

AN ABSTRACT OF THE THESIS OF

Chloe Castaneda for the degree of Bachelor of Arts in Physics presented on
April 27, 2016.

Title: An Analysis of Regioregular Poly(3-hexylthiophene-2,5-diyl) Using Kelvin
Probe Force Microscopy

There is a constant push for innovative applications of electronics. The traditional materials used to construct these devices, such as inorganic silicon, are expensive and brittle. Semiconducting conjugated polymers offer an exciting alternative to manufacturing materials, as they are flexible and affordable to mass-produce. A significant amount of work has been done in the field of organic electronics since conjugated polymers were first found to be conductive several decades ago. The approaches to studying the characteristics of these materials are varied including simulations, dielectric spectroscopy, electrostatic force microscopy, and scanning Kelvin probe microscopy. Groups have looked at how to evaluate charge carrier mobility, threshold voltage, trapping/detrapping processes and time scales, the shape and behavior of the density of states, and pinch off voltage. The focus of our interest is on understanding charge carrier transport, mobility, and the effects of trap states of these characteristics. This is studied through an unconventional use of KPFM as well as standard IV characterization. While other research groups have previously modeled trap states, we hope to understand how different manufacturing

processes passivate traps to improve mobility and how the behavior of trap states change at different back gate voltages.

This work will discuss our approach to studying P3HT, a polymer of choice for its good optoelectronic properties. We use atomic force microscopy to record traditional IV transistor curves as well as use KPFM to scan across the transistor channel and record the behaviors of charge carriers at a single point on the device

©Copyright by Chloe Castaneda
April 27, 2016
All Rights Reserved

An Analysis of Regioregular Poly(3-hexylthiophene-2,5-diyl) Using
Kelvin Probe Force Microscopy

by

Chloe Castaneda

A THESIS

submitted to

Mount Holyoke College

in partial fulfillment of
the requirements for the
degree of

Bachelor of Arts

Presented April 27, 2016
Commencement June 2016

ACKNOWLEDGEMENTS

I dedicate this to the amazing female mentors in my life, like my mother, Jennifer, and my undergraduate adviser, Kathy. These people never cease to encourage and awe me. To the physics family. If it weren't for you, I don't think I'd have stuck this out. To Jason for teaching me to use the AFM and sending me memes in my dark hour of writing. And honestly, I would like to acknowledge my own work on this paper. I never thought I was a smart kid, but with some blood, sweat and tears, I made this happen. To all young researchers, you can do it too, just persevere

TABLE OF CONTENTS

	<u>Page</u>
1 Introduction	1
1.1 Background	1
1.2 Potential and Challenges	2
1.3 Charge Transport Introduction	2
1.4 Our Focus	6
1.5 Previous Work	8
2 Charge Motion in Conjugated Polymers	10
2.1 Field Effect Transistor	10
2.2 Current Voltage Characterization	11
2.3 Density of States	14
2.4 Charge Transport	14
3 Materials and Methods	19
3.1 Sample Preparation	19
3.1.1 No Surface Treatments	20
3.1.2 Silanized Surface	20
3.1.3 Annealing	20
3.2 Testing	21
3.2.1 IV Characterization	22
3.2.2 SKPFM	22
3.2.3 Time-resolved KPFM	25
3.3 How to Read our Results	30
4 Results	31
4.1 Current	31
4.2 Mobility	31
4.3 Distance	32
4.4 Time Resolved KPFM	33
4.4.1 Single Step	33
4.4.2 Multi-step	35

TABLE OF CONTENTS (Continued)

	<u>Page</u>
5 Discussion And Summary	38
5.1 Challenges of Samples	38
5.2 Challenges of Analysis	39
5.3 Summary and Future Work	40
 Bibliography	 41
 Appendices	 44
A SOPs	45
B Materials	77

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1.1	An illustrations of the differences in energy levels, or band gaps, for conductors, semiconductors, and insulators. hyperphysics.phy-astr.gsu.edu/hbase/solids/band.html	3
1.2	(a) Energy diagram of two interacting carbon atoms. sp_2 and p_z atomic orbitals of the two individual carbon atoms combine o form pi, sigma, and nonbonding molecular orbitals. (b) A band structure starts emerging with a narrowing band gap when the conjugation length of alternating single and double bonds is increased. A HOMO and LUMO can be recognized as part of the valence band and conduction band, respectively. [5]	5
2.1	Side and top views of an inverted FET device	11
2.2	Drain bias sweeps for different gate voltages.	13
2.3	Gate bias sweeps for different drain voltages.	13
2.4	Density of states for P3HT. Experimental (symbols) and calculated (lines) mobility as a function of carrier concentration for two different conjugated polymers P3HT and OC1C10 -PPV (solid line Gaussian DOS, dashed line exponential DOS)	15
2.5	Illustration of the energy gap between the conduction and valence bands with an example of an electron being excited to the CB. . . .	16
2.6	(a) Hopping conduction, (b) band conduction with local deep states.[11] 17	
2.7	Hysteresis during a drain voltage sweep with -40 V applied to the gate.	18
3.1	Left: the sample mount with electrical feeds. Right: rhe cantilever holder and membrane for sealing the holder.	21
3.2	Illustration of the KPFM feedback loop. www.spm.iis.u-tokyo.ac.jp	23
3.3	Description of the oscillatory force caused by a difference in tip and sample bias. www.spm.iis.u-tokyo.ac.jp	23

LIST OF FIGURES (Continued)

<u>Figure</u>	<u>Page</u>
3.4 (a) The first pass, or topography scan, across the conducting channel in our FETs. (b) The second pass, or potential scan, across channel. (c) Line sections of the height information and potential.	25
3.5 Example of bias applied to gate with the single step point KPFM program. In this case, the gate is initially grounded and the KPFM records the surface potential for 1 second before a -7V bias is applied, and then after the bias is removed for 1 second.	26
3.6 Control sample surface potential responses over Au electrodes and Silicon Oxide.	27
3.7 The changes in surface potential for applying and removing gate biases.	28
3.8 The changes in surface potential for applying and removing gate biases with explanations.	29
3.9 Typical response graphs for the incremental step program, possibly showing effects of bias stress.	30
4.1 Description of the oscillatory force caused by a difference in tip and sample bias.	32
4.2 Surface potential responses for applying an -6V bias to gate at different distances away from gap for (a) recorded peak height, and (b) peaks normalized by peak height.	33
4.3 Inversion in time-resolved KPFM response peaks in measurements taken over P3HT and gold.	34
4.4 Plot of the shorter time constant extracted for every step from 0 to -50V.	35
4.5 Plot of the longer time constant extracted for every step from 0 to -50V	36
4.6 Stepping the applied gate voltage from 0 to -50V, and back to 0. We see with subsequent runs of the program, the device screens less quickly.	37

LIST OF FIGURES (Continued)

<u>Figure</u>	<u>Page</u>
4.7 Stepping the applied gate voltage from 0 to +15V, and back to 0.	. 37

LIST OF TABLES

<u>Table</u>		<u>Page</u>
4.1	Mobilities	31
4.2	Extracted Time Constants for Measurements Taken at Distances from the Conducting Gap	32

LIST OF APPENDIX FIGURES

<u>Figure</u>	<u>Page</u>
A.1 Pressure meter and valves on nitrogen canister	53
A.2 Components to assemble top of closed cell	54
A.3 Description of the oscillatory force caused by a difference in tip and sample bias.	55
A.4 Gold electrodes in contact with the sample clips	56
A.5 Where to place the ohmmeter lead to check for electrical connection on BNC cable	57
A.6 Assembled top of closed cell with clamp. Here you can see the screws on the clamp that tighten the membrane over the sample holder . .	58
A.7 Description of the oscillatory force caused by a difference in tip and sample bias.	62
A.8 Reaching under the mounted scanner head to release the clamp on the closed cell top.	63
A.9 BNC cables from controller box	65
A.10 Input with banana adapter on KEPCO	66
A.11 Crosspoint set up for dynamic gate or drain	67
A.12 How to find the Electric Tune Panel	69
A.13 A typical, good looking force curve.	69
A.14 Master Channel Panel potential tab set up	71

Chapter 1: Introduction

1.1 Background

Several decades ago, in the mid-20th century, scientists discovered semiconductivity was not a property unique to inorganic materials and observed it in a select group of polymers. These synthetic metals are conjugated polymers, meaning they contain alternating single and double carbon bonds, the fundamental property that makes them so interesting, which I explain in section 3 of this introduction. Integral early work of Heeger, MacDiarmid, and Shirakawa on polyacetylenes in the 1970s, research they later received the 200 Nobel Prize in Chemistry for, established the importance of these polymers.[1] Since then the number of publications on conducting polymers drastically increased as their versatile applications are explored. In this work we discuss the beginning of our systematic research on the electronic properties of Poly(3-hexylthiophene-2,5-diyl), or P3HT. We chose this material as it is a benchmark organic semiconductor because of its relatively high hole mobility and wide commercial availability [1, 2]. Studies of polythiophenes, the group of conjugated polymers that P3HT belongs to, came in the 1980s, a bit later than the initial publications on conjugated polymers. [3]

1.2 Potential and Challenges

The importance of conjugated polymers is made clear when one compares the production costs to that of traditional semiconductors, such as silicon. These ubiquitous traditional materials are expensive to manufacture with the desired quality and are very brittle. Organic polymer based electronics promise to significantly reduce costs, allow roll-to-roll processability, and offer the potential to create flexible devices. Today, some companies are already industrializing organic field-effect transistors (OFETs) for use in e-paper displays, circuits, and sensors. [4] The opportunities available for organic semiconductors do not end at e-paper displays; motivation for much research are long-lasting, flexible, organic light emitting diode (OLED) displays, heterojunction solar cells, and other forms of photovoltaics. The inherent compatibility of OFETs and OLEDs potentially offers devices with superior mechanical properties to those made with silicon or oxides. [4] Because this technology is at the forefront of scientific investigation, conjugated polymers will have some pitfalls. Different manufacturing techniques lead to a wide range in quality of deposited films with various types of defects, potentially leading to significant amounts of trapped charge and low mobility. By no means does that indicate a hopeless field though, as breakthroughs continue to be made.

1.3 Charge Transport Introduction

Traditional semiconductors, such as silicon and germanium, operate by electrons being excited from the valence band to the conduction band. The energy difference

contributing to the size of the band gap is intermediate between that of insulators and conductors, an illustration of which is seen in Figure 1.1.

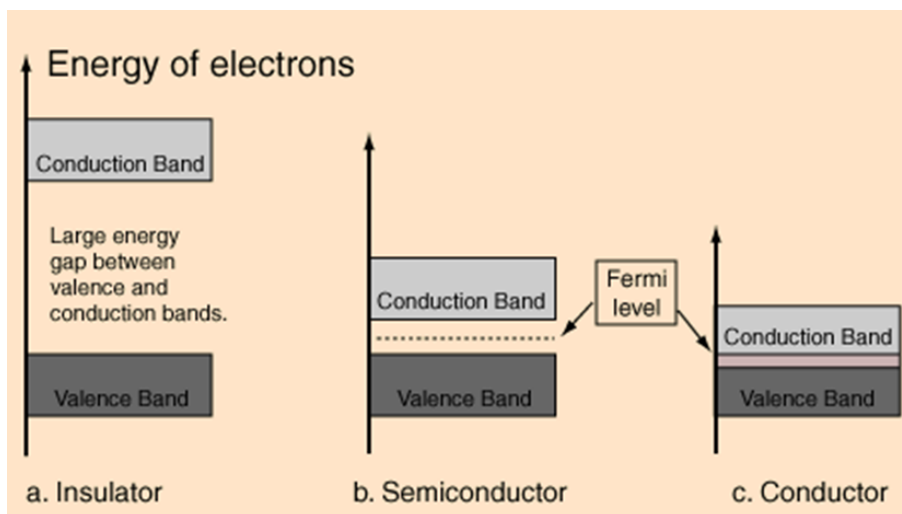


Figure 1.1: An illustrations of the differences in energy levels, or band gaps, for conductors, semiconductors, and insulators. hyperphysics.phy-astr.gsu.edu/hbase/solids/band.html

The fundamental property that gives organic materials their conductive properties are the alternating single and double carbon bonds consistent throughout the polymer backbone. This structure allows for the creation of a band gap with the properties of traditional semiconductors, and in turn the delocalization of charge. And understanding of the shapes of molecular orbitals arising from these bonds is not necessary for understanding this work, but it is important to note how their behavior contributes to the characteristic band gap. In a polymer chain, a given carbon atom has three electrons existing in sp_2 hybridized orbitals and one in a p_z orbital. Sp_2 electrons form bonds via sigma molecular orbitals; this is the only

orbital shape in single bonds. The p_z electron is used in a pi molecular orbital. Double bonds are formed through both sigma and pi molecular orbitals. If that seem a little confusing, its okay. The important result is caused by interactions between the p_z orbitals, which further spreads the energy levels of pi and pi* orbitals leading to the identification of a highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), or, essentially, the semiconductor band gap. [5] Figure 1.2 offers an illustration of HOMO and LUMO in relation to bonds and orbital splitting.

