Doctoral Thesis

On organic molecular semiconductors: Thermoelectricity and charge transport in p-type and n-type materials

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On organic molecular semiconductors: Thermoelectricity and charge transport in p-type and n-type materials

A thesis submitted to attain the degree of

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On organic molecular semiconductors: Thermoelectricity and charge transport in p-type and n-type materials

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Abstract

The understanding of electrical transport in organic semiconductors is a key ingredient for both the fundamental understanding of this material class and the development of novel technological applications. It is known that localized states within the band gap strongly affect the transport properties of electrical charges. We have devoted two different studies on the transport characterization of organic semiconductors. Following a standard approach in the first project, we investigate PDIF-CN$_2$ in a field-effect transistor (FET) geometry and report the first extensive transport study for n-type semiconductors. In the second project, we have developed and used a new Seebeck measurement setup with local on-chip thermometers for an accurate measurement of thermoelectric effects in organic semiconductors. 

The FET setup is a well established technique to characterize transport in organic materials, where the induced density of mobile charges can be tuned with a gate voltage. Measuring transfer characteristics in this setup, then allows to extract the charge carrier concentration, mobility and density of trap states (trap DOS). While p-type semiconductors have been studied extensively in the past, studies on n-type materials are generally rare. In order to fill this gap, we have investigated the n-type organic compound PDIF-CN$_2$, a semiconductor with a wide range of processing possibilities that give rise to samples, where the degree of order ranges from very disordered to highly crystalline. Indeed, starting from the same source material, we were able to fabricate spin-coated and evaporated thin-film transistors as well as single crystal FET’s and to study the performance of the FET as a function of the sample crystallinity. With the help of a transfer curve simulator, we have shown that, similar to p-type materials, the in-gap trap states are crucial for the charge transport in n-type organic semiconductors. The characteristics of PDIF-CN$_2$ turn out to be comparable, both qualitatively as quantitatively, to well known high quality p-type materials.

In order to measure the Seebeck coefficient in organic semiconductors, we have integrated a thermo-electric setup within the standard FET configuration. The experimental design involves (i) on-chip thermometers for a precise determination of the temperature drop across the voltage channel, (ii) spring pin contacts to electrode pads evaporated on the wafer for a simple and fast exchange of samples, and (iii) an inert atmosphere to account for the sample’s sensitivity to oxygen and water. We report on Seebeck measurements for Rubrene, PDIF-CN$_2$, and UBE combined with field effect transistor simulations. For all materials, the logarithmic dependence of
the Seebeck coefficient on the density of mobile charges is in agreement with theoretical predictions. Independently, we have extracted the Fermi-level position, and were able to exclude non-linear transport effects, such as phonon drag, in these materials from the absolute value of the Seebeck coefficient.
Kurzfassung

Der Ladungstransport in organischen Halbleitern spielt eine Schlüsselrolle sowohl für das Verständnis der Materialeigenschaften als auch für die Entwicklung neuer Technologien. Wie bereits früher gezeigt wurde, werden die Transporteigenschaften massgeblich von lokalisierten Zuständen in der Bandlücke beeinflusst. Die vorliegende Dissertation widmet sich in zwei Projekten dem Zusammenhang zwischen Ladungstransport und lokalisierten Zuständen. Im ersten Projekt haben wir das n-Typ Material PDIF-CN$_2$ in einer Feld-Effekt Transistor (FET) Struktur, einem etablierten Verfahren zur Charakterisierung von elektrischem Transport, untersucht. Im zweiten Projekt entwickeln wir ein neues Experiment zur Bestimmung des Seebeck Koeffizienten mit lokalen Temperatursensoren.


Um die Thermoelektrischen Eigenschaften von organischen Halbleitern besser zu untersuchen, haben wir ein neues Experiment entwickelt, welches den Seebeck Effekt in einer FET Struktur misst. Dieses Experiment hebt sich hervor durch (i) on-chip Thermometern welche eine genaue Temperaturmessung entlang des Kanals zulassen, (ii) Federpins welche den elektrischen Kontakt zum Mikroplättchen herstellen und somit einen leichtes Ein-/Ausbauen der Proben ermöglicht und (iii) einer Edelgas Atmosphäre welche der Reaktivität der Proben mit Luft und Wasser Rechnung trägt. Mit diesem Experiment haben wir Rubren, PDIF-CN$_2$ und UBE untersucht und die Effekte simuliert. In diesen drei Materialien, haben wir einen logarithmischen Zusammenhang zwischen dem Seebeck Koeffizienten und den induzierten
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Acronyms

**AFM** atomic force microscopy

**ARPES** angle-resolved photoemission spectroscopy

**cb** chlorobenzene

**cf** chloroform

**DOS** density of states

**FET** field effect transistor

**HMDS** hexamethyldisilazane

**HOMO** highest occupied molecular orbital

**LUMO** lowest unoccupied molecular orbital

**µSR** muon spin rotation

**OTS** octyltrichlorosilane

**OFET** organic field effect transistor

**PDIF-CN₂** N,N’-1H,1H-perfluorobutyl dicyanoperylene carboxydiimide

**STM** scanning tunneling microscopy

**trap DOS** trap density of states

**TFT** thin film transistor
Chapter 1

Introduction

The past decades have seen the emergence of a multitude of new material classes, including that of high-temperature superconductors, multiferroics, and organic semiconductors. A careful characterization of each new compound is the key task for revealing the underlying physical phenomena and ultimately developing these materials for technological applications. Material growth and characterization are therefore two central challenges in condensed matter physics to reveal the microscopic mechanisms responsible for the macroscopic properties of novel materials.

As of today, an immense variety of methods has been developed to study the material’s properties with spectroscopic, transport or thermodynamic techniques. The different approaches give access to complementary information on the material’s structure and composition as well as on the phases of matter and related phase transitions. Indeed, spectroscopic techniques can probe electronic states at the sample surface (e.g. ARPES, STM, AFM), bulk crystal structures (x-rays), or the local magnetic environment (neutrons, µSR), see Refs. [1–7]. Transport experiments address (among others) the electronic states in the bulk as well as properties of the lattice. Prominent examples are the original discovery of superconductivity [8] from electrical resistivity measurements, the evidence of unconventional order parameter in organic superconductors [9], or the study of charge carriers in organic materials using the Seebeck effect [10]. Finally, thermodynamic techniques study the macroscopic responses including dc and ac calorimetry (specific heat) [11] or magnetization techniques [12, 13].

In the past years, several techniques have been used to study samples of submillimetre sizes. For the family of organic compounds, a significant progress was achieved with the development of a field-effect transistor geometry [14], allowing
to control the injected charge carriers in the transport channel without doping the crystal. With this approach the electronic properties of charge transport, mobility, charge carrier density and the in-gap defect states of the organic semiconductors can be studied with unprecedented precision. The recent developments [10, 15] give access to the materials Seebeck coefficient, a quality factor for thermoelectric applications, thus complementing the electronic characterization with thermal properties. In the present thesis, we have characterized the charge transport in n- and p-type organic semiconductors with electrical conductance and Seebeck measurements. In addition, we have developed novel experimental techniques to meet with the special requirements of the small and fragile samples. In the following section the main achievements of both projects are briefly discussed.

Charge transport in n- and p-type organic semiconductors:
Charge transport in organic semiconductors is affected by localized in-gap states. These trap states arise due to various imperfections, such as structural defects [16], chemical impurities [17], adsorbed water [18] or the thermal motion of the molecules [19]. The presence of these trap states strongly affects the device performance of organic transistors, light emitting diodes and solar cells [20]. In the field of organic semiconductor technology, it is essential to understand the origin and consequences of these in-gap states and their characterization promises further advances towards application in industry. The traditional approach to characterize organic materials is via charge transport measurements. Typically these measurements are performed in a field-effect transistor (FET) setup [14], where the charge carrier density is controlled by an electric field. Most studied organic semiconductors, such as Rubrene, pentacene or anthracene, are p-type semiconductors where 'p' indicates that holes are the main charge carriers. In these materials, the transistor characteristics are well known and also analyzed in terms of the underlying density of trap states. A method to extract the density of states from transfer curves has been developed by Oberhoff et al. [21]. This matlab-based routine calculates the transfer curves for given trap densities and mobilities. The final density of states (DOS) is then obtained by adjusting the density of states until the transfer curves are well reproduced. An extensive survey over several p-type materials is provided in the work by Kalb et al. [22]. In a side-project, collaborating with a group in Minnesota, we have simulated p-type single crystals of DNTT and revealed a very low density of trap states and almost no interface traps when a vacuum-gap structure is used as dielectric [23].

Very little is known so far on n-type organic semiconductors, with 'n' denoting the dominance of electrons as mobile charge carriers. In order to shed light on these
compounds and to complement the already existing knowledge on p-type organic semiconductors, we have performed a thorough investigation on the n-type material PDIF-CN$_2$ [24]. The choice of the compound is motivated by the variety of processing possibilities: spin coating, thermal evaporation and single crystal growth. For each of these approaches the electric properties were investigated in a field effect transistor geometry. For the first time, an extended survey of the trap states in the semiconductor gap of a n-type material was achieved. The transfer curves and the trap density of states (DOS) were then simulated with the routine mentioned above. It could be concluded from this analysis that in the n-type materials the in-gap trap states are just as crucial for the device performance as in p-type compounds. Moreover, the characteristics of PDIF-CN$_2$ is comparable to common p-type materials.

This study was the first to quantitatively determining the in-gap trap states of an n-type material under the influence of different processing conditions thus helping to understand the effect of the trap states and to ultimately shape organic materials towards application.

*Seebeck effect in organic semiconductors:*

Inspired by the recent Seebeck measurements on organic semiconductors, aiming at optimizing the power factor (a quality measure for thermo-electric applications) by doping [25, 26], we have integrated a thermo-electric measurement within the standard FET configuration. To this end, we have designed and built an experimental setup, especially tailored for the demanding requirements of the organic materials. We briefly discuss these requirements and how they are addressed in the new setup. First, in order to produce the best quality samples, organic crystals are most commonly grown by physical vapor transport [27], resulting in relatively small ($\sim 100 \times 100 \times 1 \mu m^3$) and fragile samples and thus rendering the contacting of electrodes very challenging. We circumvent this issue with spring pins providing a good contact to the electrode pads evaporated on the wafer. In addition to good electrical contacts, this method ensures a gentle manipulation of the brittle crystals and facilitates the exchange of samples. Second, the reliable measurement of the accurate temperature gradient across these small samples requires local temperature probes. To this end, we have chosen an on-chip thermometer array to directly measure the temperature along the sample. As a third provision, the measurements are conducted under inert atmosphere to account for the sample’s sensitivity to oxygen and water.

With this setup several organic single crystals, including one n-type material grown by physical vapor transport have been investigated. In all of them, we have demonstrated that the Seebeck coefficient is decreasing logarithmically with the injected
charge carrier density. A theoretical description proposed by Fritzche [28] predicts a linear dependence of the Seebeck coefficient on the Fermi-level for semiconductors with a mobility edge. The model proposes additionally a parameter $A$, a dimension less constant, that gives insight on the charge transport properties in the investigated material. To investigate both, the dependence on the Fermi-level position and the constant $A$, we have performed transfer measurements of the investigated field effect transistor structures. With the help of a simulator, this allowed us to extract the density of states in the band gap from these measurements. Additionally we were able to independently determine the gate voltage dependent position of the Fermi-level. This gives rise to the possibility of fitting the simulated Seebeck coefficient with the help of the parameter $A$ to the measured curves. Thus we were able to extract this parameter for the materials Rubrene and PDIF-CN$_2$.

From the value of $A$ for the investigated Rubrene single crystals we can exclude non-linear effects on the charge carrier transport (such as phonon drag) as suggested in an earlier study, see Ref. [29] and conclude that the observed values lie closer to thermo-electric transport that takes place in conventional inorganic semiconductors. This interpretation is in good agreement with the work by Pernstich et al. [10] even so we arrive at $A$ being closer to one by taking into account the channel depth dependent charge carrier concentration leading to a depth dependent Fermi-level position and conductivity. For PDIF-CN$_2$ we arrive at a value for $A$ of being closer to zero or even slightly negative. The slope of the Seebeck coefficient was found to be a universal constant of 0.4 mV/K per decade which we could calculate as well. With this project we hope to shed light on the transport mechanisms of organic n- and p-type semiconductors from a different angle gaining insight into the intrinsic charge transport properties thus helping to optimize this material class.
Chapter 2

On transport in organic semiconductors

A general discussion on the transport mechanisms in organic semiconducting materials sets the stage for the following studies of charge transport and Seebeck effect.

In the present thesis we explore the electrical and thermal transport properties of organic molecular crystals to address the still open question of charge transport in organic semiconductors. It is the purpose of the following chapter to give an introduction on organic semiconductors, their material properties, and the experimental techniques to characterize them. We start in Sec. 2.1 with a description of the material’s molecular and crystal structure and discuss the charge transport and the role of charge trapping. In section 2.2, we introduce the field effect transistor (FET) geometry, the central building block used to characterize our materials, and elaborate on the simulator used for extracting the underlying trap density of states (trap DOS). The last section, Sec. 2.3, is devoted to the Seebeck effect, it’s possible applications and potential as an investigation method.

2.1 Organic Semiconductors

In order to understand the transport/thermal properties of organic electronics, one needs to start from the elementary building units, the atoms, understand the formation of molecules, and finally, how these molecules arrange in a crystalline (or
amorphous) structure. Organic molecules consist to a large amount of carbon, oxygen and hydrogen atoms, see few examples in Fig. 2.1. Although the electronic ground state of a free carbon atom is the $1s^22s^22p^2$, when binding to another carbon atom, the so-called sp-hybridization of the orbitals favors the $1s^22s^12p^3$ configuration with four unpaired electrons. The three electrons (sp$^2$) bind covalently to the adjacent carbon atom in the molecular plane and hence are inert. The remaining electron in the perpendicular $p_z$-orbital is only loosely bound to the molecule. The $p_z$-orbitals of adjacent carbon atoms interact and form delocalized orbitals that extend over the entire molecule (see Fig. 2.2 with a benzene ring as example). The strongly localized binding orbitals are usually referred to as $\sigma$-bonds whereas the delocalized $p_z$-orbitals are named $\pi$-bonds. The formal approach to describe the electronic configuration of the $\pi$-bonds is to determine the wave functions and energies and to populate these molecular orbitals in the ground state. At $T = 0$, electronic states are filled up to the highest occupied molecular orbital (HOMO) whereas all electronic states with energies larger or equal to the lowest unoccupied molecular orbital (LUMO) are empty. For the purpose of the following discussion, it is sufficient to consider the organic molecule as the fundamental entity where free electrons occupy the molecular orbitals.

