Fast and Slow Charge Trapping and Transport in Organic Semiconductors

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Contents

Frequently used symbols i
Frequently used acronyms iii
Abstract 1
Kurzfassung 3
About this work 5
1 Introduction 7
2 Organic semiconductors: structure, charge transport and device operation 9
  2.1 Pentacene as an example 10
  2.2 Charge transport from molecule to molecule 12
  2.3 Charge injection from a metal into an organic semiconductor 16
  2.4 The trap DOS 20
  2.5 Working principle of an organic bulk-heterjunction solar cell 23
  2.6 Working principle of an organic field-effect-transistor 25
3 Device fabrication and analysis 31
  3.1 Organic semiconductors investigated in this study 31
  3.2 Gate dielectrics used 32
  3.3 Sample preparation 33
    3.3.1 Preparation of single crystal FETs 34
    3.3.2 Preparation of TFTs 35
  3.4 Experimental setup 36
3.5 Extracting the density of trap states ........................................ 36

4 Opto-electronic simulation of organic bulk-heterojunction solar cells:
steady state and time dependent characterization 39
4.1 Introduction ................................................................. 40
4.2 Description of the numerical device model ............................ 43
  4.2.1 Optical modeling .................................................... 43
  4.2.2 Electrical modeling .................................................. 44
4.3 Estimation of the dissociation rate ..................................... 49
4.4 Sensitivity analysis ....................................................... 51
  4.4.1 Thickness dependent sensitivity .................................. 54
  4.4.2 Current-voltage curve sensitivity ............................... 55
  4.4.3 Transient current sensitivity ..................................... 57
4.5 Measurement of current transients after turn-off ................. 61
4.6 Conclusion ................................................................. 65

5 Gate-bias stress in pentacene field-effect-transistors: charge trapping
in the dielectric or semiconductor 67
5.1 Introduction ................................................................. 68
5.2 Experiment ................................................................. 68
5.3 Results and discussion .................................................. 72
5.4 Conclusion ................................................................. 74

6 From organic single crystals to solution processed thin-films: charge
transport and trapping with varying degree of order 75
6.1 Single crystal ............................................................... 78
6.2 Evaporated thin-film ..................................................... 79
6.3 Spin-coated thin-film ..................................................... 83
6.4 Comparison and density of states .................................... 85
6.5 Conclusion ................................................................. 88

7 The density of trap states and device performance of organic as well
as inorganic n- and p-type semiconductors 91
7.1 Introduction ................................................................. 92
7.2 Overview: Trap DOS and device performance ...................... 93
7.3 Experimental methods to determine the trap DOS ................ 95
7.4 Transistor performance: comparing p- and n-type materials ..... 96
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.5 New method: fully renormalized transfer curves and trap DOS</td>
<td>99</td>
</tr>
<tr>
<td>7.6 Trap DOS: organic and inorganic FETs</td>
<td>102</td>
</tr>
<tr>
<td>7.7 Trap DOS: bulk and interface</td>
<td>104</td>
</tr>
<tr>
<td>7.8 Conclusion</td>
<td>105</td>
</tr>
<tr>
<td>8 Summary, conclusions and outlook</td>
<td>107</td>
</tr>
<tr>
<td>List of Tables</td>
<td>109</td>
</tr>
<tr>
<td>List of Figures</td>
<td>111</td>
</tr>
<tr>
<td>Bibliography</td>
<td>117</td>
</tr>
<tr>
<td>Acknowledgment</td>
<td>133</td>
</tr>
<tr>
<td>Curriculum Vitae</td>
<td>135</td>
</tr>
<tr>
<td>Publication list</td>
<td>139</td>
</tr>
<tr>
<td>Contributions at conferences, meetings and workshops</td>
<td>141</td>
</tr>
<tr>
<td>Supervised projects</td>
<td>143</td>
</tr>
</tbody>
</table>
Frequently used symbols

$C_i$ Capacitance per gate unit area  
$d$ Thickness of the organic semiconducting layer  
$E_{\text{int}}$ Internal electric field  
$E_C$ Conduction band edge / mobility edge  
$E_V$ Valence band edge / mobility edge  
$E_{\text{vac}}$ Vacuum level  
$\varepsilon_i$ Dielectric constant of the gate insulator  
$\varepsilon_s$ Dielectric constant of the organic semiconductor  
$I_d$ Drain current  
$L$ Channel length  
$l$ Thickness of the gate insulator  
$\mu_{\text{eff}}$ Effective mobility  
$\mu_{\text{free}}$ Mobility of the free charge carrier  
$\Phi$ Work function  
$\Delta \phi$ Vacuum level shift  
$n_{\text{free}}$ Number of free charge carriers  
$n_{\text{trapped}}$ Number of trapped charge carriers  
$Q_i$ Number of charge carriers per unit area  
$Q_v$ Number of charge carriers per unit volume  
$\sigma$ Field-effect conductivity  
$V_g$ Gate voltage  
$V_d$ Drain voltage  
$V_{\text{th}}$ Threshold voltage  
$V_{\text{OC}}$ Open circuit voltage  
$W$ Channel width
## Frequently used acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Full Form</th>
</tr>
</thead>
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<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
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<tr>
<td>Cytop</td>
<td>Cyclic transparent optical polymer</td>
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<td>CB</td>
<td>Conduction band</td>
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<tr>
<td>DOS</td>
<td>Density of states</td>
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<tr>
<td>EA</td>
<td>Electron affinity</td>
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<tr>
<td>EIB</td>
<td>Electron injection barrier</td>
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<tr>
<td>FET</td>
<td>Field-effect transistor</td>
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<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
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<td>HIB</td>
<td>Hole injection barrier</td>
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<tr>
<td>IE</td>
<td>Ionization energy</td>
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<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
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<tr>
<td>LUMO</td>
<td>Lowest occupied molecular orbital</td>
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<tr>
<td>MIS</td>
<td>Metal-insulator-semiconductor</td>
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<tr>
<td>OFET</td>
<td>Organic field-effect transistor</td>
</tr>
<tr>
<td>OPV</td>
<td>Organic photovoltaic cell</td>
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<tr>
<td>SAM</td>
<td>Self assembled monolayer</td>
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<td>STM</td>
<td>Scanning tunneling microscope</td>
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<tr>
<td>Trap DOS</td>
<td>Density of trap states in the band-gap</td>
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<tr>
<td>TFT</td>
<td>Thin-film transistor</td>
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<td>VB</td>
<td>Valence band</td>
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Abstract

In this thesis charge transport and associated processes in organic semiconductors are investigated from various points of view to identify fundamental mechanisms limiting device performance. This will hopefully contribute to establish a more coherent picture for the charge transport and partially replace the patchwork of theories which are used nowadays.

In the first study we developed a full organic photovoltaic cell (OPV) simulator. The fundamental processes have been implemented from light incoupling to charge extraction. We then studied the limiting processes for various steady state as well as transient simulations and compared the results with actual measurements. This shows that transient measurements are an important part to identify and distinguish concurrent processes.

In the next study we investigated so called slow charge traps in organic field-effect transistor (OFET) which limit the device performance. Through careful comparison of several device stacks we have been able to identify a system where slow charge trapping occurs in the semiconductor and therefore eliminates charge trapping in the gate dielectric, which normally occurs in almost all OFET devices.

The third study is then focused on a comparison of charge transport and trapping in a n-type material. Using various processing methods we have been able to produce OFETs with a wide range of crystallinity. This is an important step for understanding how order/disorder due to morphological differences influences the spectral density of trap states (trap DOS) and thus charge transport.

The last study is a survey to summarize the trap DOS in state of the art OFETs. For this investigation we have compared publications from the last 25 years to have a coherent picture of charge traps for organic p- as well as n-type devices. A comparison to their inorganic counterparts is done as well. We also show a very simple method to extract the density of trap states from transfer
curve measurements. Furthermore we could show that organic n-type materials behave the same as the already well established p-type counterparts. Finally we have been able to produce rubrene single crystal OFETs which have the same trap DOS close to the surface as in the bulk of the single crystal.
Kurzfassung


In der zweiten Studie untersuchten wir sogenannte langsame Einfangstellen in OFETs, welche der Anwendbarkeit von diesen Transistoren im Wege stehen. Durch eine sorgfältige Durchführung der Versuche und Vergleiche zwischen verschiedenen OFETs konnten wir erstmals einen Schichtaufbau identifizieren, bei dem die Ladungsträger im organischen Halbleiter eingefangen werden. Dadurch konnten wir das Einfangen von Ladungsträgern im Isolator unterdrücken, was sonst der Normalfall ist.

Die dritte Studie beschäftigt sich mit dem Ladungstransport und Einfangstellen in einem n-typ Material. Wir benutzten verschiedene Herstellungsmetho-

About this work

Scientific achievements are not easily communicated to a wider audience, especially if the field has progressed far into very specialized topics. Even a normal day in the laboratory is hard to imagine for someone who has never worked in a laboratory environment. Therefore, this thesis does not only contain the scientific analysis and interpretation of measured data obtained from organic electronic devices, but also three illustrations. These interpretations emerged from long discussion with the designer Oliver Meier about the essence of my work. We came to the conclusion, that by illustrating the the work environment, i.e. the equipment, device structures and microscopic arrangement of organic molecules, we will be able to convey an idea about this field of research.

The three illustrations are scattered throughout this thesis and are only available in the bound version. The first image is a photograph of the tools used in the laboratory to produce and measure the organic electronic devices. The second one is a upscaled (50 times) screen printing of a standard organic field effect transistor layout used. The last one is an illustration of the polycrystalline structure of organic thin-films.
Introduction

Research is what I’m doing when I don’t know what I’m doing.

Wernher von Braun

When I started the work for this Ph.D. thesis, organic electronics was still a niche market, but the rapid development and industrial scale production changed this field in the last few years. Back then, laboratory scale organic photovoltaic cells (OPV) had efficiencies of around 5-6%, organic light emitting diode (OLED) displays where a niche market for smallest devices and organic field effect transistors (OFET) produced in a scalable process had mobilities below 1 cm$^2$/Vs.

Figure 1.1: Various organic electronic devices
Nowadays, OLED displays are widely available for up to 7.7" cell phones and tablets and large TVs up to 55" have been launched. Organic solar cells now reach 12% cell efficiency, surpassing dye sensitized solar cells and reaching the efficiencies of multijunction polycrystalline and amorphous silicon solar cells. For OFETs, solution crystallization processes have been developed with which mobilities of around 10 cm$^2$/Vs are reached, for p- as well as n-type OFETs.

Organic semiconductors are an intriguing class of materials and the research into them is exceptionally broad and interdisciplinary. First, there is a huge range of different molecules with a wide choice of different preparation and processing methods to choose from. This leads to a diverse field ranging from chemists synthesizing and analyzing single molecules or thin films, chemical engineers developing and improving preparation methods, physicist, both experimental and theoretical, trying to understand charge transport, identifying device limiting processes and establish a more coherent theory to explain and characterize these multitude of organic devices. Then there are electrical engineers which integrate organic devices into circuits and exploit their easy processing methods to combine OFETs, OLEDs, OPVs onto a flexible substrate in one processing run or even envisioning wearable electronics. Then, there are many small spin-off companies and large enterprises, with R&D budgets comparable to the GDP of smaller countries, pushing process scalability and achieving mind staggering yields. To probe and expand the market from the demand side, artists and industrial designers are envisioning new applications and integration of organic electronics to highlight the difference and advantage to the already established inorganic devices. This diverse field makes working on organic electronics extremely exciting.

In this work I will try to shed but a small light on a specific part of organic electronics, namely charge transport in crystalline and polycrystalline semiconducting layers. To tell the story, the next chapter gives an introduction to the processes involved in charge generation and transport and explains full OPV and OFET devices. The third chapter shows the different materials, discusses the various preparation methods employed and also shows the experimental setup and the data analysis. Chapter four until seven are dedicated to the investigation of charge transport and associated phenomena. For this, OPVs as well as OFETs are studied experimentally and by using simulation software. This thesis concludes with a summary of the main results in Chapter 8.
Organic semiconductors: structure, charge transport and device operation

One shouldn’t work on semiconductors, that is a filthy mess; who knows if they really exist?

---

Wolfgang Pauli, 1931

First observations of the strange behavior of inorganic semiconducting materials can be traced back to the 19th century. At the beginning they where mere reports of odd behaviors of the investigated samples. Only in the 20th century after the development of quantum mechanics and the band structure theory it was possible to properly describe the properties of these samples. Organic materials have been investigated at around the same time and already in 1948 it has been argued that phthalocyanine can be described in terms of semiconductor theory. [1]

It took another 4 decades to build and measure a working organic FET. [2, 3] Shortly after, the first working OLEDs and OPV cells have been fabricated by Tang and van Slyke. [4, 5] In 1990 spin-coating of polymers was the first time used to build a polymeric OLED. [6] All these advancements were possible thanks to various achievements in fabrication methods, right choice of materials and improved purity. The development did not stop there. Companies are investing billions of dollars to improve fabrication methods and lifetime of organic materials and nowadays electronic gadgets incorporating these organic materials are widely available.

Even though consumer products are readily available, many fundamental ques-
2. Organic semiconductors and devices

Tions regarding charge transport are not yet understood. The theoretical description of charge transport in organic semiconductors has mostly been driven by models developed for inorganic semiconductors. But organic materials are a different kind of semiconductors, as Alessandro Troisi pointed out [7]:

“The energy gap remains the only similarity between organic and inorganic semiconductors. The electronic structure, the interaction between nuclear and electronic degrees of freedom and the role of defect states are so different in organics that the analogy with standard semiconductor physics is of limited use.”

In this chapter we will discuss how electrons are distributed within a single molecule, how charges move from molecule to molecule and how we get from that to a working device.

2.1 Pentacene as an example

Figure 2.1: Pentacene structure in theory and as measured. (A) Ball and stick model. (B) STM image. (C) and (D) AFM image. [8]

In the rich field of organic materials there are many different kinds of molecules and polymers. Nevertheless all of them have some basic structure in common which allow for a distributed electron cloud on the molecule. Therefore in this chapter we will pick out a simple molecule: pentacene, which we will use as a
2.1. Pentacene as an example

Figure 2.2: Molecular orbitals of pentacene as measured using a high-resolution STM. Adapted from [9].

prototype for the wide field of organic semiconductors. Pentacene is widely used in organic electronics research and has become one of the most intensely investigated molecules. It consists of 22 carbon atoms each bound to 3 neighboring atoms. Free carbon has the electron configuration $1s^22s^22p^2$, which shows that carbon has 4 valence electrons. In a molecule, the s- and p-orbitals mix to so-called sp-hybridizations. In organic electronics the $sp^2$-hybridization, where one s- and two p-orbitals form three sp-orbitals and the $p_z$-orbital remains unaltered, is the key ingredient leading to charge transport. The three sp-orbitals form covalent bonds to three neighboring atoms, whereas the $p_z$-orbital only weakly bonds to the neighboring carbon atom. This can all be nicely seen in pentacene which consists of five benzene rings (Fig. 2.1). Every carbon atom is covalently bound to 3 neighbors, either another carbon atom or hydrogen. This leaves one electron available per carbon atom. These electrons are in the $2p_z$-orbitals which stick out of the molecular plane. The overlap of these $2p_z$-orbitals leads to $\pi$-bonds which are conjugated, i.e. every carbon atom is bound to only one neighboring carbon atom. The $\pi$-electrons in these relatively weak $\pi$-bonds are not localized.
on a single atom but are mobile within the molecule. This leads to an electronic \( \pi \)-system with wavefunctions which as a first approximation can be described using a simple particle in a box model, leading to molecular orbitals which have a discrete energy. There are two molecular orbitals which are important for conduction and therefore have a special name: the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). These two orbitals take over the role of the valence band level (HOMO) and conduction band level (LUMO) from inorganic semiconductors.

The shape and energy of these two molecular orbitals can be calculated by means of computational chemistry. Only recently it has been possible to directly map the shape using a high-resolution STM (Fig. 2.2).

### 2.2 Charge transport from molecule to molecule

![Herringbone structure of crystalline pentacene.](image)

Figure 2.3: Herringbone structure of crystalline pentacene. [10] Depending on the charge transport direction, the wavefunction overlap is different. Therefore transport properties will depend on the transport direction.

Charge transport within a single molecule results from the \( \pi \)-electrons. If two pentacene molecules are brought into close contact the molecular orbitals between the molecules begin to overlap and there is a chance that an electron might hop from one pentacene molecule to the next one. The exact shape of the molecular orbitals can be quite complicated (Fig. 2.2). Therefore the exact arrangement of the molecules in a single crystal are crucial for the conductivity. The
2.2. Charge transport from molecule to molecule

The interaction between the pentacene molecules is due the van der Waals force. This interaction is very weak, which results in semiconductor properties dominated by the properties of a single molecule, i.e. the wavefunction of a molecular orbital is not changed drastically if a molecule is in a crystal compared to a free one. This makes the simulation of charge transport in organic semiconductors a difficult task, as the interaction between neighboring molecules is not as strong as in an inorganic semiconductor (e.g. Si).

From this discussion it is evident that the charges are spatially localized on the length scale of about a single molecule. Macroscopically, the possibility for the charge carriers to hop from molecule to molecule is described by the so called

![Figure 2.4: Transport anisotropy measured in a pentacene single crystal.](image)

Where according to Yin et al. [12] the angle 0° is equal to the a axis (Fig. 2.3).

crystalline structure for pentacene has been determined by Campbell et al. [11] where it was found that the pentacene is arranged in the so called Herringbone packaging (Fig. 2.3). From this picture it can be expected that the charge transport properties depend on the crystal direction, due to a different wavefunction overlap along the a- b- and c- direction. Transport measurements clearly show this anisotropy (Fig. 2.4). As Yin et al. [12] calculated the transport anisotropy is different for holes and electrons in pentacene. This is due to the slightly different shape of the wavefunction for the HOMO and LUMO as shown in figure 2.2.
Figure 2.5: Temperature dependence of the mobility in various pentacene FETs. Depending on the processing conditions and measurement technique either “band-like” or “hopping” transport is observed. [14–16].

mobility, which links the average drift velocity $v_d$ of the charge carrier with and applied electric field $E$:

$$v_d = \mu E.$$ \hfill (2.1)

The mobility is not only crucial for understanding the transport mechanism, but it is also important for application; higher mobility leads to faster switching speeds in organic field-effect-transistors and higher efficiencies in organic photovoltaic cells and light emitting diodes.

A. Troisi calculated the maximum mobility which is expected from a simple hopping mechanism. He found the maximum mobility due to hopping from molecule to molecule to be lower than $\mu_{\text{hop}} < 0.08 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. [17] Experimentally, mobilities up to $400 \text{ cm}^2\text{V}\text{s}^{-1}$ have been measured [18] and in FET structures mobilities over $40 \text{ cm}^2\text{V}\text{s}^{-1}$ have been achieved. [19] Additionally, so called band-like transport has been observed, i.e. increasing mobility when lowering the temperature. These measurements therefore do not fit with a simple hopping
2.2. Charge transport from molecule to molecule

Figure 2.6: Left: molecular dynamics simulation of the hopping integral at different temperatures and along two directions in the crystal. Right: relative position of two anthracene molecules at 300 K which leads to the fluctuating hopping integral. [20]

model. A complication for discussion of this effect comes from the pronounced dependence of transport properties on the processing and measurement condition. Figure 2.5 shows measurements of pentacene TFTs from 3 different publications. Nelson et al. [14] (red curves) have found that different TFT samples show significantly different temperature dependent behavior even though they have been grown under nominally similar conditions. Pesavento et al. [15] (blue curves) have demonstrated that neglecting the effect of the contact resistance changes the temperature dependence from a band-like to a hopping behavior. Whereas Minari et al. [16] (dark yellow curves) have shown that when measuring a multi-grain structure a different temperature dependent behavior is found than when a single crystalline grain is measured. This illustrates the effect of grain boundaries on device characteristics.

