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Structural and electrical characterization of organic monolayers by Atomic Force Microscopy and through the nano-fabrication of a coplanar electrode-dielectric platform

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Structural and electrical characterization of organic monolayers by Atomic Force Microscopy and through the nano-fabrication of a coplanar electrode-dielectric platform

By

Florent Martin

A dissertation submitted in partial satisfaction of the requirements for the degree of

Doctor of Philosophy

in

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and the Designated Emphasis

in

Nanoscale Science and Engineering

in the Graduate Division of the University of California, Berkeley

Committee in charge:

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Professor Thomas Devine
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Spring 2011
Abstract

Structural and electrical characterization of organic monolayers by Atomic Force Microscopy and through the nano-fabrication of a coplanar electrode-dielectric platform

by

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Doctor of Philosophy in Materials Science and Engineering

University of California, Berkeley

Professor Miquel Salmeron, Chair

Correlating structural and electrical properties of organic thin films is a key requirement to understand charge transport in these materials. The electrical conductivity of organic films should be strongly dependent on how the molecules arrange to form films and crystals. Here we report on the structural and electrical characterization of organic monolayers by Atomic Force Microscopy and through the nano-fabrication of a coplanar electrode-dielectric platform.

Organic monolayers were prepared using the solution-based Langmuir-Blodgett technique and transferred to a variety of substrates. Atomic Force Microscopy was used to analyze the morphology and the microstructure of ultra-thin films at high resolution while electron diffraction measurements were instrumental in determining the lattice and orientation of crystalline domains within monolayers.

A novel Conducting probe AFM method based on the presence of an insulating oxide layer between an organic film and a conductive silicon substrate made it possible to probe the in-plane electrical conductivity in the film. With this technique, we were able to investigate the correlation between conduction properties of D5TBA monolayers and structural factors such as their molecular order and their lattice orientation.

In order to make electrical contacts with monolayer films and study them in a FET configuration, we developed coplanar electrode-dielectric substrates with roughness and surface topography in the sub-nanometer range. We present the first results on the electrical characterization of monolayers with this device which demonstrate that the coplanar geometry leads to a contact resistance by orders of magnitude lower than that found in conventional 20nm thick electrodes.
Acknowledgments

First and foremost, I would like to thank my PhD advisor, Professor Miquel Salmeron, for his support and the constant inspiration he provided me with. His enthusiasm for science and research is most amazing and I benefited numerous times from his insightful ideas and comments. I am especially grateful to Miquel for his availability even when he faced mounting responsibilities as the director of the Materials Science Division at LBNL. His door was always open and he would interrupt whichever activity he was busy with to engage with me on my PhD project. The few minutes that I requested would often extend to his next meeting sometimes two hours later.

The members of the Salmeron group have been very helpful throughout my work as a graduate student. I would like to thank Bas Hendriksen who was the central figure in the early stages of my PhD as he taught me not only about the project and techniques associated to it, but also about experimental research and how to convey results through oral presentation, posters and papers. I benefited enormously from his insight and creativity and he initiated and was part of a large amount of the scientific endeavors described in this document.

I am especially grateful to Allard Katan with whom I collaborated closely during the second part of my PhD. It was a joy to work with him and I hope to have many more collaborators with such talent as a scientist and constant willingness to help and push the project forward as a team. I am especially glad that he is the one who will transmit the work and knowledge accumulated on this project to future members of the team as he is a tireless pedagogue and his enthusiasm is contagious.

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I want to acknowledge the staff of the Molecular Foundry at LBNL, in particular the Imaging and Nanofabrication facility where I spent most of my time as a graduate student. I am grateful to Virginia Maria Altoe for her initiative and help in developing projects related to the study of AFM tips by TEM and electron diffraction on organic monolayers. I enjoyed working with her and I wish we had been able to push these investigations further. Shaul Aloni was a key collaborator for these projects and I greatly appreciated his drive, keen sense of humor, mushroom soup and even the time spent looking for him in the Foundry.

We had a strong collaboration with the Frechet group and in particular Clayton Mauldin and Jon Klopp who synthesized the molecules used in this study. We also worked closely with Lin-Wang Wang and Nenad Vukmirovic at the Materials Science Division of LBNL to develop theoretical understanding of the structure of organic monolayers and their conducting properties. Bruce
Harteneck at the Nanofabrication facility was a very valuable support for the design of the flat electrodes, especially at early stages of the project. The Berkeley Microlab now becoming the Marvell Nanolab was also key to the development of the electrodes.

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Chapter 1. Introduction and presentation of experimental techniques

The research work presented in this PhD thesis belongs to the field of organic electronics, i.e. the use of organic materials as one or all of the components of electronic devices. These include semi-conductors used as channels in transistors or light absorbing materials for photovoltaics, organic conductors as electrode materials or insulators for dielectrics. The first commercialized organic electronics devices were Organic Light Emitting Diodes (OLED)\(^1\). The elementary building blocks of these organic components are small molecules and polymers which are long-chain molecules consisting of a number of molecular repeat units called monomers.

The birth of organic electronics is sometimes pinned to the discovery by Alan G. MacDiarmid, Hideki Shirakawa and Alan Heeger that the conductivity of the polymer polyacetylene could be tuned over a wide range and up to metallic levels by doping\(^2\). They received the Nobel Prize in Chemistry in 2000 for their work. The first Organic Field Effect Transistor (OFET) was demonstrated in 1987 by Koezuka and his coworkers\(^3\). The channel was a polyethylene thin film where the carrier mobility was 2E10\(^{-5}\)cm\(^2\)V\(^{-1}\)s\(^{-1}\). OFETs have since been the focus of an extensive amount of research and record mobilities of tens of cm\(^2\)V\(^{-1}\)s\(^{-1}\) were reported for single crystals such as rubrene\(^4\). Organic electronic devices have reached the market place\(^5\) through companies such as Plastic Logic (OFETs), Konarka (organic solar cells) and numerous OLED fabricants.

The idea that organic transistors could one day replace their inorganic counterparts has been largely played down because of significant mobility and scalability limitations. Attempts to fit organic devices in a Moore’s law framework where size and density are the key evaluation criteria miss the point\(^6\), which is the fact that their low performance is compensated by other attractive features. Organic semiconductors can deliver applications unreachable by silicon\(^7\). Numerous processing techniques are available; some envisioned being very cheap such as solution or ink-based techniques. Such processes are compatible with large area fabrication\(^8\) which is critical for flat panel applications of transistors and for photovoltaic devices. The absence of high temperature annealing step permits the use of soft flexible lightweight substrates such as plastic. Finally, there is potential for very low cost since organic raw materials are cheap as well as solution based processing techniques\(^7\). A significant challenge to the widespread use of organic devices is their durability. Organic compounds are typically bonded by van der Waals forces weaker than covalent bonds in inorganic semi-conductors. They are more fragile and sensitive to environmental conditions such as light and moisture as well as chemicals and plasma techniques commonly used in device processing.
1. Characterizing organic materials at a scale adapted to their heterogeneous structure

*Structure of organic assemblies.* Organic thin films used in transistors and solar cells are significantly less ordered and more heterogeneous than their inorganic counterparts. The drawings in fig1-1 describe several microstructures that can be observed in these materials. Films made of polymers such as the widely used poly(3-hexyl) thiophene (P3HT) are semi-crystalline and usually deposited from solution by drop casting or spin-coating. As illustrated by fig1-1a, ordered regions (symbolized by rectangles) and amorphous regions coexist even after extensive annealing. The typical size of crystalline grains can vary from tens to hundreds of nm.

![Figure 1-1. A. Schematic of a semi-crystalline polymer thin film, B. Schematic of a polycrystalline small molecule monolayer or thin film, C. Schematic of a semi-crystalline small molecule film.](image)

Thin films based on small molecules can be prepared from solution or evaporated in vacuum. These films can be polycrystalline (fig1-1b) or semi-crystalline (fig1-1c). In poly-crystals, grains are separated by disordered boundaries that have been shown to strongly affect the conductivity of the thin film or even dominate charge transport. In films containing amorphous regions transport is believed to be highly inhomogeneous with some preferential conducting pathways and some insulating regions.

Finally, both polymer and small molecule thin films contain point defects such as vacancies or impurities and line defects such as dislocations. The organic materials with the highest quality are single crystals such as those prepared from rubrene which can be purified and the density of impurities reduced to a fraction equal to one impurity per $10^4$ molecules. In comparison, the impurity fraction is equal to parts per billion in inorganic semiconductors.

Based on the structure of organic materials, one can expect that the theoretical and experimental characterization of their electrical transport properties is highly challenging.

*Limited understanding.* Several decades of experimental research on inorganic semiconductors coupled to modeling of their conduction properties have led to a very high level of understanding of charge transport mechanisms and the influence of defects in these materials. On the other hand, several recent reviews of the field of organic electronics emphasize the current limited understanding in most materials used for fundamental research and considered for commercialization. These difficulties can be explained by the microstructure of organic thin films, along with the effects of room temperature thermal agitation on the position...
of molecules in organic crystals which is larger than in covalently bonded crystals. The strong electron-phonon interaction is modeled as a polaron, a quasi-particle accounting for the fact that electrons travelling through the crystal are accompanied by a deformation of the lattice.\textsuperscript{15}

**Conduction mechanism in crystalline regions.** Charge transport is best understood in single crystals due to a higher degree of reproducibility of experiments and the larger variety of techniques that can be employed to characterize them. For instance, Hall Effect measurements have been used on single crystals of rubrene.\textsuperscript{16} Even in these highly ordered materials, elucidating conduction mechanisms has proven difficult because of the coupling of electrical transport with lattice vibrations. At room temperature, the vibrations of individual molecules can cause a loss of translational order. The model for charge transport in these materials was reviewed by Coproceanu and coworkers in 2007. It is derived from the Peirls-Holstein model and accounts for the strong coupling of electrical transport with phonon modes.\textsuperscript{15} In such materials, the mobility is a combination of coherent band transport mobility and hopping mobility between localized states.

\[
\mu = \mu_{\text{tun}} + \mu_{\text{hop}}
\]

For a low polaronic coupling (smaller effect of lattice vibrations), the overall dependence of the mobility on temperature is plotted in fig1-2a.\textsuperscript{15} Band-like transport is dominant at low temperature while the loss of translational symmetry due to lattice vibrations leads to an intermediate temperature hopping regime. At high T, the mobility decreases due to scattering by atoms that vibrate around their equilibrium position. For a higher polaronic coupling, the hopping regime is dominant over the whole spectrum.

**Hopping transport.** For amorphous regions within a crystalline matrix and for fully disordered materials a hopping model derived from the Markus theory is used to describe charge transport. Hopping transport is also observed in crystalline materials in the range of temperature where it becomes dominant due to lattice vibrations. It is the case at room temperature in a number of organic crystals. In a hopping model, charge carriers are localized on molecules and move in discrete hops by diffusion or drift when submitted to an electric field. Charge hopping can be assisted by phonon vibrations. The mechanism is similar to hopping conduction in amorphous silicon as described by Spear and Le Comber in 1970.\textsuperscript{17} The hopping rate is exponentially dependent on the overlap of molecular orbitals from adjacent...
molecules such as π orbitals of conjugated small molecules. Several hopping models exist but their temperature dependence is commonly of the form\textsuperscript{18}

\[ \mu = \mu_0 \exp\left[-\left(\frac{T_0}{T}\right)^\alpha\right] \]

**PhD research.** Transport in thin films in an organic thin film transistor (OTFT) configuration has been extensively studied\textsuperscript{8,10,19}. The ease of thin-film synthesis and device fabrication accounts for the popularity of this structure for both the commercialization of OFETs and fundamental research\textsuperscript{1}. However, fig1-3a illustrates the limitation of OTFTs for experimental research aimed at acquiring a fundamental understanding of conducting mechanisms in organic materials. Thin films are typically fifty to several hundred nm thick and the width and length of the channel of OTFTs varies from tens of microns to a mm. As a result, the parameters and properties measured in this configuration are averaged over the film which is largely heterogeneous. The structural characterization, often by means of grazing incidence X-Ray diffraction (GIXD) techniques, also samples large areas of the film.

![Figure 1-3a. Schematic of an organic thin film transistor (OTFT). The inset illustrate the typical microstructure of polymers thin films composed of crystalline and amorphous domains, b. Schematic of an ultra flat FET. The channel is a monolayer organic film. The FET is combined with AFM for nanoscale structural characterization of the device.](image)

Our research project at the Salmeron group and this PhD work aims at developing solutions allowing the characterization of the structure and transport properties of organic materials at the scale of single crystalline domains (i.e. a few 100nm to a few µm in the xy plane). The materials that are investigated are ultra-thin films of organic molecules. Although not an ideal choice for commercial applications, a central benefit of using such thin films is that the samples can be characterized at high resolution by surface imaging techniques, namely the various operating modes of atomic force microscopy (AFM).

Analysis of electrical conduction mechanisms is typically carried out on thin films rather than few-layer or monolayer films. This can be explained by the difficulty to contact monolayers with electrical probes that usually damage the soft material at the contacts\textsuperscript{13}. A central goal of this PhD work was to develop a platform for non-destructive deposition and electrical characterization of organic ultra-thin layers. The device fabricated by a replica technique is
composed of gold electrodes embedded in a silicon oxide dielectric and its surface is coplanar within 1nm (see the schematic in fig1-3b). In a later stage, a metallic gate was added to the device effectively making it a Field Effect Transistor when a semiconductor is deposited at the surface. The electrodes patterned by UV lithography are separated by a gap of 500nm to 1µm but the gap could be reduced to hundreds or tens of nm by using deep UV or e-beam lithography techniques. This flat FET platform can be combined with AFM for optimal analysis of the structure of the channel material as illustrated by fig1-3b. Using this platform, the electronic properties of the organic materials bridging the electrodes can be determined and correlated to their morphology and microstructure available through AFM measurements.

2. Structural and electrical characterization techniques used in this project

**Structural characterization, AFM.** The molecular monolayers were investigated using an Atomic Force Microscope (AFM). With an AFM, it is possible to obtain topographic images of surfaces with a height resolution below one Å and a lateral resolution of about a fraction of nanometer\(^2\). An AFM is a scanning probe microscope; the data is acquired by scanning a physical probe in contact with the surface much like the stick of a blind person feeling its way along a surface. An image is formed by plotting the height of the surface measured in each pixel of a 256x256 or 512x512 array.

![Schematic of an atomic force microscope. Cross-sectional view of a substrate covered by a submonolayer of material and scanned by a cone-shaped tip (#6) attached to a cantilever (#5). The x, y and z motion of the cantilever is controlled by a piezoelectric scanner (#2).](image)

A schematic of an AFM is shown in fig1-4. A cantilever is mounted at the extremity of a scanner that contains piezoelectric domains that can extend or retract under applied bias. A very sharp tip is attached to the end of the cantilever and its extremity is in contact with the surface. The
xy position of the tip is controlled by the scanner. Its z position is measured using a laser/photodiode system: a laser beam is directed on the reflective backside of the cantilever and is reflected onto a photodiode detector which is split into four quadrants. In the initial tuning step, its position is adjusted such that the beam hits the center of the detector.

Since the cantilever is compliant, it bends when the tip encounters topographical features as it scans the surface. This causes the location at which the laser beam hits the detector to shift. The position of the beam on the detector is recorded in real time and a feedback system continuously adjusts the extension of the scanner in the z direction to keep the laser spot at the center of the detector. For instance, if the tip climbs above a 5nm tall feature causing the cantilever to bend and the laser spot to shift on the detector, the scanner will retract by 5nm to restore the initial position. It is this extension or retraction of the z position of the scanner which is plotted to from a topography image.

In addition to topographic information, an AFM can provide frictional force images of the sample by measuring the lateral force acting on the AFM tip. As the tip scans the surface of the sample and encounters regions of higher or lower friction coefficient, the cantilever is submitted to torsional movements around its axis. The reflected laser beam then shifts laterally over the photodiode detector (whereas it shifts vertically when the cantilever is deflected). This lateral shift can be plotted to form an image of the frictional force over the sample.

Using an AFM the roughness of a surface can be determined. Usually the Root Mean Square (RMS) value of the roughness is provided. This value measures the standard deviation of the topography of the surface.

\[ \text{RMS} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (z_i - \bar{z})^2} \]

In the course of this PhD work, a novel TEM based structural analysis technique was developed in collaboration with Dr Altoe and Dr Aloni who hold research staff positions at the Molecular Foundry at LBNL. These results are...
presented in chapter 4. Monolayer organic films were characterized by scanning a 100nm wide electron beam across the surface and recording the diffraction pattern produced by the crystal in real time. A brief summary of electron diffraction is provided below to introduce the topic and describe how this technique makes it possible to analyze the lattice of crystalline samples.

Electron, X-Ray or neutron diffraction techniques are among the most powerful tools to determine the structural properties of crystals which are materials composed of a periodic array of elementary building blocks. Using these tools, one can determine the spacing separating atoms or molecules composing the crystals and the symmetry in which they are arranged (hexagonal, rectangular etc...). In diffraction, an incoming beam of particles, for instance electrons, is directed at the crystalline material. Part of the incoming electrons interact with atoms and are scattered in all directions. The phenomenon is illustrated by the schematic in fig1-5a. The incoming beam is diffracted by successive planes of atoms forming the diffracted beams. Depending on their phase, these beams or electron waves can interfere with each other constructively or destructively. A geometrical calculation of the phase delay between these electronic waves shows that they interact constructively if they follow the expression

$$2asina = n\lambda$$  (1)

where $\alpha$ is the angle of the incoming and scattered waves with respect to the plane of atoms, $\lambda$ is the wavelength of the incoming wave and $a$ is the distance between neighboring planes of atoms. $\alpha$ diffracted waves that do not follow this relation interfere destructively.

In a Transmission Electron Microscope (TEM), an objective lens is positioned below the sample to focus the diffracted beams and a camera is placed in the focal plane of the lens. It records the pattern of incoming electrons which is also called a spot or diffraction pattern (see the pattern in fig1-5b). Each spot in the diffraction pattern corresponds to a direction in which scattered electron waves interfered constructively. From the distribution and precise location of spots in such pattern, one can deduce the angle $\alpha$ of the diffracted beam and therefore the distance $a$ by using equation (1). From the arrangement of the spots, one can also deduce the symmetry of the crystal. Fig1-5b shows a typical diffraction pattern obtained from an oligothiophene monolayer. The central bright spot corresponds to electrons that did not interact with the sample. The pattern has a rectangular symmetry with several missing spots consistent with the Herringbone crystal structure which is commonly observed in oligomer crystals. A top view of a Herringbone assembly of molecules is shown in inset of fig1-5b.

**Electrical characterization.** In order to measure the electrical properties of organic semiconductors, instruments with different levels of complexity can be used.

In **Conducting probe AFM**, the current flowing from the tip to the substrate is recorded as the tip scans the surface. This AFM technique requires a conductive substrate and conductive AFM cantilevers and tips. A map of the conductance of the surface of the sample is created. This mode can be used simultaneously with topography and lateral force AFM. The geometry of such measurement is vertical as the current flows from the tip into the substrates through the sample.
A horizontal 2-probe electrode system can measure the series resistance composed of the intrinsic resistance of the material and contact resistances. In order to determine these properties independently, a 4-point probe geometry can be used. Although several solutions have been designed to ensure ohmic contact between electrodes and inorganic semiconductors, the issue of contact resistance and Schottky contacts is still very prevalent in organic materials making 4-point-probe a very relevant technique.

The next level of complexity can be achieved by using a metallic gate in conjunction with 2 or 4 probes, i.e. using a transistor geometry. Schematics of transistors are shown in fig1-6a and fig1-6b. With this device, the mobility of electrical carriers can be measured. This quantity measures the velocity of charged particles under an electric field. It is related to the conductivity by equation (2)

\[ \sigma = n \mu q \]  

(2)

where \( \sigma \) is the conductivity (in S.m\(^{-1}\)), \( n \) is the density of carriers (in cm\(^{-3}\)), \( q \) their charge (+e or –e) and \( \mu \) their mobility (in cm\(^2\)s\(^{-1}\)V\(^{-1}\)). The mobility is directly related to the switching speed that can be achieved in the device.

Fig1-6a shows the typical set of IV curves that can be obtained from a transistor measurement. The electrical current passing through the channel is plotted as a function of the voltage applied between the two electrodes (also called source and drain electrodes). The conductivity of the channel can be modulated by inducing charge accumulation using an electric field applied by the gate. The flat portion of the curves corresponds to the saturation regime. The graph shown in fig1-6b is a transfer curve, a plot of the current at saturation as a function of the gate voltage.

![Figure 1-6. a. Transistor IV characteristics at varying gate voltage, b. Transfer curve, plot of the current at saturation as a function of the gate voltage.](image)

All organic field effect transistor-based studies of mobility rely on analytical methods to extract mobility from the measurements. The methods most widely used are the following\(^{22}\):
In the saturation regime, the drain current follows equation (3). The mobility can be extracted from the slope of the square of the current plotted as a function of \((V_g - V_t)\).

\[
\sqrt{I_{\text{sat}}} = \sqrt{\frac{W}{2L}} C_i \mu (V_g - V_t) 
\]  

(3)

where \(W\) and \(L\) are the channel width and length, \(C_i\) is the capacitance and \(V_t\) is the gate voltage threshold.

The mobility can also be measured in the linear regime by plotting the transconductance \(g_m\) as a function of the drain voltage.

\[
g_m = \frac{\partial I_D}{\partial V_G} = \frac{W}{L} C_i \mu V_D 
\]

(4)

The former method has been proposed by the IEEE as a standard to test organic semiconductors. These methods both present drawbacks as described in a review article by Horowitz and coworkers.

### 3. Molecules used in this study

The oligomers were prepared by the group of Professor Frechet at UC Berkeley. The protocol for the synthesis of the oligothiophene DSTBA is described in the supplemental information of a study by Chen and coworkers published in 2004 in *Langmuir*. It follows the Stile cross-coupling method. The synthesis of DHSTBA and STBA molecules has not been published to this date but is described in the PhD thesis of Dr. Clayton Mauldin.

![Figure 1-7](image)

Figure 1-7. a. 4-(5'-decyl-[2, 2'; 5', 2''; 5'', 2'''', 5'''''; 2''''''] pentathiophen-5-yl)-butyric acid (also referred to as DSTBA), b. 4-(3'''''',4'-dihexyl-pentathiophen-5-yl)butanoic acid (DHSTBA), c. 4-(pentathiophen-5-yl) butanoic acid (STBA), d. C11TSB

Fig1-7 shows the Lewis formula of the pentathiophene derivates DSTBA, DHSTBA and STBA and the oligomer C11TSB. All these compounds are made of 3 blocks, a carboxylic acid anchor, a semiconducting conjugated core and side or top alkyl chains. The carboxylic acid anchor COOH is polar and forms hydrogen bonds with the water subphase in a LB trough (see chapter 2) and with hydrophilic substrates such as mica or SiO2 on which they can be deposited. DSTBA (fig1-
7a) and C11TSB (1-7d) are functionalized with 10-carbon alkyl chain in α position of the top cycle. These non-polar groups make the molecules strongly amphiphilic which is ideal for LB preparation.

Oligothiophene and stilbene derivatives are qualified as p-type semiconductors. In contrast to p or n type inorganic semi-conductors, the terms “p type” and “n type” do not refer to the introduction of p or n type dopants. The p or n nature is related to the energy level of the highest and lowest occupied molecular orbitals (HOMO and LUMO) of the molecules with respect to the work function of conventional electrode material such as Au and Pt used for fundamental studies. The HOMO level of oligothiophene derivatives lies between -4eV and -5.5eV\textsuperscript{24}. Since their band gap ranges from 2.5eV to 3eV, LUMO levels are located further away from the Fermi level of electrodes than HOMO levels. This results in harder electron injection than hole injection which is the rationale behind referring to these materials as p or n.

4. Organization of chapters in the thesis

We will first describe the preparation of organic monolayer using the Langmuir-Blodgett (LB) method (chapter 2). In this technique, molecules dissolved in a solvent which is not miscible with water are spread at the surface of water in a LB trough. We observed that molecules self-assembled into µm large crystals during solvent evaporation. Mechanical barrier can be used to control the density of the film at the water surface before its deposition on a solid substrate for structural and electrical characterization. This method presents several advantages compared to other processing techniques including the fact that the structure of a LB monolayer that assembled at the water surface is largely independent from the substrate on which it is deposited.

The following chapters are devoted to structural characterization by AFM (chapter 3) and TEM (chapter 4). AFM can be used in situ in combination with electrical measurements to assess the morphology and microstructure of organic monolayers and correlate this information with their transport properties. At high resolution, AFM can resolve the lattice of crystalline samples. Electron diffraction in TEM is however the preferred technique to determine the crystal structure of the monolayer more accurately. Using a spot scanning method, we were able to map the crystalline structure of the monolayer and relate it to its morphology.

In chapters 5 and 6, we focus on Conducting probe AFM (CAFM ) experiments, a technique by which the conductance of a sample can be mapped as an AFM topography image is acquired. We show that in spite of the vertical geometry of the electrical measurements - the monolayer was sandwiched between a conductive AFM tip and the substrate – the in-plane conductivity of the organic film could be investigated. This is due to the presence of a layer of native oxide between the monolayer and the highly doped silicon. This insulating layer induced current to flow in the plane of the monolayer outside of the tip-sample contact area which reduced the resistance of the monolayer-SiO2/Sip+ electrical junction.
The final chapters present the fabrication, characterization and preliminary results on a novel coplanar FET platform designed to contact soft monolayers electrically without damage and combine FET measurements with AFM analysis. In chapter 7, details of the fabrication process are presented. The process involves a number of steps and several issues are described along with the way they were resolved. In chapter 8, we provide AFM data assessing the flatness of the surface of the device and providing images of the samples after monolayer deposition. Finally, electrical measurements are described which show that the coplanarity of the device is critical to improve contact resistance and study the intrinsic properties of organic monolayers. We expect to use this platform to investigate a number of fragile materials including ultra-thin films, nanowires and monolayers.

1 Loo, Y.-lin; Mcculloch, I.; Editors, G. MRS Bulletin. 2008, 33, 653-662.


21 Transmission electron microscopy: a textbook for materials science, By David B. (David Bernard) Williams, C. Barry Carter, second edition, Springer


Chapter 2. Monolayer preparation by the Langmuir-Blodgett technique

The Langmuir-Blodgett (LB) technique was used to prepare submonolayers of the oligothiophenes D5TBA, 5TBA and DH5TBA as well as C11TSB which is a trans-stilbene derivative (see chapter 1 for the Lewis formulas of these molecules). These small molecules are organic semi-conductors with band gaps which range from 2 to 3eV and were specifically designed for LB preparation by incorporating a hydrophilic anchor and a hydrophobic tail to their semiconducting core. D5TBA and 5TBA were found to self-assemble in micron scale crystalline islands at the air-water interface prior to compression in the LB trough. An additional phase composed of a porous network of grains was also observed. The air-water interface self-assembly process leading to these phases can be described by a nucleation, growth and coalescence mechanism. In addition, mixed LB films of the oligomers 5TBA and D5TBA were prepared for in-situ comparison of their structural and electrical properties. These submonolayers could be transferred on a variety of substrates with little variation over their structure and morphology.

The Langmuir-Blodgett technique was invented in 1934 by Blodgett who was Irving Langmuir’s student. She found that a monolayer of amphiphilic molecules lying at the air-water interface could be transferred onto a solid substrate by dipping the substrate out of the water. Blodgett later found that successive layers could be deposited by dipping the substrate in and out through the film lying at the interface. Although so far Langmuir-Blodgett films have had a limited number of industrial applications, they are widely used as model systems for fundamental science.

Langmuir-Blodgett films are prepared by dispersing a solution of amphiphilic molecules at the surface of a subphase (water in this study) in a Langmuir trough (see fig2-1a). Teflon barriers sliding on the trough are used to compress the layer. The evolution of the film is monitored by measuring the surface pressure at the air-liquid interface. The film in the solid phase is deposited by pulling a submerged flat substrate such as mica or silicon out of the water vertically (see fig2-1b). LB films of fatty acids monolayers have been extensively studied. When spread at the air-water interface and compressed by the barriers in the trough, these molecules go through gas, liquid and solid-like phases. Condensed solid phase are typically crystalline whereas liquid phases can be amorphous or liquid-crystalline.

