Abstract

JAFARIPAZOKI SARA. Obstacles for Carrier Transport in Organic Semiconductors: Study of Dynamic Disorder and Morphological Degradation. (Under the direction of Dr. Daniel Dougherty.)

Organic semiconductor devices have been an exciting technology due to their fantastic features such as mechanical flexibility and biocompatibility. However, organic devices are still limited in their performance. In order to improve the performance of organic devices, we need to better understand factors limit charge transport in these devices. This dissertation focuses on obstacles for obtaining a high carrier transport in organic semiconductors. Dynamical disorder which an important factor in determining charge transport was considered from a molecule in a highly order film to a fluctuating boundaries. Scanning tunneling microscopy (STM) has been a highly beneficial tool for measuring disorders impact a system. Morphology of organic films in devices was investigated in detail.

The amount of disorder in an organic semiconductor film is one of the crucial factors in determining the carrier mobility of organic devices. Therefore, it’s very important to be able to quantify disorder in organic films. In the initial research, the effect of dynamic and static disorder in fullerene system at metal-organic interface was studied using STM. We observed a reduced dynamic disorder due to the constraint of organic molecules at metal-organic interface.

To continue research on obstacles for obtaining a high carrier density in organic devices, organic field effect transistors (OFETs) were made with a promising organic molecule of 2,7-dioctyl[1]benzothieno[3,2-b][1]benzothiophene (C8-BTBT). The morphology of devices was investigated using atomic force microscopy (AFM) and kelvin probe force microscopy (KPFM). Transistors’ characterization was performed through the output characteristics and transfer
curves using a probe station and keithley 4200. We observed a thickness dependence of mobility due to degradation of organic film during contact deposition.

As the final research in this dissertation, dynamical disorder in the domain boundaries of C8-BTBT organic molecules was considered. The fluctuations of C8-BTBT domain boundaries were monitored by STM and analyzed using power spectral density and interface scaling concept. The analysis indicates trapping and releasing the molecules in the domain boundaries.
Obstacles for Carrier Transport in Organic Semiconductors: Study of Dynamic Disorder and Morphological Degradation

by
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Dedication

To my family
Biography

Sara Jafaripazoki was born on September 21, 1990 in Tehran, Iran. Her interest in physics began in high school, when she read book of Fundamentals of Physics by Halliday in addition to her textbooks. She received her Bachelor of Science in physics from K. N. Toosi University of Technology in Tehran in 2012 and started her master program after her graduation at the same university. She received her Master of Science in physics in 2015 and that same year was accepted to the physics PhD program at NC state. She traveled to the United States in August 2015 and started her PhD program at the same time. She joined Dougherty group in 2016. Her research focused on charge transport in organic semiconductors.
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I would like to thank my parents and my brother and sister for their love and support. They always encourage me to overcome difficulties during my life. Without their support, I would not have been able to achieve any success. I would also like to thank my husband, Dr. Reza Rashetnia for his support, encouragement and love. He has always had my back during my stressful times.

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Chapter 1

Introduction, Background and Motivation for Organic Electronics

Electronics is a branch of science which studies the motion and behavior of electrons in vacuum and matter. Progress in the field of electronics leads to invention of electronic devices that have revolutionized our life since the last century. Organic Electronics is the application of organic chemistry in the electronic devices. Since organic materials have different properties than conventional inorganic one, many researches have been focused in organic electronic devices. In my research, I studied the factors that limit charge transport in organic semiconductor devices. Among these factors special attention is paid to the existence of disorders in organic films. In my research, I considered different type of disorders can exist in an organic thin film. Another major problem in organic electronic devices, which studied in this research is contact issue. The electrode in organic devices usually make a poor contact with the semiconductor film and causes problems with charge injection to semiconductor films. My goal in this research is to better understand the problems in organic electronic devices in order to improve the performance of devices in future.

1.1: Organic Semiconductors

Semiconductors are a class of material that have conductivity between an insulator and a metal. In fact, semiconductors are insulators at zero kelvin. Since the Fermi level of a semiconductor is within a small band gap, the bands can be shifted with an electrical, thermal, or photonic energy to control electrical properties. The ability to conduct electricity under some circumstances (and not all the time) enables us to control the electrical current in electronic devices. Silicon and Germanium are examples of inorganic semiconductor that are traditionally
used in electronic devices such as transistors. Recently, it has been found that organic semiconductors can also be used in electronic devices for certain specific applications like high-quality, large area displays.

Organic Semiconductors are mainly composed of carbon atoms and are categorized into two groups: small molecules (or oligomers) and polymers. The former have carbon atoms in rings and are usually processed in vacuum. The latter have carbon atoms in long chains which repeat a subunit called a monomer and are usually processed with wet chemical techniques. Thus, unlike inorganic semiconductors, organic semiconductors can be processed at a relatively low temperature. This might reduce the fabrication expense and opens up the possibility of having these materials on flexible substrates which lead to emergence of flexible electronic devices [1, 2].

An important feature that causes organic crystals to have unique properties among other materials is a weak intermolecular bond. In fact, the weak Van der waals intermolecular bond in organic materials ($E_{vdw} \approx 10^{-2}-10^{-3}$ eV) are much smaller than covalently bonded inorganic crystal ($E_{cov} \approx 2-4$ eV) or an ionic lattice ($E_{ion} \approx 4-10$ eV). This weak intermolecular interaction causes only a small change in the electronic structure of molecules in the lattice so molecules in the crystal maintain most of their identity. This is much different that covalent or ionic crystals in which constituent particles are strongly bonded together so the bulk properties of covalent or ionic crystals are different than their constituent particles [3].

To further understand the electronic properties of carbon atom and its impact on organic molecules, let’s consider the electronic configuration of carbon atom in the ground state which is $1s^22s^22p^2$. Depending on molecular geometry, this atomic configuration can result in $sp^2$ hybrid
orbitals involved in chemical bonding within a molecular plane that turns out to be very relevant
to many organic semiconductors. Alternately, it can result in sp$^3$ hybrid orbitals that give rise to
a nonplanar bonding network. Carbon in this sp$^3$ configuration has four tetrahedral chemical
bonds to ligands around the atom. These single bonds are called sigma (σ) bonds. Alkanes with
general formula of C$_n$H$_{2n+2}$ are the examples of this kind of hybridization. In this case, the
electrons of carbon atom are localized. Therefore, alkanes are insulators.

A delocalized situation forms in sp$^2$ hybridization when we have 3 σ bonds formed by
overlap of the Sp$^2$ hybrid orbitals on adjacent atoms and also a pi (π) bond that results from the
remaining unhybridized p orbital. Benzene is an example of this kind of hybridization. Figure
1.1a shows two resonance forms of benzene. The 2s, p$_x$, and p$_y$ orbitals are hybridized and each
forms a sigma bond in the plane of the molecule. On the other hand, the p$_z$ orbitals of each
carbon atom are perpendicular to the plane of sp$^2$ hybridization. In this situation, the p$_z$ orbitals
of neighboring carbon atoms overlap and create a delocalized electron density above and below
the plane of carbon atoms (Figure 1.1b) [4, 5]. The delocalized π bonds in benzene can move
from one atomic site to the other one whereas the σ bonds are always fixed between carbon
atoms. Figure 1.1c represents how to show the cloud of π bonds in benzene.

![Image of benzene resonance forms and π bonds](image)

Figure 1.1: a) Two resonance forms of benzene b) p$_z$ orbitals in benzene c) depiction of
benzene structure. Images adopted from [1, 5] of chapter 1.
The molecules with delocalized \( \pi \) bonds are referred as conjugated molecules and classified as semiconductors. As mentioned above, benzene only has 2 defined resonances which are equal in energy. Larger molecules have much more resonance forms that some of them are more energetically favorable than others. One can calculate the energy levels of a conjugated molecule by considering \( \pi \) electrons as the particles and the molecule as the box. The energy levels of an isolated molecule are discrete and are known as molecular orbitals. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) known as the frontier orbitals are two important molecular orbitals for an organic semiconductor [1].

In reality, the energy levels of an organic molecule in a crystal don’t have discrete values and are broadened due to different reasons. For example, in large molecules, different segments of the molecule can have a little bit different band gap [6]. Even the weak intermolecular interaction in a crystal can have an impact on energy level of molecules [1]. Another point to notice is that molecules in a crystal can have different orientations which result in different energy levels [2]. So, the energy levels of the whole crystal can also be spread out.

In organic semiconductors HOMO and LUMO correspond to valence and conduction band in inorganic semiconductors respectively. Like other semiconductors, which previously discussed, the band gap in organic semiconductors is small so that the Fermi level can be shifted into one of the bands. In organic semiconductor, usually this manipulation of the Fermi level occurs only by applying an electric field. In inorganic semiconductors, the Fermi level is usually manipulated by doping, forming two type of inorganic semiconductors; N-type and P-type. Doping dramatically increases the conductivity of an intrinsic semiconductor. If the dopant contributes free electrons to the crystal lattice, the crystal lattice is classified as an N-type
semiconductor. If the dopant results in deficiencies of electron in valence band and creates holes, the crystal is classified as a P-type semiconductor. So, in N-type semiconductors, there are energy levels near the conduction band so the electrons can be easily exited to the conduction band and in P-type semiconductors, there are energy levels near the valence band and electrons in valence band can be exited into those levels and leave holes behind in the valence band. Therefore N-type and P-type in inorganic semiconductor has an extrinsic origin.

Organic semiconductors are also classified into two type: N-type and P-type. However, there is totally different physics behind the concept of N-type and P-type in organic semiconductors. All organic semiconductors are intrinsically semiconductors and distinction between N-type and P-type is made by comparing the HOMO and the LUMO of an organic semiconductor with the Fermi level of a metal (usually the metals that are traditionally used as the electrodes in devices). In fact, in N-type (P-type) organic semiconductors, the LUMO (HOMO) level is close to the Fermi level of the electrode and electrons (holes) can be easily injected from the electrode to the organic semiconductor. Thus, a more appropriate designation for organic semiconductors is sometimes considered to be “electron donors” (analogous to p-type) or “electron acceptors” (analogous to n-type) to indicate the tendency for charge transfer to an electrode or other molecule.

Figure 1.2 shows two examples of organic molecule: C\textsubscript{60} which is an electron donor and C8-BTBT which is an electron acceptor organic molecule. C\textsubscript{60} has one of the highest symmetries among other molecules. It has the shape of a truncated icosahedron like a soccer ball. One important point worth mentioning here is that controlling and manipulating the position of molecules on the surface have been one of the research interests in solid state physics [7]. This manipulation has been done using scanning tunneling microscopy (STM). C\textsubscript{60}, due to its
symmetry, has been the subject of many early studies to manipulate its position [8, 9] and study its motion on the surface [10].

2,7-dioctyl[1]benzothieno[3,2-b][1]benzothiophene or C8-BTBT molecule has benzene and thiophene rings at its center. Recently the organic transistors made with C8-BTBT proved to have a very good performance among other material [11]. The devices made with even a single layer of this molecule showed a mobility higher than \( 30 \frac{cm^2}{Vs} \) with resistance of 100 \( \Omega \) [12]. This is the highest reported mobility value for a 2D organic field effect transistor.

![Figure 1.2: Model structure of a) C60 b) C8-BTBT organic molecule.](image)

### 1.2: Organic Semiconductor Devices

Organic electronic devices are not viewed as a replacement for conventional inorganic devices based primarily on Si. In fact, they are designed to be a supplement to the existing silicon-based electronics. Apart from industrial application such as flexible displays, electronic paper, and sensors, organic electronic devices enable us to study electronic and optical properties of organic semiconductors. Three important organic electronic devices have been used in researches are organic field effect transistors (OFETs), organic light emitting diodes (OLEDs), and organic photovoltaic (OPV) solar cells.
An OLED is an electroluminescent device, made with three different organic layers that are sandwiched between two electrodes: an anode and a cathode (Figure 1.3). These organic layers are called hole transport layer (HTL), emissive layer (EML), and electron transport layer (ETL). In an OLED, at least one of the electrodes must be transparent to allow the light to escape out of the device. By applying a bias, electrons and holes respectively are injected from the cathode and anode and migrate from the ETL and HTL to EML. Inside the EML, electrons and holes pair up to form tightly bound pairs called excitons. Finally, excitons decay and release energy either radiatively to produce vibrant, visible colors, or nonradiatively as heat through molecular vibrations and other quenching process [13, 14].

An organic solar cell uses the photovoltaic effect which is the reverse process of electroluminescence. The photovoltaic effect refers to the process in which exposure to light creates electrical current in a material. An organic solar cell can be made in the form of a bilayer diode consisting a P-type (donor) and an N-type (acceptor) semiconductor. Light enters a solar cell through a transparent electrode (usually indium-tin oxide) and creates excitons in one of the semiconductor layers. Then excitons travel to the donor-acceptor interface and dissociate into
separate charges and these charges lead to electrical current to the sides of the bilayer. Figure 1.4a shows device structure of a bilayer solar cell (also called flat/planer heterojunction). One major problem of flat heterojunction solar cells is their efficiency. Excitons must travel through the semiconductor layer to reach the donor-acceptor interface to be split. During this process, diffusion and relaxation are competing and as a result, the thickness of the semiconductor layer play an important role. By reducing the thickness of the semiconductor layer, the number of harvested excitons decrease compared to the amount of incident photons in a bilayer solar cell, therefore the efficiency of the solar cell reduces. In order to overcome this issue, the planar arrangement can be changed into a volume structure by blending donor and acceptor to form a bulk heterojunction solar cell [5]. Figure 1.4b represents the structure of a heterojunction solar cell.

In OLEDs and OPV solar cells both optical and electrical properties of the semiconductor layer are important for determining the efficiency of devices. However, in OFETs only transport properties of the semiconductor layer are of interest. Since an important part of my research was involved with OFETs, the next section describes organic transistors in significant detail.

Figure 1.4: A device structure of a) a bilayer (flat/planer heterojunction). b) a bulk heterojunction. Adopted from [5] of chapter 1.
1.3: Organic Field Effect Transistors

A field effect transistor is an electronic device that uses an electric field to control the amount of charges in the active layer of the device. In an organic field effect transistor (OFET), the active layer is an organic semiconductor material. The organic layer has two electrodes (called the drain and source electrodes) at each side. The drain and source electrodes inject and deplete charges from the semiconductor layer. A third electrode (called the gate electrode) which is separated from the semiconductor by a dielectric layer, adjusts the amount of charges inside the semiconductor layer [15].

An OFET can be designed in 4 different structures depending on the purpose of application. These four structures are: bottom gate, bottom contact (BGBC); top gate, top contact (TGTC); bottom gate, top contact (BGTC); and top gate, bottom contact (TGBK). The first two are categorized as coplanar and the second two are referred as staggered geometry. Each of these configurations has its own advantages and disadvantages. For example, TGTC and TGBK do not
expose the semiconductor layer to ambient conditions and are useful when the organic semiconductor layer is air sensitive. However, BGBC is more helpful for quick measurement of new semiconductor materials. Another factor to notice is the difference between staggered and coplanar geometry. In staggered geometry, charges are injected along the electrode surface parallel to the channel because there is an offset between dielectric-semiconductor interface and the drain and source electrodes. In this situation, contact resistance is different from coplanar geometry which doesn’t have that offset [16].

By comparing the Fermi level of the drain and source electrodes with the frontier orbitals of the semiconductor, we note the existence of two kinds of OFETs: N-type and P-type semiconductor OFETs. Figure 1.6 presents the energy diagram of these two kinds when the transistor is off and on. The energy levels of the semiconductor and the Fermi level of the

Figure 1.6: Energy diagram for an N-type and a P-type OFET when a) no bias is applied, b and c) Gate voltage is applied with no drain voltage, d and e) both gate voltage and drain voltage are applied and the transistor is on. Adopted from [17] of chapter 1.
electrodes when no gate bias is applied is shown in Figure 1.6a. By applying a positive gate voltage, negative charges accumulate in the semiconductor at semiconductor-dielectric interface (Figure 1.7a) and the HOMO and LUMO of the semiconductor will shift down with respect to the Fermi levels of the drain and source electrodes (the situation is reverse in negative gate voltage). If the gate voltage is large enough the LUMO (HOMO) has resonance at the Fermi level of these electrodes and electrons (holes) can easily move from the electrodes to the semiconductor (Figure 1.6b and 1.6c). Now by applying a negative (positive) bias between two electrodes, electron (holes) are injected from the source to the semiconductor layer then retrieved from the drain electrode (figure 1.6d and 1.6e) [17].

![Figure 1.7: Distribution of relative charges when a) \( V_G > 0 \) and \( V_D = 0 \), b) \( V_G < 0 \) and \( V_D = 0 \).](image)

Figure 1.6 describe the operation of OFETs with zero threshold voltages and ohmic contact. However, an organic semiconductor usually makes Schottky contact with relatively large barrier height (usually \( \Phi > 0.2 \) eV). This reduces the charge injection and consequently lowers the efficiency of the device [18]. Another way to look at this problem is that there is always a mismatch between the Fermi level of the drain and source electrodes and the LUMO (HOMO) energy of an N-type (P-type) semiconductor and carriers need extra voltage to
overcome this barrier. This issue refers as contact resistance [16]. In order to solve this issue, sometime electrodes are chemically treated with self assemble monolayers (SAMs). However, this treatment can affect morphology of semiconductor films because we change the surface energy of the electrodes [19, 20, 21].

