LATERAL AND VERTICAL ORGANIC TRANSISTORS

A dissertation submitted to
Kent State University in partial
fulfillment of the requirements for the
degree of Doctor of Philosophy

by

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May 2017
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ACKNOWLEDGMENTS

I would like to express my special appreciation and thanks to my advisor assistant Professor Dr. Björn Lüssem, you have been a tremendous mentor for me. The door to Dr. Lüssem office was always open whenever I ran into a trouble spot or had a question about my research or writing. I would like to thank you for encouraging my research and for allowing me to grow as a research scientist. I would also like to thank my group members, Dr. Chang-Min Keum and Ph.D student Vikash Kaphle and Kashi Subedi. A special thanks to my close friend and group member, Ph.D student Shiyi Liu.

Also, I would like to thank The Higher Committee For Education Development in Iraq (HCED) and the National Science Foundation under grant no. 1639073 for support. I would like to thank Dr. Ina T. Martin., Director of More center, Case Western Reserve University and Wade Aldhizer, Research Machinist Specialist, Kent State University.

Words cannot express how grateful I am to my father, mother, brothers, and sisters for all of the sacrifices that you have made on my behalf. Your prayer for me was what sustained me thus far. I would also like to thank all of my friends who supported me in writing, and incented me to strive towards my goal. At the end I would like express appreciation to my beloved wife Abeer Al-khalid who spent sleepless nights with and was always my support in the moments when there was no one to answer my queries.
PUBLICATIONS AND CONFERENCES


CHAPTER 1

INTRODUCTION

The digital revolution impacts humans of all age groups and allows for a daily use of a vast variety of electronic devices, such as mobile phones, computers, tablets, and televisions. The development of electronic devices is driven by an ever-ongoing improvement and downscaling of the most fundamental electronic component - the field-effect transistor. The field-effect transistor (FET) was invented in 1947 at Bell Laboratories by a team led by physicists W. Shockley, J. Bardeen, and W. Brattain. FETs use electric fields to control the charge carrier density of a semiconductor, which allows to switch the current flowing through a semiconductor on and off. These first transistors were point-contact transistors operating similar to junction-field effect transistors as known today.

20 years after this invention, the metal-oxide-semiconductor field-effect transistor (MOSFET) was invented by Dawon Kahng and Martin Atalla in 1959. These transistors have the benefit of very low gate currents and hence low-power switching properties, which made them to the backbone of modern electronic devices.

Manufacturing of electronic components is mainly based on conventional (inorganic) semiconductors, such as Si, Ge, and GaAs. In particular Si is used widely due to its abundance and due to the almost ideal properties of its oxide - SiO$_2$ - which presented a major benefit in the beginning of the development of integrated circuits.

However, Si needs complex and expensive procedures to purify it, and manufacturing of most conventional semiconductors generates residuals harmful to the environment. Furthermore, over the last 20 years the price of an Si chip has not decreased further due to a limitation of producing.

Although silicon-based electronics has seen an incredible success during the last decades, it has a couple of drawbacks. Silicon is rigid and brittle, it is a very inefficient light emitter, and requires enormous investments to establish fabrication. These drawbacks opened the way for a new class of materials to enter the market, i.e. organic semiconductors used for example in flexible displays, wearable electronics, or bio-compatible sensor networks.

Research in organic semiconductors started in the 1960’s when researchers studied the electroluminescence of an organic diode. In 1980, the development in organic semiconductors has led to performance properties that are competitive with amorphous silicon
(a-Si), increasing their possibility to be used in commercial applications. Organic semiconductors have unique features, such as low processing cost, low weight, and mechanical flexibility. These features have attracted a large interest due to the promise of large area and flexible electronic applications. Due to large efforts both in the developments of new materials and in device processing, the industry has already started producing several organic electronic components, such as organic field-effect transistors (OFETs) used as driving electronics in flexible displays, organic LEDs (OLEDs), and organic photovoltaic (OPV).

Fundamentals of organic devices will be studied in the present work. The thesis will focus on conventional transistors (OFETs) and vertical organic transistors. By a systematic variation of the device structure the fundamental working mechanism of these transistors will be clarified.

This dissertation consists of seven chapters. Chapter one serves as an introduction to organic semiconductors, their electronic structure, as well as their charge transport mechanism. In chapter two, the theory of organic devices is presented, in particular for organic field-effect transistors (OFETs), organic permeable base transistor (OPBTs), and p-i-n organic diodes. The details of experimental preparation of these devices and their characterization will be discussed in chapter three.

In the following chapters, the research results will be discussed. Chapter four studies the effect of doping on minority charge carrier injection and conduction in OFETs. It will be proposed that minority currents are generated by the Zener tunneling effect. Chapter five studies the charge transport and characteristics of Schottky diodes. In the chapter six, the transfer and output characteristics of organic permeable base transistors (OPBTs) will be discussed. It will be shown how these transistors can be improved to show high ON-state currents and transconductance, which is a necessary pre-requisite for high-speed switching of organic transistors. A summary and outlook will be given in the last chapter of this thesis.
CHAPTER 2

PHYSICS OF ORGANIC SEMICONDUCTORS

The most fundamental principles of organic semiconductor physics are presented in this chapter. The electronic structure of organic semiconductor will be discussed, as well as charge transport and charge carrier injection from metal electrodes. The process of doping in organic semiconductors will be explained briefly as well.

2.1 Basic Principles of Organic Semiconductors

The term "organic semiconductors" refers to organic materials which possess the ability to conduct electrons. However, as organic molecules are bound by weak van-der-waals forces only, electronic coupling between neighbouring molecules is small, which leads to a very low electrical conductivity of organic semiconductors in the range of $10^{-10}$ $(\Omega \text{cm})^{-1}$.

Organic semiconductors can be classified into two categories: polymers and small molecule materials. The difference between these two categories lies in their chemical structure. Polymers are constituted by the repetition of a fundamental unit, the monomer, yielding a long chain with a molecular weight $M_w > 900$ g/mol [11]. In contrast, small molecule materials are much smaller ($M_w < 900$ g/mol). Whereas thin films of polymers are processed by wet-chemical means, e.g., by spin-coating from a solution of appropriate organic solvents, thin films of small molecules can be deposited by thermal evaporation as well.

2.2 Electronic Structure of Organic Semiconductors

In this section, the electronic structure of organic semiconductors is discussed, which is of critical importance to develop an understanding of charge carrier transport in organic semiconductors. The formation of energy levels in isolated molecules will describe first, before discussing how organic solids are formed and how charge carriers can move in the solid.

2.2.1 Formation of Molecular Orbitals and Energy Levels

To understand how molecular orbitals and chemical bonds between atoms are formed, the electronic structure of the ionized hydrogen molecule is discussed first. The molecule consists of two hydrogen atoms (a and b). The total wave function of the hydrogen molecule has the form $\Psi = \Psi(\vec{r}_a, \vec{R}_a, \vec{R}_b)$, where $\vec{R}_a$ and $\vec{R}_b$ are the spatial vectors of the
atomic nuclei and $\vec{r}$ is the spatial coordinate of the electron. The Schrödinger equation for ionized hydrogen molecule can be expressed as

$$\hat{H}\Psi = \hat{H}_\vec{r}\Psi + \hat{H}_{Ra}\Psi + \hat{H}_{Rb}\Psi = E\Psi \quad (2.1)$$

where the Hamiltonian operator $\hat{H}$ is a combination of the kinetic and potential energy of atomic nuclei and electrons. $\hat{H}_\vec{r}$ is the Hamiltonian operator of the electrons, $\hat{H}_{Ra}$ is the Hamiltonian operator of the nuclei $a$, and $\hat{H}_{Rb}$ is the Hamiltonian operator of the nuclei $b$. Although the Schrödinger equation can’t be solved analytically for $\Psi$, it can be simplified by applying the Born-Oppenheimer approximation [12]. Since the mass of electron is much smaller than the mass of the nuclei, the motion of an electron is significantly faster than the motion of a nuclei and hence the electrons almost instantaneously react to any movement of the nuclei. Therefore, the total wave function can be separated into an electronic and a vibronic part, i.e. it can be written as $\Psi(\vec{r}, \vec{R}_a, \vec{R}_b) = \Psi(\vec{r})\Psi(\vec{R}_a, \vec{R}_b)$. Eq.2.1 can be simplified to

$$\hat{H}\Psi = \hat{H}_{elec}\Psi + \hat{H}_{vib}\Psi + \hat{H}_{rot}\Psi = E_{elec}\Psi + E_{vib}\Psi + E_{rot}\Psi \quad (2.2)$$

The electronic part of the hydrogen molecule can be constructed by the atomic orbitals of atomic hydrogen, which is called the Linear Combination of Atomic Orbitals (LCAO). In this case, the electronic wave function becomes

$$\Psi(\vec{r}) = \sum_{a,b} c_i \psi_i \quad (2.3)$$

where $\Psi_a$ and $\Psi_b$ are the hydrogenic atomic orbitals (atomic wave functions) and $c_a$ and $c_b$ are coefficients. The variational method can be used to find these coefficients, which is straight forward for the hydrogen molecule. Since the two atoms are identical, the probability that the electron is near molecule $a$ must be equal to the probability that the electron is near molecule $b$. The probabilities are given by the square of the coefficients, $|c_a|^2$ and $|c_b|^2$. Consider two possibilities that satisfy the condition $|c_a|^2 = |c_b|^2$, i.e. $c_a = c_b = c_+$ and $c_a = -c_b = c$. These two cases produce a symmetric wavefunction $\Psi_+$ and an anti-symmetric wavefunction $\Psi_-.$

$$\Psi_+ = c_+(\Psi_a + \Psi_b) \quad \text{and} \quad \Psi_- = c_-(\Psi_a - \Psi_b) \quad (2.4)$$

$\Psi_+$ and $\Psi_-$ differ in the probability to find an electron between the two nuclei. For $\Psi_+$ the probability density is enhanced between the two nuclei, whereas it is diminished for
2.2.2 Hybridization of Carbon

Molecular semiconductors are based on hydrocarbons which are composed of carbon and hydrogen. The huge variety of aromatic hydrocarbons compounds, e.g. \( \text{C}_2\text{H}_2 \), \( \text{C}_2\text{H}_4 \), or \( \text{C}_2\text{H}_6 \), is caused by the formation of carbon atomic hybrid orbitals. Hybridization is the creation of new atomic orbitals by linear combination of two or more nearby atomic orbitals of the same kind. The atomic number of carbon is 6 and its ground state configuration is \( 1s^22s^22p^2 \). Hence, the 2p sub-shell has only two electrons and is not completely filled. To minimize its energy, new hybrid orbitals are formed by a linear combination of electron wave functions of the 2s and 2p orbitals.

Depending on the precise mixing of s and p orbitals, carbon can form \( \text{sp}^3 \), \( \text{sp}^2 \), and \( \text{sp} \) hybrid orbitals. Figure 2.2 shows the mechanism of carbon hybridization. In the \( \text{sp}^3 \) hybridization, the hybrid orbital is formed from one electron of the 2s orbital and
three electrons of the 2p orbital. The four sp\(^3\) hybrid orbitals form a tetrahedron shape with a bonding angle of 109.5°. Carbon sp\(^2\) hybridization occurs when one electron from the 2s orbital hybridizes with two electrons from the 2p orbital. The three sp\(^2\) hybrid orbitals form a triangular shape (i.e. these hybrid orbitals are all in plane and the remaining p orbital perpendicularly to this plane) with a bonding angle of 120°. Carbon sp hybridization occurs when one electron from the 2s orbital hybridizes with one electron from the 2p orbital, as shown in the bottom of Figure 2.2. The sp orbitals form an angle 180° and the remaining p orbitals are oriented perpendicular to the orientation of the sp orbitals.

2.2.3 Formation of π- and σ-Bounds

The formation of π- and σ-bonds can be explained by hybridization as well. Ethylene is a simple example of an aromatic compounds. Ethylene consists of a double bonded pair of carbon atoms which are both sp\(^2\) hybridized and has two carbon-carbon bonds, as shown in Figure 2.3a. One bond can be attributed to the bonding of hybridized sp\(^2\) orbital, which is known as σ-bond. The second bond is formed by overlapping unhybridized \(p_x\) orbitals, which is known as π-bond [13].
2.2.4 Delocalized π-Electron System

By increasing the molecular size, their electron density becomes more complicated. Benzene is an example of the bonding structure with both single and double bonds. Carbon atoms in a benzene ring are bound by covalent bonds, as shown in Figure 2.3b. The carbon atoms are sp$_2$ hybridized, i.e. three sp$_2$ orbitals are formed. Additionally, the p$_z$ orbital remains unhybridized and is oriented normal to the plane of the sp$_2$ orbitals. Most electrons existing in the benzene ring are bound in these hybrid orbitals and therefore form covalent σ-bonds. However, a small number of electrons remain in the p$_z$ orbitals. These electrons form π-bonds that are delocalized across the whole benzene ring. This delocalization of electrons along the molecule provides a way to move charge across the molecule.

The individual p$_z$ orbitals of all 6 carbon atoms in the benzene ring can be combined differently to form different molecular orbitals with varying energy, as shown in Figure 2.3b. These orbitals are filled with the 6 electrons donated by the p$_z$ orbitals to the molecular state. The highest occupied molecular orbital (HOMO) is usually formed as
a bonding orbital, whereas the lowest unoccupied molecular orbital (LUMO) is an antibonding orbital. The energy difference between HOMO and LUMO mostly depends on the spatial extend of the conjugated $\pi$-system. The more extended the $\pi$-system is, the smaller the energy difference becomes between the HOMO and LUMO (bandgap) of the organic semiconductor[14].

The formation of energy levels of single organic molecules has been briefly discussed. In the next section, the formation of organic solids will be explained.

2.2.5 From Single Molecules to Molecular Solids

In the following it will be discussed how the electronic structure of single molecule changes if it becomes part of a thin organic film. Figure 2.4a shows the electric potential of an individual molecule. The potential well is formed by the superposition of the potential of the nuclei of the molecule and the effective average potential of all other electrons [5][2]. The potential wells of the nuclei are merged together in the upper part to form a delocalized molecular orbital.

When molecules are brought close and form an organic solid, the electronic structure changes to the structure sketched in Figure 2.4 b and c. Since the molecules in many organic solids interact only by weak van der Waals forces, the wave functions of molecular orbitals (MOs) are usually localized in each molecule. Only in some cases, in particular for organic single crystals with very high purity, extended bands are formed, which however are very narrow (bandwidth of $< 0.2$ eV) [15][16][17]. Thus, in most cases, the electronic structure of an organic solid preserves that of the individual molecule and the validity of usual band theory is often limited [17][18].

2.2.6 Polarization Effects

The change in energy levels from the isolated molecule to a molecular solid is shown in Figure 2.4 b and c. Here, $I_g$ and $A_g$ denote the ionization energy and electron affinity of the molecules in the gas phase, whereas $I_s$ and $A_s$ denote the ionization potential and electron affinity of the solid. The difference between the ionization energy and electron affinity in the gas and solid phase can be explained by polarization effects.

When an hole (electron) is introduced into the HOMO (LUMO) state of the solid, the molecular structure and the lattice of the solid are deformed. Polaron are formed, which are quasi-particles incorporating the charge carrier itself and its associated relaxation processes. These polarons include polarization effects due to an electronic rearrangement, molecular deformation, and lattice polarization.

Due to these polarization effects, the ionization energy and the electron affinity of the solid are different to the ones of an isolated molecule [19][20] (see Figure 2.4). The
ionization energy of the solid is lowered by a polarization energy $P^+$, while electron affinity is increased by a polarization energy $P^-$ in comparison to single molecule values, i.e. [2]

$$I_s = I_g - P^+ \quad \text{ and } \quad A_s = A_g + P^-$$  \hspace{1cm} (2.5)

The polarization effects can be classified by the time scales of the relaxation process. When a charge carrier is introduced into a neutral molecule, neighboring molecules are polarized, which forms a dipole. The formation of such an electronic polaron occurs in short time scales of $10^{-16}$ s to $10^{-15}$ s and their interaction energy is up to 1 eV. The deformation of the molecule (vibronic polarization) is much slower, and has a relaxation time in the range of $10^{-14}$ s and an interaction energy in the range of 0.1 to 0.3 eV. The slowest polarization effect is lattice polarization, which corresponds to the interaction of charge carriers with the lattice forming a lattice polaron. The relaxation time of the process is in the range of $10^{-13}$ s to $10^{-11}$ s and the required energy for this process is in the range of 10 to 30 meV.

2.3 Charge Transport in Organic Semiconductors

Charge carrier transport in organic semiconductor materials whose constituent molecules are kept together mainly by weak van der Waals interactions is much harder to describe than charge carrier transport in delocalized bands of inorganic semiconductors.

Charge transport is quantified via the charge carrier mobility $\mu$ that reflects the ease
for holes or electrons to move in a conducting medium. When an electric field $F$ is applied to an isotropic material with a homogeneous distribution of charge carrier distribution $n$, the current density is defined by

$$j = \sigma F = qnv_d$$

(2.6)

where $\sigma$ is the conductivity, $q$ is the electron charge, and the charges drift in the opposite direction to the field with a drift velocity $v_d$. The drift velocity depends linearly on the electric field

$$v_d = \mu F$$

(2.7)

and hence the electric conductivity becomes

$$\sigma = qn\mu$$

(2.8)

In metals and crystalline semiconductors, charge carriers are scattered by phonons and impurities. [21]. The charge carrier mobility becomes

$$\mu = \frac{q\tau}{m^*}$$

(2.9)

where $\tau$ is the mean relaxation time between two scatter events collisions and $m^*$ is the effective electron mass. The mobility in metals depends on temperature. At high temperatures, the probability of electron collision increases due to the vibration of lattice, thus the mobility will decrease because of a shorter mean relaxation time. Eq. 2.9, a result of the so called Drude’s model used in metals and inorganic semiconductors, can be used for crystalline organic semiconductors as well.

### 2.3.1 Charge Transport in Crystalline Organic Semiconductors

Charge carrier transport in crystalline or single crystal organic semiconductor is often described by band transport [22]. Charge carriers are de-localized over the lattice defined by the energy band structure as a function of wave vector $K$. At the band extrema, the $E(K)$ dispersion can be approximated by a parabolic expression, i.e. [3]:

$$E(K) = \frac{\hbar^2 K^2}{2m^*}$$

(2.10)

with the effective mass $m^*$ of the charge carriers, which is defined as

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{d^2E}{d^2K}$$

(2.11)
in crystalline materials, the electron in a periodic potential is accelerated relative to
the lattice in an applied electric field. The charge carrier mobility is limited by lattice
scattering and is given by
\[ \mu = \frac{q\tau(T)}{m^*} = \frac{q\lambda}{\sqrt{3k_B T m^*}} \] (2.12)
where \( \tau \) and \( \lambda \) are the mean free time and mean free path between two collision, respectively.

Figure 2.5 exhibits the temperature dependence of ultra-pure naphthalene [3][22]. The
charge carrier mobility shows a strong temperature dependence. At high temperatures,
the charge mobility is limited by phonon scattering and the charge mobility decreases
with increasing temperature, since the scattering probability increases with increasing
occupation of the phonon states. Standard inorganic band theory predicts that this be-
havior leads to a law \( \mu \propto T^{-3/2} \) [3]. However, for most organic semiconductors, the
temperature dependence of the mobility deviates from the ideal law \( \mu \propto T^{-3/2} \) and the n
values (power dependence on T) are in the range 0 to -3, which is explained by a strong
coupling of the charge carriers to lattice deformations. [3][23][24]. At low temperatures,
scattering of charge carriers at charged defects (ions) becomes dominant[3][22]. In crys-
talline organic semiconductors, ions can form through capture of charge carriers in traps,
which are still existing even in highly purified materials. Scattering at ionized defects can
be described by Rutherford scattering, which relies on the Coulomb interaction between
the traps and charge carriers. Hence, at low temperatures, the charge mobility decreases
with decreasing temperature following the law \( \mu \propto T^{3/2} \).

Charge transport in organic semiconductors can only be discussed in the framework
of band transport if two conditions are fulfilled:

1. the mean free time (\( \tau \)) must be larger than \( \hbar/W \) (\( \tau \gg \hbar/W \); where W is the energy
   band width)

2. the mean free path \( \lambda \) of the charge carriers must be large in comparison to the
   lattice constant a (\( \lambda \gg a \)) [3]

These conditions are usually only fulfilled for ultrapure crystals of organic semicon-
ductors. In particular in disordered organic semiconductors charge carriers are localised
on the individual molecule and band transport can’t be applied any more.

