{sh}\) measurements, \(J\text{SC}\) decreases (except for the lowest t\text{PEDOT}) and FF increases (except for the largest t\text{PEDOT}) with raising t\text{PEDOT}. Taking into account
**Fig. 4.4:** J-V (a) and PCE (b) measurements of hybrid P3HT/Si solar cells employing PEDOT:PSS top contacts with different thicknesses $t_{\text{PEDOT}}$.

The statistical data, the exceptions can be attributed to process fluctuations. The devices with the thinnest PEDOT:PSS layer show $J_{SC}$ which is more than twice that of the Au reference. This matches with the measured transmittance improvement. Furthermore, as expected by the significantly higher $R_{sh}$ of the PEDOT:PSS layers compared to the Au reference, all devices with PEDOT:PSS contact exhibit a notably reduced FF.

Besides, the devices with PEDOT:PSS top contacts feature a higher $V_{OC}$ compared to the reference. This is attributed to an additional suppression of the reverse electron current by the hole-selective PEDOT:PSS contact (cf. Sec. 3.2.2). However, for the achieved $J_{SC}$, $V_{OC}$ of $\sim 0.56$ V is expected. The lower $V_{OC}$ of 0.524–0.529 V implies that $J_0$ is not limited by the hole current in this devices. The measured $V_{OC}$ corresponds to $J_0$ of $2.7–3.4 \times 10^{-8}$ mA/cm$^2$ ($J_{0,h} \approx 6.9 \times 10^{-9}$ mA/cm$^2$, cf. Sec. 1.6.3). Because this effect is not observed for devices with a Au grid on top of the PEDOT:PSS layer (cf. Sec. 3.2.2 and next subsection), the larger $J_0$ is probably related to additional recombination losses (cf. [47]) caused by the limited $\mu_h$ of the PEDOT:PSS layer.

The highest PCE of 7.2 % is achieved for a PEDOT:PSS thickness of 85 nm which seems to be the best compromise between high $\tau$ and low $R_{sh}$. Compared to the Au reference, this is a relative improvement of 44 %.
4.1.2 Supporting Gold Grid

As expected due to the limited conductivity of PEDOT:PSS, the devices with PEDOT:PSS top contact exhibit a significantly lower FF compared to the reference device with a semitransparent Au top contact. As a consequence, a supporting Au grid contact on top of the PEDOT:PSS layer is employed. Since the electrical conductivity ($\sigma$) of Au ($4.1 \cdot 10^5$ S/cm [139]) is significantly higher compared to $\sigma$ of PEDOT:PSS (470 S/cm), this decreases the effective resistivity of the top contact. However, to achieve a sufficient conductance, the Au grid cannot be processed semitransparent. Hence, the grid reduces the effective active area of the solar cell and in turn $J_{SC}$.

**Grid layout**

The layout of the Au grid is shown in Fig. 4.5. It consists of a 200$\mu$m wide horizontal line and three 100$\mu$m wide vertical lines. This results in an active area coverage of 9.8%. The thickness of the grid contact is 300 nm.

![Grid layout](image)

*Fig. 4.5: Layout of the Au grid contact (blue: active device area of 5 x 5 mm$^2$). The widths of the horizontal and vertical lines are 200$\mu$m and 100$\mu$m, respectively.*

Due to the highly conductive Au grid, $\sigma$ of PEDOT:PSS is not the key parameter in this case. As a consequence, to partially compensate the $J_{SC}$ reduction caused by the surface coverage of the Au grid, the PEDOT:PSS thickness is reduced to 65 nm instead of 85 nm. According to Fig. 4.2, this increases the average transmittance of the PEDOT:PSS layer by 2%.

**PV characteristics**

The PV characteristics of hybrid P3HT/Si solar cells with PEDOT:PSS-based top contact and supporting Au grid are shown in Fig. 4.6 and Tab. 4.2. For comparison, the characteristics of devices with PEDOT:PSS-based top contact (85 nm) and no Au grid are included.
As expected due to the coverage of the Au grid, $J_{SC}$ of the device with grid contact is lower compared to the device without grid. The $J_{SC}$ reduction of 7% correlates well with the expectations by the coverage of the grid (-10%) and the reduced PEDOT:PSS thickness (+2%). Furthermore, as desired, the supporting Au grid significantly improves the FF. Compared to the device with PEDOT:PSS top contact and no grid, the FF is improved by 59% (relative).

Besides, the device with the Au grid shows a significantly higher $V_{OC}$ of 0.567 V which perfectly correlates with the expected value for the achieved $J_{SC}$ and a $J_0$ limitation by the minority carrier current (cf. Sec. 1.6.3). As described before, the lower $V_{OC}$ of the device without Au grid is probably attributed to increased recombination losses caused by the limited conductivity of the PEDOT:PSS layer.
In summary, the huge FF improvement and the higher $V_{OC}$ of the device with the supporting Au grid clearly overcompensates the lower $J_{SC}$. As a result, a PCE of 11.3% is achieved which is a relative improvement of 57% compared to the device without Au grid.

### 4.1.3 Conclusion

In this section, the semitransparent Au top contact with a limited average transmittance $\tau$ of only $\sim 40\%$ is replaced by a PEDOT:PSS-based top contact with a supporting Au grid which exhibits an average $\tau$ of $\sim 83\%$ (including the coverage of the grid). A comparison of the PV characteristics of both device types is shown in Fig. 4.7 and Tab. 4.3.