We observed that the Langmuir-Blodgett preparation of thiophene and stilbene based oligomers differed from the theoretical framework established for fatty acids. These molecules were found to self-assemble into a crystalline solid phase even when the low density of molecules spread at the air-water was predicted to lead to a gas phase of non-interacting molecules. Similar observations have been reported for oligomers such as squaraines and hemicyanines as well as for oligothiophenes in a study from Chen and coworkers at the
Salmeron group. Several in-situ techniques such as Brewster Angle Microscopy (BAM where optical images of the film are acquired at a grazing angle) and grazing X-Ray diffraction can be used to monitor the evolution of the film in addition to following the evolution of the surface pressure at the air-water interface.

As a result of this self-assembly mechanism, submonolayer made of micron size crystalline islands could be prepared and studied. By compressing these islands together, we were able to obtain full monolayers with grain boundaries separating crystalline domains. For height measurements, and lateral force AFM studies (see chapter 3), submonolayers are preferred over full monolayers. The size of crystalline islands was typically between 500nm and a few µm. From understanding of the nucleation and growth mechanisms of monolayer islands, strategies aimed at controlling their size can be designed.

The variety of structures that can be obtained by the Langmuir-Blodgett technique as well as the ability to deposit them on virtually any substrate make LB oligothiophene monolayers an ideal model system to unravel structural and electrical properties in organic materials. As opposed to self-assembled monolayers (SAMs) prepared from solution at the liquid-solid interface, the structure of a Langmuir-Blodgett monolayer does not rely on the covalent binding of a head group to a surface. It is therefore independent from the substrate on which it is deposited. Hydrophilic substrates such as oxides and mica are especially suited due to the polar interactions with the COOH groups located at the bottom of the molecules. However, the Langmuir films can also be transferred to hydrophobic substrates by horizontal deposition, a technique described in chapter 4. The versatility of this technique made it possible to deposit monolayers on heterogeneous substrates, such as an oxide patterned with embedded metallic electrodes for conduction measurements (see chapter 7).

1. Self-assembly of amphiphilic molecules at the air-water interface

**Experimental.** Solutions of DSTBA in chloroform were prepared with nominal concentration ranging from 0.05mM to 0.1mM by dissolving DSTBA powder into chloroform in an Erlenmeyer.
Solutions were treated in an ultrasonic bath (referred to as sonication below) for periods of time ranging from a few minutes for less concentrated solutions to an hour for saturated solutions. Solutions with a nominal concentration of 0.05mM became clear after short sonication time indicating that 0.05mM is below saturation. Small particles could still be observed in the solution, likely due to impurities present in the powder. Solutions with nominal concentration of and above 0.1mM still contained precipitates after extended sonication time and are therefore saturated. Long sonication led to clearer solutions and the clarity decreased when the solution was left to rest. This indicates that sonication helps dissolving molecular aggregates but that molecules start re-aggregating after sonication stops. These results also show that the saturation concentration of D5TBA solutions in chloroform is between 0.5 and 0.1mM.

Whatman filter paper with a pore size of 0.2µm was used to filter solutions. For LB preparation, 0.5mL to 1mL of solution was deposited on the surface of MiliQ water (the subphase) in a KSV LB trough. A 200µL pipettor was used. Droplets were deposited gently from close above the surface to prevent them from penetrating into the water subphase. Substrates used for LB deposition include freshly cleaved mica, highly p doped silicon, gold films on mica, gold electrodes embedded in a silicon oxide dielectric (see chapter 7) and various types of substrates for TEM analysis (see chapter 4). Silicon substrates were covered with their native oxide film and cleaned by sonication in acetone and ethanol. Langmuir films were deposited on solid substrates at a speed of 3mm/min. No dependence on deposition speed was observed. Deposition on solid substrates was carried out at various stages of compression in the Langmuir trough including no compression at all.

We varied parameters such as time before compression, rate of compression, length of the stabilization period before deposition, deposition rate and found that they had little effect on the morphology of the LB film deposited on substrates. The morphology was also the same whether the Langmuir film was deposited on mica and the native oxide of a silicon wafer. When deposited on gold, the density of islands was very low even when a full monolayer was located at the air-water interface. This shows that the monolayer did not adhere well to the substrate when it was pulled out vertically from the water due to the lack of affinity between the gold film and the carboxylic acid end group of the molecules.

A similar protocol was used to prepare STBA LB monolayers. STBA is expected to be less soluble than D5TBA in chloroform due to the absence of the top alkyl chain. On the other hand, DHSTBA and C11TSB were both fully dissolved at nominal concentrations of 1mM so the protocol was similar but filtration was not required.

**Surface pressure curve.** The evolution of the film of molecules (also known as a Langmuir monolayer) is followed by recording the force exerted at the air-water interface on a thin plate hanging in the water. The plate is connected to a spring and is used as a balance that measures the surface pressure. This quantity is defined as

\[ \pi = \gamma_0 - \gamma \]

where \( \gamma \) is the surface tension and \( \gamma_0 \) the surface tension of the bare subphase (in the absence of molecules). The surface pressure therefore varies as the opposite of the surface tension. The
The preparation of LB monolayers of oligothiophene and stilbene derivatives and C11TSB differed from conventional LB preparation with fatty acids. The surface pressure isotherm curve was only composed of 2 stages before the layer started collapsing at high pressures (see fig2-2b), in contrast to typically 3 to 4 stages for fatty acids (see fig2-2a). These stages correspond to different phases that the Langmuir film goes through during compression (typically labeled gas, liquid, liquid condensed and solid phases). Fig2-2a shows a surface pressure isotherm obtained from pentadecanoic acid which is a fatty acid. In the vapor (or gas) phase, the density of molecules at the surface is so low that they do not interact. The surface pressure increases when molecules start interacting in the liquid phase and it rises sharply at the tilted and untilted mesophase stages. The latter stages are condensed solid phases where the monolayer is typically crystalline while liquid phases are amorphous or liquid-crystalline.

Fig2-2b shows surface pressure isotherm obtained when preparing LB monolayers of D5TBA from a filtered saturated solution. The surface pressure is plotted as a function of the trough area (instead of area per molecule) because of the uncertainty regarding the exact concentration of D5TBA solutions after filtration. The surface pressure curves were similar for C11TSB, 5TBA and DH5TBA. The Langmuir film only went through 2 stages. The small variations of the surface pressure observed from 250cm$^2$ to about 100cm$^2$ are mechanical artifacts of the LB apparatus and observed even in the absence of molecules at the interface. The surface pressure did not vary until the trough area became close to 100cm$^2$ at which point it increased sharply until the collapse at 15-20mN/m (not shown in fig2-2b). At collapse, the surface pressure started leveling off before becoming unstable.

These surface pressure isotherms differ largely from curves obtained from fatty acid Langmuir monolayers. Chen and coworkers also observed a 2-stage surface pressure-area isotherm for
squaraine amphiphiles similar to the molecules used in this study as they are composed of a polar anchor terminated by a COOH group, a semiconducting core and alkyl tails\textsuperscript{4}. Mussone and coworkers studied Langmuir films of poly(vinyl stearate)\textsuperscript{10}. They obtained a 2-stages curve and observed a leveling off of surface pressure gradient at high pressure that they explained by buckling of the monolayer under high compressive forces.

**Morphology at various stages of compression.** In order to investigate the nature of the Langmuir film at the two stages of compression, successive depositions at various trough areas and surface pressures were carried out. The series of topography AFM images shown in Fig2-3a to 3e were acquired after deposition of the Langmuir film on a mica substrate at levels of compression indicated by arrows on the surface pressure curve in fig2-3g. As illustrated by fig2-3a, a Langmuir film composed of micron scale islands formed at early stages. In fact, deposition minutes after spreading the chloroform DSTBA solutions at the surface of water led to the same structures. We should note that a phase of small porous grains (100-200nm large) was also observed in other samples which will be described in the next section.

The surface pressure started increasing at stage b when these islands start contacting each other. At stage d, there is almost no space left between islands while. At stage e (not shown on the surface pressure curve), a full monolayer of islands was formed and appears dark in the image while the bright regions correspond to molecules located between islands that have been pushed up due to the pressure applied by barriers.

![Figure 2-3. a. to e. Topography AFM images of a LB monolayer of DSTBA deposited at different stages of compression indicated on g. f. Schematic of the self-assembly and compression processes at the air water interface as deduced by experiments, g. Typical surface pressure curve obtained when preparing a LB monolayer of DSTBA.](image)

These results indicate that shortly after deposition on the water surface molecules diffused and self-assembled into islands (see fig2-3f for a schematic of the process). The molecules presumably diffused mostly during solvent evaporation, which took a few minutes. Once all the
solvent evaporated, we found that depositing the film immediately or after several hours led to similar results.

These results are in agreement with several studies showing that aggregation can occur at the air-water interface prior to compression. Lusk and Bohn studied a hemicyanine dye by Brewster Angle microscopy and fluorescence spectroscopy. They reached the conclusion that spectroscopic features that are characteristic of crystalline aggregates were present before compression. They found that the signature of these aggregates did not change upon compression. Kajiyama found that depending on the pH, fatty arachidic acids layers transferred to sample for TEM analysis prior to compression were crystalline.

**Molecular area calculations.** In fig2-3g, the surface pressure is plotted as a function of the area of the air-water interface delimited by barriers moving across the trough. This parameter can be converted into area per molecule if the number of molecules deposited at the air-water interface is known. In the case of D5TBA and 5TBA LB films, the molecular area that can be calculated from the nominal concentration is underestimated for the 2 following reasons. First, amphiphilic molecules can form micelles and travel through the subphase away from the air-water interface. This can cause the actual number of molecules deposited at the interface to be lower than the nominal value. Second, solutions were filtrated before being spread at the surface of water which decreases their effective concentration (with respect to the nominal concentration).

We calculated the nominal value of the molecular area for a Langmuir film deposited on mica after compression at the air-water interface: when 0.5mL of a D5TBA solution with a nominal concentration of 0.05mM was spread at the water surface after filtration, the trough area at deposition was 41nm$^2$. At that point, the surface pressure had reached 6N/m. AFM measurements of the D5TBA monolayer after transfer to the solid substrate showed that the coverage was close to 100%. From these parameters, the nominal area per molecule at deposition was calculated to be 21Å$^2$. As mentioned above, this number is a lower limit but it is rather consistent with measurements of the unit cell size by high resolution AFM and electron diffraction described in chapter 4 and chapter 5.

2. Control over the morphology of the Langmuir-Blodgett monolayer

Oligothiophene derivatives assembled in Langmuir-Blodgett monolayers composed of two phases with distinct morphologies, the porous phase and the island phase. Here the term “phase” is not used in its thermodynamic acceptation since their morphological differences are likely due to growth kinetics. Results presented in chapter 4 suggest that both phases are in fact crystalline with a Herringbone lattice. The morphology of the two phases is illustrated by fig2-4 that shows images of three different samples. For the sample shown in fig2-4a, the layer was mostly composed of micron large islands. In fig2-4b, it is composed of a network of grains which
are between 50 and 200nm in diameter constituting the porous phase. Fig2-4c shows an image where the layer is composed of roughly half island phase and half porous phase.

![Figure 2-4. Topography AFM image of a submonolayer of DSTBA on mica, a. Island phase, b. Porous phase, c. Mixture of Porous phase and island phase.](image)

The morphology of oligothiophene monolayers could be controlled by varying the concentration of the solution and its sonication time. Solutions with nominal concentrations below saturation (sample of fig2-4b) led to films composed of the porous phase. For solutions with concentrations of 0.1mM or higher, the proportion of island phase and porous phase depended on sonication time before filtration. The proportion of the island phase reached 80 to 95% (sample of fig2-4a) for extended sonication time of 60 to 90 minutes. For shorter sonication time (10-20min), the film was mixed (fig2-4b). These results show that concentration and sonication of the solution play a major role in determining the morphology of LB films. A mechanism for nucleation and growth in agreement with these experimental results will be proposed in the next section.

Island and porous phases were also observed in STBA monolayers and they were found to depend on the same parameters. Also, an image of a C11TSB monolayer on mica is shown in fig2-5 and its morphology is different than oligothiophene films. It is composed of a continuous layer with round shaped holes.

![Figure 2-5. Topography AFM image of a C11TSB monolayer on mica](image)

Finally, LB monolayers of DHSTBA were prepared and studied by AFM. These molecules assembled in large thin sheets (1nm high and tens of microns in size). Limited information could be deduced from AFM images. The fact that the edges of the monolayer sheets were not sharp or well defined suggested poor crystalline order, which was later confirmed by TEM experiments.

Several other research groups observed phases which morphology resembled the island phase and the porous phase that are described in this study. Chandra and coworkers found that the
hemicyanine derivative ODEP could form submonolayers with a variety of morphologies depending on specific compounds added to the subphase. They found an island phase that they referred to as “flowers” and a phase made of a network of grains similar to the porous phase\textsuperscript{12}. Mussone also observed porous networks and island morphologies for monolayers of the polymer poly(vinyl stearate)\textsuperscript{10}. Another common point with our study is that they observed particles at the center of monolayer islands that were also often observed at the center of 5TBA islands\textsuperscript{10}.

The fact that submonolayer aggregates with identical morphologies were reported for different compounds suggests that these structures are common for conjugated amphiphilic oligomers. It should be noted that the use of Brewster Angle Microscopy (BAM) to characterize films in situ is more widespread than AFM. The resolution of BAM is close to 10\textmu m and therefore too small to resolve the nanoscale morphology of the film. We expect that AFM images of films of conjugated oligomers studied by BAM could reveal similar morphologies.

3. Growth mechanism of Langmuir monolayers of conjugated oligomers

As described earlier, the morphology of oligothiophene and stilbene monolayer is determined by the nature of the solution rather than parameters related to the compression or deposition of the film. This indicates that the growth of the monolayer island phase and of the porous phase takes place either in solution or during solvent evaporation at the air/water interface. We did not observe similar islands in drop-cast and spin cast films of D5TBA and 5TBA which rules out assembly in solution.

We observed that 3D aggregates were often present at the center of molecular islands. This is illustrated by fig2-6a and fig2-6b which respectively show topography AFM images of D5TBA and 5TBA monolayers. In addition, morphological differences between D5TBA and 5TBA are
apparent. D5TBA islands have a radial flower-like structure while 5TBA islands are round-shaped and often faceted. Fig2-7a and fig2-7b show two different regions of a 5TBA sample prepared from a saturated solution which was not filtered. This explains the large number of aggregates that can be observed in fig2-7b. Note that based on electron diffraction results described in chapter 4, we could conclude that these aggregates are oligothiophene nanocrystals with a similar Herringbone crystal structure as monolayers. Interestingly, fig2-7a shows that in the absence of 3D clusters the monolayer is mostly composed of the porous phase while numerous islands can be observed in 7b where the density of 3D clusters is high. These results suggest that the presence of nuclei drives the formation of the island phase over the porous phase.

These observations are in agreement with the dependence of the monolayer morphology on sonication and concentration described in the previous section. For less concentrated non-saturated solutions, the molecules are fully solvated so the 3D clusters that lead to nucleation of islands are absent. The effect of sonication is twofold: it helps to dissolve some of the clusters, reducing the number of nuclei, but it also breaks up larger clusters into smaller ones, which increases the number of nuclei. Filtering enhances the latter effect, since large 3D clusters are blocked by the 200nm large pores. Sonication helps to reduce the size of the clusters below the filtration limit leading to a larger concentration of 3D nuclei in the solution used for LB preparation.

Based on these results, one can propose a mechanism for the growth of oligothiophene monolayers during Langmuir-Blodgett preparation. In the presence of a cluster of molecules, a crystalline island can nucleate and grow. In the absence of 3D nuclei, grains nucleate more homogenously forming a porous phase of small grains. The growing molecular islands absorb
smaller grains which nucleated in their vicinity. Growth stops when the solvent has evaporated. At that point, the system is essentially frozen.

This mechanism would be similar to a nucleation, growth and coalescence mechanism described by Doudevski et al for octadecyltrimethylammonium Bromide (OTAB) and octadecyltrichlorosilane (OTS) self-assembled monolayers on gold\textsuperscript{13}. They found that the shape of the islands may be rounded or fractal depending on the rate of 2D diffusion versus island growth. Crystalline islands of OTS were composed of elongated domains characteristic of self-diffusion limited growth after nucleation. This mechanism is expected in slow diffusing materials where dendrites appear during growth due to the concentration gradient formed close to the growing interface. On the other hand, molecules of OTAB assembled in round shape islands which growth is not diffusion limited. The morphological differences between D5TBA and STBA islands fall in the same categories. D5TBA islands are composed of elongated radial finger-like domains which will be described in more details in the following chapter. STBA islands are round. These results suggest that D5TBA molecules which are more amphiphilic than STBA molecules diffused more slowly at the air-water interface during solvent evaporation.

4. Mixed Langmuir-Blodgett films of 5TBA and D5TBA

**Experimental.** Mixed monolayers of 5TBA and D5TBA were prepared by using the following protocols. The monolayer shown in fig2-8a was prepared by dissolving both 5TBA and D5TBA in chloroform, then following the steps presented earlier in this chapter for sonication, filtration and LB preparation. The second method (fig2-8b) consisted in preparing two separate solutions of 5TBA and D5TBA in chloroform. After filtration, molecules were spread alternatively from the 5TBA and the D5TBA solutions 50µL at a time until 250µL of each were deposited at the air-water interface.

![Figure 2-8](image)

*Figure 2-8. a. Topography AFM image of a monolayer prepared by mixing 5TBA and D5TBA in solution, b. Topography AFM image of a monolayer prepared using two solutions, one of D5TBA and one of 5TBA and spreading them in turns at the air/water interface.*

**Results and discussion.** The topography AFM image in fig2-8a illustrates the morphology of the monolayer obtained by mixing 5TBA and D5TBA molecules in solution. Molecules assembled in
small aggregates characteristic of the porous phase. Height and friction measurements showed that 5TBA and DSTBA molecules phase segregated into grains with a typical diameter of 50 to 100nm. DSTBA grains were a few Å higher and had a lower friction.

On the other hand, depositing molecules from distinct solutions led to a monolayer composed of 5TBA and DSTBA islands as well as a porous phase, as illustrated by fig2-8b and 2-8c which were acquired in tapping mode. In this AFM mode, one acquires the phase signal together with the topography signal. A phase image is shown in fig2-8c. The phase signal is sensitive to the chemical nature of the end groups at the surface of the monolayer. This explains the strong contrast observed between DSTBA islands that appear light and 5TBA islands that appear dark. The ability to prepare intermixed crystalline structures of 2 different compounds is of great interest to study how electrical and structural properties of organic monolayers can depend on changes in their chemical structures.

5. Preliminary results: preparation of oligothiophene submonolayer using tetrachloroethane as a solvent

Experimental. Tetrachloroethane was substituted to chloroform for LB preparation. The procedure was identical to the protocol described above for molecules dissolved in chloroform. There were no obvious differences in the appearance of the solution. Although the saturation concentration is likely to differ for oligothiophene molecules dissolved in these two solvents, the difference was not significant enough to be observable. When the solution was deposited at the air-water interface in the Langmuir trough, it spread more slowly than chloroform and took longer to evaporate, which is expected from the higher molecular weight of this solvent.

Results. As described previously, 2D crystalline islands preferentially nucleate around 3D particles that remained in the solution after sonication and filtration and these islands grow during solvent evaporation. Aiming at preparing larger crystals, we used a solvent chemically similar to chloroform but with a higher ebullition temperature that evaporates more slowly. The difference was very apparent as after deposition of the tetrachloroethane solution at the air-water interface, an oil-like film was visible for a few minutes at the surface. It is not the case for chloroform which spread and disappeared almost immediately. The images obtained from AFM investigation of the LB monolayer obtained from a tetrachloroethane solution were unexpected. The molecules assembled into supramolecular structures that differ largely from what is obtained from a chloroform solution.

Fig2-9a and fig2-9b illustrate the morphology of DSTBA and 5TBA submonolayers obtained following this protocol. DSTBA molecules assembled into wire-like structure 500nm to 1µm long. A layer of material a few Å thick can be observed around the wires. This layer could be composed of lying down molecules or tetrachloroethane that has not evaporated. These 1D wire-like structures are reminiscent of the finger-like shape of internal domains of DSTBA islands prepared using chloroform. The driving force for 1D growth appeared to be enhanced by
the used of tetrachloroethane as a solvent. On the other hand, 5TBA molecules arranged in small rice grain shaped crystals as illustrated by figure 2-9b.

![Figure 2-9](image)

**Figure 2-9.** Topography AFM images of a DSTBA (fig2-9a) and 5TBA (fig2-9b) submonolayer deposited on mica and prepared from a tetrachloroethane solution.

The ebullition temperature is not the only physical property in which tetrachloroethane differs from chloroform. The viscosity of these solvents is also different (1.1 \(10^{-6}\) m\(^2\)·s\(^{-1}\) for tetrachloroethane and 0.38 \(10^{-6}\) m\(^2\)·s\(^{-1}\) for chloroform\(^{14}\)) which is expected to affect the diffusion of molecules. That could explain the very distinct morphologies obtained using tetrachloroethane. These preliminary results show that by changing parameters of the Langmuir-Blodgett preparation (the solvent but T and pH could also be explored) a variety of structures can be obtained. Since these structures are based on the self-assembly of molecules at the air-water interface, it is expected that the monolayer formed in this way are crystalline. In order to study the correlation between structural properties and electrical properties in organic materials, it is useful to be able to prepare monolayers with different morphologies, grain sizes and degrees of order. The 1D structures shown in figure 2-9a have a more simple geometry than 2D islands and could be useful to extract parameters such as the conductivity from electrical measurements.

**Conclusion.** Langmuir-Blodgett is a versatile technique that produces organic monolayers that can be transferred to various substrates including samples for TEM analysis (chapter 4) and heterogeneous metal-insulator surfaces (chapter 8) while conserving their structure and morphology. This capability coupled to the variety of different structures that can be produced by LB makes this technique an ideal tool to process model systems to investigate the relationship between the structural and electronic properties of ultra-thin organic films.

2. Website of the company that produced the LB apparatus, http://www.ksvnima.com/langmuir-blodgett-trough


Chapter 3.  AFM characterization of the structure of organic monolayers

The structural properties of organic monolayers were characterized by Atomic Force Microscopy. Topography AFM was used in contact mode and tapping mode to study the morphology of the monolayer and measure its heights to deduce the average tilt angle of the molecules. Using Lateral force AFM which is sensitive to the crystalline nature of the monolayer, it was possible to resolve the internal structure of monolayer islands. The combination of topography and lateral force AFM provided critical structural information such as the size of crystalline domains and the presence and density of grain boundaries. The lattice of molecular crystals was visualized by high resolution AFM and was consistent with the commonly observed Herringbone crystal structure. This chapter aims at providing a complete picture of the potential of structural characterization of oligothiophene monolayer by AFM.

Atomic Force Microscopy was developed in 1986 by Binnig and Rohrer at IBM and has now become a very common technique for the surface characterization of materials at the nano-scale. The morphology of organic thin-film and monolayers can be studied in contact mode, alternative contact mode (AC or tapping mode) or in non-contact. AFM can reach a lateral resolution of a few nm routinely and atomic resolution in stable imaging conditions. As mentioned in the introductory chapter, various signals can be recorded in AFM and each provides different structural, chemical or electronic information.

The main AFM techniques described in this chapter are topography AFM which provides a map of the height variations on the surface and lateral force AFM. In this contact mode technique, the frictional force between the substrate and the tip is measured by recording the horizontal deflection of the laser beam reflected off the back of the cantilever on a 4-quadrant detector. Because the frictional force depends, among other things, on the chemical interaction between the tip and the surface, this technique can provide valuable information to help identify different phases of a material or the chemical nature of a region scanned by the tip. Chen and coworkers used lateral force AFM to identify the head groups in drop-cast self-assembled monolayers and Langmuir-Blodgett monolayers.

Atomic Force Microscopy can be used at high resolution to visualize the lattice of organic monolayers or even image single molecules and defects. Most early demonstrations of lattice resolved AFM on organic materials were contact mode experiments on fatty acid LB films. Garnaes and co-workers obtained images of the lattice of a multilayer film of cadmium arachidate and could resolve boundaries between domains in a polycrystalline monolayer. It has however been shown that contact AFM often does not reach so-called “true single molecule resolution”. Even sharp tips with an apex radius of a few nm probe more than one molecule at a time. The energy potential at the surface of a crystalline material is periodical. A
sharp tip can be sensitive to this periodicity even when it is in contact with more than one unit cell since the AFM tip tends to remain longer in a lower energy configuration. The drag due to the scanning motion leads to a slip event in which the tip moves from a low energy configuration to the next. The molecular lattice can be observed in the AFM image due to this “stick-slip” motion, which is more visible in the lateral force signal. The image is the result of a convolution between the molecular lattice and the shape of the AFM tip. Since the tip averages the lattice over a few unit cells, contact mode high resolution AFM is not suitable to image individual defects. On the other hand, non-contact atomic force microscopy can resolve individual atoms, molecules and defects as Giessebl demonstrated on a Silicon (111) surface. In addition, Fukuma and coworkers studied self-assembled monolayers of alkanethiols and could resolve point defects such as vacancies present in the film.

This chapter will first focus on the applications of topography and lateral force AFM to obtain structural information on the morphology and properties of organic monolayers prepared by the Langmuir-Blodgett technique. High resolution lateral force AFM experiments will also be described as well as its applications to deduce the lattice structure of crystalline monolayers. Finally, we will describe preliminary results related to the application of the Transverse Shear AFM mode which is sensitive to the direction of crystalline grains.

1. Topography AFM in tapping mode and contact mode

Experimental. Most data presented in this chapter were recorded using an Agilent 5500 AFM. A prerequisite for scanning organic materials in contact mode is that the bond to the substrate is strong enough to prevent desorption of molecules due to shear forces applied by the tip. The molecules used in this study are terminated by a carboxylic acid group which forms hydrogen bonds with hydrophilic substrates such as mica or silicon oxide. LB monolayers based on these molecules could sustain scanning forces of up to 50-100nN before molecules were scrapped off from the substrate (equivalent to pressures of 1-2GPa). For these experiments, AFM tips with force constant in the order of 0.1N/m to 0.5N/m could be used extensively in contact without inducing observable damage. On the other hand, AFM tips with 3N/m force constant readily damaged the layer.

A description of a method used to deduce the contact area between the tip and the sample by the Derjagin-Muller-Toropov (DMT) model is provided in section 3 of this chapter treating of high resolution AFM. Based on these calculations, one can deduce the pressure applied by the AFM tip in contact provided the apex radius of the AFM tip is known. TEM images of tips used in CAFM experiments are shown in chapter 5. These metal coated tips have an apex radius of 20nm and a spring constant of 0.2N/m. At a 50nN applied force, the contact area calculated by the DMT model is 50nm^2 and the pressure is 1GPa.

Result and discussion. Topography AFM imaging in contact mode and tapping mode allows rapid determination of the morphology and height of ultra-thin molecular films. This technique can be used effectively in combination with processing method such as Langmuir-Blodgett, self-assembly in solution and spin coating to assess the nature and quality of prepared films as a
function of preparation parameters. Fig3-1a and fig3-1b show contact topography AFM images of LB monolayer islands of 5TBA and D5TBA and illustrate the morphological differences arising from differences in their chemical structures. This is likely due to differences in their diffusion constants during monolayer growth at the air-water interface (see chapter 2). D5TBA islands have a flower-like morphology that suggests a polycrystalline structure while 5TBA island have a round sometimes faceted shape that could indicate that it forms single crystals.

In addition, height measurement is a structural characterization tool that can help determine the average tilt of molecules or the number of layers that compose multi-layer films. The profiles below fig3-1a and fig3-1b were obtained along the line indicated in red on the image. From these profiles, the height of monolayers can be deduced as 2.5nm±0.3nm for 5TBA and 2.6±0.1nm D5TBA islands. The larger measurement error for 5TBA is due to the roughness of the native oxide substrate, as observed in the profile. The theoretical length of 5TBA and D5TBA molecules are 2.4nm and 3.6nm deduced from the freeware molecular editor Avogadro11.