2.3.2 Charge Transport in Disordered Organic Semiconductors

In disordered organic semiconductors, all charge carriers are localized and move
through the material by hopping from one localized state to the next [24], as shown
Figure 2.5: The temperature dependence of the charge mobilities for the holes $\mu^+$ and the electrons $\mu^-$ in ultra-pure naphthalene with an electric field applied parallel to crystal structure. Picture copied from Ref. [3] with the permission of John Wiley and Sons, copyright © 2005 Wiley-VCH Verlag GmbH Co. KGaA.

in Figure 2.6. For hopping transport, charge carriers can hop from one site to the next provided the original site is occupied and the target site is unoccupied. Charge carrier transport can thus be expressed by the master equation[25]

$$\frac{\partial}{\partial t} f_i(t) = -\sum_{j \neq i} W_{ji} f(t)[1 - f_i(t)] + \sum_{j \neq i} W_{ij} f(t)[1 - f_i(t)] - \lambda_i f_i(t)$$

(2.13)

where $f_i(t)$ denotes the occupation probability of site (i), $[1 - f_i(t)]$ denotes the probability that site (j) is empty, $W_{ij}$ represents the rate transition from site i to site j, and $\lambda_i$ reflects the decay rate of the excitation at site i. The hopping rate $W_{ij}$ can be described by the Miller-Abrahams equation. This expression is related to a phonon-assisted tunneling mechanism, and is given by [25][24]

$$W_{ij} = \nu_0 \exp(-2\gamma |R_{ij}|) \left\{ \begin{array}{ll} \exp\left(-\frac{(\varepsilon_j - \varepsilon_i)}{K_B T}\right) & \forall \varepsilon_j > \varepsilon_i \\ 1 & \text{else} \end{array} \right.$$  

(2.14)
Figure 2.6: Schematic which illustrates the hopping transport in disordered organic semiconductors with a Gaussian density of states (DOS) (cf. Eq. 2.17). Charge carriers hop along the direction of electric field (F) either to neighboring molecular sites with lower energies or to neighboring molecular sites with higher energies (cf. Eq. 2.20). Picture copied from Ref. [3] with the permission of John Wiley and Sons, copyright © 2005 Wiley-VCH Verlag GmbH Co. KGaA.

where $\nu_0$ denotes the attempt to escape frequency, which in the range of $10^{12}$ s$^{-1}$ [26]. $R_{ij}$ is the distance between sites i and j, $\gamma$ is the factor of overlap integral of the wave functions, and $\varepsilon_i$ and $\varepsilon_j$ are the energy levels of molecule sites. Equation 2.14 includes two exponentially decaying factors. The first term $\exp(-2\gamma|R_{ij}|)$ represents the tunneling process and accounts for the distance between the sites. The second exponential term is the Boltzmann factor for thermal activation, which can be understood as the probability that a charge carrier is thermally activated. This term of the rate vanishes, i.e. it equals to 1, when $\varepsilon_i < \varepsilon_j$, i.e. the target site j lies energetically deeper than the original site [25].

The Miller-Abrahams model is valid for weak electron-phonon coupling and low temperatures. In this model it is assumed that the charge carrier hops upward or downward in energy sites by absorption or emission of a single phonon. In other words, this model can be applied only for $(\varepsilon_j - \varepsilon_i)$ values smaller than the maximum Debye energy of the acoustical phonons and the energy of the optical phonon. To improve the Miller-Abrahams model, Marcus proposed another model that can be applied for large electron-phonon coupling and high temperatures. The Marcus rate is given by [27][24]

$$W_{ij} = \frac{t^2}{\hbar} \left[ \frac{\pi}{k_B T \lambda} \right]^{1/2} \exp \left[ -\frac{(\lambda + \varepsilon_j - \varepsilon_i)^2}{4\lambda k_B T} \right]$$

(2.15)

where $\lambda$ is the reorganization energy [28][29][30] and $t$ is related to the overlap integral,
where
\[ t = t_0 \exp(-\gamma R_{ij}) \]  

(2.16)

Charge carriers transport in amorphous organic semiconductors is described by hopping transport between localized states with specific energetic and spatial distribution functions. The Monte-Carlo approach (MC) [31] [32][33] promoted by Bässler et al. is a numerical model to study a hopping transport. According to Bässler, disorder is introduced by attributing a random energy \( \varepsilon \) picked from a distribution of states to each site, usually assumed to be of Gaussian shape. Hence, the energies for charge transport states are defined in terms of a Gaussian distribution function \( G(\varepsilon) \) of the density of states (DOS) [3]

\[ G(\varepsilon) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{\exp\left(-\frac{\varepsilon^2}{2\sigma^2}\right)} \]  

(2.17)

where \( \sigma \) is the DOS standard deviation and \( \varepsilon \) is the energy of DOS. As hopping is thermally activated, most derived expressions for the DOS contain the normalized width \( \tilde{\sigma} = \frac{\sigma}{k_B T} \). When sites have an energy equal or smaller than \( \langle \varepsilon_{\infty} \rangle = -\frac{\sigma^2}{k_B T} \), the hopping transport will need an activation energy with a barrier of the same order of magnitude \( \langle \varepsilon_{\infty} \rangle \) [31]. \( \frac{\sigma^2}{k_B T} \) is the equilibrium energy of charge carriers with \( F=0 \) within the density of states \( G(\varepsilon) \).

Bässler et al. were able to show that at zero electric fields, the Monte Carlo results can be fitted by the following equation for the charge carrier mobility

\[ \mu(T) = \mu_0 \exp\left[-\left(\frac{2\sigma}{3k_B T}\right)^2\right] = \mu_0 \exp\left[-\left(\frac{T_0}{T}\right)^2\right] \]  

(2.18)

where

\[ T_0 = \frac{2\sigma}{3k_B} \]  

(2.19)

At high temperatures \( T \) (i.e. \( T \rightarrow \infty \)), the mobility of a disorder free semiconductor equals \( \mu_0 \). The temperature increases the probability of charge carriers overcoming the barriers introduced by the energetic disorder in the system [3]. In the presence of external electric fields, the barrier for upward energy hops will be lowered, which allows the charge carriers to escape states in the tail of the DOS and, according to Eq. 2.20, increases the hopping rate. When the extent of energetic disorder grows, the electric field dependence becomes stronger. In the presence of energetic disorder, the Monte Carlo (MC) results yield a Poole-Frenkel behavior and the mobility is proportional to \( F^{-\frac{3}{2}} \) [34].
The general behavior of the charge mobility as a function of electric field and temperature in the presence of disorder becomes [31]

\[
\mu(\sigma, \Sigma, F, T) = \mu_0 \exp \left[ -\left( \frac{2\sigma}{3K_BT} \right)^2 \exp \left[ C \left( \frac{\sigma}{K_BT}^2 - 2.25 \right) \sqrt{F} \right] \right] \text{ for } \Sigma < 1.5
\]

\[
\mu(\sigma, \Sigma, F, T) = \mu_0 \exp \left[ -\left( \frac{2\sigma}{3K_BT} \right)^2 \exp \left[ C \left( \frac{\sigma}{K_BT}^2 - \Sigma^2 \right) \sqrt{F} \right] \right] \text{ for } \Sigma \geq 1.5
\]

where \( \Sigma \) is the positional disorder and \( C \) is a numerical parameter. When \( F=0 \) Equation 2.20 will yield Eq. 2.18. The key prediction of Equation 2.20 are that \( \ln \mu \) is proportional to \( \sqrt{\frac{F}{T^2}} \). The electric field is linked to positional disorder because the higher directionality imposed by the field prevents the charge from avoiding the sites that are only weakly electronic coupled. If the range of positional disorder \( \Sigma \) is larger than the width of energetic disorder \( \sigma \), the mobility will decrease with an increase in the electric field (c.f. Eq.2.20). The results of Monte Carlo simulations by Bössler present that the charge mobility obeys a Poole-Frenkel behavior. A main limitation of the Monte Carlo is that the energies are distributed randomly over the sites [3].

2.4 Doping of Organic Semiconductors

Doping in semiconductor technology can be described as the intentional addition of impurities into the semiconductor material to adjust and control its electrical properties, such as electrical conductivity. Organic doping resembles doping in inorganic semiconductors in the basic principles, but there are significant differences due to the difference in the structure of organic and inorganic semiconductors. In particular, the large Coulomb correlation between charge carriers, and strong polaronic coupling between localized hopping states lead to pronounced differences in the description of organic and inorganic semiconductors[4]. The working principle of doping is shown in Figure 2.7. Depending on the position of HOMO or LUMO levels of the dopant molecules in relation to the HOMO or LUMO levels of the matrix material, the matrix material is n-doped or p-doped. If the HOMO (LUMO) level of dopant molecule is higher(lower) than the LUMO (HOMO) level of the matrix material, electrons are added (removed) from the matrix. For n-type doping, the dopant donates electrons to the LUMO level of matrix. For p-type doping, the dopant withdraws electrons from the HOMO of the matrix (i.e., holes are generated).

Doping of organic semiconductors is studied by many groups. Yamamoto et al. was the first to demonstrate doping in organic semiconductors by using strongly oxidizing gases as a p-type dopants [35]. Then, Haddon et al., introduced alkali metals as a n-type
Figure 2.7: Schematic representation of the doping process for molecular p-type (left) and n-type doping (right). Picture adapted from Ref. [4].

doping [36]. Although both groups saw an increase in electrical conductivity of organic thin films, they reported several difficulties. For example, dopants tend to diffuse in the matrix material and it is difficult to control the rate of deposition of dopant and matrix. Nowadays, doping of organic semiconductors is done via co-deposition of molecular dopants and matrix materials under high to ultra-high vacuum (UHV) conditions, which allows one to minimize the impact of, e.g., contamination from processing under ambient conditions.

The most significant effect of doping is the increase in electrical conductivity. The conductivity of a layer of a phthalocyanine (ZnPc) doped with the strong electron acceptor (F4-TCNQ) can be increased by up to 6 orders of magnitude [37]. Pfeiffer et al. found that the increase of conductivity is super-linear with the doping ratio [38]. This observation was explained by a percolation model [37]. Charge carriers that are located deep in the tails of the Gaussian density of states are moving more slowly than charge carriers further up in the density of states. Upon doping the tail states are filled, charge transport happens at higher energy levels and consequently higher hopping rates, which itself increases the conductivity.

Doping of organic semiconductors improves the performance of electronic devices. In
OLED’s [39] [40] [41] and OPV [42] [43] [44], molecular doping is used to enhance the conductivity in the hole and electron transport layer and to achieve an Ohmic contacts. In OFET’s, doping is employed to enhance charge injection and to control the shift of threshold voltage [45].

2.5 Charge Carrier Injection

In this section, charge carrier injection into an organic semiconducting layer and the formation of a metal/semiconductor contact will be studied. The limitation of charge carriers injection will be discussed as well.

2.5.1 Schottky Contact

Formation of contact: When a metal and doped organic layer are in contact, an interface forms between them. According to the Schottky-Mott model, the vacuum level VL is aligned at the interface, and the barrier heights for electron injection $\phi_e$ and hole injection $\phi_h$ are given by [5]

$$\phi_e = \phi_M - \chi \tag{2.21}$$

$$\phi_h = I - \phi_M \tag{2.22}$$

where $I$ and $\chi$ are ionization potential and electron affinity, respectively.

In general, the work functions of the metal and the organic layer are different. To align the different chemical potentials of the metal and the organic semiconductor, charge is redistributed inside the organic layer, leading to a bending of the VL, the HOMO, and the LUMO [5] [3]. In Figure 2.8 a, the work function of the metal $\phi_M$ is larger than the work function of the organic semiconductor layer $\phi_{org}$ [5]. In this case, electrons migrate from the organic layer to the metal electrode and the n-doped layer is depleted, leading to the formation of a positive space charge layer inside the doped organic layer.

This redistribution of charges in the organic layer continues until the Fermi levels of the metal electrode and organic material are aligned. The potential distribution at the interface is defined by the Poisson equation. A depletion layer is formed to align the Fermi levels of both materials, which leads to the creation of a built-in potential $V_{bi}$ in the organic layer [9][15][46], which $V_{bi}$ equals the potential across the depletion region in thermal equilibrium.

The Mott-Schottky rule is often violated in real metal organic interfaces. As sketched in Figure 2.8 c, an interfacial dipole layer is usually formed at metal/organic interfaces, which leads to a potential step at this interface. Thus the presence of the dipole layer creates a discontinuity in the vacuum level VL at the metal/organic interface. Therefore,
the barrier heights of electron injection $\phi_e$ and hole injection $\phi_h$ with VL shift $\Delta$ are given by [3, 47]

$$\phi_e = \phi_M - \chi + \Delta \quad (2.23)$$
$$\phi_h = I - \phi_M - \Delta \quad (2.24)$$

The interface dipole $\Delta$ can have different origins, which are summarized in Figure 2.9. First of all, charge can be transferred between the metal and the organic layer, which results in the formation of cations and anions. Secondly, the VL shift can be explained by the image effect, i.e., the VL shift is attributed to the polarization of the electron cloud, which is attracted by the image charge formed at the metal (see Figure 2.9b). Furthermore, the VL shift can be explained by the rearrangement of the electron cloud at the metal surface. Here, the part of the electron cloud tailing into vacuum is repelled by repulsion of the electron cloud of the adsorbate (see Figure 2.9c). Similarly, a chemical reaction between the organic layer and metal can lead to an interface dipole, as shown in Figure 2.9d. The chemical interaction leads to a rearrangement of partial charge, which leads to the VL shift. Filling of interfacial states can as well lead to a shift in the vacuum level (see Figure 2.9e). Finally, for polar organic molecules, the orientation of the dipole moment can lead to a large interracial dipole, which leads to the VL shift. [5], as shown in Figure 2.9f.

**Charge Injection with Applied Electric Field:**

To inject electrons from the metal into the organic semiconductor, either the electron has sufficient thermal energy to overcome the injection barrier or it tunnels through the barrier.

However, the electron does not have to overcome the full barrier height as given in Eqs. 2.21-2.22, but the barrier height is lowered due to the so-called Schottky effect or Schottky-barrier lowering [3]. When an electron is injected at a distance $X$ from the surface of the metal, a positive charge will be induced in the metal [9] [5] (see Figure 2.10). The attraction force between the electron and the so called image charge modifies the potential barrier. The attractive force (image force) toward the metal is given by [9]

$$F = -\frac{q^2}{4\pi\varepsilon\varepsilon_0 x^2} \quad (2.25)$$

The image potential $\Phi_{\text{image}}$ is hence given by

$$\Phi_{\text{image}} = \frac{q^2}{16\pi\varepsilon\varepsilon_0 x} \quad (2.26)$$
The net potential $\Phi_e$ is given by a superposition of the image potential $\Phi_{\text{image}}$ and the initial potential modified by the applied field $\Phi_{\text{field}} = \Phi_0 - qFx$. As seen in Figure 2.10, the image potential lowers the potential barrier $\Delta \phi$, which becomes

$$\phi_B = \phi_e - \Delta \phi \quad (2.27)$$

$$\Delta \phi = \sqrt{\frac{q^3 F}{4\pi \varepsilon \varepsilon_0}} \quad (2.28)$$

The maximum of resulting potential lies at a distance $X_m$ from the surface of the metal

$$X_m = \sqrt{\frac{q}{16\pi \varepsilon \varepsilon_0 F}} \quad (2.29)$$

**Charge Injection Processes:**

The thermal energy of an electron can be sufficient to overcome the reduced injection barrier. This injection is called thermionic emission (TE) for organic semiconductor and can be described by the Richardson-Schottky equation [9] [3]

$$j_{\text{RS}} = A^* T^2 \exp \left( -\frac{\Phi_B}{K_B T} \right) \quad (2.30)$$

where $A^* = 4 \pi q m^* k_B^2 / h^3$ is the effective Richardson constant, which depends on the effective mass of the electron. Figure 2.11 presents the thermionic emission into organic semiconductor. Thermionic emission occurs when the injection barrier is small and electrons have sufficient thermal energy to overcome the image potential [3] [9]. If the potential barrier is large, electrons can tunnel through the barrier. To calculate the injected current, the potential barrier is approximated by a triangular barrier. Figure 2.11 exhibits such a triangular barrier for electron injection from the metal into the organic semiconductor. The tunneling distance and therefore the number of electrons injected depend on the applied electric field [3]. The tunneling process is called Fowler-Nordheim tunneling, leading to

$$j_{\text{FN}} = \frac{A^*}{\Phi_B} \left( \frac{qF}{\alpha K_B} \right) \exp \left( -\frac{2\alpha \Phi_B^{3/2}}{3qF} \right) \quad (2.31)$$

where $\alpha = 4\pi \sqrt{2m^* / h}$, $m^*$ is the effective mass of the electrons inside the organic semiconductor.

Thermal injection and Fowler-Nordheim tunneling can be combined to yield a large
injection rate, which is then called thermionic field injection. Effectively, electrons are tunneling through the barrier at an elevated energy between $E_F$ and $E_F + \Phi_B$, where the tunneling barrier is thinner (cf. Fig. 2.11). For the case $E=E_F$ and $E=E_F + \Phi_B$, the thermionic field emission (TEF) coincides with the thermionic emission or the field emission (FE). In effect, the injection process depends on the electric field and the temperature [3].

2.5.2 Current limitations: Injection Limited Current vs. Space Charge Limited Currents

The current flow through a semiconductor layer can be limited by the number of charge carriers injected at the contacts, leading to so called injection limited currents (ILC). However, if injection at the contacts is efficient, the current in a semiconductor can as well be limited by charge carriers accumulating in the organic layer, which is known as space charge limited currents (SCLC). Finally, the current can as well be limited by trap states in the organic layer, leading to trap-filled limited space charge limited currents (TFL-SCLC).

In the following, it is assumed that a semiconductor layer with thickness $L$ is sandwiched between two metals and that a voltage $V$ is applied between the contacts. As well, the charge carrier mobility is assumed to be constant. Furthermore, diffusion currents are ignored.

**Injection Limited Current (ILC)**

For injection limited currents, the density of thermally generated free carriers ($n_0$) inside the organic semiconductor films is larger than the number of injected charge carriers. Hence, the current flow through the organic semiconductor is limited by the amount of charge carriers injected at the contacts [3] [48]. Then, the the current density is given by

$$j \propto \exp(V)$$

which depends on the electric field ($F$)

$$F(x) = \frac{V}{d} = \text{const.}$$

Furthermore, the charge carrier density is dominated by the density of thermally generated free carriers ($n_0$). Hence, $F(x)$ and $n(x)$ are constant and independent of the position.
x within the entire sample (see Figure 2.12)

\[ n(x) = n_0 \]  

(2.34)

Figure 2.13 shows that injection limited current regime takes place only at small voltages, since the density of injected charge carriers has to be smaller than the free charge carriers present in the film due to thermal activation.

**Space charge Limited Current (SCLC)** Space charges can limit the current in a semiconductor if charge carriers are very efficiently injected into the semiconductor layer. If the injection rate exceeds the rate at which charge carriers can move away from the contacts, excess charge piles up in the organic semiconductor.

In this case, the charge carrier density \( n \) exceeds the density of thermally generated free carriers \( n_0 \). The charge carrier density \( n(x) \) becomes dependent on the distance from the contact, as shown in Figure 2.12 and is given by

\[ n(x) = \frac{3 \varepsilon \varepsilon_0}{4q d^2} \sqrt{\frac{x}{d}} \]  

(2.35)

the charge carrier density decreases for increasing distance from the contact. The electric field is found to be

\[ F(x) = \frac{3V}{2d} \sqrt{\frac{d}{x}} \]  

(2.36)

Thus the field increases away from the injecting contact, as shown in Figure 2.12. Then the current density is given by

\[ j = q \mu n F = \frac{9}{8} \varepsilon \varepsilon_0 \mu V^2 \frac{d^3}{d^3} \]  

(2.37)

This equation is called Mott-Gureny equation (Child’s law). It is clear that the current density is proportional to the square of the applied voltage \( j \propto V^2 \), as shown in Figure 2.13.

**Trap-Filled Limited Space Charge Limited Current (TFL-SCLC)**

In most cases, trap states exist in the organic semiconductor. The current density is affected by the density of the trapping states. For low current densities, all of the shallow traps are already filled and the current density is thus practically identical to the trap-free case. This is called Trap-Filled Limit (TFL). In this case, it is assumed that the trap states are treated as an energetically-discrete trapping level.
The current density is formally identical with the TF-SCLC case, but the mobility $\mu$ must be replaced by an effective mobility $\mu_{eff}$ \cite{3}\cite{49}:

$$j = \frac{9}{8} \varepsilon \varepsilon_0 \mu_{eff} \frac{V^2}{d^3}$$

(2.38)

where $\mu_{eff} = \mu \cdot \theta$, and $\theta$ is the ratio of the free carrier density to the total carrier (free and trapped) density.

Figure 2.13 presents the TFL-SCLC regime, where the current will increase rapidly from its low trap limited value to a high trap-free SCL current. $V_{TFL}$ is defined as the voltage required to fill the traps \cite{49}. $V_{TFL}$ is given by

$$V_{TFL} = \frac{q n_d d^2}{2 \varepsilon \varepsilon_0}$$

(2.39)

where $V_{TFL}$ proportional to the sample thickness $d$ ($V_{TFL} \propto d$).