![Fig. 4.7: J-V (a) and PCE (b) measurements of hybrid P3HT/Si solar cells with a semitransparent Au top contact and with the optimized PEDOT:PSS-based top contact with supporting Au grid.](image)

<table>
<thead>
<tr>
<th>contact layout</th>
<th>$J_{SC}$ [mA/cm$^2$]</th>
<th>$V_{OC}$ [V]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>semitransparent Au</td>
<td>15.1 ± 0.2</td>
<td>0.504 ± 0.001</td>
<td>66.5 ± 2.1</td>
<td>5.0 ± 0.1</td>
</tr>
<tr>
<td>PEDOT:PSS + grid</td>
<td>29.3 ± 0.2</td>
<td>0.567 ± 0.001</td>
<td>67.8 ± 2.1</td>
<td>11.3 ± 0.4</td>
</tr>
</tbody>
</table>

Tab. 4.3: PV characteristics of hybrid P3HT/Si solar cells with a semitransparent Au top contact and with the optimized PEDOT:PSS-based top contact with supporting Au grid.

As expected by the doubled transmittance of the PEDOT:PSS-based top contact, this device shows an almost doubled $J_{SC}$. Furthermore, attributed to the hole selectivity of
the PEDOT:PSS-based top contact (cf. Sec. 3.2.2), $V_{OC}$ is improved by 13%. Due to the supporting Au grid which compensates the low conductivity of PEDOT:PSS, the FF of the optimized device is even higher compared to that of the reference with the semitransparent Au top contact. This is attributed to a lower $R_S$ of 13.6 $\Omega$ compared to 26.6 $\Omega$ for the reference which clearly demonstrates the effect of the supporting Au grid.

In summary, by replacing the semitransparent Au top contact with a more transparent PEDOT:PSS-based top contact, the PCE of the hybrid P3HT/Si solar cells is relatively improved by 126%. For the best performing sample with the optimized top contact, a very good PCE of 11.6% is achieved.

### 4.2 Silicon Surface Structuring

Besides the transmittance losses in the top contact, another significant loss mechanism of the hybrid P3HT/Si solar cells is reflection losses at the organic/Si interface. Due to the higher $n$ of Si ($\sim 3.5$ [136]) compared to $n$ of the P3HT ($\sim 2$ [140]), a significant fraction of the incident light is reflected at this interface. An optical simulation (FreeSnell) of the reflectance of the hybrid P3HT/Si solar cell with PEDOT:PSS-based top contact is shown in Fig. 4.8. The dashed red line represents the average weighted (AM1.5 solar spectrum) reflectance (AWR) of 19%.

![Fig. 4.8: Simulated reflectance of a hybrid P3HT/Si solar cell with PEDOT:PSS-based top contact. Dashed red line: weighted (AM1.5 solar spectrum) average reflectance.](image)

80
One option to reduce the reflection losses is to introduce an ARC as discussed in Sec. 3.3. Another option is to structure the Si surface. Due to this, the reflected light is guided onto the surface again whereby the totally transmitted fraction of the incident light is increased (cf. Sec. 1.5.1 and Fig. 4.9).

In literature, AWR values in the range of 10–15% are reported for anisotropically etched Si surfaces in air [141, 142, 143] compared to a value of 41% for a polished Si surface [143]. This represents a relative improvement of 63–76%. Hence, in this section, an anisotropic etching step is applied to structure the Si surface to reduce the reflection losses at the hybrid organic/Si interface and as a result improve $J_{SC}$ of the devices.

Since the AWR of the hybrid P3HT/Si solar cells (19%) is significantly lower compared to that of the polished Si surface, a less pronounced AWR reduction and in turn $J_{SC}$ improvement are expected. Because the FreeSnell software is only able to simulate normal incidence, an estimation of the AWR of the hybrid solar cell on structured Si by optical simulation is not possible. However, by simply comparing the AWR values of the structured Si surface in air and of the hybrid solar cell, a $J_{SC}$ improvement in the order of 21–47% can be assumed.

In the first subsection, the mechanism of anisotropic Si etching is explained. Subsequently, tetramethylammonium hydroxide (TMAH) and potassium hydroxide (KOH) are investigated as etchants to structure the Si interface of hybrid solar cells.

### 4.2.1 Mechanism of the Anisotropic Silicon Etching

For Si, structuring the surface is easily achieved by wet-chemical etching in strongly alkaline solutions (eg. KOH, TMAH) according to the following chemical reaction [144].

$$
\text{Si}(s) + 2 \text{OH}^- (aq) + 2 \text{H}_2\text{O}(l) \rightarrow \text{Si(OH)}_2\text{O}_2^{2-} (aq) + 2 \text{H}_2(g) \quad (4.3)
$$
Due to the different activation energies of the various crystal planes for this etching reaction, the etching process occurs anisotropically [145]. For alkaline etching, the etch rate of the {100} planes is always higher than that of the {111} planes [146]. Starting with a (100)-oriented Si wafer, this results in a pyramidal surface structure formed by the exposed {111} planes of Si (cf. Fig. 4.10).

![Fig. 4.10: Schematic illustration of the anisotropically etched Si surface including the characteristic planes and angles.](image)

Due to the diamond cubic crystal structure of Si, the angle between the side faces of the pyramids ({111} planes) and the base plane ({100} plane) is 54.74°. The ratio of the etch rates for the {100} and {111} planes depends on the employed etchant. For KOH and TMAH the {100}: {111} ratios are ~300 and ~37, respectively [145].

To improve the etch rate control and the homogeneity of the anisotropic etching process, commonly, isopropyl alcohol (IPA) is added to the etching solution. IPA removes the generated hydrogen bubbles from the Si surface and increases its wettability which leads to a more homogeneous etching process [147]. Furthermore, IPA can influence the pyramid density and shape [147].

### 4.2.2 TMAH as Etchant

First, TMAH is applied for the anisotropic etching process of the silicon surface. For TMAH, promising results are demonstrated in literature [143, 148]. For the etching process, a proven and tested setup of the Institute of Semiconductor Electronics of RWTH Aachen University (IHT) is utilized. The setup has an integrated condenser to prevent the evaporation of IPA and thus improve the homogeneity of the etching process. The parameters of the TMAH etching process are listed in appendix A.3.1. TMAH etching is applied as first step in the process chain (cf. Sec. 2.3.2).