Organic materials do not strictly adhere to traditional conduction and valence band models of charge transport. The quality arises from charges existing as an intertwined combination of charge movements and structural deformation of the polymer backbone. [1] There are several proposed theories for the conduction mechanism of conjugated polymers, all of which can be found and argued for in some degree in the current literature. Peter Stallinga makes a solid point in his book, *Electrical Characterization of Organic Electronic Materials and Devices*, that settling on and agreeing with hopping versus conduction bands with deep localized trap states versus other models is not integral to exploring these materials. Fortunately, an exact model for charge transport is not necessary to our investigation, as we are more interested in the overall mobility of charges and the mechanics associated with deep trap states and how our newly developed technique, discussed in the next section, measures those characteristics. Overall, these van der Waals bonded materials offer charge carrier transport somewhere between low-mobility hopping of amorphous glass and the high-mobility of covalently bonded single crystals. [5]

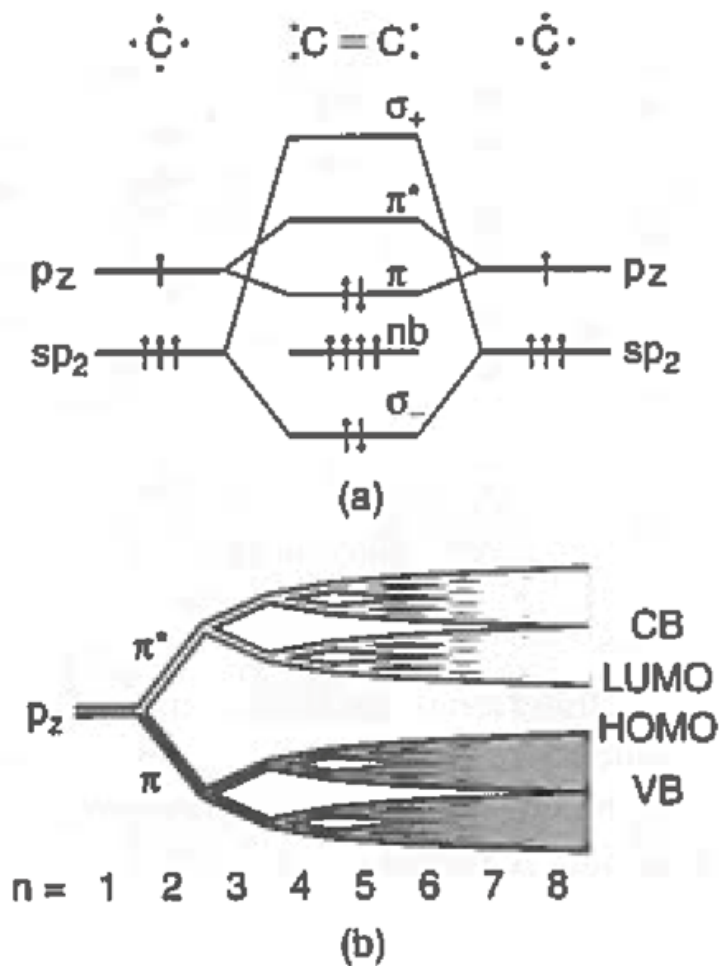


Figure 1.2: (a) Energy diagram of two interacting carbon atoms. sp_2 and p_z atomic orbitals of the two individual carbon atoms combine to form pi, sigma, and nonbonding molecular orbitals. (b) A band structure starts emerging with a narrowing band gap when the conjugation length of alternating single and double bonds is increased. A HOMO and LUMO can be recognized as part of the valence band and conduction band, respectively. [5]

1.4 Our Focus

As I mentioned previously, the purpose of our work is to explore charge carrier mobility in P3HT. More specifically, we are interested in the influence of trap states on the mobility. We look at this property by studying the electrical characteristics of three different sample preparations, using a non-traditional atomic force microscopy (AFM) technique. In addition to ac topography scans, we use Kelvin Probe Force Microscopy (KPFM) to measure surface potential. We developed a method to measure the changes in surface potential in real time at a single point in the film, implementing that and traditional scanning KPFM to explore the motion of charge carriers.

We use a field-effect transistor device architecture, illustrated in Figure 2.1, to study our samples with AFM. FETs are essentially a switch that turns on and allows current through when a voltage larger than the minimum needed, or threshold voltage, is applied to the back gate electrode. The samples are made from a silicon wafer with gold electrodes printed on top. We then put our sample through a series of baths to clean any large contaminants from the surface and use oxygen plasma for the rest. After plasma cleaning, different methods are implemented depending on the type of sample being made. The first set of samples will go directly to be spin-coated with a thin P3HT film. A second set will have a silane layer deposited on the surface of the insulator by sitting in an octadecyltrichlorosilane bath for 1.5 hours to passivate any traps in the silicon dioxide on the wafer surface and then be spin coated. A third batch will be silanized, spin-coated, and then annealed

on a hot plate at 150 degrees Celsius for half an hour to improve the crystallinity of the P3HT film. Through work done previously by other research groups, [2, 6] we understand that trap states arise from defects in our material as well as from the semiconductor-gate electrode insulator interface. This is what motivates us to manufacture our samples under different surface treatment conditions.

In our current procedure, after manufacturing our samples we test them within a day of their creation. We use an Asylum Research MFP-3D AFM to perform current-voltage characterization of our transistors, topographic measurements, and most importantly, Kelvin Probe Force Microscopy. KPFM is a technique that determines the difference in potential between the AFM probe and the chosen sample. [7] As a note, scanning KPFM, Kelvin Probe Microscopy, Kelvin Force Microscopy, and KPFM are all synonymous for the same technique. An AC bias is applied between the tip and sample, and if there is any potential difference, there will be an oscillatory force. The AFM software interprets the bias needed to minimize the force as surface potential information and attempts to return the system to its non-oscillatory state and begin the measuring process again at the next point. This is traditionally done by scanning the probe across a chosen section of the material. We use this process in addition to developing a method to record the behavior of charge carriers at a single point in the film, which will be referred to in this work as time resolved or point KPFM. We hover our probe tip above the film, both over the gold electrodes and over the silicon dioxide gate insulator, turn on the device by applying a voltage to the back-gate electrode, and the AFM software records the behavior of the holes in the P3HT. More on what we found

is discussed in the results chapter of this work.

1.5 Previous Work

Many previous studies looked at transistor devices made with organic polymers through various measuring methods, including Scanning KPFM. Tal et al. used the high lateral resolution of KPFM to calculate the density of states (DOS) around the HOMO level for their FETs and the effect of doping on the DOS. [12, 13, 14] These measurements were taken by scanning across the thin film transistor channel. In addition to their findings on DOS, they recorded behavior of their devices below the threshold voltage.

In 2015, McFarland et al. [15] expanded on Kalihari et al.'s work using KPFM to correlate local surface potentials to local morphologies in organic semiconductors by applying the knowledge to explore the effects of mono- and double-layer P3HT nanowhiskers, finding optoelectronic properties are significantly impacted by molecular packing and local environments. Moreover, in 2008, Hallam et al. [16] used scanning KPFM to investigate charge injection and trapping in zone-cast pentacene TFTs, in 2007, Smits et al. [17] used I-V and KPFM on unipolar and ambipolar OFETs to model charge transport, and in 2013, Pingel et al. [18] used the technique to look at charge injection over low and high work function metals in undoped and doped P3HT and derived a DOS from the HOMO and LUMO levels.

It is important to use complementary techniques to characterize the electronic

properties of these materials, [8] and KPFM is one that allows us to very accurately explore the motion of charge carriers. [6]

In this work, Chapter 2 discusses the intricacies of charge motion in organic semiconductors, including the importance of mobility and density of states. Chapter 3 focuses on our sample preparation methods and use of KPFM. Following that, Chapter 4 describes our results, while Chapter 5 discusses the challenges of our devices and data analysis.

Chapter 2: Charge Motion in Conjugated Polymers

A range of methods exist to study the electronic properties of organic semiconductors. Other groups have implemented current-based deep level transient spectroscopy (Q-DLTS), thermal admittance spectroscopy (TAS), Fourier transform photocurrent spectroscopy (FTPS), in conjunction with current voltage (IV) and photoluminescence (PL) measurements, [8] capacitance measurements, x-ray diffraction, [9] and KPFM and Electrostatic Force Microscopy, to study these materials. We focus on KPFM to study the behavior of charge carriers in these materials as it is able to look directly at local charge carrier motion in the P3HT film and record trapping and detrapping in real time, as well as steady state surface potential. We use an inverted FET geometry compatible with KPFM surface measurements to observe P3HT. In this chapter I discuss how FETs work as well as the mechanics for charge transport in P3HT.

2.1 Field Effect Transistor

An FET is often described in an overly simplified way as a switch. There are multiple types of FETs, our device structure is known as a thin film transistor, or TFT. One will come across two primary TFT architectures: top gate or bottom gate, also known as inverted. Our devices are bottom gated for compatibility with

AFM. Figure 2.1 is a diagram of the basic structure of an FET; the specifics of our devices are discussed in chapter 3.

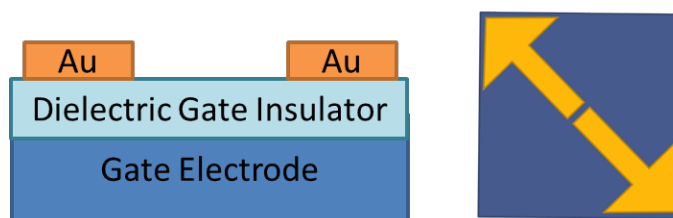


Figure 2.1: Side and top views of an inverted FET device

To turn on an FET, one applies a bias to the gate electrode. This induces an electric field in the gate material, causing a thin layer of charges to form at the interface of the electrode and the dielectric insulator. In turn, this causes a layer of opposite charge to stabilize in the conduction channel between the source and drain electrodes. The magnitude of the gate bias directly controls the density of charges in the channel, and therefore the maximum current that may pass through the FET. To initiate the flow of current through the transistor, a voltage difference is created between the source and drain electrodes

2.2 Current Voltage Characterization

The IV characteristics are critical to understanding if your FET works properly. To test the relationship between the gate voltage and current, we connect the source electrode to a FEMTO current to voltage converter. The current output information is then recorded by the program that controls the AFM. The organic

polymer we are testing is a known p-type material, meaning holes are the majority charge carrier. Proof of this is found when recording IV curves in the positive regime, as no significant electron transport is found when a positive bias is applied to the gate.

Below are two typical IV response graphs. Figure 2.2 shows the FET behavior when holding the gate bias constant while sweeping the source-drain bias. Figure 2.3 shows the opposite of holding the drain bias constant while sweeping the voltage applied to the gate. In addition to showing typical FET behavior, IV curves can also be fit to extract the mobility of charge carrier in the organic semiconductor. Mobility is one of the most important characteristics of these materials as higher mobility is required for better device performance and some applications. Mobilities near 0.1 cm²/Vs have been reported for regioregular P3HT. [9]

We use the following equations to analyze charge mobility in our devices.

