Electronic Properties of Organic Thin Films Studied by Kelvin Probe Force Microscopy

By

Oren Tal

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11/5/2006
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This Research Work was Carried Out at Tel Aviv University
in The Faculty Of Engineering
Under The Supervision of Prof. Yossi Rosenwaks

May 2006
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Prof. Yossi Rosenwaks
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I wish to thank Yiftach Nevo for his support, patient listening to my ideas and for his good advices.

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I am deeply grateful to my wife Shiri whose love, support, encouragement and patience (especially during weekends and nights of measurements…) made this research possible.

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Abstract

The field of disordered organic molecular films, and organic semiconductors in general is developing very fast, mainly due to applications as mechanically flexible and inexpensive electronic and opto-electronic devices; however, the physical properties of these materials are still ambiguous. This offers an excellent opportunity for exploring a field that combines basic research with important technological applications.

In this research we studied the electronic properties of metal/organic layered structures and organic thin film transistors in high lateral resolution using Kelvin probe force microscopy. This approach enabled us to explore the electronic energy structure of organic thin films as a function of metallic interfaces, impurities/intentional doping, and induced charge concentration.

We have developed new measurement methods and found several unique electronic phenomena:
(1) The potential distribution at the metal/organic/metal structures reveals abrupt potential changes at the interfaces, and additional long-range potential variations across the organic layer for different metals. The potential distribution across the organic layer strongly depends on its purification. In pure film the potential profile is flat, while in non-purified film there is substantial potential bending probably due to the presence of deep traps. The effect of the measuring tip on the measured potential was numerically calculated.
(2) A method for a threshold voltage determination in organic field effect transistors that is not limited by the sensitivity of the current detection was developed. The threshold voltage determines the formation of a conductive channel across the transistor and is a key factor in calculations of charge concentration and other transistor parameters.
(3) We have developed a method for measuring a generalized threshold voltage as a function of the gate voltage, which corresponds to molecular level shift versus the Fermi level at the gate oxide/organic film interface. A comparison between measured and calculated threshold voltage revealed a deviation from the conventional model for the density of states (DOS) available for hole transport.
(4) The detailed shape of the hole density of states was measured in high lateral resolution, in undoped and doped organic films. Although the DOS is a fundamental quantity that is
related to many electronic properties, experimental information on the specific shape of the DOS relevant to carrier transport in organic films has been very limited. In addition the influence of doping on the DOS is important for technological applications, and a better understanding of the DOS origin. We have found that the undoped film has a more complex distribution than the common assumed Gaussian or exponent DOS distribution, including an anomalous peak observed at sites located at interfaces between regions of different surface potentials. A DOS broadening and additional sharp peaks on the main DOS distribution were found in the case of doped film.

(5) Utilizing the DOS measurements on undoped and doped films, we have determined for the first time the Einstein relation (ER) at different locations across the molecular films. The theoretical predictions for deviation of the Einstein relation from its traditional form in the case of disordered molecular films were confirmed. The disorder parameter for non-equilibrium transport was calculated according to our results.
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<th>Symbol</th>
<th>Description</th>
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<tr>
<td>PPV</td>
<td>Poly(p-phenylene vinylene)</td>
</tr>
<tr>
<td>OLED</td>
<td>Organic light-emitting diode</td>
</tr>
<tr>
<td>α-NPD</td>
<td>N,N8-diphenyl-N,N8-bis(1-naphthyl)-1,18-biphenyl-4,48-diamine</td>
</tr>
<tr>
<td>Alq₃</td>
<td>Tris-(8-hydroxyquinoline) aluminum</td>
</tr>
<tr>
<td>F4-TCNQ</td>
<td>Tetrafluorotetra-cyanoquinodimethane</td>
</tr>
<tr>
<td>PPV</td>
<td>Poly(p-phenylene vinylene)</td>
</tr>
<tr>
<td>PT</td>
<td>Poly(3-hexylthiophene)</td>
</tr>
<tr>
<td>OFET</td>
<td>Organic field-effect transistors</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>UPS</td>
<td>Ultraviolet photoemission spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoemission spectroscopy</td>
</tr>
<tr>
<td>KP</td>
<td>Kelvin probe</td>
</tr>
<tr>
<td>φₘₐ</td>
<td>Metallic substrate work function</td>
</tr>
<tr>
<td>Eₘ⁺</td>
<td>Fermi level of a metal</td>
</tr>
<tr>
<td>IE</td>
<td>Ionization energy</td>
</tr>
<tr>
<td>φᵢₗ</td>
<td>Hole injection barrier</td>
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<tr>
<td>LVL</td>
<td>Local vacuum level</td>
</tr>
<tr>
<td>LB</td>
<td>Level bending</td>
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<tr>
<td>ZnPc</td>
<td>Zinc phthalocyanine</td>
</tr>
<tr>
<td>MIGS</td>
<td>Metal-induced gap states</td>
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<tr>
<td>VdW</td>
<td>Van der Waals</td>
</tr>
<tr>
<td>DOS</td>
<td>Density of states</td>
</tr>
<tr>
<td>Eᵢ, Eᵣ</td>
<td>Energy of localized donor states i and j</td>
</tr>
<tr>
<td>Rᵢⱼ</td>
<td>Distance between localized donor states i and j</td>
</tr>
<tr>
<td>X, Y</td>
<td>Lateral position</td>
</tr>
<tr>
<td>vₒᵣ</td>
<td>Attempt-to-hop frequency</td>
</tr>
<tr>
<td>γ</td>
<td>Inverse localization length</td>
</tr>
<tr>
<td>k</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
</tr>
<tr>
<td>Eᵢ</td>
<td>Intra-molecular reorganization energy</td>
</tr>
<tr>
<td>a</td>
<td>Distance between adjacent hopping sites/ Distance between a dopant and the nearest intrinsic hopping site.</td>
</tr>
<tr>
<td>F</td>
<td>Electric field/ Electric force</td>
</tr>
<tr>
<td>µ</td>
<td>Mobility</td>
</tr>
<tr>
<td>µₒᵣ</td>
<td>Mobility pre factor or mobility at the band edge</td>
</tr>
<tr>
<td>a-Si:H</td>
<td>Hydrogenated amorphous silicon</td>
</tr>
<tr>
<td>a</td>
<td>Ratio between the effective density of states at the transport band edge and the density of traps/ Disorder parameter</td>
</tr>
<tr>
<td>Eᵢ</td>
<td>Energy of the trap state</td>
</tr>
<tr>
<td>VRH</td>
<td>Variable range hopping</td>
</tr>
<tr>
<td>GDM</td>
<td>Gaussian disorder model</td>
</tr>
</tbody>
</table>
\( R \)  Localization radius (the typical site to site length)
\( \sigma \)  Gaussian DOS width (variance) or diagonal disorder parameter
\( \Sigma \)  Off diagonal disorder parameter
\( \bar{\sigma} \)  Gaussian DOS width normalized by Boltzmann constant times

the temperature
\( N_t \)  Number of states per volume unit
\( T_0 \)  Effective temperature
\( E \)  Level energy
\( \delta \)  Occupation fraction
\( E_{\text{a}} \)  Activation energy
\( \sigma_0 \)  Prefactor for the conductivity
\( B_c \)  Critical number for the onset of percolation
\( \sigma(\delta,T) \)  Conductivity
\( I_{\text{DS}} \)  Drain-source current
\( q \)  Elementary charge
\( \epsilon_{\text{sc}} \)  Relative dielectric constant of a semiconductor
\( \epsilon_0 \)  Permittivity of vacuum
\( V_{\text{SO}} \)  Switch-on threshold voltage
\( V_{\text{GS}} \)  Gate-source voltage
\( D \)  Diffusion coefficient
\( \text{TOF} \)  Time of flight
\( x \)  Location vector/ Lateral position
\( t \)  Time
\( G(x,t) \)  Charge carrier distribution function (Green function)
\( p \)  Hole concentration
\( j_{\text{diff}} \)  Diffusion current concentration
\( j_{\text{drift}} \)  Drift current concentration
\( \eta(x,t) \)  Local quasi chemical potential
\( \langle A \rangle \)  Average of A
\( \text{CTRW} \)  Continuous time random walk theory
\( \psi(t) \)  Waiting time distribution function
\( \text{KPFM} \)  Kelvin probe force microscope
\( \text{AFM} \)  Atomic force microscope
\( \text{CPD} \)  Contact potential difference
\( \phi_t \)  Tip work-function
\( \phi_s \)  Sample work-function
\( \text{AC} \)  Modulation, Alternating current
\( \omega \)  Frequency
\( z \)  Tip-sample separation/ Position perpendicular to a transistor
gate
\( U \)  Electrostatic energy
\( C \)  Tip-sample capacitance
\( V \)  Tip-sample potential difference/ Potential
\( V_{\text{AC}} \)  Alternating voltage amplitude
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>LIA</td>
<td>Lock-in amplifier</td>
</tr>
<tr>
<td>TFT</td>
<td>Thin film transistor</td>
</tr>
<tr>
<td>MOSFET</td>
<td>metal-oxide-semiconductor field effect transistor</td>
</tr>
<tr>
<td>$V_t$</td>
<td>Threshold voltage</td>
</tr>
<tr>
<td>$\varepsilon_{\text{ins}}$</td>
<td>Relative dielectric constant of an insulator</td>
</tr>
<tr>
<td>$F_{\text{ins}}$</td>
<td>Electric field in an insulator</td>
</tr>
<tr>
<td>$d_{\text{ins}}$</td>
<td>Insulator thickness</td>
</tr>
<tr>
<td>$F_{\text{sc}}$</td>
<td>Electric field in a semiconductor</td>
</tr>
<tr>
<td>$E_C$</td>
<td>Conduction band edge\Center of Gaussian density of states</td>
</tr>
<tr>
<td>$E_V$</td>
<td>Valence band edge</td>
</tr>
<tr>
<td>$n_i$</td>
<td>Intrinsic charge carrier concentration</td>
</tr>
<tr>
<td>$E_f$</td>
<td>Intrinsic Fermi-level</td>
</tr>
<tr>
<td>$n$</td>
<td>Electron concentration</td>
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<tr>
<td>$V_{\text{inv}}$</td>
<td>Inversion voltage</td>
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<tr>
<td>$V_{\text{dep}}$</td>
<td>Depletion voltage</td>
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<tr>
<td>$V_{\text{SC}}$</td>
<td>Threshold voltage associated with semiconductor</td>
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<tr>
<td>$V_{\text{bi}}$</td>
<td>Built-in potential</td>
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<tr>
<td>$V_{\text{FL}}$</td>
<td>Flat level voltage</td>
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<tr>
<td>$V_{\text{DS}}$</td>
<td>Drain-source bias</td>
</tr>
<tr>
<td>$W$</td>
<td>Transistor width</td>
</tr>
<tr>
<td>$L$</td>
<td>Transistor length (source-drain distance)</td>
</tr>
<tr>
<td>$C_{\text{ins}}$</td>
<td>Insulator capacitance</td>
</tr>
<tr>
<td>$V(x)$</td>
<td>Surface potential</td>
</tr>
<tr>
<td>$L_{\text{PO}}$</td>
<td>Pinch-off region length</td>
</tr>
<tr>
<td>$L_{\text{eff}}$</td>
<td>Effective conduction channel length</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra high vacuum</td>
</tr>
<tr>
<td>$F_z$</td>
<td>Tip-sample surface electrostatic force</td>
</tr>
<tr>
<td>$d\hat{n}$</td>
<td>Tip surface element normal to the surface</td>
</tr>
<tr>
<td>$\hat{z}$</td>
<td>Unit vector in the $z$ direction</td>
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<tr>
<td>$a_i$</td>
<td>Polynomial coefficient</td>
</tr>
<tr>
<td>$V_{\text{PO}}$</td>
<td>Pinch-off voltage</td>
</tr>
<tr>
<td>$C_{\text{OX}}$</td>
<td>Silicon oxide capacitance per unit area</td>
</tr>
<tr>
<td>$\text{CPD}_i(x)$</td>
<td>$\text{CPD}(x)$ at $V_{\text{GS}} = V_t$ and $V_{\text{DS}} = 0V$</td>
</tr>
<tr>
<td>$V_{\text{ox}}$</td>
<td>Voltage drop across the oxide layer</td>
</tr>
<tr>
<td>$f_{FD}(E)$</td>
<td>Fermi-Dirac distribution</td>
</tr>
<tr>
<td>$g_i(E)$</td>
<td>HOMO Gaussian DOS distribution relevant for holes</td>
</tr>
<tr>
<td>$N_i$</td>
<td>Total state density</td>
</tr>
<tr>
<td>$V_0$</td>
<td>Potential at the oxide/molecular film interface</td>
</tr>
<tr>
<td>$d_{\text{org}}$</td>
<td>Organic film thickness</td>
</tr>
<tr>
<td>$K$</td>
<td>Integration constant</td>
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<tr>
<td>$V_{\text{GAP}}$</td>
<td>HOMO - LUMO potential gap</td>
</tr>
<tr>
<td>$V_L$</td>
<td>Molecular energy levels shift</td>
</tr>
</tbody>
</table>
\[ N_A \] Total doping concentration
\[ \sigma_A \] Width of a Gaussian DOS for dopant (electron acceptors)
\[ E_A \] Center of a Gaussian DOS for dopant (electron acceptors) with respect to the HOMO center
\[ E_f' \] Fermi energy position at \( V_{GS} = V_t \)
\[ T_0 \] Effective temperature
\[ E_f'_{u} \] Undoped \( E_f' \) position
\[ E_f'_{b} \] \( E_f' \) position for undoped DOS populated with dopant induced holes
\[ p_{doping} \] Dopant induced hole concentration
\[ E_f'_{c} \] Doped \( E_f' \) position
\[ E_f^q \] Quasi Fermi level
\[ \text{ER} \] Einstein relation
\[ I_{DS\_Bulk} \] Drain source bulk current
\[ W_{dep} \] Depletion width
\[ V_{PO}^{dep} \] Pinch-off voltage at total depletion
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Figure 1. Schematic structure of some commonly used conjugated small molecules and polymers. Hydrogen atoms are not shown; single and double lines represent single and double bonds respectively where the carbon nuclei located at each line edge unless it is marked with other element. (a) α-NPD, N,N8-diphenyl-N,N8-bis(1-naphthyl)-1,18-biphenyl-4,48-diamine (b) Alq₃, tris-(8-hydroxyquinoline) aluminum (c) F₄-TCNQ, tetrafluorotetra-cyanoquinodimethane (d) PPV, poly(p-phenylene vinylene) (e) PT, polythiophene

Figure 2. (a) Bonding in conducting conjugated polymers. The sp² hybrid orbitals are shown in grey, and the unhybridized pₓ orbitals in white. Electrons are represented by black dots. The two thin sp² hybrid orbitals on the side extend in and out of the plane of the paper. (b) The delocalized cloud of π-electrons. The electronic probability density is represented by grey ovals above and below the molecule plane (hydrogen atoms are not presented)

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**Figure 32:** Top: Qualitative scheme of the hole occupation of a Gaussian DOS at different positions with respect to $\mu$. Bottom: OTFT cartoons in which the relevant charge concentration is represented in green. (a) $V_{GS} = V_t$, i.e., zero gate induced hole concentration (b) $V_{GS} < V_t$ thus holes accumulate to form a conducting channel (c) $V_{GS} > V_{GS}$ such that the hole concentration is twice larger then in (b).

**Figure 33:** Qualitative energy level scheme across the OFET far from the source and drain contacts for: $V_{GS} = V_t$, $V_{DS} = 0V$ (black curves) and $V_{GS} > V_t$, $V_{DS} = 0V$ (red curves) in the case of (a) negligible level bending and (b) level bending.

**Figure 34:** Calculated potential distribution for different $V_{GS}$ at the OFET organic film perpendicular to the gate insulator for (a) undoped and (b) doped film with doping concentration of 0.1% from the total molecule density. At $V_{GS} = 3.1V$ and $V_{GS} = 15.0V$, for undoped and doped films respectively, the level bending voltage (the difference between the voltage values at $z = 0nm$, and $z = 10nm$) is 5% of the total level shift (dashed curve).

**Figure 35:** Calculated charge concentration for different $V_{GS}$ in OFET organic film perpendicular to the gate insulator for (a) undoped and (b) doped film. At $V_{GS} = 2.8V$ and $V_{GS} = 14.6V$, for undoped and doped films respectively, the charge concentration (the difference between the charge concentration values at $z = 0nm$, and $z = 10nm$) is 5% of the total level shift (dashed curves).

**Figure 36:** Calculated channel width of 90% charge concentration as a function of $V_{GS}$ for (a) undoped and (b) doped organic film with Gaussian DOS. The doping was taken to be 0.1% from the total molecule density.

**Figure 37 (a) Inset:** $V_L$ profiles measured across an undoped transistor for $V_{GS} = 0V$ and $V_{GS}$ ranging from 0 to -16.5V. (a) $V_L$ as a function of $V_{GS} - V_t$ measured on undoped (A) and doped (B) samples. (b) DOS vs. energy relative to $E_f$ ($E_f$ at $V_{GS} = V_t$) for undoped (solid triangles) and doped (solid circles) samples. The solid curves are fitting of a Gaussian function (Eq. 5.4; curve A) and an exponential
function (Eq. 1.6; curve C) to given ranges in the undoped sample DOS curve, and a fitting of Eq. 5.5 (curve B) to the doped sample DOS curve.\footnote{76}

**Figure 38:** The calculated Coulomb effect of dopants on an exponential shaped DOS. Taken from Ref. [133].\footnote{78}

**(a) Inset:** \(V_L\) profile measured across the channel of an undoped transistor.\footnote{80}

**Figure 39:** (a) DOS distributions measured at different lateral locations across the channel marked as \(a\) to \(f\) in the inset. (b) DOS distributions measured at different lateral locations across the channel of doped transistor. Each DOS curve is an average of three curves that were measured at the same location.\footnote{81}

**Figure 40:** schematic representation of the chemical potential and the position of the DOS edge for three cases: (a) undoped sample; where ‘0eV’ denotes \(\mu\) position at the beginning of the DOS measurement at \(V_{GS} = V_L\) (b) hypothetic case of the undoped DOS populated by the dopant induced holes (represented as reddish area) (c) doped sample.\footnote{86}

**Figure 41:** (a) ER vs. hole concentration for the undoped organic film. The curve is divided into three regions: region A for \(p < 1.01 \cdot 10^{17} \text{cm}^{-3}\), region B: for \(1.01 \cdot 10^{17} \leq p \leq 1.85 \cdot 10^{17} \text{cm}^{-3}\), and region C for \(p > 1.85 \cdot 10^{17} \text{cm}^{-3}\).\footnote{87}

**Figure 42:** (a) ER, (b) DOS, and (c) hole concentration vs. energy (relative to \(\mu_{CP}\)) for the undoped sample. The curve is divided into the same three regions as in fig. 8.3.1/1 while here: at region A \(0 > E > -0.377 \text{eV}\), at region B: for \(-0.377 \geq E \geq -0.430 \text{eV}\), and at region C for \(E < -0.430 \text{eV}\).\footnote{88}

**Figure 43:** Inset: \(V_L\) profile measured across the channel of an undoped transistor (a) ER measured at different lateral locations across the channel marked as \(a\) to \(f\) in the inset.\footnote{89}

**Figure 44:** (a) ER vs. hole concentration for doped \(\alpha\)-NPD sample (0.1% F4-TCNQ). The curve is divided into two regions: region A for \(p \leq 2.1(\pm 0.4) \cdot 10^{18} \text{cm}^{-3}\), and region C for \(p > 2.1(\pm 0.4) \cdot 10^{18} \text{cm}^{-3}\).\footnote{90}

**Figure 45:** (a) ER, (b) DOS, and (c) hole concentration vs. energy relative to \(\mu\) for \(V_{GS} = V_L\) for the doped sample. The curve is divided into the same two regions as in Fig. 44 while here: at region A \(0 > E > -0.33 \text{eV}\), at region B: for \(\leq E \leq -0.33 \text{eV}\), and at region C for \(E < eV\).\footnote{91}
Figure 46: Measured DOS for undoped sample as a function of energy, where zero denotes the $\mu'_{cP}$ location as appeared in Fig. 37 (b). The red and the blue curves are exponential fittings to the measured DOS at $-0.377 \leq E \leq 0$eV and $-0.490 \leq E \leq 0.430$eV respectively.