First, to investigate the morphology of the TMAH-etched Si surface, unstructured wafers are etched and characterized by scanning electron microscope (SEM). Subsequently, hybrid P3HT/Si solar cells are processed on TMAH-etched wafers and characterized.
Surface morphology
To investigate the morphology of a TMAH-etched Si wafer, two SEM images of the structured Si surface are recorded with different magnifications (cf. Fig. 4.11).

![SEM images with different magnifications of a TMAH-etched silicon surface.](image)

**Fig. 4.11:** SEM images with different magnifications of a TMAH-etched silicon surface.

In the high-magnification image (a), the expected pyramidal surface structure is clearly visible. The pyramids cover the entire surface which can be seen more distinctly in the low-magnification image (b). The size of the pyramids varies in the range of several nm up to several µm (edge length).

PEDOT:PSS morphology
Next, the impact of the TMAH-structured Si surface on the morphology of the PEDOT:PSS layer which is deposited on top is investigated by SEM. The results are shown in Fig. 4.12.

The SEM images clearly show that the PEDOT:PSS layer covers only the top of the Si pyramids. Especially in the high-magnification image (b), the uncoated Si surface in the valleys between the pyramids is clearly visible. This is related to the in-plane oriented polymer chains which form kind of a fabric and prevent a covering of the valleys between the Si pyramids.

This effect was also observed by He et al. in [149] where it led to a reduced $V_{OC}$ of the solar cells due to increased recombination losses in the uncoated Si regions. As a consequence, a lower $V_{OC}$ is expected for hybrid solar cells which are processed on TMAH-structured Si wafer compared to reference devices on unstructured Si.
4.2 Silicon Surface Structuring

**PV characteristics**

Subsequently, hybrid P3HT/Si solar cells with PEDOT:PSS-based top contacts (with grid) are processed on TMAH-structured Si wafers and characterized by illuminated J-V measurements. The result are shown in Fig. 4.13, and the PV characteristics are summarized in Tab. 4.4. As a reference, the characteristics of devices on unstructured Si are added (cf. Sec. 4.1).

As expected due to the reduced reflection losses, the TMAH-structured device shows a significantly improved $J_{SC} (+17\%)$ compared to the reference device. The improvement is lower than predicted by the comparison of the AWR of the structured Si surface in air and that of the hybrid solar cell on unstructured Si ($21–47\%)$. This is probably attributed to the impact of the organic layers on the reflection of the hybrid solar cell which is not taken into account by that simple comparison.

Furthermore, as predicted by the non-uniform coverage of the PEDOT:PSS film, the structured device shows a significantly lower $V_{OC} (-10\%)$. In addition, the FF of the structured device is notably lower ($-9\%$ relative) compared to that of the reference device. This is probably due to a non-optimal morphology of the organic layers attributed to the incomplete coverage.

In summary, due to the lower $V_{OC}$ and FF, the TMAH-structured hybrid solar cell exhibits a lower ($-4\%$ relative) PCE compared to the unstructured reference device. Nevertheless,
Fig. 4.13: J-V (a) and PCE (b) measurements of hybrid P3HT/Si solar cells (PEDOT:PSS top contact + grid) processed on TMAH-structured Si as well a reference devices on unstructured Si.

<table>
<thead>
<tr>
<th></th>
<th>$J_{SC}$ [mA/cm$^2$]</th>
<th>$V_{OC}$ [V]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>reference</td>
<td>29.3 ± 0.2</td>
<td>0.567 ± 0.001</td>
<td>67.8 ± 2.1</td>
<td>11.3 ± 0.4</td>
</tr>
<tr>
<td>TMAH</td>
<td>34.3 ± 0.4</td>
<td>0.510 ± 0.015</td>
<td>61.7 ± 2.8</td>
<td>10.8 ± 0.9</td>
</tr>
</tbody>
</table>

Tab. 4.4: PV characteristics of hybrid P3HT/Si solar cells (PEDOT:PSS top contact) processed on TMAH-structured Si as well a reference devices on unstructured Si.

the significant $J_{SC}$ improvement clearly demonstrates the potential of Si surface structuring via anisotropically etching.

4.2.3 KOH as Etchant

As shown before, the PEDOT:PSS layer of the hybrid solar cell is not able to uniformly cover a TMAH-structured Si surface. Only the top of the Si pyramids is covered by PEDOT:PSS and thus uncoated Si regions remain which significantly reduce $V_{OC}$ of the device. As a consequence, in this section, KOH is used as etchant to structure the Si surface. Compared to TMAH, using KOH as an etchant leads to a higher etch rate for the $\{100\}$ planes and a larger difference in the etch rates of the $\{100\}$ and $\{111\}$ planes [145, 150, 151]. Thus, structured Si surfaces with smaller pyramids can be formed. This
should increase the probability to achieve a complete coverage by the organic layers which are deposited on top.

Furthermore, for the KOH etching setup, no reflux condenser is utilized to prevent the evaporation of IPA. As a result, a less homogeneous etching process is expected. This should result in a lower surface coverage of the pyramids which is supposed to further improve the coverage of the structured Si surface by the organic layers. The parameters of the KOH etching process can be found in appendix A.3.2.

**Surface morphology**

SEM images of the KOH-structured Si surface with different magnifications are shown in Fig. 4.14. As expected for KOH as etchant, the pyramids are significantly smaller (edge length <1µm) compared to their counterparts on the TMAH-etched Si surface (edge length up to several µm).

![SEM images of the KOH-etched Si surface](image)

**Fig. 4.14:** SEM images with different magnifications of a KOH-etched silicon surface.

Furthermore, as intended, the morphology of the KOH-etched Si surface is less homogeneous compared to the TMAH-etched one. As a consequence, as visible in the high-magnification image (b), the pyramids do not cover the entire surface. In turn, the gaps between the pyramids are significantly larger.