When brought together, (small) organic molecules can form a solid (with more or less crystalline order). Contrary to inorganic solids, the organic materials are bound together through very weak dipolar (van-der-Waals) interactions. It can be shown,
that these interaction forces are so weak, that they do not alter the electronic structure of the constituent molecules. Hence, the electrons independently fill the molecular orbitals and lead to mostly localized HOMO and LUMO levels (an example can be seen for Rubrene in figure 2.2). The overlap between electronic wave functions of adjacent molecules, provides a channel for electrons to delocalize in the solid expressed in terms of the transfer integral. In highly ordered crystals, this delocalization gives rise to narrow HOMO/LUMO bands extending throughout the organic semiconductor. These bands are analogous to the valence and conduction bands of inorganic semiconductors and from now on the nomenclature may be used interchangeably.
2.1 Organic Semiconductors

Figure 2.3: Modulations of the transfer integral by vertical (left) or lateral (right) displacement of two adjacent diethylene molecules. This figure and the associated calculation have been presented in Ref. [32]

2.1.1 Charge transport and trapping

As described in the last section free electrons are delocalized in π-states within a molecule. On the other hand they are almost localized on that molecule because of the small overlap between the wave functions of neighboring molecules. It is however this transfer of charges from one molecule to the next which determines transport characteristics in these materials. In order to describe charge transport, it is therefore crucial to understand this effect. The strong dependence of the hopping probability (or transfer integral) on the distance, angle, and orientation between molecules, see Fig. 2.3, already suggests that the crystalline order will play an important role for the transport characteristics.

The thermal and zero-point motion in organic molecular solids is known to be large. Taking a snapshot of the solid at a given instant of time (referred to as a frozen configuration) allows to estimate variations in distance and orientation between the molecules. It turns out that these variations are so large that they affect not only the transfer integral but also the on-site energy of the electrons. This effect leads to a broadening of the HOMO/LUMO-bands and creates electronic states that lie within band gap of the semiconductor. The influence of this so called static disorder can be seen in 2.4(left). The localization length of these in-gap states is very short, and they are usually referred to as trap states [with an associated trap density of states (trap DOS)]. The threshold energy, called mobility edge, separating localized from delocalized charges is analogous to the band edge in clean inorganic semiconductor. Upon cooling the solid, the thermal motion decreases and with it the localization. The improvement of charge transport at lower temperatures is then
referred to as 'band-like' transport.

In this frozen configuration, fluctuations cause disorder that (fully) localizes the charges. Taking into account the molecular dynamics, which are slow compared to the electronic ones, the temporal modulation of the transfer integral can assist charge transport by transferring (similar to a ferry) charges from one molecule to the next. The time-scales on which this happens are shown in Fig. 2.4(right). As the thermal motion of the molecules is reduced upon cooling and thus the efficiency of the molecules to transport charges decreases, the apparent mobility decreases as well and this is referred to as 'hopping-like' transport.

2.2 Field Effect Transistor

2.2.1 Working principle and regimes

The field effect transistor (FET) geometry is ideal to characterize the charge transport in organic semiconductors. This geometry consists of a layered structure with a gate, a dielectric layer separating the gate from the semiconductor, and two contacts, called source and drain, see Fig. 2.5. The gate plays the role of a plate capacitor. Indeed, when a gate voltage $V_g$ is applied charges accumulate at the gate and charges
2.2 Field Effect Transistor

Figure 2.5: Structure of a bottom gate bottom contact field effect transistor.

(of opposite sign) accumulate at the interface between the dielectric insulator and the semiconductor. The charges at this interface have to be provided through the source/drain contacts. In order to inject in electrons (holes) into the semiconductor the work function of the metal has to be aligned with the LUMO (HOMO) band of the semiconductor. This alignment defines whether the nature of the semiconductor: n-type (p-type) materials have a dominant electronic (hole) nature. In few known situations, the use of two different materials for the source and drain contacts can lead to an ambipolar semiconductor crossing smoothly between n-type and p-type. Irrespective of the charge carrier nature, the accumulated mobile charges at the semiconductor/insulator-interface form a conductive channel, and electrical current will flow when a bias voltage (or drain voltage $V_d$) is applied between the source to drain electrodes. In the regime of linear response (see figure 2.6), where the drain voltage is small compared to the gate voltage, $V_d \ll V_g$, the injected charges accumulate uniformly in the conductive channel and the current flow

$$I_d = \frac{W}{L} C_i \mu \text{lin} (V_g - V_{th}) V_d$$

(2.1)

is proportional to the applied drain voltage. Here $L$ and $W$ are the channel length and width respectively, $C_i$ is the capacitance of the insulator, $\mu$ the charge carrier mobility (simply called mobility), and $V_{th}$ is the threshold voltage. The above expression (2.1)
On transport in organic semiconductors

Figure 2.6: Illustration of different working regimes for a field-effect transistor. Left to right and top to bottom: At zero drain voltage, no bias is applied and the channel is homogeneous. For small biases, the channel gets slightly depleted towards the drain contact and the drain current $I_d$ is linear in $V_d$. At the onset of saturation, the conducting channel is fully depleted at the drain contact (pinch-off point) and the current stops increasing upon increasing $V_d$. Within the saturation regime, the pinch-off point moves away from the drain contact. This figure is reproduced from Ref. [34].

allows us to extract the mobility in the linear regime via

$$
\mu_{\text{lin}} = \frac{\partial I_d}{\partial V_d} \frac{L}{C_i W (V_g - V_{th})}. \quad (2.2)
$$

In the opposite limit of large drain voltages, $V_d \gg V_g$ (compare again with figure 2.6), the charge carrier concentration near the drain contact is more and more suppressed until complete depletion at the pinch-off point. A further increase of the drain voltage will not increase the current further and the drain current saturates. In this so called saturation regime the drain current can be written as

$$
I_d = \frac{W}{2L} \mu_{\text{sat}} C_i (V_g - V_{th})^2 \quad (2.3)
$$

and the mobility

$$
\mu_{\text{sat}} = \frac{L}{WC_i} \frac{\partial^2 I_d}{\partial V_g^2} = \frac{2L}{WC_i} \left( \frac{\partial \sqrt{I_d}}{\partial V_g} \right)^2 \quad (2.4)
$$
2.2 Field Effect Transistor

Figure 2.7: Saturation (left) and linear (right) regime for a field effect transistor simulated in two dimensions with the simulator developed by Blülle et al. In the saturation regime the drain voltage is higher than the gate voltage leading to a depletion of charge carriers close to the drain contact. In the linear regime the gate voltage is higher than the drain voltage and the charge carrier density decreases linearly from source to drain contact. Figure reproduced from [35].

can be extracted directly from Eq. (2.3). The second expression in Eq. (2.2) is more convenient as it allows to extract \( \mu_{\text{sat}} \) from a linear fit of \( \sqrt{I_d} \) with respect to \( V_g \).

2.2.2 Simulations

In order to gain insight into the electronic properties of the organic semiconductors, and in particular the density of trap states, we have simulated the measured temperature dependent transfer curves. Thereby two numerical routines, developed in our group over the past years, have been used. The simulator by Oberhoff, see Ref. [21], allows to study the dependence of trap DOS the FET performance on the processing conditions and/or gate dielectric, as investigated in chapter 4. The second simulator by Blülle, see Ref. [35], aims at investigating the Seebeck coefficient (and in particular its dependence on the trap DOS) in n- and p-type organic semiconductors. This program will be used in Chap. 6 below.

By similarity to an approach in numerical analysis, the working principle of both programs may be termed shooting method, as the simulator calculates the transfer characteristics from a given initial set of parameters (spectral density of states, band mobility \( \mu_0 \)). These parameters are now adjusted (typically manually) until a good agreement with the measured transfer curves is found. The sample characterization
from the optimized initial parameters is then straightforward. Both routines assume a constant density of states $n_0$ in the valence (conduction) band. Beyond this edge, the density of states is described by shallow trap states, with an exponentially decreasing density

$$n(E) = n_0 e^{-|E|/E_{\text{shallow}}}$$  \hspace{1cm} (2.5)$$

with $n_0$ the density of states (DOS) at the mobility edge, $E$ the energy away from the mobility edge, and $E_{\text{shallow}}$ the characteristic decay scale. Further away from the band edge, the density of states is dominated by so-called deep trap states

$$n(E) = n_d e^{-|E|/E_{\text{deep}}}$$  \hspace{1cm} (2.6)$$

with $E_{\text{deep}} > E_{\text{shallow}}$. Additionally, the numerical simulator can account for discrete trap states around a specific energy away from the band edge (usually with gaussian broadening). Starting from a fixed density of states and a temperature\footnote{Note that the thermal broadening is taken into account with the full Fermi-Dirac statistics.} we insert the band mobility $\mu_0$ that is extracted from the transfer measurement, see Eqs. 2.2 and 2.4. When a DOS is found that reproduces the transfer curve, the simulation is repeated for a different temperature (only the mobility might be changed). If the simulated transfer curve at the new temperature fits the measured transfer curve at this temperature, the fit is taken as a good agreement with the data. In the newer simulator, by Bluelle, the non-uniform distribution of the charge carriers within the channel thickness is taken into account self-consistently, a feature that is particularly relevant for the determination of the Seebeck coefficient.

In the range between the turn-on and threshold voltages, the drain current changes by several orders of magnitude and the simulated transfer characteristics turns out to be very sensitive to the chosen trap DOS. The reliability of this approach has been further verified by comparing it with alternative methods for DOS extraction, see Refs. [22, 36]. Furthermore, this technique has been successfully applied to various OFET configurations [22, 36–41].

### 2.2.3 Non-uniformity of the channel thickness

In a field effect transistor charges accumulate at the semiconductor insulator interface, as described qualitatively earlier in this section. When applying a gate voltage $V_g$, a
2.2 Field Effect Transistor

Figure 2.8: Total induced charge carrier density as a function of the depth into the channel, simulated for three different gate voltages.

The total charge density (per unit area)

\[ N_{\text{ind}} = C_i V_g = \frac{V_g \epsilon_0 \epsilon_r}{d}, \]  

(2.7)

is induced at this interface. Here \( \epsilon_0 \) denotes the vacuum permittivity and \( \epsilon_r \) the relative permittivity of the material. The repulsive interaction between charges causes this density to distribute (inhomogeneously) over a finite thickness, called channel thickness, perpendicular to the interface (along \( y \)). The interplay between Coulomb repulsion and screening effects results in a typical channel thickness of the order of the Debye length

\[ \lambda_D = \sqrt{\frac{\epsilon_s \epsilon_0 k_B T}{e^2 n_{\text{ind}}}}, \]  

(2.8)

with \( \epsilon_s \) the permittivity of the semiconductor. The Debye length depends on the gate voltage through the induced charge carrier density \( n_{\text{ind}} \) (per unit volume) where the latter is defined through

\[ n_{\text{ind}} = \int_{-\infty}^{\infty} dE \, n(E) f_{FD}(E, E_F, T) \]  

(2.9)
On transport in organic semiconductors

Figure 2.9: Fermi-level into the semiconductor for three different gate voltages. As the charge carrier density increases towards the interface the Fermi-level moves closer to the valence-band.

and involves the Fermi-Dirac statistics

\[ f_{\text{FD}}(E, E_F, T) = \left( e^{-\frac{E_F - E}{k_B T}} + 1 \right)^{-1}. \]

(2.10)

The simulator described above is able to take into account the full coordinate dependence along \( y \). As a result of considering the \( y \)-dependence of the induced charge carrier density, several other quantities will be altered. In order to illustrate this effect, we consider a generic density of states for an organic semiconductor in the rest of this section. From this input, we have simulated the total density of induced charge carriers as a function of the depth into the channel, see Fig. 2.8. We observe that the channel thickness decreases with increasing gate voltage due to an enhanced screening effect.

The dependence of the induced charge carrier density on the Fermi energy position, results in a \( y \) dependence of the Fermi-level, shown in Fig. 2.9. For large charge carrier densities (near the insulator/semiconductor interface), the Fermi energy is closer to the valence band (here at \( E = 0 \)) than for low densities deep inside the channel. This effect gets stronger for increasing gate voltages, where channel depth is reduced and hence the charge carrier concentration is enhanced near the interface.

Since not all induced charges are mobile, we can now evaluate the density \( n \) of mobile charges as a function of \( y \). Assuming a sharp mobility edge at \( E_V \) and an
energy-independent mobility $\mu$ below that edge, we arrive at

$$n = \int_{-\infty}^{E_F} dE n(E)f_{FD}(E,E_F,T)$$  \hspace{1cm} (2.11)

where $E_F$ is a function of $y$. The dependence of $n$ on the position across the channel thickness is shown in Fig. 2.10 for three gate voltages.

For the description of the Seebeck coefficient as we will see later (compare equation 2.17) we will need the gate voltage dependent Fermi-level of the semiconductor. As we have seen now, the position is not uniform throughout the crystal but depends strongly on the position from the interface. As we want to determine the Fermi-level that dominates the thermoelectric properties of the semiconductor we have to weight the Fermi-level with respect to the conductivity (or the free charge carrier density for a constant mobility) according to

$$E_{F}^{\text{dom}} = \frac{\int E_F(y)\sigma(y)dy}{\int \sigma(y)dy}$$ \hspace{1cm} (2.12)

We plotted the simulated Fermi-level position with respect to the induced charge carrier density for the trap density of states for a typical Rubrene field effect transistor.
Figure 2.11: Gate dependence of the Fermi-level (right) for the DOS shown on the left. As we induce more charge carriers we shift the Fermi-level closer to the Valence-band. As the Fermi-level is dependent on the position in the crystal we plot the position at the interface (red, closer to the band) and the conductivity weighted contribution (blue).

in figure 2.11. Additionally we show the Fermi-level at the interface as well. The Fermi-level moves closer to the Valence-band (at $E=0$) with increasing induced charge carrier density at the interface as well as for the weighted contribution. The slope is steeper for the interface as the charge carrier density is enhance there due to the decrease of the Debye length (see above).

## 2.3 Seebeck effect

The enormous amount of heating produced by chemical, electrical, and mechanical processes raises the question, whether this waste heat can be converted back to ‘useful’ power. As the name already suggests, the use of the thermoelectric effect promises a direct conversion of heat into electrical power. Among the different thermoelectric effects, the Seebeck effect describes how a temperature difference $\Delta T$ across a sample can give rise to an electrical voltage $V_{\text{therm}}$ between the two ends of that sample. The Seebeck coefficient $S = V_{\text{therm}}/\Delta T$, then measures the efficiency of this process. The efficiency of this effect for power generation is usually quantified with the figure of merit

$$ZT = \frac{S^2 \sigma}{\lambda} T,$$  \hspace{1cm} (2.13)


2.3 Seebeck effect

involving the base temperature $T$, the Seebeck coefficient $S$, and both the electrical $\sigma$ and thermal $\lambda$ conductivities. Ideal materials feature a large Seebeck coefficient and electrical conductivity, while the thermal conductivity, working against the thermal gradient, should be minimal. In conventional metals, the electronic contribution to the thermal conductivity dominates over the phonons. As a consequence the electrical and thermal conductivity are related through the Wiedemann-Franz law, hence limiting the figure of merit to values (typically) below unity. Extensive efforts have been undertaken over the last years, to investigate novel materials which circumvent the limitation imposed by the Wiedemann-Franz law. Pursued routes include the design of low-dimensional materials [42] and nano-structured superlattices of thermoelectric materials where the electronic and phononic modes may decouple. A novel class of this superlattice structures, based on bismuth/antimony or lead/telluride, exhibit a $ZT$ larger than two and reach the threshold value for becoming technologically relevant. The chalcogenides, with a $ZT$ larger than one, form another promising material class. The material class at the heart of our study is that of (organic) semiconductors. In these materials, where the electric and thermal conductivities are intrinsically low, the hope for large $ZT$’s resides in the Seebeck coefficient.