As shown in Figure 2.13, for voltages larger than $V_{TFL}$, the current density is fully described by Mott-Gurney law.
Figure 2.8: Schematic diagrams of energy level alignment at metal/organic semiconductor interfaces. (a) Energy level alignment of metal and organic semiconductor prior to contact. (b) Energy level alignment of metal/organic semiconductor after contact. The energy levels bend to align Fermi levels of the two solids and vacuum levels shift according to Mott-Schottky rule. (c) Realistic model of energy level alignment of the contact with vacuum level shift. Picture adapted from Ref. [5] with the permission of Advanced Material © 1999 WILEY-VCH Verlag GmbH, Weinheim, Fed. Rep. of Germany.
Figure 2.9: Possible origin of interfacial dipoles at the metal/organic layer interface. (a) Charge transfer. (b) Image force. (c) Surface rearrangement. (d) Chemical interaction. (e) Interface states. (f) Formation of permanent dipole. Picture adapted from Ref. [5] with the permission of Advanced Material © 1999 WILEY-VCH Verlag GmbH, Weinheim, Fed. Rep. of Germany.
Figure 2.10: Schematic energy band diagram between a metal surface and a semiconductor. The effective barrier is lowered by an applied electric field. The lowering is due to the combined effects of the field and the image force. Picture adapted from Ref.[3] with the permission of John Wiley and Sons, copyright © 2005 Wiley-VCH Verlag GmbH Co. KGaA.

Figure 2.11: Tunneling of electrons through a triangular barrier, thermionic emission, and field emission. Picture adapted from Ref.[3] with the permission of John Wiley and Sons, copyright © 2005 Wiley-VCH Verlag GmbH Co. KGaA.
Figure 2.12: Electric field $F$ and charge carrier concentration $n$ as a function of position $x$ in a sample with thickness $L$. (a) injection limited current (ILC). (b) space charge limited current (SCLC).
Figure 2.13: Current density-voltage J-V characteristic of organic solids at room temperature. At low applied voltages $V<V_{tr}$, the current density is exponentially dependent on the applied voltage (ILC regime). Between ($V_{tr}<V<V_{TFL}$), the current density characteristic is nonlinear and ($j \propto V^2$) (SCLC regime). For $V>V_{TFL}$, all trap states are filled, leading again to a dependency $j \propto V^2$, but with increased mobility.
3.1 Organic Field-Effect Transistors (OFETs)

Field-effect transistors (FETs) are the keystone for all electronic circuits and the ability to build FETs from organic materials has sparked interest over the past two decades. Most of the interest in OFETs stems from their potential for low cost fabrication and their mechanical flexibility. The mechanical flexibility of OFETs is caused by weak Van-der-Waals type bonding between molecules in the organic film. Furthermore, organic films can be deposited at low temperatures, which allows one to process OFETs on plastic substrates. Due to improvements in processing, material optimization, and circuit design, the performance of organic field-effect transistors exceeds that of amorphous silicon based transistors.

The first OFET was reported in 1982, when Ebisawa, Kurokawa, and Nara fabricated a metal-oxide-semiconductor (MOS) capacitor using organic semiconductor materials. The device was fabricated as a three terminal device. Polyacetylene was used as a the organic semiconductor material, polysiloxane as gate dielectric, aluminium as a gate contact, and gold for the source and drain electrodes [50]. In 1986, a breakthrough was achieved by Tsumura, Koezuka, and Ando, who processed the first OFETs with recognizable current gain [51].

These first reports started intense interest in the field, which led to an improvement in OFET performance, a reduction in cost of fabrication, a development of new OFET architectures, and through understanding of OFET operation [13].

3.1.1 Structures of OFET

The OFET is a three-terminal device consisting of a source and a drain contact, a semiconducting layer, a gate dielectric, and a gate electrode. Depending on the sequence in which the terminals are deposited, there are four different OFET architectures, which are shown in Figure 3.1.

The different OFET architectures can be distinguished by the configuration of the gate and contact electrodes: the OFET shown in (a) has a top-gate (TG) and top-contact...
(TC) configuration, (b) shows a top-gate (TG) and bottom-contact (BC) configuration, (c) a bottom-gate (BG) and top-contact (TC) configuration, and (d) is a bottom-gate (BG) and bottom-contact (BC) transistor.

Furthermore, OFETs can be distinguished by the gate/drain electrode overlap. In a staggered structure, the source/drain electrodes and the gate dielectric aren’t separated by a semiconducting layer, as shown in Figure 3.1 a and d. In staggered OFETs charge is injected only at the edge of the electrode. Furthermore, any gate/source or gate/drain overlap induces parasitic capacitances that reduces the operating speed of the OFET. Noh et al., developed a self-aligned gate (SAG) structure to minimize the effect of these parasitic capacitances and obtained cut off frequencies in the MHz regime [52, 53, 54]. In contrast to the staggered structure, in the coplanar structure, the source/drain electrodes and the gate dielectric are separated by a semiconducting layer, as shown in Figure 3.1 b and c. In the coplanar OFETs, charges are injected along the whole gate/source overlap area [27, 55, 56].

The bottom-contact (BC) configuration usually has the disadvantage of a high contact resistance, which degrades charge injection and overall transport [57, 58]. The advantage of this configuration is the ability to use high-resolution patterning techniques to define the contacts before the deposition of the semiconducting layer. Top-contact OFETs often present lower contact resistance and a better performance than BC OFETs [55]. In terms of gate configuration, bottom-gate (BG) OFETs have the advantage that the gate can safely be grown by methods that involve chemical solvents or thermal treatments that would harm the semiconductor layer in a top gate configuration. The top-gate configuration has the advantage that the gate can act as passivisation layer that protects the underlying semiconducting layer from degradation. However, processing of the TG can harm the semiconductor layer, especially during printing processes [55] [56].

3.1.2 Doping of OFET

Doping of organic field-effect transistor can be realized by channel or contact doping. Channel doping is achieved by including either a p- or an n-type doped layer at the gate dielectric of OFET (i.e. in the channel), whereas contact doping is realized by adding either a p- or an n-type doped layer underneath the contacts (source and drain), as shown in Figure 3.2. Adding doping has a profound influence on the working mechanism of OFETs.

3.1.3 Operation Principle of OFETs: A Qualitative Description

To discuss the general operation principles of OFETs, the geometry of an OFET is shown Figure 3.3 (a) The source and drain electrodes are separated by the channel with
length L. Usually, the gate electrode can be made of a metal or a conducting polymer, but very often highly doped silicon is used. \( \text{Al}_2\text{O}_3 \) and \( \text{SiO}_2 \), or polymeric insulators (poly(methylmethacrylate) (PMMA) or poly(4-vinylphenol) (PVP)) are commonly used as gate dielectric. The source and drain contacts are usually chosen to ensure an efficient charge injection, e.g., gold (Au) or platinum (Pt) for hole injection and aluminium (Al) or silver (Ag) for electron injection [59, 27].

The working mechanism of OFETs is similar to inorganic FETs. A voltage is applied between gate and source (\( V_{GS} \)) and between the source and drain electrodes (\( V_{DS} \)). The source electrode is normally grounded (\( V_S = 0V \)) and is responsible for charge carrier injection. For example, for p-type OFETs, the source is always more positive than the gate electrode (i.e., the applied gate-source voltage is negative) and more negative for n-type OFETs (i.e., \( V_{GS} \) is positive). For p-type OFETs, when no voltage is applied between the gate and source (\( V_{GS} = 0V \)), the transistor is off, because the intrinsic semiconductor material shows low conductivity only. If a negative voltage is applied between source and gate (\( V_{GS} < 0V \)), mobile charges are influenced at the insulator/organic semiconductor interface. Hence, the conductivity of the semiconductor increases and the transistor switches on. However, not all induced charges are free and will contribute to the current

---

**Figure 3.1:** Schematic cross-section of four configurations of organic transistors. Organic transistors (a) and (b) are top-gate configured, with top-contact and bottom-contact, respectively. Organic transistors (c) and (d) are bottom-gate configured, with top-contact and bottom-contact, respectively. Contacts are the source and drain electrodes.
in the FET because some charges are trapped in deep traps in the semiconductor film. Hence, charge accumulation does not start at $V_{GS} = 0V$, but an additional voltage $V_{th}$ has to be applied to the gate to fill all traps in the organic semiconductor. This additional voltage is the threshold voltage $V_{th}$ of the device. The threshold voltage furthermore accounts for differences in the Fermi level of organic semiconductor and the work function of the metal.

Without a drain-source voltage (i.e. $V_{DS} = 0V$), the charge carrier concentration along the channel is uniform. If a small drain-source voltage is applied ($V_{DS} \ll V_{GS}$), the potential $V(x)$ increases linearly from the source electrode ($x = 0, V(x) = 0$) to $V_{DS}$ at the drain electrode ($x = L, V(x) = V_{DS}$) within the channel. Hence, the charge carrier density drops linearly from the injecting electrode (source) to the extracting electrode (drain), as shown in Figure 3.3b. This behavior is called the linear regime, as the current flowing through the channel is direct proportional to $V_{DS}$.

At $V_{DS} = V_{GS} - V_{th}$, no charge carriers are accumulated at the drain, i.e. the channel is "pinched off", as shown in Figure 3.3c. This means that a depletion region is formed next to the drain electrode due to the potential difference between the potential in the channel $V(x)$ and the gate voltage.

By increasing $V_{DS}$, the current does not increase, but the depletion region will expand. Thus the channel is slightly shortened, as shown in Figure 3.3 d. Since the potential at the pinch-off point remains at $V_{GS} - V_{th}$, the current saturates at value $I_{DS,sat}$ [27].

3.1.4 Quantitative Description of the Current-Voltage Characteristics of OFETs
The current-voltage characteristics of p-doped OFET can be described by the gradual channel approximation. In this approximation, it is assumed that the electric field
Figure 3.3: (a) Cross-section of an organic transistor indicating the different voltages applied to the electrodes. Part (b)-(d) show the charge carrier distribution in the channel at the different operating regimes of organic transistor. (a) Linear regime. (c) Pinch-off of the channel at the drain. (d) Saturation regime. Picture reprinted with permission from (Jana Zaumseil and Henning Sirringhaus, Chemical Reviews 2007, 107 (4), 1296-1323 DOI: 10.1021/cr0501543). Copyright (2007) American Chemical Society.

parallel to the current flow generated by the drain voltage is much smaller than the field perpendicular to the current flow created by the gate-source voltage.

At large negative applied gate voltage, (i.e. $V_{GS} > V_{th}$), the density of free holes increases in the channel, i.e. it drops from source to drain. If $V(x)$ denotes the potential in the channel ($x$ is the distance to the source), the density of free holes $p(x)$ becomes

$$p(x) = \frac{C_{ins} W (V(x) - (V_{GS} - V_{FB}))}{qA} + N_A$$ (3.1)

where $W$ is the channel width, $e$ is the electron charge, $V_{FB}$ is the flatband voltage, which is described as the required applied voltage between the metal and the semiconductor to induce flat energy levels, and $N_A$ is the doping concentration in the channel. $A=wd$ is the cross section area of the channel, and $d$ is the thickness of the accumulation layer of holes. When holes are submitted to an electric field created by the applied drain voltage ($V_{DS}$), an electric current is flowing from source to drain. The current density is given by[9]

$$J = qp(x)E_x\mu_h$$ (3.2)
where $E_x$ is the electric field in the x-direction and $\mu_h$ is the hole mobility. By integrating equation 3.2 from source $(x = 0, V = 0)$ to drain $(x = L, V = V_{DS})$, the drain current becomes

$$-I_D = \frac{\mu_h C_{\text{ins}} W}{L} \left[ \left( V_{GS} - V_{FB} - \frac{e d N_A}{C_{\text{ins}}} \right) V_{DS} - \frac{1}{2} V_{DS}^2 \right]$$  \hspace{1cm} (3.3)$$

Equation 3.3 can be rewritten:

$$-I_D = \frac{\mu_h C_{\text{ins}} W}{L} \left[ (V_{GS} - V_{th}) V_{DS} - \frac{1}{2} V_{DS}^2 \right]$$  \hspace{1cm} (3.4)$$

Equation 3.4 matches the relation for the drain current of undoped transistors, but the threshold voltage $(V_{th})$ is altered. By assuming that the doped layer thickness $d_{dop}$ is small, $V_{th}$ can be expressed by[60]:

$$V_{th} \approx V_{FB} + \frac{q N_A d_{dop}}{C_{\text{ins}}}$  \hspace{1cm} (3.5)$$

From equation 3.5, the threshold voltage depends on the thickness of the doped channel and the doping concentration. Consequently the threshold voltage can be shifted by varying these parameters. Several research groups are confirmed that he threshold voltage can be shifted by doping either p-type or n-type transistors [45][61].

Equation 3.4 can be simplified if $V_{DS} < V_{GS} - V_{th}$. The source-drain current becomes

$$I_{DS} = \frac{W}{L} \mu_l C_i (V_{GS} - V_{th}) V_{DS}$$  \hspace{1cm} (3.6)$$

This is called linear regime, i.e. the current is linearly proportional to $V_{GS}$ and the transistor behaves as a resistor with a resistance $R$ that is controlled by $V_{GS}$. In this regime, the field effect mobility $\mu_l$ can be extracted from the gradient of equation 3.6 at constant $V_{DS}$

$$\mu_l = \frac{\partial I_{DS}}{\partial V_{GS}} \frac{L}{WC_i V_{DS}}$$  \hspace{1cm} (3.7)$$

At $V_{DS} = V_{GS} - V_{th}$ no charge carriers are accumulated at the drain, i.e. the channel pinches off. Consequently the current can’t increase anymore and saturates at $I_{DS,\text{sat}}$, as shown in Figure 3.4 a. In this regime, the source-drain current in equation 3.4 can be simplified to [62]

$$I_{DS,\text{sat}} = \frac{W}{2L} \mu_{sat} C_i (V_{GS} - V_{th})^2$$  \hspace{1cm} (3.8)$$

where $\mu_{sat}$ is the field-effect mobility. Hence, the charge carrier mobility can be extracted
from the gradient of equation 3.8, described by

$$\mu_{\text{sat}}(V_{GS}) = \frac{\partial I_{DS,\text{sat}}}{\partial V_{GS}} \frac{L}{W C_i} \frac{1}{(V_{GS} - V_{th})}$$  \hspace{1cm} (3.9)

Doped organic field-effect transistor (OFET) are commonly characterized in one of two ways, either by keeping $V_{GS}$ constant and sweeping $V_{DS}$ (typically referred to as drain sweep or output characteristics; see Figure 3.4a) or by fixing $V_{DS}$ and sweeping $V_{GS}$ (commonly referred to as gate sweep or transfer characteristics; see Figure 3.4b).

There are other important parameters of OFET that can be extracted from the transfer characteristic, which will be studied separately in the next section.

3.1.5 Fundamental Parameters of OFET

3.1.5.1 Threshold Voltage

The threshold voltage is one of the more important parameters of OFETs. For crystalline silicon transistors, the threshold voltage is defined as the voltage at which inversion is reached in the metal-insulator-semiconductor (MIS or MOS) capacitor. However, since
organic semiconductors aren’t usually operated in inversion mode, the threshold voltage is usually defined as the charge at which accumulating starts [13].

The threshold voltage is extracted from the transfer characteristic by extrapolating the linear part of the $\sqrt{I_{DS,\text{sat}}} - V_{GS}$ curve to the intercept with the $V_{GS}$ axis, as shown in Figure 3.4b. The threshold voltage depends strongly on the built-in dipoles and the difference in chemical potential of the metal and the semiconductor, impurities, interface states, and in particular charge trap states[63].

3.1.5.2 ON/OFF Ratio

Another relevant parameter is the ON/OFF ratio. It is the maximum ratio of the source-drain current in the on-state and off-state ($I_{on}/I_{off}$). The ON/OFF ratio should be as high as possible since a higher $I_{on}$ leads to higher switching speeds and a lower $I_{off}$ decreases stand-by leakage and subsequently the static power consumption.

The ON/OFF ratio can be optimized by the transistor geometry. A large ratio of the channel width over the channel length (W/L) increases $I_{on}$ while keeping $I_{off}$ constant [55]. Klauk et al., achieved a high ON/OFF ratio around $10^8$ of bottom-gate, top-contact organic thin-film transistors (TFTs) [53].

3.1.5.3 Subthreshold Swing

If gate-source voltage $V_{GS}$ below the threshold voltage $V_{th}$ is applied, the OFET operates in the subthreshold regime. The subthreshold swing is measured at the maximum slope of $\log(I_{DS})$, as shown in Figure 3.4b:

$$S = \frac{dV_{GS}}{d(\log I_{DS})} = \frac{nkT}{q} \ln 10$$

(3.10)

where $K$ is the Boltzmann constant, $T$ is the absolute temperature, $q$ is the electron charge, and $n$ is the ideality factor. The lower limit of the subthreshold swing at room temperature equals to 60 mV/decade [55].

The ideality factor $n$ is determined by the density of trap states at the gate dielectric/semiconductor interface. Hence, $n$ is given by [56]

$$n = 1 + \frac{qN_t}{C_i}$$

(3.11)

where $N_t$ is the trap state density. If $N_t/C_i$ is small, the ideality factor $n$ will be close to the ideal limit. Recently, DNTT OFET achieved 80 mV/decade, which is close to ideality [56].
3.1.5.4 Transconductance

The performance of OFETs can further be qualified by the transconductance, defined as the ratio of the drain current to the gate voltage.

\[ g_m = \frac{dI_D}{dV_{GS}} \]  

(3.12)

In the linear regime, the transconductance \( g_m \) is given by

\[ g_m = \frac{W\mu C_i}{L} V_{DS} \]  

(3.13)

where \( L \) is the channel length. In the saturation regime, transconductance is defined by

\[ g_m = \frac{W\mu_{sat} C_i}{L} (V_{GS} - V_{th}) \]  

(3.14)

The transit frequency \( f_T \) is related to the maximum switching speed of the device and is directly proportional to the transconductance

\[ f_T = \frac{g_m}{2\pi C_i W(L + 2\Delta L)} \]  

(3.15)

where \( \Delta L \) is the overlapping distance between gate and source/drain.

3.1.5.5 Contact Resistance

The contact resistance of OFETs can be defined as any resistance that is not actually associated with the conductive channel, but originates from the injection and ejection of charge carriers. The total resistance \( R_{tot} \) of OFET can be expressed as

\[ R_{tot} = R_{ch} + R_c \]  

(3.16)

where \( R_{ch} \) and \( R_c \) are the resistance of channel and the contact resistance, respectively.

To extract the contact resistance \( R_c \) experimentally, the transmission line method (TLM) is used. The TLM method relies on the observation that the contact resistance is independent of the channel length \( L \). The total resistance can be determined from the linear regime of the output characteristic of OFETs, and is given by[13]:

\[ R_{tot} = \left. \frac{\partial V_{DS}}{\partial I_{DS}} \right|_{V_{DS} \to 0} = \frac{L}{\mu C_i W(V_G - V_{th})} + R_c \]  

(3.17)

where \( \mu \) is the field-effect mobility. Hence, plotting \( R_{tot} \) vs the channel length \( L \) leads to
a linear plot with the contact resistance as y-intercept.

Contact limitations in OFETs can be minimized by reducing the charge injection barrier at the source electrode by carefully engineering the contacts by doping, or by using of self-assembled monolayers (SAMs), which leads to an energetic shift at the injection interface [64][54][65].

3.1.6 Literature Review of Doped Organic Field-Effect Transistors
3.1.6.1 Contact Doping

For high-performance OFETs charge carrier injection at the source electrode has to be optimized, which will increase the saturation current and transconductance of OFETs [60]. Charge carrier injection is limited by the interfacial properties between the metal electrodes and the organic semiconductor layer as discussed in section 2.5.1. Thus, the main role of contact doping is to reduce the contact resistance and subsequently to increase charge injection in OFETs.

Contact doping is realized by inserting a doped layer underneath the metal electrodes (source and drain). This doped layer could be either a pure dopant layer, for example, a layer of metal halides [66, 67, 68], metal oxides [69, 70, 71, 72], and molecular dopants[73, 74, 54], or a codeposition of intrinsic organic semiconductor (host)) and dopant materials, such as molecular dopants between the metal and the organic semiconductor [45][75][76][77][78].

For p-type transistors, Ante et al. studied the effect of inserting a pure dopant layer (NDP-9, Novaled GmbH) on the contact resistance of OFETs with a nanoscale channel length [54]. The OFETs consist of a thin AlOx layer as a gate dielectric, DNTT as organic semiconductor layer, and gold source/drain electrodes. It is observed that the drain current increases due to a reduction in the contact resistance at the metal electrode/semiconductor interfaces by contact doping. Tiwari et al. realized contact doping by codeposition a 10 nm thick layer of 1:1 mixture of pentacene and p-dopant \([Mo(tfd)_3] \) is selectively deposited in the source/drain electrodes area. It is seen that the contact resistance is decreased and the drain current increases about 50% by contact doping [79].