In reality, the voltage at which a device starts accumulating charge (the situation in Figure 1.6b and 1.6c) is not at $V_G=0$ [1]. In order to turn on a transistor we need an extra voltage to overcome the mismatch between the Fermi level of electrodes and the HOMO (in case of P-type) and LUMO (in case of N-type) of the semiconductor. Furthermore, the deep traps inside the channel needs additional voltage to be filled before the semiconductor conducts charges. Because of these reasons, we need to define a threshold voltage ($V_T$) at which the charges start flowing and the transistor turns on.

There are 2 ways to analyze the performance of a transistors. We can apply a constant gate voltage to a transistor with sweeping the drain voltage and measuring the current. This is called output characteristic ($I_D - V_D$ curve). The other way is to apply a constant drain voltage and sweep the gate voltage and measure the drain current. This is referred as a transfer curve.

![Graphs](image)

Figure 1.8: A typical characteristic of a P-type OFET. a) The output characteristic b) transfer curve in linear regime at $V_D=-20$ V. c) transfer curve in saturation regime $V_D=-80$ V. The transistor was made with 15 monolayers of C8-BTBT organic molecule. The width and the length were 1100 $\mu$m and 130 $\mu$m respectively.
(\(I_D - V_G\) curve). Figure 1.8 shows an example of these measurements. As shown in Figure 1.8a, by increasing \(V_D\) more carries are injected from the source electrode, so the current will increase linearly with the voltage. However, after some time these carriers will saturate in the semiconductor layer and current will remain constant. Figure 1.8b and 1.8c show the transfer curve in the linear and saturation regime respectively. We will discuss why transfer curve in linear regime is \(I_D - V_G\) and in saturation regime is \(\sqrt{I_D - V_G}\). If we assume zero threshold and ohmic contact, the charge in the channel is equal to:

\[
Q(x) = n(x)et = C_{ox}(V_G - V(x)) \quad (1.1)
\]

Where \(C_{ox}\) is the capacitance of the insulator per unit area, \(e\) is the electron charge, \(t\) is the thickness of charged layer in the channel, \(n(x)\) is the density of charges in the channel.

By assuming a threshold voltage, we have:

\[
Q(x) = n(x)et = C_{ox}(V_G - V(x) - V_T) \quad (1.2)
\]

According to eq. 1.2, when \(V_D = 0\), so \(V(x) = 0\) the charge density is uniformly distributed across the channel (it doesn’t depend on \(x\)). When we apply a small \(V_D\) that is less than \(V_G\), we have a linear gradient of charge concentration So the average value of \(V(x) = V_D/2\).

\[
Q(x) = n(x)et = C_{ox}(V_G - V_T - V_D/2) \quad (1.3)
\]

Now according to ohm’s law and conductivity definition, we have:

\[
R = \frac{V_D}{I_D} = \frac{L}{\sigma tW} \quad (1.4)
\]

\[
\sigma = ne\mu \quad (1.5)
\]
Where $\sigma$ is the conductivity, $\mu$ is the carrier mobility, $L$ and $W$ is the length and width of the channel respectively. By substituting eq. 1.3 in eq. 1.4 and using eq. 1.5:

$$I_D = \frac{W}{L} C_{ox} \mu (V_G - V_T - V_D/2) V_D$$  \hspace{1cm} (1.6)

Which usually is written as:

$$I_D = \frac{W}{L} C_{ox} \mu [(V_G - V_T) V_D - V_D^2/2]$$  \hspace{1cm} (1.7)

Now by taking derivative of $I_D$ with respect to $V_G$, one can calculate the mobility in linear regime.

$$\frac{\partial I_D}{\partial V_G} = \frac{W}{L} C_{ox} \mu_{lin}(V_D)$$  \hspace{1cm} (1.8)

$$\mu_{lin} = \frac{W}{L} C_{ox} (V_D) \frac{\partial I_D^{lin}}{\partial V_G}$$  \hspace{1cm} (1.9)

When $V_G - V_T \gg V_D$, the charges in the channel are uniformly distributed (Figure 1.9a) and $I_D - V_D$ curve is linear. As the $V_D$ increases, the carrier density inside the channel becomes nonuniform and gradually decreases at the drain voltage. Finally, it becomes zero at the drain voltage and charges are depleted at this point. This occurs at $V_G - V_T = V_D$ and the channel becomes “pinched”. This situation is shown in Figure 1.9b. By further increasing $V_D$, the pinched point moves a little bit toward the source electrode but it doesn’t result in increasing the current anymore because the potential remains constant with the value of $V_G - V_T$ at the pinched point. This condition is presented in Figure 1.9c. This corresponds to saturation regime in $I_D - V_D$ curve. Now by substituting $V_G - V_T = V_D$ in eq. 1.7, we can calculate the mobility in saturation regime.
Thus, we have:

\[ \mu_{sat} = \frac{W}{2L} C_{ox} \left( \frac{\partial |I_{D,sat}|}{\partial V_G} \right)^2 \]  

(1.11) in saturation regime.

Figure 1.9: Carrier concentration a) in linear regime when \( V_G - V_T \gg V_D \), b) when pinched off occurs at \( V_G - V_T \sim V_D \), c) in saturation regime when \( V_G - V_T \ll V_D \). Adopted from [17] of chapter 1.

Transistors are used as electronic switches in logic circuits. They also can be used to amplify a signal [15]. Therefore, two important factors for transistors performance are on/off
current and the amount of charges which they can transfer. The latter can be estimated through the mobility calculation in linear (eq. 1.9) and saturation (eq. 1.11) regime using transfer curves. The former also can be calculated from transfer curves by dividing the maximum current in on state divided by leakage current in off state.

Two major problems in OFETs need to be consider: contact resistance and gate voltage dependent mobility. Contact resistance could be a problem for any devices that used an organic or inorganic semiconductor. All equations used to extract the mobility, assume negligible contact resistance. Contact resistance originates from the fact that we need extra voltage to transfer carries from the electrode to the semiconductor. Intrinsic factors and geometry of devices have major impact on contact resistance. As mentioned before, coplanar geometries have higher contact resistance compared to staggered one [22].

Gate voltage dependent mobility is specific to organic semiconductor devices. In the next section it will be explained that the transport mechanism in organic semiconductors is hopping and charges are localized. In this situation the mobility increases with increasing the density of charge carriers. So, the mobility increases with increasing the gate voltage. This phenomenon happens through Poole-Frenkel mechanism which explains how an applied field modifies the potential near the localized levels in molecules so that tunnel transfer rate between sites increases [23].

Contact resistance, gate dependent mobility and other factors such as short channel (which can result in nonequilibrium situation during measurement) lead to nonlinearities in transfer curves. Figure 1.10 represents different kinds of nonlinearity in transfer curves. In these figures the red line is the highest slope which overestimate the mobility, the black line is
electrically equivalent ideal FET, and the green dashed line is suggested to have a better estimate slope for the mobility calculation [24]. These nonlinearities can sometimes result in overestimation of the mobility. These nonlinearities and the mobility hype related to them were the subject of many studies [25, 16, 24].

![Different nonlinearity in OFETs](image)

Figure 1.10: Different nonlinearity in OFETs. Adopted from [24] of chapter1.

Despite all inaccurate and often exaggerated statements about high mobility which has been reported in literature, certain improvements of mobility achieved during last decades is an undeniable fact. Paterson et al [25] reviewed the progress made in the last 35 years on the field of OFET. They mentioned that a high mobility in OFETs can be achieved by blending a small molecule with a polymer. The idea behind this is to combine high charge carrier mobilities typically associated with the small molecule, and the film forming traits of the polymer binder [25]. During the drying step, the blend undergoes a phase separation and ends up with a high
crystalline layer of the small molecule on top of the insulating polymer. This causes the small molecule to have a better and controllable nucleation during the drying process and reduces the density of grain boundaries in the organic film. So, this method results in decreasing disorders in the film and increasing the mobility [25]. As an example, Makita et al [26] proved that a high-performance device with the mobility of $\mu = 17 \frac{cm^2}{Vs}$ can be achieved for the organic molecule of C$_{10}$-DNBDT–NW that was spontaneously grown on the top of an amorphous insulating polymer layer of PMMA. In another study Paterson et al [27] proved that blending C8-BTBT organic molecule with C16IDT-BT polymer, plus doping the organic semiconductor with the third material of C$_{60}$F$_{48}$ increases the mobility from $\mu = 1.4 \frac{cm^2}{Vs}$ to $\mu = 7.8 \frac{cm^2}{Vs}$ and decreases the threshold voltage and contact resistance of devices.

**1.4: Charge Transport in Organic Semiconductors**

Charges transport in metals and inorganic semiconductors occurs in delocalized state and can be describe by band transport model. This mechanism isn’t applicable in organic semiconductors where molecules are held together by weak intermolecular forces. In fact, in organic semiconductors, charge transport occurs by a sequence of incoherent tunneling transitions (hopping) via localized states [28]. There is a basic difference between band transport and hopping mechanism. For example, in the former, reducing temperature result in decreasing the scattering process of phonons in the lattice, thus the mobility increases whereas in the latter one mobility increases with increasing the temperature because the carriers can get a thermal energy to overcome the barriers created by energetic disorder. There are many intrinsic and extrinsic factors that can affect charge transport in organic semiconductors such as temperature, pressure, electric field, impurity, disorder and molecular properties such as weight and size of
molecules [2]. In this section, the fundamental physics behind transport models include both band and hopping mechanism are describe in detail.

To begin with, we start from the simple tight bonding approximation or the LCAO (linear combination of atomic orbitals) approximation. In this approximation, we assume a one-dimensional chain of interacting orbital sites with the lattice constant $a$, where the wave function of each site is orthogonal to itself. By considering a periodic arrangement of molecules in a crystalline solid, we have a periodic potential. Using this potential in Schrodinger equation, we get Bloch wave functions for a carrier in the lattice which is written as the linear combination of lattice site [29]:

$$|\Psi> = e^{i k R_m} \sum_m |\phi_m>$$  \hspace{1cm} (1.12)

Where $R_m$ is the displacement vector at site $m$, $k$ is the wavevector of the wave function and $|\phi_m>$ is a lattice site orbital.

Now we use time independent Schrodinger equation:

$$H|\Psi> = E|\Psi>$$  \hspace{1cm} (1.13)

Now by projecting the above equation to a single lattice site, we have:

$$<\phi_n|H|\Psi> = E <\phi_n|\Psi>$$  \hspace{1cm} (1.14)

Using orthogonality assumption, the right-hand side of eq. 1.15 can be simplify to:

$$E <\phi_n|\Psi> = E e^{i k R_m} \sum_m <\phi_n|\phi_m>$$  \hspace{1cm} (1.15)

$$E <\phi_n|\Psi> = E e^{i k R_m}$$  \hspace{1cm} (1.16)
The left-hand side of eq. 1.15 cannot be easily evaluated unless we know the exact Hamiltonian of the system. However, we can simplify the left side by defining “on-site energy” and “transfer integral”:

\[< \phi_m | H | \phi_m > = \epsilon_m \] (1.17)

\[< \phi_n | H | \phi_m > = t_{nm} \] (1.18)

Where \( \epsilon_m \) is the site energy and \( t_{nm} \) is the transfer integral (also called the hopping integral, or electronic coupling). So, we have:

\[< \phi_n | H | \Psi > = e^{ikR_m} \sum_m \epsilon_m + e^{ikR_{n-m}} \sum_{m\neq n} t_{nm} \] (1.19)

Therefore:

\[ E = \sum_m \epsilon_m + e^{ikR_n} \sum_{m\neq n} t_{nm} \] (1.20)

If we assume that only the nearest neighbors interact with each other, by expanding eq 1.12 we have:

\[ |\Psi > = e^{ik(R-a)}|\phi_{R-a} > + e^{ik(R)}|\phi_R > + e^{ik(R+a)}|\phi_{R+a} > \] (1.21)

We recall again that \( a \) is the lattice constant. So, we have

\[ E = \epsilon + t(e^{ika} + e^{-ika}) \] (1.22)

This can also be written as:

\[ E = \epsilon + 2t \cos(ka) \] (1.23)
This is the dispersion relation in 1D when only the nearest neighbors interact. This relation describes how the energy of carrier \( E \) varies with the electron wave vector \( k \).

In the above formalism, particles and physical objects are treated using quantum wave function. This formalism is called the first quantization and is appropriate when we have a single quantum-mechanical system. There is another formalism called the second quantization and is appropriate when we are considering a complicated system such as many-body systems. In this formalism, Hamiltonian is express as the creation and annihilation operators to construct and handle the Fock states. Here, the second formalism is used in order to better understand the impact of disorders and phonons in the system. Thus, the above tight bonding Hamiltonian can be express as the product of the creation (\( a^+ \)) and annihilation (\( a \)) operators of a charge carrier:

\[
H_e = \sum_m \epsilon_m a^+_m a_m + \sum_{m \neq n} t_{mn} a^+_m a_n \quad (1.24)
\]

This is the simple Hamiltonian of a carrier that is traveling inside a periodic crystal in the absence of any disorder and without considering phonons. If we consider phonons, the Hamiltonian becomes

\[
H = H_e + H_{ph} \quad (1.25)
\]

\[
H_{ph} = \sum_{\lambda} \hbar \omega_{\lambda}(b^+_\lambda b_\lambda + \frac{1}{2}) \quad (1.26)
\]

Where \( b^+_\lambda \) and \( b_\lambda \) are the creation and the annihilation operators of a phonon with the energy of \( \hbar \omega_{\lambda} \). However, this is not enough, and we need to consider the electron-phonon interaction. This factor in Hamiltonian can be split into two Hamiltonian: local \( (H_{e-ph}^{local}) \) and nonlocal \( (H_{e-ph}^{non-local}) \) electron-phonon interaction. \( H_{e-ph}^{local} \) is related to modulation of site energies \( \epsilon_m \) due to the
electron-phonon interaction and referred as dynamic diagonal disorder. This factor reflects the intramolecular vibration. If we only keep this factor and assume that $H_{e-ph}^{non-local} = 0$, we get the standard Holstein-type polaron model. On the other hand, $H_{e-ph}^{non-local}$ describes the modulation of transfer integrals $t_{mn}$, due to the electron-phonon interaction and reflects the vibration and modification of relative position and orientation of molecules inside the crystal. This factor is called dynamic off-diagonal disorder. $H_{e-ph}^{local}$ and $H_{e-ph}^{non-local}$ represent dynamic contribution of disorders.

$$H_{e-ph}^{local} = \sum \lambda \sum m g_{\lambda m}^2 \hbar \omega a_m^+ a_m (b_\lambda^+ + b_{-\lambda}) \quad (1.27)$$

$$H_{e-ph}^{non-local} = \sum \lambda \sum m \sum n f_{\lambda mn}^2 \hbar \omega a_m^+ a_n (b_\lambda^+ + b_{-\lambda}) \quad (1.28)$$

Where $g_{\lambda m}$ and $f_{\lambda mn}$ are local and nonlocal electron-phonon coupling constants.

There is another kind of disorder in some crystal which reflects fluctuation in site energies and transfer integrals due to chemical and physical defects in a system and is presented when a system departs from the crystalline structure [30]. This is known as static disorder:

$$H_{stat\;dis} = \sum m \delta \epsilon_m a_m^+ a_m + \sum mn \delta t_{mn} a_m^+ a_n \quad (1.29)$$

Where $\delta \epsilon_m$ and $\delta t_{mn}$ denote the site energy and transfer integral modulation, respectively. So, the complete Hamiltonian of a system is sum of the above expressions:

$$H = H_e + H_{stat\;dis} + H_{ph} + H_{e-ph}^{local} + H_{e-ph}^{non-local} \quad (1.30)$$

One can distinguish the transport mechanism in a system by evaluating the contribution of each factor in the above expression. For example, if the nearest neighbor overlap energies
$t_{m,m+1}$ (which is in $H_e$) are larger than other terms in eq. 1.30, the charge transport happens through the band mechanism. If the effect of static disorder $H_{stat\, dis}$ is larger compared to the rest of factors in eq 1.30, then charge localization occurs. In this case if fluctuation in site energy goes higher than a critical value, Anderson localization happens [4]. When $H_{e-ph}^{local}$ and $H_{e-ph}^{non-local}$ contributions are larger than other factors, carriers are localized due to intermolecular and intramolecular vibrations, and one can view the motion of carriers as a series of uncorrelated hops [31]. This is the transport mechanism that occurs in organic semiconductors. Another possibility that can occur in organic semiconductor crystals is when $H_e$ is comparable with dynamic contribution. In this case the mechanism is called band like transport. This mechanism observed in many organic crystals [32, 33].