Figure 47: OFET transfer characteristics as a function of time in 10mbar air in dark. Taken from Ref. [98].
List of publications


In preparation:

Scope and outline of this thesis

Since the discovery of high conductance in doped polymers three decades ago, the field of semiconducting organic molecular films is developing very fast, driven by the enormous potential demonstrated by these materials for applications in optoelectronics and inexpensive electronics such as light emitting diodes, field effect transistors and photovoltaic cells. Although material technology advanced significantly at the last two decades, a fundamental understanding of the basic electronic and optical processes in these materials is still rather poor, and extensive research is necessary.

This research is focused on one of the basic properties of the amorphous semiconductors, which is the position of the electronic energy levels as a function of charge concentration and the density of states that defines this dependence. The levels position across an electronic device determine the performance of the device, while the density of states is a key factor that affects the behavior of many electronic properties such as the carrier mobility, Einstein relation, Debye length, and device quantities such as diode ideality factor and a threshold voltage of a transistor. Thus a fundamental understanding of the relation between energy level position, charge concentration, and the density of states is of great importance due to both scientific and technological consideration.

The study of energy level position across organic films, and the study of charge transport dependence on the density of states are both spanned along the last three decades, however there is very limited information on the level position across complete organic devices and the actual shape of the density of states is practically unknown. The unique combination of Kelvin probe force microscopy measurements and the use of different organic based structures/operational devices allowed us to measure the potential profile across organic films in lateral resolution of tens nanometers and induced local potential and charge concentration changes by different metal interfaces, impurities, intentional doping, or applied voltage.

The first chapter presents a brief introduction to the electronic structure of organic molecules, then the experimental research and the common models of the energy level structure of different metal/organic interfaces are reviewed. Finally we
introduce the concept of carrier localization and energetic disorder and review the main different models for transport in disordered organic films including the time dependent dispersive charge transport.

In chapter 2 we describe our experimental tools: The Kelvin probe force microscopy technique and the organic field effect transistor. The basic equations that describe the formation of the potential image are presented, and our Kelvin probe force microscope setup is introduced. Then the structure and operation of the organic field effect transistor are presented including the energy level structure and the current-voltage characteristics.

In chapter 3 we report on the study of potential distribution across metal-organic film layered structures. The influence of the different metals, and the purity of the organic film on the total potential structure are studied. Also the Kelvin probe force microscope lateral resolution is examined by numeric simulation.

Chapter 4 presents two different methods for the determination of the threshold voltage, which is the transistor gate voltage at the conduction channel opening. The first method allows accurate determination of the threshold voltage by direct detection of the gate electrode screening by charge. The second method detects directly the formation of the pinch-off point in which there is no charge in the channel. This enables the extraction of a generalized threshold voltage as a function of different gate voltage, which gives the molecular level shift at the gate oxide/organic film interface. The results are compared to a calculated threshold voltage based on different distributions of density of states.

In chapter 5 we describe a new method for measuring the detailed shape of the density of states in high lateral resolution by detecting the molecular level shift as a function of charge concentration. The method was applied to undoped and doped organic film in order to study the fine shape of the density of states, its lateral homogeneity, and the influence of charged dopants on the density of states. The doping influence on the Fermi level position is measured as well.

In chapter 6 the Einstein relation (i.e., the relation between the charge diffusion coefficient and the charge mobility) is calculated as a function of gate voltage and energy based on the measurements described in chapter 5. The Einstein relation behavior is described in relation to the density of states distribution and charge concentration; the findings are examined and discussed in view of a non-equilibrium transport model.
The thesis is summarized in chapter 7, and suggestions for further study are discussed.
Chapter 1: Background-organic films as amorphous semiconductors

1.1 Organic semiconductors

Electrical conduction in organic materials has been reported for the first time in the 1950’s and early 1960’s, when photoconductivity and electroluminescence were detected in crystals of organic molecules, such as naphthalene and anthracene [1–4]. Although the crystals showed high charge carrier mobility, their production and processing were very poor with little potential for applications. Latter in the 1960’s polymers doped by small organic molecules dispersed in an insulating polymer matrix were developed [5]. They possessed the semiconducting properties of small organic molecules and the mechanical properties of polymers. A breakthrough in the field of organic semiconductors was made in 1977, when the first highly conductive polymer, chemically doped polyacetylene, was reported [6]. In the 1980’s electroluminescence was reported from double layer vacuum-sublimed molecular thin film devices [7], and from conjugated polymers such as poly(p-phenylene vinylene) (PPV) [8]. Since then, a new perspective has been opened on the applicability of organic molecules into electronic devices.

![Figure 1: schematic structure of some commonly used conjugated small molecules and polymers. Hydrogen atoms are not shown; single and double lines represent single and double bonds respectively where the carbon nuclei located at each line edge unless it is marked with other element. (a) α-NPD, N,N8-diphenyl-N,N8-bis(1-naphthyl)-1,18-biphenyl-4,48-diamine (b) Alq3, tris-(8-hydroxyquinoline) aluminum (c) F4-TCNQ, tetrafluorotetra-cyanoquinodimethane (d) PPV, poly(p- phenylene vinylene) (e) PT, polythiophene.](image-url)
Beside the study of organic light-emitting diodes (OLEDs), several other research fields based on organic semiconductors have been developed in the past decade, such as organic field-effect transistors (OFETs) [9–11] and organic photovoltaics [12–14]. The organic films used in these applications are deposited either from solution using spin coating, film casting or printing techniques, or by sublimation in vacuum. These techniques can provide large-area, flexible, lightweight displays and integrated circuits. Evaporation of small molecules in vacuum enables the preparation of very clean and reproducible devices suitable for basic research while the other techniques enable low cost production, and therefore interesting for the electronic industry, mainly due to the ease of processing. But in order to be competitive, organic displays must provide comparable device performance with the already existing inorganic ones. Some commercial displays based on OLED have already become available by Philips and other companies.

Organic semiconductors are molecular films made of \( \pi \)-conjugated organic (Fig. 1 (a),(c)-(e)) or organo-metallic (Fig. 1(a)) molecules, either small molecules such as dye molecules (Fig. 1 (a)-(c)) or macromolecules like polymers (Fig. 1 (d),(e)). \( \pi \)-conjugated molecules contain alternating single and double bonds (usually carbon-carbon bonds). Single bonds are referred to as \( \sigma \) - bonds and are associated with a highly localized electron density in the plane of the molecule, and double bonds contain a \( \sigma \) -bond and a \( \pi \) -bond, where the \( \pi \) -bond is formed by an overlap.

**Figure 2:** (a) Bonding in conducting conjugated polymers. The \( sp^2 \) hybrid orbitals are shown in grey, and the unhybridized \( p_z \) orbitals in white. Electrons are represented by black dots. The two thin \( sp^2 \) hybrid orbitals on the side extend in and out of the plane of the paper. (b) The delocalized cloud of \( \pi \)-electrons. The electronic probability density is represented by grey ovals above and below the molecule plane (hydrogen atoms are not presented).
between p\textsubscript{z} orbitals of neighboring atoms along the conjugation path as demonstrated in Fig. 2 (a). The conjugation of single and double bonds establishes a delocalization of the electrons situated above and below the plane of the molecule as schematically presented in Fig. 2 (b). The conjugation between the p-orbitals forms molecular π-orbitals that are energetically split in the simple case into two low and high energetic levels: π-bonding orbital, and π\textsuperscript{*} anti-bonding orbital, respectively. The π-orbital is occupied, and the π\textsuperscript{*}-orbital is unoccupied with electrons. The highest electron-populated π-orbital is called the highest occupied molecular orbital (HOMO), and the lowest unpopulated π\textsuperscript{*}-orbital is called the lowest unoccupied molecular orbital (LUMO). The HOMO and the LUMO levels act in a similar way (although not identical) to the “valence-band”, and the “conductance-band” of inorganic semiconductors respectively and a typical HOMO-LUMO separation is in the range of 2–4eV. Consequently the intrinsic concentrations of electrons and holes are negligible in room temperature.

1.2 Energy levels alignment at metal\textbackslash organic interfaces

The interfaces between organic molecular films and metals have been extensively studied in order to reveal their electronic structure by techniques such as ultraviolet photoemission spectroscopy (UPS) \cite{15,16}, x-ray photoemission spectroscopy (XPS) \cite{17} and Kelvin probe (KP) \cite{18}. These measurements are typically done as a function of the organic layer thickness, and are effective for determination of the energy band structure and band offsets at the metal/organic interfaces.

UPS provides the relevant following quantities as described in Fig. 3: (1) Metallic substrate work function (\(\phi_m\)), i.e. the energy difference between the metal Fermi level (\(E_f^m\)) and the vacuum level, (2) Ionization energy of the deposited organic layers (\(IE\)), that is the difference between the highest occupied molecular orbital (HOMO) and the vacuum level, (3) Lowest unoccupied molecular orbital (LUMO) energy vs. to the metal Fermi energy (i.e., hole injection barrier \(\phi^h\)). (4) Organic layer vacuum level energy relative to the metal Fermi level. Using XPS, one can measure the energies of the core levels just as in the case of valence levels in UPS and these
energies should reflect the energy level alignment and position. In addition, XPS can detect chemical adsorption that induces core level shifts. The KP method is useful for the determination of the organic layers work function (vacuum level relative to the metal Fermi energy). Unlike UPS and XPS, which are limited to a molecular layer thickness up to 10-100nm due to the problem of charging, KP method enables examination of thicker layers.

It is worthwhile to elaborate more about the measured ‘vacuum level’. When an isolated electron is at rest in vacuum, it is said to be at the energy of the vacuum level. The vacuum level for an electron at rest at an infinite distance from the system is often taken as an invariant energy reference; we will call this vacuum level, vacuum level at infinite distance. The measured work function and $IE$ corresponds to the energy of an electron at rest just outside the solid, and it is still affected by the potential of the solid [19]. We will determine this as local vacuum level (LVL) as also showed in Fig. 3; thus the experimentally measured vacuum level is not that for an electron at infinite distance, and it cannot be used as an invariant reference level.

Measurements of metal/organic interfaces as a function of the organic layer thickness using UPS, XPS and KP report on abrupt shift of the LVL at the metal/organic interface along molecular layer thickness of about 2nm, which correspond, to a few molecular monolayers. In many cases this LVL offset is followed by almost no LVL change. A consensus on the analysis of this offset has yet to be reached. Several groups have identified this behavior along scales of ~10nm using UPS and XPS [15, 16, 21-23] or on length scales of ~100nm using KP [18]. These studies all identify the local vacuum level shift at the metal/organic interface as a strong polarization in the first molecular layer, which they interpret as an interface dipole. Others, however, have proposed that most of the shifts observed at low

![Figure 3: energy diagram of metal/organic film interface.](image-url)
coverage (≤5nm) are in fact due to level bending [24-27]. Schlaf et al. [27] have argued that the level-bending shift can be deduced from the shifts of the XPS atomic core levels, in the absence of strong chemical interactions at the interface, and that the true interface dipole shift is equal to the vacuum level shift minus the level-bending contribution.

In order to avoid ambiguity we define level bending (LB) as an electrostatic effect, where the potential energy of electrons is a function of position within the material. Moreover LB (and in the general case, band bending) usually refers to the situation where the mathematical form describing the energy levels as a function of position within the solid exhibits curvature. This functional dependence implies a net charge density present in the material, resulting in a nonzero second derivative of the electrostatic potential [28].

The dipole moment interpretation for the LVL abrupt shift is justified by the small film thickness over which the shift is observed (1-2nm), the extremely low intrinsic carrier density and the corresponding large screening length. Thus, one should expect level bending to be negligible across 1-2nm organic layer thicknesses [29]. On the other hand, the LB picture might fit in the following cases: when the HOMO and LUMO density of states penetrate considerably to the band gap, when the Fermi energy is shifted towards a band edge near an interface by a pinning mechanism [29] and in the case of high doping concentration.

Prior to our work long range LB was observed solely on C\textsubscript{60}metal systems. A LB of 0.33eV height near the metal (Cu) surface and a ~500nm width was reported for unpurified C\textsubscript{60} layer. The LB height was reduced to 0.13eV in purified C\textsubscript{60} based sample, which may indicate on unintentional doping that was partially removed [30]. Few works on p-type [31,32] and n-type [33] doped systems in the framework of improving carrier injection through metal/organic interfaces and lowering device drive voltage were conducted. UPS and XPS measurements on metal/organic (p-doped) systems [31,32,34] reveal, in addition to the interface LVL offset, a LB along a few nm layer-width (up to 12.8nm in the case of 0.3% F\textsubscript{4}-TCNQ doping of ZnPc\textsuperscript{**} /Au, see Fig. 4 [34]). The additional observed interface LVL offset and the organic IE were not changed upon doping; however the organic Fermi level was shifted with respect to the HOMO/LUMO energies.

\*zinc phthalocyanine (ZnPc)
When LB is measured by XPS, UPS or KP as a function of the layer thickness, the measured structure width is changing and the potential is measured on the outer organic surface; thus the measured system is different at every stage. The measured potential in a specific distance from the metal cannot represent the potential in the same distance from the metal in the case of thick organic layer. Thus the LB profile obtained by the above methods differs from the 'real' LB along thick organic layer [20]. The difference originates from reduced LB, which takes place when the organic film thickness is less than the whole width of the LB that would exist if the organic film were very thick [35].

The LVL shifts at metal/organic interfaces cannot be explained solely in terms of electron transfer between the metal and the molecules. For example, LVL shifts were observed for tetratetracontanes with a wide HOMO-LUMO gap, where electron transfer is not probable [36]. As a second factor, which may explain such cases, we can mention the image effect or the modification of the surface dipole at metal surface. The results of another good insulator, Xe, on metals also show downward LVL shift [37], and it is ascribed to the polarization of the electron cloud attracted by the image charge formed in the metal [38]. This leads to electron deficiency at the vacuum side of the molecular layer, leading to a lowering of the LVL. There is an alternative explanation for the case of Xe adsorption, the change of the work function is not due to the image effect, but due to the rearrangement of the electron cloud at the

**Figure 4:** Energy of molecular levels near the interface between Au and (a) undoped ZnPc; (b) ZnPc:0.3% F$_4$-TCNQ. The measured width of the depletion region is shown in (b). Interface LVL (here $E_{\text{vac}}$) shift, work function of Au and ZnPc and ionization energy are indicated in each case. Taken from Ref. [34].
metal surface [39]. The tailing part of the metal electronic cloud into vacuum is pushed back by repulsion with the electron cloud of the molecules, resulting in an effectively positive charging of the vacuum side by adsorption compared with the bare surface. This mechanism also leads to the lowering of the LVL. These two mechanisms may also apply to the tetratetracontane/metal systems. When the charge-transfer mechanism operates, this will work in a concerted manner with these mechanisms.

The third factor is other types of chemical interaction than charge transfer between the organic and metal layers. Various interactions lead to the rearrangement of the chemical bonds, or to the formation of new bonds. Such chemical interaction is well-known for small molecules like CO and benzene on clean metal surfaces [40], and even for Alq₃. In the case of such chemical interaction, the direction of the dipole depends on the case.

The fourth factor is the possible existence of interfacial state. Such interface state is well-known in inorganic semiconductors, and ascribed to various intrinsic and extrinsic origins such as the metal-induced gap states (MIGS) formed by the penetration of metal wavefunctions into semiconductor layer [41, 42], although the origin in the case of organic/metal contact may be much different. Finally we should mention that for polar organic molecules, the orientation of the dipole moment could lead to a large interfacial dipole.

1.3 Charge transport in disordered organic films

In this section we summarize the major theoretical approaches used to explain the charge transport in disordered organic semiconductors. The structure of crystalline inorganic semiconductors can be described in terms of a lattice characterized by long-range order and strongly coupled atoms [43]. These properties results in the formation of long-range delocalized energy bands separated by a forbidden energy gap [44]. Charge carriers move in these energy bands with a relatively large mean free path, and for pure crystalline inorganic semiconductors such as silicon or germanium, the carrier mobility is in the order of $10^4 \text{cm}^2/\text{Vs}$. Local disorder in inorganic semiconductors introduces scattering centers and energy states in the forbidden gap (both deep and shallow levels), as, for example, in the case of amorphous silicon. In
this case a strong interaction with the scattering centers and a large number of scattering centers results in a decrease of the mean free path, and the carrier mobility is in the order of $10^{-2} \text{cm}^2/\text{Vs}$. In organic crystals, such as pentacene, the molecules are held together by weak Van der Waals (VdW) forces in a long range order. This weak coupling results in a narrow width for the valence and conduction bands and the band structure can be easily disrupted by introducing disorder in the system. Although organic molecular crystals still exhibit band conduction, excitations and polarons localized on individual molecules or small molecular clusters play a dominant role. Their mobility, in the order of $10^1 \text{cm}^2/\text{Vs}$, is significantly lower than those of their inorganic counterpart.

By contrast, disordered organic semiconductors have neither well-ordered structural configuration as crystals nor small intersite separation due to covalent bonds as in inorganic semiconductors. The electronic conjugation between molecules is depressed by the relatively large separation and structural mismatch and energetic disorder is dominant. The charge carrier mobility in these materials was found to be in the range of $10^{-8} - 10^{-6} \text{cm}^2/\text{Vs}$ for OLEDs and $10^{-4} - 10^{-1} \text{cm}^2/\text{Vs}$ for OFETs, which is a few orders of magnitude lower than the mobility determined for organic crystals.

Over the past decades intense research has been carried out in order to explain the transport of charge carriers in disordered organic semiconductors, which would justify such low mobility and its dependence on charge concentration and electric field. There are several transport models showing good agreement with electrical measurements for some particular systems, but no comprehensive picture is currently available due to the diversity and complexity of these systems. The most common transport models are presented below.

1.3.1 The role of charge carrier localization and lateral energetic disorder

**Hopping between localized energy states**

In this research we focus on disordered organic molecular films, in this case there is no long range periodic structure and the electronic molecular wave functions are considered to be localized on single molecules* or a few inter-conjugated

* In the case of polymers charge carriers can be confined on a chain fragment, for example, between two structural chain twists that “break” the internal $\pi$-coupling.
molecules, and there are no continuous conduction and valance bands. As a result the description of charge transport processes in terms of standard semiconductor models is inadequate. In order to have charge transport, the charge carriers must hop between localized states that have different energies, and the carriers need to absorb or emit phonons in order to overcome the potential boundaries between the states. This process of phonon-induced hopping was originally suggested by Conwell [44] and Mott [45] in connection with conduction in inorganic semiconductors, and later by Pines, Abrahams and Anderson [46] for electron relaxation processes in silicon. Mott discussed the hopping transport in a density of states (DOS), in which he argued that the hopping over long distances and hopping to high energies are equally important. Later, Miller and Abrahams proposed a hopping model based on a single-phonon jump rate description [47]. Their treatment was made for a lightly doped semiconductor at a very low temperature. The localized states are considered to be shallow impurity levels, and the energy spread of these levels is narrow so the probability for an electron on one site to find a phonon to jump to the nearest site is high. The hopping rate of carriers from occupied $i$ to unoccupied $j$ localized donor states depends on the height of the energetic barrier $E_j - E_i$ and the distance $R_{ij}$ between the states $i$ and $j$ (Miller-Abrahams’ equation):

\[
\begin{align*}
    v_{i\rightarrow j} &= v_0 \exp(-2\gamma R_{ij}) \begin{cases} \\
        \exp\left(-\frac{E_j - E_i}{kT}\right) & \text{for } E_j \geq E_i \\
        1 & \text{for } E_j < E_i 
    \end{cases}
\end{align*}
\]

where the pre-factor $v_0$ is the attempt-to-hop frequency, $\gamma$ is the inverse localization length, $k$ is the Boltzmann constant, and $T$ is the temperature. The first exponential

![Figure 5](image-url)

**Figure 5:** schematic illustration of (a) positional disorder of localized electronic sites (b) energetic disorder of localized electronic levels, and (c) electronic density of states of 2-dimentional disordered organic semiconductor. Occupied electronic states are marked with red, and X,Y denote lateral position.
term in Eq. 1.1 represents the tunneling probability and the second exponential term accounts for the temperature dependence of the phonon density. When this model is applied to organic semiconductors, the following assumptions are made: the energetic states are nearly isolated, and Eq. 1.1 is still valid at high temperatures [47].

**Lateral energetic disorder**

In the case of disordered organic films, each molecule has a different spacing and orientation with respect to its neighbors, therefore each molecule has a slightly different potential energy, and the molecular levels have lateral energetic disorder (Fig. 5) that dominates the electronic transport properties of these films. The energetic disorder of the molecular levels is expressed in the density of states that is usually modeled as a Gaussian or exponential states distribution, and the charge transport is modeled by charge carrier hopping between the localized energetic sites where the DOS distribution gives the probability density for a state to be in a certain energy. As will be demonstrated below the shape of the DOS affects considerably the charge transport behavior.