For the purpose of this work, we shall give a more detailed description of the Seebeck coefficient in semiconductors. Starting from its definition Fritzsche [28] has derived a convenient expression

$$S = \frac{k_B}{e} \int dE \frac{E_F - E}{k_BT} \frac{\sigma(E)}{\sigma}$$

(2.14)

using Motts formula [43] and neglecting electron-electron interactions. Here, $k_B$ is the Boltzmann constant, $e$ is the electron charge, and $E_F$ is the Fermi energy. The energy-dependent conductivity $\sigma(E)$ contributes to the total electrical conductivity via

$$\sigma = \int dE \sigma(E).$$

(2.15)

Interpreting Eq. (2.14), every charge carrier contributes (in units of $k_B/e$) to the Seebeck coefficient according to its relative position to the Fermi energy (measured in $k_BT$) and to the its share $dE\sigma(E)/\sigma$ to the total conductivity. For metals, the electrons near the Fermi level, contributing most to the transport, produce a low Seebeck coefficient. In semiconductors, on the other hand, the Fermi energy typically lies inside the band-gap and the mobile charges are away from this energy level leading to a large Seebeck coefficient. The advantage of large $S$ has not yet compensated the
low electrical conductivity and the resulting $ZT$ values of semiconductors can not compete with that of current heat engines. A simple estimate allows to convert the figure of merit to a working efficiency

$$\eta = \frac{T_{\text{hot}} - T_{\text{cold}}}{T_{\text{hot}}} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + T_{\text{cold}}/T_{\text{hot}}}.$$  \hspace{1cm} (2.16)

where $T_{\text{cold}}/T_{\text{hot}}$ are the operating temperatures of the heat baths. At room temperature, and with $ZT \sim 1$, the efficiency is around a few percent. Although not competitive against heat engines, thermoelectric devices are successfully operating in niche areas, e.g., for space missions where the reliability, long lifetimes, and absence of mechanical parts strongly favor this technology.

**2.3.1 Seebeck effect in organic semiconductors**

Among semiconductors, organic semiconductors show some promising features regarding thermoelectric application, including a low thermal conductivity ($\approx 1 \text{ W m}^{-1}\text{K}^{-1}$) and high Seebeck coefficient ($\approx 1 \text{ mV K}^{-1}$). A figure of merit of 0.4 has recently been reported for PEDOT:PSS in Ref. [44] and a theoretical work on Pentacene [45] even predicts a possible $ZT$ of 0.8-1.8. First principles calculations [46] for BTBT claim that a $ZT$ of 2.4 can possibly be reached. In addition to the potential applications in thermoelectric technologies, the study of the Seebeck coefficient has the power to provide more insight into the electronic transport properties. The general expression (2.14) for the Seebeck coefficient can be simplified to

$$S = \frac{k_B}{e} \left( \frac{E_F - E_V}{k_B T} + A_V \right),$$  \hspace{1cm} (2.17)

when a sharp mobility edge $\mu(E) = \mu_0(E)\Theta(E_V - E)$ is assumed at the valence band $E_V$ of p-type semiconductors, with $\Theta$ the Heaviside function. The high value of $k_B/e = 86 \mu\text{V K}^{-1}$ gives rise to the high Seebeck coefficients observed in semiconductors. It may also be noted now, that the constant contributes with this factor to the overall Seebeck coefficient. The analogous expression for a mobility edge $\mu(E) = \mu_0(E)\Theta(E - E_C)$ in n-type materials yields

$$S = -\frac{k_B}{e} \left( \frac{E_C - E_F}{k_B T} + A_C \right).$$  \hspace{1cm} (2.18)

In the expression (2.17) [(2.18)], the dimensionless constant $A_C$ [$A_V$] reflects the dominant mechanism of charge transport in the semiconductor. An alternative derivation
of these equations is based on the Boltzmann transport theory where the system is driven out of equilibrium by the thermal gradient and its relaxation is captured in a Boltzmann transport equation (usually within a constant relaxation time approximation). Another, more direct way to arrive at the above equations is via imposing a detailed balance between the drift and diffusion currents
\[ \dot{j}_{\text{diff}} = eD \nabla n \quad (2.19) \]
\[ \dot{j}_{\text{drift}} = e\mu_0 nE. \quad (2.20) \]

Here, \( D \) denotes the diffusion constant, \( n \) the total density of mobile charge carriers, \( \mu_0 \) their mobility, and \( E \) the electrical field appearing due to the thermal gradient. The density \( n \) is obtained (here shown for a p-type semiconductor) from the density of states \( n(E) \) by evaluating Eq. (2.11) where the Fermi-Dirac distribution (2.10) defines the thermally populated states of mobile charges inside the valence band. For low temperatures, i.e., when \( k_B T \ll E_F - E_V \), we can approximate the Fermi-Dirac statistics by the Boltzmann function
\[ f_{\text{FD}}(E, E_F, T) \approx f_B(E, E_F, T) = e^{\frac{E_F - E}{k_B T}} \quad (2.21) \]

and the integral in Eq. (2.11) becomes
\[ n \approx n_0 e^{\frac{E_F - E_V}{k_B T}} (k_B T) \quad (2.22) \]

with \( n_0 = n(E_V) \) the density of states at the band edge. Expressing \( \nabla n \) as \( (\partial n/\partial T) \nabla T \) in Eq. (2.19) and combining with Eq. (2.20) we arrive at
\[ \frac{D}{\mu_0} \left( \frac{1}{n} \frac{\partial n}{\partial T} \right) \nabla T = E. \quad (2.23) \]

Evaluating the bracket on the left-hand side using Eq. (2.22) and integrating over the sample length \( L \), yields
\[ \frac{D}{\mu_0 T} \left( 1 + \frac{E_F - E_V}{k_B T} \right) \Delta T = V_{\text{therm}} \quad (2.24) \]

where \( \Delta T = L \nabla T \) and \( V_{\text{therm}} = L |E| \). Finally, using the Einstein relation for the diffusion term \( D = \mu_0 k_B T/e \), the resulting Seebeck coefficient \(^2\)
\[ S = V_{\text{therm}}/\Delta T \]
takes the form given in Eq. (2.17) with \( A_V = 1 \). The number unity obtained from the

\(^2\)The derivation for n-type materials is analogous and yields the same value for \( A_C = 1 \).
above derivation originates from few assumptions: first, the density of states below the mobility edge is assumed constant, i.e., \( n(E) = \text{const. for } E < E_V \). Second, the mobility below the mobility edge is also assumed constant, i.e., \( \mu_0(E) = \mu_0 \). Finally, the expression for the diffusion constant \( D \) was used from the Einstein relation. This corresponds to a constant relaxation time approximation within the Boltzmann transport theory. In a more general framework, the above derivation yields the result (2.17) with \( A_V \neq 1 \). Conversely, the value of \( A_V \) can give an indication of the dominant transport mechanism at work.

2.3.2 Simulations

In order to simulate the Seebeck coefficient of a p-type material, we can start from Eq. (2.17) (analogously we may use Eq. (2.18) for n-type semiconductors). The applied gate voltage will shift the position of the Fermi energy (and thereby the density of induced charge carriers) and we can extract the remaining free parameter \( A \) from fitting the simulation the experiment. This, however, requires a good knowledge of the Fermi energy, which turns out to be a non-trivial task. Indeed, the spacial distribution of mobile charges strongly depends on the coordinate \( y \) perpendicular to the dielectric/semiconductor interface. This dependence is directly linked to a position-dependent Fermi energy \( E_F(y) \) via Eq. (2.11) and raises the question of the proper definition of the 'average' Seebeck coefficient across the channel thickness. The simplest approach is to assume that the Fermi energy is uniform within this thickness (of the order of the Debye length \( \lambda_D \)). With this zeroth-order approximation, the Seebeck coefficient

\[
S_0 = S(y = 0)
\]

(2.25)

results from evaluating Eq. (2.17) with the Fermi energy taken at the interface, \( E_F = E_F(y = 0) \). In a more sophisticated approach, we divide the channel into layers of thickness \( dy \) contributing independently to a global Seebeck coefficient. Similar to multi-channel problems reported in Refs. [47–51], the individual layers are weighted with their conductivity \( \sigma(y) \) and the weighted Seebeck coefficient takes the form

\[
S_w = \int dy \frac{\sigma(y)}{\sigma} S(y),
\]

(2.26)

where \( S(y) \) is obtained from evaluating Eq. (2.17) at the depth-dependent Fermi energy \( E_F(y) \). Because of the linear relation between the Seebeck coefficient and the
2.3 Seebeck effect

Fermi energy, the above weight can be used to define a dominant Fermi energy

\[ E_{F}^{\text{dom}} = \frac{\int E_{F}(y)\sigma(y)dy}{\int \sigma(y)dy} \]  \hspace{1cm} (2.27)

for which the Seebeck coefficient (2.17) yields \( S_w \).
Chapter 3

Sample preparation methods

This chapter provides a detailed explanation of the sample fabrication including crystal and thin film growth, contact evaporation, thin film sputtering, and surface modification of substrates.

3.1 Crystal growth - physical vapour transport

All single crystals investigated in this thesis are grown by physical vapor transport. This technique requires a special oven for crystal growth, shown in Fig. 3.1, consisting of a heating wire wound around a quartz tube. The wire windings get denser from one side of the tube to the other, thereby producing a temperature gradient inside the tube. The source material is sublimated at the hotter end, is transported through an argon gas flow towards the cooler region where it crystalizes again.

Technically, quartz half-shells are placed within this oven. One of them, filled the source material (usually in powder form), is placed at the hotter end. The other half-shells are placed consecutively near the colder regions to collect the grown crystals. Before heating the coil, the oven is flooded with argon gas for 2 hours to remove all residual air. Then the temperature of the oven is ramped up and the source material starts to sublimate and is transported by the argon flow towards the cooler region where it condensates to single crystals, see Fig. 3.2. Depending on the source material, growth temperature, and desired size of the crystals, this process may take several hours up to days. When the growth is finished, the temperature is slowly ramped down with a rate of 0.5K/min to minimize thermal stress for the crystals. Growth conditions for the investigated materials are summarized in Tab. 3.1.
3.1 Crystal growth - physical vapour transport

Figure 3.1: Crystal oven for growing single crystals by physical vapor transport. The higher density of heating wires on the right produces a higher temperature where the source material can sublimate. The argon gas (flowing from right to left) transports the evaporated molecules to the cooler region.

Figure 3.2: Photographs of PDIF-CN$_2$ (left) and Rubrene (right) organic molecular single crystal as grown by physical vapor transport. These samples are highly fragile and difficult to handle, but on the other hand allow to build flexible samples. The half-shell diameter was 2cm.

<table>
<thead>
<tr>
<th></th>
<th>Rubrene</th>
<th>PDIF-CN$_2$</th>
<th>UBE</th>
</tr>
</thead>
<tbody>
<tr>
<td>growth temperature</td>
<td>510K</td>
<td>510K</td>
<td>470K</td>
</tr>
<tr>
<td>duration</td>
<td>3-4h</td>
<td>48h</td>
<td>72h</td>
</tr>
</tbody>
</table>

Table 3.1: Specifications for the growth conditions of Rubrene, PDIF-CN$_2$, and UBE. In particular we indicate for each material the growth temperature and duration.
3.2 Thin film evaporation

Evaporated thin films of the organic materials presented in this work have been grown in a vacuum evaporation chamber, see Fig. 3.3. For this purpose, the source material (powder) is loaded into boats, which can be closed with a perforated lid. The boats are then clamped into two holders to let a heating current pass through. Before evaporation, the chamber is evacuated, with a typical pressure of $4 \times 10^{-6}$ mbar. A thermocouple, attached onto the boat, monitors the boat temperature during evaporation. If needed, the substrate is heated independently (e.g. to 340K for PDIF-CN$_2$). The evaporation process is turned on by slowly increasing the applied voltage across the boat, hence increasing the heating power and the temperature of the boat. Simultaneously, the evaporation rate is followed by a crystal monitor. After several minutes, when the evaporation rate has stabilized, the shutters are opened and the material starts to accumulate on the prepared wafers. As the field effect transistor performance crucially depends on the crystallinity of the first few monolayers, the evaporation rate is kept as low as possible (around 1 Å per minute) until the film has reached a thickness of 50-100 Å. Then, the evaporation rate is slowly increased to 1 Å/s for the last layers. The final thickness of the film is about 30nm. After the evaporation, the samples remain in the vacuum chamber for 30 minutes to cool down. To minimize the degradation in air, the samples are then rapidly moved to the metal evaporation chamber for the application of gold contacts.

3.3 Metal evaporation and sputtering

3.3.1 Metal evaporation

We have used gold, evaporated with our gold evaporation system (see Fig. 3.3), to contact the sample to the external apparatus. For this purpose, the samples are mounted into a sample holder and covered with a shadow mask, see Fig. 3.4. Then the whole system is mounted in the vacuum chamber and the evaporation is performed after reaching a base pressure below $6 \times 10^{-6}$ mbar. For the source and drain contacts, 30nm of gold was evaporated at a rate of 0.1 Å/s. This low rate was chosen to prevent any harm to the modified surface (in the case of bottom contacts) or to the semiconductor (in the case of top contacts). For thermometer gold contacts on bare SiO$_2$, we first evaporated a 2nm adhesion layer with a rate of 0.1 Å/s, followed by a 50 to 70nm thick gold layer at a rate of 0.3 Å/s.
3.4 Substrate preparation

We have used purchased phosphorus doped Si-wafers with a thermally grown 270nm SiO$_2$ layer. The wafers were cut with a wafer saw in a clean-room to rectangles of a size of 13×20mm$^2$. Before use, each chip was successively cleaned in a heated ultrasonic bath of acetone and of isopropanol (15 minutes each). To minimize residual solvent on the wafer, they are finally blow-dried with nitrogen gas.

The surface states on the Si-SiO$_2$ substrates significantly reduce the performance of a field effect transistor if the semiconductor is directly placed on the bare surface. In most cases, we have therefore applied a surface modification before depositing the organic semiconductor. We use for this purpose OTS, hexamethyldisilazane (HMDS), and Cytop, see Fig. 3.5. A general overview over the selected treatments, the mixings, rotation speeds (for spin coating), and annealing parameters is provided in table 3.2.
Each treatment is discussed in more detail in the following paragraphs.

**Octyltrichlorosilane OTS** This molecule can coat SiO\(_2\) with a self-assembling monolayer and thereby render the surface hydrophobic; indeed, the water contact angle is increased to 100° [52] compared to 75° for SiO\(_2\). The central role is played by the trichlorosilane group of OTS, which anchors on the surface while the Carbon chain points out perpendicular. The anchor group functions in such a way that one arm of it binds to the surface while the others try to bind to adjacent molecules. This improves the film growth and stability. The high sensitivity of OTS to oxygen and water required the coating procedure to be conducted in a nitrogen-filled glovebox.