For drain bias sweeps (Figure 2.2):

$$I_{DS} = \frac{1}{2} * \mu * C_S * \frac{W}{L} (V_{GS} - V_T)^2 \quad (2.1)$$

For transfer characteristics, or gate bias sweeps (Figure 2.3):

$$\frac{dI_{DS}}{dV_{SG}} = \mu * C_S * \frac{W}{L} V_{SD} \quad (2.2)$$

Where μ is the field-effect mobility, C_S is the oxide capacitance per unit area, W and L are the channel width and length respectively, and V_T is the threshold voltage defined as the gate bias at which a sufficient conducting channel forms

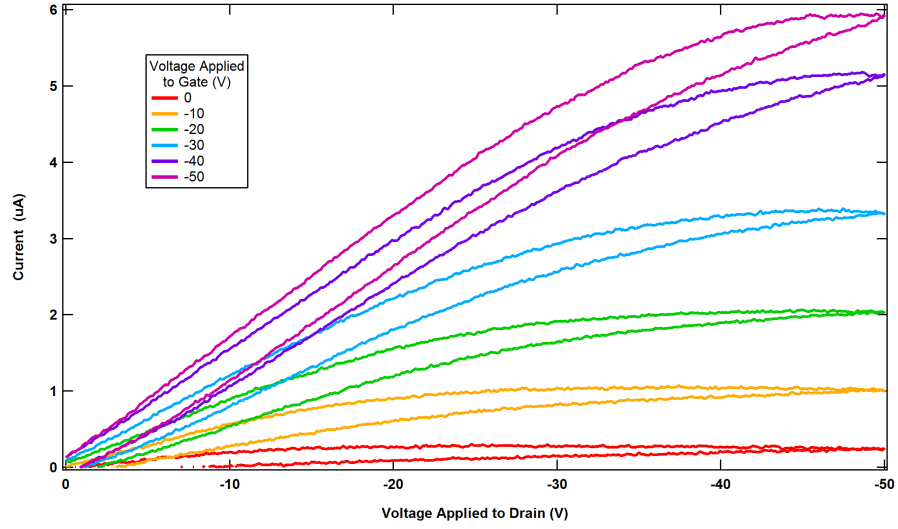


Figure 2.2: Drain bias sweeps for different gate voltages.

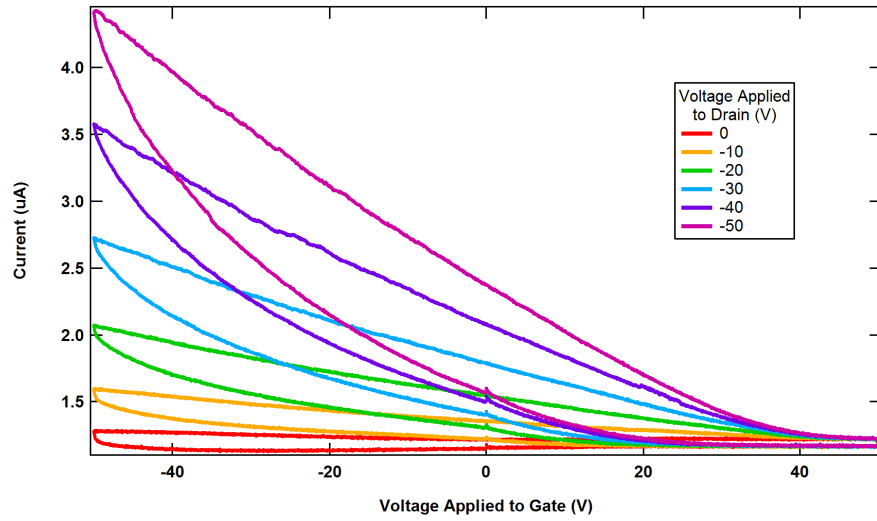


Figure 2.3: Gate bias sweeps for different drain voltages.

between the source and drain electrodes. We fit the linear regime for the V_{GS} curves and the triode, or accumulation, regime for the V_{DS} curves. A discussion

of the resulting mobilities we found is in chapter 4.

2.3 Density of States

The density of states (DOS), or the number of energy levels available for charge carriers to populate, has been investigated both experimentally and theoretically for amorphous organic semiconductors. Both Gaussian and exponential distributions are described in previous work. Torricelli et al. describe the DOS of P3HT as accurately approximated by a Gaussian function, while overall the shape depends on the material and may be Gaussian, exponential, or a combination of both. Figure 2.4 shows their experimental (symbols) and calculated (lines) mobility as a function of carrier concentration for two different conjugated polymers P3HT and OC_1C_{10} -PPV (solid line Gaussian DOS, dashed line exponential DOS).

Zhang et al. describes a method of extracting the DOS by slowly sweeping the back gate voltage at a speed of 10-20 mV/s. This research group notes the DOS reveals the energy dispersion of charge carriers and that trap states are often in the HOMO-LUMO gap of organic semiconductors.

2.4 Charge Transport

Both mobility and density of mobile charge carriers dictate the current an organic semiconductor FET can produce. Because charge transport is much more complex than in traditional crystalline materials, the effects of amorphous regions and trap

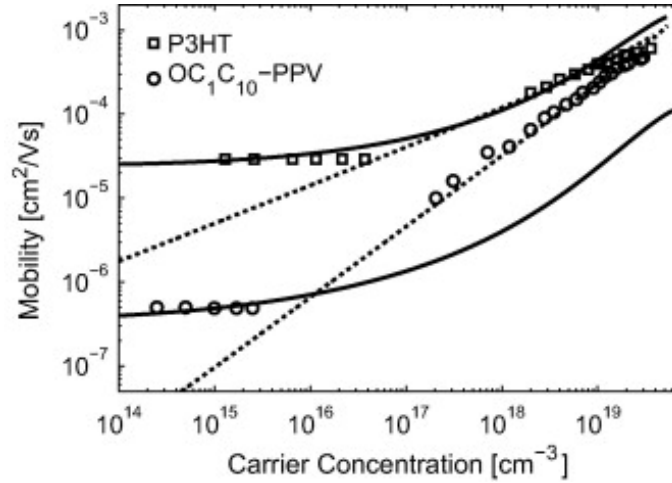


Figure 2.4: Density of states for P3HT. Experimental (symbols) and calculated (lines) mobility as a function of carrier concentration for two different conjugated polymers P3HT and OC1C10 -PPV (solid line Gaussian DOS, dashed line exponential DOS)

states become much more influential in device performance.

Multiple models of charge transport exist for organic semiconductors. Often using the traditional inorganic conduction - valence band conduction mechanism can suffice. In this model, when one maps the allowed energy levels of an intrinsic, inorganic semiconductor, they find there is an energy gap small enough that charge carriers can be excited to conduct current. The low end of this gap is known as the valence band (VB), and at absolute zero, all charge carriers exist in the VB. The upper end of the allowed levels is called the conduction band (CB). When energy is introduced into the system, electrons are able to move to the CB and contribute to current. In Figure 2.5, reproduced from Introduction to Solid State Physics by Charles Kittel (8th ed.), we see an illustration of these energy bands.

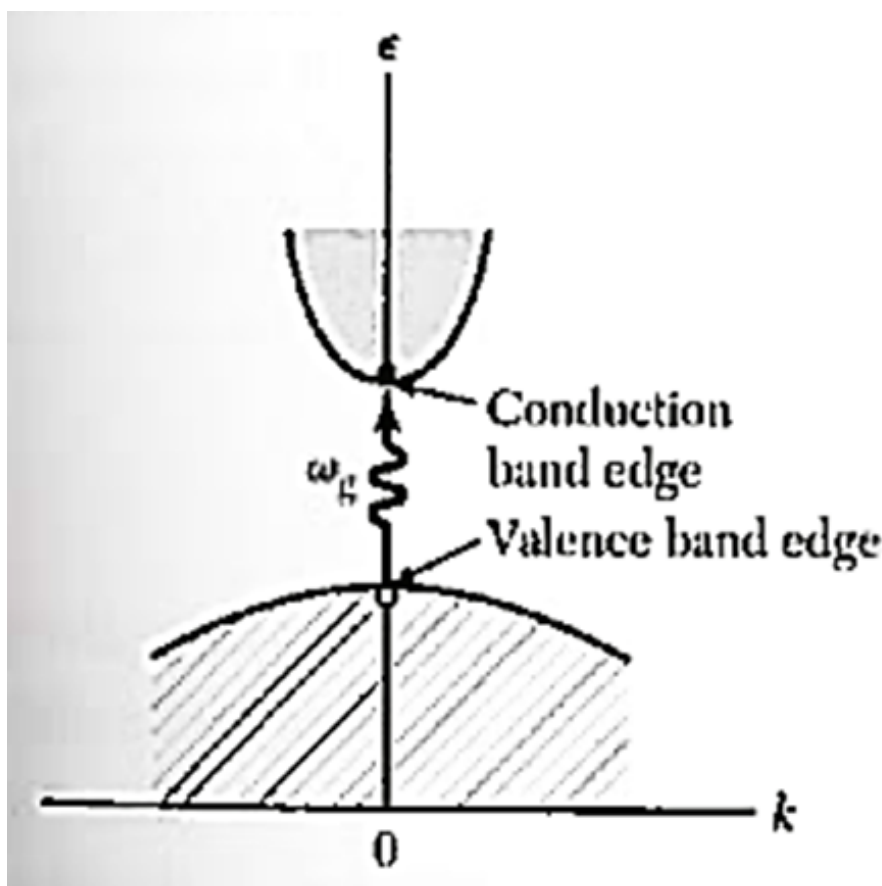


Figure 2.5: Illustration of the energy gap between the conduction and valence bands with an example of an electron being excited to the CB.

When talking about the complex behavior of organic semiconductors, the CB is frequently described as the lowest unoccupied molecular orbital (LUMO), while the VB is referred to as the highest occupied molecular orbital (HOMO). Peter Stallinga describes several proposed theories of transport in organic semiconductors in his book, two of note, one being a modification of traditional band conduction and the other described as hopping conduction. I briefly described both of these

in the introduction. The band theory describes the charges as delocalized and contributing the current in the CB but spending much of their time in deep states while with the hopping mechanism these charges only exist in the localized states and transport happens by instantaneous hops. both are illustrated in Figure 2.6

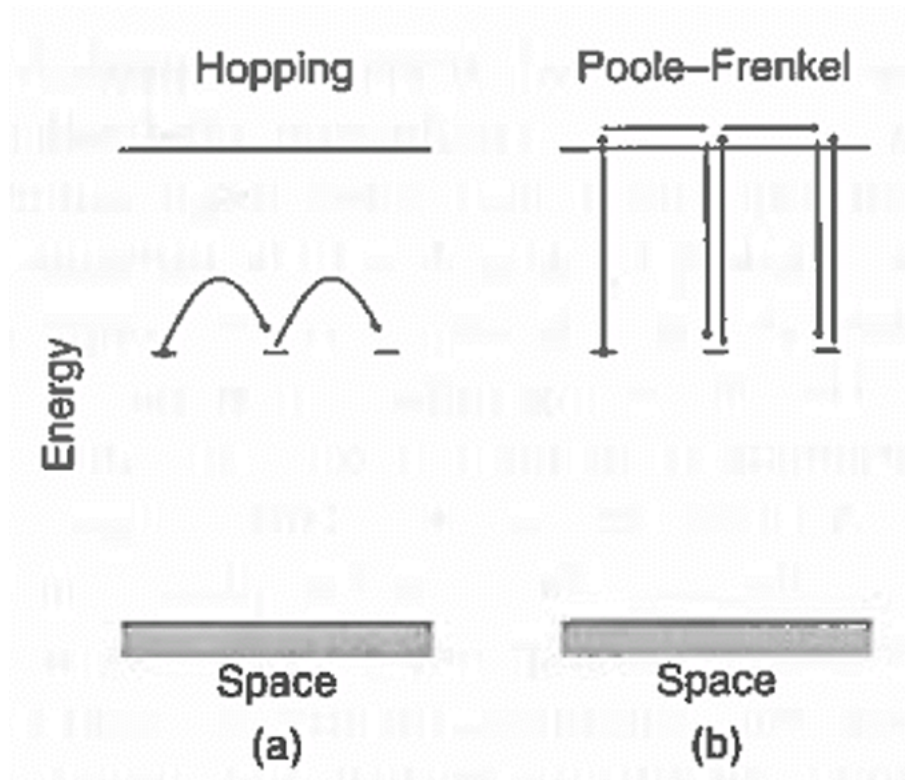


Figure 2.6: (a) Hopping conduction, (b) band conduction with local deep states.[11]

Regardless of the real mechanism, the deep local states trap charges and reduce the overall effectiveness of organic semiconductors. The origins of deep trap states are extensively described as being the semiconductor-oxide insulator interface as well as the intrinsic, disordered structure of these materials. [2, 6, 10]

An easily distinguishable influence of the difference in time for injecting charge carriers into the material versus pushing trapped charge carrier out is the existence of hysteresis in IV curves. Because hysteresis is defined as the outputs dependence on the input as well as the history of the system, we can explain the hysteresis loop in the IV curves in different directions as being related the motion of charge carriers in and out of the material. Figure 2.7 provides a clear example of hysteresis, as the recorded current varies with the direction of the sweep.