An explanation of the "band-like" transport behavior is given by the off-diagonal (or dynamic) disorder transport theory. [7, 21–23] Due to the weak intermolecular binding, the single molecule vibrates, this is also called thermal molecular motion (Fig. 2.6). These spatial changes are large enough for the wavefunction-overlap between neighboring molecules to fluctuate over time. This leads to so called dynamic localization of the electrons. This type of localization gets smaller at lower temperature, therefore the mobility increases. [24] This mechanism localizes the electron, but only dynamically and therefore allows for higher mobilities than expected from a standard hopping mechanism. This model has been applied to
calculate the mobility and its temperature dependence in a Rubrene crystal [25] where an excellent quantitative agreement with measurements was found.

2.3 Charge injection from a metal into an organic semiconductor

Injection of charges from a metal electrode into an organic semiconductor is one of the fundamental processes in any organic device. Nevertheless it is a challenge to understand it properly as there are many different mechanisms which influence charge injection. In this section we will only scratch at the surface of some of the processes which occur at a metal-organic interface.

Between the work-function of the electrode and the conduction level of the semiconductor, be it the HOMO or the LUMO level, exists a barrier. This injection barrier is in first approximation given by the energy difference of the work-function and the transport level. These values are normally taken from measurements done at the undisturbed material (Fig. 2.7). This is the so called “vacuum level alignment” case. This simplification neglects any processes which can occur as soon as the metal has been brought in contact with the organic semiconductor. These changes can be as large as 1 eV [26] (Fig. 2.8) whereas from computer simulations it is known that already an injection barrier of more than about 0.3 eV limits the device performance. This shows that this simple picture will give an idea about which organic material may be compatible with which metal electrode, but it is too simple to give a quantitative prediction of the injection barrier.

Direct measurements of the barrier at the contact between the organic semiconductor and the metal have shown that the barrier height can get larger or smaller upon contact compared with when looking at the individual material. [26] This phenomenon is called “vacuum level shift” or "interface dipole". If an organic molecule is adsorbed to the surface of the metal it can undergo simple physisorption, where the electronic structure of the molecule is rather undisturbed and interaction with the electrode is given by van der Waals force. Whereas if chemisorption occurs the organic molecule exchanges charges with the electrode and forms a covalent bond. This influences the energy and spatial distribution of the HOMO and LUMO level and thus the injection barrier.

The work function of the metal also critically depends on the crystalline orientation of the metal surface. Gold contacts show a change in the work function from 5.47 eV to 5.1 eV when going from a (100) orientation to a polycrystalline
2.3. Charge injection from a metal into an organic semiconductor

Figure 2.7: HOMO and LUMO energies for various organic semiconductors. The values are sorted by the HOMO energies. The number on top the HOMO level is the calculated value of the band gap. Additionally the work functions of various contact materials are indicated as bars.
layer. [27, 28] Normally these measurements are done in high or even ultrahigh vacuum and therefore contamination of the surface is minimized. But as soon as the electrode is exposed to air, chemical species might adsorb at the surface. These will influence the electron density at the surface of the metal and thus they will change the work function, normally to values closer to the vacuum level. [28] If the gold is treated with UV/ozone a thin Au-oxide layer forms and the work function changes to values further away from the vacuum level at around 5.5 eV. This oxide layer is stable for around one hour and after deposition of the organic layer it is stable for a few days. [26, 29, 30] Therefore depending on the preparation techniques it is also quite possible to have a gold electrode with a work function of 4.7 eV. [31] After molecule adsorption even values as low as 4.2 eV are reported. [26] The above discussed mechanisms also influence each other. Therefore it was found that a gold electrode changes its work function from 5.4 eV to 4.7 eV upon contamination (mostly carbon species and oxygen) with a broad sample variation. Whereas after chemisorption of α-NPD the interface dipole reduces due to the contamination and therefore a better hole injection was found even though the work function of the gold electrode is shifted away from the α-NPD HOMO level which would lead to higher hole injection barriers. [32]

The interaction of the molecule with the electrode also defines the alignment of the of the molecule on the surface. The angle with which the molecule attaches
2.3. Charge injection from a metal into an organic semiconductor

Figure 2.9: Gold interdiffusion into an organic layer (Diindenoperylene, DIP) on a SiO$_2$ substrate. Sample A has been cooled to -120°C, whereas sample B has been heated to +70°C during evaporation of the gold. [36]

onto the surface influences the energy level of the HOMO and LUMO. [26, 33] A study on pentacene showed the more upright the molecules are standing on the surface, the lower the injection barrier from gold. [34] Therefore applying a self assembling monolayer (SAM) changes the injection properties from a gold electrode into the organic layer. [35]

An additional mechanism which has to be taken into account is the diffusion of the electrode material into the relatively soft and weakly bound organic semiconducting film. [37] This might happen at the time of evaporation, when high energy metal atoms hit on the surface of the organic semiconductor, or later due to thermally activated diffusion (Fig. 2.9). [36]

After the molecules come into contact with the electrode a certain injection barrier is established. As soon as a charge carrier is injected into the organic semiconductor it is attracted to the image potential generated in the electrode.
2. Organic semiconductors and devices

Figure 2.10: Charge injection barrier reduction by $\Delta \Phi$ due to image charges and the internal electric field inside the organic semiconducting device. [38]

[38] This bends the injection level towards the electrode work function close to the injecting contact (Fig. 2.10). The electric field inside the device also bends the injection level which when superimposed leads to a lowering of the charge injection barrier. From this discussion it is clear that the charge injection barrier also depends on the externally applied voltage and the charge carrier distribution close to the contacts, as both of them lead to a variation of the electric field inside the organic device. Such injection models have been developed for inorganic semiconductors and have later been adapted for organic semiconductors. [39, 40]

2.4 The trap DOS

The explanation of charge transport in an organic semiconductor until now was rather simplified. Therefore many little details have been neglected in favor of a clear picture. One of these omissions are the charge traps in the band-gap of organic semiconductors. This means there are states between the HOMO and LUMO level which can be occupied by charge carriers. These charge traps may come from chemical or structural defects in the charge transporting layer. Figures 2.11 and 2.12 show the influence of such a structural defect on the band width of the HOMO and LUMO level. If there is a change in the molecular arrangement, the band width of the transport level might increase and therefore states in the band gap, which act as trapping sites, are created (Fig. 2.13). These structural defects lead to trap states close to the transport level.

Chemical defects may result in deeper lying trap states. If oxygen or hydrogen is attached to a pentacene molecule the electron distribution on the molecule is al-
2.4. The trap DOS

Figure 2.11: Band width variation of the HOMO and LUMO level depending on the intermolecular separation of two sexithienyl molecules. [41]

tered (Fig. 2.14). This leads to electrically active gap states further away from the transport level. [43–45]. These oxygen trap states have been directly observed in transport measurements on pentacene TFTs [46] a quantitative agreement has been found with the theoretical studies by Knipp et al. [45]

Figure 2.12: Band width variation of the HOMO and LUMO level depending on the translation of the two of two sexithienyl molecules. [41]
Figure 2.13: Generation of shallow traps by increasing the band width of the HOMO and LUMO level when a displacement is introduced in a otherwise crystalline pentacene structure. [42]

A further process which gives rise to trap states is the thermal motion of the organic molecules, as discussed before. [7, 21–23] This effect leads to shallow traps close to the transport level. Further discussion on the spectral distribution of trap states is given in later chapters.

The charge carriers which move in these non-perfect organic semiconducting layers get trapped in these defect states and thermally released multiple times before they reach the counter electrode. At every point in time a certain fraction of charge carriers are trapped and therefore rendered immobile. Therefore, this process reduces the effective mobility ($\mu_{\text{eff}}$) of the charge carriers,

$$\mu_{\text{eff}} = \mu_{\text{free}} \frac{n_{\text{free}}}{n_{\text{free}} + n_{\text{trapped}}}$$ (2.2)

where $\mu_{\text{free}}$ is the mobility of the free charge carrier, $n_{\text{free}}$ and $n_{\text{trapped}}$ are the number of free and trapped charge carriers respectively.

This discussion makes it evident that mobility of the charge carriers can depend on the charge carrier density as the lower lying traps get filled up and the newly injected charge carriers do not get trapped in deep states, which leads to an overall higher effective mobility. Additionally it has been found that trap states can also explain the apparent electric field dependence of the mobility. [47]

All traps discussed until now are the so called fast traps. This means that the
2.5 Working principle of an organic bulk-heterjunction solar cell

A simple picture of the involved processes governing an organic photovoltaic cell (OPV) is shown in figure 2.15. Some of the processes have been discussed before. Therefore in this chapter only the new processes will be addressed.

The thickness of an OPV cell is around 100 nm which is shorter than the coherence length of the sunlight, which is about 1 µm. Therefore the OPV cell acts as a microcavity where light which penetrates into an OPV interferences with the light reflected from the back electrode. This leads to a non-monotonous
Absorption of a photon does not directly lead to free charge carriers. First an exciton is generated which is a bound state of an electron and a hole. These excitons have a binding energy of 0.1-1 eV, which means they can not be split-up by the thermal energy. Therefore it is necessary to use a heterojunction of two different organic semiconductors which act as donor and acceptor for the charge carriers. At the interface of these two materials one charge carrier hops on the other side, increasing the distance between the bound electron and hole and thus lowers the binding energy. This so called charge-transfer exciton is very short lived and eventually splits up into two free charge carriers. As the initial exciton is only short lived and has a diffusion length of only around 10 nm, it is essential
2.6. Working principle of an organic field-effect-transistor

A field effect transistor is basically a capacitor. An applied voltage on the side of the gate leads to an accumulation of charges in the semiconductor close to the insulator (Fig. 2.18). The number of charges in the semiconductor can be calculated by \( Q = CV_g \) where \( C \) is the capacitance of the insulator. These charges are injected from the electrodes and form a conduction channel. Depending on the sign of the injected charges and the contact material used, either p-type (holes) or n-type (electrons) transport can be observed. For certain material combination even ambipolar transport is observed.

As the charges are homogeneously distributed in the channel, a small volt-
age difference ($V_d$) at the two top contacts leads to charge carriers flowing from the source to the drain contact. At low $V_d$ this current is linear to $V_d$ and $V_g$. When $V_d$ is approaching $V_g$ the charge accumulation around the drain contact gets smaller and smaller until it is zero when the gate and the drain are on the same potential. This disrupts the conductive channel and the point where the charge accumulation goes to zero is called pinch-off point. The channel current becomes independent on the applied $V_d$, i.e. it becomes saturated, but depends quadratically on $V_g$ (Fig. 2.19 and 2.20). The two regimes are called linear and saturation regime respectively. A quantitative description of this behavior can be done under following assumptions [50–52]:

- The electric field along the channel is much smaller than through the insulator (gradual channel approximation).
- There are neither interface traps nor mobile charges in the insulator.
- There are only drift currents.
- The channel is uniform.
- The mobility $\mu$ is constant.
2.6. Working principle of an organic field-effect-transistor

Figure 2.19: Charge carrier distribution and channel formation in a FET under various operation conditions.

\[ I_{d,\text{linear}} = \frac{W}{L} \mu C_i \left[ (V_g - V_{th}) V_d - \frac{V_d^2}{2} \right] \]  \hspace{1cm} (2.3)

\[ I_{d,\text{saturated}} = \frac{W}{2L} \mu C_i (V_g - V_{th})^2 \]  \hspace{1cm} (2.4)

Where \( W \) and \( L \) are the transistor width and length respectively, \( \mu \) is the mobility, \( C_i \) is the capacitance per gate unit area, \( V_g \) is the gate voltage, \( V_{th} \) the threshold voltage and \( V_d \) the applied source-drain voltage. Normally the \( \frac{V_d^2}{2} \) is neglected in the linear current.

Equations 2.3 and 2.4 are used to extract the charge carrier mobility from transistor measurements. [51]

The question which needs to be answered is how thick the conducting channel is. From the relation \( Q_i = \frac{C_i V_d}{q} \) it is known how many charge carriers are accumulated at the interface per unit area, but it is not known how deep the charges penetrate into the semiconductor. An analytic solution of the governing drift-diffusion equations does not exist. [50] A good approximation is the Debye length, which is
the length over which the charges screen an electric field:

\[ L_D = \sqrt{\frac{\varepsilon_s \varepsilon_0 k_B T}{q^2 Q_V}}, \tag{2.5} \]

where \( Q_V \) is the charge carrier density per Volume. We know that \( Q_V = \frac{Q_i}{L_D} = \frac{C_i V_g}{q L_D} \), if we substitute this into Eqn. 2.5 leads to:

\[ L_D = \frac{\varepsilon_s \varepsilon_0 k_B T}{q^2 Q_i} = \frac{\varepsilon_s \varepsilon_0 k_B T}{q C_i V_g} \tag{2.6} \]

Figure 2.21 shows the calculated channel thickness of the FET shown in Fig. 2.20. At \( V_g = 10 \) the channel is already as thin as 1 nm, which is about the length of a Rubrene molecule.

The channel becomes infinitely large at \( V_g - V_{th} = 0 \). This is only partially true, as due to the trap density in the band gap and the broadening of the Fermi-Dirac distribution there is always a certain amount of partially mobile charge carriers in the device which will give an upper limit for the channel thickness.
2.6. Working principle of an organic field-effect-transistor

Figure 2.21: Channel thickness (i.e. Debye length) at four temperatures, calculated for the Rubrene FET shown in Fig. 2.20 using Eqn. 2.6.
Device fabrication and analysis

The most exciting phrase to hear in science, the one that heralds new discoveries, is not 'Eureka!' but 'That's funny..' Isaac Asimov

This chapter gives an overview of the materials used and the methods applied. The experiments are explained in more detail in each chapter. First we discuss the organic semiconducting materials used, then we look at the preparation of the gate dielectric. Afterwards we discuss sample preparation for single crystal FETs and evaporated TFTs. As a last step we look at the method to extract trap DOS from measured transfer curves.

3.1 Organic semiconductors investigated in this study

In this studies, many different systems are being investigated and compared to each other. Most of the observed systems are organic semiconductors. The systems we prepare in-house are based on small molecules organic semiconductors (Fig. 3.1). These molecules are commercially available from either Sigma-Aldrich (Pentacene and Rubrene) or Polyera (PDIF-CN₂). Pentacene has been purified by crystallization in a physical vapor transport growth oven. [53] Whereas Rubrene and PDIF-CN₂ have been used as is.
3.2 Gate dielectrics used

to accumulate enough charge carriers into the conduction channel of a field effect transistor a very good insulator is needed. Chemical stability and a surface which does introduce additional traps is required, too. To achieve all this we used a combination of dielectrics, as every material behaves differently on the various gate dielectrics. SiO$_2$ (260 - 300 nm) has been used, sometimes modified with...
140 nm of Cytop (Asahi Glass) or a thin layer of HMDS (hexamethyldisilazane, Sigma-Aldrich) (Fig. 3.2). SiO$_2$ has the advantage of easy handling and contacting with probers, without scratching the surface, whereas HMDS and Cytop add a hydrophobic layer which lowers the interface trap density in the conduction channel of a FET. [55, 56] The two surface modifications have been applied by spin-coating and subsequent annealing of the layer on-top of SiO$_2$. Cytop has a glass transition temperature of 108°C, which gives an upper limit for the post annealing temperature of an FET on Cytop. [56, 57]

3.3 Sample preparation

Highly n-doped (phosphorous) Si wafers have been bought with a 260 - 300 nm thick thermally grown SiO$_2$ layer. The wafers have been cut into usable substrate sizes using a wafer saw. Then the substrates have been cleaned in an ultrasonic bath in hot (∼65°C) acetone for 15 min, hot isopropanol for 15 min and then blown dry with nitrogen. Afterwards the modification of the surface has been applied according to Kalb et al. [55]

Gold contacts have been evaporated either directly onto the dielectric layer (bottom contact), or after the organic layer has been deposited (top contact). The various device structures are shown in figure 3.3. This gold evaporation is done under high vacuum with a base pressure of 10$^{-8}$ mbar.
3.3.1 Preparation of single crystal FETs

Organic single crystals have been produced using a physical vapor transport oven. [53] The oven consists of two tubes. The heating tube has a wire wound around it with varying winding density. This heats one end of the growth tube to the sublimation temperature of the material, and the other end to a lower temperature. The source material is placed on a half shell inside the growth tube. A flow of argon gas then transports the sublimated molecules from the hot to the colder end of the tube, where the organic molecule deposits into half shells slowly forming high purity single-crystals (Fig. 3.4). Sublimation temperatures depend on the material, but are commonly between 250 - 350°C. This growth methods has the advantage that it also purifies the source material during the crystal growth.

The grown single crystal was then been placed on a prestructured substrate in air and afterwards transferred into a high vacuum probe chamber for electrical characterization.
3.3. Sample preparation

3.3.2 Preparation of TFTs

Organic films have been evaporated under high vacuum with a base pressure of $10^{-8}$ mbar. The substrates have been put in a substrate holder (Fig. 3.5). During the evaporation, the substrates have been kept at room temperature (pentacene) or heated to 110°C (PDIF-CN$_2$) to allow for a better film growth. The source material has been heated to 140°C and then the shutter has been opened. Afterwards, the source material has been gradually heated to 190°C ($\approx$30 min) such that the first monolayer of the film grew slowly ($\approx$10 min), whereas subsequent layers are grown faster and faster. The film thickness was around 30 nm and has been confirmed using a surface profiler (Tencore P-11). The final layout after all the evaporation steps is shown in figure 3.6.

Figure 3.5: Finished pentacene TFTs in the substrate holder.

Figure 3.6: Structured substrate for measurements of TFTs. Left: view of the whole substrate. Right: detailed view of a 4-terminal test structure.
3.4 Experimental setup

The measurements have been performed in a high vacuum probe chamber (CryoVac, Germany) which is attached to a evaporation chamber (Kurt J. Lesker) which allows to prepare and measure TFTs in high vacuum and thus study the influence of various gas exposures on the conductive properties of the organic thin-film. The probe chamber includes a cryostat which allows to do temperature dependent transport measurements. The temperature has been measured on the sample itself using a thermocouple.

3.5 Extracting the density of trap states

Field effect transistors are not only interesting because of their potential applications, but widely used because they facilitate the study of the transport properties of organic materials. In this thesis we focus on the quantification of the trap DOS in these organic materials which is done by analyzing electrical measurements of OFETs.

In this thesis we used an FET simulator which has been developed by Oberhoff et al. [58] The basic idea of the Simulator is as follows: When a gate voltage is applied in an OFET, a certain amount of charge carriers is injected into the conduction channel. From these charge carriers a certain percentage is free to move, while the rest is trapped (mobility edge model). When the gate voltage is increased, the amount of charge carriers change as well as the ratio between free
3.5. Extracting the density of trap states

Figure 3.8: Measured and simulated transfer curve of a PDIF-CN$_2$ TFT on Cytop. These simulations are used in chapter 6 to extract the trap DOS.

and trapped ones. The free charge carriers contribute to the source drain current and the mobility of these can be calculated using standard FET equations (Eq. 2.3 and 2.4).

The simulation program takes a given trap DOS as an input parameter and then calculates the expected source-drain current for a range of applied gate voltages. All input parameters are defined by the device (geometry), setup (applied voltages) or directly measurable (mobility). Therefore, the only free parameter is the underlying trap DOS. The trap DOS is adjusted until the simulated curve matches the measured one (Fig. 3.8). The DOS is assumed to be constant for the transport levels and an exponential trap DOS reaches into the band gap. Gaussian distributed trap states can be added to model discrete defect/doping states. The subthreshold region is the most important one for determining the trap DOS, as the Fermi-level fastly shifts to the transport level and thus the source-drain current increases by orders of magnitude. This program has been compared to other DOS extraction methods. [59, 60] It has been found to yield highly reliable results and has been applied to various OFET configurations previously. [55, 59–62] At very low currents, the noise level is reached, given by hopping of residual charge carriers, which is not simulated in figure 3.8. At higher currents the simulated curve might overshoot, because injection problems are neglected.
Opto-electronic simulation of organic bulk-heterojunction solar cells: steady state and time dependent characterization

If you try and take a cat apart to see how it works, the first thing you have on your hands is a non-working cat.