**1.3.2 Charge transport models**

**The polaron model**

The polaron model was first developed for inorganic crystals [48], and has later been used to explain the charge transport in molecular crystals [49] and disordered organic semiconductors [50]. This transport model takes into account a strong electron-phonon interaction. A polaron is basically a quasiparticle, which results from the combination of a charge carrier and a geometrical deformation induced by its charge. In disordered organic semiconductors it is common to assume that additional charge on a molecule, results in a molecule deformation due to an atomic rearrangement that follows the electronic redistribution within the molecule, since in most cases charge transfer from the molecule is slower than the atomic nuclei relaxation process. Consequently the charge carriers are considered to be polarons.

The transition rate for polarons as determined by Marcus is given by [51]:

\[
\tau = \frac{1}{\hbar} \left( \frac{\pi}{\hbar} \right)^{1/2} \left( \frac{\alpha}{\pi} \right)^{1/2} \exp \left( \frac{-\Delta E}{kT} \right)
\]
where $E_r$ is the intra-molecular reorganization energy. The charges moving by thermally activated hops between adjacent sites have mobility, which is electric field ($F$) and temperature dependent \[51, 52\]:

\begin{equation}
\mu = \mu_0 \exp \left[ -\frac{E_r}{4kT} - \frac{(aF)^2}{4E_r kT} \sinh \left( \frac{aF}{2kT} \right) \right]
\tag{1.3}
\end{equation}

where $a$ is the distance between adjacent hopping sites, and $\mu_0$ is slightly temperature dependent. Using Marcus theory the polaron contribution to the activation of the mobility is relatively small. The activation of the mobility using this model is around 25-75 meV \[53\], while using disorder based model the activation energy can be 420 meV \[54\].

The multiple trapping and release model

In the multiple trapping and release model a narrow band is associated with a high concentration of trap levels. The traps are localized at lattice defects or impurities in which the charge carriers are immobilized. These traps can be deep traps located near the center of the band gap, or shallow traps located close to the conduction or valence band. The model was developed by Le Comber and Spear \[55\] for hydrogenated amorphous silicon (a-Si:H), and it was used by Horowitz et al. \[56\] to explain the transport in sexithiophene based OFETs. This model assumes an exponential distribution of gap states. The charges in the organic semiconductor are trapped into localized states with a probability close to one and then released through a thermally activated process to the band where they are mobile until they are trapped again. The carrier mobility is given by:

\begin{equation}
\mu = \mu_0 \alpha \exp \left( -\frac{E_t}{kT} \right)
\tag{1.4}
\end{equation}

where $\mu_0$ is the mobility at the band edge, $\alpha$ is the ratio between the effective density of states at the transport band edge and the density of traps, and $E_t$ is the energy of the trap state. It has been demonstrated that the transport of carriers depends on the energy level of the trap states, the temperature and the voltage applied \[15\]. For further reading see Ref. \[57\] and \[58\].
The variable range hopping model

The variable range hopping (VRH) model describes the hopping transport between localized sites where in contrast to the above model all the sites are localized and there is no mobility edge that is followed by delocalized states band as in the above mentioned model. This model suggests that charge carriers may either hop over a small distance with a high activation energy or hop over a long distance with low activation energy. The main assumptions of the model are the following:

(1) The charge carrier hops between localized states, randomly distributed in space, and energetically distributed according to a DOS function. In most of the calculations the DOS is assumed to be Gaussian (as promoted by Bassler, e.g. Ref. [54]). The choice for this particular DOS shape is supported by the observation that the absorption spectra of disordered organic materials usually have Gaussian profiles [59] (although it relates to an exitonic DOS and not a polaronic DOS. The later is more relevant to charge transport processes) and by the fact that coupling between a charge carrier and a random distribution of static or induced dipoles leads to a Gaussian DOS function [60]. This assumption is known as the Gaussian disorder model (GDM).

(2) There is no phase memory between hops, and therefore "continuum band" like transport in excluded. This condition stems from the long distance/high potential boundaried between sites that dictates a slow transfer rate where compared to the inverse phase coherence (dephasing) time.

Figure 6: The effect of energy correlation. The mobility versus the square root of the electric field, as calculated by a Monte Carlo simulation, with (filled circles) and without (open circles) correlation between sites energy. Taken from Ref. [66].
(3) The hopping rate between sites is the Miller-Abrahams’ rate (see Eq. 1.1).

(4) Energies of adjacent sites are uncorrelated. This assumption was removed by Novikov [61] and later by Gartstein-Conwell [62]. The effect of energy correlation between the different sites will be discussed below.

The model described above has been solved in many different variants for charge diluted systems: e.g. analytically for 1-Dimensional wires [63], by Monte Carlo simulations for 3-Dimensional ensembles of states with or without energy correlation [54, 64], and dynamical evolution of charge carriers with time (as described below). It has been found that without energy correlation this model gives a sharp increase in the mobility in a typical electric field \( E \equiv kT / R \) (where \( R \) can be \( \gamma^{-1} \) - the localization radius or the typical site to site length), and that the Poole-Frenkel like behavior: \( \mu \propto \exp(-\alpha(T)E^{1/2}) \) observed experimentally cannot be explained [61-63, 65] for electric fields lower then \( 10^6 \) V/cm (Fig. 6). The results of the energy correlation model were described in terms of the Gaussian DOS width \( \sigma \), which is described as diagonal disorder in the state energy matrix, and off diagonal disorder \( \Sigma \), which is the degree of positional disorder. The result of the Monte Carlo simulation is the following principle equations:

\[
\begin{align*}
\mu &= \mu_0 \exp\left(-2\bar{\sigma}/3\right) \exp\left[C \left(\bar{\sigma}^2 - \sum^2\right)E^{1/2}\right] \quad \text{for } \Sigma > 1.5 \\
\mu &= \mu_0 \exp\left(-2\bar{\sigma}/3\right) \exp\left[C \left(\bar{\sigma}^2 - 2.25\right)E^{1/2}\right] \quad \text{for } \Sigma < 1.5
\end{align*}
\]

where \( C = 3 \times 10^{-4} \text{ cm}^{1/2} \text{ V}^{-1/2} \) and \( \bar{\sigma} = \sigma / kT \). This equation is often used in order to estimate the DOS shape from transport related characteristics. The origin of the diagonal disorder is still under debate. Suggested explanations for energy correlation that dictate the DOS shape and thus \( \sigma \), include charge-dipole interaction [63] (which may be reasonable only at low charge concentrations), charge-phonon interaction [67], and even fluctuation of the local micro-morphology, namely the charge states size and therefore energy may explain the energy correlation.

The variable range hopping was also used by Vissenberg and Matters in order to explain the charge transport in polymer FETs [68]. Their transport model takes into account the filling of localized states with charge carriers in contrast to former one particle models. The model predicts that at low carrier densities and low temperatures,
the transport properties are determined by the tail states of Gaussian DOS, which is approximated by an exponential DOS [68]:

\[ g(E) = \frac{N_j}{kT_0} \exp \left( -\frac{E}{kT_0} \right) \]

where \( N_j \) is the number of states per volume unit, \( T_0 \) is the effective temperature that defines the slope of the exponential DOS, and \( E \) is the energy level. It is considered that the energy distribution of the carriers at equilibrium is given by the Fermi-Dirac distribution. If the system is filled with a charge carrier density, \( \delta N_j \), which occupies a small fraction of the localized states (\( 0 \leq \delta \leq 1 \)), the position of the Fermi level is determined by the condition:

\[ \delta = \exp\left( E_f / kT_0 \right) \Gamma(1 - T / T_0) \Gamma(1 + T / T_0) \]

for \( E_f << kT_0 \), meaning that most carriers occupy the sites with energy \( E << 0 \), and

\[ \Gamma(a) = \int_0^\infty \exp(-x)x^{a-1}dx \].

This condition is fulfilled when \( \delta \) is low and \( T < T_0 \). For temperatures \( T \geq T_0 \) the function \( \Gamma(1 - T / T_0) \) diverges and the assumption that only the tail of the DOS is important is no longer valid. Using the percolation theory [69], an expression for the conductivity can be derived as a function of the occupation fraction \( \delta \) and the temperature \( T \) [68]:

\[ \sigma(\delta, T) = \sigma_0 \left( 2\pi \right)^{3/2} \frac{\pi N_j \delta(T_0 / T)^3}{B_c \Gamma(1 - T / T_0) \Gamma(1 + T / T_0)} \right)^{T_0 / T} \]

where \( \sigma_0 \) is a prefactor for the conductivity, and \( B_c \) is the critical number for the onset of percolation. For 3-dimensional amorphous systems \( B_c \approx 2.8 \) [70]. The conductivity expressed by Eq. 1.8 has an Arrhenius-like temperature dependence \( \sigma \propto \exp(-E_a/kT) \), explained by the fact that in an exponential DOS the hopping can be described in terms of activation from the Fermi level to a specific transport level, where \( E_a \) is the activation energy [71]. Moreover, the conductivity increases superlinearly with the charge carrier density \( \sigma \propto \delta^{T_0 / T} \). This is due to the fact that by increasing the carrier density deep states are filled and an activated jump to an unoccupied state at the transport energy is facilitated.

Using the described model, the following expression was determined for the Drain-source field-effect current [68]:
where $q$ is the elementary charge, $\varepsilon_{SC}$ is the relative dielectric constant of the semiconductor, $\varepsilon_0$ is the permittivity of vacuum, $V_{SO}$ is the switch-on threshold voltage of the transistor and $V_{GS}$ is the gate-source voltage. In this case $V_{GS}$ becomes $V_{GS} - V_{SO}$. Eq. 1.9 has been used to model the transfer characteristics of polythiophene derivative based OFETs with good agreement between the experimental data and the model described here (Fig. 7) [72].

The models mentioned above were performed for long enough time scales, where the charge carriers relaxed by enough inter-states hops to a near equilibrium distribution [54], or similar distribution with slightly higher effective temperature [73] (as demonstrated for exponential DOS). For this reason, the transport could be described in term of the mobility $\mu$ and diffusion coefficient $D$. Moreover, these calculations were done for charge diluted material, therefore $D/\mu$ ratio exhibit its classical value of $kT/q$, after the system has relaxed to a steady state (e.g. see Ref. [58] page 988). In the next section we summarize the evolution of the charge convection in $\alpha$ scales, before complete energy relaxatio
1.3.3 Time dependent charge transport

Dispersive vs. non-dispersive transport

The dynamic behavior of the charge transport in charge diluted amorphous organic semiconductors was experimentally explored mainly by the time of flight (TOF) experiment. In TOF technique the sample is sandwiched between two planar contacts, of which at list one is semi-transparent. The work functions of the electrodes are chosen such that there is no significant electron and hole injection into the sample. A nanosecond-duration laser pulse, incident near an electrode, is absorbed by the sample and generates non-equilibrium electron-hole pairs. Under an applied electric field between the electrodes, the electrons (holes) are swept into the near electrode, leaving a sheet of holes (electrons) to move to the far electrode and the current is measured as a function of time.

The traditional macroscopic description of carrier transport is associated with the central limit theorem. The theorem states that the average values of a large number of independent observations of a population have, under certain general conditions, an approximate normal (Gaussian) distribution. In TOF measurements, the total displacement of a carrier in a biasing field is considered to be a sequence of independent

![Figure 8](image)

**Figure 8:** sequences of “snapshots” represent packets of charge transiting a sample with time increase from top to bottom. (a) Normal non-dispersive transport of Gaussian carrier packet. (b) Dispersive carrier packet. Taken from Ref. [76].
beginnings of following displacements, called hopping times, and the lengths of individual displacements, have a narrow distribution function. The spatial distribution of the packet remains Gaussian with increasing time as described in Fig. 8 (a), while spreading of the packet due to diffusion is expressed as a Gaussian widening as long as processes such as multiple trapping or material inhomogeneity are negligible compared with the distance traveled due to the small dispersions. The velocity of the propagating packet and the current thus becomes constant until the carriers are absorbed at the electrode, at which they no longer contribute to the current. The expected current and as a function of time due to Gaussian transport is shown in curve 1 of Fig. 9.

In contrast with the current trace shown by curve 1, early experiments done on amorphous inorganic (e.g. As$_2$Se$_3$ [74]) and organic (e.g. TNF-PVK [75]) materials show an unusual current trace presented by curve 2 of Fig. 9, where the current decrease over the entire time of flight (except for a small ‘plateau’ region in some cases). The unusual current-time curves observed for disordered materials is ascribed to dispersive transport of a non-Gaussian carrier distribution as described in Fig. 8 (b). The origin of this behavior can be better understood in view of the relation between charge distribution to mobility and diffusion coefficients.
Mobility and diffusion coefficients

The charge carrier distribution function $G(x,t)$ determines the probability for a particle to be at time $t$ and location $x$ ($x$ is the location vector), given that at $t = t'$ it was at $x = x'$. Thus the carrier concentration for $x$ and $t$ is:

$$p(x,t) = \int d\mathbf{x}' G(\mathbf{x} - \mathbf{x}', t - t') p(\mathbf{x}', t')$$

where $G(x,t)$ is also the Green function satisfying the boundary condition:

$$G(x,t) = \delta(x - x')$$

For a physical system that operates with an applied external potential, at near equilibrium conditions, it is commonly assumed that there are only two components of the total current$^*$:

1. A diffusion current concentration, as described by Fick's law:

$$j_{\text{diff}}(x,t) = -D \nabla p(x,t).$$

2. A drift current concentration:

$$j_{\text{drift}}(x,t) = q \mu p(x,t) \nabla \eta(x,t)$$

where $\eta(x,t)$ is the local quasi chemical potential. The mobility and the diffusion coefficient do not have to be constant with the potential gradient (the local electrical field) in the general case. However, for normal transport at a short enough range or fixed electrical field, $\mu$ and $D$ will be constant with respect to time and space. The normal transport conditions is described by a Gaussian carrier distribution function:

$$G(x,t) = \frac{1}{(4\pi Dt)^{d/2}} \exp \left( -\frac{\mathbf{x} - \mathbf{x}' - \mu \nabla \eta t}{4Dt} \right)^2$$

where $d$ is the dimension of the system. The mobility and the diffusion coefficient are related to the first and the second moment of the carrier distribution function by:

$$\mu = \frac{1}{\nabla \eta} \lim_{t \to \infty} \frac{d}{dt} \langle x(t) \rangle$$

$$D = \lim_{t \to \infty} \frac{\langle (x(t) - x')^2 \rangle}{2dt} = \frac{1}{2d} \lim_{t \to \infty} \frac{d}{dt} \langle (x(t) - x')^2 \rangle$$

and a temporal mobility and a temporal diffusion coefficient are defined in an analogous method:

$^*$ We examine one charge carrier system, without generation or recombination of charge carriers.
Dispersive transport in disordered systems

In many systems, in particular systems that are far from equilibrium conditions the transport cannot be described as a normal (or Gaussian) transport. Namely a constant mobility or a constant diffusion coefficient cannot be defined, even at constant external field (and low charge concentration). The general term that describes this deviation is anomalous transport or dispersive transport. An extensive research has been done to describe it by continuous time random walk theory (CTRW) [76, 77-80], and later by other techniques such as generalized master equation and fractional differential equations (e.g. Ref. [80]).

The origin of the anomalous transport can be related to strong interactions between the carriers and their surroundings. In disordered organic films this property is manifested by trapping of charge carriers for long durations in deep traps/isolated traps. Scher and Montroll [77] postulated a slowly varying time dependence of the waiting time distribution function:

\[ \psi(t) \propto t^{-(1+\alpha)} \]  

(1.19)

with disorder parameter \( \alpha \), in the range of \( 0 < \alpha < 1 \) corresponding to subdiffusion process, e.g., hopping between localized states or release from a trap. They showed that one could account for the main features of dispersive transport by this long-tailed waiting time distribution. At early times in the transport process, most carriers are moving with relatively more probable short hopping times. However, with increasing time all carriers eventually encounter at least one long hopping time due to a wide statistical dispersion of effective intersite distances and deep energy levels such that those carriers are immobilized temporarily. In the long time limit, most carriers become so immobilized that the current becomes very small. This process leads to a “smearing” of charge carriers as described in Fig. 8 (b) where the maximum of charge distribution remains close to the origin. Consequently, the carrier mean position: \( \langle x(t) \rangle \) and the carrier distribution width (variance): \( \left\langle \left( x(t) - x' \right)^2 \right\rangle \) are not well defined.
In such a system the temporary diffusion coefficient and the temporary mobility coefficients are not constant but time dependent. In disordered organic films this deviation is in the power-law pattern:

\[
\sigma(t) = \sqrt{\left\langle (x(t) - x(0))^2\right\rangle} = \left(K_\alpha t^\alpha\right)^{1/2}
\]

and the temporal diffusion coefficient corresponds to the standard deviation in the displacement by

\[
D(t) = D_\alpha t^\alpha
\]

The value of \(\alpha\) determines the domain of the anomalous diffusion: subdiffusion (0<\(\alpha\)<1), as in the examined case, normal diffusion (\(\alpha=1\)) and superdiffusion (\(\alpha>1\)).

The mean position of the carrier distribution varies in time as:

\[
\langle x(t) \rangle \propto x(E)t^\alpha
\]

thus the temporal mobility has the following time dependence:

\[
\mu(t) \propto t^{\alpha-1}
\]

The relation between the different transport processes to the intrinsic physical properties of the medium in which this processes occur is given for exponential DOS (Eq. 1.6) by [76, 81]: \(\alpha = T/T_0\). For a given total DOS, a trap distribution characterized by longer tail deep into the gap corresponds to larger \(T_0\) and smaller \(\alpha\) that leads to larger deviation from non-disperssive Gaussian distribution for which \(\alpha = 1\).
Chapter 2: Experimental setups

2.1 Kelvin Probe Force Microscopy

Kelvin probe force microscope (KPFM) measures contact potential difference (defined below) at the nanoscale. It is based on the conventional atomic force microscope (AFM) invented in 1985 [82]. Martin et. al. [83], and Weaver et. al. [84, 85] used the KPFM for the first time to measure charges and potential variation on metal surfaces. In this section the basic setup of the KPFM used for our measurements is described.

2.1.1 Kelvin probe force microscopy - setup and operation

KPFM measures the contact potential difference (CPD) between a probing tip and a sample. The CPD represents the difference between the tip work-function ($\phi_t$) and sample work-function ($\phi_s$) and is defined as:

$$CPD = -\frac{1}{q}(\phi_t - \phi_s).$$

The sample work function is a sum of the intrinsic work function and any additional surface potential, thus measuring CPD across a sample surface gives local changes in the surface potential.

The basic principle of the measurement is schematically described for a metallic tip and sample in Fig. 10. When the tip and sample are not connected their LVLs are aligned but there is a difference in their Fermi levels. Upon electrical connection, electrons flows from the material with the lower work function to the one with a higher work function (in this case from the sample to the tip) as shown in Fig. 10 (a). This process continues until the Fermi levels are aligned; the two materials are now charged and there is a difference in their LVLs. Due to the charging of the tip and the sample, an electrostatic force develops as shown in Fig. 10 (b). This force can be nullified by applying an additional bias between the tip and the sample. The
The nullifying procedure is based on applying a bias to the tip-sample system; this requires that they will be in a 'capacitor' arrangement, i.e., there will be no physical contact between them. The above restriction requires that the CPD measurements will be conducted either in non-contact, or lift modes of the AFM. It is well known that in non-contact or lift modes [86] the forces between the tip and the sample are small, thus modulation (AC) techniques is used in order to increase the force sensitivity. A typical AC measurement is conducted in the following way. An AC bias at a frequency \( \omega \) is applied between the tip and the sample. It can be shown [83, 87] that the force component at this frequency is proportional to the CPD and therefore, can be nullified using a feedback loop whose input is the \( \omega \) component of the force. The most naive way to derive this force is to treat the tip-sample system as a parallel plate capacitor with one plate the tip apex, and the other the sample underneath it. [84, 85, 88] Under this assumption the force which is just the derivative of the electrostatic energy with respect to the tip-sample separation (\( z \)), is given by:

\[
F = -\frac{\partial U}{\partial z} = -\frac{1}{2} V^2 \frac{\partial C}{\partial z} \propto -\frac{1}{2} \frac{V^2}{z^2}
\]

where the electrostatic energy (\( U \)) is given for a parallel plate capacitor configuration by:

**Figure 10:** Definition and basic measurement setup of contact potential difference (CPD).
with $C$ the tip sample capacitance, and $V$ the potential difference between the AFM tip and the sample. Using the following expression for the potential difference:

\[ V = CPD - V_{DC} + V_{AC} \sin(\omega \cdot t) \]

and inserting it in Eq. 2.2 gives:

\[ F \propto \frac{1}{2z^2} \left[ (CPD - V_{DC})^2 + (CPD - V_{DC})V_{AC} \sin(\omega \cdot t) + V_{AC}^2 \sin(\omega \cdot t)^2 \right] \]

Thus the force at frequency $\omega$ is indeed proportional to the CPD.