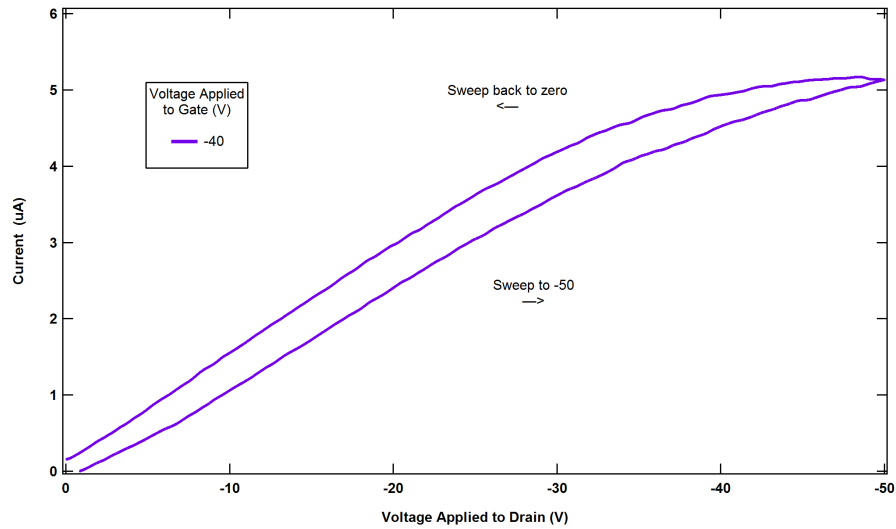


Figure 2.7: Hysteresis during a drain voltage sweep with -40 V applied to the gate.

Chapter 3: Materials and Methods

In this chapter I will discuss the details of fabricating our devices. Inverted field effect transistor device architecture is a simple and effective way to observe charge carrier motion in P3HT. Additionally, the organic semiconductor film is easily studied by KPFM as it is coated on top of the dielectric insulator and the source and drain electrodes.

3.1 Sample Preparation

Our samples are made on silicon wafers with a 200 nm layer of thermally grown silicon dioxide. The gold electrodes are deposited on the whole wafer by photolithography. The electrodes are created with a 10 micrometer gap between them. From this point, the wafer is cleaved into individual FETs and put through a series of baths. First, micro 90, then deionized water, followed by acetone, and finally isopropanol. After the fourth bath, the samples are blown dry with a nitrogen gun and placed in a pressurized, nitrogen filled glove box. From here the samples are left in a plasma cleaner under oxygen plasma for 10 minutes.

The procedure is standard up to this point for all types of samples, but subsequent steps differ depending on the characteristics being tested and compared. We are comparing three cases: (1) No surface treatments, (2) Silanized surface,

and (3) Silanized surface plus annealing of the film.

3.1.1 No Surface Treatments

After plasma cleaning, these samples are put directly on the spin coater. The surface is initially coated with anhydrous chloroform and spun at 3000 rotations per minute for 30 seconds. A P3HT solution of 3 mg per mL of chloroform is deposited on the surface and spun at 3000 rpm for 60 seconds.

3.1.2 Silanized Surface

Silanization for passivation of traps was stated in previous work [2, 6] to decrease the influence of states that arise from the dielectric interface. After plasma cleaning we soak these samples in a solution of 5 microliters of OTS per milliliter of anhydrous toluene for one and a half hours. After this we follow the same procedure for spin coating P3HT.

3.1.3 Annealing

Several groups [2, 9] discussed annealing of amorphous conjugated polymers with heat to increase crystallinity and therefore improve mobility of charges. We have not yet explored annealing without silanization first, but for some silanized samples we also annealed the spin coated P3HT on a hot plate at 150C for 30 minutes.

3.2 Testing

To test these samples in an inert environment we designed a mount to fit on our AFM, a photo of which is shown in Figure 3.1. There are three electrical leads, one

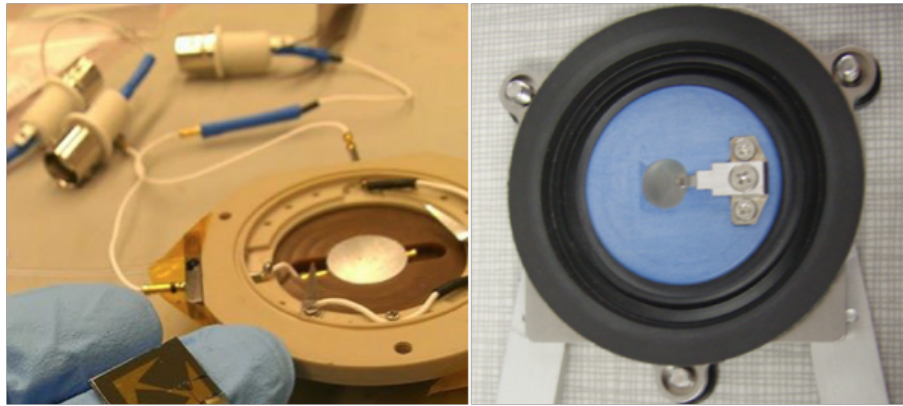


Figure 3.1: Left: the sample mount with electrical feeds. Right: the cantilever holder and membrane for sealing the holder.

for the gate which the samples sits on, and two for the source and drain electrodes which are connected to clips that screw down on top of the gold electrodes. All are soldered to BNC cables. There is also a gas feed and exhaust for nitrogen. The cantilever holder is fit with a membrane and clamp that screws into the sample mount to seal the device in the nitrogen. This clamp also holds the cantilever at a set distance above the sample so as to not crash the tip before it is released.

3.2.1 IV Characterization

To test for proper field effect transistor behavior, we conduct current-voltage tests with AFM. We take drain to source measurements by holding the gate electrode at a single voltage while sweeping the gate from +50 V to -50 V. The gate voltages are in 10 volt increments from 0 to -50V. We also gather transfer characteristics by sweeping the gate bias from +50V to -50V while holding the drain bias steady.

These measurements are done using the sealed closed cell sample mount for testing in an inert environment. The gate and drain electrodes are connected to AFM voltage outputs by means of KEPCO voltage amplifiers. The voltages output by the AFM to the gate and drain are multiplied by a factor of 5 and 10 respectively. The source electrode is hooked up to a FEMTO current to voltage converter and fed into an input. Typical IV curves are depicted in Chapter 2, section 2.

3.2.2 SKPFM

Kelvin Probe Force Microscopy is a versatile AFM technique that measures the surface potential of a sample relative to a bias applied to the cantilever tip. As is the basis for all AFM techniques, a laser is pointed at the cantilever tip and reflected back to a photodetector. As the tip oscillates according to the chosen technique, the displacement of the laser is recorded by the detector, and that information is translated by the program that controls the AFM. Figures 3.2 and 3.3 describe a simplified example of the feedback loop. KPFM is traditionally

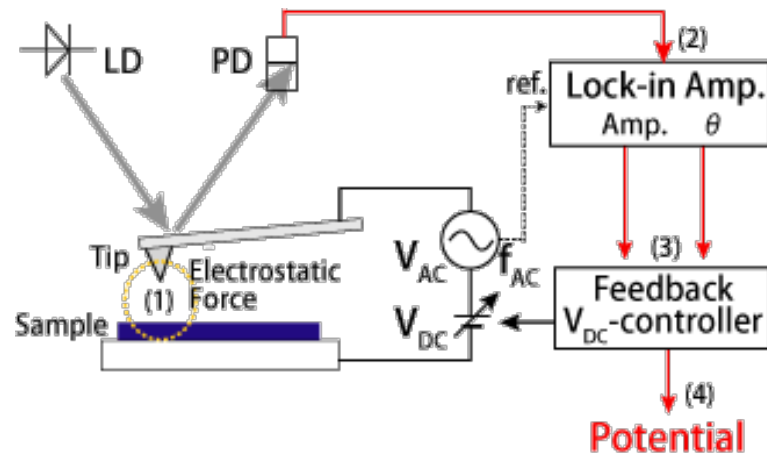


Fig. 2 General KFM system

Figure 3.2: Illustration of the KPFM feedback loop. www.spm.iis.u-tokyo.ac.jp

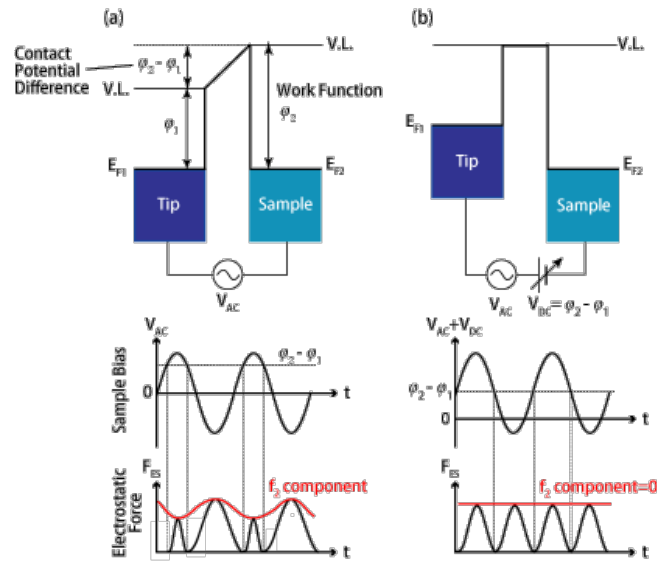


Fig. 3 Band diagram of tip and sample

Figure 3.3: Description of the oscillatory force caused by a difference in tip and sample bias. www.spm.iis.u-tokyo.ac.jp

done with a scanning technique. We use a two-pass method with the first pass using ac topography mode to gather surface height information. The second pass uses this information to lift the tip a set distance above the surface. A difference between the applied AC bias and the surface potential creates a force causing the cantilever to oscillate. The measured amplitude of the oscillation is sent back into the feedback loop of the software that controls the potential of the tip. The software then works to minimize the oscillation of the cantilever by bringing the tip voltage closer to that of the sample. Below are examples of data gathered by the two scanning KPFM passes across the conducting channel; we can see the gradual change in potential in relation a bias applied to one electrode with the other electrode grounded.

This technique allows one to gather information about the steady state surface potential of a small area of the sample. We take advantage of this to take measurements across the conducting channel to test for contact resistance. [9]

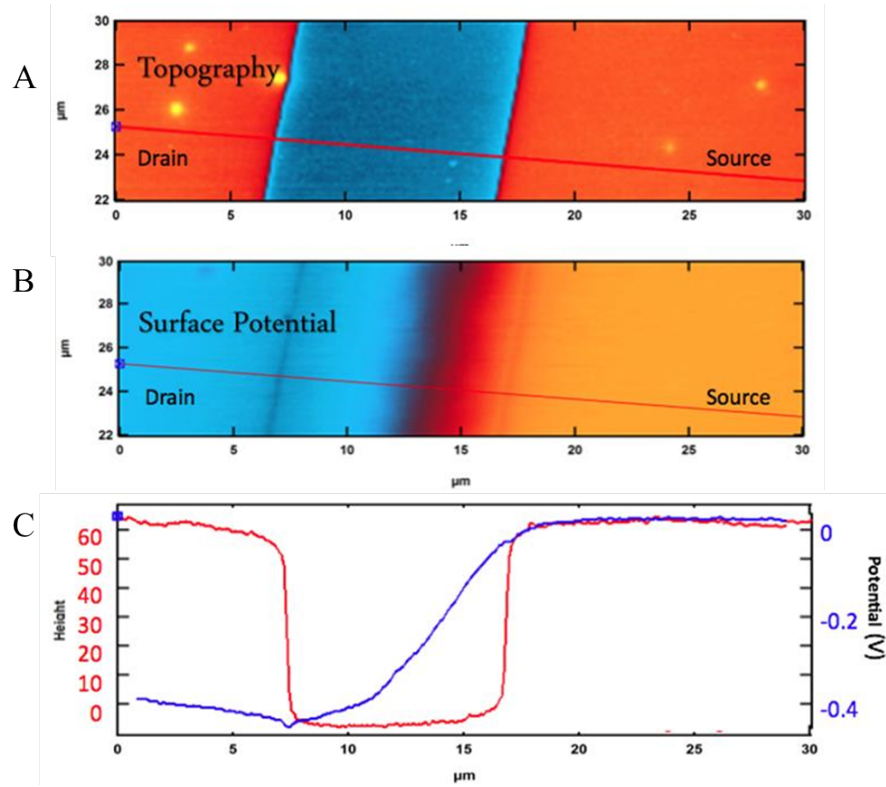


Figure 3.4: (a) The first pass, or topography scan, across the conducting channel in our FETs. (b) The second pass, or potential scan, across channel. (c) Line sections of the height information and potential.

3.2.3 Time-resolved KPFM

The downside to scanning KPFM is the time it takes to make measurements. We developed a program to control the feedback loop and cantilever enabling us to make time-resolved measurements and follow instantaneous behavior of mobile charge carriers at a single point in the material. There are two versions of this program. One applies a single, user-determined voltage to the back gate for a

period of time. Below is a plot of an applied gate voltage versus time. The drain electrode is grounded while the source electrode is connected to a FEMTO current to voltage converter.