The height measured in AFM for 5TBA is slightly larger than the fully extended length (by 1Å which is within the error bars). It is highly unlikely that the film would be composed of a tilted bilayer since the size of the 2-molecule Herringbone unit cell measured by electron diffraction was close to 40Å² (see chapter 4). Space filling simulations using the Avogadro freeware show that a bilayer could not be accommodated for such unit cell size at any tilt. The height measurements therefore indicate the 5TBA molecules stand fully upright. On the other hand, D5TBA molecules are tilted by about 45⁰ in average. Note that the tilt angle of the top decyl alkyl chain and of the butyric acid-5 thiophene bottom part could be different.
2. Lateral force AFM in contact mode

Results and discussion. In the lateral force mode, the horizontal deflection of the cantilever is plotted to form an image. This value is related to the frictional force that the tip undergoes while scanning in contact with the surface. For a given scan line, the tip scans first from left to right (the trace) and then from right to left (retrace). By subtracting the lateral force value in the trace and retrace lines, one can access the energy dissipated by frictional forces and compare the value for different regions of the sample. In order to calculate the absolute value of the dissipated energy, the measurement has to be calibrated for each new experiment following a procedure described by Salmeron\textsuperscript{12}. In this study, we used lateral force microscopy as a means to compare the properties of different regions and phases of monolayers rather than calculate absolute values of the dissipated energy.

Fig3-2a and 3-2b shows topography and lateral force images of 5TBA islands deposited on the native oxide of silicon. The lateral force image in fig3-2b was acquired during the first pass (the trace). The regions where the frictional force is lower appear darker. The frictional force is slightly larger on 5TBA molecules than on the oxide substrate. On the other hand, the topography and lateral force images of D5TBA islands (fig3-2c and 3-2d) show that the frictional force is lower on the molecules than on the substrate (fig3-2d). Note that the native oxide substrate appears brighter in fig3-2d than in fig3-2b. This is due to image treatment, not to an actual physical difference. The color coding was adjusted to emphasize the contrast. The frictional force on the oxide substrate is the same for both samples.

Figure 3-2. a. Topography and b. lateral force AFM images of 5TBA monolayer islands on SiO$_2$/Si$,+$, the Lewis formula of 5TBA is shown in inset c. topography and d. lateral force images of a D5TBA monolayer island on SiO$_2$/Si$,+$ with the Lewis formula of D5TBA in inset. The internal structure of D5TBA islands is visible in the lateral force image.

Fig3-3a shows a profile of the relative dissipated energy on the substrate and on the monolayer. It was obtained by subtracting the trace and retrace profiles and normalizing the result by the value measured on the substrate. The location where the profile was recorded is shown in inset and corresponds to a region of the image shown in fig3-2d. The dissipated energy was 5 times lower on the islands than on the substrate. This is due to the presence of alkyl chains that act as a lubricant\textsuperscript{13}.

In addition, a comparison between the topography image (fig3-2c) and the lateral force image (fig3-2d) of D5TBA confirms the presence of an internal structure within islands. Bright lines are
visible in fig3-2d. In these regions, the dissipated energy is close to 50% higher than in the rest of the island as shown on the plot of fig3-3b. The plot was acquired over 2 vertical high friction lines located 150nm from each other in the region shown in inset and extracted from fig3-2d. Frictional force is correlated to molecular order. In a well packed lattice, molecules have less freedom to move and energy dissipation modes such as gauche defects, tilting, and rotation are reduced\textsuperscript{14}. It can therefore be assumed that the internal features present in D5TBA islands are disordered boundaries between ordered domains.

Figure 3-3. a. Profile of the normalized dissipated frictional energy in the region of fig3-2d shown in inset, b. Profile of the normalized dissipated frictional energy over 2 grain boundaries. The region where the profile was acquired is shown in inset.

Lateral force measurements were also sensitive to the difference in molecular order between different phases of D5TBA molecules. Fig3-4a shows a region of a submonolayer of D5TBA where 3 distinct phases can be observed. As described in the previous chapter, oligothiophenes used for Langmuir-Blodgett preparation assemble in an island phase and in a network of smaller grains, the porous phase. In the topography image of fig3-4a, no difference in the morphology of the porous phase can be observed. The lateral force image however shows that some regions have a similar friction as crystalline islands and others have much higher friction. Based on the correlation between molecular order and friction, these results suggest that the high friction grains are amorphous, or at least much less ordered. This could be due to the presence of impurities within the monolayer.

Figure 3-4. a. Topography AFM image of a D5TBA submonolayer on a SiO2/SiP+ substrate, b. Lateral force image acquired simultaneously showing that the frictional force is not constant over the porous phase which suggest varying degrees of molecular order over this phase.
Finally, lateral force AFM was instrumental to differentiate between monolayers and multilayers of D5TBA molecules and to determine which side of the molecules was pointing up as will be described in the chapter related to TEM measurements (chapter 4).

3. Lattice resolution lateral force AFM

Experimental.

Scanning parameters. We used lateral force AFM at high resolution to investigate the crystalline nature of monolayer islands prepared by the LB technique. The small scanner (10µm range) of a 5500 Agilent AFM was used with triangular shaped SiN cantilevers purchased from Veeco. Cantilevers with spring constants between 0.25 and 0.5N/m were more effective than softer tips that led to images with a lower signal to noise ratio. Depending on experiments, scan sizes of 20, 40 or 60nm were used. For 20nm scan range, 256*256 pixel images were acquired at a rate of 2Hz to 4Hz. For 40nm and 60nm, the image sizes were respectively 512 and 1024 pixels and scan rates respectively 4 and 6Hz. The effective scan speed was therefore higher for larger range images. The advantage of using larger scan size at high scan rate is that the drift of the sample with respect to the scanner could be measured more easily.

In order to assess the influence of the force on xy resolution, AFM images were recorded at +20nN net force (fig3-5a) and -2nN net force (in the pull-off regime, fig3-5b). Fig3-5a and 5d show that the resolution of the lateral force image recorded at +20nN is higher than at negative net force at which the molecular lattice is barely visible. Fourier Transform images show that the lattice is similar for these imaging conditions indicating that differences observed between images acquired at different forces is due to changes in instrument resolution rather than to changes induced by the force. We will show in chapter 6 that the lattice changes permanently when applying forces in the order of 40nN and at higher scan speeds than used for high resolution AFM.
Effect of Drift. Even in the most stable instruments, the drift motion of the sample with respect to the scanner is an issue. Severe drift can cause the sample to shift by tens of nm per minute with respect to the scanner so that the effective scanning speed and scan size are dramatically different than nominal values entered in the AFM software. This induces distortions in the image and can cause a severe loss of xy resolution. In order to ensure a lower level of drift induced distortions in the image, high scanning rates were used (the faster the image is recorded, the less the sample drifts with respect to the tip). Also, to minimize drift induced by thermal expansion of the various elements of the microscope, the AFM was left to stabilize thermally for several days after setting up the experiments and turning the laser on. A drift rate of a few nm per minute was achieved which is sufficient for recording lattice resolution images of a monolayer.

Fig3-6a and 3-6b show Fourier Transforms of lateral force images acquired respectively with a drift speed of 5nm/min and 1nm/min for a 20nm scan (scan rate was 2Hz and the # of pixels was 256*256 so the image was recorded in approximately 2min). For higher drift speed, the lattice is distorted in the y direction which is the slow scan direction. The table in fig3-6c shows that the measured unit cell depends strongly on the drift speed with induced error as high as 50%.

Contact area. Several models are available for calculations of the contact area. The JKR and DMT models can accurately describe the contact between AFM tips and substrates. The non-dimensional Tabor parameter $\mu_T$ can help determine which of the 2 models applies to a given AFM tip-sample combination:

$$\mu_T = \left(\frac{16\gamma R^2}{9K^2z_o^3}\right)^{1/3}$$

where R the radius of curvature of the tip, K is the reduced Young modulus and $z_o$ can be approximated as the intermolecular separation in the monolayer (0.5nm). The energy term $\gamma$ is calculated from

$$P_c(DMT) = -2\pi\gamma R \quad \text{or}$$

$$P_c(JKR) = -\frac{3}{2}\pi\gamma R$$

for the DMT and JKR models respectively. $P_c$ is the adhesion force that can be measured from force-distance spectroscopy. For $\mu_T < 0.1$, the DMT model applies while the JKR model applies.
for $\mu_T > 5$. For Pt coated tips with a radius of 20nm, $\mu_T$ is close to 0.1 which indicates that it can be more accurately described by the DMT model. For sharper SiN tips used for high resolution AFM, $\mu_T$ is close to 0.05 so the DMT model also applies. The contact radius can then be determined using the following formula

$$a = \left[ \frac{R}{K} \left( P + 2\pi\gamma R \right) \right]^{\frac{1}{3}}$$

The radius of the apex of commercially available tips can differ from batch to batch but the nominal apex radius can be as low as 2nm$^{15}$. Assuming a 5nm radius for a SiN tip, a 3nN applied force and 3nN adhesion force, the contact radius between the tip and the sample is 1.2nm. For a 2nm tip apex radius, it goes down to 0.8nm such that the contact diameter corresponds to 2 to 4 intermolecular distances. The contact area is then 2nm$^2$ which corresponds to 5 unit cells. These calculations show that the AFM tip is in contact with several molecules at any point which limits the resolution of individual defects but that tip with apex radius close to 1nm could in theory achieve molecular resolution.

**Results and discussion.** Fig3-7a shows a typical high resolution image obtained on a D5TBA monolayer island. It was extracted from a larger 60nm image obtained in a finger-like domain of an island. Rows of molecules are visible in the image. The Fourier transform shown in inset was obtained from the full 60nm image. It shows that three distinct lattice directions are resolved, even though they are not readily visible from the real-space image. On the other hand, the resolution achieved in fig3-7b is less typical, the tip was likely exceptionally sharp. The drift is however more pronounced in this image.

The drift was corrected for by recording lattice resolution images of the mica substrate and comparing the experimental unit cell size with the theoretical 5.2Å hexagonal mica lattice. After correction, the spacing in the 3 resolved directions was 4.8Å with an error of 0.4Å associated with the width of the spot in the Fourier transform and statistical spread over several measurements.

According to several reviews$^{16,17}$ the most common packing of oligothiophene molecules is the Herringbone crystal structure. The results obtained here are consistent with this structure.
although the Herrigbone lattice is rectangular whereas the experimentally determined lattice is apparently hexagonal. This is due to the selectivity of high resolution AFM: only the close-packed directions of the unit cell are resolved. Fig3-7c shows a scheme of a 2 molecule-per-unit cell 2D Herringbone crystal. The green lines correspond to the planar 5T unit of DSTBA molecules. The red lines correspond to close-packed directions. There are two equivalent diagonal directions and a vertical direction. The 4.8Å row to row spacing measured experimentally would correspond to a 9.5Åx5.5Å rectangular unit cell. This structure is in agreement with TEM measurements shown in the next chapter.

Images of the 5TBA lattice were acquired but only after numerous unsuccessful trials. It appears to be much more challenging to resolve the 5TBA lattice possibly because of the higher frictional force when scanning these molecules in contact mode. The images that were obtained were not calibrated using the mica lattice so the unit cell size was not extracted. This issue could be resolved by studying 5TBA monolayer islands in TEM (chapter 4).

**Figure 3-8.** a Topography and b. Lateral force AFM image of DSTBA on SiO2/Si+. c. lateral force image obtained by zooming on the central grain boundary.

**High resolution images of grain boundaries.** Lattice resolution lateral force microscopy was used to investigate the nature of boundaries of higher friction observed in DSTBA monolayer islands (see fig3-2b). By recording 60nm large images over these regions, we confirmed their amorphous nature. Fig3-8a and 3-8b show topography and lateral force images of a section of a DSTBA island on SiO2/Si. A boundary running diagonally between two finger-like domains is apparent in 3-8b (light yellow linear feature). The bright yellow region corresponds to the substrate. Fig3-8c shows a lattice resolved image obtained in lateral force. Dark here corresponds to higher friction (the contrast is reversed in that image). The lattice can be
observed on both sides of the high friction boundary with 2 lattice directions resolved in both grains and indicated by red lines. The amorphous boundary was 5nm large, corresponding to a width of 10 molecules.

**Orientation of the lattice with respect to finger-like domains in D5TBA.** We recorded lattice resolved images in adjacent grains of a D5TBA monolayer on mica. The results are presented in fig3-9. Fig3-9a shows a topography image of a region of a D5TBA islands composed of 5 finger-shaped domains. The dotted line frames indicate locations where lattice resolved lateral force images where recorded. Fourier Transform images corresponding to the real space images are displayed in inset of fig3-9a. The directions of the molecular lattice deduced from the FT images are shown as black lines. Only 2 lines are visible in some grains because the third direction is horizontal and not resolved.

Fig3-9b shows a topography AFM image of the same region. The schematic shown in the right hand side summarizes the results of fig3-9a. The lattice orientations for each domain are drawn in blue. The non-resolved directions are included and were inferred from the orientation of the resolved directions. The lattice appears to roughly rotate with the grain orientation and one of the directions is orthogonal to the axis of the grain. As mentioned above, the spacing for the 3 lattice directions is close to 4.8Å so they cannot easily be differentiated. However, not all directions are equivalent since there are two diagonal directions and the vertical direction (as shown in fig3-7c). A symmetry argument would suggest that the direction orthogonal to grain growth, which is the axis direction, is the vertical direction. Electron diffraction experiments presented in the next chapter confirmed this assumption. Note that this vertical direction emphasized in red in fig3-7c should be referred to as the [0,1] direction based on electron diffraction terminology (this is important since otherwise the results of this chapter and the results of chapter 4 would seem to contradict).

![Figure 3-9. a. Topography AFM image showing 5 finger-like domains of a D5TBA monolayer. FT images of lattice resolved images acquired in dotted line squares are shown in inset, b. Reverse LF image of the molecular island along with a schematic showing the grain boundaries and the lattice directions.](image)

High resolution AFM in contact mode can be used to obtain useful information about the crystal structure and presence of grain boundaries in organic material. It can even be used to relate the orientation of the lattice with the morphology of molecular islands. The limitation of this technique is the lack of true molecular resolution that would allow identifying individual
defects and measuring the degree of crystallinity of the layer. STM measurements, which would yield a more accurate estimate of the decrease in molecular order, are planned in the future on molecular monolayer of D5TBA and 5TBA.

**Molecular Dynamics simulations (collaboration with Nenad Vukmioric and Lin-Wang Wang at LBNL)**. We performed classical molecular dynamics calculations to determine the most stable packing of the DSTBA molecules and compare it to experimental results. The CFF91 force field, as implemented in the LAMMPS code was used. Several structures were used as a starting point for the MD simulation, including a Herringbone structure. After relaxation, the lowest energy configurations were selected and compared. Two final structures were the lowest in energy. Both were Herringbone structures with the D5TBA molecules inclined from the substrate at an angle close to 45°. The two configurations only differed by the relative angle between the 2 molecules of the unit cell. The unit cell dimensions were a=11Å in the [0,1] direction and b=6.3Å in the [1,0] direction and the height was 2.4nm. The calculation therefore agrees with the AFM experiments when it comes to predicting the crystal structure space group (pp2g corresponding to a Herringbone motif) and the tilt. However, there is a significant disagreement regarding the size of the unit cell which is predicted to be 15% larger than measured experimentally. This discrepancy is still investigated.

4. Preliminary results: transverse shear mode AFM on D5TBA monolayers

An additional imaging mode that is closely related to lateral force AFM is the transverse shear-force imaging technique. In this mode, the AFM tip fast-scan direction is parallel to the axis of the cantilever (as opposed to the fast scan direction being orthogonal to the lever in conventional lateral force AFM). The signal that is recorded and plotted to form an image is the lateral deflection of the cantilever. As a result, this mode quantifies the transverse shear force instead of the lateral force on the AFM tip. Kalihari et al showed that this imaging mode was sensitive to the orientation of the lattice of crystals with respect to the scanning direction. The effectiveness of the technique was demonstrated on a pentacene thin film where grains were randomly oriented with respect to the scanning direction. A strong contrast was observed between grains in the transverse shear-force mode whereas no contrast was observed in conventional lateral force AFM. Using this technique, the authors could map crystal directions in grains without resorting to a high resolution imaging.

In order to apply the transverse shear force imaging mode to oligothiophene monolayers, lateral force and transverse shear-force images of a DSTBA monolayer were recorded. Both 0.2N/m Pt coated cantilevers and 0.28N/m SiN triangular shaped cantilevers were experimented. Fig3-10b and 3-10c show transverse shear force and lateral force images obtained with 0.2N/m Pt coated tips on a section of a large DSTBA island. The lateral force image (fig3-7c) shows that the island is composed of many small finger-like domains with a typical size of 100nm. White and black arrows are drawn along the local orientation of grains. As shown above, the orientation of grains and of the lattice is related.
Figure 3-10. a. Topography, b. Transverse shear force and c. Lateral force AFM images of a D5TBA island on SiO2/Si+. The direction of finger-like grains is indicated by black and white arrows in fig3-10c.

A significant contrast is observed in the transverse shear force image shown in fig3-10b. According to the study by Kalihari et al, this contrast could be related to the relative direction of the lattice and the scanning direction. The darker regions of fig3-10b correspond to regions where the angle between the grain direction and the horizontal is 0° or 90°. These are indicated by black arrows in fig3-10c. On the other hand, brighter regions in 10b correspond to 45° angle between the grain direction and the horizontal. These results are preliminary and additional experiments should be attempted to consistently compare the contrast in the transverse shear mode and the direction of finger like domains.

Note that although SiN tips are sharper than metal coated tips, we did not observe contrast in the transverse shear mode on 5TBA and D5TBA.

**Conclusion.** Atomic force microscopy can be applied to analyze the morphology and the microstructure of organic thin films. Using this technique, a map can be produced detailing the size of crystallites, the location of grain boundaries and even the orientation of the lattice for D5TBA molecules. The lattice symmetry was also determined using high resolution imaging. This structural information can be coupled efficiently to electrical measurements to deduce the conduction properties of specific components of heterogeneous organic films, as will be shown in chapters 4 to 8.

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Chapter 4. Organic monolayer and few-layer films characterization by Electron Microscopy

We used Transmission Electron Microscopy to study the morphology and crystal structure of monolayer and few-layer films of DSTBA, 5TBA and C11TSB. Organic films could be transferred to grids for TEM analysis using vertical Langmuir-Blodgett deposition and a horizontal deposition method which respectively led to monolayer and bilayer films as determined by height analysis in AFM. In order to obtain diffraction patterns of organic monolayer and few layer crystals, the dose was minimized by using a defocused beam in STEM mode and a beam diameter of 100nm. The diffraction patterns of 5TBA, DSTBA and C11TSB were consistent with a Herringbone structure. By scanning the beam over crystalline samples, we obtained spatially resolved lattice information of the monolayer. 5TBA crystalline islands were found to be single crystal or composed of 2 to 3 crystalline domains, while DSTBA islands were polycrystalline.

The study of organic materials by electron microscopy is highly challenging due to the sensitivity of these materials to the electron beam. Ultra-thin organic films can be severely damaged due to ionization and knock-on events when high energy electrons interact with molecules. On the other hand, a wealth of information can be extracted by Transmission Electron microscopy. The morphology and the microstructure of organic materials can be studied by recording real space low magnification images. For crystalline samples, the space group and lattice parameters can be obtained from electron diffraction. Finally, point and line defects can be investigated if atomically resolved real space images can be obtained. The latter is the most challenging since the dose that it requires causes very thin organic crystals to deteriorate immediately. The issue is especially critical for monolayers.

The first studies of organic crystals by TEM date from the late 70’ and 80’. Early studies focused on organic single crystals such as the work of Murata and coworker on phthalocyanine single crystals or Fryer and coworkers on paraffin crystals. The first lattice resolved image of an organic monolayer was reported by Fryer on Langmuir-Blodgett films of phthalocyanines. Cryo-microscopy has been used extensively to limit the damage induced by the electron beam. The sample is then cooled down rapidly in liquid environment to freeze its room temperature structure and study it by electron microscopy. Using this technique, Zemlin and coworkers obtained electron diffraction patterns and real space lattice images of monolamellar paraffin.

A major source of loss of signal in images of the lattice of organic materials is the beam induced motion of the specimen due to damage of the sample. Glaeser and Downing found that reducing the size of the electron beam to 100nm helped limit the motion-induced signal loss. In the so-called spot scanning technique the 50 to 200nm wide beam is scanned over the
sample and an array of real space images is produced. This technique was used on monolayers of a paraffin (C44H90) at low temperature and could even be applied to image the lattice of 20nm thick polymer crystals at room temperature.

In this chapter, we describe the preparation of organic monolayer samples for TEM experiments and the development of a technique bearing similarities with the spot-scan imaging method described above in which electron diffraction patterns of the monolayer are recorded in 100nm increments over the sample. This technique made it possible to resolve the microstructure of monolayer and bilayer organic films. The work described in this chapter is the result of a collaboration with Dr. Altoe and Dr. Aloni at the Molecular Foundry who performed the TEM experiments.

2. Preparation of TEM samples by the vertical and horizontal deposition techniques and AFM analysis

Experimental. This section deals with the experimental details of the preparation of samples for the study of organic monolayers and bilayers by TEM. Since a number of different types of electron transparent supports were used, the description is slightly lengthy.

Langmuir films of 5TBA, D5TBA, stearic acid and C11TSB were prepared at the air-water interface. These films were transferred to supports for transmission electron microscopy analysis in two ways. The films were either deposited by conventional vertical upstroke dipping (Langmuir-Blodgett) or by horizontal upstroke dipping. Langmuir-Blodgett deposition was automatic while both automatic and manual methods were tested for horizontal deposition. Various electron transparent supports were used including holey carbon Ted Pella grids (50-100nm thick film of carbon with small holes supported by a copper grid), 1824 Ted Pella grids (a continuous ultrathin film of carbon covering a holey carbon film itself supported by a copper grid) and silicon nitride SPI and Ted Pella windows.

Horizontal deposition. A schematic of the horizontal deposition method is shown in fig4-1. The TEM sample is represented as a round shape disk. Manual deposition was carried out by holding the grid with tweezers and lifting the grid upward slowly through the air-water interface. The grid was previously dipped into the subphase by a fast vertical pass through the air-water interface (while the Langmuir film was present). AFM analysis of grids after that first pass showed that no significant deposition had occurred. For SiN windows, the SiN membrane was facing up during deposition. For holey carbon films and 1824 carbon films, we observed that the Langmuir film did not adhere to the carbon film if it was facing up. This is due to the absence of affinity between the hydrophobic
carbon film and the COOH group at the bottom of the molecules. Instead, the grids were raised across the air-water interface with the copper grid side facing up. After this step, a droplet of water was usually present on the Cu face of the TEM sample with a Langmuir film presumably lying at the air-water interface. Upon evaporation of the droplet, the film was deposited both on the copper grid and on the carbon films that lies in the holes of the grid.

**Vertical deposition (conventional Langmuir-Blodgett).** Langmuir-Blodgett vertical deposition was performed by attaching self-closing tweezers to the LB lifting arm and placing a TEM grid in the tweezers. Both SiN windows and carbon based support had to be treated in an oxygen plasma. Using SiN membranes as received from the manufacturers led to transfer of a very small portion of the monolayer from the air water interface. Treating the membranes in oxygen plasma for 10 minutes rendered them hydrophilic enough for full coverage deposition of a Langmuir film. Holey carbon and 1824 supports were treated for 20s only to preserve the carbon film. SEM and TEM analysis of the 1824 grids after oxygen plasma showed that some holes had been burnt through the 4nm thick carbon films which led it to fold upon itself.

**AFM on films deposited on membranes for TEM.** AFM could be used in contact mode and tapping mode to study organic films deposited on SPI SiN membranes. The Ted Pella membranes were more difficult to study as they appeared to be highly stressed (which was visible by optical microscopy). These membranes were too compliant for contact mode or tapping mode AFM (if the spring constant of the cantilever and the spring constant of the stressed membrane are of the same order of magnitude, AFM height measurements become inaccurate).

![Figure 4-2. a. Topography AFM image of a D5TBA submonolayer deposited on a 1824 substrate, b. corresponding lateral force AFM image. Individual islands can be observed in friction. Only one island can be seen in topography towards the left of the image.](image)

Organic films on 1824 carbon supports could also be studied in AFM by placing the carbon film side on a flat mica sample and imaging the sample from the Cu grid side. This prevented the ultra-thin film from being perforated by the tip of the AFM cantilever since the film was supported by mica. Although contact mode images of the organic film over the carbon film could be recorded, the height was inaccurate. This is also due to the compliance of the carbon film. Fig4-2a and 2b show topography and friction images acquired in contact mode on a D5TBA films deposited on a 1824 support. The islands are visible in friction but hardly in topography.

When AFM imaging of the organic was not possible on the unsupported region of a SiN membrane, an alternative option was to image the supported SiN membrane which has identical properties (these TEM supports are fabricated by depositing a thin film of SiN on silicon and etching the silicon until a window of unsupported SiN films is created. The SiN membrane is therefore similar whether supported or unsupported by silicon).
**Roughness analysis of the SiN membranes.** We recorded topography images of SiN windows with Veeco SiN triangular cantilevers to measure the substrate roughness. The scan size was 2µm. We found that the RMS roughness of SPI membranes was 5.5Å while the RMS roughness of Ted Pella membranes was 3.5Å. The substrate roughness is a critical factor as rough substrate can alter the crystalline order in monolayer of organic materials, as described in section 2.

**Results.** Samples prepared by both deposition techniques were initially studied by TEM only. D5TBA islands deposited on the various TEM supports had the characteristic flower shape morphology that was described in the previous chapter. This led to the assumption that organic islands were identical whether transferred horizontally or vertically from the air-water interface. AFM analysis proved this assumption wrong.

Fig4-3a and 4-3b show topography and lateral force images of D5TBA islands transferred by horizontal deposition. The frictional force on molecular islands is similar to the silicon nitride substrate. The vertical lines that appear in fig4-3b correspond to molecules being dragged by the AFM tip as it scans towards the top of the image. This suggests that the layer of molecules in contact with the tip is loosely bound.

![Figure 4-3. a. Topography and b. lateral force images of a D5TBA submonolayer transferred on a SiN membranes by horizontal deposition, c. topography and d. lateral force images of a D5TBA submonolayer transferred on a SiN membranes by vertical LB deposition](image)

Fig4-3c and 4-3d show topography and lateral force AFM images of D5TBA islands transferred on an oxygen plasma treated silicon nitride grids by vertical LB deposition. The low friction characteristic of the presence of lubricating alkyl chains can be observed on D5TBA islands. Height measurements in topography indicate that islands in fig4-3a are 4.8nm high while islands in fig4-3c are 2.6nm high. All these observations are consistent with the presence of D5TBA bilayer islands on SiN membranes when the horizontal deposition method is used. According to the lateral force image, the carboxylic acid head groups are exposed at the top of the film which means that molecules are assembled tail to tail.

The observation that bilayers were transferred through horizontal deposition was unexpected. In the next paragraph, an explanation of the phenomenon that occurs at the interface during deposition is provided.

**Discussion.** “Overturn” of portions of the Langmuir film located at the air-water interface during the deposition process could be the cause of the formation of a second layer. In 1938 Langmuir and Schaefer published a study dealing with a horizontal deposition technique that would later be referred to as Langmuir-Schaefer (LS) deposition⁸. In this method, a bare sample
is horizontally brought in contact with an organic film lying at the air-water interface. Upon retraction of the sample, the monolayer can be transferred from the air-water interface to the solid surface if it is energetically favorable (i.e. if the right hydrophobic/hydrophilic interactions are present). Schaeffer and Langmuir observed that a layer of molecules could flip up-side down if the interaction between the solid sample and the head of the molecules was stronger than with the tails pointing out of the air-water interface. The authors called that phenomenon “overturn”. Kato observed a similar event when depositing multiple layers of an amphiphilic oligomer with the LS technique.  

A similar mechanism likely occurs in our system when the molecules are deposited through horizontal lifting across the air-water interface. As the grid crosses the surface, the monolayer comes in physical contact with the hydrophobic substrate. A portion of the monolayer could overturn and form a bilayer due to the poor interaction with the substrate upon drying of the water layer (the head groups are hydrophilic whereas the grids which are not oxygen plasma treated are not). This is illustrated by fig4-4a. Another cause could be water instability due to the vibrations induced by the manual deposition. If the first monolayer in physical contact with the membrane becomes submerged under a film of water, it becomes favorable for a second layer to assemble tail to tail with the first layer in order to expose its polar head groups to water (scenario shown in fig4-4b).