There’s another mechanism used to describe transport when highly conductive region coexists with traps associate with localized levels. This mechanism is referred as multiple trapping and release (MTR). In this model, the distribution of localized levels is close to one of delocalized bands (HOMO or LUMO). When carriers arrive at a trap, they are simultaneously captured in it with a probability close to one. Then they are release with a thermal energy (so it is a thermal activated process). The resulting drift mobility is expressed through the equation:

$$
\mu_D = \mu_0 \alpha \exp \left( \frac{-E_t}{k_B T} \right) \quad (1.31)
$$

Where $E_t$ is the trapping energy, $\alpha$ represents the ratio between the density of delocalized levels available for transport and the density of traps, $k_B$ is the Boltzmann constant, and $T$ is the temperature [15, 2].
The most common model used to describe hopping transport in disordered organic semiconductors is developed by Bässler [34] called Gaussian disorder model (GDM). This model assumed a Gaussian shape for the energy of disorders. So, density of states (DOS) is written as:

\[
g(E) = \frac{N_t}{\sigma \sqrt{2\pi}} \exp\left(-\frac{(E-E_0)^2}{2\sigma^2}\right) \tag{1.32}
\]

Where \(N_t\) is the density of traps (hopping site), \(E_0\) is the energy of center of the DOS, and \(\sigma\) is width of Gaussian shape. There is no direct experimental proof for using a Gaussian shape for DOS. The only reason for using the Gaussian distribution is the shape of the absorption band in disordered organic materials [2]. The GDM used Monte Carlo simulations for carriers hopping from one site to another with the above distribution of DOS. A carrier jumps from site \(i\) to site \(j\) based on the Miller Abraham equation:

\[
\nu_{ij} = \nu_0 \exp\left(-2\gamma R_{ij}\right) \left\{ \begin{array}{ll}
\exp\left(-\frac{E_i-E_j}{k_BT}\right); & E_j > E_i \\
1; & E_j > E_i
\end{array} \right. \tag{1.33}
\]

Where \(\nu_{ij}\) is the hopping rate from site \(i\) to site \(j\), \(R_{ij}\) is the distance between site \(i\) and site \(j\), \(\gamma\) is the decay parameter which is in the order of \(10^{10}\) m\(^{-1}\), \(\nu_0\) is the attempt hopping frequency which is about \(\sim 10^{13}\) s\(^{-1}\), and \(E_i\) and \(E_j\) are the site energies at site \(i\) and \(j\), respectively. The first exponential term describes the decrease in electronic coupling with distance. The last term is the Boltzmann factor for an upward jump in energy and it is equal to one for a downward jump [5]. Miller Abraham equation neglects electron-phonon coupling, and it is applicable only at low temperatures. A more complete model used to describe hopping rate with small electronic coupling is the Marcus model. In this model electron hopping rate is expressed as:
\[ \nu_{ij} = \frac{t^2}{\hbar} \left[ \frac{\pi}{k_B T \lambda_{\text{reorg}}} \right]^{1/2} \exp \left( -\frac{(\lambda_{\text{reorg}} + E_i - E_j)^2}{4\lambda_{\text{reorg}} k_B T} \right) \] (1.34)

\( t \) is the electronic coupling that is \( t = t_0 \exp (\gamma R_{ij}) \), \( \hbar \) is the reduced Planck’s constant, and \( \lambda_{\text{reorg}} \) is the reorganization energy. The reorganization energy is the energy costs due to geometry modification to go from a neutral to a charged state and vice versa. This reflects electron phonon coupling or intramolecular vibration. Reorganization energy is sometimes used as a parameter to characterize dynamic disorder effect [35, 30]. According to eq 1.34, a low reorganization energy results in a small geometry relaxation and a high transfer rate. This condition is true for inorganic crystal and is reverse for weakly bonded organic materials. In organic molecular crystal, the electronic coupling is small and electron phonon coupling cannot be neglected specially at high temperatures. Therefore, Marcus model is an appropriate description in this situation [2].

There are several works studied dynamic and static disorder in organic semiconductors. Tummala et al [30] studied dynamic and static disorder in fullerene systems using molecular dynamic simulation and density function theory. They concluded that the magnitude of dynamic and static disorder is comparable. Silva and Voorhis [36] also came to the same conclusion about the magnitude of dynamic and static disorder for the organic molecules. They used molecular dynamic and molecular mechanics to study disorders in the emission layer of an OLED. The organic molecules they used were PICTRZ2 as the guest, mCP, and UGH2 as the host. Therefore, according to these results, it’s important to consider both the dynamic and static disorders in organic molecules. Eggeman et al [37] and Illig et [38] al studied dynamic disorder effects in small organic molecules using thermal diffuse electron scattering. One interesting
result was that Eggeman et al [37] proved side arms like those in C8-BTBT can reduce the
dynamic disorder effect and as a result the transistor mobility have a higher value.

1.5: Characterization of Organic Semiconductors by SPM Methods

Scanning probe microscopy (SPM) is a technique which enables us to image the surfaces
on a fine scale with a physical probe. Two important techniques in SPM is the scanning
tunneling microscopy (STM) and the atomic force microscopy (AFM). The STM uses electrons
tunneling between the tip and the sample to image the surface while the AFM relies on the force
acting on the tip when it brought close to the sample. An atomic force microscope can measure
different type of forces depending on the situation and properties of the tip and sample [7]. Since
STM is based on the tunneling current between the tip and sample, a conductive substrate is
required. However, the advantage of AFM based spectroscopy is that there is no restriction on
choosing the substrate.

1.5.1: AFM based scanning probe microscopy

AFM based scanning probe has proven to be a useful tool for characterization of organic
semiconductors. In order to characterize the morphology, potential variation, electrostatic force,
and magnetic properties of a surface of an organic semiconductor film, one can use atomic force
microscopy (AFM), kelvin probe force microscopy (KPFM), electrostatic force microscopy
(EFM), and magnetic force microscopy (MFM), respectively. Since organic semiconductors are
held together by weak van der Waals interaction, they are prone to deform when the tip contacts
the sample. However, most of the AFM based scanning probe has the advantage of scanning the
organic surfaces without damaging them because they have a mode that the tip can oscillate close to the sample instead of contacting it.

An important parameter can be measured quantitively by AFM is roughness of the surface. Moreover, by looking at the morphology of the surface, one can check the coverage and growth mode of an organic film (Figure 1.11a and 1.11b). Defects such as vacancies of the film on specific spots and screw dislocations (Figure 1.11c) can sometimes be observed in organic films. Further investigation of an organic film can be done by other scanning probe techniques which are based on AFM. For example, Jaquith et al [39] studied charge trapping at localized defects in pentacene and TIPS pentacene films using electric force microscopy (EFM). Many KPFM studies probed the active channel of a transistor at its on states. Bürgi et al [40, 41] used KPFM in ultrahigh vacuum to study charge injection from the drain and source contacts into the active channel of transistors and they extracted the contact resistance from the voltage drop at the

Figure 1.11: AFM image of a) 2.5 monolayers of C8-BTBT on HMDS/SiO₂. The growth is 2D (also known as layer by layer growth or Frank-van derMerwe mode. b) same amount of C8-BTBT on HMDS/SiO₂. In this case the growth is 3D (also known as island growth mode or Volmer-Weber mode) due to contamination. c) An example of screw dislocation. More than 20 monolayers of C8-BTBT deposited on HMDS/SiO₂. All depositions were done at room temperature.

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drain and source electrode. In recent work from our group, Hoffmann et al [42] used kelvin probe force microscopy (KPFM) to study shallow traps inside the active channel of a transistors. Once the transistor turns on, we observed the onset of fluctuations in the thin film due to shallow traps which can be attributed to the dynamic disorder effect.

1.5.2 Scanning tunneling microscopy

If someone wants to observe organic molecules down to molecular scale, Scanning Tunneling Microscope is the best option. Probing individual atoms and molecule enables us to reveal properties which otherwise would remain unknown in the study of an ensemble of atoms and molecules [43]. In addition to imaging, STM of organic molecules allows us to characterize the electronic properties of molecules thorough spectroscopy. In fact, by sweeping voltage above one molecule and monitoring height or conductance changes, one can get HOMO and LUMO of the molecule. Furthermore, STM has been used to observed motions and rotations of single molecules at the surface [44, 45]. These studies can provide useful information about intermolecular interactions and relaxations. Figure 1.12 shows an example of recording the rotational motion of acetylene molecule on Cu(001) surface. The asterisks in Figure 1.12a show the fixed position of STM tip above the molecule. As the molecule rotates on the surface of Cu(001), the tunneling current changes. Figure 1.12b shows the current over time and Figure 1.12c presents the distribution of times the molecule spent in the high level of the current with a fit to an exponential decay.

As mentioned before, one application of STM is to manipulate and change the position of molecules on the surfaces. Maruno et al [46] studied the threshold condition (threshold current and voltage) required for a C_{60} molecule to start moving on the Si( 111 )-7 x 7 surface. Cuberes et al controlled displacements of C_{60} molecules along a monoatomic step of a Cu(111) surface in
order to demonstrate the feasibility of building an “abacus” at the molecular scale. All these efforts have been done to make nano scale electronic devices. However, there are still many obstacles to remove in order to develop and integrate useful molecular electronic devices [47].

Figure 1.12: a) side and top view of acetylene on Cu (001). The dashed line represents the dumbbell shaped depression in the STM image. The bottom images are the STM images of acetylene on Cu (001). The square lattice in the STM images represents Cu atoms of the substrate. b) Current during a 364 mV voltage pulse over a C₂H₂ molecule initially in the high current orientation. Each jump in the current indicates the moment of rotation of the molecule. c) Distribution of the times the molecule spent in the high current orientation with a fit to an exponential decay. The fitted time constant is 184 ms for the voltage and current in b. Adopted from [44] of chapter 1.

STM enables us to consider electronic properties of organic molecules on metallic substrates and this gives us the opportunity to investigate an important topic in organic electronic devices which is studying metal-organic interfaces. An important device problem arises from injecting charge carriers from the electrode to the organic film. Thus, STM allows us to better understand metal-organic interfaces and consider their properties in more details. Moreover, STM lets us to visualize different domains and the boundaries between domains in an organic film. The boundaries of local ordered regions can have a great impact on charge transport of organic thin film transistors (OTFT). Therefore, quantifying the dynamic of these boundaries can give us useful information about performance of organic electronic devices [48].
1.6: Conclusion

Improving the performance of OFETs necessitates proper understanding of the charge transport in organic semiconductors and the factors which can limit them. In this dissertation, I studied two important factors which influence charge transport in organic semiconductors: 1) dynamic and static disorder in organic semiconductor films, 2) the issues of contacts in OFETs. In chapter 2, the techniques which were used for these studies are explained in detail. In chapter 3, dynamic and static disorder of fullerene molecule at the interface of Au(111) are characterized using STM. Then, the effect of contact deposition on film morphology in BGTC devices made with C8-BTBT are consider in chapter 4. A thickness dependence mobility is observed in these devices due to the poor contacts with gold electrodes which became the motivation for a research question in chapter 5. In chapter 5, the dynamical behavior of grain boundaries of C8-BTBT film on gold is studied.
References:


Transport in High-Mobility Small-Molecule/Polymer Blend Organic Transistors,"


Chapter 2

Experimental Methods and Instrumentation

2.1: Scanning Probe Microscopy

In this section we review the basic principle of scanning probe force microscopy (SPM) including atomic force microscopy (AFM), kelvin probe force microscopy (KPFM), and scanning tunneling microscopy (STM). These are the tools used in this research to characterize the surfaces. In all of these tools, a physical probe rasters across the surface from point to point to form a whole image. This gives the topography and other parameters (such as surface potential difference between tip and sample) down to nanoscale.

2.1.1: Atomic Force Microscopy

Atomic force microscope was invented 1985 [1], after scanning tunneling microscope in order to image the surface of insulators. AFM uses a cantilever with a sharp tip to scan the surface. The cantilever is attached to a piezoelectric element which control the motion of cantilever very precisely. The first AFM [2] was in contact mode (C-AFM) which the tip is brought close to the sample and an electronic feedback loop is usually employed to maintain the probe-sample force constant during scanning. The motion of the cantilever is monitored through the deflection to a photo diode sensor. The feedback electronic gets the deflection of the cantilever as input and controls the distance between the tip and sample to keep the force constant (see Figure 2.1). Later the dynamic mode of AFM (also called dynamic AFM) was developed, where the cantilever is vibrated close to its resonance frequency and changes in the vibration due to tip-sample interaction are used to maintain a constant distance to the sample.
surface. Forces exerted by the tip on the sample in dynamic mode are considerably reduced compared to the contact mode [3].

In order to realize the operation process of AFM, let’s consider the interaction between the tip and the sample. As shown Figure 2.2, three different region can be distinguished [1]

(a) If the tip is far away from the surface the force between tip and sample is negligible.
(b) For closer distances an attractive (negative) force between tip and sample can be distinguished
(c) For very small distances a strong repulsive force between tip and sample occurs.
One important point worth mentioning here is that tip-sample force which is used as measured signal depends non-monotonously on the tip-sample distance. It means that for one value of the measured force in the attractive region there are two tip-sample distances, point 1 and point 2 on the force-distance curve in Figure 2.1. So, we must choose to work only on one of the branches left or right of the minimum in the force-distance curve in order to maintain monotonous force distance relation. In contact mode, the tip is brought very close to the sample and repulsive interaction between tip and sample is measured [1]. In dynamic mode, the cantilever is oscillated at or near its resonance frequency and the change in the oscillation is monitored in dependence of the tip-sample interaction [3]. In the other word, in dynamic mode, the tip–sample interaction is perturbed by attractive and repulsive forces which results in the oscillation of the AFM tip. We can consider the tip as a point-mass spring, so the z motion of an
oscillating tip can be described by the damped driven harmonic oscillator equation with a perturbation added to account for tip-surface interaction:

\[ m\ddot{z} + \frac{m\omega_0}{Q}\dot{z} + k z = F_{ts} + F_0 \cos(\omega_d t) \quad (2.1) \]

Where \( m \) is the mass, \( \omega_0 \) is the angular resonance frequency, \( Q \) is the quality factor, \( k \) is the spring constant, \( F_{ts} \) is the tip-surface interaction, \( F_0 \) and \( \omega_d \) are the amplitude and angular frequency of the driving force, respectively. In the absence of tip-surface interaction \( (F_{ts} = 0) \), the free resonance frequency is the function of the spring constant \( k \) and the effective mass \( m^* \), which depends on the geometry of the cantilever:

\[ \omega_0 = 2\pi f_0 = \sqrt{\frac{k}{m^*}} \quad (2.2) \]

When the tip is close to the surface, the tip-surface force won’t be zero \( (F_{ts} \neq 0) \). This tip-surface interaction may have different origin such as short range repulsive and chemical binding forces, the van der Waals force, and the long-range electrostatic and magnetic forces. The total short-range interatomic interaction potential comprising the repulsive and attractive part can thus be described by the empirical Lennard-Jones potential:

\[ U_{LJ} = -4\epsilon \left[ \left( \frac{\sigma_0}{r} \right)^6 - \left( \frac{\sigma_0}{r} \right)^{12} \right] \quad (2.3) \]

Where \( 4\epsilon \sigma_0^6 \equiv A \) and \( 4\epsilon \sigma_0^{12} \equiv B \) and the constants \( A \) and \( B \) are empirical parameters determined from independent measurements. A more accurate description can be obtained by considering at a specific distance what kind of force in short or long range is dominated.
However, the above model is a good approximation about how the AFM tip behaves close to the surface.

In dynamic mode, the amplitude or resonance frequency can be used as a feedback parameter to track the topography of a surface. Therefore, two operation modes in dynamic AFM are amplitude modulation atomic force microscopy (AM-AFM) and frequency modulation atomic force microscopy (FM-AFM). In fact, in AM-AFM changes in the height lead to changes in the amplitude of oscillation. The amplitude changes provide information to the feedback system to maintain the tip–sample distance constant at a pre-determined set-point. In FM-AFM mode, height changes results in frequency changes, so changes in frequency is monitored by the feedback system to keep the set-point frequency constant. Changes in frequency depends on the force gradient between the tip and the sample. Due to this reason, FM-AFM mode has higher spatial resolution than AM-AFM mode so usually the experiment in FM-AFM is performed under vacuum. On the other hand, amplitude change response occurs slowly with tip–sample interaction in vacuum, so AM-AFM mode is usually done in ambient conditions. Based on the experiment, one can choose to work with FM-AFM or AM-AFM. The alternative names for AM-AFM mode is tapping or intermediate mode intermittent contact, or AC mode. FM-AFM mode is sometimes referred as non-contact AFM [4, 5].

The AFM used to get the images in chapter 4 was MFP-3D from Asylum Research. It is operated in air at room temperature, so AM-AFM mode was used. The cantilever probes were purchased from Budget Sensors; either Tap300Al-G for standard topography measurements or ElectriMulti75-G for KPFM measurements.
Like many other microscopic techniques, in AFM problems can arise due to improper use of the microscope by the operator, a deformed or damaged tip, or some characteristics of the sample. These problems can sometimes cause artifacts or blurred images. The tip must always remain sharp during the scan. If the tip is blunt, the image becomes blurry and unclear. The tip must have an isotropic shape. If it loses its isotropic shape or anything attached to it, it may lead to image distortions or it could repeat an identical shape on the surface. Distortion in the image can sometimes be related to nonlinearity in the piezoelectric scanner. Anyone wants to analyze AFM images, has to be aware of these problems to avoid misinterpretation in analysis [6].