Figure 11 shows a schematic diagram of the KPFM measurement setup. It is based on a commercial AFM (Autoprobe CP, Veeco Inc.) operating in non-contact mode. For topographic imaging, the probing tip made of silicon coated with Pt(Ir) alloy, is driven by a piezoelectric bimorph at a frequency slightly above its first resonance [18]. An alternating voltage $V_{AC} \sin(\omega \cdot t)$ at a frequency of around 20kHz is applied to the cantilever in order to induce an electrostatic force between the tip and the sample. The CPD between the tip and the sample surface is measured by nullifying the output signal of a lock-in amplifier (LIA), which measures the electrostatic force at the frequency $\omega$. The topography and CPD are measured.

---

**Figure 11:** Schematic diagram of the KPFM measurement setup used in this project. The topography part is the solid line and the CPD part is the dashed line.
simultaneously. Consequently the electrostatic force is nullified during the topography measurement by utilizing two different frequencies for the two signals so the topography and CPD signals do not interfere with each other. Deformation of the soft organic samples due to VdW force between the tip and the sample is considerably reduced by using the non-contact mode where the tip-sample VdW force is attractive. In addition, organic samples deformation due to electrostatic forces is minimized by the electrostatic force nullification. The latter is crucial for measurements of operating organic devices under different applied voltages.

2.2 Organic Field Effect Transistors

2.2.1 Structure and basic operation

The OFET have a thin film transistor (TFT) structure, first introduced by Weimer [90], and currently widely used in most of the amorphous silicon transistors. The transistor is a three-terminal component in which the current flow between two of the terminals, the “source” and “drain”, is controlled by the bias applied to the third terminal, the “gate”. This is most simply illustrated by consideration of a conventional (inorganic) metal-oxide-semiconductor field effect transistor (MOSFET) as found in most of the modern circuits. The MOSFET consists of a conductive substrate, which is either negatively (n) or positively (p) doped, two-electrode region (oppositely doped), and a metal-oxide double layer. The basic principle of the MOSFET is illustrated in Fig. 12, where Fig. 12 (a) and (b) show the device in its off- and on-state respectively. In order to drive a current between the source and drain electrodes in the off-state, one has to apply a voltage ($V_{DS}$) across three regions: (i) a p-n junction;(ii) an n-doped bulk region; and (iii) an n-p junction. In this case, one of the junctions is always oriented in the reverse direction to the applied field and therefore the current flowing through it is based on the negligible density of minority carriers (holes in n-type region) making its value negligibly small. In the on-state, a large negative bias is applied to the gate electrode. The metallic gate, the oxide layer and the n-type bulk semiconductor act in effect as a capacitor with the gate forming one plate, the oxide acting as the dielectric spacer, and the semiconductor forming the other plate. As with any capacitor, if a bias is applied across the plates, opposite and equal charges will
accumulate on the two plates. Thus, electrons accumulate at the gate and holes accumulate at the oxide-semiconductor interface. If the bias applied to the gate is sufficiently high, the interfacial hole density will be large enough to change the semiconductor from n to p-type. In this case the current flowing through the reverse bias diode is enhanced due to the high density of holes in the n region. That is, current flows between the p-type source and drain electrodes through the intermediate p-type layer (the channel).

The basic operation of OFETs and MOSFETs are in many ways similar, although there are also important differences that arise from the different device structures involved. In general, OFETs comprise three parts: (i) a metal or doped-organic conductor, (ii) an insulator, and (iii) an organic thin film. Two typical OFET structures are shown in Fig. 13. Unlike the MOSFET of Fig. 12, there is no p-n junction involved and the source/drain electrodes are attached directly to the organic film that makes up the channel. In Fig. 13 (a) the source/drain electrodes are in direct contact with the insulator (and the channel) and in Fig. 13 (b) the source/drain electrodes are on the other side of the \( \pi \)-conjugated material. These two arrangements

![Figure 12: Schematic description of the principle of operation for “standard” semiconductor FET.](image)

![Figure 13: Organic field effect transistor (OFET) schematic typical structures: a) bottom contacts, b) top contacts. The source and the drain are metals, and the layer between the gate and the organic film is an insulator.](image)
are called “bottom contact” and “top contact” configurations respectively [91].

2.2.2 Capacitor operation

It is evident from the discussion above that the process of capacitive channel formation is critical to the FET operation. The capacitive effect determines the charge density in the channel and hence the threshold voltage ($V_t$) at which the conductivity becomes substantial (switch-on). In order to understand the operation of OFETs, we start by considering a simple metal-insulator-metal parallel plate capacitor of the kind shown in Fig. 14 (a), in which an insulating layer is sandwiched between two metallic electrodes. In this case, the entire applied voltage ($V$) is dropped across the resistive insulating, giving rise to a uniform bulk electric field of magnitude: $F_{\text{ins}} = V/d_{\text{ins}}$, ($d_{\text{ins}}$ is the insulator thickness), with no electric field penetration into the electrodes (beyond the so called skin-depth). The abrupt change of the electric field from $F_{\text{ins}}$ in the insulator to zero at the metal electrodes has its origins in the formation of vanishing thin sheets of extremely high charge density at the surface of the two electrodes. In the OFET one electrode is made of an organic semiconductor where the penetration of the electric field, which is charge density dependent, becomes more significant and hence the charge occupies a larger region near the interface as illustrated by the scheme of metal-insulator-semiconductor capacitor in Fig. 14 (b). In this case, part of the applied voltage is dedicated to the formation of this charge layer (channel depth) thus reducing the voltage that drops across the insulator and consequently reducing the total charge that accumulates at the semiconductor interface (i.e. the effective capacitance is reduced).

The threshold voltage ($V_t$) is the gate voltage required to achieve conduction between source and drain, and based on Fig. 12 (MOS technology)\* it is actually the voltage that is required to invert the type of the interface from n to p. Consider a doped semiconductor being part of a capacitor as appeared in Fig. 15; the left column describes a p-type and the right column an n-type semiconductor, respectively. Before

\* The situation of OFET technology (Fig. 13) is different and will be discussed below.
applying a voltage (top of Fig. 15) the semiconductor is electrically neutral where every dopant atom is compensated by a free charge. When a negative (positive) bias is applied to n-type (p-type) based capacitor positive (negative) charge appears near the interface.

At first it is mainly composed of dopants atoms that have been stripped of their free electron (hole). By depleting the free charges near the interface we create a depletion layer. When the voltage is made larger we arrive at a point where very close to the interface free holes (electrons) start to accumulate and create a very thin layer whose type has been inverted to p-type (n-type). In other words, the type of free charges at the interface is now opposite to what it was at the "no bias" state.

**Figure 14:** Schematic comparison between metal-oxide-metal and metal-oxide-semiconductor ($\varepsilon_{\text{ins}}$ is the relative dielectric constant of an insulator, and $F_{\text{sc}}$ is the electric field in a semiconductor).
2.2.3 Intrinsic effects

How does the process of inversion depend on the material parameters? This is commonly answered with the aid of energy band diagram (Fig. 16) where the position of the Fermi-level between the conduction band edge ($E_C$) and the valence band edge ($E_V$) depicts the density of electrons and holes in the semiconductor. For an intrinsic semiconductor there is an equal density ($n_i$) of electrons and holes, and the intrinsic Fermi-level ($E_f^i$) lies approximately at the middle of the electronic gap. When there is an excess charge then the Fermi-level shifts up (down) for excess of electrons (holes) and the charge density is:

\[
\begin{align*}
n &= n_i \exp \left( \left( E_f - E_f^i \right)/kT \right) \\
p &= n_i \exp \left( \left( E_f^i - E_f \right)/kT \right)
\end{align*}
\]

**Figure 15:** The formation of a depletion layer followed by inversion-schematic illustration.
at the low-density limit (i.e., Boltzman limit). In case of a metal the last (relevant) band is partially filled with electrons and the Fermi-level lies within the electronic band (see Fig. 16).

In order to invert the type of the material the Fermi-level at the interface has to be moved to the other side of $E_f^i$, (see Fig. 16). The voltage shift required for the inversion process is:

$$V_{inv} = \frac{2}{q}(E_f - E_f^i).$$

However, as shown in Fig. 15, before inversion is created a depletion layer is formed. The creation of this space charge is associated with a voltage drop denoted as depletion voltage [28]:

$$V_{dep} = \sqrt{\frac{2\varepsilon_x \varepsilon_0 q N_D V_{inv}}{C_{inc}}}$$

that adds to the inversion voltage. So the threshold voltage associated with the semiconductor material only is:

$$V_{SC} = V_{inv} + V_{dep}$$

Turning now to OFETs (Fig. 13). What is the gate voltage required to achieve conduction between source and drain? Based on Fig. 13 it is the voltage required to populate the organic layer with charge. Typically, a well-behaved OFET is made using an intrinsic (undoped) organic film* and the Fermi level lies approximately in the middle of the HOMO-LUMO gap ($E_f \approx E_f^i$). Therefore, following the above discussion we note that for an undoped organic film there is neither inversion nor depletion and the threshold voltage associated with the organic material only should

* The case of doped organic film will be discussed later in the text.
therefore be zero (i.e., $V_{SC} = 0V$). We will show in section 5.3 that this holds only up to threshold voltage of a few volts.

### 2.2.4 Device effects

In an OFET device an organic undoped film is placed on a highly doped n-type silicon with silicon oxide insulating layer above it and let the device reach equilibrium by a common ground. A rather simple model can demonstrate that the device structure also makes a contribution to $V_t$. In the common case the Fermi level of an intrinsic semiconductor lies about the midway between the HOMO and the LUMO and the Fermi level of the organic film lies below that of the metal contact, as drawn in Fig. 17. After making an electrical contact between the organic layer and the metal, electrons will flow from the metal to the organic film to bring the Fermi-level at the organic film up towards the metal Fermi-level; as with the single layer devices (Fig. 13), this creates a built in potential of:

\[
V_{bi} = -(1/q)(\phi_n - \phi_s)
\]

that tilts the bands of the insulator and semiconductor upwards. The width of the spacer layer determines the potential drop across the organic film, where in the limit $d_{ins} = \infty$ the potential $V_{bi}$ is dropped entirely across the insulator and in the limit $d_{ins} = 0$ the potential is dropped across the organic film. To restore the flat levels of
the organic film (and insulator) to their flat state, one has to apply a compensating external bias of \( V_{FL} = V_{bi} \). Thus, in order to reach a position where the threshold voltage is solely dependent on the organic semiconductor parameters \( V_{SC} \) we have to first apply a \( V_{FL} \) voltage to compensate for the effect of the work function difference. The total threshold voltage is therefore:

\[
V_t = V_{FL} + V_{SC}.
\]

As will be mentioned in section 4, there are other factors that affect \( V_{FL} \) in addition to the work function differences between the gate electrode and the organic film. For example, during the manufacturing process sometimes charges are trapped in the insulator (charged defects) thus affecting the charge balance across the insulator and consequently the degree of band bending and the magnitude of the flat-band voltage [28].

### 2.2.5 Current-voltage characteristics

The dependence of the drain-source current on the gate-source bias and the drain-source bias \( V_{DS} \) can be divided to three regions: the linear regime, the non-linear regime and the saturation regime. In the linear regime \( V_{GS} \gg V_{DS} \) we assume that the decrease of charge density along the channel is small and that the charge density is to a good approximation uniform along the channel (see Fig. 18 (a) and (b)). For transistor width \( W \) and length \( L \) (between the source and drain electrodes). The drain-source current is given by

\[
I_{DS} = (W/L) \mu C_{ins} (V_{GS} - V_t) V_{DS}
\]

where \( C_{ins} \) is the insulator capacitance, and there is a linear relation between the current and gate-source voltage. When \( V_{DS} \) approaches \( V_{GS} \) (Fig. 18 (c)) the main assumption underlying the linear regime (quasi-uniform charge density across the channel) breaks and the current expression becomes:

\[
I_{DS} = (W/L) \mu C_{ins} \left( (V_{GS} - V_t) V_{DS} - V_{DS}^2 / 2 \right)
\]

as demonstrated in Fig. 19.

The charge density at the channel is proportional to the potential difference between the channel and the gate:

\[
Q = -C_{ins} (V_{GS} - V_t - V(x))
\]
Figure 18: Schematic description of the charge density across the OFET channel for different $V_{DS}$. The green region represents the charge distribution in the channel. In (d) $|V_i| \ll |V_{GS}|$ is assumed, thus $V_{DS} \cong V_{GS}$ at pinch-off conditions.
where \( V(x) \) is the potential at the surface of the organic film at a lateral position \( x \). As \( |V_{DS}| \) is raised, \( V(x) \) near the drain approaches \( V_{GS} - V_t \) and the charge density near the drain is reduced thus enhancing the resistivity of the channel. When this effect takes place the slope of the current-voltage curve is reduced (Fig. 19), and the curve starts to saturate. Once \( V(x) \) is equal to \( V_{GS} - V_t \) a region empty of the channel type carriers is formed as demonstrated in Fig. 18 (d) (denote as the “pinch-off region”). When the value of \( V_{DS} \) is further raised, and \( |V(x)| > |V_{GS} - V_t| \), the pinch-off region gets wider (Fig. 18 (e)). Since this region is “empty” of channel type carriers its resistivity is very high and the entire extra potential drops across it\(^*\). Consequently, the potential at the edge of the channel is pinned at \( V_{GS} - V_t \). Since the region where the channel exists remains with a fixed boundary conditions of \( V_{GS} - V_t \) near the drain for any \( V_{DS} \) that exceeds \( V_{GS} - V_t \), the current that flows across the channel becomes independent of \( V_{DS} \) (for channel longer then the pinch-off region: \( L >> L_{PO} \)). The resulting \( I_{DS}-V_{DS} \) curve is shown in Fig. 19 and the current at this saturation regime (right side of Fig. 19) is given by:

\[
I_{DS}^{sat} = \left( \frac{W}{L_{eff}} \right) \mu n C_{ins} (V_{GS} - V_t)^2
\]

, where \( L_{eff} = L - L_{PO} \approx L \) for \( L >> L_{PO} \).

\(^*\) In principle the region that is empty of channel-type carriers (hole or electron) may be filled with the other type of carrier (electron or hole). We assume that the conductivity associated with this other-type carrier is negligibly small (low mobility, contact limited, etc).

**Figure 19:** \( I_{DS}-V_{DS} \) of an n-type transistor characteristics for several values of \( V_{GS} \) as derived by equations (2.13) and (2.15). Here, \( W/L=600, C_{ins}=50nF, \mu=10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \) and \( V_t=1V \). The dashed line depicts the transition to the saturation regime.
Chapter 3: Interface potential change and space charge region across metal/organic/metal structures.

The electronic carrier transport in, and performance of, an organic electronic device depend, to a large extent, on the electrostatic potential profile across the device and its interfaces. There is considerable interest in understanding the physical origin and location of potential shifts across the device, as these can occur due to interface dipoles, or band bending; therefore accurate potential distribution measurements are of considerable importance. To date, measurements of molecular energy levels and level offsets across metal-organic and organic-organic interfaces have been carried out mainly by UPS [92, 15, 16], XPS [17] and KP [18] measurements as a function of organic layer thickness. Yet, potential profiles, across interfaces and complete devices can only be inferred from KPFM measurements.

Many groups have used KPFM to study potential distributions across inorganic semiconductor [93, 94] and in recent years the number of studies performed on organic devices is increasing [95, 96, 97]. In the case of inorganic semiconductors, surface charges associated with gap states are present at most surfaces and limit the usefulness of KPFM study of cross-section of these materials. On the other hand, surface states are generally absent in VdW bonded molecular materials (as long as they are not oxidized [98]), making KPFM particularly suitable for the latter. We present in this chapter a study of the potential profile across Au-Alq3-M layered structures (M: Au, Al, no metal) performed in a nitrogen environment with high spatial resolution afforded by KPFM. We compared the fine features of the potential profile with the results obtained via UPS, and evaluate the KPFM resolution in the studied case using electrostatic simulation in order to avoid measurement artifacts.

3.1 Sample preparation and experimental setup

GaAs/Cr(5nm)/Au(50nm)/Alq3(1-3µm)/M layered structures (Fig. 20) were prepared by sublimation from solid sources in an ultra high vacuum (UHV) growth
chamber in Princeton University and transported under nitrogen atmosphere to the KPFM glove box at Tel Aviv University. The GaAs wafer serves as a cleavable mechanical substrate. A few nm of clean Au was evaporated in UHV on this initial Au layer (for a total thickness of 50 nm) to provide a bottom metal surface with high work function. The organic layer and the top metal layer were then deposited in the same UHV chamber.

Our KPFM [99] (Autoprobe CP -Veeco Inc.- with Kelvin probe homemade electronics [100]) was placed inside a home-built glove box with nitrogen atmosphere (<2ppm water). The samples were cleaved in-situ shortly before the KPFM measurements in the dark*. The samples were scanned in non-contact mode near the cleaved edge, and the CPD measurements were typically performed on a relatively smooth cleavage area, with a minimal metal stretching, continuous layers, and a small roughness of the organic layer.

3.2 Potential measurement across metal\organic\metal layered structures

Figure 21 shows a topography image and a CPD profile of a typical measure of layered structure. The GaAs substrate is on the left and the Alq₃ is placed between two gold layers on the right (see also the inset). The sandwich-like structure can be easily recognized due to the protrusion of the two metals (110nm with respect to the

* Except for the AFM feedback laser, which operates at 1.85eV, smaller then the optical gap of Alq₃ (~3.2 eV) but larger than the metal/Alq₃ barriers. Sample illumination was minimized by tip and cantilever shadowing and reducing the laser intensity; no changes in CPD were observed using different laser intensities.
organic surface). These protrusions are due to differences in the mechanical properties of the different layers and to low adhesion at the interfaces, which lead to an inherent effect of stretching the metal layers over the GaAs edge during the cleavage process.

The CPD profile in the proximity of the Au/Alq3 junctions in Fig. 21, i.e. the ~600 meV step down on the left and ~600 meV step up on the right can be attributed to the interface electric dipole at these junctions [101]. The constant CPD between the metal contacts indicates that the molecular energy levels are flat across the organic bulk. The two peaks observed on the inner Au layer are attributed to a lowering of the Au work function due to exposure of the GaAs/Cr/Au substrate to air [102, 103] prior to UHV-deposition of the rest of the structure (i.e., Au/Alq3/Au). UPS measurements generally show a 0.9-1.25 eV interface dipole and drop in local vacuum level energy upon evaporation of the first molecular layer of Alq3 on clean Au, as illustrated in the energy levels scheme shown in Fig. 22 (a) [15, 101, 103-105]. The smaller potential drop (~600 meV) measured by the KPFM on this interface (Fig. 21) is probably due to the fact that the Au on the “cleaved” surface is exposed to residual water and oxygen impurities in the glove box and thus has a lower work function than the Au measured with UPS in UHV. Such a contamination of Au by oxygen and water can decrease its work function by up to about 1 eV [102,103]. Figure 21 also shows that the potential shifts at the two Au/Alq3 interfaces are ~65nm wide, considerably more than observed via UPS. This is a measure of the KPFM resolution near a protruding metal layer, and is a consequence of the tip averaging effect, which will be analyzed in details below.

![Figure 21: CPD profile of cross-sections of GaAs/(Cr)/Au/Au/(purified)Alq3/Au layered structure. Inset: Topography image of the relevant area.](image)
Figure 23 shows a CPD profile (solid curve) measured across a structure comprising an inner gold layer (left) and an outer aluminum layer (right), as shown in Fig. 22 (b). In addition to the dipole-related potential drops at the two interfaces, there is a potential drop between the gold and the aluminum layers due to the difference in their work functions. This is illustrated in the UPS based energy level diagram in Fig. 22 (b). Figure 23 also shows a comparison between CPD profiles measured on GaAs/(Cr)/Au/Alq3/Al (solid curve) and GaAs/(Cr)/Au/Alq3 (dashed curve) structures. In the later case the outer aluminum layer was pilled off during the cleavage. The abrupt potential change at the outer (right) Alq3/Al interface clearly affects the whole potential distribution across the organic layer in comparison to the

Figure 22: Schematic energy levels structure (not in scale) based on UPS and inverse photoemission spectroscopy measurements [15,101,104,105] for (a) GaAs/(Cr)/Au/Au/Alq3/Au structure, and (b) GaAs/(Cr)/Au/Au/Alq3/Al structure. The data for GaAs (100)/Cr were taken from reference [17]. For the Alq3 flat energy levels were assumed.