There are several ways to try to understand a working solar cell. One is to separate the multitude of processes from each other and investigate each one in detail with an appropriate method. The approach taken here, is to simulate a complete solar cell with all the underlying processes. This comprehensive numerical model is then used to simulate various steady state and transient curves. The influence of the single processes is discussed in detail. The simulator and the findings have been published [63], whereas the transient measurements in the last section are not published.

In the first part, the optical incoupling into a multilayer stack is discussed using a transfer matrix model. From the photon absorption profile a charge transfer (CT) exciton profile is derived. We consider the Onsager-Braun mechanism to calculate the dissociation of the CT-excitons into free charge carriers. In the second
part we discuss how these free charge carriers are then modeled using a drift-diffusion model under which these charge carriers migrate towards the electrodes where they are extracted.

A general problem arising in computer simulations is the number of material and device parameters, which have to be determined by dedicated experiments and simulation-based parameter extraction. In this study we analyze measurements of the short-circuit current dependence on the active layer thickness and current-voltage curves in poly(3-hexylthiophene):[6,6]-phenyl-C_{61}-butyric acid methyl ester (P3HT:PCBM) based solar cells. We have identified a set of parameter values including dissociation parameters that describe the experimental data. The overall agreement of our model with experiment is good, however a discrepancy in the thickness dependence of the current-voltage curve questions the influence of the electric field in the dissociation process. In addition transient simulations are analyzed which show that a measurement of the turn-off photocurrent can be useful for estimating charge carrier mobilities.

In the end we compare the calculated transient photocurrent with measurements done on a P3HT:PCBM solar cell. We show, that the turn-off photocurrent is fully governed by the mobility of the charge carriers in the organic solar cell.

4.1 Introduction

After the huge progress organic light-emitting diodes have made in the last years, organic photovoltaic (OPV) devices attract more and more interest. State of the art OPV devices yield an energy conversion efficiency of around 10% to 12% for single junction cells [64] as well as tandem cells. [65] This efficiency has doubled in less than four years and is now larger than the efficiency of amorphous silicon solar cells and comparable to dye sensitized solar cells, but still less than crystalline silicon cells. [64]

OPV devices have several advantages like the possibility of low-cost production [66], room temperature processing and thin film structures. The latter two make it possible to use flexible substrates and thus the production of flexible solar cells. This leads to low-cost, flexible and transportable energy generators. Our research focuses on the influence of optical and electrical parameters on device performance.

The field of OPV’s can be separated into the planar-heterojunction devices where the donor and acceptor materials are deposited one after the other, mostly
by evaporation of small molecules and the bulk-heterojunction (BHJ) devices, where the two organic materials are diluted in the same solvent and spin coated as one layer. The advantage of the BHJ structure is that most of the generated excitons reach a nearby donor-acceptor interface where they dissociate into free charge carriers. This efficient exciton harvesting leads to higher power conversion efficiencies for BHJ devices.

Numerical models for organic BHJ devices provide insight into operating mechanisms and allow for device structure optimization. The simulation of OPV devices can be separated into two parts, firstly there is the incoupling of light into a multilayer structure and secondly the extraction of charges which needs an electrical model. The absorption of light within the multilayer structure is a crucial process and thus one of the main areas of numerical simulations. Harrison et al. [67] used analytical models and compared them to measured photocurrent action spectra. Later a transfer matrix formalism has been used by Petterson et al. [68] to calculate the absorbed optical energy within the multilayer structure. This formalism is widely used to optimize layer structures for single junction [69] as well as tandem cells. [70] Though optical models are very reliable they are only able to give an upper limit of the achievable photocurrent. Therefore electrical models have been developed to study charge generation and transport losses in planar heterojunction [71] as well as BHJ devices. [72–75] These models differ in their choice of ingredients, definition of the boundary conditions as well as in their methods to solve the drift-diffusion equations. Coupled opto-electronic models have been introduced by Kirchartz et al. [76], Lacic et al. [77] and Kotlarski et al. [78], where they connected a drift-diffusion solver with an optical thin-film simulator. All the electrical models mentioned are 1D-models and they treat every layer as an effective medium, i.e. a homogenous layer.

In this chapter we present a comprehensive numerical model which considers optical as well as electrical effects. This device model has originally been developed for the analysis of organic-light emitting diodes [79–81] and was commercialised afterwards. This software, SETFOS [82], has been extended for the simulation of organic BHJ solar cells.
Figure 4.1: Electromagnetic field penetration plot (top) is calculated using a transfer matrix formalism. This field penetration is then used to derive the photon absorption rate profile (bottom).
4.2. Description of the numerical device model

4.2.1 Optical modeling

Organic photovoltaic cells consist of a multilayer structure, with layer thicknesses on the order of the wavelength of the incident light, which is shorter than the coherence length of sunlight. Therefore an OPV is an optically coherent device. This gives rise to interference effects inside the device which can be exploited to increase the maximum photocurrent by carefully tuning the thicknesses of the individual layers [83] [68] [73]. An approach to find the optimal layer thicknesses from an optical point of view is to calculate the electromagnetic field inside the multilayer stack using a transfer matrix formalism. This approach has been used in the optical simulation of OLED’s [79] [81] and OPV’s [68] and is well established in the field of organic electronics. With this formalism the normalized optical electric field $E_{\text{norm}}$ is calculated throughout the multilayer stack (cf. Fig. 4.1). For plane waves, the optical field intensity within the stack is given by

$$I = \frac{1}{2} \varepsilon_0 c n |E|^2. \quad (4.1)$$

In the transfer matrix formalism we normalize the incident electric field such that the incoming electric field amplitude is 1. Therefore the electric field calcula-

Figure 4.2: Reflectance and fractional absorbance for each layer in the solar cell.
tion gives the field strength relative to the field strength in the surrounding medium $E_0$. This is used to calculate the absolute energy flux by looking at the ratio

$$\frac{I}{I_0} = \frac{\frac{1}{2} \varepsilon_0 c n |E|^2}{\frac{1}{2} \varepsilon_0 c n_0 |E_0|^2} \tag{4.2}$$

of the illumination intensity $I_0$ in the surrounding medium and device-internally $I$. In this study the AM 1.5 spectrum is used for $I_0$. The calculation of the device-internal intensity

$$I = n \frac{|E_{norm}|^2}{|E_0|} I_0 \tag{4.3}$$

is done wavelength and position dependent, from which the density of absorbed photons per second can be derived via

$$n_{photons} = \frac{\alpha}{\hbar c} \lambda \tag{4.4}$$

where $\alpha$ stands for absorption coefficient which is given by $\alpha = \frac{4\pi k}{\lambda}$ and $k$ stands for the complex part of the refractive index (i.e. the extinction coefficient). After an integration over the illumination spectrum one ends up with a photon absorption rate profile (cf. Fig. 4.1 (bottom)). The integration is done in the absorbing spectral range from 380 to 780 nm. The absorbance of the active layer, which is the ratio of absorbed to the illumination light intensity, drops to zero above 650 nm as is shown in Fig. 4.2. It is obvious that the thickness and refractive index is required for each layer for accurate simulation results. For this study we took these data from Monestier et al. [73]

### 4.2.2 Electrical modeling

To simulate an OPV device electrically, several processes have to be taken into account. First charge-transfer-exciton generation and dissociation, then charge drift and diffusion, and at last the charge extraction at the electrodes need to be considered. These processes will be discussed in this section.

#### Charge-transfer-exciton dissociation

The absorption of a photon generates an exciton which then diffuses to a donor-acceptor interface. At this interface the exciton dissociates and generates a charge-transfer-exciton (CT-excitons). In this model we assume that a photon directly generates a CT-exciton. Therefore only a continuity equation for CT-excitons is needed (cf. Fig. 4.3):
4.2. Description of the numerical device model

\[
\frac{dS(x)}{dt} = r_{\text{eff}} r(x) p(x) n(x) - k_f S(x) - k_d S(x) + g_{\text{eff}} G_{\text{opt}}(x). \tag{4.5}
\]

CT-exciton density \( S \) is fed by two processes: Firstly an absorbed photon directly generates a CT-exciton. \( G_{\text{opt}}(x) \) stands for the photon absorption profile shown in figure 4.1 (bottom), whereas \( g_{\text{eff}} \) is a photon-to-CT-exciton conversion efficiency, assumed to be independent of the wavelength. We set \( g_{\text{eff}} \) to zero outside of the active layer, which is P3HT:PCBM in the device under consideration here. Secondly recombination of free charge carrier pairs generates a CT-exciton. This recombination process is treated by the Langevin theory which will be discussed in the next section when the drift-diffusion model is explained.

There are also two CT-exciton state depletion mechanisms \( k_f \) and \( k_d \) which stand for the decay of a CT-state and the dissociation respectively as described by the Onsager-Braun theory. This continuity equation for CT-excitons is coupled with the drift-diffusion model which will be discussed later.

CT-exciton dissociation has been studied by L. Onsager. \cite{84} \cite{85} The initial pair separation distance is overestimated when measurements are compared with the Onsager theory. Therefore C. L. Braun \cite{86} extended the theory by Onsager. In this model a finite decay rate of the CT-exciton has been considered. The dissociation probability \( P \) is then given by

\[
P = \frac{k_d S(x)}{k_f S(x) + k_d S(x) + g_{\text{eff}} G_{\text{opt}}(x)}. \tag{4.6}
\]
4. simulation of an organic solar cell

\[ P(T, E, k_f, a) = \frac{k_d}{k_d + k_f} \]

\[ k_d(T, E, a) = \frac{3\mu e}{4\pi \varepsilon a^3} e\left(-\frac{\Delta\varepsilon(a)}{k_B T}\right) \frac{J_1\left(2\sqrt{-2b(T, E)}\right)}{\sqrt{-2b(T, E)}} \]

\[ \Delta\varepsilon(a) = \frac{e^2}{4\pi \varepsilon \varepsilon_0 a} \]

\[ b(T, E) = \frac{e^3 E}{8\pi \varepsilon \varepsilon_0 k_B^2 T^2}. \]

In equation (4.6) the mobility is the sum of the electron and hole mobility \( \mu = \mu_e + \mu_h \), \( J_1(x) \) is the Bessel function of the first kind of order 1, \( a \) is the initial pair separation distance of the CT-exciton, the pair binding energy \( \Delta\varepsilon(a) \) is calculated under the assumption that CT-excitons have the same dependence of the binding energy on the separation distance as ion pairs. \( E \) stands for the electrical field which is calculated position dependent using the drift-diffusion model explained in the next section.

To find an analytical model, the Onsager-Braun theory makes some simplifications. It does not consider disorder in energy levels as well as in the spatial distribution of the hopping sites which is present in an amorphous organic semiconductor. Koster et al. [72] and Pan et al. [87] introduced spatial disorder by integrating the dissociation probability over distribution of pair separations \( a \). A further simplification of the Onsager-Braun model is the assumption that the dissociation takes place in a homogeneous material, neglecting the presence of donors and acceptors. Veldman et al. [88] proposed that the mobility used in the Onsager-Braun model is higher than the effective mobility measured in the bulk. They attributed this to local crystallization of the PCBM molecules. This extension allows to model CT-exciton lifetimes in the order of \( 10^{-8} \) s still having a dissociation efficiency over 90%. This extension is not considered in our study. To analyze the effects of disorder and donor acceptor interfaces in more detail, Monte-Carlo simulations are used which are not the scope of this study [89–96]. Albeit all the simplifications, the Onsager-Braun theory is a widely used model to describe the dissociation of CT-excitons in organic semiconductors.

**Drift-diffusion modeling**

In the semiconductor, the following drift-diffusion equations apply:
4.2. Description of the numerical device model

\[ \frac{dE(x)}{dx} = \frac{e}{\varepsilon_r \varepsilon_0} [p(x) - n(x)] \]  \hspace{1cm} (4.7)

\[ J_e(x) = e \mu_e n(x) E(x) + D(\mu, T) \frac{dn(x)}{dx} \]  \hspace{1cm} (4.8)

\[ \frac{dn(x)}{dt} = \frac{1}{e} \frac{dJ_e(x)}{dx} - r_{\text{eff}} r(x) p(x) n(x) + k_d S(x). \]  \hspace{1cm} (4.9)

The electrical field \( E(x) \) in equation (4.7) is calculated dependent on the position \( x \). Where \( e \) stands for the elementary charge, \( n(x) \), \( p(x) \) for the electron/hole density, \( \varepsilon_0 \) for the permittivity of free space and \( \varepsilon_r \) for the relative permittivity.

Equation (4.8) is the current equation for electrons. The mobility \( \mu_e \) is assumed to be independent of the electrical field, temperature or density, which is a simplified assumption used in this chapter. The diffusion coefficient is given by the Einstein relation: \( D = \mu_e k_B T / q \).

Equation (4.9) is the continuity equation for electrons. This equation takes the creation, migration and recombination of the charge carriers into account. \( r(x) \) stands for the Langevin recombination \( r(x) = (\mu_o + \mu_p) \frac{q}{\varepsilon_r \varepsilon_0} \). The requirement for this model to be applicable is that the mean free path \( \lambda < r_c \), where \( r_c \) stands for the Coulombic capture radius \( r_c = \frac{e^2}{4\pi\varepsilon_r \varepsilon_0 k T} \) which for an average organic solid \( (\varepsilon_0 \approx 3 - 4) \) gives a Coulombic radius of \( r_c \approx 14 - 19 \)nm. This requirement is satisfied since the mean free path in this low-mobility disordered organic semiconductor is smaller than the Coulombic capture radius [97] and thus this model is applicable. The Langevin recombination efficiency prefactor, \( r_{\text{eff}} \), is a factor between 0 and 1 which has been introduced by Juška et al. [98] to take the reduced Langevin recombination into account. It will be discussed later in this chapter.

For equations (4.8) and (4.9) exist analogous equations for holes instead of electrons. The above set of equations is spatially discretised in SETFOS [82] using the Scharfetter Gummel discretisation [99] and solved iteratively in time using the Gummel scheme. [100]

**Built-in voltage**

There is a debate on the nature of the open-circuit voltage \( V_{\text{oc}} \) in OPVs and currently there are several alternative explanations. There is evidence, that the open-circuit voltage depends on the highest occupied molecular orbit (HOMO) and lowest unoccupied molecular orbit (LUMO) difference of the donor and acceptor molecules at the interface. [101] [102] Recently, this mechanism has been
looked at in more detail and a linear dependence of the $V_{oc}$ on the energy of the charge-transfer absorption has been found. [103] The open-circuit voltage also depends on the work-function of the electrodes. [104] This influence seems to be more pronounced in bulk heterojunction than in planar heterojunction device setups. [105] Furthermore the open-circuit voltage was observed to be intensity and temperature dependent. [106] This complex behavior is challenging for the simulation of these devices, because there is not a single theory which is capable of describing all of those dependencies. The approach used here assumes that every device has a built-in voltage $V_{bi}$ which is derived from the difference in the work functions of the two electrodes. This is then used to calculate the effectively applied voltage $V_{eff}$. The electric field distribution inside the device is obtained through integration of the Poisson equation (cf. Eq. (4.7)) using the effective bias $V_{eff}$ as a constraint to determine the integration constant,

$$V_{eff} = V_{appl} - V_{bi} = \int_0^L E \, dx,$$

(4.10)

where $V_{appl}$ is the experimentally applied voltage. Therefore, the electric field due to space charges is superimposed on the applied field.

### Charge extraction

When charges reach the organic-metallic interface they are extracted from the device. The current at such an interface has been described by Scott et al. [39] as a balance of injection and surface recombination. This model considers the barrier reduction at an organic-metal interface due to the electric field and the image charge potential and calculates the net injection current.

### Validation of the simulator

The model presented has been validated by varying the input parameters and analyzing their influence on the output. We have observed, that the open-circuit voltage increases slightly with illumination intensity. It also depends on the mobility of the charge carriers. Furthermore it is not equal to the built-in voltage which is assumed to be the difference between the work-functions of the electrodes in this model. The fill factor is influenced by recombination losses and thus the mobility of the charge carriers and the Langevin recombination efficiency $r_{eff}$. The short-circuit current depends linearly on the illumination intensity until recombi-
4.3 Estimation of the dissociation rate

Table 4.1: Input parameters for the thickness dependent simulation of figure 4.4.

<table>
<thead>
<tr>
<th>Description</th>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
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</thead>
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<tr>
<td>Workfunction Al</td>
<td></td>
<td>4.31</td>
<td>eV</td>
</tr>
<tr>
<td>HOMO P3HT [108]</td>
<td></td>
<td>5.3</td>
<td>eV</td>
</tr>
<tr>
<td>LUMO PCBM [108]</td>
<td></td>
<td>3.7</td>
<td>eV</td>
</tr>
<tr>
<td>Electron mobility [107]</td>
<td>$\mu_n$</td>
<td>$5 \times 10^{-7}$</td>
<td>m$^2$/Vs</td>
</tr>
<tr>
<td>Hole mobility [107]</td>
<td>$\mu_p$</td>
<td>$1 \times 10^{-8}$</td>
<td>m$^2$/Vs</td>
</tr>
</tbody>
</table>

nation losses take over and the increase becomes sub-linear. The results of this validation correspond to experimental observations.

4.3 Estimation of the dissociation rate

After describing the coupled opto-electronic numerical device model in the last section, it will be applied in this section to simulate an OPV device and extract unknown CT-exciton dissociation input parameters. The layer structure is shown in figure 4.1. The indium tin oxide (ITO) layer is 130 nm thick, it is followed by a 50 nm thick Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) layer. The active layer is modeled as a 1:1 weight ratio P3HT:PCBM blend which is covered by 100 nm Aluminum. The parameters for the electrical simulations which are taken from literature are shown in table 4.1. The two mobilities are taken from Mihailetchi et al. [107], who have measured the constant mobilities of electrons and holes in a P3HT:PCBM bulk heterojunction solar cell depending on the annealing temperature. The measurements used here are for samples which have been annealed at 140$^\circ$C for 5 minutes and the mobilities have been chosen accordingly.

The unknown parameters are the decay rate $k_f$, the pair separation distance $a$ and the photon-to-CT-exciton conversion efficiency $g_{eff}$ which have been introduced in equation (4.5) and (4.6) respectively. These parameters are determined by applying the device model to measurements of the short-circuit current dependent on the thickness of the active layer. Some reports in literature have used a simplified OPV model without CT-exciton dynamics (cf. Juška et al. [98]) and have found reduced recombination rates. Similarly our first analysis step assumes that
absorbed photons directly generate free electron hole pairs and that recombining charges are lost and not fed into the continuity equation for CT-excitons (4.5). This reduced model thus consists of equations (4.7), (4.8) and the modified version of equation (4.9) which reads as follows

\[
\frac{dn(x)}{dt} = \frac{1}{e} \frac{dJ_e(x)}{dx} - r_{\text{eff}} r(x)p(x)n(x) + g_{\text{eff}} G_{\text{opt}}(x),
\]  

(4.11)

where \( g_{\text{eff}} \) stands for the photon-to-electron conversion efficiency.