The topography data for an AFM image is saved as \(m \times m\) matrix where \(n\) is the resolution or number of lines or column. Usually these data need post-processing procedures, in order to remove some simple artifact. For example, usually the vertical oscillation of the tip is not exactly perpendicular to the \(x\) \(y\) plane of the sample. In this situation a plane-fit subtraction improves the quality of the image. After that the image can be interpret and quantify. One important parameter used in quantifying the roughness of an image is root-mean-square:

\[
RMS = \sqrt{\frac{1}{n} \sum_{i}^{n} x_i^2} \quad (2.4)
\]

Where \(x_i\) is each data in the matrix and \(n\) is the number of data. Other parameters such as variance and skew or even plotting the histograms of data are sometimes useful.

### 2.1.2: Kelvin Probe Force Microscopy

If a conductive tip is used in AFM, by applying a bias between the tip and sample, one can get the local contact potential difference between the tip and sample. The name “kelvin probe force microscopy” originate from macroscopic method developed by Lord Kelvin to
nullify the current in a vibrating plate in a parallel plate capacitor arrangement. Since AFM tip is very small, instead of current electrostatic force is measure [3]. The contact potential difference (CPD) between the tip and sample in KPFM is:

\[ V_{CPD} = \frac{\phi_{tip} - \phi_{sample}}{-e} \]  \hspace{1cm} (2.5)

Where \( \phi_{tip} \) and \( \phi_{sample} \) are the work function of the tip and sample, respectively and \( e \) is the charge of electron. Figure 2.3 shows the energy diagrams of the tip and sample. Figure 3.2a represent the situation when the tip and the sample are brought close together while there’s no electrical connection between them. In this situation, the vacuum levels are aligned. When the tip and sample are electrically connected, the Fermi levels are aligned and electron current flow, so the system will reach an equilibrium state. Now the tip and sample surface will be charged. Since the vacuum levels are not aligned anymore, an apparent \( V_{CPD} \) between the tip and sample will be formed. This is shown in Figure 2.3b. In this situation an electrical force acts on the contact area due to \( V_{CPD} \). Now an external force can be applied to eliminate the initial force. In fact, If the

![Figure 2.3: Band diagram of classic kelvin probe force microscopy. Adopted from [5] of chapter 2.](image)
applied external bias $V_{DC}$ has the same magnitude as the $V_{CPD}$ with opposite direction, the applied voltage removes the surface charge in the contact area.

Therefore, by applying an AC voltage (analogous to vibration described in dynamic AFM) plus a DC voltage to the AFM tip, KPFM measure the relative work function between the tip and the sample. We can assume that the tip-sample system acts as a parallel plate capacitors. As a result, the electrostatic force between the tip and sample $F_{es}$ can be given by the gradient of energy $U_{es}$ of the capacitor:

$$
F_{es} = -\nabla U_{es} = -\frac{1}{2} \Delta V^2 \frac{dC_z}{dz} \quad (2.6)
$$

Where $z$ is the direction normal to the sample surface, $\frac{dC_z}{dz}$ is the gradient of the capacitance between tip and sample surface, and $\Delta V$ is the potential difference between $V_{CPD}$ and voltage applied to the tip. When the applied voltage to the tip is a DC (to nullify $V_{CPD}$) and an AC (for tapping mode oscillation), the above equation becomes:

$$
F_{es} = -\frac{1}{2} [(V_{DC} - V_{CPD}) + V_{AC} \sin(\omega t)]^2 \frac{dC_z}{dz} \quad (2.7)
$$

The above equation can be divided into three part:

$$
F_{DC} = -\frac{1}{2} \frac{dC_z}{dz} (V_{DC} - V_{CPD})^2 \quad (2.8)
$$

$$
F_\omega = \frac{dC_z}{dz} [(V_{DC} - V_{CPD}) + V_{AC} \sin(\omega t)] \quad (2.9)
$$

$$
F_{2\omega} = -\frac{1}{4} \frac{dC_z}{dz} V_{AC}^2 [\cos(2\omega t) - 1] \quad (2.10)
$$
Among these, $F_\omega$ is used to measure $V_{CPD}$, using a lock-in amplifier. In fact, the output of the lock-in amplifier is proportional $V_{DC} - V_{GPD}$. By applying a $V_{DC}$ to the AFM tip, $V_{CPD}$ can be measured, such that the output signal of the lock-in amplifier is nullified and $F_\omega$ equals zero [5].

All above equations are true when we have a metal surface since we assume two parallel metal plates. In case of semiconductors, we should keep in mind that there’s always a space charge layer on the surface. Hudlet et al [7] considered the case where the metallic tip is interacting with a semiconductor surface. In this case

$$F_\omega = \frac{Q_s}{\epsilon_0} \frac{C_I C_D}{C_I + C_D} V_{AC} \sin(\omega t)$$ \hspace{1cm} (2.11)

Where $Q_s$ is the total charge on the surface of the semiconductor, $\epsilon_0$ is the dielectric constant, $C_I$ is the capacitance per unit area associated with $V_{AC}$ and the air gap between tip and sample, and $C_D$ is the capacitance per unit area associated with $V_{AC}$ and the charged layer on top of the semiconductor. Therefore, in semiconductors, the measured $V_{CPD}$ is not related to the work function of the semiconductor, but it is related to surface potential of the semiconductor.

In chapter 4, KPFM were used to study electrode-channel border properties in transistors. One important point to notice is that the surface potential that the KPFM measures is reverse in sign. The reason for this is that in the presence of a charge on the surface, the DC voltage applied to the tip nullifies the charge. So negative surface potentials are positive and vice versa. This is important for interpretation of charged surfaces.

2.1.3: Scanning Tunneling Microscopy

Surface science has been revolutionized by inventing the scanning tunneling microscope (STM) in 1982. Binnig and Rohrer who invented the STM received the Nobel prize in physics
1986 for their invention. The most amazing ability of the STM is that one can see surfaces down to the atomic scale in real space [8].

Figure 2.4a shows the schematic an STM. In STM, a voltage is applied between the metallic tip and the conducting sample. The tip is moving down toward the sample until the tunneling current flow between them. This happens exactly before the tip touches the sample’s surface. We show later that the tunneling current varies strongly (exponentially) with the distance between the tip and sample. This strong dependence to the height allows a precise vertical measurement in the STM down to picometer scale [8]. As the tip scans along the surface in $x$ and $y$ directions, a feedback system adjusts the tip’s height and moves it up and down in order to keep the tunneling current constant. Recording the up and down motion of the tip over the $x$ and $y$ directions gives us topography of the sample’s surface.

Figure 2.4: a) Schematic of a scanning tunneling microscope (STM). b) Schematic of one-dimensional metal-vacuum-metal potential barrier. Adopted from [8] of chapter 2.
To better understand the basic principle of the STM, let’s consider the Schrödinger equation for an electron in the solids (the tip and the sample or region I and III in the Figure 2.4b) and in the gap (region II in Figure 2.4b) with the barrier potential height $V_0$ and width $d$:

$$-\frac{\hbar^2}{2m} \frac{d^2}{dz^2} \psi(z) + V(z)\psi(x) = E\psi(z)$$  \hspace{1cm} (2.12)$$

$$V(z) = \begin{cases} 
V_0 & \text{for region II} \\
0 & \text{for region I and III} 
\end{cases}$$  \hspace{1cm} (2.13)$$

Where $\psi(z)$ is the wave function of the electron, $V(z)$ is the potential barrier, and $E$ is the energy of the electron. In eq. 2.13 we assume a constant potential in the barrier. In general, $V(z)$ may not be constant. However, in our discussion it’s adequate to assume a constant potential which is then called the square barrier potential [9]. The solution for wave function will be:

$$\psi(z) = \begin{cases} 
Ae^{ikz} + Be^{-ikz} & z < 0 \text{ (region I)} \\
Ce^{\kappa z} + De^{-\kappa z} & 0 \leq z \leq d \text{ (region II)} \\
Fe^{ikz} & z > d \text{ (region III)} 
\end{cases}$$  \hspace{1cm} (2.14)$$

Where $k = \sqrt{\frac{2m}{\hbar^2}} E$ and $\kappa = \sqrt{\frac{2m}{\hbar^2}} (V_0 - E)$. Note that we have right and left traveling waves in region I and II due to reflection from $z = 0$ and $z = d$ surfaces. According to eq. 2.14 and as shown in Figure 2.4b, the wave function is sinusoidal in region I and III and it is exponentially decaying with distance in region II. By assuming the amplitude of incoming wave to be unity ($A = 1$) the coefficient $B$, $C$, $D$, and $F$ can be obtained by using the fact that the wave function and its derivative must be continuous at $= 0$ and $z = d$. After calculating these coefficients, the probability of finding an electron at the end of the potential barrier can be obtained by:

$$T = |F|^2 = \frac{4k^2\kappa^2}{(k^2 + \kappa^2)^2 \sinh^2(\kappa d) + 4k^2\kappa^2}$$  \hspace{1cm} (2.15)$$
Where $T$ is called transmission factor. In the limit $\kappa d \gg 1$, we can use this approximation:

$$\sinh^2(\kappa d) \approx \frac{1}{4} e^{2\kappa d} \quad (2.16)$$

Another approximation to eq. 2.15 is to neglect that last term in denominator. Therefore, $T$ becomes:

$$T = \frac{16 k^2 \kappa^2}{(k^2 + \kappa^2)^2} e^{2\kappa d} = \frac{16E(V_0-E)}{v_0^2} \exp \left[ -2d \sqrt{\frac{2m}{\hbar^2}} (V_0 - E) \right] \quad (2.17)$$

By using the continuity equation, one can relate the probability density ($\rho(r, t) = \psi(r, t)\psi^*(r, t)$) to the current density or flux density $j(r, t)$. Using this and the time dependent Schrödinger equation, and using wave function in region III, one can write the current density is equal to [10]:

$$j = |F|^2 \frac{\hbar k}{m} \quad (2.18)$$

From here, it is proved that the tunneling current decreases exponentially with the width of the barrier (or the distance between the tip and the sample). The above description helps us to understand the basic of tunneling current occurs in STM. However, this is not a complete model and fails to consider the rate of the electrons that can pass the barrier. Obviously, this rate affects the tunneling current. A more complete model has been used to count the rate of electrons is the Bardeen Model [8, 11]. John Bardeen solved the tunneling current matrix element in his study of Metal-Insulator-Metal junction long before invention of the STM. The tunneling matrix element is given by an integration over an (arbitrary) tip-sample separation surface $S_{\text{tip/sample}}$:

$$M = \frac{\hbar^2}{2m} \int_{S_{\text{tip/sample}}} \left( \chi^* \frac{\partial \psi}{\partial z} - \psi^* \frac{\partial \chi^*}{\partial z} \right) \quad (2.19)$$
Where $\psi$ and $\chi$ are the sample and tip wave functions. Now the rate of electron transfer is determined by fermi golden rule:

\[
w_{\text{tip} \rightarrow \text{sample}} = \frac{2\pi}{\hbar} |M|^2 \delta(E_\psi - E_\chi) \quad (2.20)
\]

Where the delta function indicates only the states with the same energy level in the sample and tip can tunnel into each other. Now the tunneling current can be obtained by summing over all relevant states multiple charge of the electron and 2 due to spin degeneracy:

\[
I = 2e w_{\text{tip} \rightarrow \text{sample}} \quad (2.21)
\]

\[
I = \frac{4\pi e}{\hbar} \int_{-\infty}^{+\infty} f(E_f - eV + \epsilon) - f(E_f + \epsilon) \ \rho_s(E_f - eV + \epsilon) \ \rho_T(E_f + \epsilon) |M|^2 d\epsilon
\]

(2.22)

Where $f(E) = \frac{1}{1 + \exp \left( \frac{E - E_f}{k_B T} \right)}$ is the fermi distribution function and $\rho_s(E)$ and $\rho_T(E)$ is density of states (DOS) of the sample and the tip, respectively. When $k_B T$ is smaller than the energy resolution, the fermi distribution can be assumed to be a step function, so the above equation simplifies to:

\[
I = \frac{4\pi e}{\hbar} \int_{-\infty}^{eV} \rho_s(E_f - eV + \epsilon) \ \rho_T(E_f + \epsilon) |M|^2 d\epsilon
\]

(2.23)

It is worth mentioning that square of the tunneling current matrix is equal to transmission function in one dimensional approximation ($|M|^2 = T$) [8]. Bardeen also assumes that the magnitude of $|M|^2$ doesn’t change in the above interval. Then the tunneling current is:

\[
I \propto \int_{0}^{eV} \rho_s(E_f - eV + \epsilon) \ \rho_T(E_f + \epsilon) d\epsilon \quad (2.24)
\]
Another assumption used to simplify the above tunneling current is about DOS of the tip. If we use a metal tip, the $\rho_T$ is constant at low bias, which is true for the $\rho_T$ around the Fermi level. In this situation the density of states of the sample can be obtain by:

$$\frac{dI}{dV} \propto \rho_s(E) \tag{2.25}$$

So, the differential conductance is proportional to the density of states of the sample. The above equation leads to scanning tunneling spectroscopy (STS). In STS, the feedback loop is off, so the distance between the tip and sample is fixed above the a specific $x$ and $y$ on the surface. Then by sweeping the voltage, one can measure the tunneling current as a function of the voltage. The differential conductance is usually measured by a lock-in technique. In this technique, an AC voltage is added to the DC voltage of the STM resulting to an AC component in the tunneling current:

$$I(V + V_{ac}) = I(V) + \left(\frac{dI}{dV}\right)_V V_{ac} \sin \omega t + \frac{1}{2} \left(\frac{d^2I}{dV^2}\right)_V V_{ac}^2 \sin^2(\omega t) \tag{2.26}$$

By setting a lock-in amplifier to detect the first harmonic (the second expression in the above equation), the output signal from the lock-in amplifier is proportional to $\frac{dI}{dV} [8]$.

Pronschinske et al [12] showed that there’s another way to get the density of states of the sample. In this method the feedback loop remains on (constant current mode) and by sweeping the voltage one can monitor the height changes of the tip. In this situation:

$$\frac{dz}{dV} \propto \rho_z(E) \tag{2.27}$$
The advantage of this method is that there is no need to use a lock-in amplifier. Furthermore, constant current mode, probe the electronic structure in a more gentle way than constant height mode. Due to maintaining a constant current, $z(V)$ spectroscopy allows to probe the electronic structure at higher voltages [12].

2.2: Film and device Fabrications

In this section the procedure to make organic film and then making organic field effect transistors will be explains in detail. These devices are used in chapter 4 of this dissertation.

2.2.1: Substrate Preparation

The substrates used in this dissertation were heavily P-doped Si wafers with 300 nm thermally grown oxide layer. The Si itself was used as the gate electrode and the silicon dioxide layer was used as the dielectric for OFETs. The substrates must be cleaned prior to deposition since the debris on the surface can change the growth mode and film morphology of semiconductor layer. Before cleaning, the Si wafers need to be cut by a diamond scribe. The orientation of Si crystal in wafer was (001) which allows the wafer to be cut in straight lines by applying pressure on the corner of the wafer. During the cutting process, debris of Si were produced which can be stuck on the surface. In order to minimize the contamination at this step, we put the shiny side of wafers (the thermal oxide layer) down then applied pressure to cut them.

After cutting process, the substrates were ready for cleaning process. At first, they were rinsed with acetone, and sonicated in acetone for 10 minutes. Sonication is a process in which high frequency acoustic vibrations are used to agitate the substrate in a solution in order to remove the particles on the surface. After sonication with acetone, the substrates were rinsed with isopropanol and sonicated with isopropanol for 10 minutes. Then substrates were rinsed
with deionized (DI) water and blown dry with N₂. Then they were exposed to UV ozone for 15 minutes to remove the remaining residues on the surface. After this step, the substrates were rinsed with DI water and blown dry with N₂. After this step no residues must remain on the surface. If any trace of droplet or any kind of debris are observed on the surface, the cleaning process should repeat again.

In the next step, the substrates were treated chemically with a self assemble monolayer (SAM). In general, substrate passivation can dramatically change the film morphology. It is proved that SiO₂ surface passivation increases the mobility and on/off current ratio in OFET’s [13, 14]. Two SiO₂ surface passivation materials are octadecyltrichlorosilane (OTS) and hexamethyldisilazane (HMDS). These SAM’s make the surface more hydrophobic by decreasing the surface energy which usually results in increasing the grain size of organic molecule on the surface [15].

The SAM that I used in this work is hexamethyldisilazane (HMDS). Since HMDS is sensitive to oxygen, this step was performed in N₂ glovebox. So, the cleaned substrates were transferred to the glovebox and were annealed on a heating plate at 120°C for 30 minutes. This step is called dehydration. This step caused to desorb water or any other residue on the surface and exposed the hydroxyl group. After dehydrating the surface, HMDS was spin-coated onto the surface with 2000 rpm for 60 seconds. Then the substrates must be annealed again at 120°C for 30 minutes. This step breaks the bonds of the silizane groups and then HMDS bonds to the surface and releases ammonia as a byproduct.
After this step, organic molecules are deposited onto the surface and then for making top contact devices electrodes are deposited on the organic layer. However, for bottom contact devices, we first deposit the electrodes and then we deposit organic molecules.