![Figure 22](image_url)
case of no outer Al layer where no abrupt potential change is observed. The fact that the two CPD curves merge at the outer border on the Alq3 layer may stem from aluminum residuals (left after cleavage) that ‘pin’ the potential but do not support a macroscopic potential drop.

3.3 Calculation of the tip electrostatic averaging effect

The measured CPD equals the tip voltage that minimizes the electrostatic force between the tip and the sample as explained in section 2.1. Due to the long-range electrostatic force, the measured CPD at a point on the surface below the tip apex is a weighted average of the surface potential in the vicinity of the tip. The effect here is even stronger since the two metallic layers, which have work function considerably different from that of the molecular layer, also protrude from the sample surface, affecting the tip-sample electrostatic interaction.

The effect of the tip electrostatic averaging was calculated as follows. The three-dimensional Laplace equation was solved (using a finite element commercial code, FlexPDE Ver. 2.16f) for the following system. A metallic tip (cone shaped with a hemispherical apex, tip height: 5µm, tip opening angle: 11.3º, and apex radius of curvature of 20nm) located 20nm above a surface composed from a flat region representing the organic layer at a potential of 0V, and a protruding square strip (160nm high and 160nm wide) representing one of the metal contacts at a potential of 1V; this strip represents the ~1V potential step at the Au/Alq3 interface. For each tip location, the potential was calculated for three different tip voltages, (see, for example, Fig. 24 (a)) and the CPD was extracted in the following way. The electrostatic force between the tip and the surface was calculated by integrating the Maxwell stress over the entire tip surface [106]:

\[
F_z = -\frac{1}{2} \epsilon \int_{\text{tipsurface}} \hat{z}E_z \hat{n} d\hat{n}
\]

(3.1)

where \( d\hat{n} \) is a tip surface element normal to the surface, \( \hat{z} \) is a unit vector in the z direction (tip-axis direction), and the integral is calculated over the entire tip surface. The electrostatic force was then expanded [87] as:
to yield the voltage that minimizes the force (i.e. the CPD) through:

\[
V_{\text{min}} = -\frac{a_2}{2a_3}
\]

We use FlexPDE simulation for extracting the electrostatic forces as a function of tip-voltage; the FlexPDE solver uses finite element analysis in which the domain of interest is divided into pyramidal cells. The program solves the Laplace equation by determining the values of the dependent variables at discrete points (nodes), i.e. at the corners of pyramidal cells and at the midpoints between corners. In order to compute the solution at any point in space, the program applies a polynomial function on the known values at the cell corners and midpoints. The polynomial coefficients are determined by solving a system of linear equations.

The results are shown in Fig. 24 (b). The calculated step-like CPD profile (dashed curve) is widened by the measuring tip to a step ~290nm wide, which is larger than experimentally observed (see Fig. 21). The calculated CPD shape at the metal strip corner is attributed to the electrostatic interaction when the tip apex is in proximity of the step corner. Comparing this calculation with the dashed curve (no top Al layer) in Fig. 23 at a distance 290nm away from the junctions, we conclude that the curvature in the measured CPD may be solely due to a tip broadening of the abrupt potential drop at the Au/Alq3 interface.
3.4 Impurity effect on the potential distribution

Figure 25 shows a CPD profile measured on a GaAs/(Cu)Au/Alq3/Au structure. The upper (solid) potential profile is concave, in contrast to the profile in Fig. 21, which is nearly flat across the Alq3 layer. This interesting difference is presumably due to the different impurity contents of the two Alq3 layers; the Alq3 material used in the device measured in Fig. 25 was not purified before deposition, while the Alq3 used in the device measured in Fig. 21 was purified by multiple cycles of gradient sublimation. In the case of unpurified Alq3, unintentional doping is likely to introduce dopants with a broad energy distribution [107]. Such dopants may give rise to a space charge region, causing the observed curved CPD profile. The presence of a space charge region is also consistent with the simulation results, since the concave shape of the CPD profiles appears also at distances much larger than 290nm from the shape of the CPD profiles appears also at distances much larger than 290nm from the two contacts; thus the tip averaging effect is not likely to be the origin for the curved potential profile. The effect of unintentional doping on SCR was also demonstrated by Kelvin probe measurements on C60 as a function of film thickness. Hayashi et al. [108] showed an enhanced molecular level bending across a 600 nm thick C60 layer deposited on copper from as-received material as compared to purified C60.

![Figure 25: CPD profile measured across GaAs/(Cr)/Au/(non-purified)Alq3/Au structure under zero bias. Solid and dashed curves were before and after applying a bias respectively. Dotted curve: Topography profile.](image)
Finally, applying a $-IV$ sample-bias for 2 minutes between two consecutive CPD measurements, conducted at zero bias, lowers the CPD profile (dashed curve in Fig. 25). A similar structure that contained purified Alq$_3$ did not show any such changes in CPD. Presumably, the applied bias induces negative charging of deep dopant induced traps in the Alq$_3$ layer and thus lowers the local vacuum level, LUMO and HOMO energies; as reflected in the lower CPD across the Alq$_3$ layer.

In summary, we have measured potential profiles on a complete metal/organic/metal layered structures using KPFM. The abrupt potential drops across the metal/organic interfaces, which are often ascribed to interfacial potential dipole, and the influence of the different metal work functions, were clearly observed. Using numerical analysis, we estimated the broadening effect introduced by the tip for KPFM measurement on samples that exhibits abrupt potential and topographical steps. We conclude that non-purified Alq$_3$ layers between two metal contacts sustain molecular level bending, in contrast to purified Alq$_3$ (within our measurement resolution), which explained by the presence of deep traps due to unintentional doping in non-purified Alq$_3$. 

Chapter 4: Threshold voltage in Organic Field Effect Transistor

One of the key parameters that determine the OFET performance is the threshold voltage, defined as the gate-source voltage for which there is no space charge region in the organic film [109, 72]. $V_t$ also serves as a reference potential in the determination of charge concentration in organic thin film transistors. Thus it has a central role in the study of charge related phenomena in organic films [110] and OFETs optimization [111]. In this chapter we present new two methods for $V_t$ determination. The first one allow us to have more accurate $V_t$, and the second method provides information on fundamental quantities such as energy level shifts and the shape of the DOS available for holes.

$V_t$ is conventionally found by extrapolating the drain-source current, measured as a function of $V_{GS}$, to zero. Since the mobility in disordered organic films is charge density-dependent, the classical shape of the $I_{DS}-V_{GS}$ curve is altered [72] and the determination of $V_t$ by back extrapolation may not be correct [111, 112]. We show in section 4.2 that $V_t$ could be found without current detection by measuring the onset of the gate screening by charge accumulation in the channel [112]. In this case, a potential mapping of the channel region is conducted using KPFM [99]. In addition, we have developed a method for extraction of $V_t$ as a function of $V_{GS}$. This is done by KPFM direct determination of the pinch-off voltage ($V_{PO}$) defined as the drain-source voltage ($V_{DS}$) for which a zero-charge region is formed at the drain/channel interface, $V_t$ is then extracted from $V_{PO}$ that is measured for different $V_{GS}$. The measurements of $V_t$ as a function of $V_{GS}$ give the gate induced molecular level shift at the oxide/organic interface. Comparison between the measured and calculated $V_t$ indicate on more complex DOS then a Simple Gaussian as will be explained in sections 4.3-4.5.
4.1 Sample preparation and experimental setup

The OFET substrates (Fig. 26) were fabricated at the Technion Institute of Technology by the group of Prof. Nir Tessler. These substrates consisted of a heavily doped p-type silicon gate electrode, a thermally-grown 90\text{nm} thick silicon oxide gate insulator, and 50\text{nm} thick gold strips evaporated on the oxide to form the source and drain electrodes separated by 13\text{µm}. A thin film (50nm) of \( \alpha \)-NPD was deposited on the substrate by sublimation (evaporation rate: 1\text{Å/sec}) from solid source in an ultra high vacuum growth chamber in Princeton University by the group of Prof. Antoine Kahn, and transported under nitrogen atmosphere to the nitrogen KPFM glove box. Our KPFM was used for determination of the surface potential profile across the OFET channel, with a lateral resolution of tens of nanometers. The transistors were scanned across relatively smooth regions of the organic layer (roughness <1nm) for different \( V_{gs} \) and \( V_{ds} \) applied by a semiconductor parameter analyzer (HP 4155C), which was also used as a monitor for the drain, source and gate currents. The contact resistance [111, 95], leakage current through the gate-insulator and to the periphery of the active area, and the shift of the threshold voltage [111] due to continuous voltage application, were found to be negligible in the measured transistors.

![Figure 26: Schematic of the OFET structure and KPFM tip above the channel.](image)
4.2 Threshold voltage measurements

Here we describe the determination of $V_t$ by KPFM detection of the transition between a “bare” gate to screened gate due to holes accumulation. Figure 27 (a) shows a set of CPD curves measured for $V_{DS} = -4V$ and $V_{GS}$ ranging between 0.5V and −0.5V. Note that the separation between the upper five curves ($0.1\leq V_{GS} \leq 0.5V$) is larger than between the lower six curves ($-0.5 \leq V_{GS} \leq 0.2V$).

In order to better determine the threshold voltage, we plot in Fig. 27 (b) the potential in the channel, close to the source (at a position $X' = 6.25 \mu m$ in Fig. 27 (a)), as a function of $V_G$. As long as the gate bias is smaller than the threshold voltage ($V_{GS} < V_t$), the charge in the accumulation layer screens the gate potential and the increase of the surface potential is smaller than the increase of the gate bias ($\Delta CPD/\Delta V_{GS} < 1$). On the other hand, when the gate bias is above the threshold voltage ($V_{GS} > V_t$), there are no mobile charges between the gate and the film surface (except for a negligible charge concentration corresponding due to intrinsic carriers, unintentional doping, and electrons that overcome the relatively large electron barrier for injection). In this case the slope of the surface potential versus gate bias curve is close to one ($\Delta CPD/\Delta V_{GS} \approx 1$); the slope is not equal to unity because of the

![Figure 27](image-url)

**Figure 27:** (a) CPD curve as a function of distance from the source electrode. $V_{DS} = -4V$ and $-0.5 \leq V_{GS} \leq 0.5V$. (b) The CPD measured at position $X' = 6.25 \mu m$ (vertical arrow in (a) as a function of gate voltage for $V_{DS} = -4V$.
potential drop across the oxide. The crossover point between these two regions yields
the threshold voltage at the point of the KPFM tip in the channel. Here, the gate
voltage for which the charge accumulation onset takes place. This defines
\[ V_t(X^t = 6.25 \mu m) = 0.59 \pm 0.03 V \] and \( V_t \) at the source-channel interface (i.e., the
onset of charge accumulation in the channel) is:
\[ (4.1) \quad V_t = V_t(X^t) - CPD(X^t) = 0.56 \pm 0.03 V \]

The described method to extract the threshold voltage in an OFET,
overcomes the problem of the current detection by measuring the onset of the
gate screening by charge accumulation in the channel.

4.3 Generalized threshold voltage – concept and methodology

In this section we study the relation between \( V_t \) and related fundamental
quantities using a new method for \( V_t \) determination as a function of \( V_{GS} \). As a first
step we will focus on the origin of \( V_t \). The common OFET exhibits a p-type
behavior*: i.e., the channel majority carriers are holes, and it is in the "on state" when
\( V_{GS} \) is lower then \( V_t \). In that state, an accumulation layer is formed near the
insulator/semiconductor interface, providing a conducting channel between source
and drain. The surface charge concentration induced by the gate for an undoped
organic layer is:
\[ (4.2) \quad Q = -C_{ox} (V_{GS} - V_t - V(x)) \]
where \( C_{ox} \) is the silicon oxide (insulating layer) capacitance per unit area. \( V(x) \), the
surface potential at position \( x \) across the transistor is measured as:
\[ (4.3) \quad V(x) = CPD(x) - CPD_t(x) \]
where \( CPD(x) \) is the contact potential difference measured between the KPFM tip
and the sample at certain \( V_{GS} \) and \( V_{DS} \), and \( CPD_t(x) \) is measured at the onset of the
conduction channel, at \( V_{GS} = V_t \) and \( V_{DS} = 0 V \).

\( V_t \) can be written as the sum of two contributions [109] (see also section 2.2.4):
\[ (2.11) \quad V_t = V_{FL} + V_{SC} \]

* Mainly since p-type OFETs have in general better hole field effect mobility, and are less sensitive to
oxidation.
as described by the qualitative energy level scheme across the OFET channel shown in Fig. 28 (possible dipoles at the interfaces are ignored for simplicity). $V_{FL}$ is the flat level potential that accounts for any work function difference between the organic film and the gate, and for any physical or chemical interface dipole moment or trapped charge at the gate\oxide and oxide\organic interfaces [15], and $V_{SC}$ is the voltage drop across the organic semiconductor. $V_{SC}$ is negligible when $V_{GS}$ is in the order of a few volts [99], thus as long as $V_t$ equals to a few volts, $V_t$ measured at the onset of the conduction channel can be considered as $V_{FL}$.

According to Eq. 4.2 when $V_{DS} = V_{GS} - V_t$, a point with no gate-induced charge is created near the drain, the so-called “pinch-off point”. This takes place at $V_{PO}$, such that:

$$V_{PO} = V_{DS} = V_{GS} - V_t$$

(4.4)

When $|V_{DS}|$ exceeds $|V_{PO}|$, the pinch-off point shifts towards the source, and a pinch-off region is formed between the drain and the pinch-off point. At any $|V_{DS}|$ larger then $|V_{PO}|$, the potential between the source and the pinch-off point is $V_{PO}$, and
the excess potential $V_{DS} - V_{PO}$ drops across the pinch-off region. Since there is no hole accumulation in this region, its resistance is very high and a small extension of the region is enough to sustain an increase in the potential across it. Consequently, when $|V_{DS}|$ increases, the pinch-off region extends slightly. Our method for extraction of $V_t$ is based on determining $V_{PO}$ by direct observation of the pinch-off phenomenon using a KPFM potential mapping of the channel, and then extracting $V_t$ from $V_{PO}$.

4.4 Generalized threshold voltage measurements

Figure 29 (a) shows potential and topography profiles measured simultaneously across the transistor. The protruding regions on the left and right sides of the bottom topography profile correspond to the source and drain contacts, respectively. The potential profiles were measured for $V_{GS} = -10V$ and $V_{DS}$ ranging between 0 and $-10V$. As $V_{DS}$ approaches the pinch-off voltage, a relatively large potential drop appears near the drain (left side). Beyond a certain $V_{DS}$ value, there is almost no change in the potential between adjacent curves, except for a small region near the drain where the abrupt potential drop increases (see the five bottom curves). The large voltage drop across this region is ascribed to the abrupt voltage change that
is known to occur in the pinch-off region. As long as the (absolute) drain-source bias is smaller than the pinch-off voltage ($|V_{DS}| < V_{PO}$), the voltage drop across the accumulation layer increases as the source-drain potential increases. On the other hand, when the drain-source bias exceeds the pinch-off voltage, ($|V_{DS}| > V_{PO}$), the potential between the source and the pinch-off point does not change with increasing $|V_{DS}|$, as the excess voltage drop occurs in the pinch-off region in the vicinity of the drain. This is clearly seen in the five bottom curves in Fig. 29 (a); however the curves do not perfectly coincide due to the small shift of the pinch-off point position towards the source as $|V_{DS}|$ increases.

The pinch-off voltage can be accurately determined by plotting the channel potential measured at a specific point, i.e. 1 $\mu$m to the right of the drain (x=5.31 $\mu$m, where x is the lateral position), as a function of increasing $V_{DS}$ as shown in Fig. 29 (b). The pinch-off voltage is thus $V_{DS}$ for which $dV(x)/dV_{DS}$ becomes constant (see Fig. 29 (b) inset), since any voltage beyond $V_{DS} = V_{PO}$ drops across the pinch-off region. The non-zero derivative is due to the constant lateral shift of the pinch-off point toward the source as $V_{DS}$ increases. We determine $V_{PO}$ at a point x in the channel where the voltage difference between the curves is maximal, yet far enough from the estimated pinch-off point (~maximum curvature point) in order to minimize the tip averaging effect on the measured $V(x)$ (see reference [113] for more details about this phenomenon). Based on the pinch-off voltage definition (Eq. 4.4), we can now use $V_{PO}$ extracted at different $V_{GS}$ to determine $V_{r}$ for different $V_{GS}$ values.

![Graph](image_url)

**Figure 30:** $I_{DS} - V_{GS}$ characteristic of undoped $\alpha$-NPD based OFET.
Moreover, in the studied case $V_{FL}$ is equal to $0 \pm 0.01V$, as determined by the onset of the drain-source current (see Fig. 30), and $0.01 \pm 0.01V$ by the technique presented in section 4.2, thus $V_t$ is actually equal to $V_{SC}$ at different $V_{GS}$. In other words, $-qV_t$ is the shift of the molecular levels at the oxide/organic interface with respect to their equilibrium position as presented in Fig. 28.

4.5 Generalized threshold voltage as a measure of molecular level shift in organic Field Effect transistors

Figure 31 shows a series of $V_t$ extracted in the way described above for different $V_{GS}$ values (dark squares with error bars). The red line in Fig. 31 shows calculated $V_t$ as a function of $V_{GS}$ assuming a density of HOMO states with a Gaussian distribution. The $V_t$ is calculated as follows by the group of Prof. Nir Tessler (Technion-Israel Institute of Technology):

The Poisson equation is used:

\[
\frac{d^2V}{dz^2} = \frac{-qp(z)}{\varepsilon_o \varepsilon_{SC}}
\]

where $z$ denotes position perpendicular to the gate insulator. The hole concentration is

![Figure 31](image-url)

**Figure 31:** Measured $V_t$ as a function of $V_{GS}$ (black squares with error bars) and calculated $V_t$ as a function of $V_{GS}$ based on a single-Gaussian (full red curve) and a two-Gaussians (dashed blue curve) HOMO-DOS distribution.
given by:
\[ p(x) = \int (1 - f_{FD}(E))g_i(E)\,dE \]
where \( V \) is the potential, and \( \varepsilon_{sc} = 3 \) is the relative dielectric constant of \( \alpha-NPD \) [114], and \( f_{FD}(E) \) is the Fermi-Dirac distribution. In the above expression, \( g_i(E) \) is the HOMO Gaussian DOS distribution relevant for holes and given by:
\[ g_i(E) = \frac{N_i}{\sigma \sqrt{2\pi}} \cdot \exp \left[ -\left( \frac{E}{\sqrt{2\sigma}} \right)^2 \right] \]
where \( N_i = 1 \times 10^{21} \text{ cm}^{-3} \) is the total state density, and the Gaussian width (variance) is \( \sigma = 0.17 \text{ eV} \).

Using the equality:
\[ \frac{dV}{dz} \frac{d^2V}{dz^2} = \frac{1}{2} \frac{d}{dz} \left[ \left( \frac{dV}{dz} \right)^2 \right] \]

together with Eq. 4.5 and 4.6 we can have:
\[ \frac{dV}{dz} = \left[ K + \frac{2q}{\varepsilon_0 \varepsilon_{sc}} \int V(z) - kT \ln \left[ 1 + \exp \left( \frac{V(z) + E}{kT} \right) \right] \cdot g(E)\,dE \right]^{1/2} \]

These equations are solved with the following boundary conditions:
\[ \left( \frac{dV}{dx} \right)_{z=d_{org}} = 0 \]
and:
\[ (V)_{z=0} = V_0 \]
where \( V_0 \) is the potential at the oxide/molecular film interface, and \( d_{org} \) is the organic film thickness. \( K \), the integration constant, and \( V_0 \) are chosen to satisfy the boundary condition of the electric field being zero at the edge of the molecular layer and therefore zero surface charge. Based on the above notation, we find:
\[ V_i = (1/2)V_{GAP} - V_0 \]
\[ V_{GS} = V_{ox} + V_i \]
where \(-qV_{GAP}\) is the energy gap between the HOMO and the LUMO [115].