3. Spot scanning electron microscopy on monolayer and bilayer films

*Description of the technique.* TEM experiments were performed in a Jeol 2100F at 120kV on oligothiophene LB films deposited on various supports. Initially, only transmission electron
micrographs showing the morphology of the organic film could be obtained and no spots were observed when acquiring images in diffraction mode. Electron diffraction pattern could be obtained after tailoring the protocol to reduce the dose of electrons to avoid damaging the organic film.

Figure 4-5. Array of electron diffraction patterns obtained by scanning the beam in 100nm steps across a submonolayer of 5TBA on a SiN membrane.

A collimated parallel illumination with a spot size of approximately 100nm and corresponding flux of 10 electrons Å⁻² s⁻¹ was used. To minimize the electron dose received by the organic monolayer, the beam was scanned with a step size of 100nm and dwell time of less than a second per pixel. The spot patterns were recorded by using a capture screen routine because the regular data acquisition using the digital micrograph software led to an exposure time which was too long. Regions of the film were first scanned in diffraction mode to obtain the array of diffraction patterns before recording a scanning transmission electron micrograph of the region (see the image shown fig4-5a). The rotation between the real space image and the diffraction patterns was taken into account and corrected for. This method is a “spot-scanning” routine like the technique developed by Downing to minimize beam induced motion⁷. The main difference is that electron diffraction patterns rather than real space images are recorded here.
The specular beam is visible at the center of spot patterns shown in this chapter because the spot scanning protocol does not permit to mask it. An improved experimental set-up could be developed by modifying the camera, the imaging routine and the software to allow masking of the specular beam, minimizing beam exposure further and increasing the speed of the data capture. This would require tuning the TEM specifically for imaging of organic materials. The method described in this chapter is however applicable in most transmission electron microscopes.

**Results and discussion.** Obtaining images showing the morphology of monolayer islands is useful in itself but redundant with AFM imaging capabilities. The central contribution of this spot scanning routine is the ability to map the internal structure of ultra-thin organic crystals with a spatial resolution of 100nm. Fig4-5 shows a set of data obtained on a 5TBA submonolayer on a SiN membrane by scanning the sample in 100nm steps and recording an electron diffraction pattern at each step. The array of spot patterns is superimposed to the STEM image such that each spot pattern is located on the region of the monolayer island that it was generated from. In most pixels, first and sometimes second order diffraction spots are present. We observed that the patterns faded and disappeared within half a second of beam exposure. The diffraction patterns shown in fig4-5 were recorded in the first 0.2s of exposure.

![Figure 4-6. a. STEM image of a DSTBA bilayer on a SiN FEI membrane with the [0,1] direction of the unit cell indicated by a yellow arrow, b. Diffraction patterns obtained in the four central pixels enclosed in the blue square.](image)

The map shown in fig4-6 can help elucidate the internal structure of molecular islands. In Fig4-6a, the crystal structure of the 5TBA monolayer was mapped on the real space image by indicating the orientation of the [0,1] direction of the unit cell by yellow arrows (see fig4-7c and 7d for a detailed description of the unit cell). The diffraction patterns obtained from 5TBA crystals are consistent with a rectangular Herringbone crystal structure. The green hexagons in fig4-6a correspond to region of the films where multiple sets of spots can be observed which...
indicates that more than one crystalline domains is present under the beam. Fig4-6b shows a closer view of the 4 patterns recorded in the blue square towards the center of fig4-6a. The white spot at the centre of the island is a 3D polycrystal, i.e. a nanoparticle of 5TBA around which the island nucleated. From fig4-6a, it is apparent that 5TBA islands are usually composed of 2 crystalline domains. Interestingly, the grain boundary was not observed in topography or lateral force AFM in contrast with D5TBA grain boundaries.

![Figure 4-7. Diffraction patterns obtained from, a. a 5TBA monolayer island and b. a D5TBA monolayer island, c. Schematic of the Herringbone crystal structure of 5TBA. d. simulated diffraction pattern of 5TBA](image)

**Diffraction patterns.** Fig4-7a shows a typical diffraction pattern obtained from a 5TBA monolayer island with an exposure of 0.2 seconds. The diffraction pattern is consistent with a 7.4±0.4Å x 5.8±0.3Å herringbone unit cell. The lack of (1,0) and (0,1) reflections is a result of the glide reflection symmetry in the pgg (p2gg) space group describing the 2D Herringbone lattice. The intensity of the (2,0) reflection at 3Å is expected to be weaker than (0,2) and (1,1) reflections and is below the detection limit. The diffraction pattern in fig4-7b was obtained from a D5TBA monolayer island. It is consistent with a 9.1±0.4Å x 5.9±0.3Å herringbone unit cell. The unit cell of D5TBA crystal is therefore larger in the [0,1] direction compared to 5TBA which is consistent with the fact that D5TBA monolayers are tilted. The (1,0) and (0,1) reflections are also absent in D5TBA due to the glide reflection symmetry. Note that the intensity of the spot pattern shown in fig4-7b is above what was typically obtained from D5TBA monolayers. This subject will be described in more detailed at the end of this section

A schematic of the top view of the 5TBA unit cell deduced from fig4-7a is shown in fig4-7c. From the xyz coordinates and the scattering factor of each atom present in the unit cell, a diffraction pattern can be simulated using the electron microscopy software MacTempas. The xyz coordinates were obtained from the freeware Avogadro. Using this freeware, one can input the Lewis formula of a molecule, calculate the lowest energy configuration and extract xyz coordinates for a single molecule. Fig4-7d shows a diffraction pattern simulated from a 5TBA Herringbone crystal with a 7.4±0.4Å x 5.8±0.3Å unit cell. The simulated spot pattern is consistent with the experiments.

The crystal structure of D5TBA monolayers deduced from electron diffraction is consistent with high resolution AFM results. We mentioned that only the close-packed directions are resolved
by contact AFM and how a Herringbone structure would appear as a nearly hexagonal set of lines in AFM. There is however a slight discrepancy in the size of the unit cell measured in TEM and AFM. The 4.7 Å measured spacing in AFM corresponds to a 9.5 Å x 5.5 Å unit cell size (compared to 9.1 Å x 5.9 Å in TEM). The difference is within the experimental error of both measurement techniques. The overall size of the unit cell is very close, 53.7 Å² by TEM and 52.3 Å² by AFM.

![STEM image of a DSTBA bilayer on a SiN SPI membrane](image1)

**Figure 4-8.** a. STEM image of a DSTBA bilayer on a SiN SPI membrane with the [0,1] direction of the unit cell indicated by a yellow arrow, b. STEM image of a 5TBA monolayer on a SiN SPI membrane, c. Diffraction patterns obtained in the four central pixels enclosed in the blue square.

**DSTBA monolayers and bilayers.** We also used the spot scanning technique to map the structure of DSTBA monolayer and bilayer islands. Fig4-8a shows a STEM image of a DSTBA bilayer island with yellow arrows indicating the [0,1] direction of the unit cell deduced from electron diffraction patterns. The grey circles are due to carbon contamination and each circle corresponds to a location where a diffraction pattern was recorded. Fig4-8b shows 4 diffraction patterns corresponding to the location emphasized by a blue square. The intensity of spot patterns recorded on DSTBA was lower than on 5TBA and only the first order diffraction spots were observed. For DSTBA monolayer islands, the (1,2) reflections were absent and the (0,2) often as well. The diffraction patterns were more intense in finger-like domains than towards the center of the islands where spot patterns were composed of more than a single domain.

The map of the micro-structure shown in fig4-8a confirms the results presented in chapters 2 and 3 related to the radial and finger-like growth of DSTBA domains. Each finger is a crystalline domains and the lattice rotates with the direction of the finger. Close the center of islands where nucleation takes place, the size of crystalline domains is smaller which explains that the spot patterns are less intense.

**TSB mixed monolayer and bilayer films.** We studied C11TSB films prepared by the horizontal deposition method. We found that these films formed small bilayer islands. In several locations, bilayer islands were surrounded by a monolayer. This is illustrated by fig4-9. Fig4-9a shows a
STEM image of a portion of the film. The contrast is low but several levels of gray are present. The top left corner is slightly darker. It is an empty region where no spots where obtained in diffraction mode. Close to the top left corner, a green dotted line delineates the boundary of a slightly brighter region where spot patterns were obtained and the intensity was weak. This region is a monolayer. The slightly brighter features at the right hand side of the image are bilayer islands. AFM measurements on the same grid showed that the underlying film was 1.8nm high. This is lower than the 3.2nm theoretical height of the molecules so the layer is tilted. The second layer was 3nm higher. A topography AFM image is shown in fig4-9d. Bilayer islands can be observed throughout the image and a small portion of monolayer is visible towards the center.

The orientation of the [0,1] direction of the unit cell in the monolayer and the bilayer region was studied. The inset fig4-9c is a schematic of the local structure of the C11TSB monolayer. Yellow arrows point in the [0,1] direction while question marks indicate regions where the intensity of the spot pattern was too low to make any deductions. The schematic shows that the layer is polycrystalline with grain sizes ranging from 100 to 200nm. In addition, a second region was analyzed and illustrated by fig4-9b. The orientation of the [0,1] direction was measured in a region where a small 2nd layer island is located which showed that the second layer is in registry with the first layer.

**Diffraction intensity as a function of substrate roughness.** We used AFM to compare the roughness of Ted Pella and SPI silicon nitride windows. The Ted Pella windows were found to
have a RMS roughness of 3.5Å while the roughness of SPI grids was 5.5Å. We then compared electron diffraction patterns of D5TBA monolayers deposited on 3 different samples:
1. A SPI window support which was not treated in an oxygen plasma.
2. A Ted Pella support treated in an oxygen plasma for ten minutes.
3. A SPI support treated in an oxygen plasma for ten minutes.

All the monolayers were transferred using a vertical LB deposition. Fig4-10a shows a topography AFM image of a D5TBA island on the SPI grid that was not plasma treated (sample #1). The density of islands was very low since the COOH anchors of D5TBA molecules have no affinity for these substrates. Also, the islands appeared to have fractured. In spite of these morphological features, the spot patterns quality was higher for this sample than on hydrophilic plasma treated membranes. Both [1,2] and [0,2] reflections are clearly visible. The second best was the treated Ted Pella window (#2 shown in fig4-10c) for which the intensity was lower, the [1,2] reflections were not visible. The worst result was obtained from the treated SPI window (#3 shown in fig4-10d). [1,2] and [0,2] reflections were absent from the spot patterns and in several regions no reflections were visible.

Figure 4-10. AFM image of a D5TBA monolayer deposited vertically by the LB technique on a SPI window that was not treated with oxygen plasma, b. Diffraction pattern obtained from the monolayer shown in a. The (1,1), (0,2) and (1,2) reflections are visible, c. Typical diffraction pattern obtained from a D5TBA monolayer deposited on oxygen plasma treated Ted Pella membrane. The (1,2) and (0,2) reflections are absent, d. Typical diffraction pattern obtained from a D5TBA deposited on oxygen plasma treated SPI membrane.

The intensity of electron diffraction spot patterns is directly related to the degree of crystallinity of crystalline monolayers. These results show that 2 distinct effects play a role in the quality of oligothiophene crystals.

- First, the substrate roughness is a critical parameter: the degree of crystallinity of monolayers on membranes with 5.5Å RMS roughness is poor compared to 3.5Å RMS (sample #2 versus sample #3).
- Secondly, the nature of the interaction of the layer with the substrate appears to influence molecular order in the islands. The spot patterns shown in 10b and 10d both originate from a monolayer on the rougher SPI membranes. We checked by AFM that the plasma treatment did not affect the surface roughness. The monolayer deposited on hydrophobic membranes had a higher degree of crystallinity than those deposited on hydrophilic membranes. This is the result of the low affinity between D5TBA molecules and hydrophobic surface. The monolayer does not coat the rough surface in a conformal manner and retains the structure that it had at the air-water interface.
4. Effect of scanning in contact with an AFM tip on the crystallinity of the monolayer

A promising application of the ability to obtain diffraction patterns from organic monolayers scanned by AFM is to assess the effect of contact mode and tapping mode AFM on the degree of crystallinity of the monolayer. This section describes preliminary results obtained on a D5TBA bilayer after it was scanned in contact mode.

**Experimental.** A bilayer of D5TBA transferred by horizontal deposition was scanned in contact mode using a 0.2N/m Pt coated Budget Sensors tip. The scan size was 40µm and the scan rate was 1Hz. The applied load during scanning was 5nN and the adhesion was measured to be 5nN by force-distance spectroscopy. The grid was then studied by TEM. Bilayer islands were analyzed by recording ED patterns in 100nm increments as described above. Both the islands in the area scanned by AFM and outside of it were investigated.

![Figure 4-11. a. AFM topography image of a D5TBA bilayer deposited on a SPI SiN membrane. Two STEM images are shown in inset. Both correspond to a pair of monolayer islands that are also visible in the AFM image and indicated by white frames, b. Electron diffraction pattern obtained in a 100nm wide region of a monolayer island which was not scanned by AFM, c. Electron diffraction pattern obtained from the central island in inset c, d. Electron diffraction pattern obtained from the bottom island in inset d.](image)

**Results and discussion.** Fig4-11a shows the topography AFM image acquired in contact mode. The horizontal lines visible towards the top of the image are due to materials being displaced by the AFM tip. The bilayer islands are less stable than monolayers under the scanning motion because the tail to tail interaction between the second layer and the first is not as strong as the interaction between the COOH end group of LB monolayers and hydrophilic substrates. The region scanned in AFM was later analyzed by TEM. Electron diffraction maps were acquired in
several 2μm wide areas. STEM images of two of these areas are shown in insets c and d. The corresponding location on the AFM image is emphasized by a white frame. In addition, several areas that were not scanned in AFM where analyzed.

Fig4-11b shows a typical diffraction pattern obtained from a bilayer outside of the region scanned in AFM. The (0,2), (1,1) and (1,2) reflections are clearly visible. On the other hand, fig4-11c and fig4-11d respectively show ED patterns obtained from the areas shown in insets c and d of fig4-11a. In 11c, the contrast is very low and (2,1) reflections are absent. In fig4-11d, (0,2), (1,1) and (1,2) reflections are present but the contrast is lower than in fig4-11b. These spot patterns illustrate that scanning the bilayer in contact affects its degree of crystallinity but that the effect varies with individual islands. The load applied by the AFM tip while scanning from bottom to top was nominally kept constant. However a tip-change could have occurred during scanning and have affected the shape of the tip and its adhesion force with the sample.

These results show that the combination of AFM imaging and ED characterization can help elucidate the effects of studying soft samples with AFM. These experiments were carried out in contact mode but could be done in tapping mode or in the force volume mode recently developed by Veeco to assess the invasiveness of these techniques. Note that the effect of scanning in contact mode on the conductivity of AFM monolayers was also studied. These results will be presented in chapter 6. We found that loads in the order of 45nN were required to disturb the crystalline order of monolayer island on SiO2/Si substrates. The TEM results shown here cannot be directly compared to chapter 6 results since the sample (bilayer versus monolayer), the substrate (5Å RMS roughness SiN versus 3Å RMS silicon oxide) and the scan speed (30μm/s versus 2μm/s) were all different. Especially, the higher frictional force observed on bilayers and their fragility under the AFM tip could explain the higher sensitivity to scanning observed here compared to the results of chapter 6.

5. Lifetime of organic crystals and beam damage mechanisms

Results and discussion. The study of soft materials by TEM remains highly challenging due to the sensitivity of the substrates to electron damage\textsuperscript{2,5,6}. Ionization damage is believed to be the principal mechanism\textsuperscript{11} although knock-on damage was shown to occur even at electron energy as low as 80kV\textsuperscript{12}. Ionization occurs when the interaction between the electron beam and orbitals of the materials being irradiated leads to an electron leaving its orbital inducing the specimen to become positively charged. Knock-on damaged results from an interaction between the electron beam and the nuclei of atoms in the specimen inducing the displacement of the atom from its initial position thereby destructing covalent bonds. Assessing the parameters that play an important role in beam damage is critical to improve TEM capabilities for the study of soft matter.

The dose, the beam energy and the chemical structure of both the material of interest and its support are among the factors that must be considered. The damage rate increases roughly linearly with the dose and with the cross-section of the damage mechanism. The beam energy...
can also play a large role and the ionization of C-H bonds and of C-C bond are both believed to depend strongly on that factor\textsuperscript{13}.

We studied the dependence of beam damage on the chemical structure of 4 organic films transferred on 1824 carbon substrates by horizontal deposition. D5TBA, 5TBA, C11TSB and stearic acid films were compared. We found that the material that was the most sensitive to the beam was the stearic acid monolayer for which spot patterns faded in less than 0.1s of exposure, followed by C11TSB, D5TBA and STBA. These results can be explained by the fact that conjugated monolayers are more resistant to ionization damage because their structure can accommodate the removal of an electron. In molecules such as stearic acid, ionization of a C-C bond leads to the destruction of the alkyl chain. C11TSB and D5TBA which both have alkyl tails are therefore more sensitive to ionization damage than STBA.

In future work, the rate of disappearance of diffraction spot patterns of organic monolayers could be studied at different electron energy to assess whether ionization or knock-on are the principal damage mechanism that limit the use of TEM to study ultra-thin organic materials. Also, the effect of secondary electrons and X-Ray generated by the substrate could be studied by comparing supported and unsupported crystalline organic films.

\textbf{Conclusion.} The spot-scanning technique described in this chapter is a fast and practical method to determine the microstructure of organic films at a high resolution. Using a low dose routine made it possible to “beat” beam induced damage and obtain electron diffraction patterns of monolayers of organic molecules before the crystals became amorphous. Using this technique, the lattice and grain distribution of ultra-thin films prepared by the Langmuir-Blodgett technique and used for electrical measurements could be analyzed.

\begin{flushleft}
\textsuperscript{1} Henderson, R.; Glaeser, R. M. \textit{Ultramicroscopy}. \textbf{1985}, \textit{16}, 139-150.
\textsuperscript{7} Downing, K. H. \textit{Ultramicroscopy}. \textbf{1986}, \textit{20}, 269-278.
\textsuperscript{8} Langmuir, I.; Schaefer, V. J. \textit{Journal of the American Chemical Society}. \textbf{1938}, \textit{1115}.
\end{flushleft}
10 http://www.totalresolution.com/MacTempas.html

11 http://avogadro.openmolecules.net/wiki/Main_Page


Chapter 5. Conducting probe AFM study of oligothiophene monolayers

D5TBA monolayers deposited on highly doped silicon substrates covered with a native oxide were studied by Conducting probe AFM (CAFM). The current measured on oligothiophene monolayer islands was higher than on the SiO$_2$/Si+ substrate although the monolayer is an additional resistive layer interposed between the oxide and the conductive tip. These observations can be rationalized by the presence of in-plane conduction channels in the semi-conducting monolayer that lead to an enhancement of the number of channels for tunneling through the oxide.

In addition, the junction was observed to be rectifying with more current flowing when the sample was bias negatively. This asymmetry can be explained by the fact that molecular orbitals (MO) contributing to the current depend on the sample bias polarity. Unsubstituted oligothiophene are p type due to the proximity of their HOMO orbitals to the work function of most metals. At low negative sample voltage, efficient resonant tunneling through the HOMO takes place while a large positive bias is required for the LUMO to become resonant at positive polarity.

We also observed that the junction was sensitive to the presence of water and that its conductivity decreased with time after preparation regardless of the storage conditions. Finally, the evolution of metal coated conductive AFM tips was studied by recording TEM images of the tip before and after scanning on oligothiophene monolayers. We found that the cause of the observed increase in tip-sample contact resistance in successive CAFM images was a build-up of organic materials at the apex rather than wear.

In Conducting AFM, the current flow between a conductive AFM tip and the substrate is monitored as a topography scan is acquired in contact mode. This technique can also be referred to as Current Sensing AFM (CSAFM) or Scanning Spreading Resistance Microscopy (SSRM). Alternative conductive AFM techniques have been developed such as torsional resonance mode imaging (from Veeco) which combines an alternative contact mode with DC current measurements. CAFM can also be used in conventional tapping mode if the current is large enough to be detected in spite of the very short contact period. Another option for fragile samples is to obtain topography maps in tapping mode and measure current by point-spectroscopy in areas of interest.

It is important to note that the interpretation of current maps obtained by CAFM can be a complex issue. The applied force and therefore the tip-sample contact area are kept constant by maintaining the deflection signal at the set-point value by a feedback loop. The contact area can however vary due to local variations of the adhesive properties of the sample. Also, the contact of the tip with the sample is a point contact. This geometry has to be taken into account for quantitative analysis such as extraction of the carrier mobility from Space Charge...
Limited Current (SCLC) measurements. Additional factors that can play an important role include cooperative effects such as those we observe on oligothiophene monolayers, where materials located outside of the tip-sample contact affect the current measurements. Another critical factor is the nature and evolution of the AFM tip. The apex radius of the tip is determinant for electrical measurements and can vary even between commercial cantilevers from the same batch. Also, the radius can vary with time due to wear of the cantilevers or contamination. These experimental challenges can be controlled by obtaining SEM or TEM images of the tip of AFM cantilevers before and after use. The evolution of the tip can also be assessed in situ by force-distance spectroscopy.

The main applications of CAFM on organic materials can be divided in three categories. CAFM has been used to obtain conductivity maps of heterogeneous substrates. Recently, a number of studies focused on the nanoscale conductivity of polymer blends for solar cell applications. Ginger et al combined CAFM with light absorption measurements by using an AFM in combination with a fluorescence microscope. Bao et al used CAFM to study the conductivity of pentacene monolayers and bilayers deposited on hexamethylene disilazane (HMDS) and octadecyltrimethoxysilane (OTS) SAMs on n type silicon. They found that layers deposited on OTS were more conductive due to the higher crystallinity and grain size of pentacene grown on these substrates. In a second type of applications, CAFM has been used to study single molecules by isolating semi-conducting molecules in an insulating alkanethiol matrix. Finally, the conductive tip has been used as a mobile electrode, for instance to record the resistance at various points of a carbon nanotube connected to a gold electrode or to measure the mobility in a pentacene film deposited on an insulator at the edge of a platinum electrode.

In this chapter, we describe and explain an anomalous contrast obtained in CAFM images of oligothiophene monolayers on silicon substrates covered with native oxide. We show that the presence of the insulating oxide layer induces current to flow in the plane of the monolayer. The in-plane conductivity of the monolayer can therefore be studied in spite of using a vertical configuration where the monolayer is sandwiched between electrodes. Applications of this imaging technique are presented in the next chapter (chapter 6).

2. CAFM on oligothiophene monolayers: contrast and size dependence

**Experimental.** Current images were obtained using a 5500 Agilent AFM in contact mode in dry nitrogen and ambient atmosphere with 0.2 N/m Pt-coated silicon tips from budget sensors. Typically, a net force of 15nN was applied while recording current images to ensure good contact. The net force does not include the adhesion force between the tip and the sample which was close to 5nN, so that the total force during imaging was 20nN. The contact area for a 15nN applied force and a 5nN adhesion force can be estimated to 16nm² using the DMT model (the apex radius of Pt coated tips used for CAFM was 20nm, as measured in a TEM). For the plot of the current as a function of island size, the diameter of D5TBA islands was measured in two
perpendicular directions and averaged. The level of current for a given island was obtained by averaging the current measured on the central region of the island.

**Results.** Fig5-1a shows a topography image of a DSTBA island on SiO2/Sip+. A large polycrystalline monolayer island is located at the center and two smaller islands are located towards the left and bottom right. Smaller porous phase grains can also be observed throughout the image. Fig5-1b shows a CAFM image acquired at -0.5V sample bias. The current measured on DSTBA islands is more than an order of magnitude higher than on the substrate. This is counterintuitive since when the tip is located over the monolayer, electrical carriers have to tunnel first across molecules and then across the native oxide layer which was measured to be 2nm thick by ellipsometry.

![Figure 5-1. Topography AFM image of a DSTBA monolayer on SiO$_2$/Sip+, b. Corresponding current image at -0.5V sample bias, c. Topography AFM image of a DSTBA monolayer on SiO$_2$/Sip+, d. Corresponding current image at -2V sample bias, a plot of the current as a function of effective diameter is shown in inset. The effective diameter was obtained by taking the average of the size of molecular islands in the horizontal and vertical directions.](image)

An additional central observation is a trend towards larger conductance for larger islands. The current on the porous phase made of small grains is more than an order of magnitude lower than on molecular islands, as illustrated by fig5-1b. This size dependence was quantified by recording large scale CAFM images and plotting the average current on molecular islands as a function of size. Fig5-1c shows a topography image of a 25µm large region of a submonolayer. The corresponding current image is shown in fig5-1d and a plot of current as a function of diameter on a log-log scale is shown in inset in fig5-1c. Linear fitting with a y-intersect at 0 leads to a linear regression coefficient equal to 0.84. For comparison, the straight line corresponding to a quadratic trend is also plotted. The image in fig5-1b was also selected to show that in spite of the observed trend, some molecular islands were outliers, i.e. their conductance was
abnormally high. This is the case for the island located at the bottom right of fig5-1b. It is 200nm wide and 700nm high but its conductance is close to that of the central island. This variability could be due to the internal structure of the polycrystalline D5TBA islands. The size of finger-like grains and the nature of grain boundaries may play a significant role.

In the next paragraphs, we will provide a model that accounts for these two observations, i.e. larger current on molecules than on the substrate and a dependence of the conductance of islands on their size.

Discussion. Several effects could account for the higher current observed on molecular islands at negative sample bias:

a. The tip-monolayer contact area could be larger than the tip-oxide contact area.

b. Tunneling across the oxide could be facilitated by the presence of the organic monolayer.

c. Lateral conduction in the monolayer could enhance the tunneling area across the oxide.

a. The tip/sample contact area could be larger on the monolayer than on the substrate due to different adhesion properties. In order to evaluate the contact area over the monolayer and over the oxide, the adhesion force was measured by force distance spectroscopy and was found to be similar on the D5TBA monolayer and the native silicon oxide covering the silicon substrate. The factors that enter in the calculation of the contact area in the DMT model are the adhesion force, the size of the AFM tip and the reduced Young’s modulus of the tip and of the substrate. Of all these parameters, only the Young’s modulus differs between the tip-monolayer contact and the tip-substrate contact. Engelkes and coworkers studied alkanethiol monolayers by STM and CAFM and found that its reduced modulus was 50GPa. Using this value in the calculation of the contact area of the tip on the monolayer leads to a 70% increase compared to the area on the bare substrate. This increase is due to the indentation of the tip into the monolayer. Although significant, this effect accounts only for a small portion of the difference observed between the substrate and the monolayer conductance in CAFM.

b. The question is the following: could the presence of adsorbed molecules facilitate the tunneling across the native silicon oxide layer and account for the higher current measured on monolayer islands? Han and coworkers recently reported an increase in conductivity of a metal-TiO$_2$-metal junction upon insertion of a short alkanethiol layer between one of the contacts and the ultra-thin semi-conducting TiO$_2$. The model shown in fig5-2 describes their conclusions. In the absence of alkane monolayer, carriers face a barrier $\Phi_b$ upon injection from the left electrode (fig5-2a). In the presence of an alkane layer, most of the voltage drop is over the organic material which leads to a configuration where the work function of the metal and the conduction band of TiO$_2$ are aligned. Although electrons have to tunnel across the organic layer, its effect is compensated by the decrease of the injection barrier from the metal into the semiconductor, according to the study.
In order to assess whether a similar effect could play a role in our experiments, an energy diagram of our system is shown in fig5-3a. The Fermi energy of the degenerately doped silicon substrate is close to the valence band at 5.1eV. The work function of the platinum coated tip is in theory 5.65eV. In practice, due to air contaminants and contamination by molecules during scanning of the monolayer, its work function could be smaller by as much as 0.5eV.

Based on the UV-vis absorption spectrum obtained from a solution of D5TBA in chloroform, the HOMO-LUMO gap is 2.5eV, which is close to values measured on other pentathiophene derivatives. The location of the HOMO and LUMO levels can be roughly estimated based on Ultraviolet Photoelectron Spectroscopy (UPS) measurements on similar molecules. The HOMO level position is in the range 2.9-3.4eV and the LUMO level 5-5.6eV.