Figure 4.4 shows a purely optical simulation (top curve) to calculate the maximum achievable photocurrent depending on the device thickness. The other six curves are for coupled opto-electronic simulations where the Langevin recombination efficiency \( r_{\text{eff}} \) has been varied between 1 and 0.01. These simulation are compared with measurements by Gilot et al. [83] For devices with an active layer thickness below 50 nm losses due to charge transport can be neglected. Therefore the photon-to-CT-exciton conversion efficiency \( g_{\text{eff}} \) is fitted to this part of the curve. A value of \( g_{\text{eff}}=0.66 \) has been determined which is consistent with the analysis by Gilot et al. [83] on the same thickness dependent data. For thicker devices electrical losses play an important role. Due to measurement uncertainties it is hard to give a final value, but figure 4.4 suggests that the Langevin recombination efficiency \( r_{\text{eff}} \) in the simplified model is 10% or lower. In the full model there is an equilibrium between CT-exciton formation and dissociation. We translate the observation of the reduced \( r_{\text{eff}} \) in the simple model to the dissociation probability in the full model, since the rate \( r \times r_{\text{eff}} \) (simple model) corresponds to \( r \times (1 - P) \) (full model) (cf. with equations (4.6) (4.9)). Thus \( P \) must be 90% or higher.

With this information it is possible to determine the unknown CT-exciton parameters by analyzing the Onsager-Braun model of CT-exciton dissociation. The initial pair separation distance \( a \) can be determined under the assumption that \( k_f \) is set to \( 1 \times 10^5 \) s\(^{-1}\). The current density in figure 4.4 has been measured and calculated under short-circuit current conditions. From the open-circuit voltage which is about 0.6 V and the device thickness the internal electric field is estimated to be in the range of \( 1 \times 10^6 \) to \( 2 \times 10^7 \) V/m for thick and thin devices respectively. Figure 4.5 shows the desired dissociation efficiency (over 90%) and the internal electrical field range together with different initial pair separation distances which have been varied between 1.5 nm and 1 nm. From this plot alone the only condition for \( a \) is that it has to be larger than 1.2 nm. The best fit value for the pair separation distance \( a \) has been chosen to be 1.285 nm, by comparing experimental current-
4.4 Sensitivity analysis

In the previous section a set of parameters has been found (cf. table 4.1 and 4.2) such that the simulation fits the measurements. In this section the sensitivity
4. simulation of an organic solar cell

Figure 4.5: Dissociation probability according to the Onsager-Braun theory depending on the electrical field for several initial pair separation distances $a$. The decay rate has been fixed at $k_f = 1 \times 10^5$ s$^{-1}$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recombination eff.</td>
<td>$r_{eff}$</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Decay rate</td>
<td>$k_f$</td>
<td>$1 \times 10^5$</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>Pair separation</td>
<td>$a$</td>
<td>1.285</td>
<td>nm</td>
</tr>
<tr>
<td>Optical generation eff.</td>
<td>$g_{eff}$</td>
<td>0.66</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.2: Derived simulation parameters from figures 4.4, 4.5 and 4.6

of the model on the input parameters is investigated. This sensitivity analysis gives insight into simulation as well as experiment: First we analyze and study which parameters influence the outcome of the simulation, secondly the sensitivity analysis also helps to identify experimental setups where the influence of different parameters can be separated.

The sensitivity analysis has been conducted as follows: Firstly, a reference has been simulated with the parameters indicated in table 4.1 and 4.2. Secondly, five input parameters have been chosen, Langevin recombination efficiency $r_{eff}$,
4.4. Sensitivity analysis

Figure 4.6: Comparison of a simulated and experimentally measured current-voltage curve for an active layer thickness of 70 nm. The parameters used for this simulation are summed up in table 1 and 2.

The electron/hole mobility \( \mu_n/\mu_p \), the pair separation distance \( a \) and the decay rate \( k_f \). The first three parameters \( (r_{\text{eff}}, \mu_n, \mu_p) \) have been varied ± 10% and because the influence of the CT-exciton parameters \( (a, k_f) \) is larger, these two parameters have been varied by 3% only. Therefore in this step ten simulations have been done (five parameters with variation in two directions each). As a last step, the reference curve has then been subtracted from the varied curves. This difference between the reference curve and the varied one has then been plotted for each parameter. This procedure reveals possible correlations among the parameters.
4. simulation of an organic solar cell

4.4.1 Thickness dependent sensitivity

First of all the thickness dependence of the short-circuit current has been analyzed, the results are shown in figure 4.7. The measurements are also shown, and agree with the simulation for active layer thicknesses up to 150 nm. The two measurements around 230 nm which are shown in figure 4.4 are lying outside the axis scale in figure 4.7 and can not be modeled with the parameter set used in this study. This suggests that the different spin-speed and solvent concentrations that have been used to achieve the higher active layer thicknesses [83] also changed electrical properties of the active layer and therefore can not be modeled with a single set of parameters.

As is shown in figure 4.7, the influence of the electric input parameters are only relevant for an active layer thickness larger than about 50 nm, which has already been seen for the Langevin recombination efficiency in figure 4.4. The pair separation $a$ has the highest influence on the short-circuit current although...
4.4. Sensitivity analysis

It has been varied by only 3%. The influence of all the parameters grows with increasing active layer thickness.

Further analysis, not shown here, reveals a strong linear dependence between the three parameters pair separation distance \(a\), decay rate \(k_f\) and electron mobility \(\mu_n\). These three parameters are all involved in the dissociation of CT-excitons (cf. Eq. (4.6)). The thickness variation influences the electric field inside the device. Therefore the electric field dependence of the CT-exciton dissociation is probed. The three parameters which show the same thickness dependence are all pre-factors for the field dependence as shown in Eq. (4.6). In these equations the hole mobility is added to the electron mobility to determine the dissociation rate \(k_d\), but in the device investigated here the electron mobility is higher by a factor of 50 than the hole mobility and therefore dominates the dissociation. The hole mobility \(\mu_p\) and the Langevin recombination efficiency \(r_{eff}\) both have a unique thickness dependence, which is slightly different from each other.

4.4.2 Current-voltage curve sensitivity

Figure 4.8 shows the sensitivity analysis for a current-voltage curve with an active layer thickness of 70 nm. The current-voltage curve is the same one as in figure 4.6. The sensitivity analysis clearly demonstrates that all parameters have the highest influence on the current-voltage curve in the fourth quadrant and close to the open-circuit voltage \(V_{oc}\). Again the pair separation distance \(a\) has the strongest influence on the output. The hole mobility clearly has a different influence on the output than all the other parameters. Especially for applied voltages which are higher than \(V_{oc}\) the hole mobility has the highest influence on the current. This suggests that the hole mobility is the limiting factor for the current (photocurrent plus injected current) drawn from the device at higher voltages.

Further analysis (not shown) reveals that for the current-voltage curve under consideration there are only two clearly linearly independent sets of parameters. The first set comprises the pair separation \(a\), the decay rate \(k_f\), the electron mobility \(\mu_n\) and the Langevin recombination efficiency \(r_{eff}\), the second one is the hole mobility \(\mu_p\). Although the Langevin recombination has a slightly different voltage behavior than the other three parameters in this group it is very similar. This is interesting because in the sensitivity analysis of the thickness dependent short-circuit current shown in figure 4.7 the influence of the Langevin recombination efficiency was more similar to the one of the hole mobility.
For all the measured short-circuit current points in figure 4.4 a current-voltage curve was measured as well. An analysis of the influence of the device thickness on the current-voltage curve is performed for three representative thicknesses which is shown in figure 4.9. The short-circuit current as well as the open-circuit voltage depend on the amount of the absorbed photons. Therefore to compare the current-voltage curves for different thicknesses, the short-circuit current as well as the open-circuit voltage need to be normalized to exclude optical effects. The comparison in figure 4.9 shows, that the shape of the experimental current-voltage curve does not change for different thicknesses of the active layers. In contrast the simulated current-voltage curves show a clear dependence of the shape on the device thickness. This indicates that in the fourth quadrant the influence of the electric field on dissociation efficiency and thus recombination losses is overestimated in the device model presented in this chapter. A possible explanation for this discrepancy might be the nature of the Onsager-Braun dissociation mechanism, which does not consider energetic disorder. Though much used, the
4.4. Sensitivity analysis

Onsager-Braun model is not necessarily the best physical description of charge separation and more refined models have been developed. For instance Wojcik et al. [109] have derived an extended model based on the Onsager theory which leads to a weaker field dependence.

4.4.3 Transient current sensitivity

The sensitivity analysis in thickness dependence and current-voltage curves have shown, that several input parameters have a similar influence on the output and thus those parameters can not be determined from these measurements. In this part transient simulations are discussed and their sensitivity on parameters is analyzed.

Figure 4.10 shows the simulated transient of the short-circuit current when the light is turned on at t=0, for a thickness of the active layer of 70 nm. Again the parameter set shown in table 4.1 and 4.2 has been used. The sensitivity clearly shows that in the turn-on dynamics the Langevin recombination efficiency \( r_{eff} \) and
the decay rate $k_f$ do not play an important role, therefore the turn-on dynamics is solely defined by the pair separation distance $a$ and the two mobilities. The CT-exciton decay rate and thus the recombination of free charge carriers play no role. The electron mobility determines the first part of the turn-on and the sensitivity reaches its maximum at $0.15 \, \mu s$, whereas the hole mobility has its maximum at $0.35 \, \mu s$. Further analysis (not shown) reveals that the electron mobility $\mu_n$ has exactly the same influence on the turn-on behavior as does the pair separation $a$. This indicates that the turn-on behavior is limited by the time it takes to dissociate the CT-exciton pair. When the CT-exciton parameters are chosen such that the average lifetime of the CT-exciton is much smaller than the time it takes to extract the charge carriers, the turn-on behavior is solely defined by the two mobilities.

Figure 4.11 shows the transient of the short-circuit current when the light is turned off at $t=0$. The shape of the transient turn-off curve shown in figure 4.11 is clearly different from the turn-on curve shown in figure 4.10. The first one has
4.4. Sensitivity analysis

Figure 4.11: Sensitivity of the short-circuit current during turn-off.

A clearly visible kink at $t = 0.015 \mu s$ whereas the latter curve is more smooth without any visible kink. The sensitivity analysis of the turn-off behavior shows that the curve is solely dependent on the two mobilities. This means that CT-exciton and recombination parameters play no role and thus the recombination and subsequent CT-exciton dissociation play no role. The initial drop is given by the mobility of the electrons $\mu_n$ whose influence peaks at $t = 0.01 \mu s$ whereas the second, much slower drop is given by the hole mobility $\mu_p$ whose influence peaks at $t = 0.45 \mu s$. This difference is in the same range as the difference in the mobilities of the two charge carriers which is $\frac{\mu_n}{\mu_p} = 50$.

This last sensitivity analysis shows, that by measuring the short-circuit current during turn-off, the two mobility parameters can be estimated. This observation is similar to the findings by Pinner et al. [110] for electroluminescence transients in organic light-emitting diodes where the turn-off regime is governed by the built-in field as well. The time it takes to extract all charge carriers and thus the mobilities can be calculated under the assumption that the active layer is homogeneously
Figure 4.12: Semi-logarithmic plot of the turn-off behavior shown in figure 4.11. This plot can be used to extract the mobilities of electrons and holes.

Filled with charge carriers and that the internal electric field is given by the difference on the applied and the built-in voltage divided by the active layer thickness $E = (V - V_{bi}) / L$. We thus obtain

$$\mu = \frac{L^2}{(V_{appl} - V_{bi})\tau}. \quad (4.12)$$

The parameter $\tau$ is the time it takes for the current to drop down to 5% of the initial value. With this approach the electron as well as the hole mobility can be extracted separately.

Figure 4.12 shows the turn-off behavior as a semi-logarithmic plot. The first steep drop of the current is associated with the electrons and thus a line is fitted to it. Point A’ is defined as the point along the fitted curve were the initial current at point A is reduced to 5%. The same is done for the second drop which is associated with the holes. Again B’ is defined as the point where the current
dropped down to 5% with B as the reference point. This gives for $\tau_n=0.037 \mu$s and $\tau_p=0.56 \mu$s. With $V_{appl}-V_{bi}=0.69$ V (cf. table 4.1) and an active layer thickness 70 nm the following mobilities are extracted: $\mu_n = 1.9 \times 10^{-7}$ m$^2$/Vs and $\mu_p = 1.3 \times 10^{-8}$ m$^2$/Vs. The extracted values are in the same order of magnitude as the input values given in table 4.1. The mobility of the fast charge carriers is underestimated and the mobility of the slow charge carriers is slightly overestimated. This discrepancies stem from the assumption of a homogeneous electric field inside the device and thus the independent treatment of electrons and holes which is a simplification.

From these simulations we have learned how to extract specific parameters from a certain experiment. First we used the thickness dependence of the short circuit current for thin active layers ($< 50$ nm) to obtain the optical generation efficiency $g_{eff}$. As a next step, the mobilities can be extracted from transient turn-off measurement. From this onward, the rest of the unknown parameters can be extract from steady-state IV curves. This approach has been improved recently and is used to be able to extract OPV parameters directly. [111, 112]

4.5 Measurement of current transients after turn-off

In the last section we discussed the possibility to extract the mobility of the electrons and holes by measuring the transient current after turning-off the light. Depending on the mobility and thickness of the solar cell, these measurements have to be conducted very fast and with an accuracy over several orders of magnitude, which is challenging from the experimental point of view. Additionally the light source needs to be turned off faster than extracting the charges from the solar cell and it needs to homogeneously illuminate the solar cell for long enough to let the charge carriers come into an equilibrium.

There are several approaches to tackle these problems. Hwang and McNeill et al. [113, 114] used an InGaN LED in connection with a pulse generator (100 $\mu$s pulse length) and a digital oscilloscope. In their study they focused on the trapping detrapping of charges and compared their results to a simulator. Street et al. [115,116], used an unnamed light source chopped with 230 Hz and a lock in amplifier or an oscilloscope. In their study they focused on a direct measurement of the trap states in the band gap of an organic solar cell. Further discussion of their results and a comparison of trap states found in OFETs is given in chapter 7 on page 91.
Figure 4.13: Semi-logarithmic plot of the raw data of the turn-off behavior of a fast photodiode (Osram SFH 203 P). The transient photocurrent is measured over 5 orders of magnitude. Every sensitivity setting is reliable over a certain range only. The current has been measured over 25 µs in 10 ns steps. The influence of the different settings of the sensitivity is shown using different colors. As a guide for the eye, averaged transient photocurrent is shown as the dashed line.

For the measurements shown here, we used Luxeon Rebel LEDs which are very bright and have a fast switching time. The LED has been driven by an Agilent B1530A using the WGFMU unit which simultaneously measured transient photocurrent. This allowed us to measure changes in the current as fast as 10 ns and even as low as $10^{-8}$ A. Figure 4.13 shows a measurement done using a photodiode to calibrate the setup.

The organic P3HT:PCBM solar cell has been provided by the Laboratory for Functional Polymers at the EMPA, Switzerland. The organic bulk heterojunction solar cell has an active layer thickness of 80 nm and uses a 65 nm thick PEDOT:PSS injection layer on top of a 150 nm thick ITO (Indium Tin Oxide) electrode on glass. Aluminum is used as the counter electrode. The open circuit voltage of this cell
4.5. Measurement of current transients after turn-off

Figure 4.14: Semi-logarithmic plot of the turn-off behavior of the P3HT:PCBM solar cell under different illumination intensities. The photocurrent range was from \( 3.3 \times 10^{-5} \) A (@ 2.6 V) to \( 1.8 \times 10^{-4} \) A (@ 3.8 V). When normalized, the time evolution of the transient photocurrent is independent on the illumination intensity.

was 0.6 V.

Figure 4.14 shows a transient photocurrent measurement on the P3HT:PCBM bulk heterjunction solar cell with different illumination intensities. First of all, the measured curve looks quite different from the simulated curve (Fig. 4.12). The difference comes from the traps which are not simulated and which lead to a dispersive transport. When these curves are normalized to the initial (i.e. under illumination) photocurrent it is independent of the illumination. This is rather surprising, as one would expect a higher effective mobility at higher illumination intensities, as the more charge carriers are in the solar cell the closer is the fermi level to the respective transport level. This leads to more free charge carriers and a higher ratio of free charge carriers vs. total charge carriers. Maybe this is not observed, because the shift of the fermi level is only marginal under the different illumination intensities and thus the influence on the mobility is negligible.

From these measurements a charge carrier mobility can be calculated using equation 4.12. For the fast charge carriers (presumably electrons) a mobility of \( \mu_{fast} = 8 \times 10^{-6} \frac{cm^2}{Vs} \) and for the slow charge carriers (presumably holes) a mobility of \( \mu_{slow} = 7 \times 10^{-7} \frac{cm^2}{Vs} \) has been calculated. These values are much lower than the values measured by Mihailetchi et al. [107] where they found mobilities...
Figure 4.15: Transient photocurrent (a) depends linearly on the applied voltage. After rescaling it for the different internal electric field (b). Therefore the turn-off behavior depends on the internal electric field only and can thus be described with the mobility $\mu$ of the charge carriers. The curve for $V_{appl} = 0.5$ V decreases faster, because the device characteristics changes from a solar cell to a diode, therefore charge carriers get injected and thus this curve cannot be compared to the other ones.

from $10^{-4} - 10^{-2} \frac{cm^2}{Vs}$ for electrons and $10^{-8} - 10^{-4} \frac{cm^2}{Vs}$. But these low values are consistent with the very slow turn-off behavior of the measured solar cell.

If the observed turn-off behavior stems from the charge carrier mobility, then
the transient photocurrent should directly scale with the internal electric field in the active layer. Therefore an additional measurement has been done, where the applied bias has been varied from +0.5 V to -2 V (Fig. 4.15). The transient photocurrent depends on the internal electric field only ($E_{\text{int}} = \frac{V_{\text{OC}} - V_{\text{appl}}}{d_{\text{P3HT:PCBM}}}$). From this we can conclude it is feasible to calculate the charge carrier mobility from the transient turn-off behavior of an organic solar cell.

### 4.6 Conclusion

From the measured thickness-dependent short-circuit current for thin active layers and the optical model we estimated a photon to CT-exciton conversion efficiency $g_{\text{eff}}$ of 66%. Using this dataset the coupled opto-electronic simulation suggests a lower limit for the CT-exciton dissociation efficiency of 90%. Adding the measured current-voltage curve to the numerical analysis and assuming that $k_f$ is equal to $1 \times 10^5$ s$^{-1}$ we find dissociation parameters that are consistent with the estimated 90% dissociation efficiency. From a comparison of several current-voltage curves at different thicknesses there is evidence that the influence of the electric field on the CT-exciton dissociation process is overestimated using the Onsager-Braun model. Further investigations have to be carried out to clarify this issue.

The sensitivity analysis conducted demonstrates that the influence of the two exciton parameters and the electron mobility are correlated in the current-voltage curve and thickness scaling of the photocurrent. A sensitivity analysis of transient processes indicates that the input parameters can be separated. During turn-on, the CT-exciton decay rate $k_f$ and thus the charge carrier recombination play no role. Even more insight can be gained by looking at the turn-off behavior. In this regime the transient current density is solely defined by the mobilities of the charge carriers. This suggests that the charge carrier mobilities can be extracted. The influence of charge traps was not considered in this study.

Measurements of the turn-off behavior show, that the transient photocurrent measurements are a feasible way to characterize the charge carrier mobility in an organic solar cell.

From this discussion it is clear that simple steady-state measurements (e.g. IV characteristics) are not sufficient to disentangle the various mechanisms which govern power generation in organic solar cells. But if these steady-state measurements are combined with transient measurements we have developed a powerful tool to understand organic solar cells.
Gate-bias stress in pentacene field-effect-transistors: charge trapping in the dielectric or semiconductor

The most successful people are those who are good at Plan B.