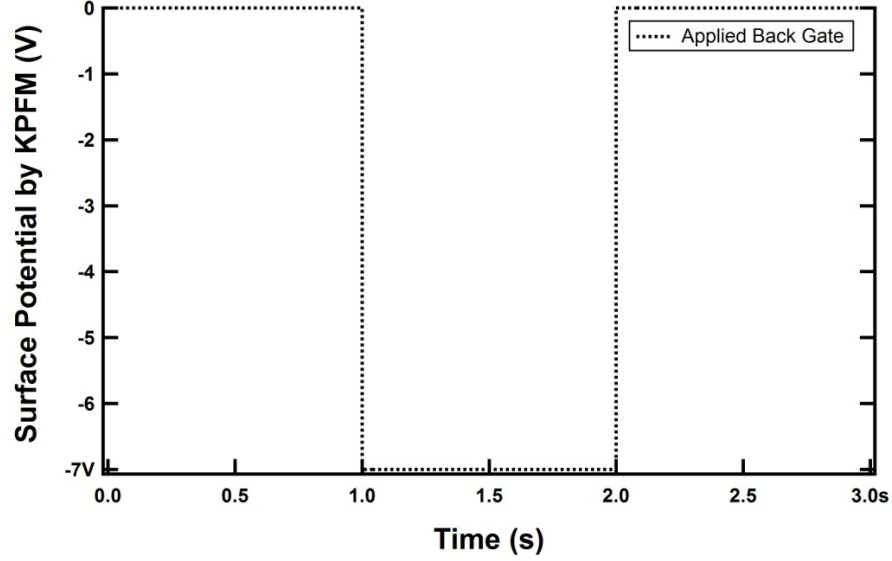


Figure 3.5: Example of bias applied to gate with the single step point KPFM program. In this case, the gate is initially grounded and the KPFM records the surface potential for 1 second before a -7V bias is applied, and then after the bias is removed for 1 second.

To characterize this method, we performed tests on control samples, illustrated in Figure 3.6. These samples consist of the cleaned silicon wafers with patterned gold electrodes and no P3HT. The measurements were taken over the gold electrodes and over the dielectric. Over the electrodes, we see no visible change in surface potential as charge carriers screen too quickly to record. We see the opposite behavior over the dielectric insulator, where the material cannot screen as there are no mobile charge carriers to negate applied bias. From the tests over the

dielectric we are also able to gather the maximum speed at which the KPFM can record a response, this time being about 3ms.

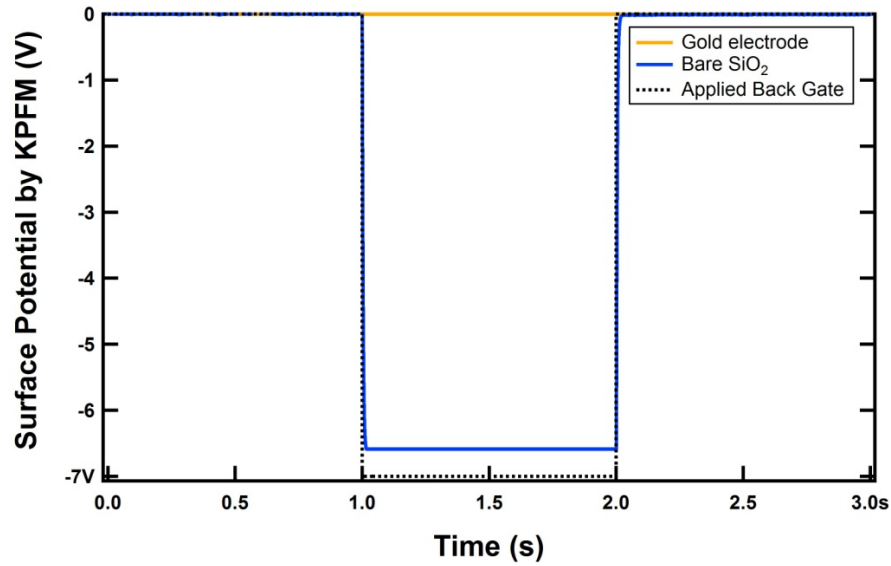


Figure 3.6: Control sample surface potential responses over Au electrodes and Silicon Oxide.

A typical response for the time resolved KPFM over P3HT and dielectric is shown below in Figure 3.7. The blue dotted line indicates the bias applied for a given time, while the red line indicates the change in surface potential recorded by KPFM.

When we position the tip above the P3HT film, some distance from the electrodes, we see an obvious spike in surface potential for every change in gate bias. The surface potential is initially at zero. When a negative bias is applied, we see a temporary negative surface potential that decays as holes rush into the film to screen. As soon as the negative bias is removed, the KPFM records a positive

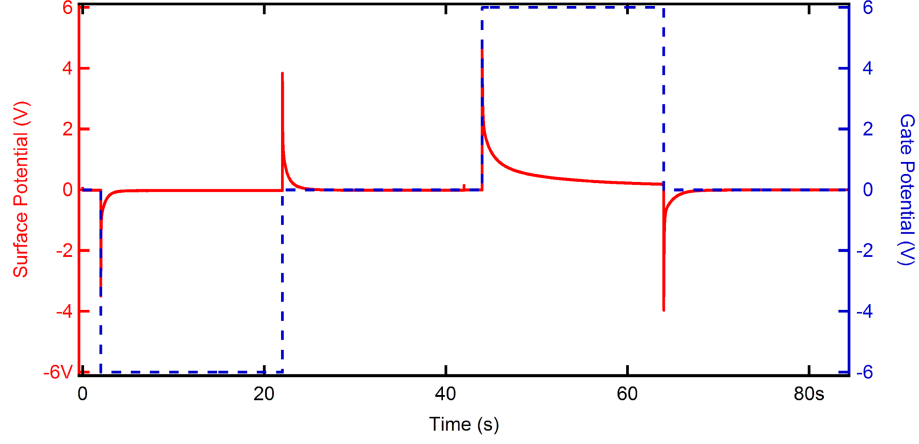


Figure 3.7: The changes in surface potential for applying and removing gate biases.

surface potential from the surplus of holes which must then be pushed out of the film to return the potential to 0. The opposite behavior is seen for a positive gate bias. Detailed notation of this is shown in the figure below. Because this material is p-type, we do not see any visible electron transport. As holes are the only mobile charge carrier, they must be pushed out of the material to screen a positive surface potential. This mechanism is made more complicated by trap states, as holes must be moved out of these states, something we found increases the screening time.

We extract information from these graphs by fitting the decays of the peaks with a double exponential equation.

$$f(t) = A_1 e^{\frac{-t}{\tau_1}} + A_2 e^{\frac{-t}{\tau_2}} \quad (3.1)$$

The two recorded time constants tell us general trends regarding the speed of charge carriers.

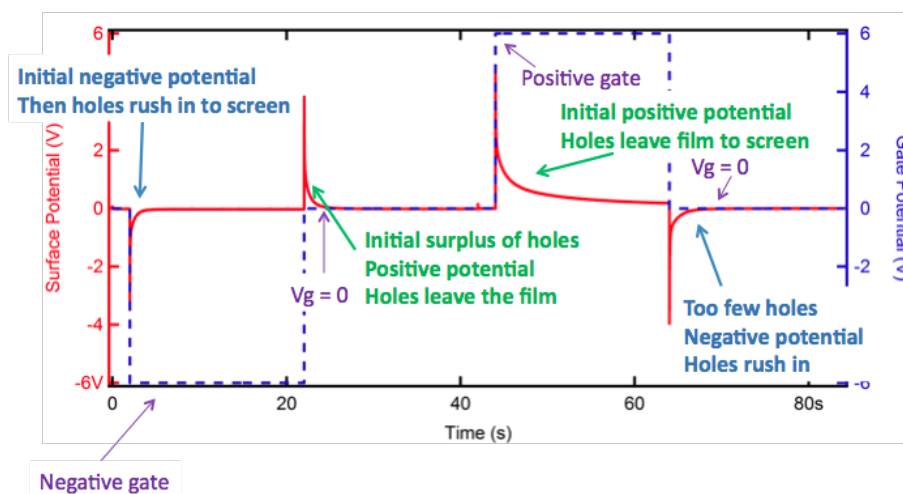


Figure 3.8: The changes in surface potential for applying and removing gate biases with explanations.

The other version of the program incrementally increases the magnitude of the back gate bias to a maximum, taking a user-determined number of steps, and then incrementally decreasing the voltage back to zero. A spike in the surface potential is recorded for each step in the gate voltage, with the same basic principle as the single bias technique. We are just beginning to explore this stepping technique.

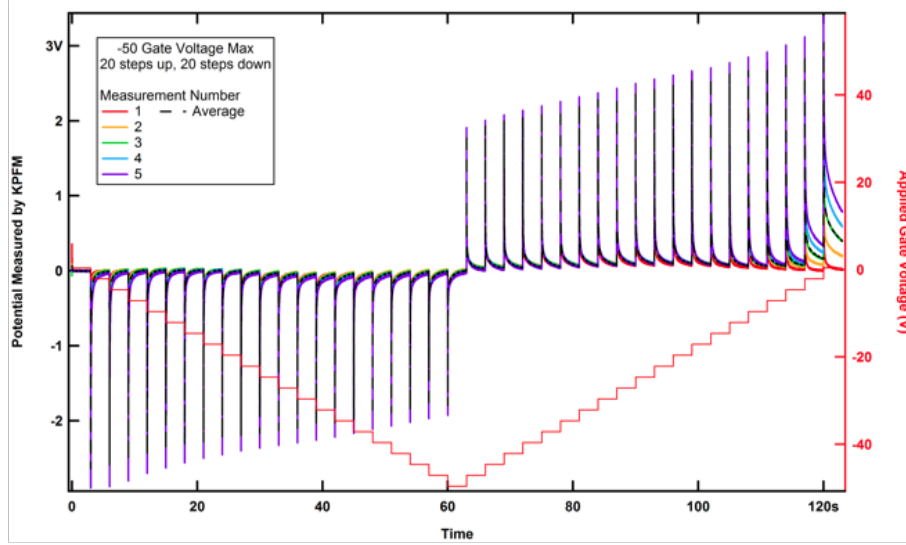


Figure 3.9: Typical response graphs for the incremental step program, possibly showing effects of bias stress.

3.3 How to Read our Results

Time resolved KPFM allows us to explore certain regimes of traps and acts as a complementary technique to others. We are confidently able to say that injecting holes into this p-type material is a significantly faster process than pushing the trapped charges out of the material. We proved that testing at significant distances at least 100 μ m away from the conducting channel does not impact the time constants. Each time resolved KPFM response peak provides two time constants describing the motion of charge carriers in the material. We can fit these peaks before or after normalizing the measured potential, and generally do both.

Chapter 4: Results

4.1 Current

From our current-voltage characteristics where we swept the voltage applied to the gate and held the drain to source voltage constant, there is clear indication of no noticeable electron transport in the positive regime. Due to sample variability we gathered a wide range of maximum currents.

4.2 Mobility

Extracting mobility from V_{gs} curves is significantly easier than for V_{ds} curves. We found a wide range of mobilities, noted in Table 4.1.

Table 4.1: Mobilities	
Type of Sample	Mobility (M^2/Vs)
No Treatments	$9.7 \cdot 10^{-5}$
Silane, No Anneal	$6.7 \cdot 10^{-5}$
Silane, No Anneal	$1.1 \cdot 10^{-5}$

4.3 Distance

Early on we focused on exploring the trends of the time resolved KPFM data taken at different areas in our sample to understand how charge carrier motion changes with distance from the conducting channel, such as at the points in Figure 4.1.

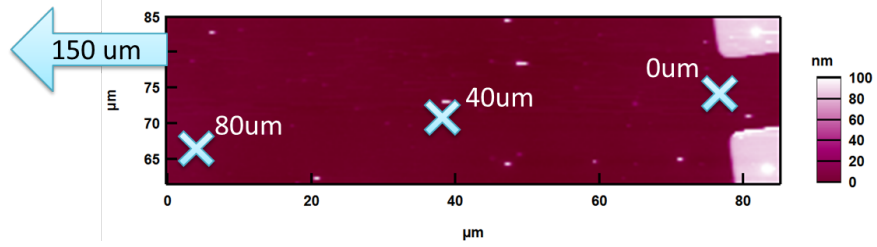


Figure 4.1: Description of the oscillatory force caused by a difference in tip and sample bias.