![Molecular structure of the substrate materials OTS (left), Cytop (middle), and HMDS (right).](image)

Figure 6.4: Molecular structure of the substrate materials OTS (left) and HMDS (right).
### 3.4 Substrate preparation

<table>
<thead>
<tr>
<th></th>
<th>OTS</th>
<th>HMDS</th>
<th>Cytop 30nm</th>
<th>150nm</th>
<th>310nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixing</td>
<td>1 OTS(^1) 500 Solvent</td>
<td>already in solvent</td>
<td>1 Cytop 10 Solvent</td>
<td>2 Cytop 3 Solvent</td>
<td>3 Cytop 2 Solvent</td>
</tr>
<tr>
<td>Spinning</td>
<td>—</td>
<td>20s at 500rpm</td>
<td>10s at 500rpm</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>20s at 1000rpm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Annealing</td>
<td>2h at 430K</td>
<td>1h at 370K</td>
<td>40min at 360K and 40min at 400K</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.2: Specification overview for the various surface modifications: OTS, HMDS and Cytop (at three different thicknesses). The table indicates for each case the mixing ratio with the solvent, the spinning speeds, and the annealing times and temperatures.

After dissolving 0.02ml of OTS in 10ml of anhydrous toluene, the wafers have been immersed in this solution for at least 18 hours to ensure a complete coverage of the surface. In order to remove any unbound molecules the wafers are then rinsed thoroughly with toluene. The completion of the cross-links between neighboring molecules (and the removal of residual solvent) is achieved by annealing the chip at 430K for 2 hours.

**Hexamethyldisilazane HMDS**  Similar to OTS, HMDS is a molecule that forms a self-assembling monolayer on SiO\(_2\). It is necessary to conduct this surface modification in inert nitrogen atmosphere, to account for sensitivity of HMDS to Oxygen and water. HMDS is then spin-coated onto the surface with a rotation speed of 500rpm for 20sec and 1000rpm for 20sec.

**Cytop**  This fluoro-polymer, developed by Asahi Glass, is extremely hydrophobic and can be deposited on the SiO\(_2\) surface by spin-coating. Thereby, the layer thickness strongly depends on the mixing concentration of Cytop with its solvent and on the rotation speed. Some typical mixing and spin-coating conditions are listed in table 3.2. Afterwards the Samples were annealed for one hour at 360K and then an additional hour at 400K to first evaporate the solvent and then to cross-link the Cytop layer.

\(^1\)The necessary minimal OTS content to guarantee full coverage of the wafers (four per run) was 0.02ml. Additionally, a minimal amount of toluene (10ml) was required to have enough solvent within the 18 hours of immersion, see text.
Chapter 4

Analysis of PDIF-CN2 - a n-type semiconductor

In this chapter, we investigate and characterize the n-type semiconductor PDIF-CN$_2$, processed as single crystals, evaporated thin films or spin-coated thin films. The comparison of the transfer characteristics for these different techniques allows us to study the dependence of the trap DOS on the processing conditions. The following chapter is based on two original publications [24, 41] (in collaboration with Roger H"ausermann). The text has been significantly adapted for this chapter.

4.1 Introduction

The crystalline order in organic semiconductors, based on weak van der Waals bonds, strongly influences the overlap of the $\pi$-orbitals of adjacent molecules and therefore impacts on the mechanism of charge transport [19]. For example, grain boundaries and packing defects have been shown to lead to a lower electrical conductivity [53, 54]. More generally, numerous causes are known to cause localized electronic states, so-called trap states, among which are structural defects [16], chemical impurities [17], adsorbed water [18], polarizability of the dielectric [55], or the thermal motion of the molecules [19]. An overview of these effects is given in Ref. [36]. Trap states influence the performance of an organic field effect transistor (OFET) by affecting the charge carrier mobility, the threshold voltage and the subthreshold swing. Conversely, the FET geometry can be used to study the trap density as a function of
Figure 4.1: The four PDIF-CN$_2$ based device structures employed in this study. From top left to bottom right: FET geometry for a single crystal on Cytop substrate, thin film evaporated without substrate, thin film evaporated on Cytop, and thin film evaporated/spin coated on HMDS. Center: chemical composition of PDIF-CN$_2$.

processing conditions. In order to explore the interplay between charge trapping and charge transport, we study systematically both, the transistor performance and the trap DOS with a varying degree of crystalline order. As for inorganic semiconductors, organic semiconductors are classified according to the dominant charge carrier type as n-type (for electron carriers) or p-type (for hole carriers). In the last years, several detailed trap DOS investigations have been conducted on p-type semiconductors such as Rubrene or pentacene [56–61]. Yet, very little is known about the electronic properties of n-type materials. One promising n-type organic semiconductor is PDIF-CN$_2$, also known as N1100 and synthesized by Polyera, see Fig. 4.1. In 2004, Jones et al. [62] reported PDIF-CN$_2$ as a high-mobility, air-stable n-type semiconducting material with processing versatility. Shortly later, stable OFETs based on spin-coated films of PDIF-CN$_2$ have been realized [63, 64]. The transistor performance can be further improved [65] by thermal annealing of the solution processed films, which leads to a significant reorganization of the molecules. Evaporated films were studied on different substrates showing that the various surface treatments of the substrate substantially influence mobility, threshold voltage and on/off-ratio [66]. By far the highest mobilities, consistently above 1cm$^2$/Vs, and best transistor characteristics were achieved using PDIF-CN$_2$ single crystals [67]. These samples show negligible gate bias stress effects [68]. Further improvements on the fabrication process were made using ionic liquid gates resulting in mobilities around 5 cm$^2$/Vs [69]. In contrast
to single crystals, mobilities of up to 1.3 cm$^2$/Vs have been reported in a solution based thin film transistor (TFT) setup when using a solution crystallization process [70]. In the present study, we go beyond previous works in several respects: first, we have investigated the field-effect performance of PDIF-CN$_2$ for all major fabrication techniques (single crystal, evaporated thin films, and solution-processed thin film) and various gate dielectrics, see Fig. 4.1. Second, we have measured the transfer curves at different temperatures and calculated the mobility of charge carriers. Finally, we have extracted the spectral trap DOS to investigate their influence on the device performance. In the following sections, we will successively discuss each fabrication technique: solution-processed samples in Sec. 4.2, evaporated films in Sec. 4.3 and single crystals in Sec. 4.4. A thorough comparison of these processing techniques and the dependence of the transistor performance on the degree of order follows in Sec. 4.5. The main conclusions of this chapter are finally summarized in Sec. 4.6.

4.2 Spin-Coated Thin-Film

We have fabricated solution-processes thin films of PDIF-CN$_2$ by spin-coating, i.e., where the source material is dissolved in a solvent [typically chlorobenzene (cb) or chloroform (cf)] and then dropped on a fast rotating substrate (500rpm for 20s). Later, the sample is annealed for one hour at 100$^\circ$C to improve the crystallinity of the films. Up to some modifications discussed in the text, this fabrication process follows Piliego et al. [64]. In order to optimize the performance of the spin-coated thin-film transistors, we applied the spin-coating technique for various substrates, including the bare pre-cleaned Si-SiO$_2$ wafers, the SiO$_2$ wafer treated with ozone (UVO) only, UVO and hexamethyldisilazane(HMDS)-functionalized SiO$_2$, and Cytop (Asahi Glass)$^1$. All substrates are cleaned ultrasonically in hot acetone and isopropanol each time for 15 minutes and dried in nitrogen blow. The UVO treatment was performed in an oxygen flooded box under a lamp emitting ultra violet radiation. For the HMDS treatment, the HMDS solution was spin-coated onto the wafer at 500rpm for 20s and at 1000rpm for 20s. HMDS was deposited in a nitrogen filled glovebox. Independent of the substrate choice, all further preparation steps are performed in a nitrogen glovebox. Approximately 0.7%wt of dissolved PDIF-CN$_2$ is dropped onto the substrates through a 0.2µm syringe filter and then spin-coated. In a final processing

$^1$The use of Cytop as a substrate for organic semiconductors has first been proposed by Kalb and co-workers [38] and has successfully been used later, see e.g. [10, 39, 71, 72].
4.2 Spin-Coated Thin-Film

Figure 4.2: Transfer characteristics of spincoated PDIF-CN$_2$ thin film transistors for six different substrate/solvent pairs. Substrates include bare, ozon (UVO), and UVO+HMDS-treated SiO$_2$. The solvents are chloroform (cf) or chlorobenzene (cb).

Figure 4.3: Transfer curves of 14 PDIF-CN$_2$ thin-film transistors spin-coated on HMDS. The source material was dissolved in chlorobenzene. The same color is used for the devices from the same batch. Within a batch devices are similar and show a significant and reproducible hysteresis as seen by the forward and backward transfer measurements. Inset: Forward curves are in plotted on a linear scale, suggesting contact limitations for high voltages. ($V_d = 50\, V$, $L = 50\, \mu m$, $W = 900\, \mu m$)
Analysis of PDIF-CN2 - a n-type semiconductor

Figure 4.4: Histogram of mobility values of 31 spin-coated devices fabricated on HMDS-treated SiO$_2$ substrates. The mobility is extracted from the transfer characteristics in the saturation regime. The best transistor has a mobility of 0.22 cm$^2$/Vs.

step, gold top contacts (30 nm) are evaporated onto the annealed device.

The measurements of the field-effect transistors were performed with a HP 4155A semiconductor parameter analyzer under helium atmosphere. Several observations allow us to reduce the multiplicity of options (substrate, solvents): we observed that samples prepared from chlorobenzene solution yielded higher mobilities than those from chloroform, see Fig. 4.2. While all devices show high off-currents, large negative turn-on voltages and a pronounced hysteresis (see Fig. 4.2), the HMDS treated samples showed the lowest off-current, the highest on/off-ratio and the highest mobility. For the detailed discussion below, we therefore (mostly) focus on samples with HMDS substrates. Note that, Cytop turned out to be inappropriate as a dielectric layer due to its highly hydrophobic surface resulting in a poor wetting.

We have measured transfer curves of PDIF-CN$_2$ on HMDS for more than two dozen devices fabricated on a dozen different wafers. A representative selection is shown in Fig. 4.3, where the same color is used for samples fabricated in the same run. While within a run transfer curves are nearly identical, they significantly differ between runs. However the hysteresis of the curves is very similar among all devices. We have extracted the mobility of the samples using the dependence of the source-drain current $I_d$ on the gate voltage $V_g$ in the saturation regime via $\mu = (2L/WC_i)(\partial \sqrt{I_d}/\partial V_g)^2$, (where $L$ is the channel length, $W$ is the channel width, and $C_i$ is the capacitance), see Eq. (2.4). Interestingly, we can estimate the sample quality already from the visual inspection of the samples: if the film is smooth and if surface appears shiny, the
Figure 4.5: Transfer characteristics at different temperatures indicating the presence of discrete trap states. Top: Temperature dependent transfer curves for a spin-coated PDIF-CN\textsubscript{2} transistor. The sample was heated to 310K and subsequently cooled to 240K in steps of 10K. Bottom: Simulation (black) for three temperatures. The additional black curve was simulated without the discrete trap state. The hatched area highlights the influence of these gaussian broadened trap states at 0.24 eV below the conduction band (CB). (V\textsubscript{d} = 50V, L = 50\textmu m, W = 900\textmu m)

mobility is systematically higher. The best transistor had a mobility \( \mu \) of 0.22 cm\textsuperscript{2}/Vs while for most devices we found \( \mu \sim 0.1 \) cm\textsuperscript{2}/Vs, see Fig. 4.4.

In order to further investigate the devices and to calculate the trap DOS, we have cooled few samples of good quality in steps of 10K from room temperature down to 240K taking a complete transfer characteristic at each temperature, see Fig. 4.5. We have observed that the slope of the drain current is independent of temperature, while the threshold voltage shifts closer to zero (inset Fig. 4.5). For the sample shown in Fig. 4.5, we have simulated the transfer curves at 290K, 270K and 240K as described
before to gain insight into the trap DOS. The measured and simulated curves are shown in the lower part of Fig. 4.5. The trap DOS needed to successfully model the transfer curves is based on a discrete trap states with a density of $5 \times 10^{19} \text{cm}^{-3} \text{eV}^{-1}$ at -0.24eV. These discrete trap states are crucial to describe the transfer characteristics accurately, without which the simulation leads to a transfer curve shown as black (long-dashed) line. The effect of the trap state is graphically indicated by the hatched area between the two simulated curves. We have learned from our analysis that the presence of a discrete trap state can be concluded from the flattening of the transfer characteristics in the subthreshold region, particularly visible for low temperatures. We have seen this feature in all devices always around -60V gate voltage, see Fig. 4.3. On other substrates (bare SiO$_2$ or UVO treated SiO$_2$) these discrete traps did not show up. As discussed below, these trap states are also absent in the evaporated thin-films on HMDS. Hence, we tentatively associate the occurrence of these discrete traps to the solution processing on HMDS.

### 4.3 Evaporated Thin-Film

An alternative technique to fabricate thin-film transistors is by evaporation. We have applied this approach for three different gate dielectrics, the bare and HMDS-functionalized SiO$_2$, as well as SiO$_2$ coated with 140nm of Cytop, see Fig. 4.1. The substrate preparation is identical to that described in Sec. 4.2. Placed in a high vacuum evaporation system with base pressure $p_{\text{base}} < 10^{-7}\text{mbar}$, the substrates are heated to 110°C during evaporation, in order to improve the crystallinity of the deposited PDIF-CN$_2$ films [64]. In order to guarantee identical growth conditions of the thin films, the TFTs differing by their substrates have been produced in the same run. In a last step, gold source and drain contacts are evaporated and the finalized FETs are moved to the attached probe chamber without breaking the vacuum.

Figure 4.6 shows the measured transfer curves of the three device structures. The thin-films on Cytop have a turn-on voltage very close to 0V whereas the transfer curve for the transistor with bare SiO$_2$ is shifted to about $-10\text{V}$. An even larger shift of about $-25\text{V}$ is observed for the transistor with a HMDS modified SiO$_2$ interface. Furthermore the lowest off-current of the TFTs is achieved with Cytop. For devices with HMDS the level of the off-current depends on the sweep direction.