James Yorke

This chapter is concerned with the gate-bias stress effect which is due to slow charge trapping. During a standard FET transfer curve measurement, slow trapping and detrapping of charge carriers have not reached equilibrium yet, therefore the transfer curve slowly shifts into the direction of the applied gate voltage. The findings presented here have been published. [62]

Gate-bias stress instability in organic field-effect transistors (OFETs) is a major conceptual and device issue. This effect manifests itself by an undesirable shift of the transfer characteristics and is associated with long term charge trapping. We study the role of the dielectric and the semiconductor separately by producing OFETs with the same semiconductor (pentacene) combined with different dielectrics (SiO$_2$ and Cytop). We show, it is possible to fabricate devices which are immune to gate-bias stress. For other material combinations, charge trapping occurs in the semiconductor alone, or in the dielectric.
5.1 Introduction

Charge trapping in organic field-effect transistors (OFETs) happens on various time scales. Trapping due to gate-bias stress is a relatively slow process which takes place on the timescale of fractions of seconds up to several days, posing a challenge to the experiment as well as the conceptual understanding. Previous studies produced OFETs with a gate-bias stress stability comparable to that of a-Si thin-film-transistors (TFT). [117]

Several mechanisms have been proposed to explain the threshold-voltage shift under gate-bias stress: (i) trapping of charges in the bulk of the semiconductor [118], (ii) trapping in disordered areas of the semiconductor [119], (iii) trapping in regions in-between crystalline grains of the semiconductor [120], (iv) trapping in states at the semiconductor/dielectric interface [121] and (v) formation of bipolarons in the semiconductor [122, 123] as summarized by Sharma et al. [124]

From temperature dependent measurements gate-bias stress effects were found to be thermally activated with a comparable activation energy of $E_\tau \approx 0.6$ eV over a wide range of organic materials. [125] This has been taken as an indication that the underlying process is the same for all tested organic materials. Recently, charges have been shown to be trapped in the SiO$_2$ if it is used as gate dielectric. [126] Although the mechanism behind this trapping is still unclear, Sharma et al. [124,127] explain it by a proton migration mechanism involving water, whereas Lee et al. [128] assume direct drift/diffusion of holes into the dielectric.

In this chapter we present a comparative study of OFETs with either SiO$_2$ or Cytop (a highly hydrophobic fluoropolymer) as dielectric and with pentacene thin-films or single crystals as semiconductor. The focus is on a quantitative measurement of the threshold voltage shift $\Delta V_{th}$ over an extended time range ($10^{-1}$ to $10^3$ s) in response to an applied gate voltage. By combining the semiconductor either in thin-film or single crystal form with the two different gate dielectrics, charge trapping can either be completely suppressed in the OFET, or it occurs (a) in the semiconductor or (b) in both the semiconductor and the dielectric.

5.2 Experiment

Usually the threshold voltage shift $\Delta V_{th}(t)$ is analyzed by measuring transfer curves at various times. With a gate bias applied in between. This straightforward measurement has some drawbacks, however: Firstly, it is slow, therefore
5.2. Experiment

Figure 5.1: The influence of the gate-bias stress on the threshold Voltage $V_{th}$ has been measured in two ways: (i) the decrease of $I_d(t)$ over time has been measured, (ii) $V_{th}$ has been calculated from the shift of the transfer curve over time. These two methods agree with each other in determining the threshold voltage shift $\Delta V_{th}$.

information about the first few, or even fraction of seconds is not accessible. Secondly, some devices, especially thin-film-transistors (TFTs) do not show a linear regime and thus deriving a threshold voltage is not straightforward, even as the transfer curve clearly shifts.

Therefore we use a different method to measure the gate-bias stress influence over time. Instead of measuring a full transfer curve, the evolution of the drain current $I_d$ is measured at a certain applied gate voltage $V_g$ and source-drain voltage $V_{d}$.[129] The decrease of $I_d(t)$ over time can be translated into a shift of the transfer curve (and therefore $V_{th}$). These two methods give the same result (Fig. 5.1). A “relative threshold voltage shift” $\Delta V_{th}/\Delta V_{th,max}$ is used to compare different devices. $\Delta V_{th,max}$ is given by the difference between the initial threshold voltage $V_{th}(t=0)$ and the applied gate bias $V_{g,appl}$.

The 3 devices, differing in their semiconductor/dielectric combination, are shown in figure 5.2. Device A is a flip-crystal OFET [130, 131] with Cytop as the gate dielectric [55, 132] and the crystals grown according to Laudise et al. [53]. For Devices B and C, the pentacene thin-films and the gold contacts have been evaporated in $10^{-7}$ mbar vacuum, the devices are transferred to the attached probe station, where they can be exposed to various atmospheres in a controlled way: in this study 1 hour of air at 0.2 bar was chosen. The single crystal device has been exposed to ambient air during sample preparation.
Figure 5.2: Different mechanism at work resulting in gate-bias stress effects. This compilation of graphs on these two pages show the device setup (first row), the measured transfer curves (middle row) and the drain current $I_d(t)$ or relative threshold voltage shift over time (bottom row).

**Device A:** $(C_i=6.6 \times 10^{-5} \text{ F/m}^2)$ Transfer curves at various temperatures before and after stress do not show any gate-bias stress effects. The same for the measurement of the drain current. $I_d(t)$ is stable over the measured time with a slight increase which is attributed to self heating of the device.
Device B: \( (C_i=7.4 \times 10^{-5} \text{ F/m}^2) \) Shows a gate-bias stress effect in the transfer curves. The time and temperature dependent measurement of the relative threshold voltage shift (bottom row) shows this effect to strongly depend on temperature. After exposure to ambient air for 1 hour, the underlying process for long term charge trapping completely changes and becomes temperature independent.

Device C: \( (C_i=1.3 \times 10^{-4} \text{ F/m}^2) \) Also shows gate-bias stress visible in the transfer curve and the time/temperature dependent measurement. After exposure to air, the gate-bias stress effect stays strongly temperature dependent.
The devices have been analyzed as follows: A transfer-curve has been measured using a series of short $V_g$ pulses (50 ms) in order to minimize the stress. Afterwards the source-drain current, $I_{sd}(t)$, has been measured at a fixed $V_g$ and $V_d$. At the end, again a pulsed transfer-curve has been measured, with a $V_g$ offset between two pulses equal to the previously applied gate bias during stressing, to check that the shape of the transfer curve has been conserved. We repeat these series of measurements at several temperatures. In addition the transfer characteristics are the basis for calculating the trap density-of-states (trap DOS) in the band-gap using a FET simulator developed by Oberhoff et al. [58], applied to other OFET configurations previously. [59–61]

5.3 Results and discussion

For Device A, the single crystal OFET, most significantly no gate-bias stress effect is visible after stressing for 17 minutes at $V_g$=-20 V. Even when monitoring the source-drain current during applied gate voltage (Fig. 5.2 bottom) no reduction of the current is seen which would indicate stress effects. The hole mobility is $\approx 0.6 - 0.7 \text{ cm}^2/\text{Vs}$ at room temperature. Additionally the trap DOS is very low (Fig. 5.3). Therefore, the combination of Cytop together with a pentacene single-crystal results in an extremely good interface [55, 133], and long term charge trapping is effectively suppressed in the dielectric. Obviously, no long term charge trapping occurs in the pentacene crystal either.

Device B, consisting of polycrystalline thin-film evaporated onto Cytop dielectric, shows gate-bias stress effect. The extensive study of $\Delta V_{th}(t)$ reveals long term charge trapping to be strongly temperature dependent when the device is always kept in vacuum. From Device A we learned that charges are not trapped in the Cytop, and thus in Device B it occurs in the polycrystalline pentacene thin-film. Exposing Device B to air causes several changes. The mobility approximately doubles from 0.08 to 0.15 cm$^2$/Vs. Turn-on and threshold voltage $V_{th}(0)$ are significantly reduced. A more peculiar effect after exposure to air is seen when analyzing the temperature dependence of $\Delta V_{th}(t)$: the gate-bias stress effect becomes essentially independent of temperature.

Device C shows similar turn-on behavior as Device B except at a much lower initial threshold voltage. Again $\Delta V_{th}$ due to gate-bias stress is clearly visible in the transfer curves as well as in the threshold voltage shift over time. In passing, we note $\Delta V_{th}(t)$ to be stronger by a factor of 2 in Device C compared to Device B.
5.3. Results and discussion

Figure 5.3: Comparison of different trap density-of-states for the 3 devices as calculated from transfer curves taken at different temperatures. The two thin-film devices have essentially the same trap DOS, whereas in the single crystal OFET the trap DOS is one to two orders of magnitude lower.

Exposure to air increases the mobility (0.1 to 0.15 cm$^2$/Vs) and shifts the transfer curves to lower gate voltage. After exposure to air, the relative threshold voltage shift remains temperature dependent, in contrast to Device B, where the temperature dependence vanishes after exposure to air.

For further discussion, we would like to point out that the mobilities in the two thin-film devices are essentially identical and the trap DOS is similar too (Fig. 5.3). Thus from the conduction measurements before and after exposure to air these two films behave the same. Therefore it appears that whatever their morphological differences may be, they have no effect on the DC properties. Additionally, as Miyadera et al. [134] have found, the morphology of a pentacene film does not significantly change the long term trapping dynamics, thus the distinctly different behavior between Device B and C can not be attributed to a different film morphology.

The shift of the initial threshold voltage after exposure to air in Devices B and C is due to filling of charge traps, where oxygen acts as a hole donor. This shift is the same for Device B and C, in terms of induced charge ($5 \times 10^{18}$ e/cm$^3$), assuming a channel thickness of 1.5 nm. This is in quantitative agreement with the analysis...
by Kalb et al. [46], where trap states were created in the band gap due to oxygen exposure. Therefore, since long term charge trapping in devices with SiO$_2$ is known to be due to trapping in the SiO$_2$ [126], exposure to oxygen which alters the semiconductor only, does not change this mechanism significantly. But in devices where long term charge trapping occurs in the semiconductor, changes of the semiconductor due to oxygen exposure can be expected to alter this mechanism. This is exactly what has been observed as the difference between Device B and C.

5.4 Conclusion

In Summary we have shown that it is possible to fabricate OFETs using Cytop and pentacene single crystals which do not show gate-bias stress effects and have a very low trap density. The device with pentacene thin-films on Cytop does show gate-bias stress effects which is due to trapping of charges in the semiconductor. When this device is exposed to air, the gate-bias stress effect becomes temperature independent which is an additional hint of the different origin of the charge trapping mechanism when compared to the OFET with SiO$_2$ as gate dielectric. Therefore we conclude that long term charge trapping occurs in the semiconductor thin-film if charge trapping in the dielectric is suppressed.
From organic single crystals to solution processed thin-films: charge transport and trapping with varying degree of order

Science is composed of laws which were originally based on a small, carefully selected set of observations, often not very accurately measured originally; but the laws have later been found to apply over much wider ranges of observations and much more accurately than the original data justified.

Richard Hamming The Unreasonable Effectiveness of Mathematics', The American Mathematical Monthly (Feb 1980), 87 No.2.

In this chapter we discuss how different preparation techniques alter the transport characteristics of an organic semiconductor. We discuss this difference by quantifying the origin thereof, namely the trap density of states. The findings discussed here arose from a collaboration with Kristin Willa who built and characterized the solution processed thin-films. Therefore the solution processed thin-films are not discussed in great detail here, except where they are needed for comparison with the other preparation techniques. For a complete discussion of all the prepared samples we therefore suggest to read the original publication. [135]
We have fabricated single crystal, thermally evaporated and spin-coated thin-film transistors (TFTs) from the same organic semiconductor PDIF-CN$_2$ using various combinations of deposition methods and gate dielectrics to investigate how the charge transport properties vary with the degree of crystalline order. Never before has a semiconductor been studied in such a wide variety of processing methods, allowing cross-comparison of the microscopic factors influencing the charge transport, and in particular the trap density of states.

Excellent transistor performance was achieved for PDIF-CN$_2$ single crystals in combination with Cytop as a dielectric layer resulting in a mobility of up to 6 cm$^2$/Vs, an on/off-ratio exceeding 10$^8$ and a subthreshold swing of 0.45 V/dec. Furthermore gate-bias-stress effects are not present in these transistors and we observed low stress effects in the evaporated TFTs with Cytop as the gate dielectric.

These findings are reflected in the density of trap states (trap DOS). Single crystal FET with Cytop has a low trap DOS, whereas in evaporated TFTs the trap DOS is higher by 2-3 orders of magnitude. Surprisingly the trap DOS of the spin-coated TFT is similar to that in evaporated TFTs, except for additional discrete trap states centered around 0.24 eV below the conduction band.

The crystalline order in organic semiconductors strongly influences the overlap of the $\pi$-orbitals of adjacent molecules and therefore the mechanism of charge transport. [21] Grain boundaries and packing defects lead to a lower conductivity. [136, 137] For practical applications the trade-off between achieved high crystallinity and facile thin-film processing of the semiconductor has thus to be optimized. Numerous causes are known for trap state formation; e.g. structural defects, [138] chemical impurities, [139] adsorbed water, [140] polarizability of the dielectric, [141] or even the thermal motion of the molecules, [21] as summarized by Kalb et al. [60] In organic field-effect transistors (OFETs) traps adversely affect the mobility, the threshold voltage and the subthreshold swing. In order to explore the interplay between charge trapping and charge transport, we study systematically both, the transistor performance and the trap DOS with a varying degree of crystalline order.

For well known p-type materials such as Rubrene or pentacene several detailed trap DOS investigations have been conducted already, [142–147] yet for n-type materials quite little is known quantitatively on the electronic properties in general and the trap DOS in particular. One promising n-type material is N,N'-1H,1H-perfluorobutyl dicyanoperylene carboxydiimide (PDIF-CN$_2$) synthe-
Figure 6.1: The four PDIF-CN$_2$ based device structures employed in this study.

sized by Polyera, also called N1100. It was first reported by Jones et al. [148] as a high-mobility, air-stable n-type semiconducting material with processing versatility. Stable OFETs based on spin-coated films of PDIF-CN$_2$ have been reported. [149, 150] Thermal annealing of the solution processed films leads to a significant reorganization of the molecules and thus to improved transistor performance. [151] Evaporated films were studied on different substrates showing that the various surface treatments of the substrate substantially influence mobility, threshold voltage and on/off-ratio. [152] By far the highest mobilities, consistently higher than 1 cm$^2$/Vs, and best transistor characteristics were achieved using single crystals of PDIF-CN$_2$. [153] These single crystals show negligible gate bias stress effects. [154] Additional improvements on the fabrication process were made using ionic liquid gates resulting in mobilities around 5 cm$^2$/Vs. [155] For solution processed TFTs mobilities as high as 1.3 cm$^2$/Vs have been achieved using a solution crystallisation process. [156]

In this chapter we present an exhaustive study of this high performance n-type organic material PDIF-CN$_2$: gate-bias-stress measurements were performed and quantitatively compared to pentacene, the field-effect performance of spin-coated, thermally evaporated and single crystal transistors of this material on various gate dielectrics (c.f. Fig 1) were investigated. We measured the transfer curves at different temperatures and calculated the mobility. To investigate the influence of the processing conditions on the device performance, we extracted the spectral trap DOS and compared the results.
6. From single crystal FETs to solution processed TFTs

6.1 Single crystal

Single crystals of PDIF-CN$_2$ have been grown by physical vapor transport [53] and the same conditions as for Rubrene crystals have been proven to be appropriate. The crystals have been placed on pre-patterned substrates. [157] To minimize interface traps a 140 nm layer of Cytop (Asahi Glass) is spin-coated on top of 260 nm thermally grown and pre-cleaned SiO$_2$. Cytop was first introduced by Kalb et al. [55] and has shown great performance in many application afterwards. [62, 158–160]

Figure 6.2 shows the temperature dependent transfer curves of a single-crystal transistor on Cytop. The turn-on is at $V_g = -4$ V and the on-off ratio exceeds $10^8$ at low temperatures. Peak mobilities of up to 6 cm$^2$/Vs have been measured (see in section 6.4). The subthreshold swing is 0.45 V/dec, comparable to what is found in high quality p-type single crystal transistors. [55, 161] Furthermore no gate-bias-stress is discernible. This again shows, the very good

Figure 6.2: High performance FET with a PDIF-CN$_2$ single crystal on Cytop with a mobility of up to 6 cm$^2$/Vs. The quality is reflected in the turn-on and threshold voltage close to 0V, the very steep subthreshold swing of 0.45V/dec and the high on/off ratio exceeding $10^8$. Simulations are done with the same DOS for all temperatures and lie on the measured curves. ($V_d = 25$ V, $L = 50 \mu$m, $W = 520 \mu$m)
performance achievable in organic field effect transistors when Cytop is used as a gate dielectric and is the result of the low density of trap states at the interface between the single crystal and Cytop. The drain current $I_d$ increases at lower temperatures (best seen on a linear scale, inset 6.2).

To extract the spectral trap DOS, the transfer characteristics of field effect transistors measured at different temperatures were analyzed using a Matlab based simulating program developed by Oberhoff et al. [58] The simulated transfer curves for the single crystal device lie within the line-width of the measured ones for all temperatures and are thus not shown. The resulting trap DOS is plotted in figure 6.10 and compared to the other devices (section 6.4).

### 6.2 Evaporated thin-film

We have fabricated evaporated thin-film-transistors with three different gate dielectrics. First, the highly doped Si substrate with a thermally grown SiO$_2$ layer was pre-cleaned with acetone and isopropanol in an ultrasonic bath. The dielectric consists of either bare or hexamethyldisilazane (HMDS)-functionalized SiO$_2$ or the same oxide coated with Cytop (140 nm) (figure 6.1). These substrates have then been placed in a high vacuum evaporation system ($p_{\text{base}} < 10^{-7}$ mbar). They have been heated to 110°C during evaporation, in order to improve the crystallinity of the PDIF-CN$_2$ films. [150] The different TFT structures have been produced in the same run, therefore the growth conditions were exactly the same for all three PDIF-CN$_2$ films. As a last step, gold source and drain contacts have been evaporated. Afterwards the FETs have been moved to the attached probe chamber without breaking the vacuum.

Figure 6.3 shows the measured transfer curves of the three device structures. The thin-films on Cytop have a turn-on voltage very close to 0 V, whereas the transfer curve for the transistor with bare SiO$_2$ is shifted to about -10 V. An even larger shift of about -25 V is observed for the transistor with a HMDS modified SiO$_2$ interface. Furthermore the lowest off-current of the TFTs is achieved with Cytop. For devices with HMDS the level of the off-current depends on the sweep direction.

All three device structures have been measured at several temperatures from 250K to 300K. These measured curves have then been simulated to extract the trap DOS. Figure 6.4 shows the transfer measurements at different temperatures of the device with Cytop and the corresponding simulation results. This device
From single crystal FETs to solution processed TFTs

Figure 6.3: Representative transfer plots for an evaporated PDIF-CN$_2$ TFT on various gate dielectrics. The TFT on Cytop has the highest on-off ratio, steepest subthreshold slope and highest mobility of the three evaporated FETs. ($V_d = 20$ V, $L = 450$ $\mu$m, $W = 1000$ $\mu$m)

and the two other devices on HMDS and SiO$_2$ could be very accurately simulated.

The influence of oxygen and air was studied by exposing the three samples simultaneously to the gases. First, they have been exposed to oxygen for 1 hour at 200 mbar and have been remeasured. In a second step all samples have been exposed to air at 200 mbar for an additional hour. In figure 6.5 the transfer curves of the three devices are plotted against the induced charge carrier density, defined as the applied gate voltage $V_g$ multiplied by the gate capacitance. Both exposures shift the transfer curves towards the left, which indicates an enhanced carrier density in the conduction channel after exposure to oxygen and air. Overall, the shifts are of comparable magnitude. Nevertheless devices with SiO$_2$ have the largest shift after both oxygen and air exposure, whereas TFTs with Cytop or HMDS are less affected. This can be explained by the more hydrophobic nature of Cytop and HMDS compared to bare SiO$_2$. Another influence can be the different film growth of PDIF-CN$_2$ on these three dielectrics, as seen in the different mobility, as well as the different trap DOS (both discussed later). TFTs with HMDS seem not to be affected by oxygen, but the high off-current would mask a possible small shift, if there was one. The off-currents seen in figure 6.5 varied
6.2. Evaporated thin-film

Measurements of PDIF-CN$_2$ on Cytop

Gate voltage $V_g$ [V]

Drain current $I_d$ [A]

Figure 6.4: Representative transfer plots for an evaporated PDIF-CN$_2$ TFT on Cytop. The transfer curves, measured at different temperatures, are well simulated by the same DOS (black lines). The corresponding DOS is shown in figure 6.10 (blue line). ($V_d = 20$ V, $L = 450 \, \mu m$, $W = 1000 \, \mu m$)

strongly, depending on the sequence in that the measurements were carried out.