The dependence of \( V_i \) on the shape of the DOS can be understood by considering that the \(-qV_i\) shift is actually the shift of the molecular level with respect to its position in equilibrium at the oxide/organic interface near the source. Increasing \( |V_{GS}| \) increases the induced hole concentration in the channel, which shifts the Fermi
level towards the center of the DOS. For a Gaussian DOS, the shift is large when the DOS in the distribution tail is small. However, as $|V_{GS}|$ increases, holes accumulate in states of higher density (as the Gaussian is wider towards its center) and only small molecular level shifts are required for populating a large number of states. Consequently the calculated $V_t$ shift for a Gaussian DOS is large for small charge concentrations ($|V_{GS}| < 2V$) and moderate for higher concentrations ($|V_{GS}| > 2V$). The measured $V_t$ presented in Fig. 31 shows a different behavior.

The dashed blue line in Fig. 31 is a calculation of the $V_t$ shift based on a DOS distribution shaped as one main Gaussian ($\sigma = 0.17eV, N_i = 1 \cdot 10^{21} cm^{-3}$) plus a small secondary Gaussian ($\sigma = 0.1eV, N_i = 1 \cdot 10^{17} cm^{-3}$) located deeper in the energy gap. The calculated $V_t$ curve based on the two-peak DOS distribution fits the measured $V_t$ very well. This is a strong indication that a realistic edge DOS might deviate considerably from the commonly assumed Gaussian distributions [61, 71]. It is important to emphasize that the calculated $V_t$ based on the double Gaussian DOS distribution is not a the only solution that fits to our results, however this DOS distribution is a simple and yet reasonable one since an additional secondary Gaussian can model an additional DOS distribution due to unintentional doping [116]. Other DOS distributions, different from a simple Gaussian distribution, may also fit the experimental results (i.e., other linear combinations of Gaussian and exponential functions).

In this chapter we have introduced a KPFM based method that does not depends on current detection limitations to extract the $V_t$ at the onset of the induced conducting channel by detecting the gate screening due to induced charge. In the case that $V_t$ is in the order of a few volts it is actually equals to $V_{FL}$ since $V_{SC}$ is considered to be negligible in the low (a few volts) $V_t$ regime. Then we have showed a new method for direct determination of the pinch-off voltage for different gate voltages using KPFM; based on this method, the $V_t$ was extracted for different $V_{GS}$. Changes in this generalized threshold voltage reflect the voltage drop across the organic film perpendicular to the gate electrode (i.e., $V_{SC}$), and should be taken into consideration when calculating charge concentrations in organic thin film transistors. A calculated $V_t$ based on a single Gaussian shaped DOS distribution does not fit the
measured threshold voltage, while calculation based on a main Gaussian density of states with an additional secondary Gaussian state distribution located deeper in the energy gap describes the measured data well. This result provides strong evidence, in this particular case, for deviation of the HOMO-DOS edge from the single Gaussian distribution that is commonly used for its description.
Chapter 5: Direct determination of the hole density of states in undoped and doped amorphous organic films with high lateral resolution

The DOS for charge carrier transport in organic molecular films and the impact of electrical doping on the DOS are of fundamental importance for understanding charge transport in organic films. As described in detail in section 1.3, transport in amorphous organic semiconductors is generally described in terms of charge-carrier hopping between disordered localized energy states [54]. The energy disorder (manifested in \( \sigma \) for Gaussian DOS models) is ascribed to the different environment of each molecule: static and dynamic disorder in position and orientation affect the molecular energy levels through electrostatic [61, 117] and steric [67] interactions. This disorder leads to a DOS usually modeled by a Gaussian [61] or exponential [68] distribution (section 1.3.2). The insertion of dopant molecules, i.e. electron donors or acceptors or optical dopants, further modifies this DOS. Dopants are introduced either intentionally to improve the film conductivity [118], modify charge injection barriers [119], add functionality (e.g. a \( pn \) junction [120]), and modify the film optical properties [121], or unintentionally as synthesis impurities [122], solution residuals [123] and chemically induced doping [124], which deteriorate the performance of the organic material. In any case, an accurate understanding of the DOS energy distribution and how it is affected by molecular doping is one of the keys to advancing basic research on, and technological applications of, organic semiconductor films, since most electronic properties of organic semiconductors are closely related to the shape of the DOS [125, 126].

The influence of dopants on the DOS distribution has been studied indirectly by assuming a Gaussian DOS distribution and extracting function parameters from carrier mobility measurements as a function of doping concentration. It was found that the DOS distribution broadens with increasing doping concentration [118], a tendency that was attributed to potential fluctuations caused by the Coulomb field of the randomly distributed dopant [127, 128]. However, experimental information on the specific shape of the DOS relevant to carrier transport in organic films has been
very limited and the influence of doping on the DOS has never been explored directly. Lang et al. have used current-voltage measurements as a function of temperature in OFET to extract the density of gap states in amorphous and single crystal pentacene [129], and Hulea et al. have used electrochemically-gated transistor to measure a wide energy range of the HOMO DOS in poly(p-phenylenevinilene) by injection of holes and ionized dopants in different concentrations during the measurement [130].

In this chapter, we report on direct determination of the DOS around the HOMO level in undoped and doped amorphous organic thin films using KPFM measurements on an OFET structure. We observe a broadening of the DOS distribution, as well as sharp doping-induced peaks in the DOS distribution. Exploiting the KPFM nanoscale lateral resolution, an additional peak is observed in the main DOS distribution of the undoped film at specific sites located at interfaces between regions of different surface potential, while the doped films exhibit a laterally more homogeneous DOS distribution.

5.1 Sample preparation and experimental setup

The α-NPD based OFETs were prepared as described in section 4.1. However, in this case, the width of the thin film was reduced to 10nm. In addition, OFETs with p-type doping were fabricated by co-evaporation of F4-TCNQ with the host (α-NPD) molecules [115] on the same substrate structures that were used for the undoped transistors. The measurement setup is described in section 4.1.

5.2 Density of states determination – methodology

The measurement concept can be explained in a simple way by assuming a Gaussian distribution of the HOMO-DOS, as shown schematically in Fig. 32 (a). When \( V_{GS} = V_t \) there is no induced charge in the organic film, and the DOS is located below the Fermi energy level. However, when \( V_{GS} < V_t \), holes are injected into the organic film from the grounded source and drain electrodes in order to screen the gate. The holes populate the tail states of the HOMO, and the molecular energy levels
During the measurement, the Fermi energy is kept constant by the grounded source and drain contacts, and the molecular energy levels are shifted with respect to the Fermi energy by the gate induced voltage. When $|V_{GS}|$ is further increased (see Fig. 32 (c)), such that twice as many holes are injected into the film then in the former case, the HOMO level is shifted less than before because there are more states available as the density of states is wider near the Fermi Level. The above description illustrates the relation between the charge concentration and the HOMO shift to the specific shape of the density of states: a low state density results in a larger HOMO shift for a certain increase of hole concentration while at higher state density the HOMO shift is reduced for the same hole concentration increase. We use the transistor structure to control the hole concentration by applying different $V_{GS}$ while we measure the level shift with the KPFM.

Assuming negligible level bending, the shift of the energy levels ($V_L$) for different $V_{GS}$ with respect to the level position at $V_{GS} = V_t$ denoted as $V_{L_t}$, can be
measured directly by the KPFM:

\[ V_L(x) = \text{CPD}(x) - \text{CPD}_t(x) \]

That is, under the above assumption: \( V(x) = V_L(x) \) (see Eq. 4.3 and Fig. 33 (a)). The measured \( V_L \) gives the level shift at the outer organic film/nitrogen interface. In the case of level bending (Fig. 33 (b)), the detected \( V(x) \) at the outer surface does not give information about the level shift across the organic film, perpendicular to the gate, since the level position changes as a function of distance from the gate oxide. In this case: \( V(x) < V_L(x) \).

The hole concentration can be extracted using:

\[ p(x) = -\frac{C_{\text{ox}}}{q d_{\text{org}}} (V_{GS} - V_t - V_L(x)) \]

Eq. 5.2 is based on Eq. 4.2 (where \( V_L(x) = V(x) \)) and it is valid when the charge concentration is homogeneously distributed across the organic film width. Having the holes concentration and the level shift, the hole DOS is then calculated using (appendix B):

\[ g(qV_L(x)) = \frac{C_{\text{ox}}}{d_{\text{org}} q^2} \left( \frac{dV_{GS}}{dV_L(x)} - 1 \right) \]

This analytic expression has no fitting parameters and has a single solution.
5.3 Negligible level bending limit

Our method for DOS measurement is feasible when the energy level bending perpendicular to the gate can be neglected. In addition, the 2-dimentional DOS can be expended to 3-dimensions for approximately homogeneous charge distribution perpendicular to the gate (see appendix B). Here, we examine the validity of these two assumptions by determination of the level bending and charge concentration in an organic film using the numeric simulation that was originally used in section 4.5 to determine $V_r$.

In this section the organic film width in the calculation is $10\text{nm}$ as in the measured samples, and the DOS of the organic semiconductor is modeled by a Gaussian distribution with a width of $\sigma = 4kT$, and a total density of HOMO states of $N_e = 1 \cdot 10^{21} \text{cm}^{-3}$ (these quantities where defined for Eq. 4.7). Whereas for doped organic semiconductor the model was modified as described in appendix A. In this case the dopant (electron acceptors) energetic distribution was modeled by a narrow Gaussian with a width of $\sigma_A = 2kT$ and a total doping concentration of $N_A = 1 \cdot 10^{21} \text{cm}^{-3}$ located $E_A = 0.3eV$ from the HOMO center towards the forbidden

![Figure 34](image_url)

**Figure 34:** Calculated potential distribution for different $V_{GS}$ at the OFET organic film perpendicular to the gate insulator for (a) undoped and (b) doped film with doping concentration of 0.1% from the total molecule density. At $V_{GS} = 3.1V$ and $V_{GS} = 15.0V$, for undoped and doped films respectively, the level bending voltage (the difference between the voltage values at $z = 0\text{nm}$, and $z = 10\text{nm}$) is 5% of the total level shift at $z = 0\text{nm}$ (dashed curve).
gap. The above mentioned parameters where chosen to describe a realistic case based on our measurements and others [54, 114].

In the following we use the numeric calculation to demonstrate that for a certain gate voltage range and a typical parameters chosen to describe the organic film, the negligible level bending and homogenous charge transport assumptions are reasonable. In addition, the simulation provides a better understanding of the channel formation in disordered film.

The calculated potential distribution across the film (i.e., perpendicular to the gate) is presented in Fig. 34 (a) and (b) for different $V_{GS}$ values in the undoped and doped (0.1% from the total molecule density) films respectively. The level bending is negligible with respect to the total level shift (less then 5%) up to $V_{GS} = 3.1V$ for the undoped film, and up to $V_{GS} = 15.0V$ for the doped film. Similar behavior has already been reported elsewhere for undoped films [109,56]. In addition it can be seen that there is a rather distinct transition between the lower gate regime in which the level shift is dominant, to the higher gate voltage regime in which the level bending is dominant. Thus we can assume that for an undoped or doped organic films in an
OFET configuration there is a certain range of $V_{GS}$ in which the energy levels are mainly shifted due to the applied bias and the level bending is negligible.

Figures 35 (a) and (b) show the calculated charge concentration in the organic film as a function of distance from the gate insulator for different $V_{GS}$ values in the undoped and doped cases respectively. The charge concentration is almost constant across the film (i.e., less than 5% difference between $z = 0\, nm$, and $z = 10\, nm$) up to $V_{GS} = 2.8V$ for the undoped film and up to $V_{GS} = 14.6V$ for the doped film. Thus the assumption of approximately constant charge concentration is valid up to a certain $V_{GS}$ which is slightly lower than in the case of negligible level bending.

According to Poisson equation (see Eq. 4.5) a constant charge concentration across the organic film requires a parabolic potential distribution, whereas we assume a negligible level bending or approximately constant potential across the film. However for a parabolic potential curve that is almost linear the two assumptions can hold together. The different gate voltage limits for the two assumptions can stem from the high sensitivity of the charge concentration to small variation in the voltage curve since the charge concentration is proportional to the voltage second derivative in position.

Figures 36 (a) and (b) show the calculated channel width of 90% of the charge as a function of $V_{GS}$ for the undoped and doped films respectively. Above a certain voltage, the charge that forms the conducting channel is squeezed abruptly towards

![Figure 36: Calculated channel width of 90% charge concentration as a function of $V_{GS}$ for (a) undoped and (b) doped organic film with Gaussian DOS. The doping was taken to be 0.1% from the total molecule density.](image-url)
the gate insulator, where in the case of the undoped organic semiconductor the channel narrowing is sharper. The gate voltage that denote the onset of the channel width reduction is somewhat higher than the gate limit for approximately constant charge concentration, and the charge is distributed across the entire organic film width for about $V_{gs} \leq 3.5V$ and $V_{gs} \leq 15.6V$ for undoped and doped samples respectively.

We can offer a tentative explanation for the negligible level bending and approximately constant charge concentration across the organic film in the low $V_{gs}$ regime. In an undoped film, this behavior can be expected for hole occupation of energies with low DOS values where the probability for states available for holes at a certain volume is relatively low, and for these energy regime holes are distributed across the whole film width rather then solely near the gate oxide. In doped OFET our calculations reveal that the charge is spread almost homogeneously over the entire film and the level bending is negligible for even higher gate voltages. In this case, up to a gate voltage of several voltages, a negative gate voltage will cause a shift of dopant-induced holes toward the gate insulator to screen its negative potential (the dopant are already ionized at equilibrium [127] for $\text{LUMO}_{\text{F4-TCNQ}} - \text{HOMO}_{\alpha - \text{NPD}} = 0.28eV$ [114]). This will results in a formation of a region near the nitrogen/organic interface of negative ionized donor that are not screened by the doping induced holes. Consequently, holes will be injected from the contacts into the film region that is close to the nitrogen/organic interface to screen the ionized dopants at this region.

In conclusion, our numeric calculations demonstrate that for organic semiconductor with a Gaussian DOS, up to a certain gate voltage the level bending can be considered as negligible, where the levels tend to shift rather then bend, in addition the charge concentration is almost uniform across the film. Beyond this range of gate voltage the channel thickness is abruptly reduced, and the level shift is small in comparison to the level bending. Note that the fine details of this trend such as the gate voltage limit, and the transition rate between the different trends can be varied by different parameter selection (i.e., different $\sigma, \sigma_A, N_j, N_A, E_A$) however, the phenomena essentially remains the same.

In order to expand the range of gate voltage in which the level bending and charge concentration changes are negligible we have used a rather thin organic film (10nm) but thick enough to sustain energy correlation in 3-dimensions between the localized electronic states that constructs the energy distribution of states. The lateral
energetic correlation is considered to be in the range of a few nanometer either due to steric [131] or electrostatic [65] reasons. In addition it was observed that a sexithienyl film exhibits steady transport properties only above two molecular monolayers. Thus in order to sustain enough percolation pathways for carriers, a film of several nanometers should be used. This enables to obtain an equilibrium condition by carrier transport all over the film. The 10nm thickness is enough for efficient charge injection from the source and drain electrodes as well. [132]

5.4 Density of states measurements

5.4.1 Dopant effects

The inset of Fig. 37 (a) shows the voltage shift, $V_L$, measured across an undoped transistor. The potential of the grounded source and drain appears as the flat portion at each end of the curves, and the potential distribution across the organic channel is seen in between. The curves were measured for $V_{DS} = 0V$ and $V_{GS}$ ranging from 0 to -16.5V. Figure 37 (a) shows $V_L$ measured as described in the inset across the organic film far from the drain and source electrodes, as a function of $V_{gs} - V_{f}^{*}$ for undoped (curve A) and doped $\alpha - NPD$ (curve B). The doping concentration is $1.4(\pm 0.4) \cdot 10^{19} \text{cm}^{-3}$ ($\sim 0.1\%$ of the total molecular density; see Ref. [98] and appendix. C). Each curve is an average of 50 curves measured at different locations on the transistors to reduce the experimental uncertainty. Measurements on different transistors gave very similar results.

The curves for both undoped and doped layers show that the change in $V_L$ is largest at small $|V_{gs}|$, then decreases and finally saturates as $|V_{gs}|$ increases. During this process, the HOMO shifts toward the Fermi energy and holes are injected into available states near the Fermi energy. A low state density results in a larger change in $V_L$ and vice versa; hence, the slope of the $V_L/(V_{gs} - V_{f}^{*})$ curve is inversely proportional to the DOS. It points to an increase in the DOS as the Fermi energy

* $V_{f} = 0.1 \pm 0.1V$ and $V_{f} = 0.8 \pm 0.1V$ as extracted from current-voltage curves taken on the undoped and doped OFETs respectively according to Ref. [111].
Figure 37 (a) Inset: $V_L$ profiles measured across an undoped transistor for $V_{DS} = 0$V and $V_{GS}$ ranging from 0 to -16.5V. (a) $V_L$ as a function of $V_{GS} - V_t$ measured on undoped (A) and doped (B) samples. (b) DOS vs. energy relative to $E_j'$ ($E_j$ at $V_{GS} = V_t$) for undoped (solid triangles) and doped (solid circles) samples. The solid curves are fitting of a Gaussian function (Eq. 5.4; curve A) and an exponential function (Eq. 1.6; curve C) to given ranges in the undoped sample DOS curve, and a fitting of Eq. 5.5 (curve B) to the doped sample DOS curve.
penetrates deeper into the HOMO state distribution, while the fine structure observed on the curves is a result of finer changes in the DOS. The $V_L$ saturation at large enough $|V_{GS}|$ possibly stems from the onset of large level bending near the gate insulator at high charge concentrations, or from the Fermi energy pinning at high DOS.

The DOS vs. $qV_L$ in Fig. 37 (b) is obtained for undoped (triangles) and doped (circles) samples by applying Eq. 5.3 to the data of Fig. 37 (a). The energy scale in Fig. 37 (b) represents the energy relative to $E_f'$ defined as $E_f'$ position at $V_{GS} = V_f$, and the negative sign denotes values below $E_f'$. The sharp increase in DOS near the high-energy end of the curves (left side of Fig. 37 (b)) should be considered as a measurement artifact that reflects the termination of the level shift ($V_L$ saturation as appears in Fig. 37 (a)). While the DOS of the undoped sample has a single peak around $0.408 \pm 0.005 eV$ in the measured energy range, the DOS of the doped sample exhibits several peaks at $(0.356, 0.393, 0.431, 0.456, 0.472, 0.518, 0.534, 0.560, 0.850) \pm 0.005 eV$. These peaks imply the presence of several doping induced energy levels. A variety of dopant configurations, i.e. dopant clusters with various sizes or different configurations of dopant and host-molecules, can lead to local shifts in potential energy and result in several discrete energy levels, as is measured here.

The DOS in the undoped sample can be divided into three main regions: a tail, a single peak around $E = 0.408 \pm 0.005 eV$, and a region that can be fitted to a Gaussian distribution [125] (curve A in Fig. 37 (b)):

$$g_i(E) = \frac{N_i}{\sigma \sqrt{2\pi}} \exp \left[ -\frac{(E - E_c)^2}{2\sigma} \right]$$

Inserting the total state density $N_i = 1.2 \cdot 10^{21} cm^{-3}$ for $\alpha - NPD$ (equivalent to one state per molecule), we find a Gaussian width $\sigma = 0.10 \pm 0.01 eV$ centered at $E_c = -0.84 \pm 0.04 eV$. This width should be considered with care, since the Gaussian function is fitted to a relatively small range of the measured DOS curve, however, it can serve as a guiding parameter that can be applied to an analytical expression that describes the influence of doping on the DOS [127]:

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where \( g_i(E) \) is given by Eq. 5.4, the doping concentration is \( N_A = 1.4 (\pm 0.4) \cdot 10^{18} \text{ cm}^{-3} \), \( a = 0.6 \text{ nm} \) is the distance between a dopant and the nearest intrinsic hopping site [127], \( \varepsilon = 3 \) is the relative dielectric constant of \( \alpha - \text{NPD} \) [19], and \( E_c = -0.88 \pm 0.04 \text{ eV} \) (appeared in \( g_i(E) \), Eq. 5.4). The lateral electric field (i.e., \( F \)) between the source and the drain is considered equal to zero since the drain-source voltage is zero. Eq. 5.5 yields the curve B in Fig. 37 (b), and describes well the main DOS distribution of the doped sample. According to [127], the second term of Eq. 5.5 expresses the shift of states toward the center of the gap due to the presence of dopants; note that its contribution in curve B is observed mostly at \( E \geq -0.49 \text{ eV} \).