2.2.2: Organic Molecular Beam Deposition

Organic molecular beam deposition is a process at which organic molecules are deposited onto a substrate through vacuum sublimation. In general, organic molecules can be deposited onto a substrate through OMBD or a chemical wet process (such as spin-coating drop-casting, blade-coating, or printing). Each of these methods has its advantages and disadvantages. One advantage of OMDB is that one can be sure about the purity of deposited material since the impurity in material has different sublimation temperature. Another important advantage of OMBD is that one has a precise control over the thickness and the rate of deposition. The advantage of deposition through a wet chemical process is that we can have the organic material on large scales, so it has been a good method for making large scale organic displays. Since most of organic molecules have low solubility, OMBD is a typical method to make thin film of organic molecules [16].

OMBD were used in this dissertation to make thin films of organic molecules. This method enabled us to make different thicknesses of the organic molecule from a sub monolayer up to 50 monolayers. Figure 2.5 presents the schematic of the box chamber used for OMBD process. The box itself was purchased from Kurt J. Lesker Company and its interior is about 35x35x60 cm³. A rough pump and a turbo pump are used to pump down the chamber to the pressure of ~ 1x10⁻⁶ torr. It usually takes more than 8 hour to reach this pressure. Inside the chamber the organic molecule is placed inside a crucible. A tungsten wire is wrapped tightly
around the crucible over its entire length and each end of the wire is attached to an electrode. The end of each electrode is accessible from the outside of the chamber in order to be connected to a power supply to apply a current. By applying the current, the crucible warms up and reaches a temperature that the organic molecule sublime. A quartz crystal microbalance (QCM) is placed close to the substrate holder to monitor the flux. By depositing the molecules on the QCM, there’s a frequency shift for the quartz natural resonance. This frequency is constantly measured internally and then converted into a flux using the density of the material. Since the frequency of QCM is sensitive to temperature, cooling lines filled with water are used to keep the temperature constant. We usually outgas the organic molecule for the first time we put the molecule in the crucible to remove the impurity (If there’s any) mixed in the material. The organic molecule that I mostly used was C8-BTBT which was purchased from Sigma Aldrich. For C8-BTBT, we outgassed the material for 3-4 hours. During the outgassing, a shutter blocks the substrate. After the outgassing and once the rate is constant and desirable, we can rotate the shutter in a way that it doesn’t block the substrate anymore to start deposition.

![Diagram of the OMBD process](image)

Figure 2.5: The schematic of the chamber used for OMBD process.
The substrate holder has a small heater on it. The heater was calibrated before by attaching an extra thermocouple to read the exact temperature of the substrate and compared to the thermocouple which was attached originally closed to the substrate. In chapter 4 it will be shown that annealing the substrate during deposition can have a dramatic effect on the growth.

2.2.3 Electrode Fabrication

For top contact devices, after OMBD, the substrates were loaded into a shadow mask to deposit the drain and source electrodes. Figure 2.6 shows the shadow masks that were used for this dissertation. Each mask has more than 100 transistors with different length and width. The widths are changing from 900 μm to 3500 μm and the lengths were changing from 80 μm to 175 μm. We usually choose to measure transistors within the same width and length range (usually the length was between 100 μm to 150 μm and width was 950 μm to 1100 μm). When the shadow masks are positioned on the substrate, we should minimize the air gap between them. We usually attached a very small carbon tape on the corner of each mask to the layer beneath the substrates to make sure, we minimize the air gap between the mask and substrate. We avoid

Figure 2.6: a) a shadow mask used for electrode deposition. b) placing 5 shadow mask in a larger mask to load to the chamber. c) The Visible light microscope image (VLM) of a transistor.
letting the carbon tap attach to the substrate since it causes contaminations. We always used the carbon tape on the side of the mask which won’t touches the substrate.

Metal deposition was performed in our collaborator Dr. Harald Ade’s lab. The box chamber is a MB ProVap 5G purchased from MBRAUN. It is placed in the N₂ glovebox. The gold wire with diameter of 0.2 mm was purchased from Alfa Aesar. About 15 cm of the wire is wrapped around a clean tweezer and cut from the roll. The wrapped gold is placed on a tungsten boat. After pumping down the chamber (p ~ 2 x 10⁻⁶ torr) a current will apply to the boat to evaporate the gold onto the substrates through the shadow masks. A QCM monitors the thickness and the rate of deposition. In this work, 30 nm of gold was deposited onto the substrates with the flux of 0.2 A/s.

For bottom contact devices, after cleaning the substrates and treat them chemically with HMDS, they were placed into the shadow masks. For these devices, 5 nm of Cr with the rate of 0.1 A/s was deposited as an adhesion layer prior to gold deposition.

The gold electrode for some bottom contact devices were functionalized with the pentafluorobenzene thiol (PFBT). The functionalizing electrodes is performed in order to modify the work function of the gold electrode so that the charge injection usually improves in devices [17, 18]. The pentafluorobenzene thiol (PFBT) treatment in this work was done by soaking the cleaned substrates with prepattern Cr/Au electrodes in a 50 mM solution in high purity ethanol for 30 minutes, then sonicated in ethanol for 30 minutes.
2.3: Sample preparation for STM

The sample’s surface has to be cleaned for imaging by STM. The substrate used in chapter 3 and 5 of this dissertation for the STM study was Au(111). As shown in Figure 2.6, the surface has step edges and inside the step edges the herringbone pattern is visible. The Au(111) is kept in the ultra-high vacuum (8x10^{-11} torr) and before imaging is cleaned by Ar⁺ ion sputtering followed by annealing. In sputtering with Argon, the Argon atoms are leaked into the chamber. There’s a filament inside the sputter gun that emits electrons through thermionic emission. As the electrons collide with Argon atoms inside the sputter gun, Ar⁺ ions are produced. These Ar⁺ ions are then accelerated by a voltage toward the sample. The Ar⁺ ions strike the sample’s surface and remove surface matter by momentum transfer and over enough time the surface will almost become free of any contaminant. After sputtering, the surface will be very rough, since sputtering ions also strike the substrate atoms. In this situation, annealing the sample at high temperature can repair the surface and let the surface atoms to reconfigure into flat surface planes. For Au(111) substrate, we sputter the surface for 1 hour and anneal it at 700 K for 30 minutes. We let the substrate too cool down before depositing organic molecule.

![STM image of Au(111) surface. Image taken at V=1V and I=100 pA.](image_url)

Figure 2.7: STM image of Au(111) surface. Image taken at V=1V and I=100 pA.
Once the substrate is cleaned the organic molecule can be deposited on the surface. For this, we transfer the substrate from the preparation chamber to the fast entry lock (FEL) chamber which is separated from the main chamber by a gate valve (See Figure 2.8). The pressure in the FEL is $\sim 4 \times 10^{-7}$ torr. The deposition process is same as the process explained in OMBD section. Again, a QCM monitors the thickness and the rate of deposition. After molecule deposition, the sample is transferred to the STM chamber for imaging. The STM used in this dissertation was the Omicron VT-STM XA which was a variable temperature STM. The range of the temperature this STM can operate is from liquid nitrogen temperature ($\sim 140$ K) to 600 K.

Figure 2.8: Top-down view of STM set up.
References


Chapter 3

Suppression of Dynamic Disorder in Fullerenes at Metal-Organic Interfaces

3.1: Preface

This chapter is a reproduction of the work that is in press in The Journal of Chemical Physics.
Suppression of Dynamic Disorder in Fullerenes at Metal-Organic Interfaces

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Abstract: Organic semiconductors are prone to strong disorder effects that often exhibit significant dynamic character. In this study, static and dynamic disorder of fullerene molecules at the interface of Au (111) are directly distinguished using Scanning Tunneling Microscopy (STM) and Spectroscopy (STS). We consider an STM image consisting of hundreds of different molecules, as an ensemble which exhibits conductance fluctuations due to both dynamic and static disorder. On the other hand, local conductance measurement of single molecules over time reflects only dynamic disorder. We demonstrate that dynamic disorder is always smaller than static disorder at the C60/Au (111) interface due to structural constraints of molecules at interface. Dynamic disorder in our experiment is due to small librations of individual molecules that are restricted by metal surface, while static disorder is related to different bonding orientations of the C60 cage that are frozen-in at room temperature. Our experimental results can be modeled with direct simulations of differential tunneling conductance.

3.2: Introduction

Carrier mobility in organic semiconductors is a figure of merit that is relevant to all developing optoelectronic device applications. It has long been recognized that disorder effects in organic molecular solids often determine the carrier mobility [1, 2]. Even the best single
crystal materials can have a high enough density of charge traps to dominate transport at sufficiently low temperature and these traps also control device noise levels [3]. While static factors like structural defects and chemical impurities can often trap charge, intrinsic dynamical motion of molecules within the solid can also distort the potential landscape enough to localize charge carriers [4, 5].

Vibrations in molecular solids couple to electronic degrees of freedom and can give rise to what has been termed “dynamic disorder” [6, 7, 8] where molecular motion changes the transfer integral between sites in a transient way [9]. The importance of dynamic disorder reflects the key fact in organic molecular solids that energy scales associated with vibrational coupling can be comparable to intermolecular electronic couplings (i.e. hopping integrals). Vibrations can thus give rise to an effectively time-dependent electronic landscape in the solid that, in addition to disorder due to fixed defects, is a dominant factor in organic electronic device performance.

Recent observations have illustrated dynamic disorder effects in small molecule organic semiconductors and how they can be controlled by judicious placement of side-arms [6, 7]. In particular, for planar acene molecules, molecular sliding motions [10, 11] along the long-axis have been calculated to cause large dynamic changes in transfer integrals [12]. It was argued that placement of side-arms along small molecule aromatic planes can impede long-distance molecular sliding and thus mitigate dynamic disorder [7]. These insights have been enabled by the realization that the very small molecular motions associated with dynamic disorder can be measured using thermal diffuse scattering features in electron diffraction patterns in state-of-the-art low-dose Transmission Electron Microscopy experiments [6]. In addition, recent work from
our group has shown an onset of low frequency fluctuations occurring uniformly throughout a transistor channel precisely at its threshold voltage [13]. This fact is consistent with a significant dynamic disorder contribution to shallow charge traps due to relatively lower frequency molecular motion of molecules in the transistor channel.

A recent calculation by Tummala et al. of the relative magnitude of dynamic to static disorder was undertaken by comparing molecular dynamics calculations with equilibrium density functional theory calculations for various fullerenes [14]. This study showed dynamic disorder made an essentially equal magnitude contribution as static disorder to the total energetic disorder in fullerene solids. Thus, both types of disorder are essential to understand and control. The origin of dynamic disorder in the fullerenes was argued to be coupling to intramolecular cage vibrations based on the similarity between isolated molecule and solid state dynamics [14].

Similar calculations have been used to quantify the ability to control dynamic disorder by substituent groups attached to the fullerene core. It was found that fullerenes such as PCBM with flexible substituents had significantly large dynamic contributions to energetic disorder than more rigidly functionalized counterpart, indene-C\textsubscript{60} [15]. Furthermore, the role of dynamic disorder effects on nonradiative recombination in polymer-fullerene solar cells has been evaluated [16]. These calculations include assessment of the effects of dynamical bending along polymer chains that should be relevant to many state-of-the-art devices.

In this paper, we experimentally distinguish dynamic and static disorder at the single molecule level at the interface between a gold electrode and fullerene-C\textsubscript{60}. This is carried out by comparing time-resolved and spatially-resolved Scanning Tunneling Microscopy (STM) and spectroscopy measurements. The collection of different adsorbed C\textsubscript{60} molecules represents an
ensemble that includes both static and dynamic disorder. Alternatively, each individual molecule can be addressed over time to observe only dynamic disorder effects (albeit on relatively slow time scales). For a very well ordered monolayer of $C_{60}$ on Au(111) we find that the temporal fluctuations of tunneling conductance are systematically smaller than the spatial fluctuations. This illustrates that the structural constraints in a monolayer organic on a metal subvert the relative magnitudes of dynamic and static disorder, making the later more significant. In particular, dynamic disorder in our experiments arises from small librations of individual molecules that are constrained by interactions with the metal surface at a given site. By contrast spatial disorder arises from the numerous bonding orientations of the $C_{60}$ cage that cannot be interconverted at room temperature.

### 3.3: Experimental Methods

A single monolayer of $C_{60}$ was prepared on the Au (111) surface by depositing several layers of fullerene-$C_{60}$ (Sigma-Aldrich) at room temperature in a chamber described previously [11]. Subsequently, the multilayer film was annealed at ~ 600K to desorb all $C_{60}$ but the first layer as confirmed by direct STM imaging (e.g. in Figure 3.1a). Scanning Tunneling Microscopy imaging was carried out using a commercial instrument (Omicron VTSTM-XA) in constant current mode with home-etched tungsten tips that were annealed by electron bombardment in ultrahigh vacuum. All STM experiments were carried out with the sample held at room temperature. Differential tunneling conductance was measured using standard lock in amplifier techniques with a modulation frequency of 10 kHz and a $0.06 \text{ V}_{\text{rms}}$ amplitude.

An important part of this paper is to describe our methodology for comparing dynamic to static disorder using single-molecule STM. This is a variation on the time-dependent STM
studies that have been developed in the past for single-molecule chemistry studies [17]. It is important to address a highly controlled approach to comparing time-dependent tunneling observations to spatially-resolved tunneling observations including characterizing the instrument noise baseline.

To begin with, we measured traditional constant-current tunneling conductance maps at different tip-sample biases to establish an “ensemble” that includes both static and dynamic disorder effects as well as electronic instrument noise. Next, we measured time-series of tunneling conductance values above fixed C_{60} molecular adsorption sites. This measurement includes only dynamic disorder and instrument noise and is identical to the well-established time-dependent STM measurements for single molecule dynamics and chemistry. Furthermore, we take care to observe time series for total times equal in length to the total imaging time for a spatial conductance map. This permits a direct comparison where possible low frequency molecular dynamics are expected to also appear in the ensemble. Finally, instrument conductance noise was quantified by repeating each of the above measurements with the STM tip moved just barely out of tunneling range so that it includes preamplifier noise as well as any cross-talk from the high voltages that control STM tip scanning.

3.4: Results

Figure 3.1 shows the STM observations leading to our comparison of static and dynamic disorder. Corresponding to the topographic image in Figure 3.1a, Figure 3.1b shows a conductance map measured at +1.0 V where the local tunneling conductance fluctuates across the ordered overlayer. The value of +1.0 V is chosen since it closely corresponds to the well-
known peak in the tunneling density of states (DOS) assigned to the Lowest unoccupied molecular orbital (LUMO) [18, 19].

In Figure 3.1c, a time series of conductance values measured at a fixed point above a single C_{60} molecule is shown. The major purpose of the analysis in what follows is to quantitatively compare the spatial fluctuations in conductance (Figure 3.1b) to the temporal fluctuations in conductance (Figure 3.1c) for the purpose of disentangling dynamic and static disorder. As already mentioned, this is analogous to comparing a time average and an ensemble average such as done in the calculations of Tummala et al [14].

Figure 3.1 a) STM image (20 nm x 20nm, +1 V, 200 pA) showing the C_{60} monolayer on Au(111) ; b) STM conductance map corresponding to a); c) Time series of conductance values measured (+1 V, 200 pA) above a single molecule in the monolayer.
Figure 3.2 shows histograms of the raw conductance values for spatial and temporal conductance measurements. The spatial histogram is made by tabulating the conductance values at the center of ~ 400 molecules with the average conductance value shifted to zero. Temporal histograms are shown for a collection of individual molecules and have been shifted so that the average taken over all the molecules is at the same zero as the spatial average (but each individual molecule average may not be at zero). The important observations from these histograms are 1) The temporal histograms are always narrower than the spatial histogram; and 2) The set of all temporal histograms measured for all of the many different molecules closely approximates the total width of the spatial histogram. Figure 3.2a shows the data for +1.0 V bias near the LUMO of the C₆₀ adsorbates. Figure 3.2b shows conductance histograms at -1.7 V, the approximate energy of the highest occupied molecular orbital (HOMO) and Figure 3.2c shows histograms for -0.5 V in the gap between orbital –derived states. The general trends of fluctuations are independent of bias as discussed in more detail in Section 4.c.

Consideration of the experimental data in Figure 3.2 establishes a connection to the theoretical predictions of Tummala et al. [14] Indeed it shows that the ensemble of molecules corresponding to the spatial fluctuations includes both dynamic and static contributions to disorder in the LUMO similar to the ensemble calculations, as expected qualitatively from the theoretical calculations. To further quantify the relative contributions of various disorder sources, we fit each spatial histogram to a Gaussian function and decompose the total width as

\[ \sigma_{tot}^2 = \sigma_s^2 + \sigma_d^2 + \sigma_{tot,f}^2 \]  

(3.1)
Where $\sigma_s$ is static disorder $\sigma_d$ is the dynamic disorder, and $\sigma_I$ is the separately calibrated instrumental noise (which is $\sigma_{tot,I} = 14.1 \pm 0.1$ pS). In the spatial histogram all terms in Eq. (3.1) are included. In the temporal histogram, only dynamic and instrumental noise are included ($\sigma^2_{d,tot} = \sigma^2_d + \sigma^2_{d,I}$ with, i.e. $\sigma_{d,I} = 6.98 \pm 0.16$ pS). This allows direct extraction of $\sigma_s$ and $\sigma_d$ since the other two quantities are measured experimentally by fitting histograms in Figure 3.2 to a Gaussian function.