All three device structures have been measured for several temperatures between 250K and 300K and the transfer curves have been simulated to extract the trap DOS. Figure 4.7 shows the transfer measurements at different temperatures of the Cytop-
4.3 Evaporated Thin-Film

Figure 4.6: Representative transfer plots for evaporated PDIF-CN$_2$ TFTs on various gate dielectrics. The TFT based on Cytop has the highest on-off ratio, steepest subthreshold slope and highest mobility of the three evaporated transistors. ($V_d = 20\text{ V}, L = 450\mu\text{m}, W = 1000\mu\text{m}$)

Figure 4.7: Representative transfer plots for an evaporated PDIF-CN$_2$ TFT on Cytop. The transfer curves, measured at different temperatures, are well reproduced by a single choice of trap DOS (black lines). The latter is shown in Fig. 4.11 (blue line). ($V_d = 20\text{ V}, L = 450\mu\text{m}, W = 1000\mu\text{m}$)
Analysis of PDIF-CN$_2$ - a n-type semiconductor

based device (with the best transfer characteristics among different substrates) and the corresponding simulation results. The two other devices based on HMDS and SiO$_2$ have been investigated as well and the simulation results are shown in Fig. 4.11. We conclude from our analysis of PDIF-CN$_2$ thin-film transistors that the best performances are achieved on Cytop substrates, with the highest mobility, lowest gate-bias-stress effect and a turn-on close to zero gate voltage.

4.4 Single Crystal

The highest crystallographic order is achieved in PDIF-CN$_2$ single crystals, which we have grown by physical vapor transport [27]. For the growth conditions, the parameters used for Rubrene crystals have proven to be appropriate here. Further details can be found in Tab. 3.1. The crystals have been placed on pre-patterned substrates [14]. In order to minimize interface traps, a 140nm layer of Cytop is spin-coated on top of a precleaned Si-wafer with 260nm thermally grown SiO$_2$.

The temperature-dependent transfer curves of a single-crystal transistor, shown in Fig. 4.8, feature a very sharp turn-on at $V_g = -4$V and an on-off ratio exceeding $10^8$ at low temperatures. The peak mobilities reach up to $6 \text{cm}^2/\text{Vs}$, see discussion in Sec. 4.5 below, and the sub-threshold swing of 0.45V per decade is comparable to that of high quality p-type single crystal transistors, see Ref. [38, 73]. Furthermore no gate-bias-stress is discernible. An increasing drain current $I_d$ upon lowering the temperatures, as seen in the inset of Fig. 4.8 is only found in very pure single crystals. It has been suggested, this "band-like" transport requires a spacing layer between the $\pi$-stacked orbitals and the interface [71].

The simulated transfer curves for the single crystal device lie within the line-width of the measured ones for all temperatures and are thus not shown. The extracted trap density of states is very low and is comparable to very good Rubrene single crystals. All these results highlight the very good characteristics achievable in single crystal organic field effect transistors. This excellent performance is associated as well with the low density of trap states at the interface between the single crystal and the chosen gate dielectric Cytop.
4.5 Comparison and Density of States

In order to allow for a quantitative comparison of the results of the previous sections, all transfer curves are plotted on the same graph in Fig. 4.9. For this purpose the drain-current is scaled by the sample area ($WL$) and by the applied drain voltage $V_d$. Furthermore, the gate voltage was converted to the number of field induced charge carriers per unit area by multiplication with the gate capacitance ($C/e$). For Cytop-based samples (single crystal FET and evaporated TFT) the turn-on voltage is close to $V_g = 0$, while for other substrates the turn-on voltage is (sometimes significantly) shifted. The pronounced shift for the spin-coated sample on HMDS indicates a large amount of negative charge carriers in the conduction channel. Regarding the second characteristics, the turn-on is by far the sharpest for the single crystal FET, while the Cytop-based samples show the best performances among the evaporated TFTs. The broad turn-on of the transfer curve for the spin-coated film reflects the large density of trap states. A third parameter, the stress measurement, revealed no gate-bias-stress effects in the single crystal, small effects for the evaporated TFT, and a large and clearly visible hysteresis for the spin-coating technique. The degree of gate-bias-stress effects appears to be qualitatively related to the trap DOS (see below).
Figure 4.9: Transfer characteristics of PDIF-CN\(_2\) based FETs with different degrees of order. The single crystal and the TFTs on Cytop show the best transistor performance with a high on-off ratio and a sharp turn-on at vanishing gate voltage. The transfer curves of the other evaporated thin-film transistors are slightly shifted, most for the HMDS treated sample. The spin-coated transistor has a broad turn-on indicating the presence of a large number of trap states. For a better comparison, the axes have been renormalized, see text.

suggesting that the charges are dominantly trapped in the semiconductor rather than in the gate dielectric [39].

From the transfer measurements at various temperatures for the spin-coated, evaporated and single crystal FETs we have extracted the charge carrier mobility according to equation 2.4 in the saturation regime, see Fig. 4.10. Compared to reference values for p-type semiconductors [41], the mobilities are relatively high both for single crystals and thin-film devices. The linear decrease of the mobility of the thermally evaporated thin-films upon lowering the temperature indicates "hopping" transport and the slope is independent of the chosen substrate. On the contrary, the mobility in the single crystal increases upon cooling and hence related to a "band-like" transport. This trend is consistent with the picture correlating the material’s order with the carrier mobility: ordered single crystal exhibits high-mobility "band-like" transport whereas more disordered thin-films show "hopping" transport with a lower mobility. Interestingly we find a flat temperature-independent mobility for the spin-coated device.
4.5 Comparison and Density of States

Figure 4.10: Temperature dependent mobility of the spin-coated, evaporated and single crystal FET devices. The single crystal has by far the highest mobility, increasing with lower temperature. The evaporated TFTs show a uniform temperature behavior on all substrates corresponding to a linear increase in mobility upon increasing temperature. The mobility of the spin-coated device remains constant over the whole measurement range.

All the charge transport properties discussed so far can be understood within a simple model, consisting of a conducting band (CB) of delocalized, mobile states and a finite density of localized (or trap) states within the semiconductor band gap. The sample’s degree of order will strongly affect the density of these trap states, a quantity that we extract from simulating the transfer characteristics of our samples, see Fig. 4.11. We find that the evaporated devices on either bare SiO$_2$, Cytop or HMDS-treated SiO$_2$ exhibit similar DOS. In agreement with our previous observations, the evaporated device on Cytop (with the highest mobility) has the lowest trap density. The single crystal has by far the lowest trap DOS which explains the sharp turn-on of the transfer curves in Fig. 4.8. The spin-coated films on HMDS-treated SiO$_2$ feature a discrete trap states centered around 0.24eV below the conduction band. The distribution is relatively narrow $\sim 0.01$eV. For this sample, the discrete trap states dominate the transfer characteristics and explain the significant difference from the other samples.

The region close to the conduction band is not directly accessible from experiments. Hence, the simulated transfer characteristics might depend on the model for the trap DOS in this region. While our approach uses a steep exponential, an earlier
Figure 4.11: Trap density of states for all PDIF-CN$_2$ n-type FETs studied in this paper. The single crystal (red) has a 2 to 3 orders of magnitude lower trap DOS compared to the polycrystalline thin-film FETs. The evaporated thin-film on Cytop has the lowest trap DOS of the thin-film FETs. The spin-coated FETs are dominated by a gaussian-shaped trap level around $-0.24$ eV. Otherwise, the trap DOS of the spin-coated FET is comparable to the evaporated ones. Two typical trap DOS of polycrystalline and amorphous silicon (a-Si:H) are shown as dashed lines. They are comparable to the DOS of the organic semiconductors [74, 75].

work is based on a Gaussian shape [71]. It appears that the results are not very sensitive to this choice: indeed, we have (energy-)integrated the DOS of Minder et al. [71] resulting in a density per unit area of $N_{2D} = 2.0 \times 10^{12} \text{cm}^{-2}$. Starting from our density of states, we obtain a density per unit volume of $N = 6.7 \times 10^{19} \text{cm}^{-3}$ trap states. With a conducting layer of thickness of 3nm the findings of Minder and co-workers agree with our results. A conduction channel of this thickness agrees with the lattice plane spacing of 2nm measured for PDIF-CN$_2$ [66].

4.6 Conclusions

We succeeded in fabricating and characterizing field effect transistors of the organic n-type semiconductors PDIF-CN$_2$ based on various processing techniques: as single crystal, as thermally evaporated thin-film and as spin-coated thin-film. Additionally, we have studied the dependence of the FET performance as a function of the substrate (gate dielectric). Our transistors range from the high performance single
4.6 Conclusions

![Scaled transfer curves of various organic and inorganic p and n-type semiconductors.](image)

Figure 4.12: Scaled transfer curves of various organic and inorganic p and n-type semiconductors. The colors indicate the processing technique: Single crystals (red), evaporated thin films (blue), solution processed thin films (orange) and inorganic samples (green/purple).

Crystal transistors via good evaporated thin film transistors to poor spin-coated TFTs dominated by trap states. For the first time, the transport properties have been studied on such a wide range of performance in a single material. We have investigated the trap density of states (trap DOS), intrinsically responsible for the transport characteristics, and hence we have been able to connect the electrical performance to the microscopic material properties. In the single crystal, the trap DOS is extremely low and as a result the subthreshold swing is very steep and the charge mobility increases up to 6 cm$^2$/Vs upon lowering the temperature. These excellent performance characteristics are reduced in the evaporated films where more disorder is present and where the trap DOS is found to be several orders of magnitude larger. Furthermore, the turn-on is broader and the mobility changes from a "band-like" to a "hopping-like" temperature dependence. All these features originate from the increased trap DOS. We have found that the trap DOS of the spin-coated films is similar to the thermally evaporated films except for a large density of discrete trap states situated about 0.24eV below the conduction band. These discrete trap states, reminiscent of the chemically induced trap states of p-type materials [37, 76], drastically reduces the device performance. In absence of discrete trap states, the spin-coated films would
be of high performance similar to the evaporated films.

In addition to the technique used to process the semiconducting material, the choice of the gate dielectric strongly affects the trap DOS and hence the FET performance. This is best observed in the evaporated films (Fig. 4.11). Gate-bias-stress effects have only been studied for evaporated thin films and single crystals and have shown to be absent in the PDIF-CN$_2$ single crystals on Cytop [24]. In the evaporated samples, these effects are much less pronounced than in pentacene.

Finally, in order to place this trap density of states calculations into a broader context, we have collected [41] a representative choice of trap densities of various organic and inorganic p- and n-type materials that have been extracted with the help of a field effect transistor structure. In this collaborative work together with Roger Häusermann, we investigated various materials in field effect geometries published in literature or measured in-house. We have shown that by scaling the transfer curves properly we can directly compare the quality of different transistors without the need of simulating the transfer curves. The proper scaling that has to be done is shifting the gate voltage with respect to the turn-on voltage and scaling with the gate capacitance. The drain current has to be corrected by the geometry (length $L$ and width $W$) and the mobility $\mu$. The resulting curves are directly proportional to the free charge carrier density and thus a measure of the ratio of free versus total number of induced charge

![Density of states of various organic and inorganic p and n-type field effect transistors. Single crystals are shown in red, evaporated thin films in blue, solution processed thin films in orange and inorganic samples in green or purple.](image)

Figure 4.13: Density of states of various organic and inorganic p and n-type field effect transistors. Single crystals are shown in red, evaporated thin films in blue, solution processed thin films in orange and inorganic samples in green or purple.
4.6 Conclusions

carriers. They can be seen in Fig. 4.12. Single crystals are shown in red, evaporated thin films in blue, solution processed thin films in orange and inorganic samples in green or purple. Additionally the theoretical maximum for a field effect transistor is indicated by a black dashed line. This maximum was lately almost achieved for a Rubrene single crystal field effect transistor [77]. To substantiate our scaling theory we performed simulations with the simulator developed by Oberhoff to extract the trap density of states for every device. The result can be seen in Fig. 4.13. Single crystals are shown in red, evaporated thin films in blue, solution processed thin films in orange and inorganic samples in green or purple.

From this quantitative comparison we can conclude first that our scaling approach already gives first insights which materials have a low trap density of states even though for an absolute number of trap states simulations have to be performed. Second we can clearly see, that PDIF-CN$_2$ can compete with the best p-type organic materials in the evaporated thin films as well as in the single crystals. We thus conclude from this microscopic study that PDIF-CN$_2$ is highly promising for practical applications thanks to the broad variety of applicable processing methods and its excellent intrinsic electronic properties reflected in the exceptionally low trap DOS as low as in the best p-type single crystal FETs [10, 36].
Chapter 5

Setup for the Seebeck measurements in organic semiconductors

To measure the Seebeck coefficient in organic semiconductors special requirements need to be met. In order to develop the best measurement methods possible we have built a new setup to measure the thermal voltage drop across an organic semiconductor within a field-effect transistor geometry.

5.1 Introduction

The Seebeck effect, directly converting heat (or temperature gradients) into electric power is named after Thomas J. Seebeck [78] and is a fascinating thermoelectric effect with many promising technological applications. Pursuing the quest for materials with better power conversion many new candidates have emerged in the recent years, among which bismuth telluride, lead telluride or the copper chalcogenides play an important role. Beside technological applications, the Seebeck effect allows to address fundamental questions on the materials transport properties. In particular, the Seebeck coefficient $S = V_{\text{therm}}/\Delta T$ measuring the generated electrical voltage $V_{\text{therm}}$ upon applying a thermal gradient $\Delta T$ provides a complementary view on the charge carrier’s transport properties.

In the recent years, renewed attention has been given to organic semiconducting materials as promising alternatives to silicon-based semiconductors. In contrast to
their inorganic counterparts, organic semiconductors feature mechanical flexibility and the possibility of cheap roll to roll fabrication. The major difficulty to study electronic and thermal properties of organic semiconductors is their (typically) low density of mobile charge carriers. In order to circumvent this issue these materials can be studied as doped thin films, or placed in a field-effect transistor (FET) geometry, where charge carriers are injected by a capacitive gate voltage $V_g$, see Fig. 2.5.

Following the second route, we have designed and implemented a new Seebeck measurement setup within a FET geometry, which allows for a simultaneous control of (i) the charge carrier density, (ii) the base temperature, (iii) the thermal gradient. The purpose of this chapter is to describe the setup and to discuss in some detail the experimental challenges. Beside the final setup version, we will also mention alternative implementations which have been tested and later rejected. We will first comment on the field effect transistor layout on the chip where also an on-chip thermometer array is positioned to accurately monitor the applied temperature gradient. Then we will focus on the application of the temperature gradient, the cryostat and the employed instruments. In a last but important part we will discuss the two different measurement protocols that were used to determine the field induced charge carrier dependent Seebeck coefficient.

## 5.2 Chip design

The organic semiconductor, incorporated in a FET geometry on a prefabricated Si-SiO$_2$ wafer ($20\times13\text{mm}^2$), is at the heart of our experiment. On the same chip, we have evaporated gold thermometers to measure locally the temperature and thermal gradient $\Delta T$ across the sample, see Fig. 5.1. In this section, we briefly sketch the FET geometry (a more detailed discussion can be found in Sec. 2.2), we discuss the on-chip thermometers, and we elaborate on the electrical contacting technique.