Similar to p-type contact doping, a wide range of materials have been proposed to induce n-type doping, leading to an improvement of electron injection. Singh et al. illustrated the reduction of contact resistance by using rhodocene dimer as selective contact doping in bottom-gate and top-contact \(C_{60} \) OFETs [80]. They observed that the drain current increases by contact doping and the off-current remains unchanged by contact doping, which is an evidence that the only structured area underneath the
source/drain contacts are doped. Singh et al. studied as well the influence of contact doping in $C_{60}$ OFETs on the contact resistance by using the TLM method. The contact resistance is reduced from 9.7 K$\Omega$ cm for undoped OFETs to 5.5 K$\Omega$ cm for contact-doped OFET.

It has been found that the contact resistance can be influenced by the structure of OFETs. OFETs using the staggered structure (bottom-gate and top-contact OFETs or top-gate and bottom-contact OFETs) usually exhibit a lower contact resistance than coplanar OFETs (bottom-gate and bottom-contact OFETs or top-gate and top-contact OFETs), which is due to the relatively large charge carrier injection area[60]. But from industrial point of view, the coplanar OFETs, especially bottom-gate and bottom-contact architectures, present the possibility to employ high-resolution lithography to structure OFETs without damaging the organic semiconductor layer[60]. This configuration offers a way to structure the doped injection layer by lithography, to avoid unwanted channel doping and decrease in the ON/OFF ratio of the device.

3.1.6.2 Channel Doping

Channel doping introduces a way to fine-tune the transistor characteristic.

Most research group studied the influence of the doping on the threshold voltages, Lüssem et al. [4], proved that the thickness of doped layer can be used to tune the threshold voltage (according to equation 3.5) [45]. They prepared p-doped transistors using pentacene as organic semiconductor layer. A thin layer of p-doped pentacene (pentacene with constant thickness and different concentration of $F_6TCNQ$, and pentacene with different thicknesses and specific concentration of $F_6TCNQ$) on top of Al$_2$O$_3$, and a another p-doped layer underneath the source and drain electrodes is structured by the same shadow mask as used for the electrodes. The transistors showed that the threshold voltage can be shifted by increasing the doping concentration $N_A$ and the thickness of the doped layer $d_{dop}$, as described by equation 3.5. The threshold voltage shifts linearly from -3.6 V for the undoped transistor to 0.8 V for thicker doped layer. This result confirms that the shift of threshold voltage isn’t due to filling of traps at insulator/organic interface, but due to an actual doping of free charges into the transistor channel.

However, in some materials combinations, doping can also fill the charge traps at the interface between the gate dielectric and organic semiconductor or in the organic semiconductor layer itself [60]. Olthof et al., showed the influence of ultra-low densities of an n-dopant ([RuCp*(mes)]$_2$) either to as received (unpurified) or highly purified $C_{60}$ in OFETs. Both unpurified and purified $C_{60}$ transistors showed a shift in the threshold voltage by doping, but unpurified $C_{60}$ OFETs presented a threshold voltage shift that is
much stronger than purified $C_{60}$ OFETs. This effect is attributed to filling the charge trap states in the devices by doping [81].

Doping can improve the stability of organic transistors through passivisation of charge traps in the doped organic layers or at the gate dielectric/organic semiconductor interface. Wei et al., demonstrated that PCBM can be effectively doped by a solution-processable n-type dopant (N-DMBI). As well, doping leads to a strong improvement in air stability of n-channel OFETs by compensating for electrons trapped in ambient air [82].

3.2 Vertical Organic Transistors (VOTs)

Lateral organic transistors are limited in their switching speed. Due to the relatively low charge carrier mobility in combination with channel lengths in the range of several $\mu m$, the transit frequency of OFETs is in the low MHz regime only (cf. Eq. 3.15). In vertical organic transistors, the channel length is defined by the thickness of the organic layer, which can be in the nm regime. Therefore, VOTs can easily reach high currents and switching speeds.

3.2.1 Organic Permeable Base Transistors (OPBTs)

In general, vertical organic transistor can be structured by stacking three metallic or highly conductive electrodes in a sandwich structure, separated by organic semiconducting layers (cf. Figure 3.5). From top to bottom, the top electrode is called emitter, the bottom electrode is called collector, and the middle electrode is known as the base electrode. The base electrode is unstructured and very thin (thickness in the range of 10 to 20 nm).

The middle electrode (base) forms a Schottky diode with the top electrode (emitter) or
the bottom electrode (collector). These Schottky diodes are connected back to back and operated at different bias. The top Schottky diode between emitter and base is operated in forward direction, while the bottom Schottky diode between base and collector is operated in reverse direction, as shown in Figure 3.6a.

The working principle of an n-type OPBT is sketched in Figure 3.6. The current injected at the emitter $I_E$ is controlled by the emitter-base potential difference $V_{BE}$. This current drifts toward the base electrode. The base electrode is permeable for charge carriers, i.e., most charge carriers are injected at the emitter are transmitted through the base, forming the current $I_{EC}$.

The base-collector diode is operated in reverse direction. Thus, the transmitted current $I_{EC}$ is collected at the collector. Combined with the reverse current of the base collector diode $I_{BC}$, the total collector current is given by [6]

$$I_C = I_{EC} + I_{BC}$$

However, not all charge carriers injected at the emitter are transmitted across the base (i.e. $I_{EC} < I_E$), but a fraction of the emitter current leaks into the base, providing for the current $I_{EB}$ flowing from emitter to base electrode.[6]

3.2.1.1 Key Parameters of OPBTs

There are several parameters that characterize the performance of OPBTs:
ON/OFF Ratio  The ON/OFF ratio determines the ratio between the collector current in the OFF- and ON-state. It is given by

\[
\text{ON/OFF ratio} = \frac{I_C(\text{ON-state})}{I_C(\text{OFF-state})} \bigg|_{V_{CE}=\text{const.}}.
\]  

(3.19)

The OFF-state current is determined when the potential difference between the base and emitter (\(V_{BE}\)) is zero or if the base has even negative potential relative to the emitter potential. In this case, there is no injected electrons at the emitter, but there is an injected current at the base \(I_{BC}\), which represents the OFF-state current of the device [6].

The ON-state current is determined when the base potential is positive relative to the emitter potential. Hence, a large current is injected at the emitter, which is transmitted at the base and reaches the collector.

Current Gain or Amplification \(\beta\) and Transmission \(\alpha\)  The current gain \(\beta\) represents the ratio of transmitted current \(I_{EC}\) to base current \(I_{EB}\) and is given by

\[
\beta = \frac{I_{EC}}{I_{EB}} = \frac{I_C - I_{BC}}{I_B + I_{BC}}
\]  

(3.20)

The transmission \(\alpha\) represents the ratio of transmitted current \(I_{EC}\) to the total injected current at the emitter \(I_E\) and is given by

\[
\alpha = \frac{I_{EC}}{I_E} = \frac{I_C - I_{BC}}{I_E}
\]  

(3.21)

From Eq. 3.21 and 3.20, it can be deduced that the amplification and transmission are related as follows

\[
\beta = \frac{\alpha}{1 - \alpha}
\]  

(3.22)

Transconductance \(g_m\)  Similar to OFETs, the transconductance of OPBTs can be defined by the first derivative of collector current \(I_C\) with respect to the base-emitter potential at a fixed collector-emitter voltage, i.e.

\[
g_m = \frac{\partial I_C}{\partial V_{BE}} \bigg|_{V_{CE}=\text{const.}}.
\]  

(3.23)

Two different concepts are discussed in the literature to explain the transmission of vertical current across the metallic base electrode: transmission across an unstructured base electrode due to hot charge carrier transport or transmission due to pores in the
metallic base. The pores can either form spontaneously in the thin base electrode or they can be created by additional structuring steps.

3.2.1.2 Transmission across an Unstructured Base Electrode

Transmission Due to Hot Charge Carrier Transport  Transmission across the metallic base electrode is explained by some authors by a ballistic transport of charge carriers injected into the thin base electrode. In fact, OPBTs can be seen as one example of a hot electron metal-base transistor, proposed by Atalla et al. in 1962 [83][84]. Ballistic transport can occur if electrons are injected into the base at an energy level, which is significantly exceeds the Fermi level in the metal (see Figure 3.7). These electrons are called hot electrons. They will be scattered several times and will relax quickly toward the Fermi energy. However, if the base electrode is very thin (i.e. much thinner than the mean free path length $\lambda_B$) and if the electrons are injected at a higher energy compared to the injection barrier between base and the organic semiconductor, the injected electrons at the emitter can pass the base without scattering before reaching the collector electrode. Thus, they are injected into the collector semiconductor and are in fact transmitted through the base electrode[6].

The hot charge carriers transmission mechanism depends on the base, emitter, and collector materials. In most hot carriers OPBTs with aluminum base electrode, the transmission is rather low ($\approx 0.1$ [85] or 0.7 [86]). In 2013, Cheng et al., improved the performance of p-type OPBTs and reached a transmission 0.99. This increase in

Figure 3.7: Schematic of the hot charge carrier based transmission process across the base electrode of OPBTs. Picture adapted from Ref. [6] with permission of IOP.
transmission was realised by inserting a multilayer of organic semiconductors between the emitter and base with gradually increasing HOMO energies[87].

Transmission Due to Pores in the base electrode  High transmission in OPBTs can be explained as well by a microscopic perforation of the base electrode. Perforation of the base electrode can be represented by pinholes or pores, which are randomly distributed across the base electrode. However, the size of pores or pinholes has to be small compared to the thickness of the device[88][89], to ensure a high ON/OFF ratio of the device.

In 2005, Fujimoto et al. proposed an OPBT which consists of Ag/C₆₀ as an emitter, a thin Al base electrode, and Me-PTC/ITO as a collector. These OPBTs showed a current amplification of 180 and an ON/OFF ratio of around 100. Fujimoto’s group found by TEM and AFM measurements that the thin Al base is perforated. Furthermore, their OPBTs showed a bidirectional operation, which means the OPBTs can be operated using the top electrode as emitter and the bottom electrode as collector or vice-versa, which excludes any hot carrier based transmission mechanism[90][6].

Nakayama et al., in 2009, showed that the base electrode deposition conditions are significant to improve the performance of OPBTs. OPBTs showed a high ON/OFF ratio around $10^5$ after exposure of the thin Al base to ambient air and annealing it in ambient air, which can increase the oxidation of the Al base and reduce the leakage current of base-collector diode (i.e., the OFF-current of OPBT)[91].

Fischer et al. used the same structure of OPBTs as proposed by Fujimoto et al., but replaced the Me-PTC layer by an additional C₆₀ layer and added a doped layer underneath the emitter electrode to enhance the charge carrier injection[92]. These modifications led to an increase in the ON-current to up to 1 A/cm² at low base-collector voltages and an ON/OFF ratio of around $10^4$ [92]. Furthermore, they proved that OPBTs are bidirectional, similar as Fujimoto’s group found.

A few research groups proposed methods to control the size of pore and distribution. Zhao et al demonstrated a p-type OPBTs and proposed a method to control the pores size by co-evaporation Al with pentacene to form the base electrode. They showed that the pore size depend on the relative ratio of the Al and pentacene. Their OPBTs reach a current amplification of 135, corresponding to a transmission of larger than 0.99 [93].

In 2014, Hyeonggeum et al. demonstrated high amplification n-type OPBTs by using C₆₀ as the emitter, thin Al film as the base, and Me-PTCDI as the collector. Because of the granular structure of the Me-PTCDI surface, the nano-porosity of the Al base film can be optimized by tuning the nominal thickness of the Al base film. A high current amplification of approximately 476 was achieved. Furthermore, based on their device
simulation results, the pore size is more significant than the pore density for current saturation because the potential effect within the pore depends on the size of pore [94].

3.2.1.3 Transmission across Structured Base Electrodes

VOTs with a structured base electrode have the same general structure as organic permeable base transistors, but are usually referred to as organic static induction transistors (OSITs). In OSITs, high resolution structuring techniques are required as the feature size of the patterning must be in the range or smaller than the overall thickness of the device in order to achieve reasonable ON/OFF ratios [7, 6]. In 2009, Chao et al. proposed a structuring process, which depends on a monolayer of polystyrene (PS) spheres[7, 8, 95, 96], as shown in Figure 3.8. A monolayer of polystyrene spheres is deposited onto the emitter electrode. It serves as a patterning mask for the deposition of the base electrode. After the deposition of the base electrode, the monolayer of spheres is removed leaving behind the base electrode with circular openings whose size can be controlled by the size of the polystyrene spheres. Usually, the diameter of these openings
is in the range of 100-200 nm[95].

The resulting structure is shown in Figure 3.9. The emitter electrode (ITO) is covered by a thin layer of insulator (PVP), and the Al base electrode is structured by PS spheres. An insulator layer (SiO) is deposited onto the base electrode. Removing the PS spheres leaves behind openings with a well defined size, which are used as etch mask to etch deep holes into the PVP layer. The organic semiconductor P3HT is used to fill the holes and to form the collector layer.

The reason of depositing an insulator layer such as SiO is to minimize base leakage currents and maximize the ON/OFF ratio, i.e., improving the performance of the transistors[8, 7].

Several researchers tried to optimize the process of base electrode structuring, in particular as resolution of the lithography based on PS spheres is too small. In 2000, Kudo et al. proposed a process to minimize the feature size by using shadow masks by introducing a small gap between mask and substrate, which induces a shadowing effect at the edges of the structure. By using this technique, Kudo et al achieved a distance of 7 µm between adjacent lines of their slit mask[6, 97].

### 3.3 Organic p-i-n Diodes

Organic p-n or p-i-n diodes are often discussed in the context of organic solar cells or organic light-emitting diodes (OLEDs). The structure of an organic p-i-n diode is shown in Figure 3.10. It consists of two charge transport layers: the p-doped layer (transporting holes) and the n-doped layer (transporting electrons). In between these two layers is an intrinsic (i) layer, which is undoped. Usually, the p and n layers are highly doped, which ensures an efficient charge carriers injection at the contacts, i.e., Ohmic contacts are formed, which allows to focus on the charge transport inside the organic material.
3.3.1 Thermal Equilibrium (Zero Bias Applied)

If there is no voltage applied across the p-i-n junction, the junction is in thermal equilibrium. Figure 3.11 exhibits the energy bands and the associated space charge distribution in a p-i-n junction at thermal equilibrium. In order to compensate the different chemical potentials in the doped layers, depletion layers are formed at doped/intrinsic layer interfaces [10]. The thickness of the depletion layers can be found by solving Poisson’s equation. The Poisson equation is given by:

\[-\frac{\partial^2 \phi(x)}{\partial x^2} = \frac{dE(x)}{dx} = \frac{\rho(x)}{\varepsilon \varepsilon_0}\]

(3.24)

Here, the p-i-n junction is a homojunction, thus the permittivity of p-type layer, intrinsic layer, and n-type layer are equal ($\varepsilon_p = \varepsilon_i = \varepsilon_n = \varepsilon \varepsilon_0$). An abrupt junction, i.e. a sharp interface between the depletion layer and the doped layers, is usually assumed and it is assumed that the space charge layer is rectangular. This assumption is justified because the Debye length of the organic semiconductor is much smaller than the depletion layer widths in the p- and n-type regions [98]. Hence, the space charge density in the p-i-n junction is given by:

\[\rho(x) = \frac{1}{\varepsilon \varepsilon_0} \begin{cases} -qN_A & -x_p < x \leq 0 \\ 0 & 0 < x \leq d \\ qN_D & d < x \leq x_n \end{cases}\]

(3.25)

where $N_A$ and $N_D$ are the density of ionized p-type and n-type dopants, respectively, $d$ the thickness of the intrinsic layer, and $x_p$ and $x_n$ are the depletion layer widths in the p- and n-type regions, respectively. According to boundary and transition conditions and with respect to charge neutrality ($N_D x_n = N_A x_p$). Equation 3.24 can be integrated
so that the potential drop across each layer can be described as

\[ \phi_p = \frac{qN_A x_p^2}{2\varepsilon\varepsilon_0}, \quad \phi_n = \frac{qN_D x_n^2}{2\varepsilon\varepsilon_0}, \quad \text{and} \quad \phi_i = \frac{qN_A x_p}{\varepsilon\varepsilon_0} \]  

(3.26)

The sum of these three potential drops equals the built-in potential of the junction (\(\phi_{bi}\)). Hence, one finds (V: applied voltage V):

\[ \phi_{bi} - V = \frac{qN_A x_p^2}{2\varepsilon\varepsilon_0} + \frac{qN_D x_n^2}{2\varepsilon\varepsilon_0} + \frac{qN_A x_p}{\varepsilon\varepsilon_0} d \]  

(3.27)
From equation 3.26, 3.27, and the charge neutrality, the depletion zone widths for p-type and n-type layer are found as follows

\[
x_p = \sqrt{d^2 + \frac{2\varepsilon \varepsilon_0 (N_A + N_D)}{q} \left( \frac{N_A}{N_D} \left( \phi_{bi} - V \right) - d \right)} - \frac{1 + \frac{N_A}{N_D}}{1 + \frac{N_D}{N_A}}
\]

\[
x_n = \sqrt{d^2 + \frac{2\varepsilon \varepsilon_0 (N_A + N_D)}{q} \left( \frac{N_D}{N_A} \left( \phi_{bi} - V \right) - d \right)} - \frac{1 + \frac{N_D}{N_A}}{1 + \frac{N_A}{N_D}}
\]

The total depletion zone width can be defined as \( \omega_d = x_n + x_p + d \)

\[
\omega_d = \sqrt{d^2 + \frac{2\varepsilon \varepsilon_0 (N_A + N_D)}{q} \frac{N_A N_D}{N_A N_D} \left( \phi_{bi} - V \right)} - d
\]

From equation 3.30, the capacitance of depletion layer of the p-i-n junction is found as

\[
C_d = \frac{\varepsilon \varepsilon_0 A}{\omega_d} = \frac{\varepsilon \varepsilon_0 A}{\sqrt{d^2 + \frac{2\varepsilon \varepsilon_0 (N_A + N_D)}{q} \frac{N_A N_D}{N_A N_D} \left( \phi_{bi} - V \right)}}
\]

The capacitance of the depletion layer of the p-i-n junction depends on the density of ionized p-type and n-type dopants \( N_A \) and \( N_D \) and furthermore on the thickness of the intrinsic layer \( d \), and the total electrostatic potential variation across the junction \( \phi_{bi} - V \).

3.3.2 Applying an External Bias \( V \)

Figure 3.12a plots the charge carrier distribution under forward bias. To explain the the current-voltage characteristic of organic p-i-n diodes at small electric fields, it is assumed that charge carriers do not recombine within the charge depletion zones and are able to diffuse into the opposite site of the neutral region (i.e., electrons diffuse into the p-doped layer and holes diffuse into the n-doped layer). According to this assumption, the I-V characteristic of pn-diode becomes

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

where \( J_0 \) denotes the saturation current. This equation is called the Shockley equation. The assumptions Shockley used to derive his equation can’t be directly applied to organic p-i-n diodes, because charge carriers can’t diffuse through the whole intrinsic layer without recombination. More detailed studies showed that the Shockley equation has to
be adapted to describe the current in an organic p-i-n diode:

\[
J = \frac{V}{R_{||}} + J_0 \left( exp \left( \frac{qV}{\theta_i(n, T, V)} \right) - 1 \right)
\]

(3.33)

where \( R_{||} \) denotes a parallel resistance and \( \theta_i \) is an empirical function, which depends on temperature and applied voltage.

Charge carrier transport in the p-i-n diode under reverse bias depends on the electric field strength. At low fields, a reverse charge carrier transport can arise from either minority charge carrier diffusion, thermally activated generation of free charge carriers in the intrinsic layer, or direct shunt paths through the junction [10].

At reverse bias, minority charge carriers diffuse through the intrinsic layer, i.e. electrons diffuse into the p-type region and holes into the n-type region. These minority charge carriers recombine in the doped layer, which generates a reverse current. The diffusion process is independent of the voltage, thus the reverse current is constant and
is mainly limited by the diffusion constant of charges within the junction. Another main
contribution to reverse current is caused by free charge carriers thermally generated
within the depleted layers of the junction. These charge carriers can be either generated
via inter-gap trap states or via direct transition from the HOMO to the LUMO states.
The latter case is less pronounced in case of organic semiconductors that have an energy
gap in the range of 2-3 eV.

The last contribution of reverse current is provided by direct shunts. Direct shunts can
be caused by the intrinsic roughness of organic layers or by contaminations. Weak spots
form in the device layers which lead to a direct contact between the metallic electrodes.
Thus, direct shunt paths show in the I-V characteristics as an Ohmic behavior[10].

At high electric fields the p-i-n junction can break down, which is seen by a very large
reverse current. Basically, there are two breakdown mechanisms: avalanche breakdown
and Zener tunneling. Avalanche breakdown or impact ionization occurs at very high
reverse bias voltages. The field is so strong that thermally generated charge carriers gain
enough kinetic energy to ionize atoms within the semiconductor, generating more free
charge carriers leading to an abrupt increases in current. However, in organic semicon-
ductors an avalanche breakdown is unlikely, as the free path length of charge carriers is
very small, i.e. free charge carriers cannot gain enough energy to ionize additional charge
carrier.