Figure 3.2: Temporal and spatial conductance measured at a) $V = +1$ V (LUMO); b) $V = -1.7$ V (HOMO); c) $V = -0.5$ V (in-gap);
Table 3.1 compiles the dynamic and static disorder in tunneling conductance for the LUMO as well as the highest occupied molecular orbital (HOMO) and an energy within the HOMO-LUMO gap. The width of each conductance can be changed if we measure it at different tip condition. However, as shown in Figure 3.3, the relative width of $\sigma_s/\sigma_d$ is always constant at the specific sample voltage. We discuss about the deciding factor in the width of conductance in more details in section 4.3. In all cases, the dynamic disorder width is significantly smaller than the static disorder width. This contrasts with the theoretical study for a fullerene solid which predicts that the two effects will be almost identical in magnitude. Evidently, the relative role of dynamic and static disorder is different at a metal organic interface compared to a bulk crystal.

![Graph showing $\sigma_s/\sigma_d$ vs Experimental Trials]

Figure 3.3: The relative width of static and dynamic disorder at +1.0 V in tunneling conductance, measured on different days with different tip conditions.
Table 1. Parameters extracted from conductance fluctuation measurements for C₆₀/Au(111).

The total width of the raw histogram from conductance maps is \( \sigma_{\text{tot}} \), the total width of the instrumental conductance histograms for the spatial maps is \( \sigma_{\text{tot},I} = 14.1 \pm 0.1 \text{pS} \), and the instrumental widths for the dynamic measurements of single molecules is \( \sigma_{d,I} = 6.98 \pm 0.16 \text{pS} \). The intrinsic static and dynamic contributions to conductance fluctuations are then extracted as described in the Equation 3.1.

<table>
<thead>
<tr>
<th>Voltage</th>
<th>Orbital</th>
<th>( \sigma_{\text{tot}} )</th>
<th>( \sigma_s )</th>
<th>( \sigma_d )</th>
<th>( \sigma_s / \sigma_d )</th>
</tr>
</thead>
<tbody>
<tr>
<td>+1.0 V</td>
<td>LUMO</td>
<td>37.25 \pm 2.67</td>
<td>33.05 \pm 3.01</td>
<td>9.83 \pm 0.36</td>
<td>3.35 \pm 0.33</td>
</tr>
<tr>
<td>-1.7 V</td>
<td>HOMO</td>
<td>54.07 \pm 4.09</td>
<td>46.42 \pm 4.77</td>
<td>23.88 \pm 0.60</td>
<td>1.94 \pm 0.20</td>
</tr>
<tr>
<td>-0.5 V</td>
<td>In-gap</td>
<td>50.13 \pm 3.42</td>
<td>45.20 \pm 3.80</td>
<td>16.50 \pm 1.25</td>
<td>2.92 \pm 0.24</td>
</tr>
</tbody>
</table>

To understand the origin of this effect, we need to consider the local tunneling spectra measured for different molecules in the spatial ensemble as shown in Figure 3.4. The vertically offset spectra are local conductance measurements for different individual molecules while the inset of Figure 3.4 show the spatial average over all of the molecules. In each spectrum we see the HOMO-derived peak at \( \sim -1.8 \) V and the LUMO derived peak at \( \sim +0.9 \) V, in agreement with previous tunneling spectroscopy measurements [18, 19]. However, the precise peak positions seen to vary between different molecules in the vertically offset curves. Each peak position can vary by at least a few tenths of a volt across the monolayer.

The spatial variation in local electronic structure is expected based on the previous consideration of different molecular orientations at different sites on the surface. As described in the DFT study of Wang et al., these different orientations can have significantly different local
electronic properties [20]. For example, a C_{60} adsorbate oriented with a hexagon directly facing the Au surface has been calculated to have a larger energetic shift of its LUMO orbital than one with a pentagon facing the surface. These orientations have slightly different adsorption energies but they are known [18, 21] to coexist within many C_{60} monolayers after being kinetically frozen in during the deposition (and/or annealing) process. Thus, the static spatial variation in dI/dV arises predominantly from different fullerene adsorption orientations.

The dynamic variations in dI/dV must arise from different effects. Direct interconversion of different orientations is overwhelmingly improbable since past experiments have demonstrated and quantified the kinetics of such interconversion and found large energetic barriers [22]. Moreover, if interconversion were possible, the conductance distribution for dynamic and static measurements would be identical. Possible small scale motions of C_{60} molecules that could lead to the observed conductance differences are translational lattice

Figure 3.4: Tunneling spectra measured above different C60 molecules in the monolayer showing ensemble variations in the conductance at different energies. Inset: Average tunneling spectrum over a total of 44 C60 molecules.
phonons or librational modes [23]. The later are frustrated rotations that are normally only important at low temperatures in bulk fullerene solids due to the rotational freedom above ~ 260 K [24]. However, the presence of the Au(111) substrate clearly changes the rotational dynamic and makes librations are very likely cause of the observed dynamic disorder. A static C\textsubscript{60} orientation is frozen in upon creation of the monolayer and librations cause small changes to the local conductance. The following section discusses the implications of the relative effects of the observed dynamic and static disorder and how it can be incorporated into a phenomenological tunneling model.

3.5: Discussion

3.5.1 Connection to Theoretical Studies of Dynamic Disorder in Fullerenes

A key point to emphasize about the observations reported in this paper is that they refer to relatively slow rotational motion of the fullerene molecules. In contrast, the recent calculations of dynamic disorder in fullerenes focus on molecular vibrational motion that occurs on time scales far too rapid to be dynamically accessible to typical STM measurements. Nevertheless, it is possible to make a few useful comparisons and contrasts between previous theory and our experimental observations. Most importantly, our measurements provide a proof of principle demonstration that it is possible to experimentally differentiate dynamic from static effects by comparing time dependent single-molecule STM to a space-dependent ensemble STM. In the case considered here the expected distinction between dynamic and static effects of molecular orientation changes makes the delineation clear.

It has long been known that rotational motion in fullerite crystals is thermally active at room temperature [24, 25]. Thus, in the absence of the metal interface present in our experiment,
we would expect the effects of static and dynamic rotational disorder to be of essentially equal magnitude. In this case, at any given, instant a molecule at any given site would be equally likely to be in any possible orientation. Conversely, any site averaged over time would sample all possible orientations. Our observations thus illustrate another example of how interfaces in organic electronic devices can have significantly different disorder effects than bulk materials. In the past, it has been noted that there are several scenarios where static disorder at interfaces can be dramatically different than the bulk [26, 27, 28]. Clearly the interfacial interactions can also modify dynamical effects.

Computational studies indicate that rotational motion and average orientation of C60 adsorbates have a significant impact on the local density of states [20] and therefore in part determine the charge injection properties (e.g. the effective Schottky barrier) into the organic material. Evidently, the most important aspect to consider at the interface may be the static structural order since dynamic motions can be strongly constrained. This contrasts with bulk effects where dynamic and static disorder effects are often comparable or where dynamic disorder is even suspected to be the dominant factor in determining charge transport [14, 29].

3.5.2 Ergodicity Breaking at the Metal-Organic Interface

The constraints imposed by C₆₀ interactions with the metallic substrate make temporal and spatial averages different. This is an example of ergodicity breaking and implies that equilibrium statistical mechanics does not rigorously apply at this particular metal-molecule interface. This could have practical implication in how we view modeling of injection processes. It highlights the question of whether it is correct to assume a well-defined macroscopic temperature and chemical potential that governs charge injection. Importantly, the fact that static
and dynamics disorder were calculated to be the same for bulk fullerene solids [14] suggests that this is indeed an interfacial effect.

Similar ergodicity breaking has recently been noted in molecular motion in biological systems. For example, molecular diffusion controlling ion motion at membranes in neuron cells has shown non-ergodic signatures due to trapping in the ion channels [30]. In granular materials, non-ergodicity is a defining fact that determines approaches to understanding macroscopic characteristics analogous to thermodynamics [31]. Frustrated rotational motion of grains has been observed to lead to nonergodic behavior in the case of packed pentagonal plates [32, 33]. This is an interesting connection to the frustrated rotations we observe since our experiments observe thermally-activated motion while granular matter is completely athermal [31]. The important connection between all of these situations and the C$_{60}$/Au(111) interface that we have studied is that strong constraints render the system inhomogeneous at a microscopic level. The constraints prevent the microscopic degrees of freedom at different sites from all accessing the same regions of phase space as time evolves and breaks the standard ergodic hypothesis.

3.5.3 Model for Tunneling Conductance Fluctuations

The conductance fluctuations measured in our STM experiments arise as the tip position responds to the different molecular orientations either in space or in time. Under the constant current feedback conditions used to measure fluctuations, the tip will move vertically as the local conductance changes. The differential tunneling conductance can be expressed as follows [34]:

$$\frac{dI}{dV} = B \rho_T \rho_s (eV) T(z, V, eV) - \frac{aezI}{4\sqrt{\phi}} \quad (3.2)$$
Where $\rho_s$ is the density of electronic states of the sample, $\rho_T$ is the density of electronic states of the tunneling tip (assumed independent of energy), $T(z, V, EV)$ is the transmission function for a square potential barrier, $z$ is the distance between the tip and the sample, $\alpha$ and $B$ are numerical constants, $\phi$ is the effective energy barrier for the square potential, $V$ is the potential difference between the tip and sample, $e$ is the electronic charge. In this equation, we neglect variation of $z$ with $V$ since conductance histogram measured in Eq. (4.1) are measured at fixed potential difference. Our basic approach in using Eq. (4.1) is to focus on fluctuations of the parameter $z$ that arise from either different molecular orientations or librational motions.

The reason to focus on fluctuations in $z$ is that the transmission function $T(z, V, eV)$ is an exponential function of the distance $z$ between the tip and sample. Therefore, any small height changes on the surface or the tip will dominate the conductance values. One effect of the inherently uncontrolled tip properties, which change substantially from day to day, is that the absolute magnitude of the conductance values and their fluctuations change with the tip. However, this occurs in both ensemble and dynamic conductance measurements and leads us to focus on the relative width of $\sigma_s / \sigma_d$ for each measurement with a stable tip. The other possibly relevant parameter in Eq. (4.1) is the density of states of the sample which clearly varies somewhat between different molecules in the ensemble (see Figure 3.4). However, these effects are small compared to the $z$ fluctuations in the transmission function and are also averaged over the modulation bias of 0.06 Vrms. This is only slightly smaller than the typical static energetic disorder broadening for a fullerene solid [14] and so from the standpoint of the STM tunneling conductance measurements here, the density of states is approximately constant. We consider typical values for all of the parameters given in Eq. (4.1) similar to those used in Pronschinske et
al. [34] and simulate statistical conductance distributions for comparison with the experimental data in Figure 3.2.

Figure 3.5 shows simulated conductance histograms for an assumed Gaussian distribution of tip sample separations z centered on 0.25 nm. The blue circles represent static disorder where the fluctuation in z about its average value is set to the experimental spatial variation of tip height of 0.031 nm. This value is extracted from STM topographic images such as Figure 3.1a. The red squares represent dynamic disorder due to the much smaller on-site librational motions. We assume z fluctuations due to librations to be ~ 0.01 nm and observe that the relative width of the dynamic and static histograms agrees with our observations.

![Simulated conductance histograms using Eq (2) and assuming a Gaussian distribution of z-values for the STM junction width.](image)

Figure 3.5: Simulated conductance histograms using Eq (2) and assuming a Gaussian distribution of z-values for the STM junction width. The blue circles represent static disorder with a large z variance due to different frozen-in molecular orientations in the monolayer. The red squares represent the narrower dynamic distribution simulated by assuming a smaller variance of z-values corresponding to librational motions at fixed sites.
There are some interesting differences between the simulation and the experiments. Both of the simulated distributions are strongly asymmetric due to the dominance of the exponential transmission function in Equation (2). In the limit where tunneling conductance variation due to random z values is the only physical effect relevant to conductance fluctuations, the conductance distribution would be rigorously log-normal since we place a Gaussian random variable (z) inside an exponential function. The experimental histograms do not allow a clean distinction between a Gaussian and log-normal distribution even though the simulation suggests that this should be at least qualitatively evident with the quantity of data used in each individual histogram. This difference could in part be attributed to the square barrier transmission function we employ. A more realistic barrier shape might give a closer correspondence between simulation and experiment. However, the key aspect is that the relative size of dynamic and static conductance fluctuation can be produced with realistic parameters in this simplified tunneling model.

3.6: Summary and conclusion

In summary, we have studied the relative contribution of dynamic and static disorder of C60 on the Au(111) surface by comparing temporal and spatial variation in conductance of C60 molecules. We believe STM experiments can be an important experimental tool for measuring different disorder effects at the single molecule level. We have outlined several experimental considerations including instrument noise characterization and matching time scales of dynamic and ensemble measurements, as well as a basic phenomenological model for STM-based conductance fluctuations in constant current mode.
Our results for $\text{C}_6\text{H}_{60}/\text{Au}(111)$ show that spatial conductance fluctuations are always larger than temporal conductance fluctuations in this system. This is in contrast to predictions for bulk $\text{C}_6\text{H}_{60}$ solids [14] and shows that interfacial constraints can alter the relative importance of static and dynamic disorder. Such constraints evidently break ergodicity in the $\text{C}_6\text{H}_{60}$ monolayer, making ensemble statistics different from temporal statistics’ This raises the interesting question of the validity of thermodynamic equilibrium concepts at metal-organic interfaces. The constraint of the surface prevents free rotation of $\text{C}_6\text{H}_{60}$ adsorbates but leaves in place a frozen-in distribution of random $\text{C}_6\text{H}_{60}$ bonding orientations. This is incorporated into a tunneling model by assuming that dynamic fluctuations in tip-to-sample distance are much smaller than those between different adsorption sites.

The observed suppression of dynamic disorder at the metal-organic interface has implications for organic electronic device physics where, in an injection limited circumstance, it may be more important to control static disorder than dynamic disorder. Importantly, this is opposite to what might be expected in devices that are limited by transport processes away from the metal-organic interface where dynamical effects can be comparable to static ones and thus more consequential for device optimization.
References:


semiconductors by suppressing large-amplitude thermal motions," *Nature Communications*, vol. 7, no. 10736, 2016.


Chapter 4

Thickness-Dependent Mobility Controlled by Morphology Evolution During Contact Processing in C8-BTBT Field Effect Transistor

Abstract: The most promising carrier mobilities in recent years for organic semiconductors have been obtained in films of the small molecule C8-BTBT. We find generally good carrier mobilities in films grown by organic molecular beam deposition. This unexpected thickness dependence is found to be the results of morphology evolution induced by top contact deposition.

4.1: Introduction

Organic Field Effect Transistors (OFET’s) are technologically important as candidate active backplanes for display technologies [1, 2] and also occupy a dominant role in empirical characterization of charge transport in organic semiconductors [3, 4, 5]. The field effect mobility determined from these devices is the primary figure of merit for assessing the limits of charge transport in the material class. The highest values obtained are on the order 10-20 cm²/Vs and typically found in single crystal samples [3, 5]. In thin film OFET’s, complex morphological evolution during growth and processing determine carrier mobility by controlling defect density and film connectivity.

The thin film approach has been taken to extreme limits by considering single layer OFET’s. In this field, one vision is that morphological control of a single active layer could be more reliable when compared to thicker films that presumably undergo more complex growth processes. Using self-assembled monolayers or monolayer films created by single layer organic
molecular beam deposition (OMBD), it is possible to create functional transistors that can be integrated into logic circuits [6]. Moreover, the effective low dimensionality of these ultrathin OFET’s acts as a separate experimental knob to test existing charge transport models in organic semiconducting materials [7, 8, 9]. Single layer transistors have also very recently been cast from very dilute polymer solution, promising new solution-based routes to precise structural and morphological control in OFET’s [10].

The small molecule C8-BTBT has shown good performance in OFET’s created by solution casting [11, 12, 13, 14], vapor deposition techniques [15], and novel hybrid processing methods [16, 17]. Vacuum deposition was employed to make single layer transistors on hexagonal boron nitride with carrier mobilities reported to be of order 30 cm2/Vs [18]. Contacts to these very thin molecular channels were made by the unusual approach of micromanipulation of pre-deposited gold flakes with a transport probe station tip. Vacuum deposited films with more traditional top contacts showed lower mobilities (5-10 cm2/Vs) consistent with early solution-based devices.

This situation is a prime example of the importance of processing details in organic electronic device performance. The same materials can show dramatically different figures of merit in devices depending on the precise processing steps. This is intimately connected to the impact of organic film morphology on the very complex and often disordered charge transport pathways in soft materials [7].

In this paper, we report on morphological effects controlling charge transport in C8-BTBT OFET’s with particular attention to the processing steps involved in contact creation. We have found an unexpected thickness dependence to the field effect mobility for C8-BTBT
OFET’s grown by OMBD methods with source and drain contacts grown by traditional vacuum deposition methods. The carrier mobility increases with thickness for many molecular layers despite the fact that the accumulation layer in OFET’s is typically found to exist within the first few layers [19, 20, 21]. This origin of the extended thickness dependence is traced to film morphology degradation caused by electrical top contact deposition that is most severe for the thinnest films. The effect can be suppressed but not totally eliminated by depositing contacts at cryogenic temperatures, indicating that the nonequilibrium diffusivity of “hot” metal atoms arriving from the vacuum is the decisive factor.