For distance measurements we found some variation in the peak height, but when normalized, the effects were negligible, Figure 4.2 shows the spread, while Table 4.2 shows the extracted time constants. We took measurements up to 150 μm from the conducting channel.

Table 4.2: Extracted Time Constants for Measurements Taken at Distances from the Conducting Gap

Distance From Gap	Time 1	Time 2	Time 1	Time 2
0 μm	0.037	0.93	0.082	1.7
40 μm	0.041	1.3	0.083	1.9
80 μm	0.049	1.4	0.10	1.9
150 μm	0.042	1.4	0.074	1.5

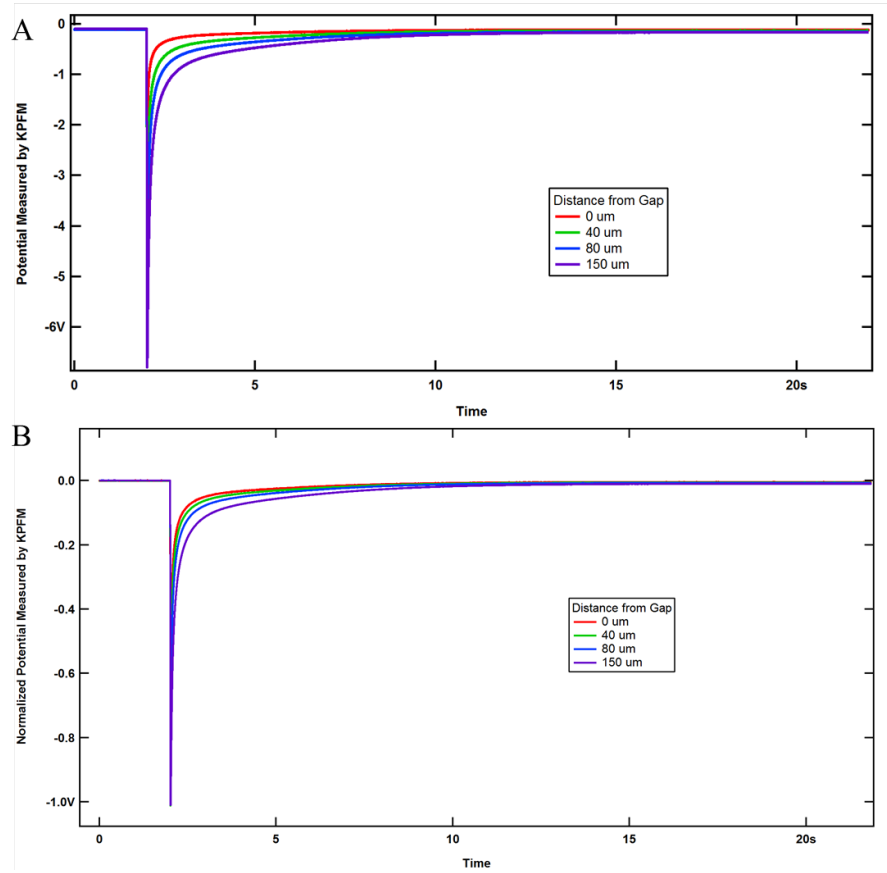


Figure 4.2: Surface potential responses for applying an -6V bias to gate at different distances away from gap for (a) recorded peak height, and (b) peaks normalized by peak height.

4.4 Time Resolved KPFM

4.4.1 Single Step

There is a clear difference in time constants between the untreated samples and the OTS treated and annealed samples. Unfortunately the data for the OTS treated

but not annealed samples, or OnA, is inconclusive. Additionally, we explored the curious phenomena, depicted in Figure 4.3, resulting from time resolved KPFM measurements taken above P3HT coated on the gold electrodes. We see an inversion of the response peaks. As of now, this is unexplained.

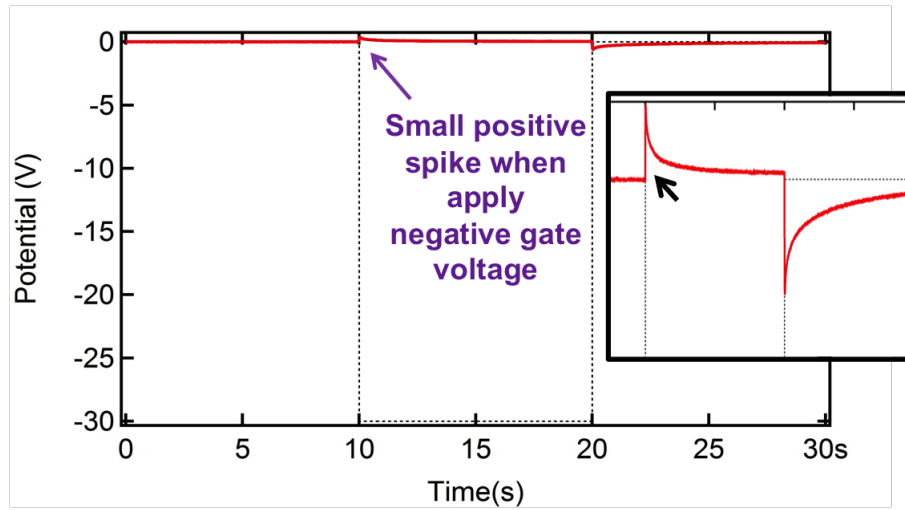


Figure 4.3: Inversion in time-resolved KPFM response peaks in measurements taken over P3HT and gold.

4.4.2 Multi-step

As for results from the multi-step time resolved KPFM, we have found non-monotonic behavior in the longer of the two extracted time constants, depicted in Figure 4.5. Again, unfortunately, results regarding the effects of silanization are inconclusive as to whether or not it removes or reduces the influence of trap states arising from the oxide interface.

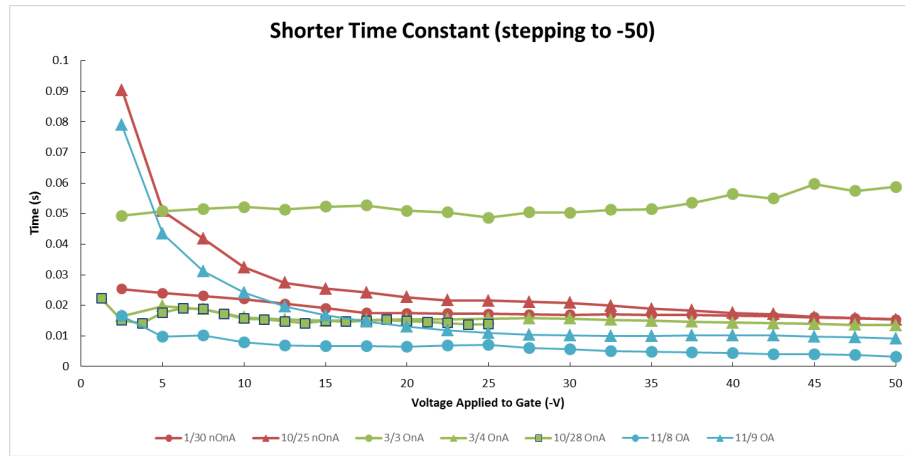


Figure 4.4: Plot of the shorter time constant extracted for every step from 0 to -50V.

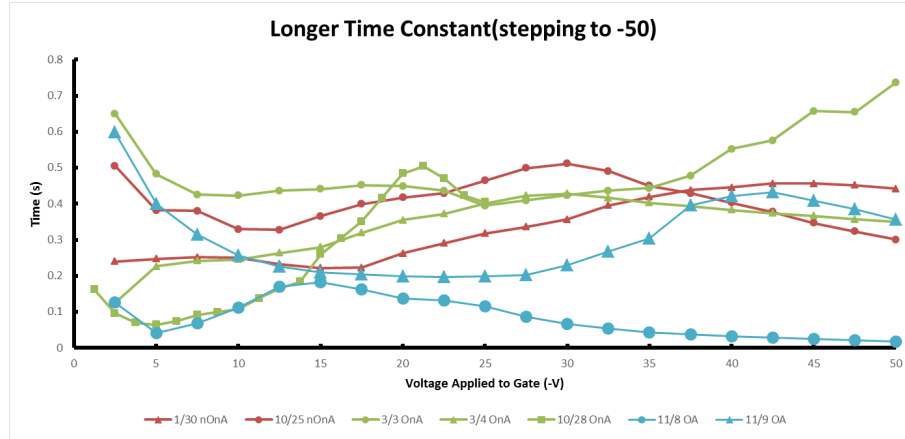


Figure 4.5: Plot of the longer time constant extracted for every step from 0 to -50V

For some samples we see it takes longer and longer to screen the positive surface potential and eventually the device is unable to screen in the time allotted for each step, this is depicted in Figure 4.6 on the indicated right hand side of the graph. We propose this may be from accessing very deep trap states where it is very difficult to push holes out of.

For stepping to a maximum positive gate potential of 15 V, we find that the device is very quickly unable to screen, Figure 4.7, but the speed of screening does increase with each subsequent measurement.

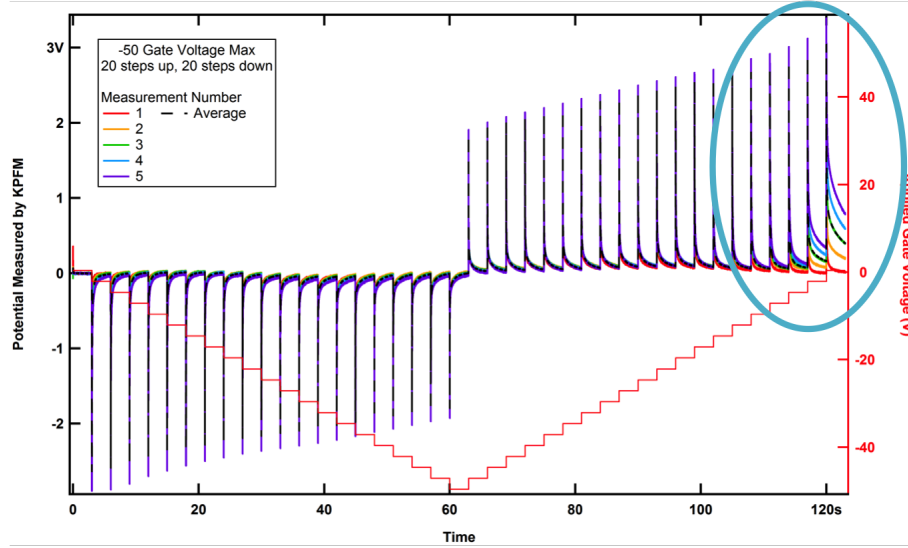


Figure 4.6: Stepping the applied gate voltage from 0 to -50V, and back to 0. We see with subsequent runs of the program, the device screens less quickly.

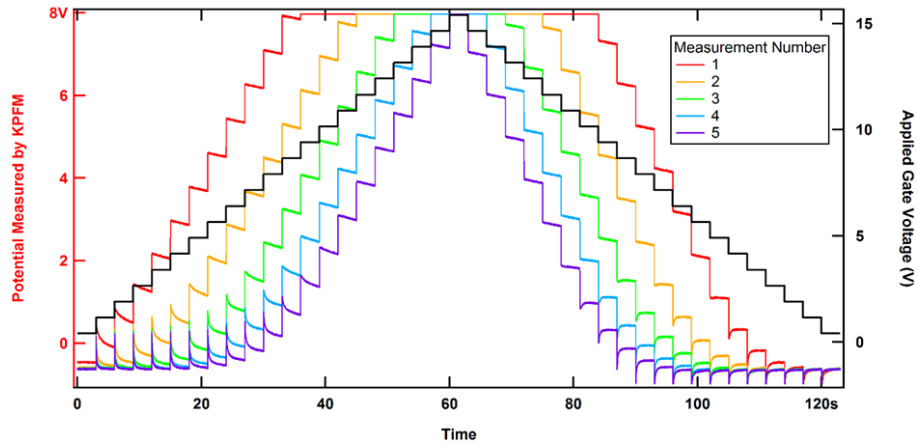


Figure 4.7: Stepping the applied gate voltage from 0 to +15V, and back to 0.

Chapter 5: Discussion And Summary

In this chapter I will discuss the challenges of this project in regards to both the samples and data analysis. Additionally I will describe some future directions for the work.

5.1 Challenges of Samples

While P3HT is a highly utilized material, it is not perfect. The processing conditions are highly influential on device performance. The type of solvent used greatly impacts the uniformity and degree of crystallinity of the material. Chloroform has been shown to produce low crystallinity film, but with high uniformity. [2] In addition to the effects of processing materials, spin coating, while speedy and accessible, does not at all guarantee a high-quality film. Because this is a messy process, we often found our devices would short and we were unable to test them. Day to day differences such as humidity and lighting conditions may also impact the device. These are all things to consider moving forward, but for now it gives reason for our significant issues with repeatability from device to device.