Figure 5-2. Model for enhanced conductivity upon adsorption of an organic layer proposed by Han et al. a. An injection barrier exists due to the mismatch between the work function of the tip and the conduction band (CB) of the TiO2 ultra-thin film. b. The presence of a short alkanethiol monolayers substitutes a narrow tunneling barrier to the injection barrier in a.

Figure 5-3. a. Energy diagram for the tip-D5TBA-SiO2- p+Si junction at equilibrium, b. tunneling across the molecules and the oxide at negative tip bias, c. tunneling across the oxide at negative tip bias.
By comparing the energy diagrams in 2a and 3a, one can realize that the 2 junctions are dissimilar. The native oxide is the highest and widest tunneling barrier in the junction. For carriers tunneling from the silicon electrode to the Pt electrode, the presence of the molecules does not affect the height of the barrier which is determined by the Fermi level of the silicon electrode and the band gap of the oxide. For carriers tunneling in the reverse direction however, the presence of the molecules could facilitate tunneling of electrons (or holes) across the oxide if most of the voltage drop was across the C10 alkyl chain. The oxide barrier height would then be reduced by $W_{\text{pt}} - E_a$ for electrons and $E_i - W_{\text{pt}}$ for holes (where $E_a$ is the electron affinity and $E_i$ the ionization energy). Fig5-3b and 3c illustrate this scenario for electron conduction at negative tip voltage (equivalent to positive sample bias). A similar schematic could be drawn for hole conduction through the HOMO at negative sample bias.

If the decrease in the oxide barrier height could compensate the additional tunneling barrier (the C10 chain), these models suggest that the presence of the monolayer could facilitate tunneling across the oxide. These predictions are however based on the assumption that the voltage drop is mostly across the C10 chain and not across the oxide. This is at odds with the relative widths of the two barriers unless one considers the large contact area between the monolayer and the oxide compared to the size of the tip-monolayer contact.

Although the presence of the monolayer could enhance tunneling across the oxide, this effect does not explain the observed dependence of current on the size of monolayer islands. The last mechanism that we describe, lateral conduction through the monolayer, accounts for both the size dependence and enhanced CAFM current on the monolayer compared to the oxide.

c. Lateral conduction model. The resistance of the oxide film is the largest in the electrical junction, larger than the intermolecular resistance between neighboring oligothiophene molecules and the tip/monolayer contact resistance. When the tip is in contact with a crystalline organic island, additional pathways are available for conduction since carriers can travel in the layer before tunneling through the oxide. This is illustrated by models shown in fig4a and 4b where the junction is represented as resistors in series and parallel.

![Figure 5-4. a. lateral conduction model explaining the observed current dependence, b. parallel resistor model](image)

Since the native oxide is the limiting step for carrier transport, the area over which carriers tunnel through the oxide is a critical parameter. This area is equal to the tip/sample contact area (tens of nm$^2$) when the tip scans over the substrate. However, as a result of lateral conduction, the tunneling area through the oxide can potentially be as large as a crystalline island (in the µm$^2$ range) for low intermolecular resistance.
The oxide layer between the layer of molecules and the conducting substrate greatly enhances the contribution of the lateral current flow relative to the vertical conduction through the junction. Several STM studies reported a size dependence of measured current similar to our results but at a smaller length scale: Yokota et al.\textsuperscript{16} and Kafer et al.\textsuperscript{17} reported that the apparent height and therefore the conductance of nanoscale clusters of semiconducting organic molecules embedded in an alkane matrix increased with the size of the clusters. They proposed a parallel resistor model to explain their findings. Ishida et al.\textsuperscript{18} studied a similar system with CAFM in vacuum and found that the resistance of 2 to 10 nm large clusters decreased with size.

A simplified resistor based model is shown in fig5-4b in which the electrical circuit is composed of 3 types of non-linear resistors assembled in series and parallel (the injection resistance $R_{\text{tip-mol}}$, the intermolecular resistance $R_{\text{mol-mol}}$ and the resistance of the native oxide $R_{\text{mol-subs}}$). A modeling of the current as a function of the size of a 2D cluster of molecules predicts a quadratic increase of current with size for $R_{\text{mol-mol}} \ll R_{\text{mol-subs}}$. When the size of the cluster is such that the sum of intermolecular resistances from the center to an edge of the cluster approaches $R_{\text{mol-subs}}$, the dependence becomes linear. Experimentally, we have observed a linear dependence over the distribution of sizes of the porous phase grains and islands (see the inset in fig5-1c).

As a control, stearic acid monolayers (with the chemical formula $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$ and a thickness of 1.8nm) were prepared and studied in CAFM. There were no detectable currents when the tip was in contact with stearic acid molecules deposited on SiO2/Si substrates. Stearic acid is a non-conjugated molecule in which charge carriers cannot be injected. This control confirms the role played by the semi-conductor core of the molecules in CAFM experiments.

\textit{In the next section, we will describe results related to the dependence of the monolayer electrical properties on environmental conditions as well as data related to the rectifying character of the junction.}

### 3. Rectification and environmental effects

\textbf{Experimental.} DSTBA monolayers were prepared by the Langmuir-Blodgett and deposited on SiO2/Si substrates. A Langmuir film was prepared by spreading 0.5mL of a saturated DSTBA solution on water. This film was deposited simultaneously on two SiO2/Si+ substrates. One sample was placed in a glass bottle containing dry nitrogen by using a glove box. That sample was heated in an oven at 100°C for 12 hours. The other sample was kept in ambient conditions. Both samples were imaged in CAFM. To ensure that the sample heated in dry nitrogen was not exposed to ambient air. It was transferred to the environmental chamber of the AFM trough a glove box. It was subsequently imaged at negative and positive sample bias. In order to study the effect of water re-adsorption, the “dry” sample was exposed to air and imaged again in CAFM. The humidity level in the glove box and the AFM environmental chamber were below 0.5%. The results of these experiments are presented below.
**Results.** The AFM images shown in figure 4-5 as well as the experimental IV curves summarize the findings of this study. The results are complex as several effects are described and analyzed including a rectification effect and the qualitative differences observed between CAFM images acquired on “wet” and “dry” samples. Note that section 5 describes some CAFM experiments carried out in vacuum that had limited results due to critical tip contamination issues.

The first series of images (5a,b,c) were acquired in ambient atmosphere on a sample shortly after preparation. This sample did not undergo any heat treatment and is referred to as a “wet” sample because it is expected to contain water resulting from the LB preparation. The data points on the curve shown in 5d were obtained by averaging the current measured on a D5TBA island. For each data point, a CAFM image was recorded. The second series (5e,f,g) was acquired on heated sample and in dry nitrogen following the procedure described in the experimental section. Fig5-5h shows the corresponding IV curve.

![AFM images and IV curves](image_url)

**Figure 5-5.** a. Topography AFM image of a D5TBA monolayer island on SiO\textsubscript{2}/Si+, b and c. corresponding CAFM images acquired at +3V and -0.5V in N\textsubscript{2}. The sample was heated at 100°C for 12 hours, d. IV characteristic obtained by average current measured in CAFM on the central island, e. Topography AFM image of a D5TBA monolayer island on SiO\textsubscript{2}/Si+ which was not dried after preparation, f and g. corresponding CAFM images acquired at +3V and -0.5V in air, h. IV characteristic obtained by averaging current measured in CAFM on the central island.

**Rectification.** We observed that D5TBA monolayers deposited on p doped silicon covered with native oxide were rectifying and that the strength of rectification depended on the environmental conditions. Fig5-5b and 5f were acquired at +3V sample bias while 5c and 5f were acquired at -0.5V. The monolayer could not be studied at -3V sample bias since the upper limit of measurable current in our CAFM set-up is 1nA. The current on D5TBA islands reached that limit and saturated for biases below -2V. As shown by IV curves, the rectification coefficient was measured to be between 10 and 100 depending on the environmental conditions. The rectification is stronger in dry conditions with the current being 100 times higher at -1V than at +1V bias. The lower rectification on “wet” samples is mainly due to the
higher current levels measured at positive sample polarity compared to dry conditions. The causes of the observed rectification will be discussed in the next section.

**Qualitative differences in current images.** In addition to the rectification observed by comparing the magnitude of current at + and – sample polarity, there were strong qualitative differences in the appearance and contrast of CAFM images. As mentioned previously, for negative sample polarity, the current was consistently higher on D5TBA islands and scaled up with size. The current within islands was roughly constant except towards the end of fingerlike domains where it was smaller. At positive sample polarity on a “dry” sample, this size dependence was not observed below 2.5V and the current on islands and the substrate was of the same magnitude. Above 2.5V (see fig5-5b), the current was slightly higher on islands and a weak size dependence was observed. In the image shown in fig5-5b, a number of bright spots can be observed which are likely due to defects in the native oxide layer where its resistance is lower. These observations indicate that lateral conduction is reduced or absent when imaging dry samples at positive bias.

On the other hand, in images acquired at positive polarity on a “wet” sample in air (see fig5-5f), the current was higher on islands and depended strongly on the size of D5TBA islands. Also, internal grain boundaries were visible in current images and appeared to be more conductive. These results show that water plays a significant role for positive sample polarity CAFM imaging of D5TBA monolayer by enhancing the lateral conductivity in the monolayer. The stronger effect observed on grain boundaries is likely due to the preferential adsorption of water in these regions of the layer.

On the other hand, for negative sample bias, no differences could be observed between wet and dry samples. The current level and the contrast were similar. This suggests that water does not play a significant at negative sample bias and that heating at 100°C does not have annealing effect on the conductivity on the monolayer and therefore its structure. At higher temperature (150-170°C), the monolayer was permanently damaged. In section 3, we will propose a model accounting for the observations described in this section according to which HOMO and LUMO orbitals become resonant at respectively negative and positive sample polarity.

**Additional remarks.**

a. When a “dry” sample was exposed to air and imaged in CAFM at positive polarity, the dependence of current on island size was found to increase slightly as well as the current measured on islands. It however never reached the level observed on “wet” samples. The water initially present after LB preparation can therefore be removed by heating the sample and does not re-adsorb completely after the sample is exposed to air. This suggests that the adsorbed water is located in between the monolayer and the substrates or between molecules. This is in agreement with the hydrophilic nature of COOH head groups (whereas the alkyl chains tails are hydrophobic).

b. As mentioned in the previous section, stearic acid monolayers were prepared and studied in CAFM. The fact that there were no detectable currents when the tip was in contact with stearic acid molecules deposited on SiO2/Si substrates confirms that the size dependent contrast
observed in CAFM is not due to ionic conduction through water adsorbed under molecules. Otherwise, similar water induced conduction would be observed for stearic acid monolayers.

c. We measured the conductivity of heated and non heated samples a month after preparation and found that the current level at negative and positive polarity had decreased by 30 to 50% compared to initial values measured after the heating procedure. After two months, the conductivity had decreased further. It was 70% lower than after preparation showing that the monolayer slowly degrades with time. Oligothiophene and polythiophene have a better environmental stability than most organic semi-conductors but after an extended time and in the absence of encapsulating layer, they can be expected to degrade. Oxidation of the thiophene core is the most likely mechanism although the samples were kept in a N₂ store box (and in the dark).

4. Cause of the rectification observed in oligothiophene monolayers

Results. The rectification mechanism was investigated by comparing IV characteristics on the 
SiO₂/Si substrate and islands of different sizes. CAFM images were acquired in dry atmosphere 
on a D5TBA monolayer heated in N₂ after preparation. Fig5-6 shows a friction image and 
current images obtained at -1V (fig5-6b) and +2.5V(fig5-6c) sample polarity. The current was 
lower on the D5TBA island than on the substrate at 2.5V positive bias. Similar images were 
obtained at a range of different voltages, and the current was averaged in 4 different locations 
of the CAFM images to obtain IV curves corresponding to islands of different sizes and on the 
SiO₂/Sip+ substrate. Fig5-6d shows the IV curves obtained using that method.

Figure 5-6. a. Lateral force image, b. current image at Vsample= -1.0V, c. current image at Vsample= +2.5V of 
D5TBA on SiO₂/Sip+ in dry N₂. The outline of the D5TBA islands in a. has been superimposed in b. and c. , d. 
Current-voltage spectra acquired in the four different locations marked in a. The current is obtained by 
averaging inside selected regions of the islands. The arrows point to the bias voltages used in b. and c.

The results presented in fig5-6 show that the rectifying nature of the electrical junction is due 
to the presence of the organic monolayer since the IV characteristic acquired on the substrate is symmetric. They also confirm the lack of size dependence of the current at positive sample polarity. Note that the current measured at -1V is in the range of 50-70pA (fig5-6b). This is lower than the level of current in the IV shown in fig5-5d. This is due to the fact that these measurements were obtained a few weeks after the sample was prepared. As mentioned in the
previous section, we observed that the conductivity of oligothiophene monolayers decreased with time.

In the next paragraphs, several models accounting for rectification observed in organic/inorganic systems are presented. We show that pinning of the molecular levels to the substrate is consistent with rectification observed in our system. This subject was already touched upon briefly in fig5-2 since the scenarios of fig5-2b and fig5-2c (voltage drop over the alkyl chain) correspond to pinning of the HOMO and LUMO levels to the substrate.

**Cause of rectification.** Rectification was observed in a number of organic systems including single molecules, monolayers and thin films. Several molecule/electrodes geometry can lead to asymmetric IV characteristics. In particular, the electrodes work function and the energy of molecular orbitals play a crucial role. Three main mechanisms can cause molecular rectification. Among the first molecular systems observed to cause rectification were the Aviram-Ratner donor-acceptor molecules. These compounds are made of donor and acceptor components separated by a linker. Rectification occurs due to the relative position of HOMO and LUMO levels of the donor and acceptor parts of the molecules. Since oligomers used in this study are not donor-acceptor molecules this mechanism cannot be the cause of rectification observed in our system. Other studies invoked the formation of Schottky barriers at the contacts as a cause for rectification. The fact that the monolayer investigated in this study is 2.5nm thick with a 1.8nm wide semiconducting core makes this hypothesis unlikely. Finally, rectification was observed to be caused by pinning of the molecules energy levels to the electrodes that serve as contacts. This mechanism will be described below.

**Pinning.** Unsubstituted oligothiophenes are p-type semiconductors with HOMO levels ranging from 4 to 5.5eV below the vacuum level, which is close to both the Fermi level of the Pt tip and the Si substrate. The observed current-voltage characteristic at negative polarity (see fig5-6d) is the result of resonant tunneling through a molecular orbital. Since the onset of current is close to -0.5V, the resonant orbital is the HOMO which is in accordance with the p nature of oligothiophene molecules. At positive sample bias the current increases rapidly only above +2V. The zero-current plateau from -0.5V to +2.0V is close to the optical 2.5eV HOMO-LUMO gap of DSTBA in solution. In addition, there are clear qualitative differences between the spatial distributions of conduction at negative and positive sample polarity, which suggests that resonant tunneling at opposite polarities involves different molecular orbitals. Both observations point to the LUMO as being the orbital that becomes resonant at positive polarity.

Conduction through the HOMO at negative polarity and the LUMO at positive polarity is best explained by pinning of the molecular orbitals to the sample Fermi level, i.e. they move together with the sample when a bias voltage is applied. Similar behavior was observed to be the cause of rectification in various Self-Assembled Monolayers (SAM) on silicon by Lenfant and coworkers. Such pinning, in spite of the interposed oxide film, can be rationalized first by the strong bond between the butyric acid head group and the substrate, as compared to the weak Van der Waals interaction between the tip and the methyl end groups of the alkyl chain. Secondly, the lateral conductivity of the monolayer effectively enhances the contact area between the thiophene part of the molecular film and the Si substrate.
The energy diagrams shown in figure 5-7 illustrate the shift of molecular levels with the applied bias in a scenario of full pinning to the substrate which is a simplified scenario (incomplete pinning is more likely in practice but the mechanism is essentially the same). The LUMO and HOMO levels of the molecules are drawn in green with the HOMO level located close to -5eV and the LUMO level 2.5eV above. At equilibrium, the HOMO level is positioned below the tip and substrates Fermi level. As negative bias is applied, the levels shift with the substrate and the HOMO become resonant at a low bias. On the other hand, LUMO orbitals can participate in the charge transport by injection of electrons from the tip at bias voltages above +2V.

![Energy diagram illustrating the explanation of rectification by pinning of the molecular levels to the substrate.](image)

Figure 5-7. Energy diagram illustrating the explanation of rectification by pinning of the molecular levels to the substrate, a. at equilibrium, b. at negative sample bias the HOMO becomes resonant at -0.5V, c. at positive sample polarity, the LUMO becomes resonant above 2V.

The smaller current observed at positive sample voltages and the absence of size dependence of the current measured in CAFM on monolayer islands would imply a reduced lateral mobility of the electrons injected into the LUMO. Several studies reported that organic systems contain a higher density of trap states for electrons than for holes, especially in the presence of oxygen. Our results point to a reduced mobility of electrons in the LUMO compared to holes transported in the HOMO which is in agreement with these observations.

5. Transient effects and charge trapping in D5TBA/SiO2/Sip+ junctions studied by CAFM and KPFM.

We observed that applying a large voltage for several minutes with the tip in contact with the monolayer on SiO2/Sip+ had a significant effect on subsequent CAFM images obtained in the
same regions of the film due to the trapping of charges. We used KPFM to determine the nature of the charges trapped by using this procedure.

**Experimental.** Charge trapping was studied by CAFM on a D5TBA monolayer in nitrogen atmosphere. The sample had been heated for 10 hours in nitrogen at 100°C after preparation and before CAFM. After recording a 5µm large image, the tip was positioned in contact at the center of a monolayer island. The force was 20nN (5nN adhesion force and 15nN net force). The sample was biased to -3V during 3min and the current recorded in real time. Topography and CAFM images were then recorded at negative and positive sample polarity to assess the effect of local current flow on the full monolayer scale. The experiment was repeated on a different molecular island but this time the sample was biased to +3V while the tip was positioned in contact.

This procedure was applied in another set of experiments on a D5TBA monolayer on SiO2/Si which was studied by Kelvin Probe Force microscopy in vacuum in a RHK AFM. Topography and surface potential images were recorded in one pass in frequency modulation mode. A Nanosurf EASY Phase Lock Loop (PLL) system was used to excite the cantilever at its resonance frequency (60kHz) and measure the frequency shift, which was used by the imaging feedback to create a topography image. To obtain the surface potential image, an AC bias was applied to the tip at a 2kHz frequency. A separate controller (Stanford Research Systems) was used to apply the DC bias that minimizes the AC electrostatic force on the cantilever. The applied DC bias at each pixel was used to form the surface contact potential image.

**Results.** Fig5-8a and 8b show topography and current AFM images of a monolayer island after applying -3V locally in the location indicated by a red cross. Fig5-8b was recorded at -0.5V sample bias. A yellow contour is drawn on fig5-8b to indicate the edge of the island. A region of the island where the current is 90% lower appears darker in the current image. The region of lower conductivity extends as far as 500nm from the point of injection. Fig5-8c and 8d show topography and current AFM images of the monolayer island where +3V was applied in the location marked a red cross. Fig5-8d was recorded at +0.5V sample bias. The current is higher close to the location where the bias was applied and below 0.1pA everywhere else.
**Nature of the trapped charges.** These results show that charge trapping occurs while current flows between the tip and the sample through the molecules and native oxide layer. These charges have a significant effect on the conductance of the monolayer as shown by fig5-8b and fig5-8d.

![Figure 5-9.a Surface potential AFM images of a D5TBA monolayer island after a. Applying -3V in contact in the location indicated blue arrows, b. Applying +3V in contact, c. Graph of the potential measured along the dotted line before injecting charges (red curve), after applying -3V (blue curve) and after applying+3V (green curve). + indicates that positive charges have been trapped and – that negative charges have been trapped.](image)

To assess the nature of the charge trapped, we performed KPFM on the monolayer after injecting charges locally with the tip. Fig5-9a and 9b show surface potential images acquired after applying -3V and +3V with the tip in contact. In fig5-9a, the potential was 150mV lower in the region where the tip was in contact (see the blue profile shown in fig5-9c), indicating positive charges. This is consistent with resonant tunneling through the HOMO at negative polarity. On the other hand, the potential was 150mV higher after applying +3V with the tip in contact with the layer (fig5-9b) indicating injection of negative charges, consistent with LUMO conduction. The results of these experiments are summarized in Table 1 which describes the sign of the trapped charged depending on the polarity of the applied sample bias during charging, followed by the effect of these traps on subsequent AFM images as a function of the imaging conditions (sample bias polarity).

<table>
<thead>
<tr>
<th>Sample polarity during charging</th>
<th>Trapped charge polarity</th>
<th>CAFM Image Polarity (sample bias)</th>
<th>Effect of trapped charges on CAFM current</th>
</tr>
</thead>
<tbody>
<tr>
<td>Negative</td>
<td>+</td>
<td>-</td>
<td>Decrease (shown in fig8b)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+</td>
<td>Increase</td>
</tr>
<tr>
<td>Positive</td>
<td>-</td>
<td>-</td>
<td>Increase (shown in fig8d)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+</td>
<td>Increase</td>
</tr>
</tbody>
</table>

Table 5-1. Summary of the CAFM and KPFM measurements of charge trapping.

**Location of the trapped charges.** Charges could be either trapped into the oxide or into the monolayer. In separate KPFM experiments, we observed that bare SiO2 could be charged in the same manner as the monolayer/SiO2 junction by bringing the tip in contact with the native oxide substrate and applying a bias. The sign of injected charges was the same as for the
monolayer/SiO2 charging experiments. These results prove that charges can be injected into the oxide but do not rule out injection in the monolayer (or both). The mechanism described in the following paragraph is consistent with charge injection into the oxide whereas no model accounting for all the observations described so far could be designed based on permanent charging of the monolayer.

**Gating mechanism.** Assuming that the charges are trapped into the oxide, the observation that they locally reduce or enhance the conductivity of the monolayer points towards a mechanism of local gating. We showed in fig5-8b that the HOMO conductivity of the monolayer became lower after the trapping of holes. The energy diagram in fig5-10a illustrates the gating effect that trapping holes in the SiO2 layer could have on the molecules. The local positive charges shift the level of molecular orbitals to lower energies. As a result, the HOMO level is located further from the tip and the sample Fermi levels which induces a decrease in the conductivity of the monolayer at negative sample bias. The LUMO level however shifts closer to the electrodes Fermi levels so the LUMO conductance increases.

![Energy diagram illustrating the effects of charge trapping into the oxide on HOMO and LUMO conduction, a. positive traps induce a downward shift of MOs, b. positive traps induce an upward shift of MOs](image)

In the reverse situation (electrons injected), the energy diagram in fig5-10b shows how a shift of molecular orbitals towards higher energy values would occur due to gating by negative charges. This shifts the onset of resonant tunneling through the LUMO to higher values and therefore leads to a lower LUMO conductivity. According to results shown in fig5-8d however, the conductivity locally increased after injecting negative charges which seems at odds with the prediction that was just made. But fig5-10b also illustrates how the shift of the HOMO can lead
it to become resonant with the silicon substrate valence band which is likely the cause the observed increase in conductivity.

Additional experiments such as Ultra-violet Photoelectron Spectroscopy (UPS) or CAFM using tips coated with metals with different work functions or using samples with different Fermi energies could help investigate this question further. UPS would determine the exact position of the energy levels of the molecules while additional CAFM experiments would permit to test the hypothesis according to which MO energy levels are pinned to the substrate.

6. CAFM experiments in ultra-high vacuum (UHV).

We used a RHK ultra-high vacuum AFM to image monolayers of DSTBA on SiO2/Sip+ in UHV at pressures ranging from $10^{-9}$Torr to $10^{-10}$Torr. We found that tip contamination was a critical issue since after only a few scan lines of the tip on the sample, the measured current had dropped to a few tenths of pA due to the increase of the resistance of the tip-monolayer contact. Fig5-11a and fig5-11b show lateral force and CAFM images obtained on a DSTBA monolayer. The flower shape morphology is clearly visible in friction. The particles dispersed throughout the islands are made of silicon oxide which was determined by studying a similar monolayer by TEM. Once we started filtering the DSTBA solution systematically before use, these particles were not observed anymore. They presumably came from the glass container of the solution which might release particles upon repeated sonication.

The current image was acquired by scanning downwards. In the first few lines of the image, the current was 35pA on the island and 10-15pA on the substrate. After scanning approximately 10 lines, the current had decreased by more than 20 times. The horizontal streaks visible throughout the image correspond to tip changes. For instance, the tip-monolayer contact briefly improved ¾ towards the bottom of the image were bright lines are located.

![Figure 5-11. a. Lateral force AFM image acquired on a DSTBA submonolayer on SiO$_2$/Sip$^+$ in UHV, b. CAFM image of the same region of the monolayer at -2V](image)

The tip used for these experiments was Pt coated on a cantilever with a spring constant of 3N/m (instead of the 0.2N/m cantilevers used in dry N$_2$ and air). We observed that for softer
cantilevers, the tip could not be withdrawn from contact because of the large adhesion and the limited range of the z component of the piezoelectric scanner (330nm). For experiments performed in air and N\textsubscript{2}, we have found that molecules were very readily desorbed when scanning with 3N/m cantilevers. As a result, contamination of the tip by molecules is aggravated by using cantilevers with a large spring constant. UHV experiments could be attempted using AFM tips made of materials that either lead to a lower adhesion, or have a lower affinity for molecules. For instance, we observed that conductive diamond coated AFM tip were contaminated more slowly than Pt coated tip.

7. Study of tip contamination and wear by Transmission Electron Microscopy

We have used high resolution and analytical TEM to study wear and failure mechanisms of platinum coated silicon tips used for conductive AFM of monolayers of D5TBA on silicon. The level of current measured in CAFM is generally observed to decrease with time until the probe becomes insulating\textsuperscript{1}. The issue was more severe in ultra high vacuum since the resistance of the tip-sample contact increased dramatically within a few scan lines.

Figure 5-12. a. Transmission electron micrograph of a Pt coated AFM tip before use. The apex radius of the tip is about 20nm, b. Dark field TEM images showing the presence of a single Pt grain at the apex of the tip, c. Dark-field TEM image showing the silicon core of the tip, d. Transmission electron micrograph of a Pt coated AFM tip after use on a D5TBA submonolayer on SiO\textsubscript{2}/p+Si in contact. The tip was worn out as evidenced by the flat at its extremity and a molecular film had been transferred to the apex.
Tips were characterized by high-resolution TEM imaging, electron-diffraction, and energy-dispersive x-ray analysis. A number of different processes were observed including flat wear of the tip apex, transfer of material from the substrate to the tip, and plastic deformation of the tip. Our studies show that the decrease of the tip-sample conductivity results from the formation of transfer film at the tip apex, and not from fracture or delamination of the metallic coating of the AFM tips. The TEM measurements were performed by Dr. Altoe at the Molecular Foundry on AFM tips used on D5TBA submonolayers.

**Experimental.** TEM analysis of the tips before and after use was performed under a field emission transmission electron microscope JEOL FETEM 2100-F equipped with an energy dispersive x-ray spectrometer (Oxford). AFM cantilevers were mounted in a home built adaptation of the JEOL single tilt TEM holder making it possible to image the same tip before and after AFM use. Several Pt coated Si tips (3N/m and 0.2N/m) were characterized by TEM before use showing very strong similarities. Figure 5-12a shows details of a typical Pt coated Si tip before use. The apex radius measured from TEM images for several tips ranged from 20 nm to 22 nm. Very often we have observed a predominant single grain of Pt on the apex of the tip. That is revealed by dark field TEM images such as fig5-12b where the grain located at the apex is clearly visible. Dark field images such as fig5-12c were used to measure the thickness of the coating layer which was very close to the nominal specification of 30 nm.