Zener tunneling, however, is often observed in organic p-i-n junctions. Here, charge
carriers tunnel from the HOMO states to the LUMO states of neighboring molecules,
hence generating free charge carriers. The tunnel barrier has a triangular shape with the
maximum height given by the energy gap, as shown in Figure 3.12 c.

A few research groups discussed organic p-i-n diode. In 2005, Harada et al. demon-
strated the first stable and reproducible organic p-i-n homojunctions based on Zinc-
Phthalocyanine as an intrinsic semiconductor layer, p-doped ZnPc layer is processed
by co-evaporation of ZnPc with F_{4}TCNQ, and n-doped ZnPc layer is processed by co-
evaporation ZnPc with Ru(terpy)$_{2}$. The device characteristics are described by a devi-
ation from the Einstein relation for disordered materials[99]. In 2010, Kleemann et al.
demonstrated an organic Zener diode. The structure of the diode consists of Meo-TPD-
F$_{4}$TCNQ as p-doped layer, Balq$_{2}$NPB as intrinsic layer, and Bphen-Cs as a n-doped
layer. Kleemann et al. observed that the reverse current of the diode decreases exponen-
tially with increasing interlayer thickness and showed that the breakdown voltage of
the organic Zener diode can be controlled precisely by varying interlayer thickness and
increasing the doping concentration of p-doped layer[100].

Recently, Keum et al. discussed trapping in the organic p-i-n Zener diodes. The
charge trapping mechanism and its influence on the electrical characteristics of the diodes are studied by developing a novel bias stress protocol. As well, Keum et al. found that the molecular doping efficiency and the effective charge depletion zone are systematically correlated with the charge trapping in the intrinsic layer[98].
CHAPTER 4

EXPERIMENTAL METHODS

The properties of the materials used in this work are presented. All fabrication steps from cleaning to measuring devices are summarized. Mask layouts of the devices are discussed, as well as the characterization methods used later on.

4.1 Materials

All materials used in the organic field-effect transistors (OFETs), diodes, and organic permeable- base transistors (OPBTs) are presented.

4.1.1 Pentacene

Pentacene is a flat polycyclic aromatic hydrocarbon molecule made of five fused benzene rings, as shown in Figure 4.1. This structure leads to an extended conjugation and a high charge carrier mobility. The individual molecule has an energy gap separating the HOMO and LUMO states of 1.1 eV [101]. Pentacene is one of the most promising small molecule semiconductor (p-type semiconductor) due to its high field effect mobility of up to 5.5 cm²/Vs in thin films and 35 cm²/Vs in single crystals [102] and resonable air stability. Furthermore, pentacene and its derivatives can form well-ordered thin films on glass, silicon, and plastic substrates [103, 104]. Intrinsic pentacene is purchased from Sensient, Wolfen, Germany.

4.1.2 C₆₀

Fullerene (C₆₀) consists of 60 carbon atoms arranged in the form of a hollow sphere, as shown in Figure 4.1. To complete the sphere, the carbon atoms form 20 six-membered and 12 five-membered rings. C₆₀ is often referred to as Buckminster fullerene and is chemically and thermally stable. In 1985, fullerene was firstly discovered by Richard Smalley, Robert Curl, James Heath, Sean O’Brien, and Harold Kroto at Rice university. C₆₀ is a promising n-type semiconductor. It is commonly used as electron transport layer in organic photovoltaic cells (OPV), vertical transistors (OPBT) [92], and organic diodes [105] due to its high electron mobility. OFETs based on C₆₀ have achieved a high electron mobility of up to 4.9 cm²/Vs [106].

4.1.3 Spiro-TTB

Spiro-TTB is used here as insulating layer to define the active area of OPBTs and to block unwanted currents. Spiro-TTB is known as p-type organic semiconductor material
and used as electron blocking material and hole transport material in OLEDs [107]. Figure 4.1 shows the molecular structure of Spiro-TTB. Basic properties of Spiro-TTB are a ionization potential (IP) of 5.1 eV [108]. Furthermore, it is stable in air for up to at least 4 months and only shows a decrease in mobility of up to 13% upon exposure to ambient air [108]. Due to its twisted form, Spiro-TTB has a high glass temperature, allowing to anneal the devices in this work. Spiro-TTB is purchased from Lumtecc and used as received.

4.1.4 Tetratetracontane (TTC)

Tetratetracontane (TTC) is a long-chain alkane molecule with the chemical formula (CH$_3$(CH$_2$)$_{42}$CH$_3$). TTC is an insulator material with a large bad gap of about 9 eV. TTC can be evaporated by thermal evaporation technique at temperature around 100°C. It is hydrophobic and is commonly used as a dielectric for organic field-effect transistors. It can enhance the crystallinity of the organic semiconductor grown on top and passivate the insulator/organic semiconductor interface [109, 110]. Furthermore, it can be used as a passivation layer for OFETs to protect the device from ambient air, which increases their stability [111]. Tetratetracontane (TTC) is purchased from Sigma-Aldrich and used as received.
4.1.5 Silicon Monoxide (SiO)

In 1887, SiO was discovered by Charles F. Maybery at the Case School of Applied Science in Cleveland. SiO is an inorganic insulator and is commonly used to manufacture poly-crystalline silicon solar cells and in the field of nanoelectronics [112]. In this work, SiO is employed to structure the active area of OPBTs and to block unwanted currents. SiO is a brown-black glassy solid with density of 2.13 g/cm$^3$ and a melting point 1702$^\circ$C. SiO is purchased from Sigma-Aldrich and used as received.

4.1.6 N-dopant W$_2$(hpp)$_4$

The n-dopant W$_2$(hpp)$_4$ is a dimetal complex of tungsten with the anion of 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidine (hpp). The chemical formula of W$_2$(hpp)$_4$ is C$_{28}$H$_{48}$N$_{12}$W$_2$. In 2002, W$_2$(hpp)$_4$ was first synthesised by Cotton and coworkers [113]. Figure 4.1 shows the molecular structure of the W$_2$(hpp)$_4$.

In this work, the n-dopant W$_2$(hpp)$_4$ is synthesised by the Bunge group at Kent State University. The synthesis of W$_2$(hpp)$_4$ is performed in a slightly modified manner to that first described by Cotton and co-workers [113]. A sample of commercially available W$_2$(hpp)$_4$Cl$_2$ (0.2 g, 0.2 mmol) is added to 15 mL of tetrahydrofuran (THF). Potassium metal (0.5 g) is subsequently added and the solution stirred for approximately 1 h until turning a dark red color. The reaction is refluxed (80 − 85$^\circ$C) for 3 h. The reaction mixture is then cooled to room temperature and the THF is removed under vacuum. Toluene is added (10 mL) and the insoluble material is removed via centrifugation. The toluene solution is brought to dryness under vacuum producing a deep-red solid. We obtain an isolated yield 0.1 g, 52%. To isolate crystals suitable for single crystal X-ray diffraction, the solid is dissolved in 5 mL of THF and placed in a freezer at −35$^\circ$C. After one week, small red block-shaped crystals suitable for X-ray diffraction are collected. The crystallographic data is similar to the previous report [113]: a = 8.28 Å, b =9.58 Å , c = 10.08 Å, $\alpha = 86.0^\circ$, $\beta =70.96^\circ$, $\gamma = 81.06^\circ$, V = 747 Å$^3$, T = 105 K. All materials used to synthesize W$_2$(hpp)$_4$ are purchased from Sigma-Aldrich and are used as received.

The molecule W$_2$(hpp)$_4$ has a very low ionization energy of 3.51 eV [113]. This extremely low ionization energy has the benefit that electrons can transfer easily to molecules with high electron affinity, for example C$_{60}$. However, as a drawback, the low IP makes W$_2$(hpp)$_4$ unstable in air, i.e. it reacts rapidly with oxygen. Devices using W$_2$(hpp)$_4$ become air sensitive and either should be kept in a glovebox (nitrogen environment) or encapsulated before exposing to ambient air. The sublimation temperature of W$_2$(hpp)$_4$ is in the range of 187 to 210$^\circ$C. The n-doped C$_{60}$ (C$_{60}$:W$_2$(hpp)$_4$) films achieve a conductivity of up to 4 S/cm [114].
4.1.7 P-dopant $F_6^{-}TCNNQ$

The p-dopant $F_6^{-}TCNNQ$ (1,3,4,5,7,8-hexafluorotetracyanonaph thoquinodimethane) has a structure relatively similar to another molecular p-dopant - $F_4^{-}TCNQ$, as shown in Figure 4.1. $F_6^{-}TCNNQ$ was first reported in the scientific literature by Koech et al. in 2010[115]. The electron affinity of $F_6^{-}TCNNQ$ is 5 eV, which makes it a perfect p-dopant for many matrix materials [116].

4.2 Device Preparation

All devices in this work are fabricated on glass substrates. The glass substrate dimension is 21 x 21 mm$^2$ and glass thickness is 1 mm. Glass substrates are purchased from Thin Film Devices Inc. USA.

Glass substrates are cleaned via a defined procedure before fabrication of the devices. In a first step of the cleaning procedure, the substrates are placed in an ultrasonic bath with soap (Laboratory Cleaning Detergent) and DI water for 20 min. Afterwards, the samples are rinsed with DI water before they are put again in an ultrasonic bath with DI water for 20 min. This is followed by rinsing with Acetone, Methanol, and Isopropyl alcohol for 20 min each. Then, substrates are dried by Nitrogen gas. Afterwards the substrates are transferred to glovebox and loaded into the deposition tool.

4.2.1 Deposition of Device Layers

Device layers are deposited by thermal evaporation with a background pressure below 10$^{-7}$ Torr. Figure 4.2 shows the setup of the deposition chamber used here.

Organic materials are sublimed in the chamber from aluminium nitride crucibles. Al is evaporated from graphene boats, SiO from molybdenum boats, and Cr from Chrome Plated Tungsten Rods. The crucibles and boats are heated electrically. The layer thickness and rate of deposition are monitored by a quartz crystal micro balances (QCMs), fixed above the crucible. The working mechanism of QCM is based on the change of resonance frequency of the QCM with the deposited material mass m. Therefore, the thickness of the deposited layer d can be calculated from the relation $d=m/\rho$, where $\rho$ is the density of the deposited material. The layer thickness can be monitored with a reading accuracy of 1 Å at real time and the rate of deposition can be monitored with a reading accuracy of 0.1 Å/s. Furthermore, the layer thickness on the substrate and layer thickness read by the QCMs have a fixed ratio, which is called the tooling factor, which is determined during calibration of the QCM. The deposited thin films are structured by shadow masks, which are attached to the substrates. The deposition process is done
under high vacuum conditions to avoid scattering of the evaporated material by undesired particles in the chamber and to protect the organic materials from degradation due to oxygen or moisture. Molecular doping is achieved by co-evaporation of the host and dopant materials and by using separate QCMs, as shown in Figure 4.2.

4.2.2 Encapsulation

Due to the low air stability of some organic semiconductors, devices are encapsulated inside the glovebox. The encapsulation process is done by gluing a glass lid by an epoxy glue onto the sample as shown in Figure 4.3. The glue is cured by leaving the device overnight inside the glovebox.

4.3 Mask Layout

The devices are structured by different shadow masks. The device active area is defined by the overlap area of all layers.

4.3.1 OFET Mask Layout

OFETs samples are fabricated at the Institut für Angewandte Photophysik, TU Dresden. Figure 4.5 presents the mask setup of OFET. Each sample has three independent devices. All devices in each sample have the same channel width of 30 mm and different
channel length (T1 = 0.3 mm, T2 = 0.15 mm, T3 = 0.1 mm).

From bottom to top, the bottom electrode mask (yellow) is the gate mask, which used to structure the gate and gate electrode, followed by the organic material mask (green), which is employed to structure the doped (channel), and the intrinsic organic layer. Then, the source (black) and drain (turquoise) masks are used to structure the doped injection layer and the metal contacts. Furthermore, the purple squares are metal pads to connect the three electrode strips.

4.3.2 P-i-n Diode Mask Layout

P-i-n diode samples are processed on glass substrates. The mask layout is shown in Figure 4.5. There are 3 devices per sample. The cathode electrode is deposited first, which is followed by the red mask used to structure the n-doped, intrinsic, and p-doped layers. At last, the anode is structured by the green mask. The overlap area of all layers
represents the active area, which has a size of 2.56 mm$^2$.

4.3.3 Layout of OPBTs with Large and Small Active Area

The mask layout of OPBTs with large active areas is shown in Figure 4.6a. Each sample has three independent devices with the same active area. The collector mask (yellow) is used first, followed by the organic layers mask (green). Then, the base mask (turquoise) is used, followed by the organic layers mask (green). The last mask is the emitter mask (red), which connects all devices. The active area of all devices equals 4 mm$^2$.

In this work, another set of OPBTs with small active areas are processed to study the effect of size active area of OPBTs. Figure 4.6b shows the mask setup of these OPBTs. The masks sequence is same as in the OPBT with large active area, but the active area size is 0.25 mm$^2$. There are five independent devices per sample.

In the OPBTs, the misalignment between masks is critical, as it can lead to a direct contact between collector and base, base and emitter, or collector and emitter. This problem can be solved by structuring the active area of the devices. Figure 4.7 shows the concept of active area structuring, which be discussed in detail in Sec.7.3.3. Structuring of the active area of OPBTs can be realized by two subsequent shadow masks. Two sets of insulating layers are deposited, one horizontally aligned layer (blue, Ins.1) and another vertically aligned (light brown, Ins.2), Therefore, an active area (red square) shown in Figure 4.7a is formed.

Figure 4.5: Mask layout to process p-i-n diodes with an active area 2.56 mm$^2$. 
4.4 Characterization of Devices

4.4.1 Electrical Characterization

Current-Voltage characteristics of devices are measured with a parameter analyzer Keithley SCS-4200. This instrument has three medium power SMUs and one high power unit. OFETs and OPBTs are three terminal devices, while p-i-n diode and $C_{60}$ diodes are a two terminal devices. Each electrode is connected to one SMU. In the measuring mode, the accuracy of the measured voltage value is better than $\pm 0.02\%$ and $\pm 0.06\%$ for the measured current.

4.4.2 Temperature Dependent Characterization

All $C_{60}$ diode samples are encapsulated inside the glovebox before transferring them to ambient air to do temperature dependent measurements. The design of the temperature stage is shown in Figure 4.8. The setup consists of a fan, a thermometer, a power supply, and a Peltier element. The Peltier element can cool the samples down to $-20^\circ C$ and can heat up to $60^\circ C$. 
Figure 4.7: Structuring the active area of OPBTs. (a) Mask Ins.1 and Ins.2 are used to structure the active area. (b) Mask Ins.2 and emitter mask are used to structure the active area.

Figure 4.8: Schematic sketch of the temperature dependent measurements.
CHAPTER 5

DOPED ORGANIC FIELD-EFFECT TRANSISTORS

The injection of minority charge carriers into n-doped organic field-effect transistors will be discussed\(^1\). It will be shown that minority charge carriers (holes) can be efficiently injected into the transistor via Zener tunneling. Moreover, the shift of onset minority conduction by lightly n-doping the channel region of the transistor will be studied.

5.1 Structure of n-Doped OFETs

The structure of the n-doped OFETs is shown in Figure 5.1. The transistor consists of pentacene as matrix material, Al\(_2\)O\(_3\) (120nm) as gate oxide, and source drain electrodes made of aluminum. To avoid trapping of electrons at the oxide interface, an aliphatic and insulating layer of TTC is added to the device as a passivation layer \([110, 117, 118, 109]\). The source and drain regions are doped by the n-dopant \(W_2(hpp)_4\) (50 nm, 2wt\%). Furthermore, in some transistors a thin layer of n-doped pentacene (1 wt\% \(W_2(hpp)_4\), thickness 0, 2, 4, and 6 nm) is sandwiched between the gate oxide and the intrinsic pentacene layer, i.e. the channel region is lightly n-doped. OFETs are fabricated by thermal evaporation under high vacuum conditions (base pressure of \(10^{-8}\) mbar). During deposition the substrate temperature is kept at 60\(^\circ\)C. All layers are deposited on glass substrates with 50 nm Al as a gate and 120 nm Al\(_2\)O\(_3\) as gate oxide. Al\(_2\)O\(_3\) is deposited by atomic layer deposition (ALD)\([45]\). To passivate trap states at the organic/oxide interface, a layer of the insulating long alkane chain tetratetracontane (TTC, C\(_{44}\)H\(_{90}\)) is deposited on top of Al\(_2\)O\(_3\)[110]. This deposition is followed by a thin n-doped pentacene layer (doping concentration varies from 1 wt\% - 16 wt\% \(W_2(hpp)_4\) and thickness ranges from 0 nm to 8 nm), an intrinsic pentacene layer (50 nm), n-doped pentacene layers as injection layers underneath the contacts \([(50 \text{ nm, 2wt\% } W_2(hpp)_4) \text{ or } (150 \text{ nm, 4 wt\% } W_2(hpp)_4)]\), and aluminum as source and drain contacts (50 nm). The layers are structured by shadow masks with a channel length of 0.3 mm and a channel width of 20 mm.

Doping is realized by thermal co-evaporation of matrix and dopant materials. The doping ratio is set by the deposition rates of two independent quartz crystal microbalances (QCMs). All OFETs are encapsulated under nitrogen atmosphere before transferring them to air.

\(^1\)This chapter is based on my publication "Minority Currents in n-Doped Organic Transistors" [61]
5.2 Conductivity of n-Doped Pentacene Films

The n-dopant $W_2(hpp)_4$ is synthesized according to the description in Section 4.1.6. Figure 5.2 a shows the setup of devices used for measuring the conductivity of n-doped pentacene films. The conductivity of n-doped pentacene films are measured to show that n-doping pentacene by $W_2(hpp)_4$ is effective, the current-voltage characteristics of n-doped pentacene films (Al(50 nm)/Pentacene:$W_2(hpp)_4$ (100 nm, [1,2,4,8, and 16 wt%])] on cleaned glass substrates with sample length 1.27 mm and width 4.4 mm are shown in Figure 5.2 b. The linear trend of the plots indicates that n-doping is indeed functioning. The conductivity of n-doped pentacene films ranges from $2.6 \times 10^{-6}$ S cm$^{-1}$ for 1 wt% to $2.5 \times 10^{-4}$ S cm$^{-1}$ for 16 wt% as shown in Figure 5.2 c.

In comparison to p-doped pentacene by F$_4$-TCNQ or F$_6$-TCNNQ, the conductivity is much lower[119], indicating that n-doping is not as efficient as p-doping. Furthermore, the strong increase in conductivity from 1wt% to 2wt% can be explained by filling of trap states by doping, seen as well in doped films of $C_{60}$[81, 120].

5.3 Transfer Characteristics of n-Doped OFETs

The transfer characteristics of n-doped OFETs are shown in Figure 5.3 a. At positive voltages, a quasi-Ohmic contact for majority charge carriers (electrons) [121] is formed, leading to efficient electron injection and clear n-type behavior of the transistors. However, at negative gate voltages, minority (hole) conduction is seen as well. Furthermore, doping the channel strongly influences minority conduction of the transistor. As seen in
Figure 5.2: (a) Setup of devices used for measuring the conductivity of n-doped films. (b) Current-voltage characteristics of pentacene films doped by $W_2(hpp)_4$ (1, 2, 4, 8, and 16 wt%). (c) Conductivity of n-doped pentacene films at various doping ratios.

Figure 5.3 a, the onset of hole conduction shifts with increasing thickness of the doped channel layer (cf. Figure 5.3 b as well).

At first sight, the fact that minority charge carriers are efficiently injected into the transistor channel is counter-intuitive: The n-doped injection layer in fact increases the injection barrier for holes and should suppress any hole injection into the transistor. However, the minority charge carriers injection into the transistor channel can be explained by Zener tunneling underneath the drain contact of n-doped OFETs.

5.4 Injection of Minority Charge Carriers by Zener Tunneling

Charge generation by Zener tunneling is well known from inorganic semiconductors[122, 123] and commonly observed in organic p-i-n diodes as well[10]. It is used for example in charge generation layers of stacked OLEDs [124, 125] or AC driven OLEDs[126], and in injection layer for inverted OLEDs[127].

Thus, the charge generation by zener tunnelling in organic p-i-n diode should be
studied to understand the minority charge carriers injection into the transistor channel.

5.4.1 Structure of Organic p-i-n Diode

The design of the p-i-n diode is shown in Figure 5.4. The p-i-n diode samples are prepared by thermal evaporation at base pressure $10^{-8}$ mbar. The diodes consist of p-doped pentacene (F$_6$-TCNNQ, 50 nm, 4 wt%), intrinsic pentacene of varying thickness (30, 40, 50, 60, 70, and 80 nm), and n-doped pentacene (W$_2$(hpp)$_4$, 50 nm, 8 wt%). Aluminum is used as anode and cathode material (50 nm). The samples are structured by shadow masks with an active area is $2.56 \text{ mm}^2$.