Further examination of the measured DOS of the undoped sample reveals a DOS tail at \(-0.38 \leq E \leq 0 \text{ eV}\) that can be fitted to an exponential function [68] (curve C in Fig. 37 (b)):

\[
g(E) = \frac{N_i}{kT_0} \exp \left( -\frac{E}{kT_0} \right)
\]
with a total trap density \( N_t = 3.4(±0.1)\cdot10^{15} cm^{-3} \) and an effective temperature \( T_o = 1350±2K \). In the case of the doped sample, a moderately sloped exponential-like DOS tail, which deviates from curve C, appears at \(-0.31 \leq E \leq 0eV \). The observed flattening and rising of the exponential tail due to doping has been previously described with an analytical model for an exponential DOS tail [133] as shown in Fig. 38 for several choices of dopant concentrations. The described changes point to a DOS broadening due to doping, as was also observed indirectly by other methods [118].

5.4.2 High resolution lateral measurements

KPFM topographic measurements across various transistor regions show a smooth organic film surface, yet concomitant CPD measurements show randomly distributed potential fluctuations in both doped and undoped samples. The inset of Fig. 39 (a) shows such fluctuations in \( V_L \) profile measured across the central region of an undoped transistor channel at \( V_{GS} = -0.1V \). The DOS presented in Fig. 39 (a) is measured at the center of the potential depressions and protrusions (locations a, c, and e in the inset) and at their interfaces (location b, d and f). An additional peak appears at \( E = 0.408±0.05eV \) on the main DOS distribution measured at these interfaces. A possible origin for this additional intensity in the state distribution is the presence of interface states between molecular aggregates with slightly different averaged molecular orientation, leading to differences in the measured CPD. For the doped sample, DOS distributions measured at five different locations (Fig. 39 (b)) show the same distribution of the main peaks with different amplitudes. The additional peak seen in the DOS of the undoped film (Fig. 39 (a)) may be masked by the dopant-induced changes in the DOS of the doped film. The average lateral separation between the dopants is around 10nm; this is less then the KPFM spatial resolution estimated to be tens of nanometers, thus DOS fluctuations in the vicinity of a specific dopant are most likely not detected, and the different peak amplitudes at different locations may stem from changes in the relative contributions of the various dopant energies.
5.4.3 Fermi energy position

The Fermi energy position is subjected to two opposite effects due to the introduction of dopants into the molecular film. According to Bassler et al. [127], holes can be transferred from the dopant LUMO to the host HOMO even if the dopant...
LUMO would be ~ 0.8eV below the dopants HOMO host. This is due to stabilization by Coulomb interactions between ionized dopants and released holes localized in nearby hopping sites. In our case \( HOMO_{host} - LUMO_{dopant} \approx 0.28eV \) [114] and, practically all the dopants are already ionized in equilibrium. As illustrated schematically by Fig. 40 (a) and (b) respectively, the dopant induced increase in the hole concentration, shifts \( E_f' \) from its original position \( (E_f')_a \) towards the HOMO center (position \( (E_f')_b \)). This shift (-0.535eV) was calculated by finding the upper limit \( (E_f')_b \) of an integral on the measured undoped DOS that equals to the dopant induced hole concentration \( p_{doping} \):

\[
(5.6) \quad p_{doping} = N_a = 1.4 \cdot 10^{18} \text{cm}^{-3} = \int g(E)_{undoped}(1 - f_{FD}(E))dE
\]

However, dopants induce a DOS broadening or conversion of shallow states into deep states in the HOMO-LUMO gap as schematically shown in Fig. 40 (c). This effect should shift back \( E_f' \) away from the HOMO center. Based on the fitting of Eq. 5.4 and Eq. 5.5 to the measured DOS, the HOMO-DOS centers of the doped and the undoped samples are located at \( E_c = -0.88 \pm 0.04eV \), and the \( E_f' \) shift between the

**Figure 40:** schematic representation of the chemical potential and the position of the DOS edge for three cases: (a) undoped sample; where ‘0eV’ denotes the \( E_f' \) position at the beginning of the DOS measurement (i.e., at \( V_{GS} = V_c \)) (b) hypothetic case of the undoped DOS populated by the dopant induced holes (states occupied by holes appeared in red) (c) doped sample.
undoped sample to the doped sample is only 34meV away from the HOMO center ($E_{f_c}'$ position). According to this observation, in the studied case, the broadening effect is somewhat more dominant than the effect of hole contribution by the dopants.

The above behavior is unique in the sense that the DOS of crystalline inorganic semiconductors does not change upon similar dopant insertion. Consequently, introduction of p-type dopants causes $E_f'$ to shift towards the valance band. Another difference in the $E_f$ behavior can be seen in Fig. 37 (a), where for the same increase in $|V_{GS}|$ the position of $E_f$ vs. the molecular levels is changed abruptly when the DOS is narrow and moderately when the DOS gets wider. In crystalline inorganic semiconductors the shift of $E_f$ as a function of charge concentration is relatively moderate and monotonic, and the DOS shape does not play a significant role for that matter since even near the band edge, large densities of states are already available.

In conclusion, the KPFM-based method described here allows the direct determination of the DOS distribution in a molecular film and of the influence of doping on this distribution, with a lateral resolution of tens of nanometers. The DOS of the undoped organic film exhibits an exponential-like tail and a more complex structure, including an additional peak at specific physical locations on the film that correspond to interfaces between regions with different surface potential. Doping broadens the DOS and induces several discrete peaks on the main distribution. DOS distributions measured at different lateral positions on the doped samples have similar shape and peak energies, but different peak heights. Introduction of dopants into the organic film change slightly the Fermi energy position with respect to the HOMO center due to two opposite effects on the Fermi energy position: the doping induced additional charge and the broadening of the DOS.
Chapter 6: Generalized Einstein relation

In this chapter we determine for the first time the Einstein relation (ER) at different locations across molecular thin films and examine the effect of doping on its value. We confirm the theoretical predictions for deviation of the Einstein relation from its traditional form in such cases, and compare the detailed structure of the ER with the fine structure of the DOS tail that was described in section 5.4. The findings are discussed in context of non-equilibrium transport.

The generalized ER, which is the relation between the diffusion coefficient and the mobility \( \frac{D}{\mu} \), is very widely used in its traditional form:

\[
\frac{D}{\mu} = \frac{kT}{q}
\]

in the analysis of charge transport in non-degenerated semiconductors and semiconductor based devices. In the case of disordered semiconductors deviation from Eq. 6.1 was measured for amorphous silicon using time of flight measurements [134], and was inferred in the frame of non-equilibrium dispersive transport [77, 81] to account for the unusual current-time characteristics obtained by TOF measurements in both amorphous inorganic and organic semiconductors [135, 136]. In this case the diffusion coefficient and the mobility are not well defined, and are time dependent as explained in section 1.3.3. The influence of disorder and electric field on the ER was further studied by Monte Carlo simulation of hopping transport [137, 138]. Several phenomena, such as the broad rise of the turn-on photocurrent in OLEDs [139], and the temperature dependence of the ideality factor in organic diodes [140], were explained by ER deviations from \( \frac{kT}{q} \) for disordered materials. However, such deviations were also found in crystalline inorganic semiconductors as they become degenerate [28, 141]. In a disordered semiconductor, with distributions of tail states penetrating into the energy gap region, degeneracy effects should be even more pronounced [142]. Accordingly, it has been shown that deviation from the traditional form of ER can be expected under equilibrium condition for disordered semiconductors since they tend to be degenerate [139]. In this case ER depends on the shape of the DOS [139, 142, 143].

For hole current the ER is derived from the current equation:
\[ J_h(x) = q\mu_h p(x)E(x) - qD_h \frac{dp(x)}{dx} \]  

where \( J_h(x) \) is the hole current density, \( \mu_h \) is the hole mobility, and \( D_h \) is the hole diffusion coefficient. At equilibrium, no net current flows in the semiconductor \( (J_h(x) = 0) \) and the relation between \( D_h \) and \( \mu_h \), which is a generalized form of ER, can be obtained \([144]\):

\[ \frac{D_h}{\mu_h} = - \frac{p(x)}{dp(x)} \frac{dV_f(x)}{dV_f(x)} \]

or in more formal presentation, using the fact that a difference in potential between two points is defined as the difference in \(-E^q_f/q\), where \( E^q_f \) is the quazi Fermi level \([139, 140, 144]\):

\[ \frac{D_h}{\mu_h} = 1 \frac{p(x)}{q} \frac{dp(x)}{dE^q_f} \]

Under non-degenerate carrier concentration, the Fermi-Dirac distribution can be approximated to a classical (Boltzman) distribution and the conventional form of Einstein relation, which is presented in Eq. 6.1 is derived \([144]\).

The detailed structure of the DOS should influence the ER through the charge concentration and the position of \( E^q_f \) since:

\[ p = \int_{-\infty}^{\infty} g(E) f_{FD}^h(E)dE \]

such that \( f_{FD}^h(E) \) is the Fermi-Dirac distribution for holes \( (E^q_f(E) \equiv \frac{1}{1 + e^{\frac{E-E_f}{kT}}}) \), and

using Eq. 6.4:

\[ \frac{D_p}{\mu_p} = \frac{1}{q} \int_{-\infty}^{\infty} g(E)\frac{df_{FD}^h(E)}{dE^q_f}dE \]

* For \( q\mu_h pE \approx qD_h \frac{dp}{dx} \) Eq. 6.2 can be regarded as a good approximation.
and for $g(E)$ much wider then $\frac{df_{FD}(E)}{dE_f^q}$:

$$\frac{D_h}{\mu_h} \approx \frac{1}{q} \frac{p}{g(E_f^q)}$$

(6.7)

Thus we can study the ER in view of the charge concentration and the DOS.

**Note:** The sample preparation and experimental setup are described in sections 4.1 and 5.1.

6.1 Einstein relation determination – methodology

Inserting Eq. 5.2 to the generalized form of ER (Eq. 6.3) and enable us to extract the ER from the KPFM measurements of organic thin film transistor as:

$$\frac{D_h}{\mu_h} = \frac{V_{GS} - V_i - V_L(x)}{1 - \frac{dV_{GS}}{dV_L(x)}}$$

(6.8)

The measurements are conducted at $V_{DS} = 0V$, and different $V_{GS}$ values as in section 5 (see Fig. 37 (a) Inset). In this way we can obtain GER as a function of $p$, and the shift of $\mu_{CP}$ from its position at $V_{GS} = V_i$. The measurements are assumed to be under equilibrium condition, since $I_{DS}(x)$ is negligible at $V_{DS} = 0V$, long enough time after setting a new value of $V_{GS}$. $E(x)$ is negligible far enough from the contacts where the organic layer potential is constant.

6.2 Einstein relation measurements

6.2.1 Undoped $\alpha$-NPD

Figure 41 presents the ER that was extracted from measurements on $\alpha$-NPD thin film transistor as a function of charge concentration. This curve is an average of 50 curves measured at different locations on the transistor. Measurements of different transistors
yield similar results. ER is larger then $kT/q$ for the whole range of the measured charge concentration, and its distribution can be divided into three regions: ER increasing for $p < 1.01 \cdot 10^{17} \text{cm}^{-3}$, region B: for $1.01 \cdot 10^{17} \leq p \leq 1.85 \cdot 10^{17} \text{cm}^{-3}$, and region C for $p > 1.85 \cdot 10^{17} \text{cm}^{-3}$.

According to Eq. 6.7 the ER is approximately proportional to the charge concentration divided by the DOS available for the respective $\mu_{cp}$ position, thus the behavior of ER in the above-mentioned three regions can be understood in view of the DOS shape, and the charge concentration extracted from the same measurements. Figure 42 shows the ER (a), the DOS (b), and charge concentration (c) as a function of Energy with respect to $E_f$ position, where regions A, B and C are defined as in Fig. 41. The charge concentration curve, which was calculated using Eq. 5.2, is smoother then the DOS distribution since it is approximately an integral on the DOS up to $E_f$, and therefore less sensitive of the DOS local fluctuations. The charge concentration increases exponentially without substantial differences across the three

Figure 41: (a) ER vs. hole concentration for the undoped organic film. The curve is divided into three regions: region A for $p < 1.01 \cdot 10^{17} \text{cm}^{-3}$, region B: for $1.01 \cdot 10^{17} \leq p \leq 1.85 \cdot 10^{17} \text{cm}^{-3}$, and region C for $p > 1.85 \cdot 10^{17} \text{cm}^{-3}$.
Figure 42: (a) ER, (b) DOS, and (c) hole concentration vs. energy (relative to $E_f$) for the undoped sample. The curve is divided into the same three regions as in fig. 8.3.1/1 while here: at region A $0 > E > -0.377eV$, at region B: for $-0.377 \geq E \geq -0.430eV$, and at region C for $E < -0.430eV$. 
regions, while the DOS has a different behavior at each region, therefore according to Eq. 6.7, the fine structure of the DOS distribution determines the shape of the ER curve. In region A (Fig. 42 (c) and (a)) the slope of the charge concentration, which is the numerator in Eq. 6.7, is larger than the slope of the DOS distribution, which is the denominator in Eq. 6.7, thus the ER increases in this region. The opposite dependence in region C yields a reduction in the ER for energies closer to the HOMO center, and in region B there is a single depression in the ER function due to the single DOS protrusion at the same region.

As is demonstrated above the measured ER is very sensitive to the rich DOS structure. Towards the end of the measured energy region (more negative energy) the ER seems to approach $kT/q$. Thus the transition from relatively flat DOS distribution to steeper distribution reduces the ER deviation from $kT/q$.

6.2.2 Lateral measurements

Utilizing the lateral resolution capability of KPFM we have determined the ER at different locations across the transistor channel. The ER was extracted from the CPD lateral measurements presented in section 5.4.2. As shown in the inset of Fig. 43(a), the lateral CPD measurements revealed randomly distributed potential

**Figure 43:** Inset: $V_L$ profile measured across the channel of an undoped transistor (a) ER measured at different lateral locations across the channel marked as a to f in the inset.
fluctuations. The ER curves in Fig. 43 (a) were measured at the center of the potential depressions and protrusions (locations a, c, and e in the inset) and at their interfaces (location b, d and f). The depression of the ER curve, which is centered at $E = 0.408 \pm 0.05eV$ is measured solely at these interfaces. This feature corresponds to the DOS peak at the same energy (see Fig. 39 (b)), which might be a consequence of interface states between molecular aggregates as suggested in section 5.4.2. The additional feature on the ER curve at specific positions across the thin film is an example for the implication of the energetic disorder on a fundamental transport characteristic, that is the ER.

6.2.3 Dopant effects

Introduction of dopants into the organic thin film widens the DOS distribution by shifting states into the HOMO-LUMO gap, according to the DOS measurements of doped and undoped $\alpha$-NPD films in section 5.4.1, and previous theoretical and experimental works [133, 118]. Since the ER values are affected by the DOS structure one can expect for changes in the ER due to the presence of dopants in the molecular film. In the case of undoped $\alpha$-NPD, the ER deviates from $kT/q$ even for zero space charge region ($V_{GS} = V_i$); this indicates that Eq. 6.1 does not hold and the system is always degenerate for any measured value of hole concentration (i.e., $f_{FD}(E)$ cannot be approximated by the Boltzman distribution) as was also demonstrated theoretically for Gaussian DOS shape [145]. However, it is important to mention that in the general case, a large state density inside the gap due to doping is expected to lead the system into degeneracy even for a relatively large separation between $E_f$ and the HOMO center, simply due to the DOS broadening. At sufficiently high doping concentrations crystalline semiconductors are degenerate as well, however in this case it stems solely from $E_f$ shift toward one of the energy bands due to dopant induced charge concentration, while in disordered organic films both factors (induced charge and DOS widening) play a role.

Figure 44 presents the ER measured on $\alpha$-NPD doped with 0.1% $F_4$-TCNQ as a function of charge concentration; the ER was calculated using:
This equation takes into account also the doping induced charge \( qN_A \) assuming complete ionization \(-\)see section 5.4.3\). In region A of Fig. 44 \( (\rho \leq 2.1(\pm0.4) \cdot 10^{18} \text{ cm}^{-3}) \) a high values of ER appeared followed by a decay of the ER main curve towards \( kT/q \) at region B \( (\rho > 2.1(\pm0.4) \cdot 10^{18} \text{ cm}^{-3}) \); in addition, several peaks on top of the main ER curve appear in this region.

Figure 45 shows the ER (a), DOS (b) and charge concentration (c) as a function of energy with respect to \( E_f' \) position. In region A the ER increases up to \( |E| = 0.15eV \) and then decreases for more negative \( V_{gs} \). These trends originate from the almost flat DOS curve up to \( |E| = 0.15eV \), consequently the increase in the charge concentration determines the ER increase. At \( -0.33 < E < -0.15eV \) the DOS rises towards the negative energies as a relatively moderate exponent that leads to an ER decrease. In region B the sharp increase of the DOS with decreasing energies causes ER decrease, since the charge concentration (an integral over the DOS) increases.

\[
(6.9) \quad \frac{D_p}{\mu_p} = \frac{V_{gs} - V_f - V_L(x) - \frac{qd_{org}}{C_{ox}} N_A}{1 - \frac{dV_{gs}}{dV_L(x)}}
\]
Figure 45: (a) ER, (b) DOS, and (c) hole concentration vs. energy relative to $E_f$ for the doped sample. The curve is divided into the same two regions as in Fig. 44 while here: at region A $0 > E > -0.33 eV$, at region B: for $-0.33 eV \leq E$, and at region C for $E < eV$. 

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slower then the DOS itself. The multiple peaks on the main ER curve in region B demonstrate again how the DOS fine structure is expressed in the ER.

The significant ER divergence from $kT/q$ in the case of doped sample stem from almost flat DOS tail at energies close to $E_f$ (i.e., at energies close to zero in Fig. 45 (a)). Thus the validity and possible origin of the flat DOS tail should be further studied although this behavior is theoretically expected for doped film (see Fig. 38). Similar to the undoped case, the deviation from $kT/q$ is reduced at energies in which the DOS increase is steeper.

6.2.4 Einstein relation in equilibrium and non-equilibrium conditions

We have shown that ER deviations from $kT/q$ under equilibrium conditions can be explained as a consequence of a DOS with a flat tail distribution, whereas local changes in ER as a function of charge carrier concentration (or $E_f$ position) stems from the fine structure of the DOS distribution. The implications of our measurements on ER under non-equilibrium conditions can be examined in view of the CTRW formalism (section 1.1.3).

Recall that the time dependence of the temporal diffusion coefficient and the
temporal mobility are related to the disorder parameter $\alpha$, as appeared in Eqs. 1.21 and 1.23, where the value of $\alpha$ determines the domain of the anomalous diffusion: subdiffusion ($0<\alpha<1$), normal diffusion ($\alpha=1$) and superdiffusion ($\alpha>1$). Scher et al. [77] suggested that the shape of an exponential DOS is related to the disorder parameter in the following way:

\begin{equation}
\alpha = \frac{T}{T_0}
\end{equation}

where $T_0$ is the effective temperature that determines the slope of an exponential DOS as defined in Eq. 1.6.

We will demonstrate the determination of $\alpha$ in the case of an undoped sample since the measured DOS in this case can be approximated to two exponential distributions as shown in Fig. 46. The red curve presents the fitting of Eq. 1.6 to the measured DOS at $-0.377 \leq E \leq 0eV$ with $T_0=1350 \pm 2K$ and thus $\alpha = 0.2170 \pm 0.0007$ while the blue curve presents the fitting of Eq. 1.6 to the measured DOS at $-0.490 \leq E \leq 0.430eV$ with $T_0 = 300 \pm 3K$ and therefore $\alpha = 0.98 \pm 0.01$. Thus we can conclude that the flat exponent fitting implies on subdiffusion conditions and therefore on deviation of ER from $kT/q$ when $E_f$ is in this DOS region, or for charge concentration in the range of $p < 1.01 \cdot 10^{17} \text{ cm}^{-3}$. Above this region the deviation from $kT/q$ is expected to decrease since $\alpha = 0.98 \pm 0.01$ for $E \geq -0.490$ and the system approach normal diffusion condition ($\alpha=1$). The reduction is not abrupt as the flat tail still plays a roll, however new occupied states in the DOS region that give $\alpha = 0.2170 \pm 0.0007$ do not contribute to the subdiffusion behavior and more carriers exhibit normal diffusion as $E_f$ shift to the exponential like DOS region with the higher slope (i.e., at $-0.490 \leq E \leq 0.430eV$). The ER in equilibrium presents similar behavior as a function of $E_f$ as is implied for non-equilibrium condition based on $\alpha$ values. Thus there is a straight relation between ER in equilibrium and in non-equilibrium conditions as both are related to the DOS shape.