Compared to the TMAH-etched Si surface, the significantly smaller pyramids and the lower surface coverage of the pyramids should improve the coverage by the organic layers deposited on top. As a consequence, for the KOH-etched hybrid solar cells, a higher $V_{OC}$ compared to that of the TMAH-etched devices is expected. However, the smaller pyramids
and their lower surface coverage should lead to higher reflectance losses and as a result lower $J_{SC}$ compared to that of the TMAH-etched hybrid solar cells.

**PV characteristics**

The PV characteristics of hybrid P3HT/Si solar cells (PEDOT:PSS top contact) processed on a KOH-structured Si wafer are shown in Fig. 4.15 and are summarized in Tab. 4.5. The characteristics of unstructured and TMAH-structured devices are added for comparison (cf. Sec. 4.2.2).

As expected by the morphology, the KOH-etched hybrid solar cell shows an improved $V_{OC}$ compared to the TMAH-etched device (+16%). Its $V_{OC}$ is even higher than that of the unstructured device (+4%) which may be attributed to a different chemistry of the etched.

<table>
<thead>
<tr>
<th></th>
<th>$J_{SC}$ [mA/cm²]</th>
<th>$V_{OC}$ [V]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unstructured</td>
<td>29.3 ± 0.2</td>
<td>0.567 ± 0.001</td>
<td>67.8 ± 2.1</td>
<td>11.3 ± 0.4</td>
</tr>
<tr>
<td>TMAH</td>
<td>34.3 ± 0.4</td>
<td>0.510 ± 0.015</td>
<td>61.7 ± 2.8</td>
<td>10.8 ± 0.9</td>
</tr>
<tr>
<td>KOH</td>
<td>32.1 ± 0.6</td>
<td>0.592 ± 0.003</td>
<td>66.8 ± 1.1</td>
<td>12.7 ± 0.3</td>
</tr>
</tbody>
</table>

**Fig. 4.15:** $J$-$V$ (a) and PCE (b) measurements of hybrid P3HT/Si solar cells (PEDOT:PSS top contact) processed on KOH-, TMAH- and unstructured Si.

**Tab. 4.5:** PV characteristics of hybrid P3HT/Si solar cells (PEDOT:PSS top contact) processed on KOH-, TMAH- and unstructured Si.
Si surface (due to e.g. interface dipole, reduced surface trap density). This clearly indicates that the organic entirely covers the Si surface without forming voids.

Furthermore, as predicted by the smaller pyramids and the lower surface coverage of the pyramids, the KOH-etched device shows a lower $J_{SC}$ (-6%) compared to that of the TMAH-etched reference. However, its $J_{SC}$ is still significantly larger than that of the unstructured hybrid solar cell (+10%).

As a result of the improved $J_{SC}$ and $V_{OC}$, the KOH-etched hybrid solar cell exhibits a notably higher PCE (+12% relative) compared to the unstructured reference device.

**4.2.4 Conclusion**

In this section, an anisotropic etching process of Si is investigated to reduce the reflection losses of hybrid solar cells and thus improve its $J_{SC}$.

The largest $J_{SC}$ improvement of 17%, is achieved for TMAH-etched devices. However, due to the formation of voids between the organic material and Si, $V_{OC}$ of these devices is significantly lower compared to that of unstructured reference devices. As a result, the TMAH-etched devices exhibit a lower PCE than the reference.

By using KOH as etchant, the voids between the organic material and Si could be prevented due to the formation of smaller pyramids with larger gaps in between. As a result, the hybrid solar cells on KOH-etched Si possess $V_{OC}$ which is even higher compared to that of the unstructured reference. As expected, their $J_{SC}$ is lower compared to that of the TMAH-etched devices but still significantly higher than $J_{SC}$ of the unstructured devices.

For hybrid solar cells processed on KOH-etched Si, a PCE of 12.7% is achieved. This is a relative improvement of 12% compared to the unstructured reference and clearly demonstrates the effect of Si surface structuring on the performance of the hybrid solar cells.

**4.3 Backside Contact Optimization**

In literature, various organic and inorganic materials have been studied as interlayers to improve the electron collection at a Al/Si contact [152, 153, 154, 155]. Among other things, promising results have been achieved by using a LiF interlayer (15%
relative PCE improvement) [152] and a PFN (cf. Sec. 2.1.2) interlayer (30\% relative PCE improvement) [154]. As a consequence, these two materials are investigated as interlayers in the previously discussed hybrid solar cells. Hereby, the FF and in turn the PCE of the solar cells should be improved.

4.3.1 LiF Interlayer

In OLED technology, the combination of LiF and Al is widely used as an electron injection layer [76]. Here, it is assumed that elemental lithium (Li) is formed in a reaction of LiF and Al during evaporation, which then acts as a dopant for the underlying layer [77]. In Si, elemental Li is known as an interstitial shallow donor with a low diffusion rate ($\sim 10^{-18}$ cm$^2$/s) [156, 157]. Therefore, it is assumed that a thin highly n-doped region is formed at the interface to the backside contact by Li, which diffuses into Si. This should improve the electron extraction at the backside contact. Therefore, an improvement of the FF due to a lower $R_C$ is expected. Hence, hybrid solar cells with a 0.5 nm LiF interlayer between Si and the Al backside contact are processed.

Device layout

Due to restrictions of the e-beam deposition tool which has been used for the contact deposition so far, the LiF/Al backside contact has to be deposited by thermal evaporation using a different setup. Furthermore, the change of the deposition tool necessitates the substitution of the top grid material. For the devices with LiF interlayer, silver (Ag) is employed instead of Au for the grid contact. The corresponding device layout is depicted in Fig. 4.16. The hybrid P3HT/Si solar cells are processed on KOH-etched Si (cf. Sec. 4.2.3).