4.2: Experimental Methods

Thin films of (C8-BTBT) were grown by organic molecular beam deposition (OMBD) in a high vacuum chamber that has been described previously [22]. A quartz crystal microbalance (QCM) was used to monitor the flux (≈ 0.1 - 0.2 A/s) and film thicknesses were calibrated by direct AFM imaging after growth. The substrates were Si(001) wafers with a 300 nm thermal oxide that were cleaned with acetone sonication and isopropanol sonication each for 10 minutes, then rinsed with DI water and blown dry with N\textsubscript{2}, followed by UV ozone exposure for 15 minutes, and again rinsed with DI water and blown dry with N\textsubscript{2}. Then the substrates were chemically treated with a hexamethyldisilazane (HMDS) monolayer in a glove box as described before [22]. The substrate temperature during growth was controlled by an integrated heater on the substrate stage that had been calibrated.

Atomic Force microscopy experiments were carried out with a commercial instrument (Asylum MFP-3D) using commercial non-contact tips for imaging (Budget Sensors Tap300Al-G) and Kelvin probe studies (Budget Sensors ElectriMulti75-G).
Top contact Organic Field Effect transistor devices were made by depositing 30 nm of Au source and drain contacts (with the flux \( \sim 0.2 \) A/s) through a shadow mask onto the C8-BTBT thin film channel. For bottom contact devices, 5 nm of Cr was deposited prior to 30 nm Au deposition on HMDS treated substrate. The pentafluorobenzene thiol (PFBT) treatment was performed by soaking the cleaned substrates with prepatteren Cr/Au electrodes in a 50 mM solution in high purity ethanol for 30 minutes, then sonicated in ethanol for 30 minutes. In all devices, the gate contact was made by scratching the back side of the Si wafer with a diamond scribe and applying silver paint to contact the highly doped Si. Transistor output and transfer curves were measured with a semiconductor parameter analyzer (Keithley 4200) in a commercial probe station (Janis CCR5) in vacuum \( (\sim 10^{-4} \) torr).

4.3: Results

4.3.1: C8-BTBT Film Structure and Morphology

The nucleation and growth on C8-BTBT films during OMBD on HMDS-treated silicon wafers is quite similar to known behavior of other related small molecules. Figure 4.1 shows a series of AFM images for submonolayer \( (\sim 0.5 \) ML) films grown at different temperatures. At room temperature, there is a relatively high nucleation density of islands with height measured by AFM to be just above 3 nm, consistent with the length of the upright molecule. At higher temperature, the nucleation density significantly decreases due to the enhanced surface diffusivity that allows more deposited molecules to find existing nuclei on the surface as opposed to creating stable new nuclei. This situation has been observed for pentacene [23] and other films on a variety of substrates and is in line with standard predictions of submonolayer nucleation theory [24].
The nucleation of behavior of C8-BTBT films is promising for device considerations since growth at temperatures ~ 70°C results in very large nuclei with dimensions of several micrometers. Such a nucleus could potentially span a set of source drain electrodes and act as a channel for a single layer OFET with minimal structural defects. However, we have found that films grown at substrate temperatures above room temperature tend to result in poor transistors that either do not turn on at all or have low mobility. We attribute this to the fact that, for large nuclei, there can be relatively large crack-like defects between nuclei that dominate device performance.

![Incomplete monolayer of C8-BTBT on HMDS treated substrates deposited a) at room temperate, b) at 40°C, c) at 70°C.](image)

As the thickness of the films is increased for growth on a room temperature substrate, we find a typical wedding cake film morphology that has also been seen for pentacene and related small molecules in OFET’s [25]. Figure 4.2 shows a series of such films at different thicknesses from 1.5 layers up to ~ 50 layers. For films thicker than ~ 10 layers, we can begin to note the presence of high needle-shaped mounds. These features represent an alternate crystal polymorph
that has been reported in the past [17]. These needles do not percolate across the film and so their impact on OFET performance is assumed to be relatively minor.

Figure 4.2: 10nm * 10nm AFM images of C8-BTBT film a) 1 complete layer, b) 2 complete layers c) 5 complete layers d) 10 complete layers e) 25 complete layers, f) 50 complete layers. The black regions in a), b), and c) are substrates. After 10 complete layers, the needle growth appears on the film as shown in d). Since the imaging quality exacerbate for 25 and 50 complete layers, we find areas without needle growth to scan.
4.3.2: Organic Field Effect Transistor Performance

We have measured transistor performance for OFET’s with active layers from ~ 2 complete layers up to ~ 50 complete layers in a top-contact, bottom-gate configuration. Example output and transfer characteristics for a two layers OFET are shown in Figure 4.3a and 4.3b respectively. The threshold voltage in our devices is quite high, similar to other ultrathin C8-BTBT OFET’s [18]. This fact was not found to depend on the film thickness. Other C8-BTBT transistors have been reported to have lower threshold voltages, so it is likely possible to optimize this aspect beyond what we have achieved.

Figure 4.3: a) Output and b) transfer characteristics in saturation $V_{d}$=-20 V for a 2 layers devices. c) Output and d) transfer characteristics in saturation $V_{d}$=-80 V for a 25 layers device.
The reliability factor of the OFET curves in our experiment was calculated according to the recommendations of Choi et al [26] and found to be in the range of 6-40%. This is far from ideal, but high enough to consider the devices as functional. The low values for the reliability factor are probably indicative of some impacts of contact resistance on the precise value of extracted mobilities.

![Graph](image)

**Figure 4.4:** Mobility versus thickness. The black and red dots represent transistors in which the drain and source electrodes deposited at room temperature and at cryogenic temperature, respectively.

The mobility in our films was found to increase with film thickness from ~ 0.1 cm²/Vs to ~ 2.5 cm²/Vs in going from a two layers film (Figure 4.3a and 4.3b) to a many layer film (Figure 4.3c and 4.3d). The fact that mobility continues to increase for many layers is at odds with what would be expected based on previous understanding of the ultrathin accumulation region in OFET’s. Figure 4.4 shows the thickness dependence of mobility for a series of devices with Au source and drain top-contacts grown with the device film held at either at room temperature or at liquid nitrogen temperature. It shows increasing mobility in both cases with no clear sign of saturation out to more than 50 layers. The mobilities for the devices with contacts grown at low temperature were systematically higher than those with room temperature contact growth. This implies some important impact of the contact creation step on ultimate device performance.
4.3.3: The Impact of Top-Contact Deposition on C8-BTBT Film Morphology

Despite the fact that bottom-contact geometries have been commonly used in OFET fabrication using films of small molecules, we were not able to obtain reliable results for our C8-BTBT films. The reason is clear from Figure 4.5a. Here we show a failed OFET where C8-BTBT was deposited on top a region with predefined source and drain contacts. There is a severe morphological discontinuity between the contacts and the channel. In fact, there seems to be depletion region where relatively little evidence of a molecular film is found near the contacts.

The problem of discontinuities in film growth morphology between a channel and source/drain electrodes was identified years ago within the OFET community. An interesting solution has been to functionalize the electrodes with a thiolate SAM so that they are energetically more similar to the silane-functionalized gate dielectric region. This strategy has been used with considerable success to improve diF-TES-ADT transistors using a halogenated benzenethiolate SAM’s [27]. We found that this approach resulted in improvements to our device morphology as illustrated in Figure 4.5b, where it can be seen that C8-BTBT islands extend continuously across the contacts. However, we also found that OFET performance in such devices was not as good as for devices using a top contact geometry. From here we consider only the top contact case.

Figure 4.5c shows an AFM topographic image that indicates very good morphological continuity between the channel and the top contacts. In fact, it is not so easy to discern where the contacts begin based on film morphology alone. In part this is due to the use of a shadow mask which makes the 30 nm contact thickness accumulate relatively gradually. However, direct imaging of surface potential using KPFM shown in Figure 4.5d reveals an abrupt potential shift where the contact begins. Evidently, the gold metal is continuous and forms a film
consisting of grains smaller than the spatial resolution of the AFM. These grains can be
noticeable by comparing the right and left sides of Figure 4.5c.

Figure 4.5: AFM images of channels and drain and source electrodes. The black and red lines
indicate the electrode and the channel part, respectively. a) more than one monolayer of C8-BTBT
on bottom contact devices. The blue arrow indicates the discontinuity. The first monolayer covers
the channel and the 2nd and 3rd layer is forming in the channel. The branched growth forms on
electrodes. b) more than one monolayer of C8-BTBT deposited on bottom contact device in which
the electrodes are chemically treated with PFBT. The discontinuity between the channel and
electrodes was eliminated. c) 2.5 monolayers of C8-BTBT film in top contact geometry. d) KPFM
of the transistor in c. In all images, the white bar is 10 nm.
On one hand, the morphology in Figure 4.5 suggests that top contact devices should perform well. Indeed, the carrier mobilities for thick films are good, albeit not records for C8-BTBT devices. However, there still remains the mystery of why the carrier mobility increases with thickness beyond the few layer regime. There are several cases where such an effect has been seen in small molecule OFET’s and associated with small morphological degradation due to the top-contact deposition process.

We found that contact growth does notably alter the morphology of the C8-BTBT films and that this effect is most significant for the thinnest films. Figure 4.6 shows AFM images of films before and after Au top contact deposition. It is readily apparent for the very thin (~ 2 layer) film in Figure 4.6a and 4.6e that significantly more “low” areas (in the case the HMDS/SiO2 substrate) are present after deposition than before. The same trend is visible to a
lesser extent in the thicker film case as shown in Figure 4.6. This is similar to reports of the effect of top-contact deposition in tetracene OFET’s [28].

![Figure 4.7: The percentage of changes in film morphology before and after contact fabrication versus thickness.](image)

We quantify the changes in film morphology by measuring the percentage of the dark regions (for 2, 3, and 5 monolayers the dark regions are HMDS/SiO$_2$ and for 8 monolayers it is the lowest layer seen in AFM image). Figure 4.7 shows the changes before and after gold deposition, each point is the averaged over 20-40 AFM images which are taken before and after top-contact creation. The change decreases as film thickness increases and we attribute the thickness dependence of mobility shown in Figure 4.4 to these morphological changes. Evidently, the thinnest films in our experiment have their morphology significantly degrade by top contact deposition. For thicker films, the top layers provide some immunity to contact-induced changes of the active channel in the first few layers near the gate dielectric.

4.4: Discussion

The thickness-dependent mobility we report here is similar to that reported for pentacene and tetracene OFET’s in the past. The prior experiments used an empirical model for the dependence that to fit the mobility data given by [28, 29]:

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\[ \mu = \mu_{\max} \left( 1 - \exp \left( - \left( \frac{d}{d_c} \right)^\beta \right) \right) \quad (4.1) \]

where \( d \) is the film thickness, \( \beta \) is a fitting exponent, \( \mu_{\max} \) is the maximum (i.e. saturated) carrier mobility, and \( d_c \) is the characteristic film thickness where the mobility has nearly obtained its maximum value. The solid lines in Figure 4.4 show examples of this function plotted with the mobility data for Au contact deposition on a room temperature substrate and on a substrate cooled to \( \sim 80 \) K. Evidently, the critical thickness, and saturation mobility are significantly different for the two contact deposition protocols. The critical thickness is larger (\( d_c \sim 12.0 \) ML) for the case when contacts are grown at room temperature compared to contacts grown at low temperature (\( d_c \sim 7 \) ML). This reflects the fact that the morphology changes are likely to be more severe at room temperature where the intrinsic diffusion of the C8-BTBT molecules is more rapid. Thus the thickness required to protect the lower layers where the active channel exists is larger.

The functional form of Eq. (1) is indeed empirical and the small number of data points in Figure 4.4 make interpreting the solid lines as fits not particularly compelling. Nevertheless, it is interesting to note that the empirical formula is an example of stretched exponential function that was initial applied to discharging of glassy capacitors. The connection to transport in the disordered landscape of an organic molecular film is apparent, especially in light of the relatively routine use of this model in previous data.

Despite the semi-quantitative similarity between our OFET observations and previous reports of anomalous thickness-dependent mobilities, there are significant distinctions. The most instructive comparison is to tetracene, where the explicit connection between mobility and morphology degradation has been clearly made for top contact devices [28]. The morphology
degradation we report in Figure 4.6 and Figure 4.7 appears more significant than reported for tetracene. This is most likely attributable to the side arms of C8-BTBT that give it more opportunity for rapid surface diffusion than the fully aromatic tetracene. The relatively facile diffusion of the C8-BTBT species is evident from its low temperature liquid crystal phase transition at \( \sim 110 \, ^\circ C \) [30]. One may speculate that the arrival of “hot” gold atoms on top of the film during contact growth can locally induce a liquid crystal-like environment that heals imperfectly as the deposition energy is dissipated, thereby degrading film morphology.

Another important difference is found in comparison to pentacene films, which also have shown an anomalous thickness dependent mobility for top contact devices. For this molecule, it is possible to create functional transistors using a bottom contact approach. In-situ transport experiments show that the thickness dependence of mobilities is in line with the expectation of a very thin (even submonolayer) active channel. By contrast, we have not found functional devices using a bottom contact approach unless the contacts are first functionalized with PFBT SAM’s. The low mobilities we found for these functionalized contact devices arise from the degraded connectivity of films and are a further indication of the extreme sensitivity of charge transport to film morphology. We can in some sense regard the devices created on PFBT-treated electrodes as having undergone a morphological degradation similar to what occurs during top contact deposition, possibly due to an enhanced overall diffusion rate.

Finally, we discuss the connection between our device measurements and C8-BTBT devices made using solution processing techniques. Early experiments showed that solution-deposited films could have remarkably high carrier mobilities of \( \sim 5 \, \text{cm}^2/\text{V}s \) [13]. Different processing condition such as blending with polymers and dopants [12] and nucleation of microwires [11] reproduced and even improved this notable performance metric. In particular,
all of these good results used top-contact deposition onto relatively thick C8-BTBT films that would not be expected to suffer from much top-contact-induced degradation. In fact, our best thick devices show carrier mobilities comparable to those reported for thick solution-grown films. It has not been checked whether morphological degradation occurs for top contact deposition onto ultrathin films cast from solution. We view this as very likely to occur for thin enough films especially because the film morphology in some spun-cast films\textsuperscript{26, 27} is nearly identical to what we observe by OMBD. Alternate solution processing techniques would likely differ in the impact and detail of top contact deposition.

\textbf{4.5: Summary and Conclusions}

In summary, we have studied morphological properties of C8-BTBT in OFET’s and their impacts on charge transport in C8-BTBT layer. The thin bottom contact devices showed discontinuity in some areas between the electrodes and the channels since the surface energy and growth mode is different between these two. Functionalizing the electrodes with SAM could eliminate the discontinuity problem and improve the growth but also dramatically decreased the performance of devices. A thickness dependence mobility was found in top contact devices up to 50 monolayers. However, the mobility should have saturated after the first few layers in organic molecules created by OMBD. We realized that this thickness dependence mobility is due to a morphological degradation of C8-BTBT film during top contact deposition. This degradation of the film ameliorated with increasing in thickness which explained the thickness dependence of mobilities. The degradation didn’t eliminate but improved with depositing electrodes at cryogenic temperature.
The impact of morphology on charge transport is an undeniable fact. Therefore, the factors affect morphology must be considered and morphology of organic molecules has to be engineered in each circumstances. C8-BTBT has shown a promising material for OFET’s. However, without proper attention to fabrication process specially contact engineering, we can’t obtain the maximum charge transport in the organic layer.
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Chapter 5

Dynamical Behavior of C8-BTBT Domain Boundaries at Metal-Organic Interface

Abstract: Domain boundaries are a determining factor in the mobility of organic devices since they can trap mobile carriers. We have observed the dynamical behavior of these boundaries and suggest that their thermal fluctuations are a new source of dynamic disorder in organic films. Here, we study the dynamical behavior of C8-BTBT monolayer films with dynamical domain boundaries at a metal-organic interface. Power spectral density of fluctuating boundaries indicates a single molecular trapping and release event to the domain boundary. By quantifying the dynamics of the boundaries, we realized that the dynamical scaling at early times shows a growth exponent of $\frac{1}{2}$ indicating uncorrelated diffusive motion of molecules. This is followed by the saturation of the boundary edge width to a value that falls within the size of a molecule.

5.1: Introduction

Organic electronic devices are increasingly attracting attention over the last two decades due to their potential application in flexible electronics [1, 2] and bio-compatible electronics [3, 4, 5]. However, charge transport is still limited and complex in these devices due to disorder in the organic layer. Disorders can have both dynamic and static components [6] and it has been shown that the magnitude of both can be comparable for organic materials [7, 8]. In general, the vibrational motion of organic molecules can couple to carriers, resulting in dynamic disorder that influences carrier transport [6]. Typically, structural disorder such as dislocations, vacancies, impurities, and domain boundaries, is viewed as entirely static [9]. It should be borne in mind that structural defects can also have a dynamical aspect since molecules can move in their
immediate vicinity. However, the dynamical behavior of molecule near these defects remains a challenge because of the complexity in simulation and difficulty of monitoring these motions with the instruments accessible to the time scale of their fluctuation.