In conclusion, using the KPFM measurements conducted on undoped and doped OFETs the ER was determined as a function of the chemical potential position and charge concentration. We have found rich ER behavior and deviations from its
traditional value, $kT/q$; this behavior was explained in view of the measured DOS and charge concentration. Variations in ER were found at specific lateral locations on undoped $\alpha$-NPD film in which interfaces between regions with different surface potential were observed. In the case of doped films, significant deviation from $kT/q$ was found for low gate induced charge concentrations and were explained by relatively flat DOS distribution. The validity of this behavior should be studied. In both cases (doped and undoped films) the ER deviations from $kT/q$ were reduced at higher charge concentrations possibly due to large increase in the DOS available at the chemical potential position as the chemical potential approaches the DOS center. Finally, a good agreement was found between the measured ER in equilibrium conditions and the disorder parameter that determines the nature of diffusion under non-equilibrium conditions as both are related to the DOS shape.
Chapter 7: Conclusions and future trends

This thesis described the study of organic molecular thin films using the KPFM technique. We have shown how the application of KPFM for the study of metal/organic interfaces and operating OFETs can provide new information on the electronic structure of organic films. More specifically we utilized the influence of metallic interfaces, impurities, intentional doping and voltage biased electrodes to induce potential changes that can be probed by the KPFM and shed light on the behavior of organic film energy levels, and density of states.

The important contribution of this thesis can be divided into three main categories:

A. Measurements of the potential distribution across metal/organic interfaces.
B. The study of molecular level response to induced voltage.
C. High resolution spatial determination of the density of states and Einstein relation in undoped and doped organic films.

The findings, their context in a wider perspective and suggestions for future studies are summarized below:

A1. The measured potential across metal/organic/metal structures, revealed the abrupt potential drop across the metal/organic interfaces, the organic film potential response for two metal interfaces with different work functions, and the influence of impurities on the spatial potential distribution (sections 3.2-3.4.). As the examined structure is a simple prototype for OLEDs*, the extracted information provides a first step for a better understanding of the potential distribution across such structures, which is important for improving OLED functionality. The next necessary step would be the determination of potential distribution across such structures under applied voltage between the metal layers, simultaneously with current-voltage measurements. Such a study will enable extensive characterization of organic films electronic properties in OLED-like structures. For example, using the appropriate metals to have a favored injection of a single type of charge carriers (i.e., electrons or holes) the carrier

* The used layered structures are wider than typical OLEDs as was required due to the limit of tens-nanometer lateral resolution of the KPFM measurements.
mobility can be extracted as a function of lateral electric field, charge concentration, and location.

A2. Based on numerical analysis, we calculated the broadening effect introduced by the tip for KPFM measurement on samples that exhibit large potential and topographical changes (section 3.3). This analysis expanded our understanding for the limitation of the KPFM as a measurement tool for interfaces, and regions with sharp potential and topography height changes in general. Consequently, during our work with OFETs we have modified the OFETs structure to reduce the electrostatic effect of the protruding drain and source electrodes on the probing tip while sustaining an efficient carrier injection. In order to reduce the electrostatic tip effects in future measurements of different sample structures, a deep understanding of data potential distribution between the tip and sample is required. Thus tip-sample electrostatic simulations should be further developed. The use of KPFM measurements can be extended to regions with large potential change by applying deconvolution techniques to extract the surface potential from the distorted measured potential. For example, this will allow more reliable study of charge injection near electrode interfaces.

B1. We have developed a new method to determine the threshold voltage by KPFM (section 4.2). Since this method overcomes the problem of the current detection by measuring the onset of the gate screening by charge accumulation in the channel, the method can be used as a standard way for threshold voltage determination while studying OFETs with KPFM. Furthermore, the proposed method provides a tool for local detection of the channel formation at any lateral point across the transistor channel. Thus it can be used in the future for studying percolation paths for charge carrier transport across organic films.

B2. Using KPFM for direct detection of the OFET pinch-off voltage we have measured the threshold voltage as a function of the gate voltage, which gives the gate induced molecular energy level shift at the gate-oxide/organic interface (sections 4.3-4.5). This method utilizes the combination of OFET and KPFM in order to expand the use of KPFM, which is a surface probing technique to detection of potential at sub-surface interfaces. Practically, this study provides an important evidence for
“effective” threshold voltage at each gate voltage, which should be taken into consideration in the development process of OFETs and OFET based electronic circuits, since it can crucially affect their performances. From experimental consideration, the unique threshold voltage behavior should be considered while analyzing OFETs.

**B3.** The comparison between the measured threshold voltage as a function of gate voltage and calculated threshold voltage extracted from numerical simulation based on different DOS distributions, revealed a deviation from a simple Gaussian distribution of the holes DOS. This provided indirect, however significant, evidence for the oversimplification of the DOS distribution used for modeling charge carrier transport and in organic films. This study presents an essential relation between a technological device parameter: the threshold voltage, and a basic physical parameter: the DOS, which expends the physical understanding of organic films electronic behavior and hopefully will enable more efficient OFET development. The relation between gate induced charge, molecular level shifts, and the organic film DOS was realized during this project and later was utilized for the determination of the DOS distribution.

**C1.** Numerical simulation revealed a low gate voltage range in which the level bending perpendicular to the gate electrode is negligible for undoped and doped organic films. This behavior was reported before (section 5.3) for undoped organic films and could be expected for DOS with a long tail distribution as explained in the relevant section. In the case of doped film, the origin of this behavior is not fully understood by us and should be further investigated. The transition between negligible and substantial level bending is accompanied with fast reduction in the charge carrier channel width. This behavior expands the understanding of carrier channel formation, which is important from technological considerations. Future experimental study of the above mentioned behavior is necessary in order to gain comprehensive understanding of the simulation observed phenomena. For example, comparison between threshold voltage shift and surface potential shifts (i.e., $V_L$) measured on organic film with the same width as a function of gate voltage, gives the molecular

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* Effective threshold voltage - in the sense that the threshold voltage in not merely the flat level voltage.
level shifts at the gate-oxide/organic and organic/nitrogen interface respectively. The difference between these shifts at the opposed interfaces of the OFET’s organic film yields the level bending voltage drop across the organic film (far from the drain and source electrode) as a function of the gate voltage. Thus allow direct comparison to our simulation.

**C2.** We report on a determination of the detailed shape of the DOS relevant to hole-transport in molecular films. In the case of undoped amorphous \( \alpha-NPD \), a more complicated DOS structure then the commonly assumed Gaussian (or exponential) was revealed, including an anomalous peak observed at specific sites located at interfaces between regions of different surface potential (section 5.4). Since the DOS distribution shape is related to many electronic properties and there is a very limited knowledge on the DOS shape, such a determination is of fundamental importance both from scientific and technological considerations. Furthermore, the lateral fluctuations in the DOS provide a direct evidence for a lateral energetic disorder. In the future, the above (C1) proposed comparison between the threshold voltage and \( V_L \) on the same transistor can support these results. It is important to stress that the measured DOS in OFETs with thin organic films is expected to be substantially affected by interfacial properties. Thus future examination of interfacial effects on the measured DOS is important, and can be conducted for example as a function of different chemical treatments applied to the gate oxide, or different types of molecular monolayer adsorbd on the oxide. In addition it would be of great importance to compare between mobility measurements as a function of charge concentration and calculated mobility based of our measured DOS.

**C3.** We have used the DOS measurement technique to study the influence of dopants on the DOS shape. We revealed a doping-induced broadening of the DOS, which is in agreement with theoretical predictions and indirect evidences for DOS broadening. Moreover we detect several doping-induced sharp peaks on the main DOS distribution, which might be ascribed to different doping levels (section 5.4.1), and observed that the position of the chemical potential at flat level condition is shifted towards the forbidden gap due to the DOS broadening in contrast to the case of crystalline inorganic semiconductors (section 5.4.3). These results provide better understanding of the origin of the DOS distribution. From technological
considerations, as evident by the measured doping effect on the DOS, any addition of doping or presence of impurities that act as dopants have a substantial effect on the DOS and consequently on other electronic properties (e.g., chemical potential position). Future DOS measurements of a specific organic layer with several different doping concentrations is expected to provide additional information on the doping effects such as internal screening effects, and a better understanding of the used DOS measurement technique.

**C4.** Based on the DOS measurements on undoped and doped films, we extracted the ER at different locations across the molecular films, and have found an agreement with theoretical predictions for deviation of the Einstein relation from its traditional form in the studied case. These results demonstrate the implication of the DOS shape on related factors. The deviation in ER should be taken into consideration with relation to charge transports and level bending in organic films. Consequently these finding has a direct influence on the performance of organic device. Since this is the first measurement of ER on organic films, our findings should be confirmed in the future by different methods for GR measurements.

In conclusion, the application of the KPFM method on organic film structures provided new and unique information on key factors related to the electronic structure of organic films and organic based devices.
Appendix A: Numeric simulation model of doped organic field effect transistor

In section 4.5 the level bending, charge concentration and channel width in OFET were calculated using the numeric simulation presented in chapter 4. Here we present the necessary modifications for accounting doped OFET.

In section 4.5 the calculation was based on the following equations:

The Poisson equation:

\[
\frac{d^2V(z)}{dz^2} = -\frac{qp(z)}{\varepsilon_0\varepsilon_{sc}}
\]

where the hole concentration is given by:

\[
p(z) = \int (1 - f_{id}(E)) g_i(E) dE
\]

and the DOS is given by a Gaussian distribution:

\[
g_i(E) = \frac{N_i}{\sigma \sqrt{2\pi}} \exp \left\{ -\left( \frac{E}{\sqrt{2}\sigma} \right)^2 \right\}
\]

Thus:

\[
\frac{d^2V(z)}{dx^2} = -\frac{q}{\varepsilon_0\varepsilon_{sc}} \cdot \left[ \frac{N_i}{\sigma \sqrt{2\pi}} \int_{-\infty}^{\infty} \frac{dE}{1 + \exp \left( \frac{V(z) + E}{kT} \right)} \exp \left( -\frac{E^2}{\sqrt{2}\sigma^2} \right) \right]
\]

In the case of doping with acceptors an additional narrow Gaussian distribution of the dopants \( g_A(E) \) is added to Eq. A.1:

\[
\frac{d^2V(z)}{dx^2} = -\frac{q}{\varepsilon_0\varepsilon_{sc}} \cdot \left[ \frac{N_i}{\sigma \sqrt{2\pi}} \int_{-\infty}^{\infty} \frac{dE}{1 + \exp \left( \frac{V(z) + E}{kT} \right)} \exp \left( -\frac{E^2}{\sqrt{2}\sigma^2} \right) - N_A + \int_{-1}^{\infty} \frac{dE}{1 + \exp \left( \frac{V(z) + E}{kT} \right)} \cdot g_A(E) \right]
\]

Eq. A.2 can be reduced to first order differential equation utilizing the following two equalities:
\[
\frac{dV}{dz} \frac{d^2V}{dz^2} = \frac{1}{2} \frac{d}{dz} \left( \left( \frac{dV}{dz} \right)^2 \right)
\]

(A.3)

and:

\[
- \frac{q}{\varepsilon_0 \varepsilon_{sc}} \frac{N_A}{\sigma \sqrt{2\pi}} \int_{-\infty}^{\infty} \frac{dV}{dz} \exp\left(-\frac{E^2}{(\sqrt{2}\sigma)^2}\right) dE =
\]

\[
- \frac{q}{\varepsilon_0 \varepsilon_{sc}} \frac{N_A}{\sigma \sqrt{2\pi}} \int_{-\infty}^{\infty} \left(V(z) - kT \ln \left[1 + \frac{qV(z) + E}{kT}\right]\right) \exp\left(-\frac{E^2}{(\sqrt{2}\sigma)^2}\right) dE
\]

(A.4)

to have:

\[
\frac{dV(z)}{dx} = \left[ K + \frac{2q}{\varepsilon_0 \varepsilon_{sc}} V(z) - \frac{2q}{\varepsilon_0 \varepsilon_{sc}} \int_{-\infty}^{\infty} \left(V(z) - kT \ln \left[1 + \exp\left(\frac{V(z) + E}{kT}\right)\right]\right) \exp\left(-\frac{E^2}{(\sqrt{2}\sigma)^2}\right) dE - \frac{N_A}{\sigma \sqrt{2\pi}} \exp\left(-\frac{E^2}{(\sqrt{2}\sigma)^2}\right) - \frac{N_A}{\sigma \sqrt{2\pi}} \exp\left(-\frac{(E - E_A)^2}{(\sqrt{2}\sigma_A)^2}\right) \right]^{1/2}
\]

(A.5)

here the dopant distribution is:

\[
g_A(E) = \frac{N_A}{\sigma_A \sqrt{2\pi}} \exp\left(\frac{(E - E_A)^2}{(\sqrt{2}\sigma_A)^2}\right)
\]

(A.6)

where \( N_A = 1.4 \times 10^{18} \text{ cm}^{-3} \), \( \sigma_A = 0.3 \text{ eV} \), \( E_A = 0.3 \text{ eV} \) these parameters were chosen to be as close as possible to our studied case. Eq A.5 is then solved numerically in a similar way to Eq. 4.9 in section 4.5 by the following boundary conditions:

\[
(4.10) \quad (dV / dz)_{z=d_{org}} = 0
\]

and:

\[
(V)_{z=0} = V_0
\]

where \( V_0 \) is the potential at the oxide/molecular film interface, and \( d_{org} \) is the film thickness. \( K \) and \( V_0 \) are chosen to satisfy the boundary condition of the electric field being zero at the edge of the molecular layer. \( V(z) \) is given by Eq. A.5, \( p(z) \) is calculated by Eq. 4.6 and the width of 90% of the charge concentration by finding the \( z \) that gives 90% of the total charge in the film.
Appendix B: Extraction of density of states

The charge concentration is given by:

\[ p = \int_{-\infty}^{\infty} g(E) f_{FD}(E) dE \]  

(B.1)

Since \( E'_f \) is the Fermi energy level position at \( V_{gs} = V_t, V_{ds} = 0V \), then \( qV_L \) is the shift in the quasi Fermi level \( E'^q_f \) with respect to \( E'_f \) (recall that \( qV_L \) also equals to the electronic level shift with respect to their position at \( V_{gs} = V_t, V_{ds} = 0V \)). After derivation by \( V_L \) we have:

\[ \frac{dp}{dV_L} = \int_{-\infty}^{\infty} g(E) \frac{df_{FD}(E)}{dV_L} dE \]  

(B.2)

in this presentation Fermi-Dirac distribution is given by:

\[ f_{FD}(E, V_L) = \frac{1}{1 + \exp \left( \frac{E - E'_f - qV_L}{kT} \right)} \]  

(B.3)

and its derivation by \( V_L \) is:

\[ \frac{df_{FD}(E, V_L)}{dV_L} = \frac{q}{kT} \frac{\exp \left( \frac{E - E'_f - qV_L}{kT} \right)}{\left[ 1 + \exp \left( \frac{E - E'_f - qV_L}{kT} \right) \right]^2} \]  

(B.4)

when the width of \( \frac{df_{FD}}{dV_L} \) is much narrower relative to that of \( g(E) \) it can be approximated by a \( \delta \) function:

\[ \frac{\exp \left( \frac{E - E'_f - qV_L}{kT} \right)}{\left[ 1 + \exp \left( \frac{E - E'_f - qV_L}{kT} \right) \right]^2} = \delta \left( \frac{E - E'_f - qV_L}{kT} \right) \]  

(B.5)

Inserting (D/4) and (D/5) to (D/2) we get:
(B.6) \[ \frac{dp}{dV_L} = \frac{q}{kT} \int_{-\infty}^{\infty} g(E) \delta \left( \frac{E - E_f' - qV_L}{kT} \right) dE \]

Using:

(B.7) \[ \delta \left( \frac{x}{a} \right) = a \delta(x) \]

we have:

(B.8) \[ \frac{dp}{dV_L} = q \int_{-\infty}^{\infty} g(E) \delta(E - E_f' - qV_L) dE \]

and applying:

(B.9) \[ \int f(x) \delta(x - a) dx = f(a) \]

we have:

(B.10) \[ \frac{dp}{dV_L} = q g(E_f' + qV_L) \]

Thus the DOS as a function of \( qV_L \) is:

(B.11) \[ g(E_f' + qV_L) = \frac{1}{q} \frac{dp}{dV_L} \]

Finally we apply Eq. B.11 on Eq. 5.2 \[ p(x) = -(C_{ox} / qd_{org})(V_{GS} - V_t - V_L(x)) \] to have Eq. 5.3:

(B.3) \[ g(qV_L(x)) = \frac{C_{ox}}{d_{org} q^2} \left( \frac{dV_{GS}}{dV_L(x)} - 1 \right) \]

where we define \( E_f' \) position as zero
Appendix C: Determination of doping concentration

In an undoped OFET the conductivity is zero unless charge carriers are injected to the organic film by the applied gate-source bias. In the cases of doping in the organic layer, dopant induced carriers lead to a finite bulk current in the organic film given by:

\[ I_{DS_{Bulk}} = qN_A \frac{W}{L} \mu d_{org} V_{DS} \]

for the case of p-type doping at \( V_{GS} = V_t \). Recall that \( N_A \) is the acceptor doping concentration, and \( d_{org} \) is the organic film thickness.

Figure 47 shows the \( I_{DS} - V_{GS} \) characteristics of a polymer based thin-film transistor with ring geometry as a function of air induced p-type doping. The curve taken under vacuum condition shows a typical \( I_{DS} - V_{GS} \) behavior of undoped OFET while in case of doping, the additional contribution of the bulk current to the total current is manifested in the \( I_{DS} - V_{GS} \) curve as an additional “shoulder” towards positive values of \( V_{GS} \) (the additional curve shifts to the right stem from doping induced \( V_t \) shift). As \( V_{GS} \) is raised beyond \( V_t \) the conduction channel is in OFF state and the current, which is solely a bulk current, is decreasing due to formation of a depletion layer that reduces the hole concentration. The bulk current is nullified when the depletion width \( (W_{dep}) \) matches \( d_{org} \). In this case, all the dopant induced holes are injected out from the organic film.

For a small source-drain field we assume that the depletion of the semiconductor takes place uniformly over the entire channel length and that the dopants are uniformly distributed throughout the semiconductor layer. The depletion layer width in a doped semiconductor is given by [28]:

\[ W_{dep} = \varepsilon_0 \varepsilon_{org} \left( \sqrt{1 + \frac{2C_{ins}^2 (V_{GS} - V_t)}{qN_A \varepsilon_0 \varepsilon_{org}^2} - 1} \right) \]

and the insulator capacitance per unit area is:

\[ C_{ins} = (\varepsilon_0 \varepsilon_{ins}) / d_{ins} \]

The current drops to zero once the depletion layer extends across the entire organic
film. If we know the gate voltage at which it happens we can use Eq. C.2 and C.3 to derive the dopant density ($N_A$) under the condition $W_{dep} = d_{org}$:

\begin{equation}
N_A = \frac{2(V_{PO}^{dep})\varepsilon_0}{q\left(d_{org}^2 + \frac{2d_{org}d_{ins}}{\varepsilon_{org}/\varepsilon_{ins}}\right)}
\end{equation}

where $V_{PO}^{dep} = V_{GS}\big|_{I_{dV}} - V_t$.

\textbf{Figure 47:} OFET transfer characteristics as a function of time in 10mbar air in dark. Taken from Ref. [98].
Bibliography

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ארוך טל
ה novità עם כלת החנה "דוקטור פילוסוף"

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בכרך פרמי גוסה רוזנבויק
כسن תשמ"ח
עבודה ו нескחת הנדרכת
פropolis יוסי רונהוכס
תקציר

המלהמה של מוליכים למוליך מתוארת בגאמה אינפראונדרית ומופיעה בצורת שני גלונים - אינפראונדרי אינפראונדרי למוליך גביש לערב.

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מ״ה ב׳." ו׳ ג׳ מ׳ ת׳ ק׳ (במקהל של שיבתה ארגרות מороות, התחהלת החתחה והחElapsedTimeות של גפונות המגאביקומ הסורים וה��ובים על התפקדות המרכזים המרכזים [ותן ת￡ה אאמרerg ברמות.
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