### 5.2.1 Field effect transistor

The basic setup of a FET consists of a back gate, separated from the sample by a thin insulating layer, and two electrodes, called source and drain, in contact with the sample. The gate/insulator/semiconductor structure forms a plate capacitor. This geometry allows to induce mobile charge carriers at the semiconductor/insulator interface when a gate voltage $V_g$ is applied. The source and drain contacts, separated by the channel length $L$, provide these charges. Additionally, a bias voltage between
Figure 5.1: Left: Layout of the sample chip. The semiconductor is laminated in the green area covering the source/drain contacts. Source and drain contacts are indicated as long yellow strips underneath the sample. The thermometer array is evaporated on the lower part. The temperature is measured as a change in resistivity of the thin-film gold strips (purple). The gold wires lead to square patches connecting to the spring pins. The temperature gradient is suggestively shown as a color gradient. Right: Microscope picture of the real setup with a single crystal on the upper channel. The gate is contacted with silver paint to the backside of the wafer.

source and drain can be used to measure electrical transport properties of the sample. For the purpose of our study, we measure the voltage drop $V_{\text{therm}}$ between source and drain upon applying a thermal gradient $\Delta T$ across the channel length $L$. Beside the dependence of the Seebeck coefficient $V_{\text{therm}}/\Delta T$ on the base temperature $T$, the FET geometry allows us to study $S$ as a function of the charge carrier density by changing the gate voltage $V_g$.

5.2.2 On-Chip Thermometers

Determining the accurate thermal gradient across the semiconducting sample is crucial for precise Seebeck measurements. A simple method to evaluate the temperature drop across the semiconductor is to combine the temperature difference between both ends of the chip, as obtained from platinum thermometers (see below), with geometric scalings (chip length vs. channel length). The measurement of $\Delta T$ is significantly increased when the thermometers are placed near the sample. Therefore, we have chosen to sputter on-chip thermometers next to the transistor channel. This
5.2 Chip design

resistance-based thermometry extracts the local temperature from changes in the resistance of the sputtered material. The material requirements hence include a strong dependence of the resistivity upon changing temperature, i.e., large temperature coefficient \( (1/\rho)(\partial \rho / \partial T) \) and a high reproducibility over many heating/cooling cycles.

**Gold Sensors**

Gold has turned out to be a suitable and reliable material for resistive thermometry. Since the rest of the electrical circuit is also based on gold contacts, we did not have to worry about contact resistances, and their temperature dependences. We have sputtered gold thin films on precleaned Si-SiO\(_2\) substrates, in pure argon atmosphere at a power of 50W, an argon gas pressure of \( 4.9 \times 10^3 \) mbar and for 110 sec leading to a film thickness of around 36nm. The resistance is than measured in a four-point geometry.

**Zirkonium Nitride Sensors**

Comercial temperature sensors based on Zirkonium nitride (ZrO\(_x\)N\(_y\)) are available for many years already, e.g., Cernox\textsuperscript{TM}. In these sensors, the material films are reactively sputtered onto sapphire substrates within an atmosphere of argon, nitrogen and oxygen. Later, the sensitive area and the top gold contacts are then formed by photolithography. The resistivity strongly depends on the ratio of nitrogen to oxygen gas during sputtering and the temperature dependence is that of a semiconductor (negative temperature coefficient). Two main arguments are in favor of using ZrO\(_x\)N\(_y\) thermometers for our experiment: first, the high resistance, as compared to the
Setup for the Seebeck measurements in organic semiconductors

Figure 5.3: Resistivity (left) and temperature coefficient (right) of ZrO$_x$N$_y$ against the partial nitrogen pressure during sputtering.

resistance of the gold contacts, allows for an accurate four-point measurement with a high voltage drop across the thermometer and assures a higher sensitivity. Second, the material’s resistivity shows a very strong temperature dependence.

When searching for the optimal gas mixture, we noticed, that the lowest possible partial oxygen pressure of our sputtering was already too high, leading to insulating behavior with highly non-linear current-voltage characteristics. Next, we limited our search to ZrN$_x$ by varying the nitrogen gas pressure with respect to the argon gas...
5.2 Chip design

pressure by several orders of magnitude. The partial nitrogen pressure of 0.35 gives a suitable balance between resistance and temperature coefficient. Unfortunately, the intense use of the sputtering chamber for other research purposes, possibly oxidizing the zirconium target, prevented a systematic reproducibility of the thermometer performance. We therefore opted for the gold-based thermometry.

5.2.3 Electrical contacts

The electrical structures are deposited on the wafer via shadow mask evaporation or sputtering. Given the fixed wafer geometry and a rigid contacting system (see below) one basic chip layout (sketched in Fig. 5.1(left) and shown in Fig. 5.1(right)), has been used throughout the entire project. It consists of two source/drain contacts and a thermometer array. The three sensors allow to measure base temperature and the

![Figure 5.5: Side-view of the setup with the sample mounted between the two holders and contacted from above with spring pins (upper picture) and a schematic drawing (below).](image)

...
thermal gradient over all sensor pairs, and hence to check the linearity of the gradient. The gold wires end in large square gold pads which are electrically contacted to the measurements devices via spring pins, see Fig. 5.5. Contacting with spring pins has proven to be very useful as mounting a new sample does not require any soldering or conductive gluing and hence makes it possible to exchange a sample chip within seconds. The shape of the source and drain contacts can influence the measurement of the thermal voltage significantly leading to a wrong Seebeck coefficient [79]. We therefore tried to optimize the contact shape according to this reference by using elongated and thin contacts.

5.3 Applying a temperature gradient

The basic ingredient for measuring the Seebeck coefficient is the application of stable and controllable base temperature $T$ and temperature gradient $\Delta T_h$ across the sample. In the case of our organic semiconductors, incorporated in a FET on a prefabricated Si-SiO$_2$ wafer, we clamp the wafer between two holders (stainless steel), see Fig. 5.6. For a better handling when exchanging the samples, the holders are free to move unidirectionally on a rail.

A temperature difference between the two holder results automatically in a temper-

![Figure 5.6: Technical drawing of the two holders mounted in the socket rail. Each holder is perforated with a cylindrical hole for the heating coil. The sample chip is clamped in the slits and bridges between the two holders.](image)
5.3 Applying a temperature gradient

In order to generate and rapidly control this temperature difference, we have opted for a 'heating while cooling' procedure where both holders are permanently cooled at the socket with liquid nitrogen, while each holder is heated separately by a heating coil. The latter, made from constantan wire, is embedded in a cylindrical hole within the holder. Platinum sensors (Pt1000) placed close to the bridge monitor the holder’s temperature and feed the apparatus regulating the heating power of the coils. With this approach, the temperature gradient can be controlled precisely and changed at rates up to 0.5K/s, Fig. 5.7. The ramping rate of the temperature gradient and the absolute temperature (< 1K/min) ensures optimal relaxation of the temperature on the sample and keeping the thermal stress for the semiconductor small.

Peltier elements present an alternative route for temperature control and reversal. Those devices use the Peltier effect (inverse Seebeck effect) for generating a temperature difference between their upper and lower side when applying a voltage. Using Peltier elements over Ohmic heating coils circumvents the need for permanent cooling. Indeed, flipping the sign of the applied voltage across the Peltier element, switches it from a heating to a cooling device and vice versa. For the purpose of our study, where we aimed for the base temperature to achieve around 200K. But at low temperatures the waste heat generated by the Peltier elements overcompensates the cooling power making their use inappropriate.
5.4 Cryostat

The entire setup, as described so far, is embedded in a cryostat to ensure optimal environmental conditions. Most importantly, we have used a vacuum pump to exchange the atmosphere (3 times) inside the cryostat by argon gas to prevent the sensitive organic semiconductors to be in contact with water and Oxygen. A slight overpressure during the experiment keeps the air outside the cryostat. A positive side-effect of this procedure is the strong reduction of water condensation induced by the nitrogen-cooled heater socket. The latter is in direct contact with a copper rod, piercing out of the cryostat. The outer end of the copper rod is directly immersed in a liquid nitrogen bath and the cooling power can be regulated by changing the immersion depth.

5.5 Instruments

The experimental setup has been used in different probing modes discussed in the following. We will aim at highlight the advantages and disadvantages of each mode.

5.5.1 Version A

In a first version of the setup the Pt1000 sensors necessary for the regulation of the heating coils are monitored by two Lakeshore 335 Temperature controllers. These controllers define from the readout, a temperature set-point, and carefully chosen PID parameters the necessary heating power. The on-chip thermometer and the Seebeck voltage are measured with a Keithley Electrometer using a scanner card to switch the channel. This electrometer also supplied the gate voltage. The transfer curve of the transistor is measured by an Agilent 4155A Parameter Analyzer. As the source and the drain contact served as contacts for the Seebeck measurements as well as for the transistor measurements, we changed the connections between the measurements with three relais switches from the Keithley to the Parameter Analyzer. The relais switches, controlled by an Arduino, have the advantage of completely decouple the electrical circuits. This measurement version is fast because the temperature control is internally done by the Lakeshore devices. The disadvantage lies in the measurement of the Pt1000 sensors by the Lakeshore Temperature Controllers. The resistance readout is done pulsed which induces a high noise level in all cables nearby leading to a high off-current in the transfer curves. The noise on the thermal voltage however
5.5 Instruments

Figure 5.8: Electrical network (Version A) used for Seebeck measurement. The temperature is controlled by the Lakeshore equipment. This facilitates the measurement but induces a high noise level in the Pt1000 because of the Lakeshore pulses. Relais switches at the source, drain, and gate contacts are controlled by an Arduino.

did not increase.

5.5.2 Version B

In a second version we have improved our setup by measuring the outer Pt1000 temperature sensors with two lock-in amplifiers thus reducing the noise level in our circuit. The effect could be directly seen in the transfer curves of our transistor measurements where the off-current decreased by two orders of magnitude. The lock-in readout is monitored with a computer program that calculates the needed heating power with given PID parameters and feeds the result to the Lakeshore temperature controllers that still provide the necessary heating power. The disadvantage of this setup is the handling as setting up the lock-ins, the computer and the calibration takes more time and effort but the decrease in off-current in the transfer curves enables a better analysis of the sub-threshold swing which is otherwise below the noise-level.
Figure 5.9: Electrical network used to measure the Seebeck coefficient of organic single crystals. The outer temperature sensors are measured with a Lock-in amplifier to reduce noise in the circuit. The heating power needed is calculated with a computer program and fed to the Lakeshore temperature controllers. The switches at the source, drain and gate contact are relais switches controlled with an Arduino.

5.6 Measurement Protocols

With our setup, we are now able to measure the Seebeck coefficient $S$ in a field effect transistor and hence to study its dependence on the gate voltage. The natural protocol to carry out the experiment is to fix the gate voltage $V_g$ and to scan the thermal gradient through $0 \rightarrow \Delta T_{\text{max}} \rightarrow -\Delta T_{\text{max}} \rightarrow 0$, see Fig. 5.10(left). The temperature sweep is then repeated for other gate voltages. This approach has been used in an earlier work by Pernstich and co-workers [10]. It accounts for a peculiarity in many organic semiconductors, namely a large off-set in the thermal voltage, i.e., a non-zero thermal voltage even in absence of a thermal gradient. This off-set voltage can be
5.6 Measurement Protocols

Figure 5.10: Illustration of the traditional protocol for measuring the Seebeck coefficient (left) and the protocol used in this thesis (right). Instead of sweeping the temperature gradient at fixed gate voltages (left), we sweep the gate voltage for fixed thermal gradients (right). On both panels, the dots represent individual measurements and the lines connect the measurements within one sweep. Each sweep is indicated with a different color. Independent of the protocol, the Seebeck coefficient \( S(V_g) \) is obtained from the slope of the thermal voltage against the temperature gradient for each gate voltage \( V_g \) (black lines). For illustrative purposes the temperature gradient is only varied between zero and \( \Delta T_{\text{max}} \) whereas in the experiments the temperature gradient scanned the full range between \(-\Delta T_{\text{max}}\) to \( \Delta T_{\text{max}} \).

larger than the variation of the thermal voltage between \( \pm \Delta T_{\text{max}} \). The origin of this phenomenon is not fully understood and the proposed measurement protocol excludes possible effects of a drift in this off-set voltage. There are two major drawbacks of this technique: first, the time \( \tau_T \) required to stabilize the thermal gradient after each step is of the order of a minute per Kelvin while the voltage relaxation \( \tau_V \) for each gate voltage is much faster; depending on the conductivity of the channel \( \tau_V \) ranges between 4 and 30 seconds. As a result of the long duration and the numerous thermal sweeps of this protocol the sample deterioration due to residual oxygen, water or thermal or gate stress affects the Seebeck measurement. A transfer curve measured before and after one Seebeck measurement can be seen in figure 5.11.

In an alternative protocol, illustrated in Fig. 5.10(right), the gate voltage is tuned at a fixed thermal gradient. The latter is then changed for the next scan through \( V_g \). The Seebeck coefficient \( S(V_g) \) is then obtained from the measured thermal voltages from different sweeps of \( V_g \). With this protocol a speed-up of up to a factor\(^1\) 10 is

\(^1\)The duration for measuring the full \( S(V_g) \) with this sequence approximately equals to take one
Setup for the Seebeck measurements in organic semiconductors

Figure 5.11: Demonstration of sample degradation using the ramping protocol for Seebeck measurements. The two transfer measurements are taken before (red) and after (purple) one full Seebeck measurement with the ramping protocol (left) and with the gate sweep protocol (right). Almost no degradation can be seen for the gate sweep protocol.

achieved compared to the protocol mentioned above and, hence, the effect of sample degradation is minimized. Note that for this new protocol to be applicable, the offset voltage has to be very stable disregarding of the measurement history. Having verified this, we were able to minimize the deterioration due to large gate biases (gate bias stress) by turning the gate voltage off between when changing to a new thermal gradient. The sensitivity of this approach to hysteretic effects of the offset voltage and/or temporal deterioration of the sample turns out to be a positive feature. Indeed, when the measured points $V_{\text{therm}}(\Delta T)$ lie on a straight line, both effects can be ruled out. In order to further establish the reliability of this approach we have measured a transfer curve before and after the Seebeck measurement for both protocols. In the traditional approach, a deterioration is clearly observed, see Fig. 5.11(left), while the new protocol leads to almost identical transfer characteristics, see Fig. 5.11(right). In all experiments, we have opted for equidistant steps in the temperature gradient $\Delta T$, while we have chosen a variable number of gate voltage steps depending on the desired resolution. The gate voltage steps were chosen with a logarithmic spacing giving a higher sensitivity in the turn-on region.

温度 sweep at one voltage with the traditional protocol. The speed-up factor is therefore linear with the number of steps in $V_g$ (here $\approx 30$).
5.6 Measurement Protocols
Chapter 6

Seebeck coefficient of organic semiconductors

We study simultaneously the charge transport and the Seebeck effect of organic semiconductors in a specially designed experiment, where the standard field-effect transistor is embedded in a setup suited for thermoelectric measurements. Single crystals of the p-type semiconductors Rubrene and UBE are studied as well the n-type semiconductor PDIF-CN$_2$. The position of the Fermi-level is controllably varied by the gate voltage tuning the Seebeck coefficient over a wide range. Similarities and differences among the various organic semiconductors are discussed.