P-type pentacene TFTs have also been studied on bare SiO$_2$ and Cytop. [62] In contrast to PDIF-CN$_2$ pentacene shows similar film properties on both substrates, whereas surprisingly PDIF-CN$_2$ grows differently on each substrate. Furthermore it is remarkable that oxygen acts as an electron donor in PDIF-CN$_2$, whereas in pentacene it has been identified to act as a hole donor. [46] Obviously the influence of oxygen and air on n-type semiconductors is a topic for further research.

All three transfer curves in figure 6.3 show minimal hysteresis, indicative of very few slow traps which would lead to gate-bias-stress effects. To quantify this, the source-drain and gate voltage were maintained constant and the drain current was monitored over time (Fig. 6.6). Most remarkable is the minimal stress effect in the TFT with Cytop. Also striking is the very similar stress behavior of the TFTs with bare SiO$_2$ and HMDS. For p-type materials HMDS acts as an effective passivation layer and reduces gate-bias-stress induced long-term charge trapping. The reduction of the gate-bias-stress effect is due to the hydrophobic nature of HMDS which prevents water to reach the dielectric interface. [48] But for PDIF-
Figure 6.5: Representative transfer curves for three evaporated TFTs. The devices have been fabricated in high vacuum and subsequently have been exposed to oxygen and air. For all 3 dielectrics the transfer curves shift to the left; exposure to oxygen and air leads to more free charge carriers in the conduction channel of the FET. (The different values of the device capacitance have been taken into account.)

CN$_2$, the HMDS treatment has no significant effect on long-term charge trapping. This might suggest that the long term charge trapping is not mediated by water molecules at the dielectric/semiconductor interface for this n-type semiconductor. [48] These stress measurements can be compared to similar measurements performed in pentacene. [62] From this follows, that a thin-film of PDIF-CN$_2$ is much less affected by gate-bias stress than a pentacene thin-film is. Stress measurements on single crystal FETs of PDIF-CN$_2$ on Cytop show a negligible small gate-bias-stress effect, [154] which shows that this n-type semiconductor is very promising for applications.

As a summary of this section of evaporated thin-film transistors, it can be concluded, that PDIF-CN$_2$ films on Cytop show the highest mobility, lowest gate-bias-stress effect and a turn-on close to $V_g=0$ V.
6.3. Spin-coated thin-film

Various substrate preparation methods were investigated to optimize the performance for thin-film transistors with spin-coated PDIF-CN$_2$. We found that samples prepared from chlorobenzene solution usually yielded higher mobilities than those from chloroform. All devices show high off-currents, large negative turn-on voltages and a pronounced hysteresis. The HMDS treated samples showed the lowest off-current, the highest on/off-ratio and the highest mobility, thus they were selected for further studies. Cytop could not be used as a dielectric layer due to its highly hydrophobic surface leading to a poor wetting.

Transfer curves were measured on more than two dozen devices fabricated on a dozen wafers. We find a strong correlation between the macroscopic appearance of the film and the mobility; if the film is smooth and macroscopically defect-free, i.e., if the surface appears shiny, the mobility is higher. The best transistor had a mobility $\mu$ of 0.22 cm$^2$/Vs. In most other devices $\mu$ was below 0.1 cm$^2$/Vs. Transfer curve measurements at different temperatures have been
6. From single crystal FETs to solution processed TFTs

Figure 6.7: Transfer characteristics at different temperatures indicate the presence of discrete trap states. Top: Temperature dependent transfer curves for a spin-coated PDIF-CN$_2$ TFT. The sample was heated to 310K and then cooled to 240K in 10K steps. Bottom: Simulation (black) for three temperatures. The additional black curve was simulated without the gaussian trap state, thus highlighting the influence of these $5 \times 10^{19}/\text{cm}^3$ gaussian broadened trap states at 0.24 eV below the conduction band (CB). ($V_d = 50 \text{ V}, L = 50 \mu\text{m}, W = 900 \mu\text{m}$)

done (Fig. 6.7). Surprisingly the slope of the drain current is independent of temperature, while the threshold voltage shifts closer to zero (inset fig. 6.7).

For three different temperatures the transfer curve have been simulated (Fig. 6.7 bottom). To successfully model the transfer characteristics discrete trap states had to be included ($5 \times 10^{19}/\text{cm}^{-3}$ eV$^{-1}$ at -0.24 eV). An additional simulated
6.4 Comparison and density of states

transfer curve is plotted in black to show how the transfer characteristics would look if these discrete trap states were not present. The effect of the trap state is graphically indicated as the hatched area. The presence of a discrete trap state can be spotted already in the flattening (kink) of the transfer characteristics in the subthreshold region, particularly visible for low temperatures. We have seen this feature in all devices always around -60V gate voltage. Regarding these discrete traps we made the following observations: the discrete traps did not show up when spin-coating was performed on bare SiO$_2$ or UVO treated SiO$_2$; there are no discrete traps in the evaporated thin-films on HMDS. We thus tentatively associate the occurrence of these discrete traps with the solution processing on HMDS.

6.4 Comparison and density of states

![Figure 6.8: Temperature dependent mobility of the spin-coated, evaporated and single crystal FET devices. The single crystal has by far the highest mobility, increasing with lower temperature. The evaporated TFTs show a similar temperature behavior on all substrates which means a higher mobility at higher temperatures. The mobility of the spin-coated device stays constant over the whole measurement range.](image)

From the transfer measurements at various temperatures for the spin-coated,
evaporated and single crystal FETs the mobility was extracted at each temperature (figure 6.8). Overall the mobility values are relatively high for both single crystals and thin-film devices. The mobility of the thermally evaporated thin-films decreases linearly upon lowering the temperature, indicating “hopping” transport and the slope is comparable, independent whether the gate dielectric is bare SiO₂, Cytop or HMDS-treated SiO₂. The single crystal device shows an increasing mobility with decreasing temperature, often referred to as “band-like” transport. This is consistent with the picture of order and disorder present in semiconducting materials as the high mobility, ordered single crystal exhibits “band-like” transport whereas the lower mobility, more disordered thin-films show “hopping” transport. Surprisingly the mobility of the spin-coated device remains constant over the whole measured temperature range.

Figure 6.9: Transfer characteristics of PDIF-CN₂ based FETs with different degrees of order. The single crystal and the TFTs on Cytop show the best transistor performance with a high on-off ratio and a sharp turn-on at 0V. The transfer curves of the other evaporated thin-film transistors are slightly shifted, most for the HMDS treated sample. The spin-coated transistor has a broad turn-on indicating the presence of a large number of trap states. (The drain current has been corrected for length and width of the FETs and the applied drain voltage. Additionally the different capacitances have been taken into account.)

All transfer curves are replotted in a single graph in figure 6.9. For a quan-
6.4. Comparison and density of states

titative comparison of the transfer characteristics, the drain-current is scaled by
the width and length of the device and the applied drain voltage \( V_d \). Additionally
the gate voltage was converted to the number of field induced charge carriers per
unit area by multiplying it with the gate capacitance. The turn-on voltage of all
devices on Cytop (single crystal FET and evaporated TFT) is very close to zero
gate voltage, whereas the turn-on voltage for all the other evaporated TFTs is
shifted, most pronounced for the HMDS treated samples. The turn-on voltage for
the spin-coated sample is remarkably moved to the left indicating a large amount
of negative charge carriers in the conduction channel. The turn-on is by far the
sharpest for the single crystal FET. For the evaporated TFTs, the one with Cy-
top as a gate dielectric again showed the best performance. The broad turn-on
of the transfer curve for the spin-coated films reflects the large density of trap
states. Stress measurement revealed no gate-bias-stress effects in the single
crystal FET and very little effects for the evaporated ones. For the spin-coated
FET the influence of the gate-bias-stress is clearly visible in the large hysteresis
between the forward and backward measurements. The degree of gate-bias-
stress effects appears to be qualitatively related to the trap DOS (Fig. 6.10), as
one would expect if the charge is mainly trapped in the semiconductor and not in
the gate dielectric. [62]

Essentially all the discussed charge transport properties can be traced back
to the density of trap states in the band gap (figure 6.10). As expected from the
charge mobility and transfer characteristics, the evaporated devices on either bare
SiO\(_2\), Cytop or HMDS-treated SiO\(_2\) exhibit similar DOS within one order of mag-
nitude. The evaporated device on Cytop with the highest mobility has the lowest
trap density. The single crystal has by far the lowest trap DOS which of course
is the origin of the sharp turn-on of the transfer curves (figure 6.2). The spin-
coated films on HMDS treated SiO\(_2\) shows a very particular behavior as there are
discrete trap states centered around 0.24 eV below the conduction band. The
distribution is relatively narrow and if fitted with a gaussian the width is 0.01 eV.
These trap states dominate the whole transfer characteristics. Without them the
trap DOS of the spin-coated films would be comparable to the evaporated ones.

The detailed increase of the DOS approaching the conduction band depends
on the modeling mechanism as this is a region that is not directly accessible from
the experiment. Our model uses a steep exponential whereas also a gaussian
shape is possible. [159] Gratifyingly the results of both models are comparable.
We integrated the DOS of Minder et al. [159] resulting in an area density of \( N = \)
From single crystal FETs to solution processed TFTs

Figure 6.10: Trap density of states for all PDIF-CN₂ n-type FETs studied in this chapter. The single crystal (red) has a 2 to 3 orders of magnitude lower trap DOS compared to the polycrystalline thin-film FETs. The Evaporated thin-film on Cytop has the lowest trap DOS of the thin-film FETs. The spin-coated FETs are dominated by a gaussian-shaped trap level around $-0.24$ eV. Otherwise, the trap DOS of the spin-coated FET is comparable to the evaporated ones. Two typical trap DOS of polycrystalline and amorphous silicon (a-Si:H) are shown, which are comparable to the DOS of the organic semiconductors. [162, 163]

For our density of states we calculated a volume density of $N = 6.7 \times 10^{19} \text{cm}^{-3}$ trap states. If we assume a layer thickness of 3 nm, the findings of Minder et al. agree with our results. A conduction channel with this thickness seems reasonable as a lattice plane spacing of 2 nm was measured for PDIF-CN₂. [152]

6.5 Conclusion

We succeeded to fabricate FETs where the same semiconducting material PDIF-CN₂ is incorporated either as single crystal, as thermally evaporated thin-film or as spin-coated thin-film. These various transistors show a diverse behavior starting from the high performance single crystal transistors to good evaporated thin-film transistors to the highly trap dominated spin-coated ones. For the first
time, such a drastic variation of the transport properties has been quantitatively analyzed in one and the same material with respect to their origin, the trap density of states (trap DOS) and thus connected electrical performance with microscopic material properties.

In the single crystal the trap DOS is very low and is the reason for the steep subthreshold swing and the increasing mobility at low temperatures up to $6 \text{ cm}^2/\text{Vs}$. These excellent performance characteristics are somewhat reduced in the evaporated films where more disorder is present and the trap DOS is higher by several orders of magnitude; the turn-on is broader the mobility changes from a “band-like” to a “hopping”-like temperature dependence. This is reflected in the increased trap DOS. Surprisingly the DOS for the spin-coated films is comparable to the thermally evaporated films except for the additional discrete trap states, that are reminiscent of the chemically induced trap states of p-type materials. [46, 61] These discrete trap states greatly affect the device performance resulting in an extremely broad subthreshold region. If they could be avoided the spin-coated films would be of high performance.

In addition to the semiconducting material also the choice of the gate dielectric strongly affects the total trap DOS relevant for the FET transistor performance. This is visible for the evaporated films (fig. 6.10), where Cytop used as a gate dielectric strongly reduces the number of trap states and thus improves the device performance (fig. 6.9).

No gate-bias-stress effect has been visible for the single crystal FET, whereas the evaporated thin-films clearly showed stress effects. However these effects are much less pronounced than in pentacene TFTs. Spin-coated TFTs are significantly affected by an applied gate voltage.

We conclude from this microscopic study that PDIF-CN$_2$ is highly promising for practical applications thanks to its wide choice of processing methods and its excellent intrinsic electronic properties reflected in the exceptionally low trap DOS as low as in the best p-type single crystal FETs. [60, 158]
The density of trap states and device performance of organic as well as inorganic n- and p-type semiconductors

God made the bulk; surfaces were invented by the devil. 

Wolfgang Pauli

This chapter is a comprehensive compilation of the trap DOS in various semiconductors, organic and inorganic, p- as well as n-type under various processing conditions. To get a full picture, we screened publications from the last 25 years and present the main findings derived from typical data in all the materials. We found a new method to qualitatively calculate the trap DOS and we will show, that the trap DOS surface of rubrene is the same as the bulk of rubrene and thus the famous saying by Wolfgang Pauli does not hold for rubrene.

Trap states, present in any real semiconductor, do not only influence charge transport, but also various other physical processes relevant for device performance. Therefore quantifying the density of trap states (trap DOS) in a semiconductor is a crucial step into understanding and improving field effect transistors (FET) and other devices. In addition to the standard SCLC and FET simulation we show a simple method to determine the free vs. total charge carrier density and therefore the trap DOS through full renormalization of the transfer curve. We analyze and compare compare the trap DOS for a wide range of materials, or-
ganic as well as inorganic, and fabrication methods, leading to various degrees of order/disorder. The quantitative analysis of the trap DOS reveals that organic materials have a similar trap DOS as inorganic materials, for a similar morphology. Surprisingly, p- and n- type materials have a similar trap DOS. We show that it is possible to have a very low trap DOS in inkjet printed organic polymers, close to the trap DOS of organic single crystals. A comparison of trap DOS close to the surface with the bulk trap DOS in rubrene reveals that no surface trap states are present in this organic small molecule single crystal and that the trap DOS in organic bulk heterojunction solar cells is similar as in polymer FETs.

7.1 Introduction

Organic electronics has come a long way from a field for mere scientific curiosity [1] to devices that are readily available in the mass market. Nevertheless we lack a proper understanding of the inner working of the charge transport in these semiconducting layers. It is known that a reduced device performance has its origin in localized charges which have a lower probability of hopping to a neighboring molecule. [164] This localization occurs at so called trap states which are energetically located in the band-gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). These trap states are categorized into shallow traps, which are close to the respective transport level and deep traps situated further away from the transport levels.

There has been intense research to quantify and understand the influence of trap states on charge transport, especially for organic p-type semiconductors. Still, the various origins of trap states which then lead to charge localization are widely discussed and many details are not very well understood. Therefore to quantify the spectral distribution of the density of charge trap states (trap DOS) is essential to widen our knowledge in the field of organic semiconductors and to finally understand their charge transport properties.

In this study we present a comprehensive comparison of measurements of the trap DOS for numerous organic as well as inorganic p- and n-type semiconductors, various processing conditions and therefore a wide range of purity and crystallinity. First we will summarize the influence of the trap DOS on device operation and performance, then we will compare measurements of transfer curves of organic field effect transistors (OFET) and inorganic FETs, which leads us to a comparison of their respective trap DOS. In the end a comparison of various
organic devices (not only FETs) and their trap DOS is shown and discussed.

7.2 Overview: Trap DOS and device performance

Some disorder which leads to localization of charge carriers is always present in organic semiconductors be it single crystals or polycrystalline/amorphous thin-films. In general localization may be caused by the dynamic motion of the molecules [20, 165], grain boundaries (or more general: structural defects) [136, 137], impurities [166], doping [142, 167, 168], adsorbed polar molecules [55, 61, 144, 169] or the gate dielectric. [159, 170] The trap DOS can also be modified after producing the devices by exposing the organic semiconductor to gases [46, 171], UV-Ozone [172], ions [173], x-rays [174, 175] or by thermal annealing. [176]

Depending on the material, preparation, purity and crystallinity of the semiconductor, the charge mobility is phenomenologically classified as “thermally activated” or “band-like”. [135, 159, 177, 178] There has been intense research, how charge transport is influenced by charge localization using either charge modulation spectroscopy [178] or electron spin resonance spectroscopy. [179] Shallow traps are found to influence the measured mobility [180] and also its temperature dependence in field effect transistors [178], thus leading to a “band-like” or an activated temperature dependent behavior. These shallow traps have a spatial extension over several molecules, whereas deeper lying traps further localize the charge carrier to about 1.5 molecules. [181]

For low charge carrier densities the charges spend most of their time in a localized state far away from the transport level in the band gap. Through accumulation of charge carriers by either a gate bias, absorption of photons or injection through the electrodes, the deeper lying traps will be subsequently filled and more and more charges will be in the delocalized states in the transport level which then determine the charge mobility. [25] This filling of the trap states through charge injection is also able to explain the apparent electric field dependence of the mobility observed in SCLC measurements of organic photovoltaic cells (OPV) and organic light emitting diodes (OLED). [47] The spatial distribution of traps might also be inhomogeneous and the trap DOS may shift in energy or increase/decrease depending on the position in the device. [167] To summarize this: the trap DOS is the connection between the microscopic arrangement of the molecules and the macroscopic measurable charge transport properties.
Recently it has been found that the trap DOS is not only the basis of charge transport itself, but also influences other properties of organic semiconductors. To have a good charge injection the work function of the metal needs to be close to the transport level of the semiconductor. This alignment is influenced by the presence of trap states at the interface. [37] At organic-organic heterojunctions the energy level alignment between the two films is highly dependent on the trap states close to the HOMO or LUMO level. The more trap states are present, the larger the shift between two adjacent organic HOMO levels. [182] This alignment of adjacent organic layers not only influences the hopping of charges over that interface, but also the open circuit-voltage achieved in an organic photovoltaic cell [183] and can even lead to an interface dipole. [184] Also the diffusion of charges depends on the trap DOS which leads to a deviation from the generally used Einstein relation. [185] Recombination of electrons and holes are also influenced by the presence of trap states in the semiconductor, where they act as recombination centers for non-radiative recombination. This mechanism lowers the efficiency of OLEDs [186], and reduces the fill factor in OPVs. [174, 187]

For solar cells an additional process is influenced by the presence of trap states: charge generation. After absorption of a photon, the generated exciton has to efficiently dissociate into free charge carriers. This happens at organic-organic heterojunctions. The high binding energy of the exciton leads to a high barrier for the dissociation, this is mitigated by allowing the electron and the hole in the exciton to hop to lower energy states (i.e. trap states) at both sides of the interface and thus allowing them to spatially separate and overcome their coulomb attraction. [116, 188]

Therefore knowing the density and the spectral distribution of the trap states in the band-gap not only helps to understand the charge transport itself, but also helps to explain energy level alignment and charge generation/recombination, especially in more complex device structures.

One part of trapping which is not discussed in this paper are the so called slow trap states. [48,49,62] Where charge carriers are trapped for longer periods of time (up to weeks). These processes are still poorly understood and their connection to the measured trap DOS for the “fast traps” discussed here is not yet clear.
Various methods have been developed to measure the trap DOS. Here, the methods are only briefly discussed and the interested reader can get a more detailed description in the respective original publication. Additionally, a wide range of preparation methods have been used to make the devices compared here which are also not discussed in detail.

To determine the trap DOS in OFETs, the established analytical methods developed for inorganic FETs have been applied. To account for specific properties of organic semiconductors, specialized computer simulation programs have been developed. All these methods for FETs are based on the knowledge that as the gate voltage $V_g$ is increased, the deep trap states are filled which then leads to more charge carriers being excited into the conduction level where they are mobile.