![Figure 5-13. Series of transmission electron micrographs of a Pt coated tip, a. before use, b. After use on a bare silicon wafer covered by its native oxide, c., d. and e. were acquired after scanning 50mm, 100 and 150mm on a submonolayer of D5TBA. The film of transferred molecules grew at the side of the top rather than at the apex.](image)

**Results and Discussion.** Fig5-12d shows an image of a tip after use in contact mode on a submonolayer of D5TBA on SiO2/Si. This image exemplifies how scanning in AFM in contact mode on organic/inorganic heterogeneous surfaces modifies the tip in two ways: the transfer of molecules from the substrate to the tip and wear of the tip apex. Only a limited part of the overall Pt conductive coating is worn indicating that the increase in the tip/sample resistance is caused by the transfer of organic materials rather than wear. Transfer of D5TBA from the substrate to the tip apex was consistently observed after the tip stopped conducting. For CAFM
experiments on D5TBA done in UHV we found that a thickness of about 2 nm of the material deposited at the tip apex was enough to prevent conduction between substrate and tip. This thickness needed to increase to about 10-15nm to stop conduction when the CAFM experiments were done in air. The differences between UHV and ambient is presumably due to the presence of water at the tip-sample contact. Water has been shown to dope organic molecules even at very low concentration. Also, the tip-sample contact area can be effectively increased due to a water meniscus forming at the contact.

The series of images shown in fig5-13 illustrate how a single AFM tip can be used in contact and imaged in TEM alternatively to measure the evolution of the apex with scanning. The tip was first used on a silicon substrate covered with native oxide and then on a high coverage monolayer of D5TBA on SiO2/Si. After the first step on silicon, the apex of the tip had been worn by close to 20nm. After scanning on the monolayer, a film was gradually transferred and seemed to have diffused from the apex to the side of the tip.

**Conclusion.** In this chapter, we showed that the presence of the insulating oxide layer interposed between monolayer organic crystals and a substrate induced electrical current to flow in the plane of the monolayer in CAFM experiments. This technique constitutes a novel way to probe the in-plane conductivity of the monolayer and its key advantage is that the contact from a soft AFM tip is less invasive than by macroscopic electrodes. Chapter 6 describes applications of this method to study the relationship between the conductivity of the organic monolayers and factors such as the degree of crystallinity and the symmetry of the lattice.

On the other hand, limitations of the method are the complexity of the electrical circuit and the difficulty to extract quantitative information from CAFM images. A simple model such as the resistor network shown in fig5-4b does not permit to deduce a key parameter such as the carrier mobility in the monolayer. The flat transistor platform described in chapters 7 and 8 was developed to improve the quantitative understanding of the electrical properties of ultra-thin organic films and access properties such as the mobility of electrical carriers, the resistance at the contacts and grain boundaries and the position of molecular orbitals with respect to the work function of electrodes.


11 BudgetSensors ElectriCont G AFM probes


15 Murphy, A. R.; Fréchet, J. M. J. Chemical reviews. 2007, 107, 1066-96.


Chapter 6. Structure-conduction correlation in monolayers: mechanical manipulation and conduction anisotropy

Two applications of the CAFM technique described in chapter 5 are presented here. Both confirm the lateral conduction model that was proposed to account for the size dependent contrast observed in current images of DSTBA on SiO2/SiP+ substrates. First, mechanical manipulation of the monolayer crystalline structure and the influence of molecular order on its conduction properties are described. In the second part of the chapter, theoretical work is combined to structural and electrical characterization to investigate conduction anisotropy in DSTBA monolayers.

We found that applying force with AFM tips in the 40-100nN range irreversibly reduced the conductance of the organic monolayer. Lattice resolved images revealed that the decrease in current measured in CAFM was due to a reduction of molecular order in the 2D organic crystal. These results demonstrate that AFM tip manipulation is a useful method to study the relationship between structural and electrical properties in organic monolayers.

In addition, we studied the dependence of conductivity on crystalline orientation in oligothiophene monolayers. Molecular dynamics simulations predicted that the conductivity was 30% higher in the [1,0] direction of the Herringbone unit cell. The relative orientation of the lattice and the growth axis of finger-like domains was determined by electron diffraction. We then used size dependence analysis and a nanopatterning technique to obtain experimental evidence of the conduction anisotropy.

Mechanical manipulation. Intense efforts have been devoted to correlating the structure of organic thin films and monolayers with their electrical properties. A number of structural parameters can affect electrical conduction including the presence of amorphous domains within a crystalline matrix\(^1,2\), the presence of grain boundaries\(^3,4\) and local defects\(^5\). The impact of these structural factors on the carrier mobility and the threshold voltage in field effect transistors has been particularly investigated\(^6\). For microstructure characterization, X-Ray diffraction has been used extensively and provides information on the lattice structure and intermolecular spacing. This technique is however not sensitive to material inhomogeneity. In addition, it cannot be used to determine the absolute degree of crystallinity of a monolayer or a thin film. X-Ray diffraction can however be used to compare the quality of thin films and optimize their preparation protocol. A conventional way to correlate order and electrical transport in thin films is therefore to combine an OFET measurement of the average mobility with X-Ray diffraction.

In the first section of this chapter, we describe a direct nanoscale observation of the correlation between the molecular order in a monolayer and its conductivity which is obtained through...
mechanical manipulation. This study is based on applying the CAFM technique presented in chapter 5 and combining it with high resolution AFM to investigate the effect of applying large pressure in the order of a GPa with the AFM tip on both electrical and structural properties of a monolayer.

Conduction anisotropy. The dependence of conductivity on crystalline orientation has been studied in several organic materials. Sundar and coworker used a stamp-like technique to connect a macroscopic single crystal of rubrene to electrodes and found that conductivity along the [1,0] direction of Herringbone crystals was higher than in the [0,1] direction due to a better overlap of the Pi orbitals of the system. Polymer thin film systems, as well as thin films of pentacene and oligothiophene derivatives were also investigated. It should be noted that the origin of conduction anisotropy differs for small molecules and polymers. In polymer thin films, anisotropy can arise from differences between inter and intramolecular conduction mechanisms since the conductivity along the backbone is higher than in directions orthogonal to the polymer chain. For small molecules crystals, conduction anisotropy can be observed in two configurations:

- 3D crystals often have a “layer by layer” structure. The conduction in the xy plane of the layers and in the z direction can be significantly different.

- For 2D crystals or layered 3D crystals, a conduction anisotropy can arise from the asymmetry of the 2D crystal structure due to the anisotropic overlap between molecular orbitals. This type of anisotropy which is related to the crystalline lattice is the focus here.

Conduction anisotropy in monolayers has been little studied due to two majors challenges, 1. Establishing a non-invasive electrical contact to monolayer materials, 2. Obtaining large enough crystalline grains to measure the dependence of conduction on lattice directions within a single grain. In this chapter, we describe the use of CAFM and a nano-patterning method to measure conduction anisotropy in oligothiophene monolayers and correlate experimental data to molecular dynamics simulation.

1. Correlation between conductivity and molecular order through mechanical manipulation of D5TBA monolayers

1.1 Experimental. The effect of scanning at high force in contact mode AFM was investigated. Using a Pt coated BudgetSensors tip (0.2N/m spring constant), topography, lateral force and current images of a region of the submonolayer were acquired. The applied force for these initial images was +15nN. A force distance curve was then recorded and the set point was modified to obtain the desired force: 45nN in experiments described in 1.3 and 80nN for those shown in section 1.5. A new scanning area was defined by zooming in the initial image and an image was recorded at a scanning rate of 1Hz. The region where high force was applied was close to 2µm large. Following this image acquired at 45nN or 80nN at applied force, the net force was decreased to +15nN, and topography, lateral force and current images were acquired.
at an increased scan size to compare the area scanned at high force with the surrounding. A 5500 Agilent AFM with a 10µm scanner was used.

The AFM tip had to be changed between CAFM and high resolution experiments. Silicon nitride triangular shaped cantilevers with force constants of 0.27N/m or 0.58N/m were used for to record lattice resolved images. In order to find the molecular islands scanned at high force after changing the AFM tip, a landmark was created by scratching the edge of the sample. A 80µm large scanner was then used to map a 150µm large area of the monolayer close to the landmark. After applying force to an island located in the mapped region, the cantilever was changed and the map was used to find the island for lattice resolved AFM. Using an instrument with more accurate xy positioning would help bypass these technical complications. The Veeco Icon recently purchased by the Salmeron group would therefore be more convenient than the 5500 Agilent used in this study although it is less suited to high resolution AFM because of its large 90µm scanner. The protocol for the acquisition of lattice resolved images was described in chapter 3.

The data shown in section 1.4 were acquired on a submonolayer of D5TBA on mica so no current images were recorded. For that experiment, triangular shaped silicon nitride cantilevers were used both to apply force and image the lattice of the monolayer.

1.2 Introductory results. We showed in the previous chapter that the conductance of molecular islands depended on their size due to lateral conduction in the monolayer. It appears that size is not the only parameter that can have an effect on the level of current recorded in CAFM. Fig6-1 shows topography, lateral force and current images recorded on a D5TBA submonolayer on SiO2/Sip+.

Figure 6-1.a. Topography and b. lateral force AFM image of a D5TBA monolayer on Sip+/Si, c. Corresponding current image at -0.5V sample bias

The monolayer is composed of a few molecular islands and of a large amount of porous phase which have a similar height. A contrast can however be observed in the lateral force between different regions of the porous phase. The frictional force on the network of grains located at the left hand side of the image was lower than on the grains located towards the center. A corresponding contrast can be observed in the CAFM images. The current on the low friction grain was 50% higher than on the high friction grains. Xiao and coworkers showed how lateral force AFM could be used as an indicator of the degree of crystallinity in organic monolayer11. Based on the lateral conduction model proposed in chapter 5, one expects the conductance of monolayer clusters and islands to depend on crystallinity. The observation of a higher current and lower friction in distinct regions of the porous phase is a strong indication that different
degrees of order exist within that phase. In the following sections, we describe how the degree of order in D5TBA polycrystalline islands can be modified by applying pressure with and AFM tip and how it affects their local conductance.

1.3 Mechanical manipulation of monolayer islands at +45nN force. The protocol described in the experimental section was followed to assess the effect of scanning the monolayer in contact at 45nN and 80nN applied force. Fig6-2a and 2b show topography and current AFM images of a D5TBA film on SiO2/Sip+. As described in chapter 5, the current was higher on the D5TBA islands than on the bare substrate and the current level scaled up with the island size due to lateral conduction in the monolayer.

After recording the images shown in fig6-2a and 2b, a square area of 2.25µm side was scanned at a +45nN force at a scan rate of 1Hz. Fig6-2c shows a topographic image obtained after zooming out and reducing the force back to 15nN. As can be seen, there is no detectable changes in the topography of the layer after the scan at the higher force, the height remaining constant within less than 1Å. A faint vertical line can be observed towards the center of the left hand side island where the monolayer is 2Å higher. This line corresponds to the left boundary of the region scanned at high force. The current image in fig6-2d acquired simultaneously, shows a sharp contrast between the regions inside and outside of the central square scanned at 45nN, where the current was about 50% lower. The experiment was repeated several times at forces ranging from 40 to 50nN. A similar set of data is shown in fig6-3. The current in the region scanned at high force in fig6-3d was 60% lower than on the pristine region.

The decrease in conductivity with no height or morphology changes can be explained by structural modifications of the crystalline lattice of the molecular layer in the form of disorder.
that produces local configurations with decreased $\pi$-overlap between neighboring thiophene units. Qi and coworkers reported a similar local decrease in conductivity of stilbene oligomers SAMs on Au after scanning at forces in the range of 100nN$^{12}$. In addition Fang and coworkers studied the dependence of current on applied force on an anthrylacetylene derivative monolayer. They found that the current remained constant with increasing applied force whereas it is expected to increase due to the larger tip-sample contact area. They explained these results by a decrease in molecular order balancing the increase in contact area$^{13}$.

Figure 6-4. Lateral force high resolution AFM image obtained in the pristine region of the D5TBA film in fig6-2d, the FT of the image is shown in inset.

We investigated the origin of the observed decrease in conductivity by imaging the monolayer at high resolution with silicon nitride cantilevers. Fig6-4 shows a 60nmx60nm lateral force image acquired on the monolayer island at the left hand side of images in fig6-2d. It was recorded in the region of the monolayer located outside of the low conductance square area. The Fourier transform in inset shows that 3 crystalline directions corresponding to the close-packed directions of the Herringbone lattice are resolved (as described in chapter 3).
On the other hand, the image in Fig6-5 was acquired on the same monolayer island but in the lower conductance square where a 45nN force was applied in contact. It is apparent from the real space images and their Fourier Transform that the modified region has a much lower degree of crystallinity as a result of scanning with the tip at +45nN. The decrease of the molecular order in areas scanned at high force is therefore responsible for the increased resistance of the electrical junction. Several lattice resolved images were acquired both inside and outside of the lower conductance region with similar results.

![Image](image.png)

**Figure 6-5.** Lateral force high resolution AFM image obtained in manipulated region of the DSTBA film in fig6-2d, the FT of the image is shown in inset.

The degree of molecular order is reflected in the intensity of the peaks in the Fourier Transform images. Fig6-6a and 6b show intensity profiles obtained from the FT in fig6-4 and fig6-5 in the direction indicated by a red dotted line.
The area under the peak is 55% lower in the modified region compared to the pristine monolayer. Quantification of the molecular order through measurements of the intensities of spots in the FT images is only approximate because in contact mode the images do not show true molecular resolution as the tip is in contact with more than a single unit cell of the lattice and thus produces an average of the intermolecular distances. STM measurements, which would yield a more accurate estimate of the decrease in molecular order, are planned in the future.

1.4 Zoom on the boundary. In order to compare the degree of crystallinity between pristine and manipulated regions of the monolayers, lattice resolved images were acquired at the edge of the manipulated area. Fig6-7a shows a topography AFM image of a D5TBA monolayer on mica. Towards the center of the island, a square can be observed were the layer was scanned at 50nN. The square is visible because its edges are higher by a few angstroms. This could be caused by a reduced molecular tilt due to pressure applied by the tip.

Fig6-7b shows a zoomed-in topography image on the left edge of the square which appears as a bright vertical line at the center of the image. Finally, a lattice resolved lateral force image was acquired by zooming in on the boundary. It is displayed in fig6-7c. A set of lines corresponding to rows of molecules can be observed on the left hand side of the image. The right hand side where the layer was scanned at high force appears disordered. In addition, the friction is lower on the darker left half of fig6-7c, in agreement with the correlation between molecular order and friction.
Figure 6-8. a. Topography, b. friction, c. current AFM images of DSTBA over SiO2/Si+ after scanning in contact applying a 80nN net force at the center of the image, d. FT image of a lattice resolved image obtained in the scanned region

1.5 **Effect of scanning at higher force.** The effect of scanning the monolayer at higher forces, in the range from 75 to 100nN, was also investigated. As illustrated by fig6-8, scanning at these forces resulted in removal of the molecular film in certain regions while in others the film structure was strongly modified, with changes in topography, friction and electrical properties.

Figure 6-9. Lateral force AFM image of a region of the monolayer scanned at +80nn. The Fourier transform is shown in inset. At least 5 distinct ordered directions are observed.
The height of the monolayer decreased permanently by about 20% (fig6-8a), its friction increased (fig6-8b) and the current decreased by 90% (fig6-8c). Lattice resolution images revealed that although some regions of the monolayer remained ordered, the lattice was randomly oriented. This is illustrated by the image shown in fig6-9 where numerous distinct lattice directions are observed.

In addition, five independent pairs of spots can be observed in the Fourier transform of the image which is shown in fig6-8d and in inset of fig6-9. These results suggest that the tip motion can “reorder” the monolayer since some of the crystalline directions observed in fig6-9 were not lattice directions of the initial monolayer.

1.5 Lattice order induced by applying force. Interestingly, in several instances applying force with the tip induced the opposite effect, i.e. decreased frictional force and increased conductivity in the monolayer. These effects were observed in experiments where the tip was used to scrape off molecules by repeatedly scanning the same line at high forces. Molecules under the tip were scrapped off but the conductance of the surrounding monolayer, which was presumably in contact with the blunt sides of the tip, had increased.

The images in fig6-10 are extracted from an experiment where a large polycrystalline islands was “diced” in smaller domains using the tip to scrape off molecules and define boundaries. The bright lines in fig6-10a correspond to bare substrate regions where molecules have been removed by the AFM tip. Several dark vertical stripes where the frictional force is smaller are indicated by white arrows. Two stripes are adjacent to boundaries of scrapped off molecules and were created by the AFM tips while applying high force. The radius of curvature of the AFM tip used in these patterning experiments can be expected to be very large since the tip was used repeatedly at high force to scrape off the molecules. Both wear and plastic deformation can result from such treatment (a tip used in similar conditions was studied by TEM and its apex radius was 50nm).

Figure 6-10. a. Lateral force image of a DSTBA monolayer island after using the tip to scrape off molecules and nanopattern domains, b. Current image acquired at -1V sample bias in the same region of the monolayer.

Fig6-10b shows a CAFM image. Regions where the friction is lower are more conductive, which suggests an enhanced crystalline order. These results show that in specific circumstances, the tip can induce or modify the molecular order in the layer. These experiments were however much less reproducible than mechanical manipulation described previously in this section.
1.6 Conclusion and Future work. The mechanical manipulation method described in this section is interesting in two aspects. First, it constitutes a direct proof of the relationship between crystalline order and conductivity in an organic monolayer. Such results can be drawn from a combination of FET and X-Ray diffraction measurements on thin films but these techniques typically probe a large amount of heterogeneous materials and average their properties. Here we demonstrate control over the crystallinity of the monolayer at the nano-scale.

Secondly, this manipulation protocol could be implemented in monolayer FETs to quantify the relationship between carrier mobility and molecular order by comparing the mobility of the film at various degrees of crystallinity. In highly ordered materials, a shift from band conduction to hopping conduction could be observed and tracked by temperature dependant experiments. Ideally, true molecular resolution characterization would be needed to quantify the density of defects and the degree of crystallinity. This could be achieved by non contact AFM or ex-situ by STM.

2. Conduction anisotropy in AFM monolayers investigated by AFM tip nano-patterning

As mentioned in the introduction, several groups reported that the conductivity along the [1,0] direction of Herringbone crystals was higher than in the [0,1] direction. In this section, we describe how we applied CAFM to study whether the conduction in DSTBA monolayer was isotropic. Theoretical results predicting a higher conduction along the [1,0] direction of the DSTBA unit cell are first presented, followed by AFM and TEM structural characterization specifically aimed at determining the relative orientation of finger-like domains and the crystalline lattice. Finally, a nanopatterning technique is used along CAFM to measure the degree of anisotropy experimentally.

2.1 Molecular Dynamics (MD) simulations (calculations by Dr. Nenad Vukmirovic and Dr. Lin-Wang Wang at LBNL). We used molecular dynamics simulations to assess the dependence of conductivity on lattice direction in Herringbone crystals of DSTBA. The unit cell size presented in chapter 3 was used. We showed that the theoretical unit cell was 15% larger in both [1,0] and [0,1] directions than determined experimentally. Based on the calculation described below, because the size difference is the same in both directions, the predicted anisotropy would be the same in magnitude for the calculated unit cell and for a 15% smaller one.

We calculated the system hole wavefunctions and their overlap at room temperature in order to estimate the degree of anisotropy of the hole mobility. The calculation was performed using the charge patching method\(^4\), which has an accuracy similar to that of density functional theory in the local density approximation. In a system composed of 7×7 unit cells, the wavefunctions of the top ten highest occupied orbitals were calculated. At room temperature, the orbitals of the system are strongly localized. Fig6-11a shows a snapshot of the top five hole wavefunctions extracted from the MD simulation. The globular shapes are isosurfaces enclosing regions with 98% probability of finding the hole inside the surface. The overall shape of the isosurfaces is indicative of the direction of strongest coupling along which light blue lines were drawn.
From the overlap of wavefunctions, we quantified the angular dependence of hole hopping. We estimate the hopping probability (which is linearly related to carrier mobility\(^{15}\)) between the wavefunctions \(k\) and \(m\) as being proportional to the square of the wavefunction moduli overlap

\[
W_{km} \propto M_{km}^2 = \left[ \int |\psi^{(k)}(r)| |\psi^{(m)}(r)| \, dr \right]^2
\]

where \(\psi^{(k)}\) and \(\psi^{(m)}\) are the wavefunctions for the realistic room temperature atomic structure obtained as a snapshot from molecular dynamics simulation. In recent work\(^{16}\), we have shown that such overlap integral approximates very well the full hopping matrix calculated by taking into account the electron-phonon interaction. We then quantified the angular dependence of hole hopping by projecting the hoping probability on \(x\) and \(y\) axes of the unit cell and weighting the projections with the length of the hop by defining the function \(g\) as

\[
g(\alpha) = \left\{ \left( x_k - x_m \right) \cos \alpha + \left( y_k - y_m \right) \sin \alpha \right\}^2 M_{km}^2
\]

with \(g(0)\) the projection along the \(x\) axis (parallel to \([0,1]\)) and \(g(90^\circ)\) the projection along \(y\) (parallel to \([1,0]\)).

![Figure 6-11. a. Top five hole wavefunctions corresponding to a snapshot in a room temperature molecular dynamics simulation of the 7x7 Herringbone structure. The globular shapes are isosurfaces enclosing regions with 98% probability of finding the hole inside the surface. The lines indicate the directions of strongest coupling. The energies of the levels are 2.787eV (blue), 2.758eV (red), 2.746eV (pink), 2.738 (black), 2.735 (gray), b. Plot of \(g\) as a function of \(\alpha\).](image)

The dependence of \(g\) on the direction \(\alpha\) is plotted in fig6-11b. The hole mobility is 30% larger in the \([1,0]\) direction than in the \([0,1]\) direction which is a moderate anisotropy. Although in rubrene and pentacene crystals the anisotropy factor was found to be between 5 and \(10^{7,9}\), Uno and coworkers found a weaker anisotropy in an oligothiophene derivative with a factor of \(1.5^{10}\) which is close the factor 1.3 which is predicted here for D5TBA. The next paragraph describes how the orientation of the Herringbone unit cell is related to the growth of finger-like domains and therefore the morphology of D5TBA islands.
**Structural characterization.** The relative direction of the finger-like grains and the crystalline lattice in D5TBA islands was studied at high resolution. Figure 6-12 summarizes results related to structural characterization by lattice resolved AFM images and electron diffraction in TEM that were partially described in chapter 3 and chapter 4. Fig6-12a shows a topography AFM image of a D5TBA monolayer while fig6-12b and 12c respectively show STEM images of a monolayer island transferred by LB deposition and a bilayer island prepared by horizontal deposition on a SiN membrane.

![AFM image of D5TBA monolayer islands deposited on mica, b. Scanning transmission electron image of D5TBA monolayer islands deposited on a Si3N4 membrane, a typical TEM diffraction pattern obtained from an individual grain of an island is shown in inset, c. Scanning transmission electron image of D5TBA bilayer islands with a typical diffraction pattern shown in inset, white arrows in fig a, b and c indicate individual grains and are parallel to the grain direction, d. scatter plot of grain direction versus direction of the a lattice vector [0,1] obtained for single grains by TEM on monolayer islands (red circles), bilayer islands(orange diamonds) or AFM (yellow squares). The solid line depicts the $\alpha=\beta$ equality and is plotted as a guide to the eye.]

The angle $\alpha$ is used to measure the orientation of the direction of finger-like domains with respect to the vertical. Since these domains are not perfectly straight, an error is associated with this measurement corresponding to the statistical deviation of 3 independent
measurements. The angle $\beta$ is defined as the angle between the [0,1] direction of the unit cell and the vertical. No error is reported for TEM measurements due to its higher accuracy. For AFM, the error is associated to the finite width of spots in the Fourier Transform of lattice resolved AFM images. We mentioned in chapter 3 that resolved directions could not be ambiguously assigned to unit cell directions. Based on the TEM results, it could be confirmed that the crystalline direction which was roughly orthogonal to the orientation of finger-like domain was [0,1] (although the line of molecules resolved in the real space AFM image is along [1,0]).

Each data point of the scatter plot in fig6-12d corresponds to an individual finger domain where $\alpha$ and $\beta$ were determined from the morphology of the island and electron diffraction in TEM or high resolution AFM. The solid line corresponds to $\alpha = \beta$. Most data points fall close or along this line, which shows that the axis of finger domains is parallel to the [0,1] direction of the unit cell in both monolayer and bilayer islands. Based on the results from hopping conductivity calculations described in the previous section, one can be expect the conductivity to be lower in the radial direction of D5TBA islands, which is also the grain growth direction.

In the next paragraphs, we describe how the CAFM technique described in chapter 5 was applied to the experimental investigation of conduction anisotropy.

2.3 Current versus size dependence. The first method that was used is based on a current versus size analysis. Fig6-13a shows a plot of the current as a function of the size of molecular islands. In addition, the current as a function of “local width” is plotted (orange data points). Fig6-13b illustrates what “local width” refers to. It is defined as the size of the island in the [1,0] direction of the unit cell, i.e. perpendicular to the axis of finger-like grains. Fig6-13a shows that the dependence on local width is well fitted by a straight line. From these measurements, one can indirectly deduce that the dependence on length (i.e. dimension of the [0,1] direction) is weak. Indeed, since the current scales linearly with width, if it also scaled linearly with length, then the overall dependence on island size would be quadratic whereas it is measured to be linear experimentally.

Figure 6-13. a. Dependence of the current on average island diameter (yellow squares) and on the local width $w$ (orange diamonds) within islands, as illustrated in b. The data was acquired at -2V sample bias, b. Schematic illustration of the structure of a D5TBA island with a depiction of the “local width” $w$ which corresponds to the local size of the island in the [1,0] direction of the unit cell.
**Limitations of the method.** These experimental results agree qualitatively with calculations of the hopping mobility obtained from MD simulations. However its application to the extraction of quantitative data is limited by the fact that “local width” is coupled with “local length” in D5TBA islands. To obtain more quantitative results, one would need measurement of the conductance on crystals which would have the same length but different widths and vice versa.

**2.4 Nanopatterning.** In order to obtain a more accurate and quantitative experimental determination of the anisotropy, we used the AFM tip to create sub-domains within D5TBA crystals.

**Principle of the experiment.** We used nanopatterning to carve boundaries within molecular islands. The domains were rectangles 150nm wide and 600nm long. The domains were created by applying large forces in contact with the AFM tip which induced desorption of molecules from the surface. The aim of these physical boundaries is to prevent current flow and limit lateral conduction is D5TBA islands. Fig6-14 illustrates the method. Fig6-14a shows a topography image of a D5TBA island and fig6-14b the corresponding lateral force image where finger-like domains are visible due to the higher frictional force over grain boundaries. Fig6-14c shows a topography AFM image obtained after physical boundaries were created by removing molecules. A current image acquired on the nanopatterned island is shown in fig6-14d.

The domains created by nanopatterning are rectangular. The orientation of the lattice with respect to the large and short edges of the rectangles varied across the island. The friction image (figure 6-14b) shows that domain boundaries mostly run radially from the center of the island to the periphery. In the rectangle labeled C, the growth axis of crystalline domain (also the [0,1] direction of the unit cell) is along the large edge. In A, it is the [1,0] direction of the unit cell which is along the large edge of the rectangle. The domain labeled B is intermediate since the axis of finger-like domains is oriented along the diagonal.

**Figure 6-14:** a. Topography and b. lateral force AFM image of a D5TBA monolayer island over SiO2/Si, c. Topography AFM image after creating rectangular domains by scrapping off molecules with the AFM tip, d. CAFM image recorded at -0.5V sample bias.

Calculations predict that the hopping mobility is anisotropic and larger in the [1,0] direction of the unit cell. This anisotropy can be expected to induce higher current levels in nanopatterned domains where the long edge of the rectangle is parallel to the high conductivity direction. The images in fig6-14 describe one of 3 similar experiments that were carried out to test this hypothesis. In the CAFM image of fig6-14d, the current recorded on the rectangle labeled A is 40% higher than recorded in C. This is in agreement with conduction anisotropy predictions. A
more detailed set of results for the three series of measurements is presented in fig6-16 and fig6-17.

**Experimental.** In order to created boundaries, the monolayer was scanned in contact mode at 70nN applied force with the slow scan direction disabled. As a result, the AFM tip was scanning along the same line repeatedly which led to the desorption of D5TBA molecules. Using this technique, boundaries could be carved artificially within monolayer islands of D5TBA. Fig6-14a and 14c illustrate the morphology of a monolayer island before and after scrapping off molecules.