![Fig. 4.16: Schematic cross section (a) and top view (b) of a hybrid organic/Si solar cell with Ag grid contact and LiF interlayer at the backside contact.](image-url)
4.3 Backside Contact Optimization

**Changed top contact material**

First, hybrid P3HT/Si solar cells with Au grid (e-beam evaporation) and Ag grid (thermal evaporation) top contacts and without LiF interlayer are processed and characterized to investigate the impact of the change in grid material. Since the main function of the supporting metal grid is to reduce the effective sheet resistance, and the resistivity of Au and Ag is comparable (Au: $2.2 \cdot 10^{-8} \, \Omega \, \text{m}$, Ag: $1.6 \cdot 10^{-8} \, \Omega \, \text{m}$ [158]), no significant change in the properties of the hybrid solar cells is expected.

The results of the illuminated J-V measurements are shown in Fig. 4.17, and the PV characteristics are summarized in Tab. 4.6.

![Fig. 4.17: J-V (a) and PCE (b) measurements of hybrid P3HT/Si solar cells with either Au or Ag as top grid material.](image)

<table>
<thead>
<tr>
<th>grid material</th>
<th>$J_{SC}$ [mA/cm$^2$]</th>
<th>$V_{OC}$ [V]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>32.1 ± 0.6</td>
<td>0.592 ± 0.003</td>
<td>66.8 ± 1.1</td>
<td>12.7 ± 0.3</td>
</tr>
<tr>
<td>Ag</td>
<td>31.6 ± 2.4</td>
<td>0.595 ± 0.002</td>
<td>66.7 ± 1.9</td>
<td>12.5 ± 0.6</td>
</tr>
</tbody>
</table>

**Tab. 4.6:** PV characteristics of hybrid P3HT/Si solar cells with either Au or Ag as top grid material.

As expected, the measurements show that the impact of the changed top contact material on the PV characteristics is insignificant. $V_{OC}$ and FF are altered less than 1%, and $J_{SC}$ is modified by 1.6%. The higher $J_{SC}$ might be due to minimal deviations of the grid
dimensions attributed to the different evaporation systems which may result in a slightly varied surface coverage of the grid contact.

**Impact of the LiF interlayer**

To investigate the impact of the LiF interlayer, hybrid solar cells with and without LiF interlayer are processed and characterized by illuminated J-V measurements. The PV characteristics are summarized in Fig. 4.18 and Tab. 4.7.

![Fig. 4.18: J-V (a) and PCE (b) measurements of hybrid P3HT/Si solar cells w/ and w/o LiF interlayer.](image)

<table>
<thead>
<tr>
<th></th>
<th>$J_{SC}$ [mA/cm$^2$]</th>
<th>$V_{OC}$ [V]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>w/o LiF</td>
<td>31.6 ± 2.4</td>
<td>0.595 ± 0.002</td>
<td>66.7 ± 1.9</td>
<td>12.5 ± 0.6</td>
</tr>
<tr>
<td>w/ LiF</td>
<td>31.9 ± 2.5</td>
<td>0.597 ± 0.003</td>
<td>68.5 ± 2.3</td>
<td>13.0 ± 0.9</td>
</tr>
</tbody>
</table>

**Tab. 4.7: PV characteristics of hybrid P3HT/Si solar cells w/ and w/o LiF interlayer.**

For the devices with LiF interlayer, all parameters are improved. While the improvement of $J_{SC}$ and $V_{OC}$ is negligible (<1%), the FF increase is more pronounced (+3% relative). The FF improvement is mainly attributed to a reduced $R_S$ of 14.8$\Omega$ compared to 17.0$\Omega$ for the reference device without LiF. This matches the expectation resultant from an improved electron extraction. Overall, the devices with LiF interlayer at the backside contact show a 4% (relative) improved PCE compared to the devices without LiF.
Compared to the previously mentioned PCE improvement of 15% demonstrated in [152] for PEDOT:PSS/Si solar cells, the relative improvement achieved here is significantly lower. However, the devices presented here exhibit a PCE of 13% which is remarkably higher compared to a PCE of 11% in that publication. The lower PCE improvement is related to the already high $J_{SC}$ and $V_{OC}$ of the devices without LiF interlayer due to the structured Si interface and the additional electron-blocking P3HT interlayer. In contrast, the achieved relative FF improvement matches with that demonstrated in [152] (+3%).

### 4.3.2 PFN Interlayer

PFN is presumed to form a strong interface dipole reducing the effective WF of the Al contact by 0.67 eV to a value below that of Si [154]. This is expected to improve the electron extraction at the Al backside contact and in turn FF and $J_{SC}$ of the solar cell. Furthermore, the reduced effective WF of Al is expected to improve $V_{OC}$ of the solar cell due to an enhancement of the built-in electric field [154]. As a consequence, PFN is investigated as backside contact interlayer in this work.

#### Device layout

PFN is dissolved in a mixture of methanol and acetic acid (500:1). It is deposited via spin-coating (1000 RPM) on the backside of the Si wafer after the processing of the front side organic materials and before the evaporation of the Al backside contact. The corresponding device layout is shown in Fig. 4.19. The solar cells are processed on TMAH-etched Si wafers.

![Device layout](image)

*Fig. 4.19: Schematic cross section (a) and top view (b) of a hybrid PEDOT:PSS/Si solar cell with PFN interlayer.*
PV characteristics

The processed devices are characterized by illuminated J-V measurements to analyze the impact of the PFN interlayer on the PV characteristics. The results are shown in Fig. 4.20 and Tab. 4.8.

![Graph showing J-V and PCE measurements](image)

**Fig. 4.20:** J-V (a) and PCE (b) measurements of hybrid PEDOT:PSS/Si solar cells w/ and w/o PFN interlayer at the backside contact.