Bulk properties of organic thin-films and single crystals have been measured by means of space charge limited current (SCLC) measurements or the improvement thereof: temperature-dependent SCLC. A recent review studied and compared the trap DOS for p-type semiconductors calculated using FET and SCLC measurements.

For amorphous multilayered organic light emitting diodes (OLEDs), a wide body of theories and simulation software has been developed. A different approach analyzes the charge carrier density dependence of the mobility to directly extract the underlying trap DOS. Only recently has the trap DOS in organic photovoltaic cells (OPV) been quantified by transient photoconductivity measurements. For this method, an OPV is exposed to a short laser pulse (less than 10 ns) and the resulting transient photocurrent is measured over several orders of magnitude in time as well as current. It is assumed that the long tail of the photocurrent is due to the slow charge carrier. Therefore, information about the trap DOS relatively far away from the respective transport band of the slow charge carrier can be extracted.

Many of the analytical and numerical trap DOS extraction methods are based on a mobility edge model, where it is assumed that there is a clearly defined energy level which separates localized, immobile, charges from delocalized, free-to-move charges. This mobility edge separates the transport level from the trap states. Salleo et al. [190] found that the mobility edge model is best at describing the transport in organic polymers. An additional mechanism, which some models
consider is the hopping from one localized state to a neighboring one with similar trapping energy. This has been discussed by McMahon and Troisi [164] where they found that this mechanism is unlikely to contribute to the transport, especially in more crystalline semiconducting layers and is normally overshadowed by the process of exciting a charge carrier into the transport level where it is free to move around. The various analytical models for FETs have been discussed and compared to a numerical model by Kalb et al. [59], where it is found that the trap DOS calculated using analytical and numerical models agree very well, but the analytical models have a certain spread depending on the assumptions, whereas the numerical model by Oberhoff et al. [58] gives a more reliable result. In this study we use this numerical model to analyze the trap DOS for all organic FETs.

7.4 Transistor performance: comparing p- and n-type materials

As discussed before, the trap DOS influences the macroscopic charge transport properties in organic field effect transistors. Therefore it is possible to directly see its influence on the transfer curve. In this section we compare measured transfer curves from various publications. In the next section these curves are renormalized properly and in the end we compare the respective trap DOS. For this we screened publications from the last 3 decades for relevant papers, where transfer curve as well as trap DOS calculations have been done. From these publications suitable ones have been chosen according to the following criteria: device geometries are published, dielectric layer thickness and material was mentioned, the trap DOS was plotted with an energy scale relative to the distance of the respective transport level and last, but very important: the transfer curves have been measured at low source-drain voltages \( V_d \ll V_g \). We would like to stress the last criterion a bit more: for large \( V_d \) the device exhibits a wide saturated regime between the subthreshold and linear regime. As only the subthreshold and linear regime can be directly compared within this wide range of device geometries and measurement protocols, a wide saturated regime would mask any effect originating from a difference in the trap DOS.

Figure 7.1 shows the renormalized transfer curves for the chosen p- as well as n-type FETs and thin-film transistors (TFT). The respective materials are listed in table 7.1 with a reference to the original publications. The applied gate voltage has been corrected for the various dielectrics used and plotted against the sheet
### 7.4. Transistor performance: comparing p- and n-type materials

<table>
<thead>
<tr>
<th>Material</th>
<th>fabrication method</th>
<th>DOS extraction</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>p-type:</strong></td>
<td></td>
<td></td>
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<tr>
<td>Rubrene</td>
<td>single crystal on Cytop</td>
<td>Simulator [58]</td>
<td>here</td>
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<tr>
<td>Rubrene SCLC</td>
<td>single crystal</td>
<td>TD-SCLC [172]</td>
<td>here</td>
</tr>
<tr>
<td>Pentacene</td>
<td>single crystal on Cytop</td>
<td>Simulator [58]</td>
<td>[62]</td>
</tr>
<tr>
<td>Pentacene SCLC</td>
<td>single crystal</td>
<td>TD-SCLC [172]</td>
<td>[60]</td>
</tr>
<tr>
<td>Pentacene</td>
<td>Evaporated thin-film on Cytop or SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Simulator [58]</td>
<td>[62]</td>
</tr>
<tr>
<td>PQTBz-C12</td>
<td>inkjet printed on SiO&lt;sub&gt;2&lt;/sub&gt; with ODTS SAM treatment</td>
<td>Simulator [58]</td>
<td>[196]</td>
</tr>
<tr>
<td>PQT-12</td>
<td>inkjet printed on SiO&lt;sub&gt;2&lt;/sub&gt; with ODTS SAM treatment</td>
<td>Simulator [58]</td>
<td>[196]</td>
</tr>
<tr>
<td>P3HT</td>
<td>inkjet printed on SiO&lt;sub&gt;2&lt;/sub&gt; with ODTS SAM treatment</td>
<td>Simulator [58]</td>
<td>[196]</td>
</tr>
<tr>
<td>a-Si</td>
<td>amorphous silicon on SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Transfer curve measurements [197]</td>
<td>[198]</td>
</tr>
<tr>
<td>Poly-Si</td>
<td>polycrystalline silicon on SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Transfer curve and C-V measurements</td>
<td>[199]</td>
</tr>
<tr>
<td>P3HT:PCBM</td>
<td>P3HT:PCBM bulk heterojunction solar cell</td>
<td>transient photoconductivity</td>
<td>[116]</td>
</tr>
<tr>
<td>PCDTBT:PCBM</td>
<td>PCDTBT:PCBM bulk heterojunction solar cell</td>
<td>transient photoconductivity</td>
<td>[116]</td>
</tr>
<tr>
<td><strong>n-type:</strong></td>
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<tr>
<td>PDIF-CN&lt;sub&gt;2&lt;/sub&gt;</td>
<td>single crystal on Cytop simulator [58]</td>
<td></td>
<td>[135]</td>
</tr>
<tr>
<td>PDIF-CN&lt;sub&gt;2&lt;/sub&gt;</td>
<td>evaporated thin-film on SiO&lt;sub&gt;2&lt;/sub&gt;, HMDS or Cytop simulator [58]</td>
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<td>[135]</td>
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<tr>
<td>PDIF-CN&lt;sub&gt;2&lt;/sub&gt; SCLC</td>
<td>PDIF-CN&lt;sub&gt;2&lt;/sub&gt; single crystal SCLC measurements of the bulk TD-SCLC [172]</td>
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<tr>
<td>a-Si</td>
<td>amorphous silicon on SiN</td>
<td>Transfer curve measurements</td>
<td>[200]</td>
</tr>
<tr>
<td>Poly-Si</td>
<td>polycrystalline silicon on SiO</td>
<td>Transfer curve and C-V measurements</td>
<td>[199]</td>
</tr>
<tr>
<td>a-IGZO</td>
<td>amorphous indium-gallium-zinc-oxide on SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Transfer and C-V measurements using a simulator</td>
<td>[201]</td>
</tr>
<tr>
<td>ZnO</td>
<td>zinc-oxide on SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>C-V measurements</td>
<td>[202]</td>
</tr>
</tbody>
</table>

Table 7.1: Overview of the semiconducting materials studied here for the comparison of the transfer curves, the trap DOS or both.
7. Trap DOS in organic and inorganico semiconductors

Figure 7.1: Normalized transfer curve of the analysed p- and n-type organic FETs. The steeper the subthreshold slope, the lower the trap DOS. The higher the conductance, the higher the mobility. Organic single crystal FETs have a very steep subthreshold region and high mobility, whereas the evaporated TFTs have a broad subthreshold region and lower mobility. The inkjet printed polymers have a subthreshold region close to that of single crystals, but a mobility close to that of TFTs. The two inorganic FETs have a very broad subthreshold region.

To compare the various dielectrics, device geometries and applied voltages, the sheet conductance is plotted against the induced charge carrier density, given by applied gate voltage times capacitance.

conductance. First of all there is a trend for p- as well as n-type to be shifted to the left or to lower $V_g$. Which is due to the Fermi level being far away from the valence band (or HOMO) and closer to the conduction band (or LUMO). Therefore generally it seems to be that the Fermi level is rather closer to the conduction band.
than to the valence band, leading to a deficiency of holes (p-type) or excess of electrons (n-type).

The steepness of the subthreshold region directly relates to the trap DOS close to the turn-on voltage, i.e. when the Fermi level is far away from the conduction band, whereas the maximum achieved current depends more on the mobility. The three organic single crystal FETs (pentacene, rubrene and PDIF-CN\(_2\)) show the steepest subthreshold region, whereas the evaporated thin-film transistors (Pentacene and PDIF-CN\(_2\)) all show a broader subthreshold region which is comparable for p- and n-type FETs. The three printed polymer transistors by Jang et al. [196] exhibit a very steep subthreshold region somewhere between the thermally evaporated thin-film transistors (TFT) and single crystal FETs, but the mobility of these devices is below 0.2 cm\(^2\)/Vs.

The a-Si TFT has a similar subthreshold region for n- and p-type transport which is comparable to the thermally evaporated TFTs. But it shows a very low mobility for the p-type transport, whereas the electron mobility is close to one and thus better as the evaporated PDIF-CN\(_2\) TFTs. The polycrystalline Silicon has a very high mobility \(\gtrsim 20\) cm\(^2\)/Vs for electrons as well as holes, but the subthreshold region is very broad and thus the number of traps is high in this FET. The amorphous IGZO FET is an n-type transistor which shows a very high mobility (20 cm\(^2\)/Vs) but otherwise has a performance comparable to polycrystalline silicon.

Figure 7.2 shows a compilation of the mobility of all the discussed devices. It shows a range of the mobilities which can be expected in the various materials depending on processing conditions and the value of the mobility of the devices discussed here. These mobility ranges easily span several orders of magnitude even in the same material.

### 7.5 New method: fully renormalized transfer curves and trap DOS

Until now we have only been able to discuss the density of deep trap states via the subthreshold slope. To compare the trap DOS over the whole measured range, the transfer curves need to be further normalized for the mobility and shifted for the turn-on voltage. Figure 7.3 shows all these normalized curves for p- as well as n-type FETs. Additionally the theoretical maximum value derived from the gradual channel approximation is plotted. In the linear regime \((V_d \ll V_g)\) we have:
Figure 7.2: Mobility of the FETs shown in Fig. 7.1. The red squares (single crystals) and triangles (TFTs) are for the materials studied in this paper. Whereas the range indicates the highest and lowest value which can be expected for a certain material. The mobility range easily spans several orders of magnitude even in the same material. A wide body of references has been used for this graph. [19, 62, 135, 159, 198–200, 203–213]

\[ I_d = \frac{W}{L} \mu C_i (V_g - V_{th}) V_d. \] (7.1)

With \( W \) and \( L \) being the width and length of the FET channel, \( C_i \) the capacitance per unit area, \( \mu \) the mobility and \( V_{th} \) the threshold voltage. Applying the same normalization as for the measured transfer curves and with \( V_{th} = 0 \), which in this case is equal to the turn-on voltage, the equation transforms to:

\[ I_d \frac{L}{W V_d \mu} = C V_g. \] (7.2)

This gives an upper limit for all transfer curves in any FET. Any deviation from this maximum is due to the presence of trap states. This theoretical maximum does not account for the subthreshold region and might overestimate the achievable current close to the turn-on voltage. But the difference is only marginal and

\[ I_d = W \mu C_i (V_g - V_{th}) V_d. \] (7.1)

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7.5. New method: fully renormalized transfer curves and trap DOS

Figure 7.3: Direct representation of the free vs. total charge carrier density in the studied FETs through fully normalized and shifted transfer curves. The deviation from the theoretical maximum directly reflects the number of trap states. Single crystal FETs (red) are very close to the theoretical limit and the limit is even reached for rubrene. The evaporated TFTs (blue) are much more dominated by traps. The inkjet printed polymers (orange) are in between the single crystal FETs and evaporated TFTs. All inorganic FETs, except for n-type a-Si are very much trap dominated.

not relevant in our discussion. This renormalization is not only convenient because it gives an theoretical upper limit, but it is a direct representation of the free vs. total charge carrier density when both axis are divided by the elementary charge q (Fig. 7.3).

The first observation is the symmetry between the organic n- and p-type materials in figure 7.3. The single crystal curves as well as the evaporated TFTs look the same independent of n- or p-type. This leads to the conclusion that the preparation technique has a dominating influence on the trap DOS and not the materials itself. Therefore we can conclude, that the device performance for n-type FETs can be as good as for the established p-type semiconductors.

The single crystal FETs are already very close to the theoretical maximum and it is even reached for the rubrene single crystal FET. A further reduction of the trap DOS will therefore not improve the shape of the transfer curve significantly.

As seen before, printed polymers (P3HT, PQT-12 and PQTBTz-C12) show an excellent device performance which is comparable or even better than for the
evaporated TFTs. PQTBTz-C12 shows a sharp subthreshold region comparable to the single crystals, but at higher induced charge carrier densities the performance seems to be closer to the evaporated thin-film FETs.

The p-type polycrystalline Silicon FET not only has a very broad subthreshold region, but the whole transfer curve is extremely broad. The p-type amorphous Silicon FET shows a performance comparable to the evaporated organic thin-film FETs, except for the subthreshold region. The n-type amorphous silicon is generally better than the evaporated organic thin-films, whereas the a-IGZO and n-type polycrystalline Silicon show a lower performance and are comparable to the evaporated thin films. The ZnO TFT shows a very broad turn-on behavior and seems to be strongly trap limited.

### 7.6 Trap DOS: organic and inorganic FETs

The compilation of the fully normalized transfer curves discussed before (Fig. 7.3) gave an estimation of the spectral trap DOS and connected it directly to the transfer curve. However to properly calculate the spectral trap DOS either a simulation program or an analytical method is needed. Different calculation

![Figure 7.4: Trap density of states for p- and n-type FETs. It is similar for p- and n-type materials. The 2-3 orders of magnitude gap between single crystal FETs and evaporated TFTs is closed by the inkjet printed polymeric TFTs. The inorganic FETs have a high trap DOS close to the transport level, which dominates the transfer curve.](image-url)
methods have been compared to each other by Kalb et al. [59] For all organic FETs discussed here, the simulation program by Oberhoff et al. [58] has been used. Therefore the results are directly comparable. For the inorganic FETs, various methods have been used by the authors, which leads to discrepancies about the parameters used for the extraction and thus to a higher uncertainty about the exact number of traps.

The spectral trap DOS for all analyzed FETs is shown in figure 7.4. The first observation is that the trap DOS for organic FETs is composed of two exponential curves. A steep one close to the respective transport level and a broader one further away. This observation is supported by various other measurements: an analysis of the Seebeck coefficient in organic semiconductors [158] showed a logarithmic dependence on the induced charge carrier density. This can be directly explained by an exponential trap DOS. Direct measurements of the electron states close to the HOMO level of pentacene and MeO-TPD by UPS measurements show a steep exponential decay around the transport level by 2 to 3 orders of magnitude. [214, 215] Measurements of the trap DOS using Kelvin probe microscopy show these features as well. [167, 216] There has also been a direct observation of the double exponential shape of the trap DOS: thin-films of C$_{60}$ have been doped with extremely low concentrations during evaporation. A shift of the work function is observed upon doping [217], which exhibits two exponential regimes. A fast shift at low doping ratios and a slower one at higher doping ratios. This shift is directly connected to the shape of the spectral trap DOS. Similar measurements with the same conclusions have been made on α-NPD and CBP. [218]

The next observation is that the trap DOS looks very similar independent of n- or p-type transport, for the single crystals as well as the thin-films. This has also been found by Ha et al. [219] where they investigated the trap DOS in an ambipolar transistor.

The evaporated thin-films have a trap DOS which is about 1 to 3 orders of magnitude higher than the single crystal FET. For the evaporated TFT, there is a slight variation of the trap DOS depending on the dielectric used. The polymer FETs show that it is possible, by careful processing, to reduce the trap DOS and come close to the trap DOS of the pentacene single crystal, which is even more impressive considering the polymer samples have been inkjet printed onto the substrate and not deposited in a high vacuum environment as the evaporated TFTs.
For the inorganic p-type transistors having a comparable or lower performance in the transfer curves (Fig. 7.1 and 7.3) compared to the evaporated thin-films it is not surprising to see that they have a trap DOS which is equal and higher than the trap DOS of the evaporated organic TFTs. For the inorganic n-type transistors, the poly-Si shows a similar or higher trap DOS than the evaporated organic TFTs. The a-Si TFT shows a very low trap DOS in between the trap DOS for organic single crystals and evaporated thin films. Both observations are consistent to what has been seen in the normalized transfer curves (Fig. 7.3).

The two oxide semiconductor TFTs, ZnO and and a-IGZO, both show a DOS lower than the evaporated organic TFTs even though in the fully normalized transfer curve plot (Fig. 7.3), they show a comparable or worse performance compared to the evaporated organic TFTs. This discrepancy could be due to the different methods to determine the trap DOS. For both samples a CV method has been used to determine the trap DOS. Therefore it seems that this method does not lead to a result which is consistent with trap DOS determination methods based on measured transfer curves. This is consistent with what has been found while analyzing the 3 polymer TFTs. The trap DOS found using the simulator by Oberhoff et al. [58] resulted in a trap DOS about 1 order of magnitude higher than what has been published before with the same data [196] but analyzed using a CV method. The origin of this discrepancy between the two methods is unclear and needs further research.

### 7.7 Trap DOS: bulk and interface

After the discussion of the spectral trap DOS in FETs and the implication on charge transport, we will compare it to the trap DOS found in the bulk of organic semiconductors. To measure bulk properties different method are used: for organic single crystals SCLC measurements [172] and the time dependence of the photocurrent for OPVs. [116]

The bulk trap DOS for the rubrene single crystals is extremely low and varies by about an order of magnitude among the samples (Fig. 7.5). It is very remarkable, that the trap DOS in rubrene close to the surface (FET measurement) is as low as the one measured in the bulk (SCLC measurement).

For the pentacene this is only true about 0.3 eV from the valence band, where the bulk trap DOS and interface trap DOS are of similar value. Closer to the valence band the pentacene has a higher trap DOS at the interface by 1 to 2
7.8 Conclusion

We have discussed how traps influence various characteristics of organic devices and especially how it influences charge transport. By normalizing the transfer orders of magnitude.

The PDIF-CN$_2$ already shows a very low trap DOS at the interface to the dielectric in the FET. And SCLC measurements show a slightly lower trap DOS in the bulk. This again highlights, the potential this material has as being a high performance n-type organic semiconductor comparable to the best p-type counterparts.

Most remarkably, the two measurements of the trap DOS in bulk heterojunction solar cells (P3HT:PCBM and PCDTBT:PCBM) exhibit a similar trap DOS as the polymeric FETs. This is surprising, as the active film of the bulk heterojunction solar cell is expected to be more disordered compared to the FETs. Therefore one would have expected a higher trap DOS.

Figure 7.5: Trap density of states for p- and n-type organic materials, not only FETs. Rubrene has the same trap DOS in the bulk (SCLC measurement) as close to the surface (FET). The trap DOS in bulk-heterojunction solar cells (P3HT:PCBM and PCDTBT:PCBM) is as low as in polymeric TFTs. PDIF-CN$_2$ single crystals are already very close to the bulk trap DOS value, but there is still some room for improvement.
7. Trap DOS in organic and inorganic semiconductors

curves appropriately the free vs. total charge carrier density and thus the trap DOS can be directly compared within different FET configurations. Nevertheless for a quantitative and spectral analysis of the trap DOS a proper analysis is necessary.