Creating domains of a similar size required being able to place the AFM tip very precisely where a boundary needed to be created. First, a topography image was recorded at low force to locate the position where boundaries would be created. Then, since a force of 70 to 100nN is necessary to scrape molecules off, one needs to increase the force and position the tip at the correct location. However, the tip does not remain at the same location when the applied force is raised. A 0.2N/m Pt-Cr coated tip typically slides by 50 to 200nm when the force is raised from 0 to 50nN. This can significantly limit the positioning accuracy.

The following method was used to circumvent this issue: an image of the monolayer island was acquired at 5nN applied force and a landmark was chosen along the line where the first boundary was to be located. The applied force was raised to 70nN and a scan was started outside of the molecular island. When the landmark was reached the slow scan direction was turned off (i.e. the tip started scanning the same line repeatedly and scrapping off molecules). The process was followed in real time since the AFM image is recorded even when the tip scans along the same scan line over and over. Fig6-15 shows the topography image that was acquired while scrapping the layer off. The monolayer appears in yellow in the image. The scan goes from left to right. As the tip scans in contact at high force, the width of the monolayer is reduced until no more molecules remain at the right hand side of the image.

![Figure 6-15. Topography image recorded as the tip scans the same line repeatedly (slow scan direction turned off) at 50nN. As the tip scans repeatedly the same line, molecules are scrapped off so that the width of the molecular island decreases until no molecules remain at the right hand side.](image)

When the first line was fully scrapped off, the scan was stopped. The center of the image was translated by 150nm to start creating a second boundary parallel to the first one. The slow scan direction was momentarily turned on to let the scanner adjust its position, and turned off
before starting to pattern a second line. The image center adjustment and the line patterning procedure were repeated for as many lines that needed to be patterned.

**Figure 6-16.** Summary of the results obtained by three nano-patterning experiments, a, b and c correspond to series 1, 2 and 3 in the graphs of fig6-17. In each case, a molecular island was imaged in topography and lateral force AFM to obtain the morphology of finger-like domains (grain boundaries are reproduced as dark lines). The islands were then nano-patterned by scrapping off molecules. The size of rectangular domains was 150nmx600nm.

**Results.** Fig6-16 shows schematics of the nanopatterned islands along with the current measured in the domains. Black lines indicate the location of grain boundaries deduced from lateral force AFM images. From the orientation of grain boundaries, one can deduce the direction of finger-like domains and therefore the direction of the [1,0] and [0,1] directions of the Herringbone lattice. A question mark is located in regions of the islands where the grain boundaries were not visible in the lateral force image. Fig6-16a corresponds to the series of images shown in fig6-14. Fig6-16b and fig6-16c correspond to two additional experiments. For each island, the values of current measured in the rectangular domains were obtained by averaging 3 CAFM images acquired at -0.5V sample substrate (and 6 images for series #1). Images were acquired at various angles (0°, 45° and 90° scanner rotation) to average out variations due to tip contamination. The result is 3 series of current values measured in nano-patterned domains.

The trend displayed by the results is summarized in the graphic of fig6-17 where the current as a function of the angle between the [0,1] direction of the unit cell and the long edge of the domain is plotted.

In fig6-17, the current is plotted as a function of the angle between the finger-grain axes (i.e. [0,1] direction of the unit cell) and the direction of the large edge of the rectangular domain. Each data point corresponds to a domain. Fig6-17a shows a plot of the absolute current while in the plot of fig6-17b, the data were normalized to account for variations between the 3 series due to the use of different AFM tips and different samples. This normalization also makes the observed trend more visible. Each current value was normalized as a relative value of the lowest current value in the series. In #1, the lowest value was for the data point (21.3°, 5pA), in #2 it was (32°, 4.5pA) and in #3 (53°, 6.6pA).
**Discussion.** A trend towards higher current value in domains were the large edge is perpendicular to the grain-growth direction can be observed. Fig6-17b shows that in series #1 and series #3, the conductance increased by 30 to 45% as the angle between the growth axis (predicted low conductivity direction) and the large edge of the domains increased. The data in series #3 follows that trend somewhat poorly with a clear outlier at the data point (14°, 13.2pA). This nano-patterned domain had the highest conductance in the series and clearly goes against the trend observed in series #1 and series#3 (It should be noted that the size of the domains in series #3 was not constant and that the outlying domain was the largest as described in endnotes17). Note that a higher conductance was measured in domains orthogonal to the grain-growth direction in spite of the higher density of grain boundaries in these domains compared to those oriented along grain-growth. The weak effect of grain boundaries is consistent with results shown in chapter 8.

![Figure 6-17. a. Plot of the current measured in nano-patterned domains as a function of the angle between the grain growth direction and the long edge of rectangular domains. Each data point corresponds to a domain in fig6-16, b. Plot of the normalized current. The current was normalized by dividing the measured values by the lowest value of the series.](image)

**Applied force during CAFM.** The current values shown in fig6-16 were deduced from CAFM images acquired at a higher force than normally used for CAFM. As mentioned in chapter 5, a 10-15nN applied force was required to ensure a stable electrical contact between the tip and the sample in CAFM. The applied force for series 2 and 3 was 28nN and it was 38nN for the series #1. This additional 15-20nN applied force was aimed at enhancing the contrast between nano-patterned domains. Indeed, the total resistance of the junction can is the sum of two terms, the injection resistance which is insensitive to anisotropy and a second term which depends on anisotropy (this term includes the in-plane resistance of the monolayer and the monolayer-substrate resistance). Decreasing the injection resistance with respect to the second term therefore leads to a greater contrast accounting for the intrinsic conduction properties of the monolayer. The contrast between nano-patterned domains was lower in images acquired at 15-18nN applied force. In the series #3 for instance, the current was larger in domain A than in domain C but only by about 20% (as opposed to 40% at 38nN). After a few images at such force, the conductance of the nano-patterned domains decreased permanently. This can be explained by the invasive effect of scanning the monolayer with the tip as described in the first part of this chapter.
Conclusions on conduction anisotropy. The experimental results described in this section are in agreement with the moderate level of anisotropy predicted by calculations (30% compared to 500% as measured in rubrene single crystals\textsuperscript{7}) and in the same range as other results obtained on oligothiophene derivatives\textsuperscript{10}. The trend displayed in the graphs of fig6-17 is moderately strong due to the weak level of anisotropy. Using molecules in which the Pi orbitals are stacked parallel to each other would lead to a much larger anisotropy and much higher contrast in CAFM images of nano-patterned domains. Molecules such as Tips-pentacene derivatives where side groups force the molecules into a face to face arrangement could be explored.

In addition, the nano-patterning technique described in this section can be used to tailor the shape of soft materials in order to analyze their properties. In a 2 electrodes or FET configuration, one could pattern the organic material used as the channel to simplify its geometry and facilitate the simulation and calculation of its properties.


17 The size of the domains in series #3 was not constant across the island since the size of small edge was 135nm long for (14°, 13.2pA) and respectively 85nm and 100nm long for the data points (78°, 8pA), (52°, 6.6pA) and (47°, 6.8pA), (78°, 8.4pA), (45°, 7.8pA). The domain with 13.2pA current was therefore the largest but would still go against the observed trend if attempt was made of normalizing the current by the size.
Chapter 7. Nanofabrication of coplanar electrodes and FETs: technical details

A protocol for the fabrication of embedded gold electrodes and coplanar field effect transistors is described in this chapter. The devices are aimed at studying the electrical properties of ultra-thin organic films while characterizing their structure using scanning probe microscopy. The method is a so-called replica technique where gold electrodes and an insulator are deposited on a smooth silicon wafer and replicate its flatness. That initial template is subsequently polished and etched away revealing the surface composed of gold electrodes embedded in a dielectric.

A detail introduction of the motivations behind fabricating this device and similar attempts made in other research groups is given in the next chapter.

1. Summary of the steps involved in the fabrication of embedded electrodes and coplanar FETs

The process for the fabrication of coplanar embedded electrodes and coplanar FETs is shown in fig7-1 and described below.

**Fabrication of the electrodes by UV lithography (fig7-1a).** 6” silicon wafers were used as a template. Gold electrodes were patterned by UV lithography. The gap between electrodes varied between 2µm and 500nm and gold was evaporated with nominal thickness ranging from 12 to 15nm. Note that no adhesion layer was used since it is incompatible with the rest of the process. A lift-off step followed.

**Deposition of the dielectric and the gate followed by anodic bonding (fig7-1b, 1c and 1d).** The next step was the plasma enhanced chemical vapor deposition (PECVD) of a layer of silicon oxide (150nm) from a silane precursor at 350°C. For embedded electrodes with no gate, the wafer was then directly bonded to a 6” borofloat glass wafer by anodic bonding at a temperature of 300°C. For coplanar FETs, a gate layer was evaporated with a nominal thickness of 80nm followed by an additional layer of PECVD oxide before anodic bonding. To minimize gate leakage, an additional UV lithography step was used so that there was no overlap between electrode pads and the gate. This is described in section 7.

**Dicing, polishing and etching.** The wafer was then diced in 1cmx1cm pieces with a diamond pen. The pieces were polished mechanically with a lapping machine until approximately 50 microns of silicon remained. The rest of the silicon was etched away in a bath of TMAH 25%. First the pieces were etched at 70°C. When only a few µm of silicon remained, the pieces were transferred to a room temperature 25%TMAH bath.
Using a room temperature bath helped increase the selectivity of TMAH towards silicon and limited the etching of silicon oxide. It was also observed that gold electrodes could be damaged if left in contact with TMAH at 70°C. The room temperature etching took several hours.

2. Lithography and gold evaporation

**Lithography.** A pattern containing sets of electrodes with 10 different geometries was defined on a 6” polished silicon wafer using standard UV lithography. Each set was composed of 4 electrodes. The gap between electrodes at the center of the sets varied between 2µm and 500nm, which is the resolution limit of the stepper (GCA 8500 at the Nanolab at UC Berkeley). This resolution limit could easily be extended by using a DUV stepper or e-beam lithography, since the other steps of the process are not sensitive the method used to define gold electrodes (E-beam, UV or deep UV lithography).

The layout of the mask is shown in fig7-2a. It is made of 10 rows labeled A to J. Each contains ten sets of electrodes labeled I to X. The size of the gold patch for these electrodes is 100µm. We will describe below how these pads can be contacted by wire bonding or using a probe station. Ten sets with larger gold pads (500µm) are visible at the bottom of fig7-2a. Fig7-2b shows the design of the centers of electrode sets labeled I to X which correspond to sets I to X of a given row of electrodes.
The rationale behind having a number of different designs is that the coplanar FET platform can be applied to study a number of different materials including monolayers, thin films, nanowires and others. The designs I, V, VI and VII are aimed at maximizing the width of the channel whereas designs such as III and IV are aimed at facilitating 4-point probe measurements. Sets IX and II are well suited to contact single nanowires. The pattern of the mask contains 110 sets of electrodes. The size of that pattern is close to 10mm and is repeated over the surface of a 6'' wafer leading to a very large number of sets of 4 electrodes.

![Figure 7-2.a. Lay-out of the patterned electrodes. The mask is composed of 10 rows labeled A to J each composed of 10 sets of 4 electrodes with small contact pads, and an additional row with large contact pads at the bottom, b. central design of each set of electrodes. Each design is composed of 4 parts each connected to one the 4 electrode pads that form a set.](image)

Gold electrodes. Gold was evaporated using a ULTEK E-Beam Evaporator at the Nanolab\textsuperscript{2} or a Semicore e-beam and thermal evaporator at the Molecular Foundry at LBNL. The gold film was evaporated at the lowest possible thickness for 2 reasons. First, the height step at the edge of embedded electrodes shown in the schematic of fig7-1f is expected to increase with electrode thickness (we will show in the next chapter that embedded electrodes are not fully coplanar with the oxide but that a step of a few Å to 1nm always exists). Secondly, the CVD oxide is conformal over the patterned wafer. The surface topography due to the presence of gold electrodes is therefore conserved at the surface of the oxide which is subsequently bonded to glass. Thick electrodes would lead to large height variations and could result in a lower quality bond.

Titanium is routinely used as an interfacial layer between SiO\textsubscript{2} and metals such as platinum and gold because it improves adhesion and wetting of the metal to the substrate. The replica method that we describe in this chapter is not compatible with the presence of an adhesion layer unless this layer would be conductive and resist etching in TMAH. Indeed, this adhesion layer would be located between the silicon wafer and the gold. It would therefore be exposed after etching the silicon wafer and would be at the surface of the embedded electrodes. Most adhesion layers form an oxide in air and would therefore not be suitable as electrode material.
In the absence of an adhesion layer, gold electrodes do not wet or adhere well to SiO$_2$ during evaporation. This imposes a lower limit on the thickness of gold electrodes since below 10nm the gold film is composed of a network of grains that do not interconnect. Such electrodes would not be conductive. This is illustrated by SEM images of evaporated electrodes shown in Fig7-3. Fig7-3a shows a micrograph of a gold electrode evaporated on a 6” silicon wafer with a nominal thickness of 10nm. The film is not closed and not conductive. The gold film shown in Fig7-3b was evaporated with a nominal thickness of 12nm. The film is not close but grains are interconnected so electrodes are conductive. Finally, the gold film in Fig7-3c had a nominal thickness of 15nm and is nearly closed.

3. Chemical Vapor Deposition of the dielectric and anodic bonding

Choice of the PECVD material. The two main factors directing the choice of a dielectric material are the dielectric strength and the dielectric constant (or relative permittivity $\varepsilon_r$). Materials with a higher dielectric constant are preferred as dielectrics for transistors since the capacitance is proportional to $\varepsilon_r$ and the field effect induced by the gate increases with capacitance. The dielectric strength defines the electric field at which catastrophic breakdown of the insulator occurs.

Commonly available materials for PECVD are silicon oxide (SiO$_2$) and silicon nitride (Si$_3$N$_4$). The dielectric constant of SiO$_2$ is 3.9 and its dielectric strength is 10MV/cm but can be lower in case of contamination, especially by hydrogen from the silane precursor. Si$_3$N$_4$ has a similar dielectric strength but its dielectric constant is 7.5. Another possible choice of dielectric is TEOS (tetrathyl ortho silicate) which has a similar dielectric constant as SiO$_2$ (4.2) but typically a higher strength due to the higher purity of PECVD TEOS.

SiO$_2$ was selected over Si$_3$N$_4$ because the anodic bond appeared to be of higher quality when using this material. TEOS was not tested because it is not available in the Oxford Plasmalab.
80plus PECVD system at the Microlab at UC Berkeley but could be an improvement with respect with SiO$_2$. The deposition was carried out at 300°C at a rate of 50nm/min.

**Anodic Bonding.** The anodic bonding of the wafer to glass is a necessary packaging step. Since the silicon wafer used as a template is set to be polished and etched away in the last steps of the process (see fig7-1), a thick support is needed to able to handle the device after removing Si. Borofloat glass is resistant to silicon etchant and can easily be glued or bonded so it is a natural choice.

In order to bond a Si wafer to a glass wafer, various techniques are available. In anodic bonding (see inset in fig7-4a), the wafers are placed in contact and positioned between 2 electrodes. The top electrode in contact with the glass is heated to 350°C and grounded while a -1000V bias is applied to the bottom electrode. Anions present in the glass migrate to the top electrode. Close to the interface between the two wafers, the charge deficit is compensated by the migration of cations and formation of covalent liaisons, resulting in a strong bond between the two wafers. To test the quality of the bond, one can dice the wafer and verify that the glass and silicon adhere well along the dicing lines. If the quality of the bond is poor, the two wafers typically detach during dicing.

![Diagram of anodic bonding process](image)

**Figure 7-4.** Photograph of a 6" wafer patterned with gold electrodes and a PECVD oxide bonded to glass, inset. Schematic of the anodic bonding process (for a wafer with no metallic gate layer).

An alternative to anodic bonding is thermo-compression bonding which is carried out by applying a strong force on wafers at high temperature. It can be done at room temperature if both the glass and silicon wafers are treated in an oxygen plasma. The plasma treatment creates dangling bonds at the interface that lead to covalent bonds when the wafers are brought in contact. This alternative was not tested in this study but could be explored in order to substitute room temperature processing steps to high temperature ones which could induce changes in the gold electrodes due to gold diffusion.
**Bonding quality and failures.** Fig 7-4 shows a typical bond obtained by applying -1000V to the bottom electrode at 350°C in a Karl Suss thermo-compression and anodic bonder at the Berkeley Nanolab. The bond is often poor at the center of the wafer. Any impurity located at the surface of the glass or silicon wafer leads to a local bond defect. Anodic bonding was carried out immediately after SiO$_2$ PECVD. Bonds of good quality could be obtained without extensive cleaning of both wafers. Fig 7-4 shows half of a 6” wafer after bonding. The electrodes are visible especially the ones with large gold pads. At this stage, the electrodes are encapsulated between the silicon and the glass. Bubble-like features can be observed in several locations where the bond failed. The density of these defects is typically higher at the center and at the edge of the wafer. Interference fringes are visible due to the sub-micron air gap between the glass wafer and the SiO$_2$ in defective regions.

Initially, the overall process was tested on embedded electrodes with no gate (as shown by the inset in fig 4a). When a gold layer and a SiO$_2$ layer were added to the process, consistent bond failure was observed. Interference fringes could be observed over most of the interface, indicating that the two wafers were not physically in contact. After a few hours, the two wafers came off from each other. Large regions of gold had been bonded and transferred from the silicon wafer to the glass due to poor adhesion to the oxide. By evaporating a 3nm Ti layer before evaporating gold, the problem could be solved and bonding was successful. This shows that an adhesion layer is needed for the metallic gate layer but not for the thin electrodes pads.

**Electrical contact to the gate.** When the gated devices were bonded to glass, we observed that bond quality was higher when there was an electrical connection between the bonding electrode and the gate layer. The PECVD gate dielectric insulates the metallic gate from the Si wafer and the top electrode. To solve this issue, a small section of the wafer was shielded during PECVD oxide deposition. In this region of the wafer, the metallic gate is in direct contact with the p doped Si substrate wafer itself in contact with the bonding electrode. After bonding, the 6” wafer is diced in centimeter size wafers. The region where the gate dielectric is absent due to shielding is then discarded.

### 4. Polishing and etching the silicon away to expose the active FET surface

**Mechanical polishing.** After dicing the 6” wafer into pieces, 90% of the 0.65mm thick silicon wafer was polished away mechanically in a Logitech lapping machine at a rate of 10μm/min. Five 1cmx1cm large pieces were polished in each run.

**Etching.** The samples were then transferred in a Tetra Methyl Ammonium Hydroxide 25%(TMAH) etch bath heated at 75°C where 99% of the remaining silicon was etched at a rate of 1 to 2μm/min. The samples were monitored and transferred to a room temperature TMAH 25% solution when a color change could be observed on the silicon surface, which indicated that the thickness of the remaining silicon was close to 1μm. The samples were left to etch at room temperature for close to 6-12 hours. After etching, the samples were transferred in a distilled water beaker using tweezers and agitated to clean off the TMAH from the surface. The
samples were finally transferred in a second water beaker using a clean pair of tweezers. In case of improper cleaning, leftover TMAH could be observed in optical microscopy. It appeared as a multicolor paste with interference fringes.

**Importance of etching at room temperature.** Some silicon remained on the surface and could not be removed even if the sample was left in the etchant at room temperature over a long period of time. Fig7-5a shows a 50x optical image of embedded electrodes after etching. The remaining silicon is mostly located on gold electrodes. Electrodes bridged by silicon cannot be used as contacts to study conduction in organic monolayers or other materials. We are currently exploring which additives could be added to the TMAH solution to reduce the amount of patches of left-over silicon.

![Figure 7-5. a. 50x optical image of embedded gold electrodes after etching in TMAH25%, b. 1000x image of the center of a set of 4 electrodes with most of the surface still covered by silicon. Black arrows point at yellow regions. AFM topography imaging showed that these features correspond to smooth height variations on the oxide dielectric that could be due to stress relaxation close to the Au-SiO\textsubscript{2} interface.](image)

The room temperature step was necessary to preserve gold electrodes. If the samples were left in hot TMAH for the whole etching procedure, gold electrodes came off from the surface or were damaged. This is due to the low adhesion between electrodes and SiO\textsubscript{2}. In addition, although TMAH is a silicon etchant, it can also etch silicon oxide but although at a reduced rate. At 70°C, the specificity of TMAH towards Si versus SiO\textsubscript{2} is lower than at room temperature. The RMS roughness of the oxide of samples left in the hot etchant was 5-6Å whereas it was 3Å for samples etched at room temperature.

**Stress relaxation.** In the optical image of fig7-5b, black arrows point at regions of wafer with a yellowish color. At first sight, one could assume that these features are defects or some material such as resist or left-over etchant. It was determined by topography AFM that this color contrast was coincided with smooth height variations at the surface of the wafer. These features were not present before polishing and etching of the silicon as evidenced from optical images acquired from the glass side of the packaged wafer. We suspect that stress relaxation causes these height variations. The deposition of PECVD oxide is conformal so the surface of the wafer that is bonded to the glass has height variations where the 12-15nm thick electrodes are located. After the silicon is polished and etched away, the stress due to these height variations
is has more freedom to relax leading the electrodes and surrounding SiO₂ to protrude out by 10-20nm. We will show in the next chapter that this topography has not effect on material deposited on top of the device.

5. Sacrificial layer

In order to protect the Au- SiO₂ surface from being damaged by TMAH during etching, a strategy based on the use of a sacrificial Cr was experimented. Although it initially led to improvements, it was abandoned for reasons described below. The layer was evaporated on top of the silicon wafer before patterning the gold electrodes and depositing the oxide by PECVD. During the last etching step of the electrode fabrication, this chromium layer was interposed between the silicon and the Au- SiO₂ surface as shown by the schematic of fig7-6a. It was then etched in a Cr etchant which has less effect on Au and SiO₂ than TMAH.

Figure 7-6. a. Schematic of a flat FET fabricated using a Cr sacrificial later, b. AFM image of a portion of a molecular island on a native oxide/Si substrate. The roughness of the molecular layer was 3Å, c. AFM image of a portion of a molecular island on the dielectric of an Au-SiO₂ surface. The roughness of the molecular layer that reproduces the substrate roughness was 6Å.

The presence of a Cr layer did help protect the oxide layer from being etched and the gold electrodes from being damaged. However, its surface was rougher than the initial silicon wafer. As mentioned above, it is crucial that the starting substrate roughness is as low as a few Å RMS since the Au-SiO₂ interface replicates the roughness of the substrate. Fig7-6b shows an AFM image of a D5TBA island deposited on the native oxide of a silicon wafer with 3Å RMS roughness. Fig7-6c shows an image of a D5TBA island on the SiO₂ dielectric of a coplanar FET fabricated with a Cr layer. The height scale is the same for both images. The roughness over the dielectric and therefore the monolayer was 6 Å RMS. The molecular order in the monolayer can be expected to be strongly perturbed by the roughness of the substrate, as shown by TEM measurements presented in chapter 4. The use of a sacrificial layer would therefore be relevant only if a layer as flat as the silicon wafer is used.
6. Contacting the gold electrodes by wire bonding, macroscopic probes and home-made electrodes.

The device obtained at the end of the fabrication process is shown in fig7-1f. In order to do electrical measurements on materials bridging the electrodes, electrical contacts to the electrode pads are necessary. Several methods were used depending on the required applications.

**Wire bonding.** In order to combine AFM and electrical characterization, the most suitable method was wire bonding. A critical limitation when using a scanning probe apparatus in conjunction with personalized characterization tools is access and space. Bonded wires take little space and run just above the surface of the sample. The only constraint is that the number and density of bonded electrodes is limited since an access path is required for the AFM tip.

A West-bond wedge bonding tool was used to connect gold electrodes to the electric leads of a socket with aluminum wires. The wedge bonding technique is illustrated by the schematic shown in fig7-7a. The wire passes through a wedge and is pressed in contact with the electrodes. The tool is vibrated to induce melting of the metal by frictional heating. When the first bond is done, the wire is threaded through the wedge while the tool is moved towards the second contact. A second bond is formed by vibrating the tool after which the wire is cut (see fig7-7b). Fig7-7c shows a scanning electron micrograph of an aluminum wire bonded to a gold pad by this technique. Wire bonding tools are not specified for electrode thickness below 500nm but wires could be reliably bonded to 10-15nm thick electrodes. We observed that the first bond was usually stronger than the second bond. As a result, the first bond was always located on the thin electrode and the second on the gold pad of the socket.

![Figure 7-7. a. and b. Schematic of the first and second bonds of the wire bonding process, c. Scanning electron micrograph of an Al wire bonded to gold (reproduced from Semipark©)](image)

**Home-made electrode.** An electrode was fabricated out of a thin copper sheet which was cut in a triangular shape. The base of the Cu triangular sheet was glued to a magnet which adhered to the metallic sample holder. The point of the Cu triangle was worked into a hook and sharpened. This electrode could be used to connect the large electrode pads shown in fig7-2a. The electrodes was connected to the sample bias of the Agilent 5500 sample plate. Using this
device, CAFM measurements between a conductive AFM tip and a gold electrode could be performed. The results are shown in the next chapter.

**Probe station.** For conventional conduction measurements of organic materials deposited on gold electrodes, a Rucker probe station was used in ambient using soft probes. Probe stations in inert atmosphere and in vacuum with low temperature capability are available at the inorganic facility of the Molecular Foundry. Experiments are planned on these instruments in the future.

### 7. Second lithography step to solve gate leakage issues

The quality of silicon oxide deposited by PECVD is lower than thermal oxides grown from silicon wafers in furnaces. Both top and bottom contact Field-Effect transistors used for electrical measurements on organic thin films typically employ highly doped silicon as a gate and 100 to 200nm thick thermal SiO$_2$ as the gate dielectric. Due to the lower quality of the oxide, we observed gate leakage at biases as low as a few volts in the initial Coplanar FETs that we fabricated.

In order to reduce gate leakage, a second lithography step was used to pattern the gate and limit its overlap with gold electrodes (instead of depositing a full 80nm metallic layer over the 6” wafer). Fig7-8a shows an optical image of a wafer processed with this 2-step lithography at stage d of the process (see fig7-1). Regions where the gate is present have a gold color while the thin electrodes are grayish. A higher magnification image is shown in inset). Local defects either due to local bonding failure or lift-off defects are also emphasized by red frames.

![Image](image.png)

**Figure 7-8.** a.Optical image of a section of a 6” wafer after the anoding bonding packaging step. A zoomed image is shown in inset. The gold colored background corresponds to regions where the 80nm thick gate later is present. Au electrodes are thinner (12-15nm and appear in grey). The gate extends at the center of each set of 4 electrodes. Defects are emphasized by dark red frames, b. IV measurements between source and drain at various gate voltages. The offset between curves corresponds to leak currents.

Even after minimizing the overlap between the gate and electrodes, leakage remained an issue. Fig7-8b shows a graph of the current measured between the source and the drain at different
gate biases as the source-drain voltage is ramped from -20V to 20V. The leakage is a few pA at 10V gate bias. In some devices it reached 1nA at 30V. Although this is a significant improvement compared to the leakage in non-patterned gate wafers, these specifications limit the range of available gate bias. 40 to 50V gate bias are routinely applied in OFETs with gate dielectric thickness of 150-200nm.

To improve the gate dielectric characteristic further, an additional step could be implemented. A layer of Hafnium oxide could be deposited by Atomic Layer Deposition. The layer, located in-between the PECVD SiO$_2$ and the gate, would provide an additional insulating barrier against gate leakage.

**Conclusions.** The overall process is made of a number of steps and processing of a wafer takes 2 to 3 full days of work using 7 to 10 different instruments (spin-coating, lithography x2, evaporation x2, PECVD x2, anodic bonding, polishing and etching). However a key advantage of the technique is the sheer number of working electrode sets produced in a single run. A single 6” wafer can thus be used for an extended period of time due to the amount of samples prepared in one run.