5.2 Challenges of Analysis

Fitting the response curves of the time-resolved KPFM turned out to be a much more complex process than we had anticipated. As discussed previously, we find that IGORs double exponential curve fitting follows the trend of the decay in surface potential very closely for most samples. Our concerns, now that we have mostly automated the fitting process are threefold. First, we want to figure out if there is a significance to the values of the coefficients, as this would indicate whether or not normalizing by the height of the response peaks is beneficial or not. Second, another group using similar techniques but different materials found their FET devices that had not had the oxide surface passivated had two time constants relating to charge motion, while the passivated devices only had one. [6] We do not see this behavior in our fits and would like to check for a triple exponential fit while holding one or more of the times constant to check if silanization significantly decreases the influence of deep traps resulting from the oxide interface. Lastly, in addition to exploring the physical mechanisms related to the extracted time constants, we want to double check the quality of the curve fitting itself. This would mean holding the values constant, changing them significantly, and seeing how the second or third part of the exponential equation changes. If there are significantly different results, we must be critical of IGORs analysis.

5.3 Summary and Future Work

Organic semiconductors are complex and finicky materials with a great deal of potential. P3HT is very sensitive to processing conditions and our methods of sample preparation lead to a large degree of variability in device performance. Additionally, one must always think critically about data analysis and stay a step ahead of their computer. As soon as we solidify our understanding of data analysis, this project and quickly move forward with completing our understanding of the effects of surface treatments and annealing while taking into account stricter standards for processing conditions, such as light levels. Following this, we can explore the effects of bias stress on the devices in ambient and inert environments.

Bibliography

- (1) Davis, A. (2014). Visualizing and Controlling Charge Transport in Conjugated, (May).
- (2) Majewski, L. A., Kingsley, J. W., Balocco, C., Song, A. M. (2006). Influence of processing conditions on the stability of poly(3-hexylthiophene)-based field-effect transistors. *Applied Physics Letters*, 88(22), 222108. doi:10.1063/1.2208938
- (3) Street, G. B., Clarke, T. C. (1981). Conducting Polymers: A Review of Recent Work. *IBM Journal of Research and Development*, 25(1), 5157. doi:10.1147/rd.251.0051
- (4) Sirringhaus, H. (2014). 25th Anniversary Article : Organic Field-Effect Transistors : The Path Beyond Amorphous Silicon, 13191335. doi:10.1002/adma.201304346
- (5) Stallinga, P., ebrary Academic Complete. (2009). Electrical characterization of organic electronic materials and devices. Hoboken, NJ: John Wiley and Sons.
- (6) Zhang, Y., Ziegler, D., Salmeron, M. (2013). Charge trapping states at the SiO₂-oligothiophene monolayer interface in field effect transistors studied by kelvin probe force microscopy. *ACS Nano*, 7(9), 82588265. doi:10.1021/nm403750h
- (7) Asylum SPM techniques manual
- (8) Bozyigit, D., Wood, V. (2014). Electrical characterization of nanocrystal solids. *Journal of Materials Chemistry C*, 2(17), 31723184. doi:10.1039/C3TC32235A
- (9) Grecu, S., Roggenbuck, M., Opitz, A., Br??tting, W. (2006). Differences

of interface and bulk transport properties in polymer field-effect devices. *Organic Electronics: Physics, Materials, Applications*, 7(5), 276286. doi:10.1016/j.orgel.2006.03.005

(10) Torricelli, F., Kovcs-Vajna, Z. M., Colalongo, L. (2009). The role of the density of states on the hole mobility of disordered organic semiconductors. *Organic Electronics*, 10(5), 10371040. doi:10.1016/j.orgel.2009.05.013

(11) Kittel, C. (2005). *Introduction to solid state physics*. Hoboken, NJ: Wiley.

(12) Tal, O., Rosenwaks, Y. (2006). Electronic properties of doped molecular thin films measured by Kelvin probe force microscopy. *The Journal of Physical Chemistry. B*, 110(50), 255214. doi:10.1021/jp065246q

(13) Tal, O., Rosenwaks, Y., Preezant, Y., Tessler, N., Chan, C. K., Kahn, A. (2005). Direct determination of the hole density of states in undoped and doped amorphous organic films with high lateral resolution. *Physical Review Letters*, 95(25), 256405. doi:10.1103/PhysRevLett.95.256405

(14) Tal, O., Rosenwaks, Y., Roichman, Y., Preezant, Y., Tessler, N., Chan, C. K., Kahn, A. (2006). Threshold voltage as a measure of molecular level shift in organic thin-film transistors. *Applied Physics Letters*, 88(4), 043509. doi:10.1063/1.2167395

(15) McFarland, F. M., Brickson, B., Guo, S. (2015). Layered Poly(3-hexylthiophene) Nanowhiskers Studied by Atomic Force Microscopy and Kelvin Probe Force Microscopy. *Macromolecules*, 48(9), 30493056. doi:10.1021/ma502411n

(16) Hallam, T., Duffy, C. M., Minakata, T., Ando, M., Sirringhaus, H. (2009). A scanning Kelvin probe study of charge trapping in zone-cast pentacene thin film transistors. *Nanotechnology*, 20(2), 025203. doi:10.1088/0957-4484/20/2/025203

(17) Smits, E. C. P., Mathijssen, S. G. J., Clle, M., Mank, A. J. G., Bobbert, P. a., Blom, P. W. M., De Leeuw, D. M. (2007). Unified description of potential profiles and electrical transport in unipolar and ambipolar organic field-effect transistors. *Physical Review B*, 76(12), 16. doi:10.1103/PhysRevB.76.125202

(18) Pingel, P., Neher, D. (2013). Comprehensive picture of p -type doping of P3HT with the molecular acceptor F 4 TCNQ. *Physical Review B*, 87(11), 115209. doi:10.1103/PhysRevB.87.115209

APPENDICES

Appendix A: SOPs

A.1 Sample Manufacturing

The substrates are prepared in a clean room environment by the trained postdoc in the Aidala lab. You will receive a doped Si disk with multiple gold electrodes patterned on top. As of May 2016, the Aidala lab only uses substrates with a 10um conducting channel. You must use a diamond scribe to CAREFULLY cleave the disk into individual substrates.

A.1.1 Standard Cleaning

Once the individual substrates have been cut from the disk, you run them through a series of baths to remove large particulate. In the fume hood of the Arango lab you will find 4 bath beakers and a sonicator that will run for 5 minutes.

1. Micro-90 bath
2. DI water bath
3. Acetone bath
4. Isopropyl alcohol bath
5. Blow dry with nitrogen gun

It is recommended that you warm up the plasma cleaner while the sonicator is running. Remember that the area between the gloveboxes where the oxygen tank is located is considered "clean", so you must disrobe to enter it.

1. Open the valve on top of the tank completely
2. Open the right-most valve completely (the center valve SHOULD NOT be touched)
3. Turn on the plasma cleaner and check the parameters in Setup Menu. I always set my plasma time to 10 minutes. The recommended settings for the other parameters can be found in the Arango lab
4. In the Commands Menu start the warm up
5. While the plasma cycle is running, rememebr to record the oil level/color and oxygen pressure
6. Once the cycle is complete, end it in the Commands Menu

The substrates must now be transferred into the glovebox for plasma cleaning. In addition, you should use this as an opportunity to place any materials for polymer solution making, silanizing, or spin-coating in the wet glove box.

Once the substrates have been placed in the glovebox for plasma cleaning, put them in the plasma cleaner, seal the door, and run the plasma cycle again.

A.1.2 Silanization

For P3HT samples you are silanizing, you will need to put several additional materials in the wet glovebox:

- 3 mL syringe for toluene
- syringe needle for toluene
- wipes
- Aluminum foil
- chemical resistant bags for waste
- XL nitrile gloves

Some items that should already be in the glovebox, check to make sure:

- Teflon dish and lid
- micro-pipette and tips
- Toluene rinse for samples
- Waste vial for used OTS solution
- Plastic tweezers for use in OTS

NOTE: OCTADECYLTRICHLOROSILANE IS VERY REACTIVE TO MOISTURE, OXYGEN, AND METALS. I recommend running the glovebox autopurge

while preparing the solution. You must ALWAYS use the plastic tips provided for the micro-pipette to measure out OTS.

NOTE: OTS will be located in the refrigerated storage in the wet glove box. It is recommended that you remove it while running the plasma cycle to allow it to thaw.

You will create a solution of 5 uL OTS to 1 mL of toluene.

1. Roll out aluminum foil on flat surface
2. Spread wipes on top of foil
3. Gather teflon dish, toluene, waste, and rinse containers
4. Place XL nitrile gloves over glovebox gloves for protection from OTS
5. Place plasma cleaned substrates into teflon dish
6. Measure out 3 mL of toluene with syringe and put in dish
7. Measure out 15 uL of OTS with micro-pipette and put in dish
8. Cover dish
9. Allow substrates to sit for 1.5 hours (90 minutes)
10. When bath is complete, rinse substrates in toluene bath and add a tally mark to the number of uses on the bath vial. Do not use a bath more than 6 times.
11. Dry each rinsed substrate with nitrogen gun

12. Dump OTS solution in waste vial
13. Move substrates for spin-coating and place all waste that may have touched OTS in a chemical resistant bag

A.1.3 Spin-coating

If there is no pre-made P3HT solution in the wet glovebox, you will need to prepare more. The solution should contain 3 mg of P3HT solid for every 1 mL of chloroform. I would recommend measuring out at least 9 mg of P3HT to make enough solution. Items you will need:

- Syringe for chloroform
- Syringe for P3HT
- Needle for chloroform
- Filter for P3HT
- Wipes
- Aluminum foil
- Slices of yellow tape, 4 for each sample

Prepare your P3HT solution if needed. Just measure out the proper amount of chloroform and put it in the vial containing the solid P3HT and shake the vial a bit so all of the solid dissolves.

You'll need to make sure the spin-coater is programmed to spin at 3000 rpm for standard P3HT samples. It's worth it to just check for a pre-programmed recipe. To do this, hit the "mode" button to enable editing. Use the left and right arrow buttons to select the parameter you want to edit and the up and down buttons to increase or decrease the value. Hit enter to set your selection and mode again to return to recipe selection.

You will have to program the second stage to 3000 as the first stage apparently has no bearing on the actual rotation.

1. Cover edges of samples with yellow tape
2. Extract some chloroform
3. Extract some P3HT and place a filter on the syringe
4. Place a substrate on the spin-coater, being careful to center it
5. Deposit some chloroform on the substrate, close the coater, and spin for 30 seconds, then end the cycle
6. Now either open the coater and deposit P3HT OR clear the "short cycle" error and drop P3HT through the lid. DO THIS AS FAST AS POSSIBLE
7. Allow the sample to spin for 60 seconds
8. Remove yellow tape

A.1.4 Annealing

Annealing is probably the simplest part of the sample-making process. Heat the hot plate to 150 degrees Celsius, once the samples have been spin-coated, place them on the plate for 30 minutes.

A.1.5 Sample Mounting

A.2 Closed Cell Set Up

1. The sample must first be mounted on a steel chuck. The steel chuck allows the sample to be magnetically held in place in the cell. Makes an electrical connection between the sample and the chuck. Note, if using the silver paint this must be done at least one hour ahead of time to ensure sufficient drying.
2. If your sample is air-sensitive, you may want to do this in the glovebox (which requires its own training). However, it can be done in the lab as well.
3. Carefully use a diamond scribe to scratch through the back-side of the sample to get through the oxide that has built up to the conductive doped Si beneath it. Once you have made a decent scratched area, wipe off the scratch with a Kim Wipe in order to remove the silicon dust you have made. DO NOT USE A SOLVENT, you can unintentionally damage the film on the other side of the wafer.
4. Remove a steel chuck and place it flat. Using the silver paint, place a single

drop on the steel chuck, and quickly place the sample (centered) atop it. Note: you do not want to inhale this solvent, so open the door and only open the bottle as long as you have to.

5. At this point you must let the solvent dry. Whether you performed this procedure in or out of the glovebox, the transfer chamber on the glovebox is a good way to speed drying – pumping down the vacuum will remove most of the solvent. If leaving the sample in the vacuum to speed the drying, wait at least 30-45 minutes. Remember, however, that other people may need to use the transfer chamber.
6. Be sure there is sufficient nitrogen, so open the main valve on the gas canister and see what pressure the regulator reads on the canister pressure meter before beginning. If the pressure is very low, let one of the post-docs know so a new canister can be ordered. The gas line is shown in Figure A.1, below.