<table>
<thead>
<tr>
<th></th>
<th>$J_{SC}$ [mA/cm²]</th>
<th>$V_{OC}$ [V]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>w/o PFN</td>
<td>31.9 ± 0.8</td>
<td>0.519 ± 0.014</td>
<td>64.3 ± 1.7</td>
<td>10.6 ± 0.4</td>
</tr>
<tr>
<td>w/ PFN</td>
<td>32.6 ± 0.6</td>
<td>0.518 ± 0.006</td>
<td>68.6 ± 0.9</td>
<td>11.6 ± 0.3</td>
</tr>
</tbody>
</table>

**Tab. 4.8:** PV characteristics of hybrid PEDOT:PSS/Si solar cells w/ and w/o PFN interlayer at the backside contact.

It is visible that all PV parameters except $V_{OC}$ are improved ($J_{SC}$: +2%, FF: +7% relative, PCE: +9% relative). Apart from $V_{OC}$, this corresponds to the results Sheng et al. have published in [154] for PFN in hybrid PEDOT:PSS/Si solar cells. While the $J_{SC}$ improvement is significantly lower, the achieved FF improvement is larger compared to those results ($J_{SC}$: +11%, FF: +5% relative). The FF improvement is mainly ascribed to a lower $R_S$ of 10.6Ω compared to 13.8Ω for the reference device without PFN interlayer. Hence, the PFN interlayer mainly improves $R_C$ of the backside contact and thus $R_S$ of the solar cell.
The lower $J_{SC}$ improvement is attributed to the TMAH-structured Si surface. As a result, even the devices without PFN show a $J_{SC}$ which is larger than that of the devices with PFN in [154] (29.6 mA/cm$^2$). Furthermore, the anisotropic etching step may also be the reason for the missing $V_{OC}$ improvement compared to the published results. Since both sides of the Si wafer are etched, the etching probably has an impact on the functionality of the PFN interlayer due to a different termination and morphology of the Si backside.

4.3.3 Conclusion

Two different materials, LiF and PFN, have been investigated as interlayers to improve the Al backside contact of hybrid organic/Si solar cells.

With a LiF backside interlayer, the PCE of P3HT/Si solar cells is relatively improved by 4\%. As expected, this is almost completely attributed to an enhanced FF. For the best performing sample, an excellent PCE of 14.2\% is achieved.

Utilizing a PFN interlayer in PEDOT:PSS/Si solar cells, a more pronounced relative PCE improvement of 9\% is reached. Again, this is mainly related to FF enhancement.

4.4 Conclusion

In this chapter, several parts of the hybrid organic/Si solar cell are optimized to improve the device performance.

First, the semitransparent Au top contact is replaced by a combination of PEDOT:PSS and an Au grid. Hereby, the transmittance of the top contact is more than doubled which results in a significant $J_{SC}$ improvement of 94\%. Furthermore, due to the electron selectivity of PEDOT:PSS and the higher conductance of the PEDOT:PSS/grid combination, $V_{OC}$ (+13\% relative) and the FF (+2\% relative) are enhanced as well. In summary, by optimizing the top contact, the PCE of hybrid P3HT/Si solar cells is remarkably improved by 126\%.

Next, an anisotropic etching step was introduced to structure the Si surface and thus reduce the reflection losses at the organic/Si interface and as a result improve $J_{SC}$ of the hybrid solar cells. The largest $J_{SC}$ improvement of 17\% is achieved by using TMAH as etchant. However, due to the formation of voids between the organic material deposited on
top and the structured Si surface, these devices show a significantly declined $V_{OC}$ (-10\%) and as a result a lower PCE (-4\% relative). Hence, KOH is utilized as etchant and the etching setup is changed to generate smaller Si pyramids and a lower surface coverage of the pyramids. Hereby, the voids and in turn the $V_{OC}$ reduction are prevented. For the KOH-etched hybrid P3HT/Si solar cells, a $J_{SC}$ improvement of 10\% and as a result a relative PCE improvement of 12\% are achieved.

Finally, two different interlayer materials (LiF and PFN) are investigated to improve the electron extraction at the backside contact and as a result FF of the hybrid solar cells. With a LiF interlayer, the PCE of P3HT/Si solar cells is relatively improved by 4\% which is almost completely attributed to an enhanced FF (+3\% relative). An even higher relative PCE improvement of 9\% is reached with a PFN interlayer in hybrid PEDOT:PSS/Si solar cells. Again, this is mainly ascribed to an improved FF (+7\%). For the best performing hybrid P3HT/Si solar cell with LiF interlayer, an excellent PCE of 14.2\% is achieved which so far is one of the highest efficiencies published for this type of solar cells.

The successive improvement of the PV characteristics of the hybrid solar cells attributed to the different optimization stages is concluded in Fig. 4.21 and Tab. 4.9. As visible here and in accordance with the photo-electrical calculations and the optical simulations, the dominant loss mechanisms of the unoptimized P3HT/Si reference device are optical losses (reflection at the hybrid interface: -9\% $J_{SC}$, absorption in the semitransparent Au top contact: -44\% $J_{SC}$) and a non-optimal blocking of the reverse electron current (-16\% $V_{OC}$). In comparison, the FF losses are only marginal (-3\%). This indicates that the charge extraction is only a minor problem of the reference device.
Fig. 4.21: J-V (a) and PCE (b) measurements of hybrid P3HT/Si solar cells in the different optimization stages.