Most Seebeck studies on organic semiconductors are based on doped thin films. The charge carrier concentration is varied by changing the doping concentration thus indirectly changing the position of the Fermi level but in an uncontrolled and irreversible way [80–84]. Only recently, the Seebeck effect has been studied within a field effect transistor structure [10, 29, 85]. This new paradigm allows one to induce (non-destructively and reversibly) mobile charges and hence to control the charge carrier concentration by shifting the Fermi energy. In the first work based on this new approach [29], the authors have investigated Rubrene and reported a rather large Seebeck coefficient $S$ in this material but no dependence on the gate voltage was observed. It has been recognized later that the large off-set voltage at $\Delta T = 0$ had not been accounted for properly. In a later work, Pernstich and co-workers [10] have shown that the Seebeck coefficient in Rubrene decreases logarithmically with the density of induced charge carriers. Other works on organic thin films and polymers
Figure 6.1: Photographs taken under a microscope for UBE, PDIF-CN\(_2\), and Rubrene (from left to right) single crystals on Cytop. Channel length is 500 \(\mu\text{m}\) for PDIF-CN\(_2\) and 250 \(\mu\text{m}\) for Rubrene and UBE. The observed mobility range is indicated below for each material class.

also observe this behavior [85–88]. The value for \(A_V \approx 3\) extracted for Rubrene and Pentacene, see Ref. [10], is higher than expected for a conventional semiconductor with a constant density of delocalized states. The value of \(A\) has been attributed to an energy dependent scattering rate, again in the conceptual framework of band transport. In this chapter, we use our combined FET/Seebeck setup to measure simultaneously the transfer characteristics and the Seebeck coefficient as a function of the induced charge carrier density. We then extract the position of the Fermi-level from comparing the measurements with numerical simulations. Finally, we compare our results for the n-type material PDIF-CN\(_2\) with the earlier work on Rubrene. As a third material we investigated UBE, a p-type material with low mobility compared to Rubrene [10]. Our samples thus span a mobility range over three decades (a photograph taken under a microscope of a representative sample of each material is shown in Fig. 6.1 together with the measured range of mobilities) thus giving us additionally the possibility to investigate whether the Seebeck coefficient in organic semiconductors changes over this wide range of mobilities.
Seebeck coefficient of organic semiconductors

Figure 6.2: Top: Thermal voltage of a Rubrene single crystal on Cytop with an applied outer temperature difference of -10K (left) and 10K (right) as a function of the gate voltage $V_g$ for the gate sweep protocol. Bottom: Thermal voltage as a function of the applied temperature difference for two different gate voltages as done in the ramping protocol. Here the slope is directly proportional to the Seebeck coefficient and the decreasing slope with increasing gate voltage is visible.

6.1 Seebeck and transport measurement

In order to verify the smooth operability of our setup, we have started our investigation with Rubrene single crystals, known for their stability and processing reliability. In this section, we use this archtype material to discuss the experimental procedure and the data analysis to validate our new measurement setup, and to demonstrate the accuracy of the alternative measurement protocol proposed in Sec. 5.6. Discussions on the physical implications are deferred to Sec. 6.2.
6.1 Seebeck and transport measurement

Figure 6.3: Thermal voltage (in V) against the eight measured on-chip temperature gradients (in K) sorted for each gate voltage. Only a selection is shown here. For each gate voltage $V_g$ (in V), the a fit is determined from a linear regression. For each figure we display the fit quality (coefficient of determination $R^2$), a quarter of the Seebeck coefficient ($S$ in these figures) and the off-set voltage $Y$ in V.

6.1.1 Thermal voltage measurement

If the thermal voltage is measured in the (traditional) ramping protocol, the temperature difference across the sample is varied changing the temperature on both sample holders simultaneously up and down respectively. This ramping is performed at a constant gate voltage and both the thermal voltage and thermometer resistances are measured continuously. After each thermal cycle, the gate voltage is increased to the next value. While the outer temperatures provide a sufficiently good estimate of the temperature drop across the sample (necessary for the experimental protocol), the Seebeck coefficient can be determined more precisely by evaluating the on-chip thermometers, and results from the slope of a linear fit of the thermal voltage against on-chip temperature gradient.

For the (new) gate sweep protocol, the local temperature is only measured before and after every gate sweep. The linearity of the temperature gradient can be checked by evaluating all three thermometers. The data set is now sorted for the different gate voltages and the Seebeck coefficient is extracted from a least square linear fit, see Fig. 6.3. All curves $V_{\text{therm}}(\Delta T)$ for different gate voltages are shown in Fig. 6.4. Notice the large off-set of the thermal voltage ($\sim -1\text{mV}$) at $\Delta T = 0$ and an off-set ($\sim 0.5\text{K}$) of the local $\Delta T$. Although generically observed, the origin of this off-set is...
still unclear. Nonetheless, Fig. (6.4) demonstrates beautifully its stability.

Accounting for the difference between thermometer distance and the channel length for the thermal voltage, the extracted $\partial V_{\text{therm}}/\partial \Delta T$ slopes can be converted to the Seebeck coefficient, Fig. 6.5. In order to plot the Seebeck coefficient as a function of the induced charge carrier density we subtract the on-set voltage from the gate voltage and multiply this quantity by $C/e$ with $C$ the gate capacitance and $e$ the electric charge, i.e.,

$$N_{\text{ind}} = \frac{(V_g - V_{\text{on}})C}{e}. \quad (6.1)$$

This step allows for a direct comparison between different samples, fabrication procedures, and gate dielectrics [41]. This scaling brings the graph in Fig. 6.5 from the left to the right side and additionally changing from a linear gate voltage axis to a logarithmic one which directly shows to the logarithmic dependence of $S$ on the induced charge carrier density.
6.1 Seebeck and transport measurement

Figure 6.5: Seebeck coefficient of Rubrene against the gate voltage (left) and induced charge carrier density (right). Notice the logarithmic scale for $N_{\text{ind}}$, demonstrating the logarithmic dependence of $S$ on the induced charge carrier density.

6.1.2 Characterisation of the Transistor

Independent from the Seebeck measurements, we have performed transfer characteristics for every sample. For the Rubrene transistor shown in Fig. 6.6(left), the extracted mobility is $\sim 11\text{cm}^2/\text{Vs}$, both from the saturation and linear regime. Its increase upon cooling to 275K suggests "band-like" transport while cooling further the mobility drops again. The sub-threshold slope of 180mV per decade indicates a low trap density of states of the semiconductor and hence the good quality of the transistor. The turn-on was shifted slightly towards positive gate voltages.

Similar to the shift of the gate voltage in the Seebeck measurements, see Eq. (6.1), we shift the transfer curves for better comparison and simulation. For this we proceed as follows: from measurements and simulations we know [77], that a perfect, i.e. trap-free, transistor at room temperature turns on at a gate voltage of $0.4\text{V}$. The turn-on is defined as the voltage for which the current raises above the level of $I_d = 10^{-14}\text{A}$. Similarly, the sub-threshold slope is found to be $58.5\text{mV}$ per decade. Since we are able to measure currents only above $I_d = 10^{-11}\text{A}$, we shift the transfer curves towards an apparent turn-on at $0.2\text{V}$. This approach neglects possible trap or dopant states below the Fermi-level at the turn-on. These states can not be accessed within the resolution of our experiment. Furthermore, close to the turn-on where the density of charge carriers is really low, we may not trust the Seebeck measurements, which require a reliable build-up of the thermal voltage. By shifting the transfer curves, we disregard the behavior in the off-set regime of the transistor. The simulated transfer
Figure 6.6: Top left: Temperature dependent transfer curves of a Rubrene single crystal on Cytop. The extracted mobility is to 11cm$^2$/Vs. Top right: Measured (black lines) and simulated transfer curves (dots) for two different temperatures. Bottom left: Density of states of the Rubrene single crystal 17_05 with a constant density in the valence band, an exponential tail of shallow trap states, and deep trap states far from the valence band. The mobility edge is shifted by 0.1V away from the valence band. Bottom right: Density of totally induced and free charge carriers as a function of the Fermi-level position. When the Fermi energy is close to the valence band, (almost) all induced carriers are mobile.

curves, shown in Fig. 6.6(right), show a good agreement with the measured data. The band density of states used here is 3 per molecule and eV, a standard value found in literature [35]. From a trivial scaling with the unit cell volume of Rubrene (containing 4 molecules) 2800Å$^3$, we find for the density of states the value $4 \times 10^{21}$ cm$^{-2}$eV$^{-1}$. With the typical band width of 0.7eV, we arrive at a total $2.85 \times 10^{21}$ band states per cm$^2$.

Recent low-temperature space-charge-limited current experiments indicate that the
mobility edge is slightly shifted away from the valence band edge into the shallow tail states. For the simulations at 300K, we fixed the mobility edge at 0.1eV away from the valence band. In comparison with the situation where the mobility edge coincides the valence band edge, it turns out that the transfer curves do not significantly differ. The DOS input taken for the simulation can be seen in Fig. 6.6 (lower left). The simulator calculates for a given position of the Fermi energy and a given temperature the total density of thermally activated (or induced) charge carriers and which fraction of it is mobile (free charge carriers), see Fig. 6.6 (lower right). Notice, that when the Fermi energy is sufficiently close to the valence band (at around 0.3eV), almost all induced charge carriers are mobile. For determining the current density distribution in the conducting channel, the coordinate dependence of density of free charge carriers in the direction perpendicular to the surface needs to be studied. The mobile charges screen the gate potential on the typical Debye length, see Sec. 2.2.3.

Simulating this screening effect, we obtain a coordinate-dependent Fermi-level position and, as a result, the ratio between free and induced charge carriers across the transport channel thickness. This allows us to simulate a realistic transfer curve. Conversely, the knowledge of the total density of free charge carriers can be used to extract the gate voltage and position-dependent Fermi energy from the simulator.

### 6.1.3 Reproducibility of the measurements

One declared goal of this section is to provide a thorough discussion on the reliability of the Seebeck measurements with the new setup. For that purpose, we have studied the dependence of the Seebeck coefficient on (i) the measurement protocols, (ii) the protocol details, and (iii) the temporal aspects (several runs). The agreement between the two suggested protocols, see 5.6, is validated in Fig. 6.7(left). This figure shows that Seebeck coefficient of Rubrene can be reproducibly measured with an accuracy of ±25mV/K. In this experiment, the measurement is repeated four times by alternating between the gate-sweep (squares) and ramping (filled circles) protocols (sequence red squares, red dots, blue squares, blue dots) showing a high reproducibility. Notice the much higher number of data points collected for the gate-sweep protocol than for the ramping protocol, although both experiments have similar duration. At low gate voltages, where the resistance in the conducting channel is large, we have a high measurement uncertainty due to fluctuations in the thermal voltage. In this region the ramping data is more reliable since the thermal voltage is averaged over several
Figure 6.7: Seebeck coefficient measured for Rubrene single crystals on Cytop at 295K. Measurements based on the ramping protocol are shown as circles, while rectangles indicate measurements in the gate sweep protocol. In the sample on the left four runs have been measured alternating between ramping and gate sweeps.

In a second experiment, shown in Fig. 6.7(right), we have varied the gate-sweep protocol by either waiting (5min) between each point, taking a full transfer curve between each point, or repeating the experiment the next day. The deviation in this data is slightly larger than in the first experiment but remains in a small range ±50mV/K. Once more the long lifetime and stability of Rubrene single crystals on Cytop becomes evident in our measurements.

### 6.2 Seebeck coefficient for p-type Rubrene

The measurement and data evaluation procedure described in the previous section has been applied to several Rubrene single crystals. Detailed results for three single crystals on Cytop will be discussed in the following, see Fig. 6.8. The large variation in the turn-on voltage suggests possible interface dipole effects. The simulations, based on the input DOS shown in Fig. 6.8(bottom right), provide a good agreement with the experiment. The mobility used for the simulations was extracted from the transfer curve. All three devices show a very similar low trap density of states. A first indication of the trap DOS can already be extracted from the transfer curves after shifting by the turn-on voltage and scaling by the mobility, the geometry and the gate capacitance, see Fig. 6.8. Indeed, the slope of these curves [41] is directly

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1We have observed a typical time scale of 5 minutes for the thermal voltage to stabilize.
6.2 Seebeck coefficient for p-type Rubrene

Figure 6.8: Top left: Transfer curves for three Rubrene single crystals. The extracted mobilities are 11 cm$^2$/Vs for sample 17_05, 12 cm$^2$/Vs for sample 05_04 and 18 cm$^2$/Vs for sample 04_03_02 respectively. Top right: Transfer curves additionally shifted by the turn-on voltage together with respective simulations (squares). Bottom left: Transfer curves additionally scaled by the mobility indicating the ratio between free and induced charge carriers. Bottom right: Density of states used as an input for the transfer curve simulations.

We evaluate the Fermi-level, following both routes discussed in Sec. 2.3.1. For both approaches (interface and dominant) the traces $E_F(N_{ind})$, shown in Fig. 6.9, almost coincide for different samples. These Fermi energies can be used to evaluate $S_0$ [Eq. (2.25)] and $S_w$ [Eq. (2.26)] respectively. At this point, the only free parameter left in Eq. (2.17) is the constant $A$, vertically shifting Seebeck coefficient curves. Note that the slope comes intrinsically from the shift of the Fermi-level and can not be changed proportional to the ratio between induced and free charge carriers (as discussed earlier in this work).
Figure 6.9: The measured (black squares) and simulated Seebeck coefficient for the weighted (blue) and interface (red) contribution fitted with the indicated values for $A$ for three different Rubrene single crystals. Fermi-level as extracted from the simulations with the respective DOS as can be seen in the lower left graph of Fig. 6.8.

by changing $A$. A comparison between the measured Seebeck coefficient and the simulated curves is provided in Fig. 6.9 for three different samples. The agreement between the simulated and measured Seebeck coefficient and all three samples have similar values of $A$. When using the interface expression $S_0$ for the Seebeck coefficient, we find a good agreement for $A \approx 3.5 \pm 0.2$. The weighted approach $S_w$ suggests a value $A \approx 1.5 \pm 0.2$.

We have repeated the Seebeck/transfer measurements for numerous samples. The representative selection of measurements, shown in Fig. 6.10, demonstrates the good agreement of both the absolute value and slope of the curves and underlines the linear dependence of the Seebeck coefficient on the induced charge carrier density. The fact that the Seebeck data lies within a narrow band is an indicator of the high
6.2 Seebeck coefficient for p-type Rubrene

Figure 6.10: Summary of Seebeck coefficient measurements of various Rubrene single crystals on Cytop at 295 K. Curves with circles have been measured with the ramping protocol, curves with rectangles are measured with fixed ∆T steps and gate sweeps. The shaded region of width 0.2 mV/K and slope 0.4 mV/K highlights the good agreement between the different curves.

quality and reproducibility of Rubrene single crystals on Cytop. Our data agrees well with the values reported by Pernstich and co-workers [10]. Following their interface dominated approach for extracting the constant A, namely using the formula for $S_0$, we find a value 3.5 in agreement with previously extracted value $\sim 3$. With the simulator developed by Blülle, we can simulate the dependences of all quantities along the channel thickness. By evaluating a weighted Seebeck coefficient $S_w$, we find for $A$ a value closer to unity. Both values (3.5 for $S_0$ and 1.5 for $S_w$) are within the range reported in classical inorganic semiconductors. This is surprising because in
these materials (and in strong contrast to ours) charges are transported ballistically through an almost perfect crystal with rare scattering events.