3 http://microlab.berkeley.edu/labmanual/chap6/oxford2.pdf

4 http://nanolab.berkeley.edu/labmanual/chap9/9.02ksbonder.pdf
Chapter 8.  Nanofabrication of a platform coplanar electrodes and FETs: AFM structural and electrical analysis

In order to make electrical contacts with soft organic materials such as monolayers, electrode platforms with feature dimensions comparable to molecular sizes are necessary. We achieved this with coplanar electrode-dielectric substrates with roughness and heights in the sub-nanometer range, as shown by AFM images of the fabricated devices. With this platform, we probed the electrical properties of organic monolayers in combination with AFM characterization. A D5TBA submonolayer was deposited on the substrate by the Langmuir-Blodgett technique. By spatially mapping the current flowing laterally from the AFM tip through the submonolayer to the embedded electrodes, we could study the conductivity of the monolayer in relation with its crystallographic structure, as well as its contact resistance to the electrodes. In comparison with traditional 20nm thick electrodes overlayed on SiO2 we found that the contact resistance on the embedded electrodes was at least 40 times lower than the best non-coplanar devices.

Various techniques have been employed to design an electrical contact that can probe organic thin-films non-invasively. Actuated compliant probes that can contact soft organic systems with minimal damage have been developed. Boggild et al designed multi actuated probes for 4-point measurement on ultra-thin organic films and could combine this set-up with scanning probe to study working devices in Kelvin probe force microscopy. Monolayer field effect transistors (FET) were fabricated by Smit et al by under-etching gold electrodes and preparing a silane based self-assembled monolayer on the SiO2 dielectric. The SAM extended underneath the under-etched electrodes which provided a reliable electrical contact.

Another method is to embed metallic electrodes in an insulator to create a coplanar metal-insulator-metal junction for bottom contact organic FETs. In addition to reducing the damage at the contact, a planar configuration makes it possible to study the interface at high resolution by AFM. In several attempts to fabricate such devices, a pattern was created by etching a silicon oxide substrate, followed by the evaporation of a layer of gold with a thickness equal to the etched material. Xu and coworkers used this technique and obtained a coplanar device. However spikes at the edges of the electrodes due to the evaporated gold adhering to the walls of the resist were present. Higuchi added mechanical polishing to that protocol in order to smoothen the device. Using a similar method, Singh obtained a co-planar surface but the electrodes were decorated by a trench which was 50nm and 5nm deep. Xu and Singh compared the performance of their coplanar transistors with regular non-planar devices and found that the mobility was 30% to 70% higher, while the contact resistance and threshold voltage were up to 50% lower in the planar configuration. Xu studied 60nm thick films of pentacene while Singh focused on P3HT nano-fibrils that were 50 to 100nm thick. These
materials are thicker than the 2.5nm thick monolayer investigated in this study and less sensitive to the planarity of the device and to defects such as trenches or spikes. Finally, Tsutsui et al used a replica technique that has several similarities with our method and could obtain nearly coplanar devices with less than 1 nm peak to peak roughness. Applications of these devices have not been reported to this date.

In this chapter, we describe the AFM analysis of the coplanarity of the platform which fabrication process was presented in chapter 7. We also present preliminary results related to the electrical characterization of organic monolayer films using coplanar Au embedded electrodes and coplanar FETs. We show that the contact resistance between the monolayer and electrodes is at least 40 times lower when using embedded electrodes compared to regular 20nm thick.

1. AFM analysis of coplanar electrodes and coplanar FETs after fabrication.

General characteristics. We used AFM to acquire topography images of the coplanar embedded electrodes and the coplanar FETs fabricated by the replica technique detailed in chapter 7. Figure 8-1a illustrates the morphology of 4 electrodes embedded in a silicon oxide dielectric. The gold electrodes are visible as their roughness is higher than the surrounding SiO2.

The critical parameters that we use to assess the quality of the coplanar electrodes are:

a. The height step at the interface between the electrodes and the dielectric.
b. The RMS roughness of the dielectric.

c. The RMS roughness of the electrodes.

A height profile acquired in the location indicated by a black dotted line is displayed in fig8-1b. Black arrows indicate the location of the Au/SiO2 interface in the topography image and in the profiles. The height steps were respectively 1nm and 0.3nm for the top and bottom interfaces in fig8-1a. These values are representative of the spread observed around the electrodes with steps ranging from a few angstroms to 2nm. The average step height measured at ten locations of the Au-SiO2 interface for the electrode located at the top of fig8-1a was 9Å with a standard deviation of 6Å. Fig8-1c shows a close up image of the electrodes and the heterogeneity at the Au-SiO2 interface. In the next section of this chapter (see fig8-6), we discuss the effect that the heterogeneity of the height step is expected to have on the contact between the electrodes and organic materials deposited on top of the device.

![Figure 8-2. a. Topography AFM image of Au electrodes with a nominal thickness of 12nm. The electrode is composed of a network on inter-connected grains and its RMS roughness is 11Å, b. Line profile taken along the whole width of the topography image, c. AFM image of Au electrodes with a nominal thickness of 15nm. The electrode is composed of a coplanar gold films with holes a few nm deep. Its RMS roughness is 5.3Å over the coplanar top surface and 11Å when the measurement includes the holes, b. Line profile taken along the whole width of the topography image.]

The height step at the Au/SiO2 interface is mostly due to the transition from a flat dielectric to a rough electrode surface. The gold RMS roughness was 1nm due to its grainy structure. We will show in the next section that for more closed and flat gold films, a trench was observed at the Au-SiO2 interface. Such trench is detrimental to the quality of the contact between soft materials and electrodes. Improving the flatness of electrodes and solving trench related issues could therefore be key to the performance of the device.

Along with the step height at Au/SiO2 interfaces, the roughness of the silicon oxide dielectric is a central specification of the device. Materials that serve as the channel between electrodes are supported by the dielectric. Its roughness should be low enough to ensure the integrity of
fragile thin materials such as monolayers. We showed by electron diffraction experiments (chapter 4) that there was a significant difference in the quality of diffraction patterns obtained from monolayers deposited on support with 3.5Å and 5.5Å RMS roughness. The dielectric in fig8-1a and fig8-1c has a surface roughness of 3Å. This number compares well with thermal oxide employed for dielectric in a number of organic FETs, which roughness is in the order of 4-5Å RMS.

In addition, some height variations can be observed as dark regions within the oxide in fig8-1a. These height variations are smooth as the topography varies by less than 10nm over micrometers (as opposed to the sharp step observed at the SiO2/Au interface). We described the origin of these features in chapter 7. They have no influence on organic material deposited on the device.

**Gold electrodes.** Depending on the nominal thickness of evaporated gold electrodes, the morphology of gold electrodes was different. Fig8-2a shows a topography image of 12nm thick gold electrodes embedded in SiO2. A profile is shown in fig8-2b. The gold layer is composed of interconnected grains separated by 1-2nm gaps. The RMS roughness of these electrodes was 11Å. On the other hand, fig8-2c shows an image of a gold electrode with 15nm nominal thickness. The gold film appears to be much more closed. A number of holes a few nm deep can be observed but the rest of the film is flat with a RMS roughness close to 5Å. If the holes are included in the measurement, the roughness is 11Å. As mentioned earlier, the flatness of the gold film is less critical than other specifications of the coplanar electrodes.

![Figure 8-3. a. Topography AFM image of gold electrodes embedded in silicon oxide, b. Zoomed-in topography image showing the interface at higher resolution, c. Height profile taken along the white line on at the center of b.](image)

**Trench.** When electrodes were evaporated with a nominal thickness of 15nm, they were surrounded by a trench which was a few tens of nanometers large and 1 to 5nm deep. The topography image in fig8-3a shows the interface between a gold electrode and the dielectric. A dark line can be observed along the edge of the gold.
The zoomed-in topography AFM image in fig8-3b shows that the trench is irregular. A height profile was taken along the white line and shows that the trench is 3 to 4nm deep and 30 to 40nm large (fig8-3c). The average height of the electrode is 1nm higher than the dielectric. The effect of this topographical feature on the connectivity of monolayer deposited on Au/SiO2 substrates has not yet been fully investigated but it is expected that in regions where the trench is the widest, the monolayer cohesion would be affected (although we observed that the monolayer could bridge holes in holey supports for TEM analysis). The origin of this feature is not clear. They could be caused by two main effects: non-wetting of the SiO2 CVD dielectric during deposition or shadow effects could be responsible. Expansion and contraction of the gold grains upon heating and cooling of the wafers during PECVD and bonding could also explain this phenomenon.

2. AFM characterization of organic monolayers on coplanar electrodes and FETs

A sub-monolayer of the oligothiophene D5TBA was deposited on the surface of a coplanar electrodes platform by the Langmuir-Blodgett technique. As mentioned in chapter 2, the advantage of this preparation method is that crystals formed at the air water interface can be transferred on a variety of different substrates while retaining the same morphology and the same crystal structure.

Figure 8-4. Topography AFM image of a submonolayer deposited on embedded Au/SiO2 substrate showing that monolayer islands prepared by the Langmuir-Blodgett technique are deposited on both Au and SiO2 and have the same morphology, b. Corresponding lateral force image. The internal boundaries are visible for islands deposited on the SiO2 but not over Au which indicates that the roughness of the gold cause defects in the monolayer.

Fig8-4a shows a topography AFM image of several D5TBA islands overlapping between the silicon oxide dielectric and a gold electrode (which is located at the bottom of the image). Islands are continuous over the interface. The grain boundaries between crystalline domains of D5TBA islands are visible in the lateral force image (fig8-4b) for islands located over the oxide. The boundaries are not visible over the gold, instead the contrast seen in lateral force mirrors
the height contrast observed in topography. This is due to the grainy structure of the gold films. The D5TBA polycrystal is deposited and coats the grainy substrate in a conformal manner which leads to the creation of subdomains within the islands.

Figure 8-5. Topography AFM image of 3 gold electrodes embedded in silicon oxide, b. Height profile acquired along the black dotted line. 2 and 4 indicate height steps due to the Au/SiO2 transition. Both steps are close to 5Å. 1 and 3 indicate height steps corresponding to the monolayer islands which are 2.6nm high, c. Zoom on a D5TBA island overlapping the SiO2/Au interface showing that the monolayer adopts the grainy structure of the Au electrodes due to conformal deposition.

Fig8-5a shows a topography AFM image of several monolayer islands over 3 gold electrodes and the dielectric surface. Although no single island bridges two electrodes, islands are physically connected to each other. We will show in the next section that electrical carriers can be transported across boundaries between islands. A height profile is provided in fig8-5b with arrows pointing at several specific features. The cyan arrows #1 and #3 indicate discrete 2.6nm height step at the edge of the molecular islands. Blue arrows #2 and #4 correspond to the edge of the electrodes where the step height was in the order of a few Å.

Figure 8-6. a. Topography AFM image of a D5TBA island at the interface between Au and SiO2. The interface is heterogeneous. A narrow and shallow trench is visible in locations designated by arrows. The contact between the monolayer and the electrode is likely worse in these regions. On the contrary, the height step is small in regions designated by a dotted line square where the contact is likely better.

We recorded images of the boundary between the dielectric and the electrodes at higher magnification. Fig8-6a and fig8-6b show 1μm large topography and friction AFM images of a D5TBA island located at the edge. As described in the previous section, the interface is not homogeneous due to the roughness of the gold electrode. In locations indicated by rectangular frames in fig8-6a, the oxide and the gold are almost coplanar. The black arrows point at
locations where the step is larger, in the region of 1nm. One can expect the electrical contact between the monolayer and the gold to be better in coplanar regions.

A lattice resolved analysis of the monolayer at the boundary between the dielectric and the gold could assess the effect of the height step on molecular order. These experiments have not been carried out at this time but are planned in the future.

**P3HT thin film on coplanar electrodes.** In order to test coplanar FETs on a well-documented model system, we spin coated films of P3HT on the surface of the device. The solution was deposited on the wafer and the spinner was set to 2500 rotations per minute for 40s. The sample was then imaged in contact mode AFM. Fig8-7a shows a topography AFM image of the centre of a 4-electrode set. The Lewis formula of a 3-monomer section of P3HT is shown in inset. The sample was scanned in contact at high load (100nN) to assess whether a film had been deposited. Fig8-7b shows an image centered on a gold electrode acquired after zooming out from the region scanned at high load.

![Figure 8-7. a. Topography AFM image of the surface of a coplanar FET after deposition of a P3HT film (the Lewis formula of 3 P3HT monomers is shown in inset), b. Topography image obtained after scanning the central rectangular at 100nN applied load. The film in this region was scrapped off allowing measuring the film height which was 3nm.](image)

The part of the image labeled as “bare substrate” was 3nm lower than the rest of the sample. In this region, the P3HT film had been removed. The bright yellow portions located at the boarder of the bare region correspond to the material that has been removed from the surface and displaced by scanning. These results show that although it is not obvious from fig8-7a, a 3nm thin P3HT film had been deposited and that it coated the wafer conformally. Electrical measurements on these samples have not been performed yet.

*These results of this section are very encouraging as they show that the critical dimensions of the coplanar electrode-dielectric surface match the scale of organic monolayers. The next part of this chapter is devoted to electrical characterization of the contact between organic monolayer and gold electrodes using CAFM.*
3. Electrical characterization of organic semiconductors by combining CAFM with coplanar electrodes

**Proof of concept.** In order to investigate the nature of the contact between the monolayer and the electrodes at the gold-oxide interface, we used atomic force microscopy in the conductive mode and measured the current flowing from a conductive tip, through DSTBA monolayer islands to an electrode. A schematic of the set-up is displayed in inset of fig8-8a. Topography, lateral force and current images acquired at the edge of a gold electrode embedded in SiO2 are shown in fig8-8a, b and c. In fig8-8a, a black dotted line is drawn to locate the SiO2-Au boundary which is clearly visible in the lateral force image (fig8-8b). The friction is higher on the electrode which is located on the right hand side than on SiO2. The dark areas of the topography image correspond to the same smooth height variations that were described in section 1 of this chapter and in the previous chapter.

![Figure 8-8](image-url)

Figure 8-8. a. Topography AFM image of a DSTBA submonolayer on a SiO2 (left) and an embedded gold electrode (right). A dotted line indicates the location of the edge of the electrode. The dark regions are smooth height variations at the surface due to stress relaxation, as described earlier, b. Corresponding lateral force AFM image. Molecular island appear darker than the porous phase and the SiO2 and Au substrates. The frictional force of islands located on Au is higher which could be due to reduced molecular order or weaker bonding due to the weak interaction between the COOH termination and Au, c. Corresponding current image acquired while applying xV to the electrode while the tip was grounded.

The height step between the SiO2 and Au is between a few Å and 1nm along the edge of the electrode. As shown by the lateral force image, several islands overlap between the Au electrode and the SiO2. The current image in fig8-8c acquired at -5V sample bias shows that the monolayer is electrically connected to the electrode since current is detected on islands located
on the dielectric. Interestingly, the islands which are not in direct physical contact with the electrode are also connected showing that inter-islands boundaries have a finite resistance but can transport current. Images in fig8-8 were acquired in ambient conditions. We have described in chapter 4 how CAFM experiments led to the conclusion that water could enhance conductivity in the monolayer by a doping like mechanism.

When repeating the AFM experiments of fig8-8 on a dry sample and in N2 atmosphere, we found that the current measured on the monolayer was 50 to 70% lower. These results are intriguing and require further investigation. In a recent Physical Review Letters paper, Leary and coworkers described how the presence of water could gate oligothiophene molecules and enhance their conductivity by shifting the onset of resonant tunneling. In chapter 5, we described CAFM results pointing at an enhancement of the conductivity of D5TBA monolayer at positive sample polarity, i.e. when the LUMO was involved. Based on the work function of the Pt tip and of the Au electrode, and on the proximity of the HOMO to these levels, the orbital involved in transporting current in fig8-8c is most likely the HOMO. These results suggest that the effect of water might apply to both the HOMO and the LUMO.

**Comparison between coplanar electrodes and regular electrodes in CAFM.** For comparison with the traditional non-coplanar electrode devices we patterned similarly shaped 20 nm thick electrodes on silicon substrates with 100 nm of thermally grown oxide. We recorded CAFM images of a LB D5TBA submonolayer close to the edge of an electrode. The tip was grounded while a -5V bias was applied to the gold electrode. A schematic of this experiment is shown in fig8-9b.

![Figure 8-9](image-url)

**Figure 8-9. a.** AFM topography image of D5TBA crystalline islands deposited on a silicon oxide wafer patterned with 20nm thick gold electrodes. The contour of a molecular island is emphasized in white, b. schematic of the CAFM set-up used to probe the conductivity of the monolayer and the contact resistance between the monolayer and the gold electrode, c. CAFM image showing 2 monolayer islands electrically connected to a gold electrode located at the top of the image. The image was stopped when the tip reached the electrode because it was found that tip contamination occurred when scanning over the electrode. A current profile acquired along the dark dotted line is shown in inset.

Fig8-9a and fig8-9c show topography and current images of the monolayer. The electrode is located at the top (bright yellow region). The current image shows that two islands which are in physical contact with the electrode are also connected electrically although unequally. The
island with the highest current level is emphasized by white contours in both fig8-9a and fig8-9c. Close to the electrode, the current level is -50pA so that the total series resistance between the two contacts (the sum of the tip-monolayer resistance, the intrinsic resistance of the film and the contact resistance at the electrode) is approximately 100GΩ at -5V.

This 100GΩ total series resistance is dominated by the electrode-monolayer contact resistance. Indeed, an upper limit to the tip-monolayer contact resistance can be estimated at 5GΩ, since when the tip is in contact with the monolayer located on top of the electrode, the current measurement is saturated, which implies the current is >1nA. Also the results of CAFM on embedded electrodes shown below (fig8-10) prove that the resistance of the monolayer is in the range 1-20GΩ, well below the total 100GΩ series resistance. In addition, we observed that most molecular islands that appeared to be in physical contact with the electrode did not show any current when contacted by a conductive AFM tip, implying that they are not connected electrically. These islands are probably disordered or otherwise damaged at the electrode interface.

Figure 8-10. a. AFM topography image of D5TBA crystalline islands deposited on a silicon oxide with 12nm thick embedded gold electrodes, b. Schematic of the CAFM set-up used to probe the conductivity of the monolayer and the contact resistance between the monolayer and the embedded electrode, c. CAFM image showing 3 monolayer islands electrically connected to a gold electrode located at the top of the image. The central island is emphasized by a white contour. The current level measured in various parts of the islands is displayed on the image. A profile acquired along the black dotted line is shown in inset.

Fig8-10a and 10c show topography and CAFM images of a D5TBA monolayer at the edge of an embedded gold electrode. The current varied from tens of pA to ≥1nA (saturation of the current amplifier) close to the electrode edge. The current profile in the inset shows a sharp gradient (0.5nA in 50nm) and the current reached saturation when the tip was 100nm away from the electrode. By extrapolating the current gradient, the current would be higher than 2nA at the Au-SiO2 interface so that the sum of the tip-monolayer and monolayer-electrode contact resistances was below 2.5GΩ. The contact resistance is therefore at least 40 times lower than in the non-planar geometry. It should be noted that for the experiment shown in fig8-9, the island with the best contact was used. So for most islands, the contact resistance is orders of magnitude higher in the non-planar configuration compared to the coplanar device.
The details of the current image show that in the planar configuration, the measured current displayed clear variations within single islands. This implies that the electrical circuit was not dominated by contact resistance, but by the conductance of the islands themselves. Several levels of current can be observed, as indicated on the image. Close to the electrodes, the current was saturated. It dropped to 0.3nA in the top left region of the molecular islands, which corresponds to an increase in resistance in the order of 10GΩ. In the top right-hand region of the central island, at the same distance to the electrode, the current was only 200pA and there appears to be a sharp boundary between these two regions.

The fast scan direction of the AFM tip in fig8-10c is horizontal, so that the appearance of a sharp vertical boundary cannot be attributed to a change in the state of the AFM tip. Finally, the current reads 80pA on the bottom island which is in physical contact with the large central island through an inter-island boundary. Both variations correspond to series resistance increase of about 10GΩ. From these results, one can reach two conclusions. For regular 20 nm thick non planar electrodes where the contact resistance varies between 100GΩ and infinite resistance, little information can be obtained about the conductivity of the organic monolayers because the contact resistance masks any features specific to islands. For embedded electrodes, the contact resistance is below the resistance of the crystalline monolayer and grain boundaries.

Interestingly, only one boundary with significant resistance is present in the D5TBA island measured in fig8-10. From lateral force measurements images shown in chapter 3, we know that a D5TBA island is typically composed of a number of finger-like domains separated by boundaries. Based on analysis of fig8-10c, most of those grains boundaries have little effect in a current measurement. Such conclusion would be in agreement with the fact that we could detect current anisotropy in D5TBA islands in spite of the presence of grain boundaries (chapter 6).

4. Injection barrier at the Au-monolayer interface

IV spectroscopy measurements were done in the CAFM configuration. We found that the IV characteristic was asymmetric with higher current flowing when the gold electrode was negatively biased in both the coplanar and regular electrodes configurations. Fig8-11a shows an IV curve recorded on the same monolayer island from which the data in fig8-9 was obtained using the set-up shown in the schematic of fig8-9b. The current flowing when the gold electrode is positively biased is negligible compared to the current at negative bias.

As mentioned in chapter 5, the HOMO of D5TBA and 5TBA is located between 4 and 5.5eV. Oligothiophene are qualified as p-type because the work function of conventional electrodes used in organic electronics such as Pt and Au is closer to the HOMO than the LUMO. As a result, charge injection is easier in the HOMO than the LUMO. The term “p-type” is therefore related to the energy level of frontier orbitals rather than the intrinsic hole or electron transporting properties of the molecules. The molecular orbital involved in experiments described here is therefore most likely the HOMO.
The asymmetry of the IV characteristics is related to hole injection from the electrodes into the HOMO so the rectification could be due to the formation of a Schottky barrier at the metal-semiconductor interface. The origin of this barrier is the mismatch between the electrode work function and the Fermi level of the molecules which causes the accumulation of charges at the metal-semiconductor interface, as illustrated by fig8-11b. Upon contact, holes flow from molecules into the electrode inducing a local negative charge at the interface. The potential barrier induced by this local charge limits the injection of holes from the electrode into the molecules.

Figure 8-11. a. IV characteristic measured by CAFM on the molecular island shown in fig8-10, b. Schematic of the formation of a Schottky diode at the interface between metallic electrodes and the monolayer.

The size of the Schottky barrier increases with the energetic difference between the work function of the electrodes and the Fermi energy of the monolayer. The nominal work functions of gold and platinum are 5.1eV and 5.65eV respectively. This difference could account for the higher current measured when holes are injected from the Pt tip compared to an Au electrode. A very detailed study of charge tunneling across an alkanethiol monolayer showed that the conductance could vary by orders of magnitude depending on the metal coating the AFM tip. The current was the highest with the tip that had the lowest work function.

Finally, another factor that could be critical is the fact that the Pt tip is a point contact which induces an electric field distribution distinct from that of an electrode.

5. Gating effects in CAFM

We used a CAFM configuration similar to experiments shown in fig8-10 but with a buried gate to measure the effect of gate bias on the conductivity of a D5TBA monolayer. The 2 CAFM images in fig8-12a and fig8-12b were acquired simultaneously. In each scan line, a first pass was done at 0V gate bias and a second one at +20V gate bias. A gold electrode is visible on the right hand side of fig8-12. A red contour shows the initial location of the electrode. As evidenced by the CAFM image, the electrode was damaged during fabrication. Three more electrodes are located at the bottom, top and left of the location shown in the image.

A molecular island is electrically connected to an electrode located below and not shown in the image. Although a molecular island is visible at 0V gate bias, no current is recorded at +20V gate bias, indicating that the conductivity of the D5TBA monolayer decreased upon applying a
positive gate voltage. The current level is very low in this experiment because the tip became contaminated when scanning on the monolayer located on gold electrodes (molecules tend to desorb from the Au electrode when scanned in AFM). The effect of positive gate bias is in accordance with the p-type nature of D5TBA oligomers since applying a positive gate bias induces a depletion of holes in the monolayer which forms the channel of the transistor. At negative gate bias, the conductance of the island increased but not significantly.

These results of gated experiments are encouraging but still preliminary. In order to bypass the issue of tip contamination, a solution would be to obtain topography images of the layer in tapping mode or non-contact mode. Current measurements would then be carried out by bringing the tip in contact locally and doing IV spectroscopy at various gate biases to obtain transistor IV characteristics. With the tip immobile in contact, the contamination by organic molecules would be less severe.

![Image](image_url)

**Figure 8-12.a** CAFM image recorded at -1V electrode bias and 0V gate bias. A few pA flow between the AFM tip and an electrode (not visible in the image) through a molecular island. **b**. CAFM image recorded at -1V electrode bias and +20V gate bias. No current flows through the central island which is therefore not visible in the image. Fig8-12a and fig8-12b were recorded simultaneously by switching the gate bias on and off at each scan line.

**Conclusion.** Through topography AFM analysis, we showed that the surface of electrode-dielectric platforms was coplanar with an average step of 1nm at the Au-SiO2 interface. It is likely that the contact to the monolayers is the best in the region where this step is a few Å. The height of the step could be reduced by solving issues related to the roughness of the gold electrodes. The specifications of the coplanar devices fabricated by the replica technique are above those of reported embedded electrode devices described in the introduction that were tested by using thin films or 50nm thick polymers fibrils.

The electrical characterization of soft organic material using this platform is still in an early stage. We showed that the contact resistance was improved by a factor between 40 and several orders of magnitude for the coplanar electrodes compared to regular 20nm thick ones. In addition to monolayers, we plan to characterize organic nano-wires and polymer ultra-thin films using this platform.


Chapter 9. General conclusion and outlook

This research work aimed at developing solutions to shift the characterization of organic semiconductors from macroscale averaging techniques to the scale of single 2D crystalline grains to account for the fundamentally heterogeneous nature of these materials. Analysis of both the structural and electrical properties of these semiconductors is needed as the two are strongly correlated and a mechanism for electrical conduction can only be based and confirmed by understanding the way molecules arrange in thin films and crystals. In this thesis, the application of established techniques and the development of new methods for the structural and electrical investigation of ultra-thin organic films were described, along with the Langmuir-Blodgett method.

For the preparation of organic monolayers and few-layer films, the LB technique was selected because of several unique features. Monolayer crystals were prepared at the air-water interface and could be transferred on essentially any substrate with little or no variation of their structure (chapter 2). These monolayers were robust and sustained both AFM and TEM analysis with an amount of structural damage that did not prevent key information from being extracted.

Atomic Force Microscopy was used to analyze the morphology and the microstructure of ultra-thin films at high resolution. This technique can be used in-situ while performing electrical measurements (chapter 3). Spot scanning electron diffraction in a TEM microscope provided detailed structural maps of the crystalline lattice and its orientation in 2D crystals (chapter 4). Both TEM and AFM are applicable to a wide range of ultra-thin film materials and not limited to oligothiophene monolayers described in this study.

The electrical analysis techniques used in this work were Conducting probe AFM, coplanar electrodes and field effect transistors. A novel method based on the presence of an insulating oxide layer between an organic film and a bottom silicon electrodes made it possible to investigate in-plane electrical conductivity in monolayers in CAFM (chapter 5). This technique has two key advantages. It can be used to study fragile materials easily destroyed by macroscopic probes thanks to the high level of control of the force applied with the AFM tip. In addition, its implementation is simple as it only requires a microscope with CAFM capability and environmental control. With this technique, we were able to investigate the correlation between conduction properties of DSTBA monolayers and structural factors such as their molecular order and their lattice orientation (chapter 6). We also developed methods that can be implemented for in-plane two and three-terminal measurements (the mechanical manipulation and nano-patterning techniques).
In order to make electrical contacts with monolayer films, we developed coplanar electrode-dielectric substrates with roughness and surface topography in the sub-nanometer range. The fabrication technique involves a number of processing steps (chapter 7) but produces wafers composed of a large amount of samples. Analysis of the nano-fabricated platform by topography AFM showed that coplanarity in the range of a few Angstroms to 1nm had been achieved (chapter 8). The electrical characterization of the monolayers with this device is still in a preliminary stage but we could demonstrate that the use of a coplanar substrate induces critical improvements in the electrical contact between the ultra-thin film and metallic electrodes.

The tools and methods developed in this PhD work can now be applied to a variety of organic materials including p and n type semi-conductors, small molecules and polymers assembled in monolayers or ultra-thin films with varying degrees of crystallinity. There is potential for further improvement of coplanar FETs in terms of electrodes roughness and leakage through the dielectric. The platform is compatible with additional techniques such as Kelvin Probe Force Microscopy with which one can map the potential distribution across working devices and study charge trapping mechanisms in OFETs.