5.4.2 Zener Tunneling in an Organic p-i-n Diode

Zener tunneling in organic diodes was thoroughly studied in the past. It was found that the tunneling current depends exponentially on the thickness of intrinsic layer and only weakly on the temperature, confirming the tunneling nature of the current [100, 128, 129]. Furthermore, it was found that the breakdown voltage increases for increasing intrinsic layer thickness and lower doping concentrations [100]. Zener tunneling is effective in pentacene homojunctions as well. Figure 5.5 a displays I-V curves of pentacene p-i-n diodes with different intrinsic interlayer thicknesses (30 nm to 80 nm) prepared as described in the experimental information and as sketched in Figure 5.4.

In forward direction a sharp increase in current at about 2V is seen. In accordance to
other reports on organic diodes, the current onset in forward direction does not depend on the interlayer thickness of pentacene[100].

In reverse direction, the current exponentially rises at large reverse voltages. In contrast to the forward direction, the onset of the backward current, i.e. the breakdown voltage of the Zener diode, depends strongly on the interlayer thickness and shifts by approximately -1.5 V for each additional 10 nm of intrinsic interlayer.

The dependency of the backward current on the intrinsic interlayer thickness is shown in Figure 5.5 b. A purely exponential dependency is found, which is in accordance to the results of Kleemann et al.[100].

The almost linear increase in breakdown voltage leads to an approximately constant breakdown field shown in Figure 5.6 a. Overall, a fairly constant breakdown field of around 1.2 - 1.33 MV cm$^{-1}$ is observed.

The mechanism of Zener tunneling in an organic pentacene p-i-n diode is illustrated in Figure 5.6 b. Under reverse bias the applied voltage drops across the intrinsic layer resulting in large electric fields. If the electric field exceeds the breakdown field, electrons can tunnel from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of neighboring molecules. Effectively, electron and holes are generated within the junction, which are transported to the n- and p-doped layer, respectively, by the applied electric field.
Figure 5.5: (a) Current-voltage characteristics of organic p-i-n diodes with different intrinsic interlayer thicknesses. (b) Reverse current density at -7V vs. intrinsic interlayer thickness. The p-i-n device consists of Al(50 nm)/pentacene:F$_{6}$-TCNNQ(4 wt%, 50 nm)/intrinsic pentacene (x nm)/pentacene:W$_{2}$(hpp)$_{4}$(8 wt%, 50 nm)/Al (50 nm).

5.4.3 Zener Tunneling in n-Doped OFETs

Zener tunneling as observed in the pentacene p-i-n homodiodes can explain the observed minority injection into the transistor channel as shown in Figure 5.7. At negative gate voltages, a large voltage drops between gate and drain electrode. If the electric field in the intrinsic pentacene layer exceeds the threshold for Zener tunneling, free electrons and holes are generated. Electrons will drift back to the n-doped drain electrode, whereas holes are injected into the transistor channel.

To show that the electric field inside the intrinsic pentacene layer underneath the drain electrode is indeed in the range of the breakdown field, the voltage drop across the intrinsic pentacene layer is estimated by modeling this part of the transistor by a simple series connection of the capacitance of the gate insulator ($C_{\text{ins}}$, 120 nm of Al$_{2}$O$_{3}$ and 25 nm of TTC) and the intrinsic pentacene layer ($C_{\text{intr}}$ 50 nm). Hence, for transistors without channel doping, the electric field in the intrinsic pentacene layer $E_{\text{intr}}$ becomes:

$$E_{\text{intr}} = \frac{1}{d_{\text{intr}}} \frac{C_{\text{ins}}}{C_{\text{intr}} + C_{\text{ins}}} (V_{DS} - V_{GS}),$$  (5.1)

where $d_{\text{intr}}$ denotes the thickness of the intrinsic pentacene layer.

Without channel doping, hole conduction sets in at $V_{GS} = 0.5V$ (OFETs with 0 nm n-doped channel) (cf. Figure 5.3 a), resulting in an electric field strength in the range 1.19 MV cm$^{-1}$ ($C_{\text{ins}} = 3.7 \times 10^{-8}Fcm^{-2}$; a dielectric constant $\varepsilon_r = 3$ is assumed for
organics, close to the breakdown electric field shown in Figure 5.6a confirming the assumption that Zener tunneling is responsible for minority injection.

5.5 Influence of Doping on Minority Channel Formation

Only transistors without channel doping were discussed in the previous section. However, as seen in Figures 5.3a and b, doping the transistor channel has a strong influence on the formation of the hole (minority) channel as well. The onset of hole conduction shifts by approx. 4.5V due to an increase in thickness of the doped channel by 6 nm.

Two mechanisms can cause this strong shift in onset of minority conduction. First of all, the injection mechanism itself can explain the observed dependency. Hole injection by Zener tunneling can only be efficient if the n-doped layer at the insulator/semiconductor interface is fully depleted by the applied negative gate voltage. Otherwise, all holes are generated inside the intrinsic pentacene layer will recombine with electrons still remaining in the n-doped channel. Hence, an increase in the doped layer thickness leads to an increase in the voltage needed to fully deplete the layer from electrons, which in turn increases the onset voltage as seen in Figures 5.3a and b.

The voltage shift resulting from an increase in thickness of the doped channel layer can be estimated by straightforward arguments. The voltage across the insulator and doped layer needed to fully deplete an n-doped layer at the insulator-semiconductor interface
Figure 5.7: Equivalent circuit of the region of the OFET underneath the drain electrode at reverse bias. If the electric field in the intrinsic pentacene layer exceeds the breakdown field, electrons and holes are generated by Zener tunneling.

\[
V = V_{FB} + \frac{eN_D^+d_{dop}^2}{2\varepsilon_0\varepsilon_{P5}} \left( 1 + 2\frac{d_{ins}\varepsilon_{P5}}{d_{dop}\varepsilon_{ins}} \right) \]

(5.2)

with \( V_{FB} \) the flatband voltage, \( e \) the elementary charge, \( N_D^+ \) the density of ionized, i.e. active dopants, \( d_{dop} \) the thickness of the doped layer, \( \varepsilon_{P5} \) the dielectric constant of pentacene, \( d_{ins} \) the thickness of the gate insulator, and \( \varepsilon_{ins} \) the dielectric constant of the gate insulator.

Assuming that the capacitance of the depleted doped channel layer \( C_{dep} \) is much larger than the capacitance of the gate insulator \( C_{ins} \) and the intrinsic pentacene layer \( C_{intr} \) and Equation 5.1 can re-arrange and solve for \( V_{ins} \), i.e. the voltage dropping across the insulator:

\[
V_{ins} = \frac{C_{intr}}{C_{intr} + C_{ins}} (V_{DS} - V_{GS}) \]

(5.3)

By using Equations 5.2 and 5.3, \( \Delta (V_{DS} - V_{GS}) \) is the shift in onset of hole conduction. It can be modeled for a given concentration of free electrons in the doped layer \( N_D^+ \). A good agreement to the experimental data is reached for a density of active dopants \( N_D^+ \) of approx. \( 9.5 \times 10^{17} cm^{-3} \), which is shown as straight line in Figure 5.3b. This electron density corresponds to a doping efficiency defined as the ratio of active dopants \( N_D^+ \) to the total density of dopants \( N_D \) of 11%. However, this number is only valid under the assumption that the shift in the onset voltage is caused by an increasingly more difficult
depletion of thicker doped channel.

The other mechanism that can explain the shift in onset voltage of minority conduction is an increase in hole trapping due to an increase in the number of n-dopants. For most dopant/host combinations a low doping efficiency was observed, which means that most dopant molecules do not donate an electron to the LUMO of host material. However, these states are not entirely inactive. Although they are not sufficiently strong to donate an electron to the LUMO of the host material, they still represent trap states for holes located in the HOMO of the matrix.

Hence, an increase in the thickness of the doped layer will increase the number of traps \( N_t \) at the gate insulator/pentacene interface, which in turn will shift the onset of hole conduction according to

\[
\Delta V = \frac{N_t e d_{dop}}{C_{ins}} \tag{5.4}
\]

Following Equation 5.4 and the experimental result shown in Figure 5.3b (\( \Delta V = 4.5V \)), a density of traps \( N_t \) in the range of \( 1.75 \times 10^{18} \text{cm}^{-3} \) can be calculated.

5.6 Influence of Channel Doping on Majority Charge Carriers

Two mechanisms were discussed in the previous section to explain the shift of the onset of hole conduction: an increase in onset voltage due to the additional voltage needed to fully deplete the doped channel layer or, alternatively, an increase in onset voltage due to stronger trapping of holes by inactive n-dopants. Both mechanisms can explain the experimental results well, but show a different dependency on the doping efficiency. While a high doping efficiency increases the density of free charge carriers in the doped layer, which will make depletion more difficult, a low doping efficiency will leave more dopant molecules inactive resulting in increased trapping. Therefore, to determine which mechanism is dominating, the density of free charge carriers in the doped channel is determined and hence the doping efficiency. Using of the influence of doping on the majority charge carriers, i.e. on electron transport visible at positive gate voltages. It is known that doping leads to a shift in threshold voltage of majority charge carriers according to[45]

\[
V_{th} = V_{FB} + \frac{eN_D^+d_{dop}}{C_{ins}} \tag{5.5}
\]

Figure 5.8a shows the transfer characteristics of a series of transistors with 8nm thick doped channel and increasing doping concentrations (1wt%, 2wt%, 4wt%, and 16 wt%). A shift of the n-threshold voltage is clearly seen and summarized in Figure 5.8b. Overall, the threshold voltage shifts from approx. 7V at low doping concentrations to 4V at 16 wt%.
As seen, an increase in n-doping concentration in the channel not only increases the n-threshold voltage by increasing the density of free electrons, but suppresses the p-type behavior also. This behavior is in accordance to the observation that the onset of p-conduction increases with increasing thickness of the doped layer and is consistent with the observation of Noh et al. [132]. By using Equation 5.5, the density of free electrons in the doped channel $N_D^+$ can be deduced. The density of charge carriers is $6.7 \times 10^{16} cm^{-3}$ at a doping concentration of 1 wt%. Combined with the known density of dopants in the film this results in a doping efficiency of 0.8 % only, much lower than the doping efficiency estimated from Equation 5.2, i.e. by assuming that the depletion of the n-doped transistor channel is limiting hole conduction.

The low doping efficiency observed here therefore indicates that trapping of holes by inactive n-dopants in the channel is causing the strong shift in the onset of hole transport. Adding more dopants by increasing the thickness of the doped layers leads to an increase in trapping and consequently a shift in the transfer characteristic. Furthermore, the low doping efficiency explains why no shift in n-threshold voltage is observed at the low concentration used in Figure 5.3 and why the overall conductivity of n-doped pentacene films is much lower compared to p-doped pentacene films (Figure 5.2).
CHAPTER 6

CHARGE TRANSPORT IN C\textsubscript{60}-BASED SCHOTTKY DIODES

To fully understand the operation of OPBTs, it is essential to clarify charge transport in the individual diodes of the device. Most importantly, the OFF-state current of the OPBTs is determined by the OFF-state current of the bottom diode, i.e. to increase the ON/OFF ratio of OPBTs the OFF-state current of the bottom diode has to be minimized. Here, systematic experiments are conducted that clarify the origin of the OFF-state current of the bottom diode. Furthermore, how these OFF-state currents can be minimized will be discussed.

6.1 Structure of C\textsubscript{60}-Based Schottky Diodes Used As Bottom Diodes for OPBTs

Figure 6.1 shows the structure of the bottom diode. The device consists of 100 nm Aluminium (Al) covered by 20 nm Chromium (Cr) as anode, a layer of intrinsic C\textsubscript{60} as organic semiconductor, and a thin Al layer as cathode. Outside the device area, the cathode is enhanced by a 50 nm Al contact pad, which doesn’t contribute to the active area. After depositing the enhancement contact, the device is exposed to ambient air for 30 min, resulting in the formation of a thin native oxide layer AlO\textsubscript{X} on the surface of the base.

For the device shown in Figure 6.1a the intrinsic layer thicknesses (50 nm, 100 nm, and 150 nm) and the thickness of the top electrode (13 nm, 15 nm, 17 nm, and 19 nm) is varied. The active area of the diode sketched in Figure 6.1a is defined by the overlap of all three electrodes (anode, organic layer, and cathode), which is 4 mm\textsuperscript{2}. In the devices shown in Figure 6.1b the top electrode thickness is varied (13 nm, 15 nm, 17 nm, and 19 nm), whereas the C\textsubscript{60} layer thickness is kept constant at 100 nm. To vary the active area, additional layers of SiO\textsubscript{X} are deposited by thermal evaporation onto the bottom electrode. The active area is defined by the openings in the insulating layer of SiO\textsubscript{X} and ranges from 0.01 mm\textsuperscript{2}, 0.0225 mm\textsuperscript{2}, to 0.04 mm\textsuperscript{2}.

All samples are produced under high vacuum conditions by thermal evaporation. Shadow masks are used to structure the electrodes and the organic layers. After the exposure step, all samples are annealed for 4h at 60°C inside the glovebox, which is filled with pure Nitrogen (oxygen and humidity levels below 0.1ppm). The quality of the SiO\textsubscript{X} layers deposited by thermal evaporation is tested in Figure 6.2, which plots the I-V and C-V characteristic of a thin film (100 nm) of SiO\textsubscript{X} (glass...
Figure 6.1: Structure of the bottom diode. (a) Bottom diode with active area of 4 mm$^2$. The thicknesses of intrinsic $C_{60}$ layer and of the cathode is varied. (b) Bottom diode with structured active area are 0.01 mm$^2$, 0.0225 mm$^2$, and 0.04 mm$^2$. Cathode thickness ranges from 13, 15, 17, to 19 nm.

substrate, overlap area 4 mm$^2$). The current is symmetric in the forward and reverse bias and reaches around $3 \times 10^{-8}$ A at 3V [133, 134], which is small compared to currents usually flowing in a Schottky diode. Thus, the SiO$_X$ is a good insulator to block leakage currents between cathode and anode. Figure 6.2b plots the capacitance of SiO$_X$, which is independent of voltage. The dielectric constant of SiO$_X$ is calculated by using equation 6.1 and equals 4.23, which is close to values found in the literature [135, 136].

$$C = \frac{\varepsilon \varepsilon_r A}{d}$$ (6.1)

where $\varepsilon_r$ is the relative dielectric constant, $\varepsilon$ is the permittivity of free space, $A$ is the device area, and $d$ is the SiO$_X$ thickness.

To examine the structuring of the active area of Schottky diodes, Figure 6.3 shows the top view of an optical profilometer image of a finished device. It is clear that the active area is in the middle of all layers. Furthermore, it is observed that the structured active area is slightly smaller than the nominal area. All dimensions (width and length) are smaller by approximately 10 $\mu$m, therefore the real active areas become 0.0361 mm$^2$, 0.0186 mm$^2$, 0.0061 mm$^2$.

6.2 Characteristics of $C_{60}$-Based Schottky Diodes

Understanding the behavior of the bottom diode of the OPBT is essential for describing the operation of the OPBTs. In the following, the current-voltage characteristics of systematically varied diodes are discussed. The voltage is always applied to the cathode contact with reference to the anode and the current is measured at the anode. Figure 6.4a presents a representative I-V characteristic of the bottom diode with a 100 nm $C_{60}$
layer and 17 nm top electrode thickness. In the reverse bias, the current increases only slowly with applied voltage as shown in Figure 6.4a (regime I) and only reaches $\approx 2 \times 10^{-3}$ A/cm$^2$ at -4V.

The current is much higher at forward voltages. Below a forward bias 1V, the current exponentially increases with applied voltage (regime II). In contrast, at a forward voltage above 1V (regime III), the current levels off. Plotting the current density in regime III in a double logarithmic scale (cf. Fig.6.4b) shows that the current density depends quadratically on the voltage [137, 138] [105] ($J \propto V^2$).

To understand the current regimes in forward direction, the organic layer thickness of the diode is varied. Figure 6.5 exhibits the J-V characteristics of the diode as a function of $C_{60}$ layer thickness with 17 nm thick cathode layers (cf. Fig. 6.1). A clear dependence is seen in both forward and reverse bias. Overall, the forward and reverse current densities increase for thinner $C_{60}$ layer. As shown in Figure 6.5, at 1 V forward bias (regime II), the forward current density increases exponentially with voltage. Furthermore, in regime II, the forward current density is independent of the $C_{60}$ layer thickness. Therefore the current can be explained by injection-limited currents (ILC).

However, above 1 V (regime III), the $C_{60}$ layer thickness has a strong influence on the current density. As shown in Figure 6.6, the current density is inversely proportional to the cube of the layer thickness. Overall, the forward current density fits well to equation 6.2 $J \propto V^2/d^3$ [139], which again confirms space-charge limited currents in regime III. Combining the voltage and thickness dependency, the current in regime III can be explained by space-charge limited currents (SCLC) discussed in chapter 2. For
space charge limited currents, a square dependency of the current density is predicted [140, 139]:

$$J = \frac{9}{8} \varepsilon \varepsilon_r \mu \frac{V^2}{d^3}$$

(6.2)

where $\varepsilon_r$ is the relative dielectric constant, $\varepsilon$ is the permittivity of free space, $\mu$ is the carrier mobility, $d$ is the organic layer thickness, and $V$ is the applied voltage. Using equation 6.2, the electron mobility of $C_{60}$ can be calculated from a plot of current density versus the square of the forward bias voltage. Assuming a relative dielectric constant of $C_{60}$ of 4 [141, 142] results in an electron mobility of $C_{60}$ is $2 \times 10^{-4}$ cm$^2$/V.s.

This electron mobility is much lower compared to those reported for OTFTs [143, 144, 106] and diodes [105] based on $C_{60}$. This low charge carrier mobility can be explained by the exposure to ambient air during the oxidation of the cathode. Exposing the $C_{60}$ film to both $O_2$ and $H_2O$ is known to cause degradation of the $C_{60}$ film [145, 146, 147, 141]. A decline in the electron mobility by almost three orders of magnitude upon exposure to ambient air was reported in the literature [145, 148]. Absorption of $O_2$ and $H_2O$ molecules in the $C_{60}$ films induces an increase in the density of electron trap states, which leads to a reduction of the forward current density of the diode [145, 149, 148].

6.3 Nature of Reverse Currents

Whereas the current in forward direction can be readily explained by ILC (regime II) and SCLC (regime III), the nature of the reverse current is much less understood. To
Figure 6.4: (a) Current-voltage characteristic of the bottom diode. Three different current transport regimes can be identified. (b) log(J)- log(V) plot for the I-V characteristic in regime III showing a quadratic dependency of current on the voltage, indicating space-charge limited current (SCLC) as described by Equation 6.2.

clarify the origin of these unwanted leakage currents, several parameters that can control the OFF-state current of the diode are tested. In particular, the effect of the thickness of the C_{60} layer, of the structured active area, of the temperature, and of the top electrode on the OFF-state current of the diode is studied in the following.

6.3.1 \( C_{60} \) Layer Thickness Dependency

As shown in Figure 6.5, the current in forward and reverse direction depends on the \( C_{60} \) layer thickness. Figure 6.7 plots the reverse current density at -4V with the \( C_{60} \) layer thickness. Each value is the average of 12 devices and the error bar corresponds to the standard deviation (\( \pm \sigma \)).

At reverse bias (regime I), the current density increases slowly with applied voltage, whereas the current density obviously depends on the thickness of \( C_{60} \) layer as shown in Figure 6.5. Overall the reverse current density increases by almost one order of magnitude with decreasing the \( C_{60} \) layer thickness from 150 nm to 50 nm.

6.3.2 Active Area Dependency

The current-voltage characterises of the diode are studied to understand the influence of the size of the active area. Structuring the overlap area can be done by inserting an insulating layer (\( \text{SiO}_x \)) between anode and cathode electrode (cf. Fig. 6.1b). Figure 6.8 shows the current-voltage characteristics of the diode with 100 nm \( C_{60} \) layer, 17 nm top electrode, and varying active area (0.04 mm\(^2\), 0.0225 mm\(^2\), and 0.01 mm\(^2\)). Both,
forward and backward currents show a clear scaling with the device area, as shown in Figure 6.8.

Figure 6.9 plots the trend of the forward and reverse current as a function of structured active area. Each value in the figure represents the average of 12 devices and the error bar corresponds to standard deviation ±σ. The forward current shows a strong increase with the device area. Overall, a 4 times increase in area leads to an increase in the current by a factor of 20, as shown in Figure 6.9a.

Figure 6.9b shows that the reverse current linearly increases with active area. The current changes by a factor of 4 from small to large active areas.

6.3.3 Temperature Dependency

The diode characteristics is strongly influenced by temperature. Figure 6.10 shows the J-V characteristics of the diode with 100 nm thick $C_{60}$ layer and a top electrode thickness of 17 nm (cf. Fig. 6.1b) for temperatures ranging from 253K to 360K.