### 6.3 Seebeck effect in n-type PDIF-CN$_2$

Next, we investigated the n-type material, PDIF-CN$_2$, and present the first Seebeck measurement of a n-type single crystal semiconductor, see Fig. 6.11. All measurements and evaluations were done according to the same protocol than the Rubrene.

**Figure 6.11:** Top left: Transfer curves for three PDIF-CN$_2$ single crystals scaled by capacitance and geometry. The extracted mobilities are 0.38cm$^2$/Vs (14_07), 1cm$^2$/Vs (23_04_02), and 1.7cm$^2$/Vs (16_02) respectively. Top right: Transfer curves additionally shifted by the turn-on voltage together with simulations (squares). Bottom left: Transfer curves additionally scaled by the mobility. Bottom right: Input DOS for the simulations of the three samples given.
6.3 Seebeck effect in n-type PDIF-CN$_2$

Figure 6.12: Measured (squares) and simulated (solid red for interface and blue for weighted) Seebeck coefficients of three PDIF-CN$_2$ single crystals on Cytop.

samples in the previous section. The simulated curves agree well with the measured ones for the crystals 14.07 and 16.02, while the agreement is less good for the sample 23.04.02. This sample does not show the typical transistor behavior as already observed in the kink in the sub-threshold region. This behavior might originate from imperfect electrical contacts. The transfer curves scaled by the extracted mobility provides a rough indication of the trap DOS.

In order to simulate this n-type compound, the original simulator (designed for p-type materials) was adapted by flipping the signs of the gate and drain voltages. Since there is no intrinsic difference in the transport between p- and n-type semiconductors, this sign change does not affect the results. A good agreement between the measured and simulated transfer characteristics is found for the trap DOS shown in
Fig. 6.11(right). A key ingredient entering the simulation of transfer curves is the density of states in the valence/conduction band. This quantity can, in general, be extracted from independent calculations but is missing so-far for PDIF-CN$_2$. The known volume 700Å$^3$ of a unit cell (containing a single molecule) [89], agrees with the molecular density of Rubrene, see above. Assuming a band width comparable to Rubrene, we use for our analysis the same density of states in the conduction band. The Seebeck coefficient at the interface and the weighted contribution is then calculated with the extracted Fermi-levels at the interface and the weighted contribution respectively (compare Fermi-level in the lower right graph of Fig. 6.12). The parameter $A$ is the only free parameter now for fitting the simulated Seebeck coefficient to the measured curves. For both samples we plot a band of $A$ values (for both, inter-
face and dominant) and a best fit by eye as solid line. This data evaluation (Seebeck, transfer, simulation) was done for the three samples leading to a range of $A$ values as can be seen in Fig. 6.12. The data is overall well reproduced with a (negative) value of $A \approx -2 \pm 0.5$ (weighted contribution) and $A \approx 0.0 \pm 0.5$ (interface contribution). Since the measured curves do not lie as close together as for Rubrene, the uncertainty width in $A$ is broader. The lower $A$-value for the sample 23_04_02 may originate from the non-ideal transfer characteristics, see Fig. 6.11.

A representative choice of Seebeck measurements on PDIF-CN$_2$ single crystals on Cytop is summarized in Fig. 6.13. All curves are within a band of width 0.3mV/K with a slope of 0.4mV/K per decade.

### 6.4 Seebeck measurements on p-type UBE

As a third material, we have investigated UBE, see Fig. 2.1, a p-type semiconductor that can be grown as single crystals by physical vapor transport. The growth conditions are discussed in Sec. 3.1 and measurements are done as described in Sec. 6.1. A representative choice of Seebeck measurements in UBE single crystals is shown in Fig. 6.14. We notice large differences between different samples but also between measurement runs on the same sample. These differences are significantly larger than in Rubrene or PDIF-CN$_2$ samples. However, the data points are consistent within each measurement run. The large difference between the samples and the experimental runs is unclear. One possible explanation, based on contact resistances, could be checked in a four-point measurement which would require a new chip design. Nonetheless, the flattening of the transfer curves in the linear regime at high drain and gate voltages, see Fig. 6.15, is usually a sign for conduction in the channel that is strongly limited by contact resistance. The latter arises from an energy level misalignment at the interface between the semiconductor and the metal electrode possibly giving rise to an additional thermal voltage. Within this assumption, the deviations between different runs of the same sample can be understood as charging effects from the transfer curve measurements taken between the runs. Indeed, the applied drain voltages $V_d > 10$V are significantly larger than the thermal voltages in the order of mV that we want to measure. Statistically we observe a correlation between low contact resistances and low Seebeck coefficients. Inversely, samples which have an indication of high contact resistance (from transfer curves) show a higher Seebeck coefficient and larger variations between different runs.

The low charge conductivity is another factor possibly entering this issue. In
Figure 6.14: Seebeck coefficient of UBE single crystals on Cytop. Not only the variation between different samples but also between consecutive runs of the same sample as can be seen for sample 24_01_02 a and b (open and full green squares). There is a tendency for higher quality devices to show a lower Seebeck coefficient. Overall the slope is a reproducible feature in the UBE Seebeck coefficient measurements.

In fact, the two other materials Rubrene and PDIF-CN$_2$ showed reliable Seebeck measurements together with a conductivity larger by a factor of 10-100. Additionally the channel width in the UBE samples is very narrow, $\approx 100\mu$m, compared to PDIF-CN$_2$/Rubrene ($\approx 500\mu$m). As a result, the range of gate voltages required for a reliable build-up of the thermal voltage drastically shrinks, hence reducing the measurement range.

The precise dependence of $S$ on the gate-induced charge carrier density is difficult to determine because of the data scattering. Due to the poor reliability of the data,
6.4 Seebeck measurements on p-type UBE

![Graphs showing Seebeck measurements on p-type UBE](image)

Figure 6.15: Measured transfer curves plotted on a logarithmic (top) and on a linear (middle) scale of two UBE single crystal on Cytop. The mobility as step wise differential is plotted for both samples (lower part). The effect of high contact resistance limiting the current in sample 31_03_01 can be seen in the flattening of the transfer curves (middle right) compared to a linear regime (indicated by the dashed line).
we have forborn from extracting the $A$-value. Instead, we have extracted the slopes $\partial S/\partial \log(N_{\text{ind}})$ from linear fitting subset of each data set (neglecting significantly deviating data point). All samples/runs agree with each other with $\partial S/\partial \log(N_{\text{ind}}) \sim 0.4\text{mV/K per decade}$.

### 6.5 Comparison and conclusion

We have reported the Seebeck and transport characteristic of three different organic molecular semiconductors, processed as single crystals. This characterization has been performed in a combined FET/Seebeck experimental setup built for this purpose. With PDIF-CN$_2$, we provide the first investigation of the Seebeck coefficient for a n-type single crystal. The high quality data allows us to draw a direct comparison between Rubrene and the highly crystalline n-type PDIF-CN$_2$, see Fig. 6.16. The intrinsic difference in the sign of the dominant charge carrier reflects itself in the sign of the Seebeck coefficient and a trap DOS being either close to the valence or the conduction band. Accounting for this difference, the two materials behave almost the same Seebeck coefficient qualitatively and even quantitatively. Indeed, in both cases the Seebeck coefficient decreases logarithmically with increasing charge carrier density with the same slope and almost the same absolute value.

We have shown that the Seebeck coefficient intrinsically depends on the position of the Fermi energy rather than on the induced charge carrier density. Varying the induced charge carrier density, either via doping or via field effect, provides a simple way to shift the Fermi energy. Our experiment allows us to gain the direct relation between the density of induced charge carriers and the position of the Fermi-level, by measuring the transfer characteristics. We have paid special attention to the non-uniformity of the system perpendicular to the semiconductor/insulator interface, Sec. 2.2.3, resulting in a position-dependent Fermi energy. Combining a fully two dimensional simulation with a weighted approach for the Seebeck coefficient, we were able to account for this non-uniformity in $S$. Relating the two independent quantities $S$ and $E_F$, in Fig. 6.17, we can reveal the internal correlation, as resulting from extracting the $A$-value. This value can directly be read-off from the interception of the linear fit with the $y$-axis (after scaling $S$ by $k_B/e$). We find $A \approx 1.5$ (Rubrene) and $A \approx -2.5$ (PDIF-CN$_2$). Our analysis predicts that the slopes of the linear fits is universal $1/k_B T$, here $\approx 1/25\text{meV}$, a value that agrees perfectly with the measured data.

An overall comparison between the three studied materials is given in Fig. 6.18. It
6.5 Comparison and conclusion

Figure 6.16: Density of states and Seebeck coefficient for p-type Rubrene and n-type N1100 highlighting the similarities between both materials that can be produced in high crystallinity and in the same time showing their intrinsic difference, the sign of the main charge carrier.
Seebeck coefficient of organic semiconductors

Figure 6.17: Seebeck coefficient against Fermi-level a plot that can be made only by combining Seebeck coefficient measurements with field-effect transistor simulations. The slope of the linear fits is universal $1/k_B T$ and the interception with the y-axis corresponds to $A$.

It turns out that the slopes of all measurements ($\approx 0.4 \text{mV/K per decade}$) agree remarkably well with each other. In fact, this slope can be understood as a generic property of a semiconductor, as we shall see from the following argument.

First, let us assume a constant valence band (with density $n_0$) extending infinitely (much more than $k_B T$) to the negative energy regions, a sharp band edge at $E = 0$, and a vanishing density of states inside the band gap. The density of states per energy shall be denoted with $N_0$. Next, we assume that every charge carrier present in the valence band was induced by applying a gate voltage\(^2\). The density $n_{\text{ind}}$ of induced charges results from Eq. (2.11). By approximating the Fermi-Dirac statistics $f_{\text{FD}}$ by the Boltzmann function $f_B$, we arrive at Eq. (2.22). Solving this equation for

\(^2\)This assumption only simplifies the calculations and the notation but does not influence the result.
Figure 6.18: Seebeck coefficient of the three investigated organic materials UBE, Rubrene and PDIF-CN₂. For a better comparison we plot the absolute value of the Seebeck coefficient. The color shaded regions indicate the band width of the measured absolute value of the Seebeck coefficient whereas the slope is found to be an intrinsic parameter of a semiconductor.

\[ E_F = k_B T \ln \left( \frac{n_{\text{ind}}}{n_0 k_B T} \right) \]  

and inserting this result into Eq. (2.17) we obtain

\[ S = \frac{k_B}{e} \ln \left( \frac{n_{\text{ind}}}{n_0 k_B T} \right) \].

If we would change the volume density by an order of magnitude the change of the Seebeck coefficient would be

\[ \Delta S_{\text{vol}} = \frac{k_B}{e} \ln(10) = 0.2 \text{mV/K} \]
corresponding to a slope of 0.2 mV/K per decade. But as we have to convert the volume density \( n_{\text{ind}} \) to a density per unit area \( N_{\text{ind}} \), we assume the charges to be distributed homogeneously within a channel of thickness given by the Debye length [Eq. (2.8)], i.e., \( n_{\text{ind}} \lambda_D = N_{\text{ind}} \). Because \( \lambda_D \) depends on \( n_{\text{ind}}^{-1/2} \), we find

\[
\frac{\partial S}{\partial \ln(N_{\text{ind}})} = \frac{2k_B}{e}.
\]  

(6.5)

The change of the Seebeck coefficient per one decade in \( N_{\text{ind}} \) is then given by

\[
\Delta S = \frac{2k_B}{e} \ln(10) \approx 0.4 \text{mV/K}
\]  

(6.6)

and corresponds to the slope of \( S \) versus \( N_{\text{ind}} \) in a semi-logarithmic plot. The analytic result matches perfectly both the observed slope in the experiment and the simulations. This implies that the influence of the trap DOS on the shift of the Fermi-level position is only marginal. The overall contribution (especially in the linear regime of the transistor) comes from the overlap of the Fermi-Dirac function with the band density of states. As their density is much higher than the trap density in the band gap the filling up of band states determines the shift of the Fermi-level. From the above derivation we conclude that the slope of the Seebeck coefficient (or Fermi-level) against \( \ln(N_{\text{ind}}) \) is universal and does not depend on any material specific parameters, e.g. \( n_0, A, \mu \). Deviations from this universal value indicate a high trap density of states in the band gap as the above assumptions are not valid anymore.

On the contrary, the value of the \( A \)-parameter provides direct signatures on the trap DOS. We have analyzed \( A \) for Rubrene and PDIF-CN\(_2\). In Rubrene we find \( A \approx 1.5 \pm 0.2 \) a value that agrees well with previously reported works on this material [10] and corresponds to the typical value measured in conventional inorganic semiconductors. This latter observation is surprising because the charge transport mechanisms in these two material classes are completely different. For PDIF-CN\(_2\), we have extracted value \( A \approx -1 \pm 0.5 \) suggesting a more disordered transport mechanism. Although different from Rubrene, these values are within the range reported in inorganic semiconductors. A reliable extraction of \( A \) was not possible for the UBE system, because of large variations between samples and between different runs of the same sample. We propose that contact effects are responsible for shifting the different measurement curves with respect to each other. Hence, the absolute value does not reflect the intrinsic Seebeck coefficient of UBE. Still it appears that \( A \) is somewhat larger in UBE than in Rubrene. All three samples, however, show the universal behavior of 0.4 mV per decade.
6.6 Outlook

We have seen that the Seebeck coefficient in combination with a field effect transistor structure can be used to spot unusual transport phenomena as an enhanced $A$ reflects some additional entropy transport in the semiconductor. For the organic materials studied we did not find an enhanced value of $A$ or of the Seebeck coefficient making them not preferable as thermoelectric materials than any other semiconductors in general. The problems involving the optimization of the figure of merit are the same as for conventional materials meaning the problem of increasing the electrical conductivity by not simultaneously decreasing the Seebeck coefficient and increasing the thermal conductivity. We calculated the efficiency for one Rubrene single crystal device. From literature we know the thermal conductivity for Rubrene at room temperature $\kappa = 1\text{Wm}^{-1}\text{K}^{-1}$ [90]. This value was measured at zero gate voltage and we expect the thermal conductivity to increase with increasing charge carrier concentration as the electronic contribution to the thermal conductivity is large in organic semiconductors. Nevertheless we will take this value to approximate calculate $ZT \approx 10^{-6}T$. Inserting a reasonable temperature for organic semiconductors of 400K we arrive at a maximum $ZT = 4 \times 10^{-4}$ at a gate voltage of 15V. Assuming a temperature difference of 100K above room temperature we can calculate the corresponding Carnot efficiency $\eta = 3 \times 10^{-5}$. This efficiency is still far from being
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worth to be incorporated in any thermoelectric device and evidently the fact of the necessity of applying gate voltage would have to be circumvented by choosing an optimal chemical doping concentration. Nevertheless we think that using a field effect transistor structure to study the thermal and electrical properties of materials in a combined way can also give insights which way to optimize a material for it’s possible application.
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