<table>
<thead>
<tr>
<th></th>
<th>J&lt;sub&gt;SC&lt;/sub&gt; [mA/cm&lt;sup&gt;2&lt;/sup&gt;]</th>
<th>V&lt;sub&gt;OC&lt;/sub&gt; [V]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>reference</td>
<td>15.1 ± 0.2</td>
<td>0.504 ± 0.001</td>
<td>66.5 ± 2.1</td>
<td>5.0 ± 0.1</td>
</tr>
<tr>
<td>PEDOT:PSS + grid</td>
<td>29.3 ± 0.2</td>
<td>0.567 ± 0.001</td>
<td>67.8 ± 2.1</td>
<td>11.3 ± 0.4</td>
</tr>
<tr>
<td>KOH-etching</td>
<td>32.1 ± 0.6</td>
<td>0.592 ± 0.003</td>
<td>66.8 ± 1.1</td>
<td>12.7 ± 0.3</td>
</tr>
<tr>
<td>LiF interlayer</td>
<td>31.9 ± 2.5</td>
<td>0.597 ± 0.003</td>
<td>68.5 ± 2.3</td>
<td>13.0 ± 0.9</td>
</tr>
</tbody>
</table>

Tab. 4.9: PV characteristics of hybrid P3HT/Si solar cells in the different optimization stages.
Chapter 5

Conclusion and Outlook

This work represents a comprehensive study of hybrid organic/inorganic solar cells. In these devices, the organic semiconductor can lead to improvement based on the following fundamental processes:

- additional $I_{ph}$ generation
- blocking of the reverse electron current into the anode contact
- reduction of the reflection losses (antireflection coating)

To demonstrate these effects, devices based on various combinations of inorganic and organic semiconductors are investigated. Their performance is predicted by photo-electrical calculations as well as optical simulations, and the results are compared with the measured characteristics of the processed devices.

To demonstrate additional $I_{ph}$ generation within the organic material, a device layout based on PEN as organic and GaN as inorganic part of the hybrid solar cell is employed. Due to the lower HLG of PEN compared to the GaN band gap $E_G$, a larger fraction of the solar spectrum can be utilized. As a result, for the hybrid PEN/GaN solar cell, a higher $J_{SC}$ compared to a Schottky junction reference without PEN is expected. The measured PV characteristics of the hybrid solar cell as well as those of the Schottky reference match with the theoretically predicted values. For the hybrid PEN/GaN solar cell, a $J_{SC}$ improvement of 198% compared to the Schottky reference is achieved. This clearly demonstrates the additional $I_{ph}$ generation within PEN.

To validate the blocking of the reverse electron current into the top anode contact, hybrid solar cells based on Si as inorganic semiconductor are chosen. As organic part, two different
CONCLUSION AND OUTLOOK

polymers, P3HT and PEDOT:PSS, are investigated. While P3HT is employed as an electron blocking interlayer, PEDOT:PSS is used in combination with a Au grid as a hole-selective top anode contact. For both device types, the LUMO of the polymer forms an energy barrier which suppresses the detrimental reverse electron current into the anode contact. As a consequence, for both types of hybrid organic/Si solar cells, an improved \( V_{OC} \) compared to the Schottky junction reference without organic material is expected. The measured PV characteristics agree with the predicted values and show a significantly improved \( V_{OC} \) of the hybrid solar cells compared to that of the Schottky reference (P3HT: +73\%, PEDOT:PSS: +97\%). This clearly proves the blocking of the reverse electron current by the organic material.

To demonstrate the function as an antireflection coating (ARC), the small-molecule organic semiconductor Spiro-MeOTAD is used. As inorganic part of the hybrid solar cell, Si is utilized and as transparent top contact, PEDOT:PSS combined with a Au grid is employed. Since \( n_{PEDOT:PSS} < n_{Spiro-MeOTAD} < n_{Si} \), the introduction of a Spiro-MeOTAD interlayer between PEDOT:PSS and Si can reduce the reflection losses. To predict the impact of the Spiro-MeOTAD interlayer and to find an optimal Spiro-MeOTAD thickness, optical simulations are performed. Subsequently, hybrid Spiro-MeOTAD/Si solar cells as well as reference devices without Spiro-MeOTAD interlayer are processed and characterized. The EQE data of both device types as well as the measured \( J_{SC} \) improvement are in good agreement with the predictions by the optical simulations. This clearly validates the optical simulations and thus the function of the Spiro-MeOTAD interlayer as an ARC in the hybrid solar cell. For the best performing hybrid solar cell with Spiro-MeOTAD interlayer, an excellent PCE of 14.3\% is demonstrated.

Besides studying the different functions of the hybrid solar cells, the device layout and fabrication processes of the hybrid P3HT/Si solar cell are optimized to improve the device performance. In a first step, the semitransparent Au top contact is substituted by a combination of the conductive polymer PEDOT:PSS and an auxiliary Au grid with a significantly larger transmittance (\(~83\%\) compared to \(~40\%\)). As a result, \( J_{SC} \) of the hybrid solar cells is improved by 94\%. Furthermore, \( V_{OC} \) and FF are enhanced due to the hole selectivity and a lower \( R_S \) of the PEDOT:PSS top contact. Overall, by replacing the semitransparent Au top contact with the PEDOT:PSS-based one, the PCE of the hybrid P3HT/Si solar cells is improved by 126\% (relative) reaching a value of 11.3\%. 

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Additionally, an anisotropic etching step is introduced to structure the Si surface and thus reduce the reflection losses due to a multi-step reflection process. Two different etchants, TMAH and KOH, are utilized. For TMAH as etchant, a complete surface coverage with etched pyramids with edge lengths in the range of several nm up to several µm is demonstrated and a $J_{SC}$ improvement of 17% is achieved. However, due to an incomplete coverage of the structured Si surface by the organic materials, these devices show a significantly reduced $V_{OC}$ (-10%). Thus, KOH is applied as alternative etchant to achieve smaller pyramids with a lower surface coverage and in turn improve the coating of the structured Si surface by the organic materials. As a result, no $V_{OC}$ reduction is observed for these devices. However, attributed to the reduced surface coverage of the pyramids, a lower $J_{SC}$ improvement of 10% is reached. Overall, with KOH as etchant, the PCE of the hybrid P3HT/Si solar cells is relatively enhanced by 12% to a value of 12.7%.