In all regimes, the current increases with temperature. In regime III, the current is limited by space charges. Hence, according to Eq. 6.2, the charge carrier mobility can be deduced from Figure 6.10, which is shown as a function of temperature in Figure 6.11. As usually observed for organic semiconductors, the charge-carrier mobility exhibits an Arrhenius type temperature dependence, according to [150, 151, 152, 153, 154]

$$
\mu(E = 0) = \mu_0 \exp \left( -\frac{\Delta}{K_B T} \right)
$$

(6.3)

where $\mu_0$ is the charge-carrier mobility in the limit of infinite temperature, $\Delta$ is the
Figure 6.6: Forward current density of the diode with different $C_{60}$ layer thickness (50, 100, and 150 nm) at $V = 4\ \text{V}$.

activation energy, $K_B$ is the Boltzmann constant, and $T$ the absolute temperature. The mobility decreases over more than two orders of magnitude from $T=253\ \text{K}$ to $360\ \text{K}$ at applied voltage $4\\text{V}$. The activation energy of the bottom diode is measured by varying the temperature from $253\ \text{K}$ to $360\ \text{K}$ in ambient air. By using equation 6.3, the activation energy is calculated and equals to $0.35\ \text{eV}$. However, this value is in the same range as reported before [155, 156].

In Figure 6.12, the change of reverse current density with temperature is plotted. Figure 6.12b shows that the reverse current density decreases drastically for temperatures ranging from $360\ \text{K}$ to $253\ \text{K}$. At temperatures lower than $300\text{k}$, the reverse current becomes independent of temperature.

As seen before, the reverse current of the $C_{60}$ diode scales with the thickness of the $C_{60}$ layer, the size of the active area, and temperature. The behavior of reverse current can be explained by inhomogeneities and possible microscopic pinholes in the $C_{60}$ film, which attribute to structural properties of the $C_{60}$ layer (e.g. roughness spikes in the deposited layer). These can give rise a leakage currents in the bottom diodes. In case of a varying $C_{60}$ intrinsic layer thickness, the reverse current increases for thinner $C_{60}$ layer as the possibility of structural inhomogeneities of the $C_{60}$ layer increases.

6.4 Optimization of $C_{60}$-Based Schottky Diodes

The ON/OFF ratio of the OPBT is limited by backward currents of the bottom diode. Here, how this backward current can be reduced is studied. Three different processes are tested: optimization of the oxidation conditions and varying thickness of
Figure 6.7: Reverse current density of the diode with different $C_{60}$ layer thickness (50, 100, and 150 nm) at $V= -4$ V.

the top electrode, as well as annealing the diodes.

6.4.1 The Role of Oxidation of the Top Electrode

To understand the effect of exposure to air, the current of a large number of devices is shown in Figure 6.13. The effect of different exposure times (30 min to 3h) on the forward and reverse current of a diode with an active area 0.04 mm$^2$, 100 nm $C_{60}$ layer, and top electrode thickness 17 nm is shown in Figure 6.13. The diodes are exposed to ambient air for different exposure times and measured inside the glovebox, which is filled with pure Nitrogen (oxygen and humidity levels below 0.1ppm).

Both forward and reverse current density depend on the exposure time to air. Figure 6.13a demonstrates that the forward current decreases if the exposure time is increased from 30 min to 60 min. Overall, however, the spread of data is large, which complicates data analysis. This decrease in forward current can be explained by a degradation of the organic layer due to adsorption of moisture or oxygen in air [157, 145].

The trend is clearer for the reverse current. Here, the current decreases with exposure time as shown in Figure 6.13b. Figure 6.13b exhibits that the backward current decreases drastically by almost one order of magnitude by increasing the exposure time by 30 min. For longer times, the backward current starts to saturate (60 min to 180 min). The behavior of the reverse current with exposure time can be explained by forming the oxide layer, when Al film exposed to air. It is known that Al films are easily oxidized by oxygen in air, and a thin oxide layer (native oxide) is formed on its surface [158, 159]. Following an initial very rapid oxide growth, oxidation slows down or nearly stops, leading to a
saturation of the reverse current after 60 min [159, 160, 161, 158, 162]. The formation of a thin oxide layer can block electron injection from the top electrode, thus decreases the backward current [91, 163, 164]. The intentional control of the oxide layer by varying the exposure time is effective in suppressing the backward current and in improving the ON/OFF ratio in the OPBT [163].

6.4.2 Influence of Thermal Annealing

To study the influence of annealing on the diode performance, the devices are annealed for 4 hours at a temperature of 60°C after the cathode is exposed to ambient air. The annealing process is done inside the glovebox. Figure 6.14 shows that higher device performance is obtained by annealing. The forward current increases by almost one order of magnitude. This can be attributed to removal of oxygen and humidity from the organic layer.

By exposing the diode to ambient air the organic layer starts to degrade due to absorption of oxygen and water vapor, which create charge trap states. Thermal annealing treatment helps to remove oxygen and moisture from the organic layer and to reduce the density of trap states [145, 165] [148]. Figure 6.14 exhibits a little decrease in the reverse current of the bottom diode, which slightly helps to decrease the OFF-state current of OPBT and increase the ON/OFF ratio [91].

6.4.3 Top Electrode (Cathode) Thickness Dependency

The top electrode thickness is an essential parameter for the operation of OPBTs [90, 166, 167]. To clarify if it influences the electrical behavior of the diode, the forward and reverse current of the diode with 100 nm $C_{60}$ layer and different thickness of the top
Figure 6.9: Currents of the bottom diode with different active area. (a) Forward current at applied voltage \( V = 4 \) V. (b) Reverse current at applied voltage \( V = -3 \) V.

electrode (cf. Fig. 6.1a) is presented in Figure 6.15. The forward and backward current density of a total of 32 diodes are plotted. The error bars denote the \( \pm \sigma \). Clearly, there is no influence of the top electrode thickness on the forward current density [168, 169]. The reverse current density is independent of Al top electrode thickness [169] as well, as shown in Figure 6.15b.

6.5 \( C_{60} \)-Based Schottky Diodes Used As Top Diodes of OPBTs

The top diode is another essential part to understand the operation of OPBT. In particular, the ON-state current of OPBT is controlled by top diode. Here, by an optimization of electron injection of the top contact, the ON/OFF ratio of the OPBT can be increased. For example, Fischer et al. [92] increased the ON current of the OPBT from 100 to 1000 \( mA/cm^2 \) by doping the emitter contact. The ON/OFF ratio of OPBT can be improved by doping the \( C_{60} \) layer of the top diode to increase the electron injection as well [92].

6.5.1 Diode Setup

Figure 6.16 shows the structure of the top diode. The device is processed on glass substrates and consists of a thin Aluminium (Al) layer (17 nm) as cathode, a layer of intrinsic \( C_{60} \) as organic layer (100 nm), doped \( C_{60} \) layer (20 nm), and (20 nm) Chromium (Cr) followed by (100 nm) Aluminium (Al) as anode. The cathode layer is exposed to ambient air for 30 min, before the sample is taken back to vacuum to process the other layers. As discussed above, the air exposure step is responsible for the formation of a
thin native oxide layer AlO$_X$ on the surface of the cathode. Here, all organic layers and the anode are processed in vacuum after the air exposure of the cathode. Doping of C$_{60}$ is processed by co-evaporating of C$_{60}$ and W$_2$(hpp)$_4$ at a concentration of 2 wt% . The electron injection at the top electrode of the top diode is increased by inserting a doped C$_{60}$ layer due to a reduction of a contact resistance [114].

6.5.2 Diode Characteristics

Figure 6.17a exhibits the I-V characteristic of the top diode. There is no major difference in the behavior of I-V characteristic between top and bottom diode (section 3.2). In forward bias, the current has two different regimes depending on the applied voltage as shown in Figure 6.17a. At forward voltage below 1V, the current increases exponentially with applied voltage (regime II). In contrast, at a forward voltage above 1V (regime III), the current starts to be settle down. Figure 6.17b represents log(J)-log(V) plot in regime III, showing that the current density depends quadratically on the voltage.

In the forward bias, two regimes II & III can be explained by injection-limited currents (regime II, ILC) and space-charge limited currents (regime III, SCLC). The current density obviously increases exponentially with voltage for injection-limited currents regime, while the current density shows a square dependency with voltage in space-charge limited currents [137, 138, 105] regime according to Equation 6.2 [140, 139].

The electron mobility of C$_{60}$ in the top diode can be extracted from a plot of current density versus the square of forward bias voltage for SCLC regime. The calculated electron mobility of C$_{60}$ is $4 \times 10^{-4} \ cm^2/V.s$, where the relative dielectric constant 4 is
assumed for $C_{60}$ [141, 142].

In the reverse bias, the current increases slowly with negative voltage as shown in Figure 6.17a (regime I) and the reverse current is lower than the forward current by almost 3 orders of magnitude at $\pm 4V$. The reverse current can be explained by inhomogeneities and possible microscopic pinholes in the $C_{60}$ layer.
Figure 6.12: Current densities of the bottom diode versus temperature. a) Forward current density at applied voltage $V = 4$ V. b) Reverse current density at applied voltage $V = -4$ V.

Figure 6.13: Bottom diode currents versus exposure time. a) Forward current at applied voltage $V = 4$ V. b) Reverse current at applied voltage $V = -3$ V.
Figure 6.14: Current-voltage characteristics of the bottom diode with different annealing temperature. The diode structure is shown in Figure 6.1b with active area $0.04 \, mm^2$ and top electrode thickness 17 nm.

Figure 6.15: Top electrode dependency of the bottom diode. a) Forward current density at applied voltage $V = 4 \, V$. b) Backward current density at applied voltage $V = -4 \, V$. 
Figure 6.16: Setup of the top diode with active overlap area is 4 mm².

Figure 6.17: a) Current-voltage characteristic of the Schottky diode with voltage applied to the bottom electrode. Three different current transport regimes can be identified. b) log(J)- log(V) plot for the I-V characteristic in regime III showing a quadratic dependency of current on the voltage, indicating space-charge limited current (SCLC) as described by Equation 6.2.
CHAPTER 7

ORGANIC PERMEABLE BASE TRANSISTORS

Organic Permeable Base Transistors (OPBTs) using the small molecule $C_{60}$ as the semiconductor material are discussed. In the beginning, the fabrication of these $C_{60}$ OPBTs is explained by presenting the layer stack and essential treatments. Based on the results of the previous chapter, the operation mechanism of the OPBT is discussed. Various approaches are presented to optimize the OPBT, especially by reducing the active area of OPBTs.

7.1 Organic Permeable Base Transistor (OPBT) Structure

Figure 7.1a shows the structure of the OPBT. The OPBT is processed by thermal vapor deposition in vacuum and structured by using shadow masks. Fullerene ($C_{60}$) is the n-type organic semiconductor material (i-$C_{60}$), which is used for bottom and top layers (thickness 100 nm). The top and bottom electrode consist of a combination of Al (100 nm) and Cr (20 nm). Using aluminium in the top and bottom electrode decreases the resistance of the electrode and ensures a proper wetting of the thin film on the glass substrate. The chromium layer protects the Al layer from oxidation and supplies a sufficient electron injection into $C_{60}$. A thin Al layer with a thickness of 13, 15, 17, and 19 nm is used as middle or base electrode and is exposed to ambient air for 30 min to 60 min. The top 20 nm thick $C_{60}$ layer is doped with a highly efficient n-dopant ($W_2(hpp)_4$) to improve the electron injection by reducing the contact resistance [114]. Doping of $C_{60}$ is accomplished by co-evaporating $C_{60}$ and $W_2(hpp)_4$ at a concentration of 2 wt%. After fabrication, the devices are transferred to a glovebox filled with a pure Nitrogen (less than 0.1 ppm $O_2$ and $H_2O$). Annealing is done for 2h at temperature ranging between 150°C to 180°C.
7.2 Working Mechanism Of OPBTs

OPBTs consist of two Schottky diodes stacked back to back. The top diode is formed between the emitter and the base electrodes (BE diode) and the bottom diode is formed between the collector and the base electrodes (BC diode) as shown in Figure 7.1. As discussed in Chapter 3, the current flowing from emitter to collector is controlled by a variation of the base-emitter voltage $V_{BE}$.

In the so-called base sweep measurement, the base-emitter voltage $V_{BE}$ is increased while the collector-emitter voltage $V_{CE}$ is kept constant. This measurement is analogous to the transfer characteristic of an OFET.

Figure 7.2 shows a base sweep of an OPBT consisting of 100 nm Aluminium (Al) covered by 10 nm Chromium (Cr) as collector electrode, a layer of intrinsic $C_{60}$ of 100 nm as organic semiconductor, a thin Al layer of 13 nm as base electrode, a layer of intrinsic $C_{60}$ of 100 nm as organic semiconductor, a doped $C_{60}$ layer of 20 nm, and a 10 nm Chromium (Cr) followed by 100 nm Aluminium (Al) as emitter electrode.

Overall, the OPBT shows an ON/OFF ratio of $\approx 10^3$ and a current amplification of $\approx 15$ at 3V, as shown in Figure 7.2 a and c. This current amplification corresponds to a transmission of larger than 95% (see Figure 7.2 d), which is a strong indication that transmission of charge carriers through the base can not be explained by a hot carrier transport, as hot-electron transistors have not reached a transmission higher than 90% for 10 nm thick Al base layers [170]. Instead, the high transmission observed here can be explained by small openings in the base electrode, allowing for direct contact of the upper and the lower intrinsic $C_{60}$ layer in the OPBT.

Three qualitatively regimes can be seen in the I-V characteristics of OPBT, as shown in Figure 7.2 a and b. At base-emitter voltages $V_{BE}$ below 0V, both bottom (BC) and top (BE) diodes operate in reverse direction. Hence, current flow through the device is
Figure 7.2: a) Current-Voltage characteristics of $C_{60}$ OPBT at a driving voltage $V_{CE} = 3V$ and active area 4 mm$^2$. b) Collector current regimes with base-emitter voltage. c) Current gain or amplification. d) Transmission. $I_C$: collector current, $I_E$: emitter current, and $I_B$: base current.

blocked and no currents can be injected at the emitter. The small current observed below $0V$ are due to reverse currents of both diodes.

For $V_{BE}$ larger than $0V$, the top diode (BE diode) operates in forward direction. Hence, electrons are injected from the emitter into the device and are transmitted through the base electrode. In the voltage range $0V < V_{BE} < 1.2V$ (regime I), the collector current matches the emitter current and increases exponentially with $V_{BE}$, as shown in Figure 7.2 a and b [88, 171].

In the voltage range $1.2V < V_{BE} < 2.3V$ (regime II), the current starts to saturate and increases only slowly with applied voltage, as shown in Figure 7.2 b. The current behavior can be explained by a limitation of the charge carrier transport in the intrinsic
semiconductor layer between the emitter and the base electrode[171].

For $V_{BE}$ larger than 2.3V (regime III), the current saturates, as shown in Figure 7.2 b. It has been proposed by Kaschura et al. that the current behavior in this regime can be explained by the current through a series connection of two n-type organic layers [171].

Figure 7.2 c and d show the differential current gain $\frac{dI_C}{dI_B}$ (amplification) and differential transmission $\frac{dI_C}{dI_E}$ of the OPBT. The current gain decreases for increasing base currents (see figure 7.2a). The differential amplification can be as large as $10^3$, which corresponds to a differential transmission close to 100%. Again, these large values reiterate that the transmission process cannot be explained by a hot carrier transport, but is due to small pores in the base.

7.3 Optimization of OPBTs

Optimization of OPBT is done by applying various processes to improve the functionality of the devices. Three process steps that are found to be essential for OPBT optimization are: annealing, increasing injection by doping, and structuring the active area of OPBT. These processes are discussed below to understand their effect on the OPBT.

7.3.1 Annealing Effect

Annealing is essential to optimize the device operation. Samples are annealed in two steps: firstly, devices are annealed for 2h at a temperature of 150$^\circ$C inside the glovebox, followed by a second annealing step outside the glovebox for 2h at a temperature of 120$^\circ$C. Figure 7.3 displays the collector current of OPBTs with and without annealing versus the base-emitter voltage at a constant voltage between collector and emitter of $V_{CE} = 3$ V. Samples without annealing exhibit almost no transistor behavior and the collector currents increase weakly with base-emitter voltage in the range from 1 V to 3 V. Overall, the ON/OFF ratio is small and reaches 3 only. After annealing inside or outside the glovebox, the collector current increases and the ON-state currents (at $V_{BE} = 3$ V) can be clearly distinguished from the OFF-state currents ($V_{BE} = -1$ V). Overall, the ON-state currents increase by two orders of magnitude. It seems that annealing devices inside the glovebox increases both the ON-state and OFF-state currents, and the ON/OF ratio is only around 70. However, annealing devices outside the glovebox leads to a better performance with an ON/OFF ratio of 550. As well, the transmission of the OPBTs is increased by annealing and reaches 99.5% and 99.7% after annealing inside and outside the glovebox, respectively (cf. Table 7.1).

The ON-state currents are almost identical regardless if the samples are annealed
Figure 7.3: Collector current versus base-emitter voltage at $V_{CE} = 3$ V. Active overlap area is 4 mm$^2$ (cf. Fig. 7.1). Annealing is done inside and outside the glovebox (GB) with different annealing temperatures.

<table>
<thead>
<tr>
<th>Annealing</th>
<th>Transmission [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>After fabrication</td>
<td>19.2</td>
</tr>
<tr>
<td>150°C inside GB</td>
<td>99.5</td>
</tr>
<tr>
<td>120°C outside GB</td>
<td>99.7</td>
</tr>
</tbody>
</table>

Table 7.1: Transmission of OPBTs with and without annealing.

inside and outside the glovebox. However, annealing the samples in ambient atmosphere leads to a significant reduction of the OFF-state currents. In the OFF-state, the potential difference between the emitter and base $V_{BE}$ is zero or negative and the potential between collector and base $V_{CE}$ is large. Therefore, the OFF-state currents are caused by backward currents of the collector diodes. As discussed in Section 6.4.1, exposure of devices in ambient air can help to form an oxide layer at the $C_{60}$/Al interface, which blocks electron injection into $C_{60}$ [91]. Therefore, the OFF-state current of OPBT is decreased.

The effect of annealing outside the glovebox can be studied by Scanning Electron Microscopy (SEM). Figure 7.4 a and b show the morphology of 100 nm $C_{60}$ deposited onto Cr/Al (collector electrode), before and after annealing. The morphology of $C_{60}$ changes slightly and a grainy structure appears. Figure 7.4 c and d exhibit the morphology of a 13 thin Al film (base electrode) deposited onto the $C_{60}$ layer and Cr/Al (collector electrode) before and after annealing. The morphology of the Al layer shows large grains with deep grooves between individual grains where pinholes (openings) can form.
Figure 7.4: SEM images of (a) 100 nm $C_{60}$ on Cr/Al before annealing. (b) 100 nm $C_{60}$ on Cr/Al after annealing at 150°C inside glovebox and 120°C outside glovebox. (c) 13 nm Al on 100 nm $C_{60}$ on Cr/Al before annealing. (d) 13 nm Al on 100 nm $C_{60}$ on Cr/Al after annealing at 150°C inside glovebox and 120°C outside glovebox. The scale bar is 500 nm as shown on images.
Furthermore, the structure of the base electrode is studied by Transmission Electron Microscopy (TEM). Figure 7.5 shows a cross-section of the $C_{60}$/base electrode/$C_{60}$ stack. Pinholes (openings) in the base electrode can be identified. These pinholes in the thin Al film can be interpreted by the reorientation of molecules in the $C_{60}$ layer due to the annealing process. Therefore, the formation of pinholes can improve the current transmission through the Al base contact because these openings allow a direct contact from top to bottom $C_{60}$ layer (i.e., emitter to collector) [88, 169, 92].

7.3.2 Contact Doping

OPBTs can be improved significantly by adding a doped injection layer. The doped layer ensures that the injection from the emitter is Ohmic, leading to increased currents and an increased transconductance.

The advantages of doping are most pronounced in devices which suffer from a bad charge injection at their contacts. Similarly, doping is essential to lower the driving voltages of organic solar cells and organic LEDs [172].

Doped injection layers can be easily inserted in vertical organic transistors by adding an additional layer to the structure.

Figure 7.6 displays the collector current of OPBTs with and without doped layer. It is clear that using a doped injection layer underneath the emitter electrode increases
the ON-state current (collector current at $V_{BE}= 3$ V). The collector current is increased by one order of magnitude, i.e. although charge injection from the Cr layer of the top electrode into the intrinsic $C_{60}$ is already efficient, it can still be enhanced by the use of a doped injection layer.

Also, inserting a doped injection layer enhances the current gain of the $C_{60}$ OPBTs. Figure 7.7 displays the differential current gain versus base-emitter voltage or vs. the collector current. The current gain is increased by one order of magnitude by inserting a doped injection layer underneath the emitter. Figure 7.7b shows that the highest current gain occurs at a collector current of $10^{-2}$ A.

### 7.3.3 Effect of Active Area Structure

The performance of OPBTs is strongly affected by the device area. In this section, the overlap area will be structured to study this effect further.