We have shown that the trap DOS for n-type FETs can be as low as for the best p-type materials and is generally the same under the same processing conditions. This illustrates, that processing conditions and not the material itself, are a dominating input factor for the trap DOS. We have seen that high mobility does not directly lead to a low trap DOS and thus sharp turn-on behavior of the FET especially in the inorganic oxide semiconductors. The inorganic semiconductors do have a similar trap DOS as the organic thin-films, much higher than the organic single crystals. Whereas the mobility is higher in the inorganic thin-films especially for n-type semiconductors.

The printed polymer FETs prove that by careful choice of material and optimal processing it is possible to close the gap in the trap DOS between evaporated thin-films and single crystals. This has not been achieved yet with small molecules which indicates that the grain boundaries in the small molecules are the origin of the several orders of magnitude difference in the trap DOS between the single crystals and evaporated thin-films.

The trap DOS at the interface to the dielectric can be as low as in the bulk of the organic material which exemplifies that no further damage is imposed on the surface while handling the single crystal in air and that there are no surface states which act as charge traps in rubrene.

The bulk trap DOS measured in polymer:C_{60} bulk-heterjunction solar cells is as small as in polymeric FETs at least far away (≤ 0.2 eV) from the transport band. This illustrates that the thin-film organic bulk-heterjunction OPVs can have very low trap DOS despite the much more complex internal structure of the film which leads to a more disordered morphology.
Summary, conclusions and outlook

In the beginner’s mind there are many possibilities, but in
the expert’s mind there are few.

Shunryu Suzuki

This thesis discussed charge transport and some associated phenomena
from various points of view. Especially, how charge transport is connected with
charge generation and extraction in OPVs and how it is related to the density of
trap states.

In essence, the conclusions are as follows:

Through implementation of all physical processes in a comprehensive numeri-
cal model for organic photovoltaic cells (OPVs) we have been able to disentangle
the influence of the physical processes involved. We have shown, transient mea-
surements to be crucial to get a full picture of an organic bulk heterojunction solar
cell. Especially, as the transient turn-off behavior is dominated by the electron
and hole mobilities only. Measurements have supported the simulated findings
and they are now implemented in the characterization of OPVs.

We have built organic field-effect transistors (OFETs) using pentacene single
crystals and Cytop as gate insulator, which are not affected by gate-bias stress.
An evaporated pentacene thin-film on Cytop shows gate-bias-stress, similar to a
pentacene thin-film transistors (TFTs) using bare SiO$_2$. We have shown that even
though, the gate-bias stress looks similar in both devices, their origin is different.
When using SiO$_2$ charge carriers diffuse into the dielectric, which then leads to
gate-bias stress effect. We have been able to show, that with Cytop this does not
happen and therefore the origin of gate-bias-stress when using Cytop has to be
charge trapping in the semiconductor itself.

We have been able to build OFETs with one and the same n-type material (PDIF-CN$_2$), but with a wide range of processing methods. PDIF-CN$_2$ has been incorporated as single crystal, thermally evaporated or solution processed thin-film. This leads to a wide range of crystalline order and thus allowed for a quantitative analysis the influence of order/disorder on charge trapping and transport. In the single crystal we found a very low trap DOS, comparable to the best single crystal p-type materials, with mobilities up to 6 cm$^2$/Vs and a “band-like” temperature dependent behavior. These excellent properties are somewhat reduced in evaporated TFTs where more disorder is present and the mobility changes to a “hopping-like” temperature dependence. Interestingly, the solution processed TFTs have a similar performance as the evaporated ones, except that they have a discrete trap state around 0.25 eV below the conduction band, which dominates the TFT characteristics.

A quick and simple method has been developed to directly compare free vs. total charge carrier density and thus the trap DOS in organic as well as inorganic materials. This will help to discuss device performance on a much more fundamental level. From a comparison of the trap DOS of a wide range of materials, organic as well as inorganic, published in the last 25 years we have found that n-type materials can be as good as the established p-type OFETs. Inorganic FETs have a trap DOS which is close, or even larger, than the trap DOS for the thermally evaporated TFTs. Inkjet printed polymers do have a trap DOS which is lower than the one of evaporated TFTs, showing, that by careful choice of material and optimal processing methods the gap in the trap DOS between single crystals and thin-films can be overcome. This has not been achieved yet with small molecules, indicating that grain boundaries, especially prevalent in small molecule thin-films, to be the origin of this trap DOS gap. The trap DOS beyond 0.2 eV in bulk heterojunction OPVs is similar as in the corresponding polymer TFTs, which is rather remarkable as the morphology of the film in the OPV is expected to be more amorphous than the one of the TFTs. With rubrene single crystals we have shown, the trap DOS close to the interface to be exactly the same as in the bulk. This is in stark contrast to everything which is known from inorganic semiconductors, where surface states lead to a different trap DOS in a FET configuration.

Even though this thesis helped in elucidating some problems in organic electronics, more questions have surfaced during these studies which need to be
answered to deepen our understanding of the field. The origin and spectral distribution of slow trapping in the semiconductor which leads to gate-bias-stress in OFETs is still elusive and whether there is any connection to long charge trapping in which occurs in OLEDs is unknown. We do not know how exactly the density of states looks close to the mobility edge and how exactly to define the transition from free to trapped charge carriers. The same is true for the trap DOS far away from both conduction levels, we do not know anything about the trap DOS in the middle of the band-gap. Additionally we have quantified the so called “steady-state” trap DOS but it would be very interesting to know more about the dynamics of the trap states and especially how this dynamics is connected to the depth of the trap states.
List of Tables

4.1 Input parameters for the thickness dependent simulation of figure 4.4. 49
4.2 Derived simulation parameters from figures 4.4, 4.5 and 4.6. 52

7.1 Overview of the semiconducting materials studied here for the comparison of the transfer curves, the trap DOS or both. 97
List of Figures

1.1 Various organic electronic devices .................................................. 7

2.1 Pentacene structure in theory and as measured. (A) Ball and stick model. (B) STM image. (C) and (D) AFM image. [8] ................................................................. 10

2.2 Molecular orbitals of pentacene as measured using a high-resolution STM. Adapted from [9]. ................................................................. 11

2.3 Herringbone structure of crystalline pentacene. [10] Depending on the charge transport direction, the wavefunction overlap is different. Therefore transport properties will depend on the transport direction. .................................................. 12

2.4 Transport anisotropy measured in a pentacene single crystal. [13] Where according to Yin et al. [12] the angle 0° is equal to the a axis (Fig. 2.3). .................................................. 13

2.5 Temperature dependence of the mobility in various pentacene FETs. Depending on the processing conditions and measurement technique either “band-like” or “hopping” transport is observed. [14–16]. .................................................. 14

2.6 Left: molecular dynamics simulation of the hopping integral at different temperatures and along two directions in the crystal. Right: relative position of two anthracene molecules at 300 K which leads to the fluctuating hopping integral. [20] .................................................. 15

2.7 HOMO and LUMO energies for various organic semiconductors. The values are sorted by the HOMO energies. The number on top the HOMO level is the calculated value of the band gap. Additionally the work functions of various contact materials are indicated as bars. 17

2.8 Metal electrode/organic semiconductor interface energy level alignment. Left: vacuum level alignment. Right: vacuum level shift or interface dipole induced shift (ΔΦ) of the work function Φ.  Ed^vac: vacuum level, EIB: electron injection barrier, HIB: hole injection barrier, EA: electron affinity, IE: ionization energy. [26] .................................................. 18

2.9 Gold interdiffusion into an organic layer (Diindenoperylene, DIP) on a SiO2 substrate. Sample A has been cooled to -120°C, whereas sample B has been heated to +70°C during evaporation of the gold. [36] .................................................. 19

2.10 Charge injection barrier reduction by ΔΦ due to image charges and the internal electric field inside the organic semiconducting device. [38] .................................................. 20

2.11 Band width variation of the HOMO and LUMO level depending on the intermolecular separation of two sexithienyl molecules. [41] .................................................. 21

2.12 Band width variation of the HOMO and LUMO level depending on the translation of the two of two sexithienyl molecules. [41] .................................................. 21

2.13 Generation of shallow traps by increasing the band width of the HOMO and LUMO level when a displacement is introduced in a otherwise crystalline pentacene structure. [42] 22
2.14 Generation of deep trap states due to a chemical defect in pentacene. If a oxygen molecule is attached to two pentacene molecules a deep trap states about 0.29 eV from the HOMO level is created. Adapted from Knipp et al. [45] .......................... 23
2.15 Simple picture of the processes in an organic photovoltaic cell. .............................................. 24
2.16 A more detailed picture of an organic bulk heterojunction solar cell. .............................................. 24
2.17 Simulation of the light intensity dependence of the transfer curves of organic solar cells. The simulator is described in chapter 4. .............................................. 25
2.18 Structure of an organic field-effect transistor. .................................................................................. 26
2.19 Charge carrier distribution and channel formation in a FET under various operation conditions. .................................................................................................................. 27
2.20 Measured Rubrene single crystal FET on Cytop. Indicated are the two regimes; linear and saturation and the transfer and output curves. At high currents, the linear regime becomes sublinear, this is due to contact limitations in this device. .................................................................................. 28
2.21 Channel thickness (i.e. Debye length) at four temperatures, calculated for the Rubrene FET shown in Fig. 2.20 using Eqn. 2.6. .............................................. 29
3.1 Chemical structure of some of materials used in this study. ......................................................... 32
3.2 Materials used for the modification of the dielectric (left and middle). High hydrophobicity of Cytop (right). [54] ......................................................... 32
3.3 Various device types used for studying organic materials in this thesis. ......................................................... 33
3.4 Schematics of the physical vapor transport oven used for growing organic single crystals. 34
3.5 Finished pentacene TFTs in the substrate holder. ................................................................. 35
3.6 Structured substrate for measurements of TFTs. Left: view of the whole substrate. Right: detailed view of a 4-terminal test structure. ................................................................. 35
3.7 Vacuum probe chamber for measurements. ................................................................. 36
3.8 Measured and simulated transfer curve of a PDIF-CN$_2$ TFT on Cytop. These simulations are used in chapter 6 to extract the trap DOS. ......................................................... 37
4.1 Electromagnetic field penetration plot (top) is calculated using a transfer matrix formalism. This field penetration is then used to derive the photon absorption rate profile (bottom). ................................................................. 42
4.2 Reflectance and fractional absorbance for each layer in the solar cell. ......................................................... 43
4.3 Relevant processes for CT-exciton modeling. .................................................................................. 45
4.4 Thickness dependence of the short circuit current $J_{SC}$ with varying Langevin recombination efficiency $r_{eff}$. A purely optical simulation is also shown. The simulations are compared with measurements (□) by Gilot et al. [83] .................................................................................. 51
4.5 Dissociation probability according to the Onsager-Braun theory depending on the electrical field for several initial pair separation distances $a$. The decay rate has been fixed at $k_f = 1 \times 10^5 \text{s}^{-1}$. .................................................................................. 52
4.6 Comparison of a simulated and experimentally measured current-voltage curve for an active layer thickness of 70 nm. The parameters used for this simulation are summed up in table 1 and 2. .................................................................................. 53
4.7 Sensitivity of the current density for a thickness dependent simulation. .................................................................................. 54
4.8 Sensitivity of the current density for the current-voltage curve. ......................................................... 56
4.9 Normalized comparison between measured and simulated J-V curves for different active layer thickness. .................................................................................. 57
4.10 Sensitivity of the short-circuit current during turn-on. .................................................................................. 58
4.11 Sensitivity of the short-circuit current during turn-off. .................................................................................. 59
4.12 Semi-logarithmic plot of the turn-off behavior shown in figure 4.11. This plot can be used to extract the mobilities of electrons and holes. .................................................................................. 60
4.13 Semi-logarithmic plot of the raw data of the turn-off behavior of a fast photodiode (Osram SFH 203 P). The transient photocurrent is measured over 5 orders of magnitude. Every sensitivity setting is reliable over a certain range only. The current has been measured over 25 µs in 10 ns steps. The influence of the different settings of the sensitivity is shown using different colors. As a guide for the eye, averaged transient photocurrent is shown as the dashed line.

4.14 Semi-logarithmic plot of the turn-off behavior of the P3HT:PCBM solar cell under different illumination intensities. The photocurrent range was from $3.3 \times 10^{-5}$ A (@ 2.6 V) to $1.8 \times 10^{-4}$ A (@ 3.8 V). When normalized, the time evolution of the transient photocurrent is independent on the illumination intensity.

4.15 Transient photocurrent (a) depends linearly on the applied voltage. After rescaling it for the different internal electric field (b). Therefore the turn-off behavior depends on the internal electric field only and can thus be described with the mobility $\mu$ of the charge carriers. The curve for $V_{\text{appl.}}$=0.5 V decreases faster, because the device characteristics changes from a solar cell to a diode, therefore charge carriers get injected and thus this curve cannot be compared to the other ones.

5.1 The influence of the gate-bias stress on the threshold Voltage $V_{\text{th}}$ has been measured in two ways: (i) the decrease of $I_d(t)$ over time has been measured, (ii) $V_{\text{th}}$ has been calculated from the shift of the transfer curve over time. These two methods agree with each other in determining the threshold voltage shift $\Delta V_{\text{th}}$.

5.2 Different mechanism at work resulting in gate-bias stress effects. This compilation of graphs on these two pages show the device setup (first row), the measured transfer curves (middle row) and the drain current $I_d(t)$ or relative threshold voltage shift over time (bottom row). **Device A:** ($C_i=6.6 \times 10^{-5}$ F/m$^2$). Transfer curves at various temperatures before and after stress do not show any gate-bias stress effects. The same for the measurement of the drain current. $I_d(t)$ is stable over the measured time with a slight increase which is attributed to self heating of the device.

5.3 Comparison of different trap density-of-states for the 3 devices as calculated from transfer curves taken at different temperatures. The two thin-film devices have essentially the same trap DOS, whereas in the single crystal OFET the trap DOS is one to two orders of magnitude lower.

6.1 The four PDIF-CN$_2$ based device structures employed in this study.

6.2 High performance FET with a PDIF-CN$_2$ single crystal on Cytop with a mobility of up to 6 cm$^2$/Vs. The quality is reflected in the turn-on and threshold voltage close to 0V, the very steep subthreshold swing of 0.45V/dec and the high on/off ratio exceeding $10^8$. Simulations are done with the same DOS for all temperatures and lie on the measured curves. ($V_d = 25V$, $L = 50 \mu m$, $W = 520 \mu m$)

6.3 Representative transfer plots for an evaporated PDIF-CN$_2$ TFT on various gate dielectrics. The TFT on Cytop has the highest on-off ratio, steepest subthreshold slope and highest mobility of the three evaporated FETs. ($V_d = 20 V$, $L = 450 \mu m$, $W = 1000 \mu m$)

6.4 Representative transfer plots for an evaporated PDIF-CN$_2$ TFT on Cytop. The transfer curves, measured at different temperatures, are well simulated by the same DOS (black lines). The corresponding DOS is shown in figure 6.10 (blue line). ($V_d = 20 V$, $L = 450 \mu m$, $W = 1000 \mu m$)
6.5 Representative transfer curves for three evaporated TFTs. The devices have been fabricated in high vacuum and subsequently have been exposed to oxygen and air. For all 3 dielectrics the transfer curves shift to the left; exposure to oxygen and air leads to more free charge carriers in the conduction channel of the FET. (The different values of the device capacitance have been taken into account.) 82

6.6 Gate-bias-stress induced reduction of the normalized source-drain current for PDIF-CN$_2$ thin-film transistors. TFTs on HMDS and on bare SiO$_2$ respond similarly to gate-bias-stress, whereas TFTs with Cytop are much less affected. For comparison pentacene TFTs on bare SiO$_2$ and Cytop are shown. [62] They respond much stronger to gate-bias-stress. 83

6.7 Transfer characteristics at different temperatures indicate the presence of discrete trap states. Top: Temperature dependent transfer curves for a spin-coated PDIF-CN$_2$ TFT. The sample was heated to 310K and then cooled to 240K in 10K steps. Bottom: Simulation (black) for three temperatures. The additional black curve was simulated without the gaussian trap state, thus highlighting the influence of these $5 \times 10^{19}$/cm$^3$ gaussian broadened trap states at 0.24 eV below the conduction band (CB). ($V_d = 50$ V, $L = 50$ µm, $W = 900$ µm) 84

6.8 Temperature dependent mobility of the spin-coated, evaporated and single crystal FET devices. The single crystal has by far the highest mobility, increasing with lower temperature. The evaporated TFTs show a similar temperature behavior on all substrates which means a higher mobility at higher temperatures. The mobility of the spin-coated device stays constant over the whole measurement range. 85

6.9 Transfer characteristics of PDIF-CN$_2$ based FETs with different degrees of order. The single crystal and the TFTs on Cytop show the best transistor performance with a high on-off ratio and a sharp turn-on at 0V. The transfer curves of the other evaporated thin-film transistors are slightly shifted, most for the HMDS treated sample. The spin-coated transistor has a broad turn-on indicating the presence of a large number of trap states. (The drain current has been corrected for length and width of the FETs and the applied drain voltage. Additionally the different capacitances have been taken into account.) 86

6.10 Trap density of states for all PDIF-CN$_2$ n-type FETs studied in this chapter. The single crystal (red) has a 2 to 3 orders of magnitude lower trap DOS compared to the polycrystalline thin-film FETs. The Evaporated thin-film on Cytop has the lowest trap DOS of the thin-film FETs. The spin-coated FETs are dominated by a gaussian-shaped trap level around $-0.24$ eV. Otherwise, the trap DOS of the spin-coated FET is comparable to the evaporated ones. Two typical trap DOS of polycrystalline and amorphous silicon (a-Si:H) are shown, which are comparable to the DOS of the organic semiconductors. [162, 163] 88

7.1 Normalized transfer curve of the analysed p- and n-type organic FETs. The steeper the subthreshold slope, the lower the trap DOS. The higher the conductance, the higher the mobility. Organic single crystal FETs have a very steep subthreshold region and high mobility, whereas the evaporated TFTs have a broad subthreshold region and lower mobility. The inkjet printed polymers have a subthreshold region close to that of single crystals, but a mobility close to that of TFTs. The two inorganic FETs have a very broad subthreshold region. To compare the various dielectrics, device geometries and applied voltages, the sheet conductance is plotted against the induced charge carrier density, given by applied gate voltage times capacitance. 98

7.2 Mobility of the FETs shown in Fig. 7.1. The red squares (single crystals) and triangles (TFTs) are for the materials studied in this paper. Whereas the range indicates the highest and lowest value which can be expected for a certain material. The mobility range easily spans several orders of magnitude even in the same material. A wide body of references has been used for this graph. [19, 62, 135, 159, 198–200, 203–213] 100
7.3 Direct representation of the free vs. total charge carrier density in the studied FETs through fully normalized and shifted transfer curves. The deviation from the theoretical maximum directly reflects the number of trap states. Single crystal FETs (red) are very close to the theoretical limit and the limit is even reached for rubrene. The evaporated TFTs (blue) are much more dominated by traps. The inkjet printed polymers (orange) are in between the single crystal FETs and evaporated TFTs. All inorganic FETs, except for n-type a-Si are very much trap dominated. 101

7.4 Trap density of states for p- and n-type FETs. It is similar for p- and n-type materials. The 2-3 orders of magnitude gap between single crystal FETs and evaporated TFTs is closed by the inkjet printed polymeric TFTs. The inorganic FETs have a high trap DOS close to the transport level, which dominates the transfer curve. 102

7.5 Trap density of states for p- and n-type organic materials, not only FETs. Rubrene has the same trap DOS in the bulk (SCLC measurement) as close to the surface (FET). The trap DOS in bulk-heterojunction solar cells (P3HT:PCBM and PCDTBT:PCBM) is as low as in polymeric TFTs. PDIF-CN$_2$ single crystals are already very close to the bulk trap DOS value, but there is still some room for improvement. 105


Bibliography


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4. *Transistor Characteristics of N-Type Single Crystal OFET: Polyera N400 and N800*
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