In a last step, LiF and PFN are investigated as an interlayer between Si and the Al backside contact of the hybrid solar cells to improve the electron extraction and thus the FF of the devices. With an LiF interlayer, $R_S$ of the hybrid P3HT/Si solar cell is reduced by 13% resulting in a relative FF improvement of 3% and a PCE improvement of 4%. For the best performing sample, a very good PCE of 14.2% is achieved. With a PFN interlayer, $R_S$ is reduced by 23% leading to relative FF and PCE improvements of 7% and 9%, respectively.

In summary, the different types of hybrid solar cells investigated in this work impressively demonstrate the potential of this class of solar cells. For the best performing devices, excellent PCE of 14.3% (with Spiro-MeOTAD ARC) and 14.2% (with LiF backside contact) are achieved. These represent two of the highest values published for hybrid solar cells based on a heterojunction between an organic and an inorganic semiconductor.

Besides the achieved efficiencies, another very important aspect for the practicability of a solar cell technology is its long-term and environmental stability. While conventional Si solar cells exhibit excellent durability (degradation rates <1% per year) [159], organic materials are known to suffer from exposure to oxygen, humidity and ultraviolet light [41]. In OLED and OPV technology, this drawback is dealt with by encapsulation of the devices [41]. Nevertheless, investigations should be carried out to investigate and optimize the durability of the hybrid organic/inorganic solar cells.
Appendix A

Process Parameters

A.1 GaN-Based Devices

Formation of the ohmic contact
Deposition tool: *Pfeiffer* Classic 500 L
Annealing: 30 s @ 825 °C in a *Centrotherm* rapid thermal annealing (RTA) system

Definition of active areas via photolithography
Photoresist: AZ1518, *AZ Electronic Materials*
Developer: AZ726, *AZ Electronic Materials*
Process:
1. Spin-coating: 1 min @ 2000 RPM
2. Soft bake: 2 min @ 97 °C
3. Exposure through shadow mask
4. Developing
5. Hard bake: 30 min @ 120 °C

Deposition of the organic semiconductor
OVPD system: *AIXTRON* Gen1

Deposition of the semitransparent top contact
E-beam tool: *Pfeiffer* Classic 500 L
A.2 Silicon-Based Devices

Wafer cleaning

Cleaning procedure:

1. 5 min in DMSO (170°C or 80°C)
2. 5 min in acetone (100°C or 80°C)
3. 5 min in IPA (170°C or 80°C)
4. Rinsing with deionized water (DI water)
5. 5 min in a 1:1 mixture of hydrochloric acid (HCl) and DI water

Removal of the silicon oxide

BOE composition: 35 % ammonium fluoride, 7 % hydrofluoric acid (HF), aqueous solution
BOE dip: 5 min

Structuring via photolithography

Photoresist: AZ1518, AZ Electronic Materials
Developer: AZ726, AZ Electronic Materials
Process:

1. Spin-coating: 1 min @ 2000 RPM
2. Soft bake: 2 min @ 97°C
3. Exposure through shadow mask
4. Developing
5. Hard bake: 30 min @ 120°C

Deposition of the organic semiconductors

P3HT: dissolved in toluene @ 90°C Spiro-MeOTAD: dissolved in chlorobenzene @ RT
Drying:

- P3HT: 20 min @ 80°C
- Spiro-MeOTAD: 5 min @ RT
- PEDOT:PSS 15 min @ 100°C
A.3 Anisotropic Si Etching

A.3.1 TMAH

- TMAH concentration: 1 vol%
- IPA concentration: 10 vol%
- temperature: 80 °C
- etch time $t_{etch}$: 20–25 min

A.3.2 KOH

- KOH concentration: 2 wt%
- IPA concentration: 4 wt%
- temperature: 80 °C
- etch time $t_{etch}$: 20 min
Bibliography


[100] Sigma-Aldrich data sheet for P3HT. URL: http://www.sigmaaldrich.com/catalog/product/aldrich/698997?lang=de&region=DE.


List of Publications


Acknowledgments / Danksagungen

Im Folgenden möchte ich mich bei allen Personen bedanken, durch deren Unterstützung diese Arbeit erst ermöglicht wurde. Insbesondere danke ich:

– Herrn Prof. Dr.-Ing. Andrei Vescan, der mir die Möglichkeit gegeben hat, am Lehr- und Forschungsgebiet Compound Semiconductor Technology zu promovieren. Insbesondere bedanke ich mich für die Freiheit dir er mir bei der Durchführung meiner Arbeit gewährt hat.

– Herrn Prof. Dr. rer. nat. Uwe Rau für die Übernahme des Zweitgutachtens.

– Herrn Dr. rer. nat. Holger Kalisch für seine detaillierten Korrekturen, für seine hilfreichen wissenschaftlichen Anregungen und für das sehr freundliche Miteinander.

– Herrn Pascal Pfeiffer, M.Sc. für die ausgezeichnete Atmosphäre und zahlreiche (wissenschaftliche) Diskussionen im Büro sowie auf dem Weg dorthin.


– Frau Gabriele Nogueira-Glenski und Frau Sonja Buchholz-Trappe für ihre Unterstützung im Bereich der Lithographie.
Acknowledgments / Danksagungen

– Frau Marita Söhndel für ihre Unterstützung bei allen organisatorischen Fragen und zahlreiche sehr nette Gespräche.

– Allen (ehemaligen) Mitarbeitern und Mitarbeiterinnen des Lehr- und Forschungsgebiet Compound Semiconductor Technology für das ausgezeichnete Arbeitsklima und die Unterstützung vor und während dieser Arbeit.

Besonderer Dank gebührt darüber hinaus meiner Frau, die mich während der gesamten Promotion in jeder auch noch so stressigen Situation unterstützt hat und natürlich meinen Eltern, die mir das Studium erst ermöglicht und immer an mich geglaubt haben.