The active area of OPBT is structured by insulating layers on top of the base electrode, as shown in Figure 7.8. Therefore, the current injected at the emitter can only reach the base contact and be transmitted towards the collector within the active area.

#### 7.3.3.1 Shadow Mask Patterning

Structuring of the active area can not be achieved by a single shadow mask as it would require that a part of the mask be disconnected from the rest of the mask. Two shadow masks are designed as shown in Figure 7.9. Both masks are used subsequently which leads to a structured insulating layer with an specified opening defining the structured
Figure 7.7: OPBT with and without doped injection layer and active overlap area is 4 mm$^2$ (cf. Fig. 7.1). (a) Current gain differential versus base-emitter voltage at $V_{CE} = 3$ V. (b) Current gain differential versus collector current.

Figure 7.8: Structure of OPBT with structured active area by inserting insulator layer on top of the base electrode. The structured active area are 2.56 mm$^2$, 1.44 mm$^2$, 0.64 mm$^2$, 0.04 mm$^2$, 0.0225 mm$^2$, and 0.01 mm$^2$. 
Figure 7.9: Shadow masks to deposit the insulating layer used to structure the OPBT active area. Mask 1 and mask 2 are applied subsequently. The two insulating layers form a structure with an opening defining the active area in the middle. White area will be covered by the insulating layer, whereas the shaded area will be free and corresponds to the structured active area.
active area.

Figure 7.10 c and d show images of OPBT samples with varying active area. The active area is indicated in Figure 7.10 a and b.

7.3.3.2 Sample Fabrication

The layer stack of structured OPBTs is shown in Figure 7.8. The emitter and collector electrodes consist of aluminum (Al) (100 nm) and chromium (Cr) (10 nm). The intrinsic C$_{60}$ layers are 100 nm thick and a doped layer is inserted underneath the emitter electrode to make an Ohmic contact.

Two insulators materials are used to structure the active area SiO$_X$ and Spiro-TTB. Both materials are deposited by thermal evaporation. SiO$_X$ is used as insulator material for devices with an active area of 2.56 mm$^2$, 1.44 mm$^2$, and 0.64 mm$^2$. Spiro-TTB is used as an insulator material for the devices with an active area of 0.04 mm$^2$, 0.0225 mm$^2$, and 0.01 mm$^2$. Spiro-TTB is an organic material with a high energy band gap in the range of 3 eV, which is known as an electron blocking layer. Spiro-TTB has a LUMO level of around 3 eV below the vacuum level [173], whereas the LUMO level of C$_{60}$ is around 4 eV [174]. Hence, an energy barrier in the range of 1 eV is formed at the interface between Spiro-TTB and C$_{60}$. Both insulator materials have a low mobility, which makes them appropriate to minimize the current flow outside the active area.

After finishing, the samples are annealed according to the same protocol as for the unstructured OPBTs (inside the glovebox for 2h at 150$^\circ$C and outside the glovebox at 120$^\circ$C for 2h).

Before analyzing the transfer characteristics of OPBTs, the alignment of the masks is checked. Figure 7.11 shows the top view of an optical profilometer image of structured OPBTs. These images show that the structured area is formed in the middle of of the overlap of all layers. The active area (red) is in the center of the collector area (black box), the base area (green box), and the emitter area (blue box).

It is observed that the structured active area is slightly smaller than the nominal area. Each dimension (length an width) is approximately 10 µm smaller, leading to real active areas of 0.0361 mm$^2$, 0.0186 mm$^2$, 0.0061 mm$^2$.

7.3.3.3 Transfer Characteristics

The OPBTs without structured area and with a structured active areas of 2.56 mm$^2$, 1.44 mm$^2$, and 0.64 mm$^2$ are measured by sweeping the base-emitter voltage from -1 to 3V at $V_{CE} = 3V$, while the OPBTs with a structured active area of 0.0361 mm$^2$, 0.0186 mm$^2$, and 0.0061 mm$^2$ are measured by sweeping the base-emitter voltage from -0.5 to 2V at $V_{CE} = 2V$. The range of base-emitter voltages is determined by the ON- and OFF-state
Figure 7.10: (a) Mask layout for OPBT with a structured active area of 2.56 mm$^2$, 1.44 mm$^2$, and 0.64 mm$^2$. (b) Mask layout for OPBT with a structured active area of 0.04 mm$^2$, 0.0225 mm$^2$, and 0.01 mm$^2$. (c) Optical image of OPBT samples deposited by masks sketched in (a). Each sample consists of 3 OPBTs with different active area. (d) Image of samples structured with the masks shown in (b). Each samples consists of 5 OPBTs, where 3 OPBTs have an active area of 0.04 mm$^2$, one OPBT has an active area of 0.0225 mm$^2$, and the last OPBT has an active area of 0.01 mm$^2$. 
Figure 7.11: Top view of an optical profilometer image with outlined areas for OPBT structure with a nominal active area of 0.04 mm$^2$. The real area is 0.0361 mm$^2$. The black, green, and blue areas represent the collector, base, and emitter, respectively. The structured active area is the outlined by the red box.

Figure 7.12 shows the transfer characteristic of a device with an unstructured active area. The collector and emitter current are almost identical, which demonstrates that the current transmission from emitter to collector through the base electrode is efficient.

Figure 7.13 and 7.14 present transfer characteristics of OPBTs for different active areas. Overall, the ON- and OFF-state currents and hence, the ON/OFF ratio are strongly affected by changing the device area.

In Figure 7.15, the mean ON- and OFF-state currents of OPBTs with varying active area dimensions are summarized. The ON- and OFF-state current are determined for unstructured devices and structured devices with an area of 2.56 mm$^2$, 1.44 mm$^2$, and 0.64 mm$^2$ at $V_{BE} = 3$V and -1V, respectively, while the ON and OFF state currents for devices with an area of 0.0361 mm$^2$, 0.0186 mm$^2$, and 0.0061 mm$^2$) are measured at $V_{BE} = 2$V and -0.5V, respectively. Generally, the ON-state current increases by increasing the size of structured active area from 0.0061 mm$^2$ to 0.0361 mm$^2$ and from 0.64 mm$^2$ to 4 mm$^2$. The OFF-state current decreases exponentially with decreasing dimensions of the active area, as shown in Figure 7.15b.

Figure 7.16a plots the dependency of the ON/OFF ratio vs. structured active area. The ON/OFF ratio clearly increases by decreasing the size of active area. The current gain (amplification) depends slightly on the active area as well, which is shown in Figure 7.16b.

Both, ON-state and OFF-state currents increase with increasing active area. A major
component of the ON-state current is the transmitted current $I_{EC}$, i.e. the current, which is injected at the emitter, transmitted through the base and collected at the collector. The almost linear dependency of this transmitted current shows that the transmission occurs across the whole base electrode and is not concentrated at a "weak spot" of the base.

In contrast, the OFF-state current is mainly given by the reverse current of the bottom diode (BC diode) and direct leakage currents from emitter to collector. As discussed in Sec. 6.3.2, the reverse current of the bottom diode decreases by decreasing the active area. Furthermore, as seen in Figures 7.13 and 7.14, the OPBTs are not totally OFF at negative voltage of $V_{BE}$, which is an indication of a leakage directly from emitter to collector. This leakage current increases by increasing the structured active area.

Overall, the OFF-state current decreases much stronger with reduced active area than the on current. Consequently, the ON/OFF ratio increases by decreasing the structured active area.

Furthermore, the base current is only weakly dependent on the active area, which explains the increase in current amplification with smaller active areas.

7.4 Transconductance $g_m$

The transconductance is one of the most important performance parameters of transistors. The transconductance is directly proportional to the transit frequency of the transistor (see Sec.3.1.5.4). Thus, a high transconductance leads to devices with high switching speeds.
Figure 7.13: Transfer characteristics (base sweep) of OPBTs with different active area at $V_{CE}=3V$. (a) 2.56 mm$^2$. (b) 1.44 mm$^2$. (c) 0.64 mm$^2$. 
Figure 7.14: Transfer characteristics (base sweep) of OPBTs with different structured active area at $V_{CE} = 2V$. (a) 0.0361 mm$^2$. (b) 0.0186 mm$^2$. (c) 0.0061 mm$^2$. 
Figure 7.15: ON and OFF currents of OPBTs with varied active area. (a) ON-state current. (b) OFF-state current. For large active areas (4 mm$^2$, 2.56 mm$^2$, 1.44 mm$^2$, and 0.64 mm$^2$), OPBTs are measured at $V_{BE} = -1$ to 3V and $V_{CE} = 3V$. For small active area (0.0361 mm$^2$, 0.0186 mm$^2$, and 0.0061 mm$^2$), OPBTs are measured at $V_{BE} = -0.5$ to 2V and $V_{CE} = 2V$.

Figure 7.16: ON/OFF ratio and current gain $\beta$ of OPBTs with different active area. For large active area (4 mm$^2$, 2.56 mm$^2$, 1.44 mm$^2$, and 0.64 mm$^2$), OPBTs are measured at $V_{BE} = -1$ to 3V and $V_{CE} = 3V$. For small active area (0.0361 mm$^2$, 0.0186 mm$^2$, and 0.0061 mm$^2$), OPBTs are measured at $V_{BE} = -0.5$ to 2V and $V_{CE} = 2V$. 
Figure 7.17 shows the transconductance of the OPBTs with different structured active area. In general, the transconductance is larger for OPBTs with small active area (0.0061 mm$^2$ to 0.0361 mm$^2$) than for OPBTs with larger active area (0.64 mm$^2$ to 4 mm$^2$).

![Figure 7.17: Max. transconductance $g_m$ versus active area for OPBTs with base electrode thickness 13 nm.]

7.5 Effect of Base Electrode Thickness

The OPBTs are modulated by a base voltage, and varying the thickness of the base electrode can affect the characteristics of OPBTs. The devices are processed with different base electrode thicknesses varying from 13 to 19 nm. The effect of base electrode thickness is analyzed by studying the ON/OFF ratio and current gain (amplification) of the OPBTs. Figure 7.18 shows the ON/OFF ratio and current gain of OPBTs with an active area of 2.56 mm$^2$ at a driving voltage of 3V for different base thickness. The ON/OFF ratio increases by varying the base electrode thickness from 13 to 19 nm, and the current gain decreases with increasing of base thickness. Figure 7.19 plots the ON/OFF ratio and current gain of the OPBTs for different base thickness at a driving voltage of 2V with an active area of 0.0361 mm$^2$. The behavior of OPBTs with small active area is similar to the one of OPBTs with large active areas, i.e. the ON/OFF ratio increases and the current gain decreases with increasing of base thickness.

Again, it is seen that the ON/OFF ratio increases by minimizing the dimension of structured active area. For the large devices, the ON/OFF ratio is increased from approximately 500 to 1000 by increasing the thickness of the base electrode from 13 to 19 nm, while the ON/OFF ratio reaches 80000 for small active areas and thicker base electrodes.
The increase in the ON/OFF ratio by thicker base electrodes can be explained by the elimination of direct leakage currents between emitter and collector [78, 168].

Also, the current gain is affected by the thickness of base electrode. Obviously, the current gain gradually decreases by making the Al film thicker, which can be explained by the reduction of the density of pinholes in the base electrode. [94, 166, 90].

7.6 Output Characteristics of OPBTs

To measure the output characteristics, the OPBT is connected in the common-emitter configuration, i.e. the emitter serves as a reference terminal for the base and collector. Figure 7.20 shows the collector current as a function of collector-emitter voltage at various base currents for OPBTs with varying base electrode thickness. At low collector-emitter voltages $|V_{CE}|$, the base-emitter and base-collector diodes are operated in forward mode to provide the base current. Upon increasing the value of $|V_{CE}|$, the base-collector diode (bottom diode) starts to be reversely biased and the OPBT turns on. In order to provide a fixed base current, the base-emitter diode is operated under forward bias and the base-emitter voltage increases, thus the collector and emitter currents rise. Upon a further increase in $V_{CE}$, the contribution of base current from the collector side decreases. The base-emitter diode (top diode) becomes more forward biased and the emitter current will stop increasing when the required base current is achieved.

Figure 7.20 shows that the output characteristics of OPBTs are affected by the base electrode thickness. The collector current increases by decreasing the thickness of base electrode. This behavior is attributed to an increase in density of pinholes in the base electrode.

Figure 7.18: Parameters of OPBTs with different base electrode thickness (Al film) for structured active area 2.56 mm². (a) ON/OFF ratio. (b) Current gain $\beta$. 

![Graph](image-url)
Figure 7.19: Parameters of OPBTs with different base electrode thickness (Al film) for
structured active area $0.0361 \text{ mm}^2$. (a) ON/OFF ratio. (b) Current gain $\beta$.

base electrode for thinner base electrodes. Thus, the transmitted current from emitter
to collector will be increased.

The current gain is determined in the saturation regime at $V_{CE} = 2\text{V}$ and $I_B = 100 \mu\text{A}$
to show the effect of base thickness. Figure 7.21 shows that the current gain decreases
with thicker base electrode as observed in section 7.5.

These results are in agreement to the current gain determined from the transfer
characteristics (see Figure 7.19b), which shows the stability of the devices.

7.7 Base-Bias Stress Stability in OPBT

To study the influence of base-bias stress on the OPBTs, the transfer characteristics
are measured before, during, and after a base-bias stress of $V_{BE} = -0.5$ to $2\text{V}$ ($V_{CE} = 2\text{V}$)
is applied for 27 min. Figure 7.22 shows the transfer characteristics (base sweep
measurements) of OPBTs for different applied base-bias stress times ranging from 0 to
27 min for different active areas and a base electrode thickness of 13 nm. The base-bias
stress mainly leads to a shift of the transfer characteristics to larger voltages. The shift is
strong at the beginning of the stress test (i.e. stress time from 0 to 6 min) and becomes
smaller for longer stress times.

Figure 7.23 exhibits the voltage shift at a collector current $10^{-6} \text{A}$ for varied stress
time. Again, a strong shift is seen at the beginning, but the shift saturates for large stress
times. The voltage shift saturates approximately after 12 min of stress time especially
in the structured active area $0.00361 \text{ mm}^2$ and $0.0061 \text{ mm}^2$. Overall, the voltage shift is
independent of structured active area.
Figure 7.20: Collector current as a function of collector-emitter voltage $V_{CE}$ at different base currents for OPBTs with different base thickness. Active area is 0.0361 mm$^2$. (a) 13 nm. (b) 15 nm. (c) 17 nm. (d) 19 nm.
The base-bias stress effect in the OPBTs can be explained by charge trapping at base/organic semiconductor interface. The proposed mechanism is attributed to the existence of defect states at the interface between base and the top $C_{60}$ layer due to hydroxyl groups on the $AlO_X$ around the base electrode. In OPBTs, a thin oxide layer $AlO_X$ is formed around the base electrode by exposing the devices to ambient air during fabrication. When the OPBT is turned on, the injected electron current at the emitter flows vertically through the base electrode. Hence, the defect states at the interface between base and the top $C_{60}$ layer starts to capture electrons. Thus, the transfer characteristics of OPBTs are shifted, i.e. a more positive base-bias has to be applied to overcome the influence of the trapped electrons.

Figure 7.21: Current gain $\beta$ versus base electrode thickness at $V_{CE} = 2V$ for OPBTs with active area $0.0361 \text{ mm}^2$. 

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Figure 7.22: Collector current as a function of base-emitter voltage $V_{BE}$ at $V_{CE} = 2V$ with different stress time, different structured active area, and base thickness 13 nm. (a) 0.0361 mm$^2$. (b) 0.0186 mm$^2$. (c) 0.0061 mm$^2$. 
Figure 7.23: Voltage shift versus stress time for different structured active area at $10^{-6}$ A. (a) 0.0361 mm$^2$. (b) 0.0186 mm$^2$. (c) 0.0061 mm$^2$. 
8.1 Conclusion

An extensive study has been performed to provide a better understanding of the operation principles of doped organic field-effect transistors (OFETs), organic p-i-n diodes, Schottky diodes, and organic permeable base transistors (OPBTs). This has been accomplished by a combination of electrical and structural characterization of these devices.

The discussion of doped OFETs focuses on the shift of the threshold voltage due to increased doping concentrations and the generation and transport of minority charge carriers.

Doping of pentacene OFETs is achieved by co-evaporation of pentacene with the n-dopant $W_2(hpp)_4$. It is found that pentacene thin film are efficiently doped and that a conductivity in the range of $2.6 \times 10^{-6}$ S cm$^{-1}$ for 1 wt% to $2.5 \times 10^{-4}$ S cm$^{-1}$ for 16 wt% is reached. It is shown that n-doped OFET consisting of an n-doped channel and n-doped contacts are ambipolar. This behavior is surprising, as n-doping the contacts should suppress direct injection of minority charge carriers (holes).

It was proposed that minority charge carrier injection and hence the ambipolar characteristic of n-doped OFETs can be explained by Zener tunneling inside the intrinsic pentacene layer underneath the drain electrode. It is shown that the electric field in this layer is indeed in the range of the breakdown field of pentacene based p-i-n Zener homodiodes.

Doping the channel has a profound influence on the onset voltage of minority (hole) conduction. The onset voltage can be shifted by lightly n-doping the channel. The shift of onset voltage can be explained by two mechanisms: first, due to a larger voltage that has to be applied to the gate in order to fully deplete the n-doped layer. Second, it can be attributed to an increase in hole trapping by inactive dopants. Moreover, it has been shown that the threshold voltage of majority (electron) conduction is shifted by an increase in the doping concentration, and that the ambipolar OFETs can be turned into unipolar OFETs at high doping concentrations.

In subsequent chapters, the working mechanisms of OPBTs are discussed. OPBTs consist of two Schottky diodes (top and bottom diode), and the charge transport in these $C_{60}$-based Schottky diodes is studied first. Two transport regimes can be distinguished in forward direction - injection limited currents (ILCs) and space charge limited currents.
(SCLCs). It is found that the current increases exponentially with applied voltage in the ILC regime and depends quadratically on the applied voltage in the SCLC regime. Furthermore, it is observed that the forward and backward currents of the Schottky diode are increased by decreasing the $C_{60}$ layer thickness, increasing the active area, and increasing the temperature. Furthermore, in order to reach a high performance, various treatments have been applied. Air exposure, a variation of the thickness of the top electrode, as well as annealing of the diodes are used to optimize the diodes.

OPBTs are processed by using the semiconductor $C_{60}$ due its high charge carrier mobility and good film-forming properties. Again, the working mechanism of OPBTs is studied by electrical characterization (base-sweep measurements and output characteristics). To achieve a high performance of OPBTs, various treatments and techniques have been applied. The annealing of the OPBTs after fabrication changes the morphology of the base electrode. Thus, openings (pinholes) are formed in the base electrode, which enables a high current transfer from the upper to lower semiconductor layer. The formation of openings is proved by analyzing SEM and TEM image of the base electrode.

Adding a doped layer at the emitter is another process to optimize the OPBTs. The doped layer ensures a high charge carrier injection at the emitter, leading to a high transmission and current gain.

Furthermore, it has been observed that the ON/OFF ratio and transconductance of OPBTs increases by decreasing their active area. A very high transconductance $g_m$ of 37 S/cm$^2$ is reached, which has the potential to boost the switching speed of organic transistors to 5 MHz. Furthermore, it is shown that the base electrode thickness is an essential parameter for OPBTs. The current gain $\beta$ decreases by increasing thickness of base electrode, whereas the ON/OFF ratio increases for thicker base electrodes.

8.2 Outlook

This dissertation helps to improve the understanding of the operation principles of n-doped organic field-effect transistors and organic permeable base transistors. The results of the n-doped OFETs show that the doping efficiency of $W_2(hpp)_4$ in pentacene is low. To increase the efficiency, the relationship between dopant structure and doping efficiency has to be understood. Currently, novel dopants with varying side-groups are developed by the Bunge group, which should help to find design rules for more efficient n-dopants. Furthermore, the possibility of shifting the threshold voltage of OFETs by the doping concentration has strong implications for actual applications. For example, the switching voltage of a CMOS inverter can be controlled. More generally, studying the integration of doped OFETs and finding ways to benefit from the increased stability and variability
of these transistors is a promising future research topic.

Based on the results of the Schottky diodes and OPBTs, more work can be done to develop a better understanding of their working mechanism. Due to the influence of the OFF-state currents of the Schottky diodes on the ON/OFF ratio of the OPBTs, a better understanding of the origin of the backward currents can stimulate further progress. Hence, simulating charge transport in organic Schottky diodes and modeling tunneling currents through the native oxide layer is promising.

Still, even with reduced backward currents of the Schottky diodes, the ON/OFF ratio and current gain of OPBTs will be limited by direct leakage currents from emitter to collector. Thus, using an insulator layer with high energy gap, such as aluminum oxide $\text{Al}_2\text{O}_3$ and silicon oxide $\text{SiO}_2$ might improve the device behavior. Finally, OPBTs show much higher base currents than OFETs, which limits their application in some instances. Hence, approaches to limit base currents have to be found, e.g. by improving the native oxide layer around the base or by adding a self-organized insulation layer, e.g. by phosphonic acids.
BIBLIOGRAPHY