Among all defects leading to structural disorder, domain boundaries are highlighted in many research efforts [10, 11, 12] and their impact can be tuned by different growth [13, 14] and processing conditions [15, 16]. The reason for this attention is that domain boundaries in organic films play an important role in determining the charge transport [17]. They are one of the origins of charge traps within semiconductor films and can thus play a role in the multiple trapping and release model of charge transport [18]. The trapping and releasing of carriers has been observed by our group through the corresponding increase in fluctuations of the surface electrostatic potential as a transistor turns on [19]. Those were shallow traps distributed homogeneously inside a channel. Localized charge traps inside transistors’ channel have also been investigated by Jaquith et al [20, 21] with special attention to the domain boundaries. However, the dynamic behavior of these boundaries has not been considered. Knowledge about such dynamic behavior can help us to unravel the factors that hinder transport in organic films.

Since atomic level imaging methods have been developed and instrumented for surface sciences, significant research effort and attention have been devoted for interface fluctuation investigations [22, 23]. Interface fluctuation studies have been beneficial for understanding growth and the equilibration of surface structures [22]. The interface scaling concept [24] has been used as a quantitative analysis to understand dynamics of interfaces’ fluctuations [25, 26, 27].
In this study, we investigate the domain boundary fluctuations in C8-BTBT monolayer films at the Au(111) surface using scanning tunneling microscopy (STM). C8-BTBT has been the subject of intense researches due to its high performance in OFETs [28, 29]. We dynamically imaged the random motion of the boundary edges. Using interface scaling concepts, we obtained the growth exponent of $\beta = 1/2$, which corresponds to uncorrelated molecular motions to and from the boundary edges. We show that $G(t)$ saturates at a value comparable to the distance between two adjacent molecules in the surface unit cell. The power spectral density of the fluctuations is also found to be consistent with this uncorrelated statistical process since is shows a scaling at high frequencies. These observations suggest that steady-state thermal fluctuations of domain boundaries can be an important contributor to dynamic disorder in organic films and may contribute to the low frequency electrical noise in devices.

5.2: Experimental Methods

The experiments were performed in a multichamber ultrahigh vacuum that has been described before [30]. A Au(111) crystal was cleaned by sputtering with 1 keV Ar+ ions and then annealing at 700 K. C8-BTBT was purchased from Sigma-Aldrich and was deposited on Au(111) by organic molecular beam deposition. A quartz crystal microbalance (QCM) was used to monitor the flux of $\sim 0.06 \text{ Å/s}$. The coverage was checked by dozens of STM images all over the crystal after each deposition. A commercial variable-temperature STM, Omicron VT-XA with a home-etched tungsten tip were used for this study. All measurements were carried out at room temperature.
To monitor the fluctuation of boundaries, the STM scan angle was adjusted so that the fast-scan direction was perpendicular to the direction of fluctuating boundaries. Then the STM tip was repeatedly scanned over a fixed point on the boundary for several minutes to generate a time-dependent view of the boundary fluctuations. In order to analyze the edge motion a combination of Fuzzy logic and Sobel method edge detection algorithms in MATLAB were applied to the cropped temporal image. Each boundary contains two edges in left and right side and these were found to be uncorrelated in our experiments.

![STM images and schematic](image)

**Figure 5.1:** a) STM image of the clean Au(111) surface. The image is 150*150 nm taken at V=-1V, I=150 pA. b) Incomplete monolayer of C8-BTBT/Au(111). The image is 43*54 nm taken at V=1V, I=100 pA. The bar in both images indicate 19 nm. c) magnify image of b. The size is 14.8*14.8 nm. d) schematic depiction of the intermolecular distances for incomplete monolayer of C8-BTBT/Au(111).

### 5.3: Results

Figure 5.1a shows the cleaned Au(111) surface where the well-known herringbone reconstruction can be seen. After depositing less than one monolayer of C8-BTBT on Au(111) crystal, we observed the molecules adopt a flat lying orientation as is expected for large molecules on a metal surface due to van der Waals attractions. The molecules on Au(111)
surface appeared to have two bright spot with a dark spot in middle which we assign as the BTBT part. As shown in Figure 5.1b there is an abrupt change in orientation of the molecular unit cell in concert with the rotation of the herringbone substrate reconstruction. This is similar to the behavior of the methanethiol monolayer on the Au(111) surface [31]. These molecular domains have static boundaries as shown in Figure 5.1b. The intermolecular distances $\vec{a} = 0.92 \pm 0.02 \, \text{nm}$ and $\vec{b} = 4.08 \pm 0.06 \, \text{nm}$ are both larger that intermolecular distance of C8-BTBT crystal which are $\vec{a} = 0.5927 \, \text{nm}$ and $\vec{b} = 2.918 \, \text{nm}$ [32]. In this case, the angle between $\vec{a}$ and $\vec{b}$ is $\gamma = 103.1^\circ \pm 1.8^\circ$.

Figure 5.2: a) STM images of the complete monolayer of C8-BTBT/Au(111). b) the magnify scan of the white square in a. c) the closer view of the white square in b. All the images are taken at $I=800 \, \text{pA}, V=1\,\text{V}$. d) schematic depiction of the intermolecular distances for complete monolayer of C8-BTBT/Au(111).

However, by depositing a complete monolayer (Figure 5.2a), the C8-BTBT domains become decoupled from the underlying herringbone reconstruction. Instead of rotating the unit cell according to the substrate direction, the unit cell is now fixed and rotated by $21.3^\circ \pm 1.6^\circ$ compared to $\vec{a}$ from [11̅2] direction across huge regions of the surface as shown in Figure 5.1a.
In this saturated coverage regime, there are new domain boundaries that appear “fuzzy” which indicates fast motion of molecules in this region. Figure 5.2b and 5.2c show a closer view in Figure 5.2a from the complete monolayer of C8-BTBT/Au(111). In figure 5.2c, exact orientations of molecules in the crystal are shown. The intermolecular distances in complete monolayer of C8-BTBT/Au(111) are $\mathbf{a} = 1.10 \pm 0.03 \text{ nm}$ and $\mathbf{b} = 3.11 \pm 0.05 \text{ nm}$ with the angle between them $\gamma = 82.3' \pm 1.1'$. An interesting fact is that the molecular structure in incomplete monolayer is more dense than complete monolayer. Therefore, in incomplete monolayer, it is more favorable for molecules to make unit cell in direction of $[11\bar{2}]$ and compact together. Then by completing the layer, the crystal structure rotates 23.1’ compared to $[11\bar{2}]$ direction and molecules have more freedom and fluctuate at the boundaries.

Figure 5.3a shows an STM image where the scan angle is perpendicular to the boundaries. A cropped temporal image and its binary image are presented in Figure 5.3b and 5.3c. This image scans a line with the width of 0.98’A (50 nm divided by 512 pixel) over 420 seconds. The left edges fluctuation is shown in Figure 5.3d.
5.4: Discussion

In order to quantify the fluctuations of domain boundaries, we consider their power spectral density (PSD). Figure 5.4 shows the PSD averaged over 10 edges which follows $\frac{1}{f^2}$ spectrum. Power spectral densities scaling as $\frac{1}{f}$ [33, 34] and $\frac{1}{f^2}$ [35, 36, 37] have been observed and discussed extensively in the context of low frequency electrical noise in semiconductor devices. In general, noise in devices like transistors can have many different sources. It can originate from thermal fluctuation and random motion of carriers in the transistors. This leads to a white noise which is dominant at high frequencies. At low frequencies, $\frac{1}{f}$ noise prevails, which is originally assumed in transistors to be due to trapping and releasing carriers in the oxide layer close to the semiconductor [37, 34]. In fact, charging and discharging a trap result in random
telegraph signal which leads to a Lorentzian spectral density [36]. This Lorentzian spectral has a constant value at very low frequency and then above a corner frequency, it shows a $\frac{1}{f^2}$ scaling [38]. The combined effect of many Lorentzian spectra with different corner frequencies results in $\frac{1}{f}$ spectrum [38]. Due to this fact, by reducing the size of devices up to nanometer scale, the noise in devices often changes from $\frac{1}{f}$ to $\frac{1}{f^2}$ as device size shrinks and fewer Lorentzian contribute to the total PSD [35, 36, 37]. These low frequency noises are important and can be used as diagnostic tool for a device lifetime and reliability [39].

![Figure 5.4: PSD averaged for 10 edges. The red dashed line is $\frac{1}{f^2}$.](image)

In the analysis of our experiments, we monitored the fluctuation of a small portion of a boundary over time and obtained a $\frac{1}{f^2}$ shape of the power spectral density. By analogy to the known physics of charge transport noise, we attribute this to a trapping and releasing event at the domain boundaries. We assume this to be the motion of a single C8-BTBT molecule, though the dynamical instability makes this not directly resolved in our observations.
In order to further analyze the boundaries fluctuation, we quantified the motion of domain boundaries using interface scaling concepts. The correlation function in interface scaling can be used to characterize the roughness of a boundary [40]:

\[ G(t) = \langle (x(t + t_0) - x(t))^2 \rangle \quad (5.1) \]

Where \( x(t) \) is the position of a domain boundary at time \( t \). According to dynamic scaling [24], \( G(t) \) follows a power law relation with time:

\[ G(t) \propto t^{2\beta} \quad \text{for} \ t < t_x \quad (5.2) \]

Where \( \beta \) is the growth exponent and \( t_x \) is a crossover time that separates the power law part of \( G(t) \) from a saturation region of \( G(t) \). By understanding \( \beta \) for a set of data one can classify the behavior of an interface. The correlation function \( G(t) \) of each edge for C8-BTBT film is calculated. Figure 5.5 shows the \( G(t) \) averaged for 10 edges. The \( G(t) \) shows a power law growth for the first \( \sim 8 \) s and then saturated. The calculated exponent is \( \beta = 0.49 \pm 0.01 \). This

Figure 5.5: Correlation function averaged for 10 edges. The red line is the power law fit.
corresponds to the random deposition in dynamic scaling method. However, it is analytically shown that for random deposition the interface grows indefinitely with time without saturation. We believe the saturation observed in our experiment is due to finite horizontal width of domain boundaries. In this case, random deposition can be interpreted as uncorrelated diffusive motion of molecules. We also calculate the saturation width \( w_{\text{saturation}} = \sqrt{G_{\text{saturation}}} = 1.02 \pm 0.17 \, \text{nm} \). This width falls within the distance between two C8-BTBT adjacent molecules \( b = 1.10 \pm 0.03 \, \text{nm} \). This suggests that the fuzzy borders are the result of fluctuating a single C8-BTBT molecule at each side, in the direction perpendicular to the domain boundary. This is in agreement with PSD analysis which shows a single molecular trapping and releasing event at the edges. The upward turn at larger times after the saturation in correlation function could be the result of additional phenomena such as the cage rearrangement observed in colloidal systems near the glass transition [41]. This is outside of the scope of this study because it needs more statistics.

5.5: Summary

In summary, we studied the dynamical behavior of domain boundaries in C8-BTBT organic molecule on Au(111) using STM. We track the boundary fluctuations by time resolved imaging and quantified the fluctuations using PSD and mean-squared-widths. We obtained a \( \frac{1}{f^2} \) scaling of PSD at high frequencies which corresponds to a single molecular trapping and release event at the domain boundary edge. The mean-squared width is consistent with this interpretation since, for small times, it scaled precisely linearly in time as expected for uncorrelated motion. Interestingly, the width saturates at a value comparable to the unit cell size, indicating that
molecular motion occurs perpendicular to the direction of the boundary. In the other words, single molecules can be trapped and released to exchange across the domain boundary.

Dynamic disorder is a decisive factor in carrier mobility of organic devices. In this paper, we studied a new source of dynamic disorder which is the domain boundary fluctuation in an organic film. This work helps to understand the dynamic disorder in organic semiconductor which poorly understood due to its complexity.
References:


Chapter 6

Outlook; Significance of Disorder and Film Degradation in Organic Electronics

In order to obtain the maximum capability of organic devices, it is important to better understand decisive factors in charge transport of organic semiconductors. Among all decisive factors, disorder plays an important role in charge transport of an organic semiconductor [1] which was the focus of chapter 3 and chapter 5 of this dissertation. Earlier research classifies disorder into two categories: dynamic and static disorder [2, 3]. The effect of these two kinds of disorder is different in device performance [3] and it is important to distinguish each of them for different organic semiconductors made under different conditions. Furthermore, dynamic and static disorder can have different sources. For example, molecular librations in a crystal can lead to dynamic disorder [2] and structural defects in a crystal can result in static disorder [4]. This research mainly characterizes the amount and origin of these two types of disorder representative examples of organic films.

In chapter 3 of this dissertation, dynamic and static disorder were experimentally distinguished in fullerene film at a metal-organic interface using STM and STS. A previous study [3], using computational techniques, proved that the amount of dynamic and static disorder in bulk fullerene must be of the same order of magnitude. However, our measurements indicated that static disorder is always larger than dynamic disorder. The reason for having a less dynamic disorder in our film was the metallic substrate. In fact, the metallic substrate suppressed the libration of fullerene molecule which resulted in a reduced dynamic disorder in our measurement. This observation is significant for organic electronic community since before our
experiment, it was postulated that the amount of static and dynamic disorder is the same in organic materials while we proved that this condition will not be held at the metal-organic interface. This result is remarkable for future studies specially when charge injection to the semiconductor layer is considered. Indeed, in order to improve charge injection from the electrode to the organic film, it is more important to control static disorder than dynamic disorder.

In chapter 4, another important factor in reducing the performance of organic electronic devices which is the morphological degradation was investigated. In this research, the degradation of C8-BTBT film morphology during contact fabrication was considered. The key quantity that characterizes charge transport is the carrier mobility [2]. We observed a thickness dependence mobility in top contact organic field effect transistors (OFETs) due to film degradation during contact creation. Therefore, this degradation is very important in device performance. We showed that this degradation could be improved (but not eliminated) by creating contacts at cryogenic temperature. In general, according to this study and other studies [5, 6, 7], C8-BTBT has shown a very good device performance compare to other organic molecules. However, we showed that proper attention in fabrication process is required to obtain a better device performance. The severe film morphology degradation observed in this study for C8-BTBT films can be associated to the specific side arms of this molecule. In fact, it has been shown before that this molecule has a relatively low transition temperature from crystalline to liquid crystallin phase (the transition occurs at 110 C) [8]. Due to this fact, a liquid crystal-like environment can be locally induced during the arrival of hot gold atoms on top of the film during contact fabrication. This can cause a rapid surface diffusion for C8-BTBT molecules. Then the film morphology doesn’t fully recover after contact creation process and results in film
degradation. This degradation is very important to notice for future studies about C8-BTBT devices.

In chapter 5, we verified a new source of dynamic disorder as the fluctuations of domain boundaries in an organic film. Previously, domain boundaries have been viewed as a source of static disorder and the effect of domain boundaries on charge transport and mobility of organic devices has been studied for a long time [9, 10]. Domain boundaries can trap mobile carriers, so they are directly related to the mobility of devices. We monitored the fluctuation of domain boundaries in C8-BTBT film on Au(111). Correlation function of the fluctuating boundaries showed a single C8-BTBT molecule fluctuated at each side of the boundary until the fluctuation saturated. This fluctuation was in the direction perpendicular to the boundary. Further investigation of fluctuating boundaries which was performed by calculating power spectral density (PSD) verified that a single C8-BTBT trapped and detrapped at each side of the boundary. We suggest that this thermal fluctuation of the molecules at film boundaries can be a new source of dynamic disorder in organic films and can be a source of low frequency noise in devices.

Although these research results develop the understanding of obstacles in obtaining efficient carrier transport in organic devices, there is still much work to be done with regard to finding other obstacles for a good carrier transport and ways to improve them. The performance of electronic devices can still be enhanced, however, there may be some limitations in increasing the performance of organic devices. To illustrate, a high density of traps even in a single crystal of an organic semiconductor indicates that a high amount of disorder always presents in organic materials [11], however, by understanding the source and the amount of different kinds of
disorder, one can find ways to control them. To give an example, by considering the fact that the amount of static disorder is higher than dynamic at the metal-organic interface, one can reduce the static disorder through changing the deposition process in order to ameliorate charge injection to the semiconductor layer. Another example is that by understanding the fact that grain boundaries can increase dynamic disorder in a film, one can find ways to decrease the number of grain boundaries by changing deposition process.

One strong point about organic materials is that new structures and derivatives can be synthesized in order to tune the crystal packing and improve charge transport. Regarding this, characterizing the amount of static and dynamic disorder with the method introduced in this work, is useful in order to explain the performance of devices made with new synthetized materials. For example, the position of side arms in new synthesized materials can be changed and it has been shown that by substituting side arms in direction of long axis (like the side arm in C8-BTBT molecule), the amplitude of intermolecular vibration can be reduced which results in less dynamic disorder and improves the charge transport in the crystal [12]. However, we showed that the specific side arm in C8-BTBT molecule can sometimes have an irregular effect and cause film degradation during contact fabrication. Moreover, our results suggest that a new source of dynamic disorder which is thermal fluctuation at the domain boundaries should be also considered in organic films and more action with regard to decreasing the number of grain boundaries is required to further reduce the dynamic disorder and improve the device performance. We should note that additional investigations on domain boundaries of organic materials are necessary in both bulk materials and at the interfaces in order to understand the contribution of domain boundaries in dynamic and static disorder in a film. Finally, this work
helps to better understand disorder and other factors that are crucial in charge transport in organic films in order to improve the performance of organic electronic devices.
References:


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