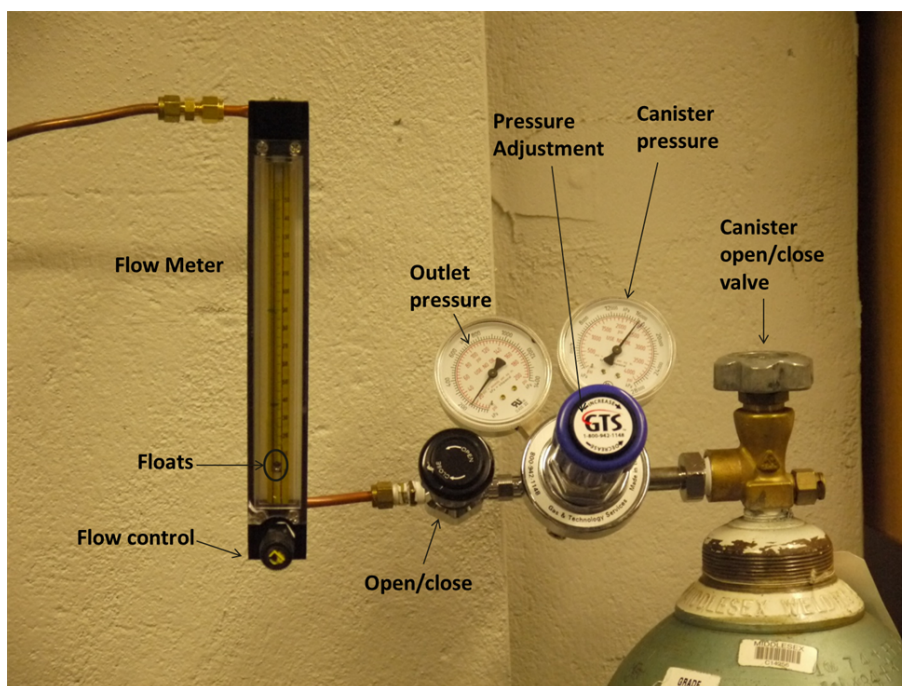


Figure A.1: Pressure meter and valves on nitrogen canister

At this point you will likely want to set up the Asylum software before mounting your sample. Information on how to do this can be found in the next section.

Assemble the top of the closed cell This is often unnecessary. You must do this BEFORE loading the tip, because it is extremely easy to break the tip while assembling the top. For this you will need a viton membrane, the ring and the wrench, shown below in Figure A.2.

Load the ring on the wrench with the not-flat side visible. Put the tip holder in the hole in the viton membrane such that only one central ridge is showing on the tip-clip side of the holder. Holding the tip holder with one hand, use the wrench to put the ring on the backside of the system and push and turn

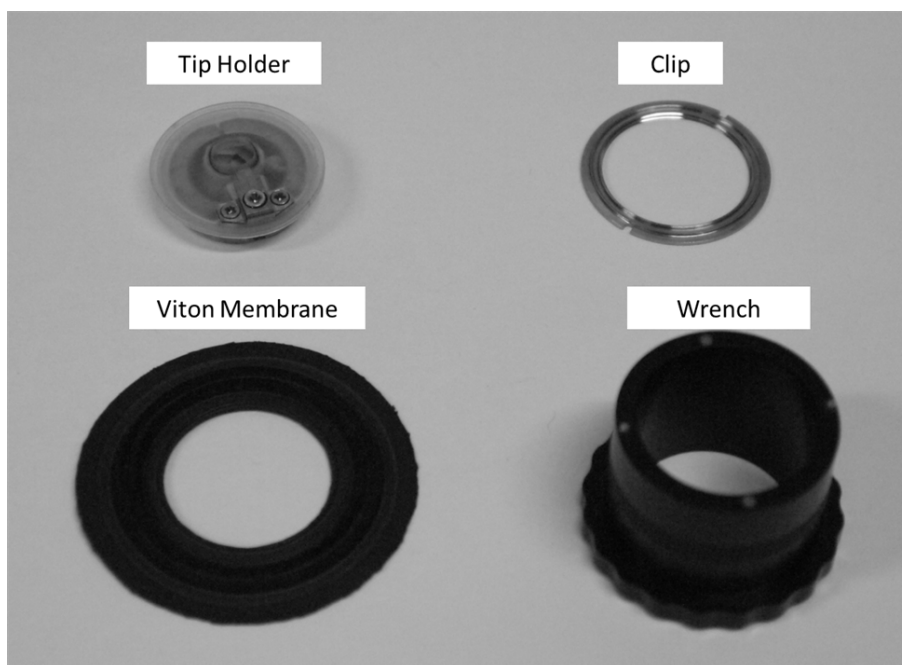


Figure A.2: Components to assemble top of closed cell

clockwise to put it into place. It is best to see if you can easily dislodge the ring at this point. If you can, it is not on very well so simply give it another shot. Once the viton membrane is held in place, you have to load the top into a clamp. This clamp is what prevents the tip from crashing into the bottom of the cell (or vice versa) while you are loading the closed cell. This part is a little tricky, as you have to figure out the necessary relative orientation of the tip holder and the cell bottom. Further information is shown in Figure A.3.

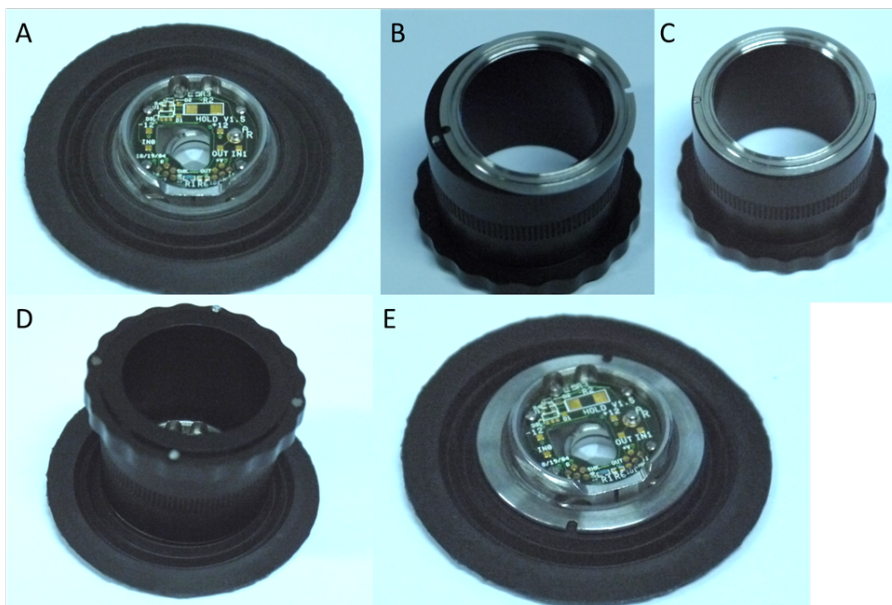


Figure A.3: Description of the oscillatory force caused by a difference in tip and sample bias.

Load and contact sample

1. The mounted sample should be placed on the metal center position of the cell bottom. There is less room to move your sample once it is loaded in the closed cell than there usually is simply mounting it on the stage, so it is imperative the feature you want to examine is as centered as you can make it.
2. Contact the two touchpads with the electrode clips, while keeping them away from the center of the sample as in Figure A.4. The further out the clips contact the gold touchpad, the less likely the AFM will contact the clips when engaging (which would prevent measurement).

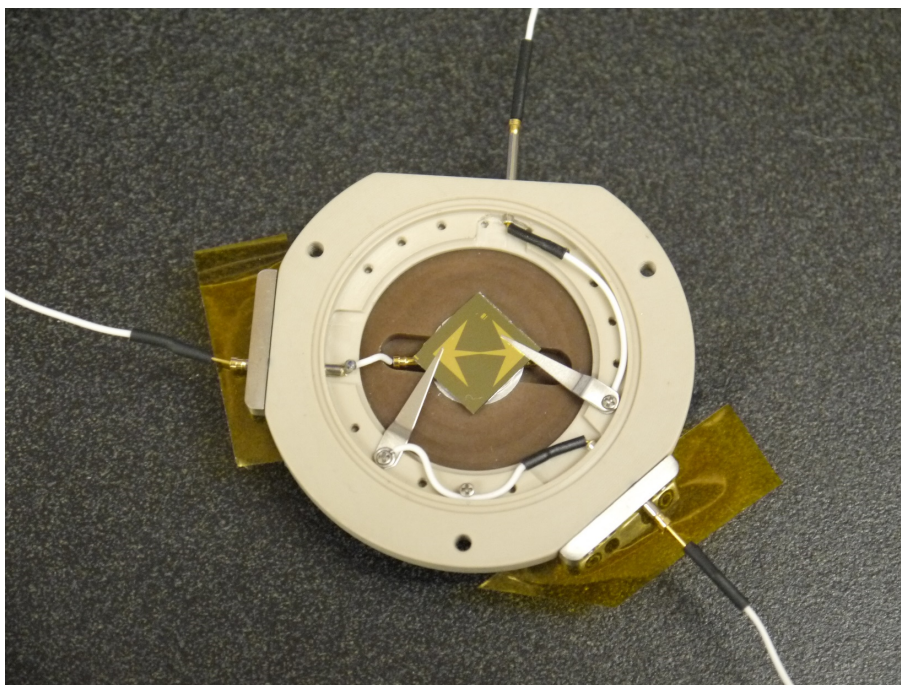


Figure A.4: Gold electrodes in contact with the sample clips

3. If the electrodes are hitting the side of the sample instead of properly going over and contacting the top, washers will be necessary. To use one or more washers, simply place it below the electrode clip in the stack that the screw goes through (washer(s) beneath electrode clip beneath wire loop beneath the screw).
4. Test the electrical contact with an ohmmeter by placing one lead on the gold electrode and the other in the center of the corresponding BNC cable as in Figure A.5.

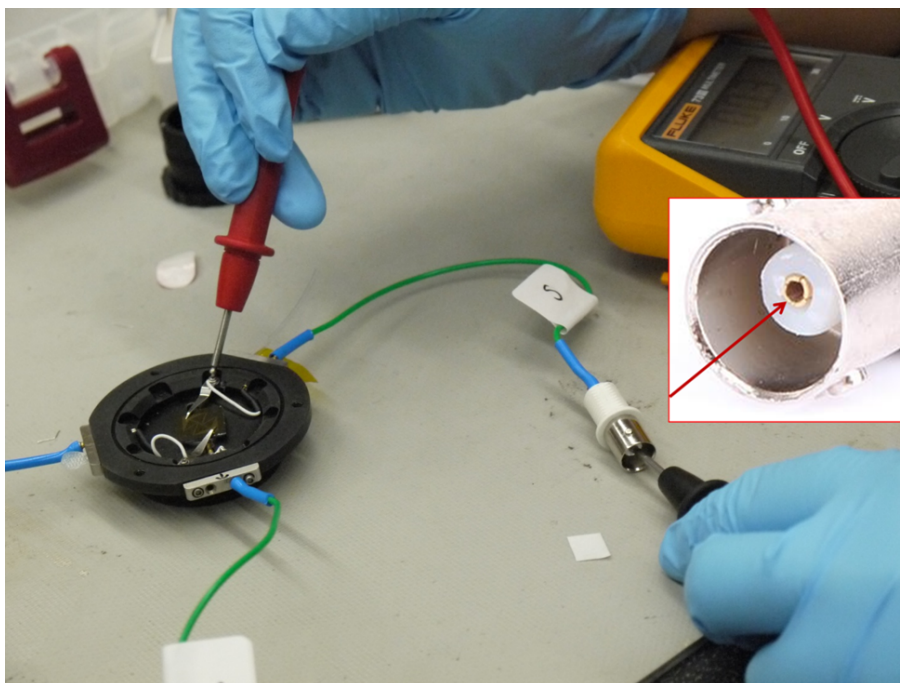


Figure A.5: Where to place the ohmmeter lead to check for electrical connection on BNC cable

5. Close the cell. The O-ring goes into the groove around the outer (top) face of the bottom of the closed cell. The ring begins too small to fit in the groove, so it must be stretched out slightly in order to fit. You can do this by sticking your pointer fingers inside the ring and rotating them in a circular motion while lightly stretching the ring. Then you can place the ring over the groove and wait for it to contract enough to sit snugly in the groove.
6. Closing the cell is relatively simple if you loaded the clamp properly on the cell top. Simply flip over the cell top, align it properly and screw the thumb-screws finger-tightly into the holes.

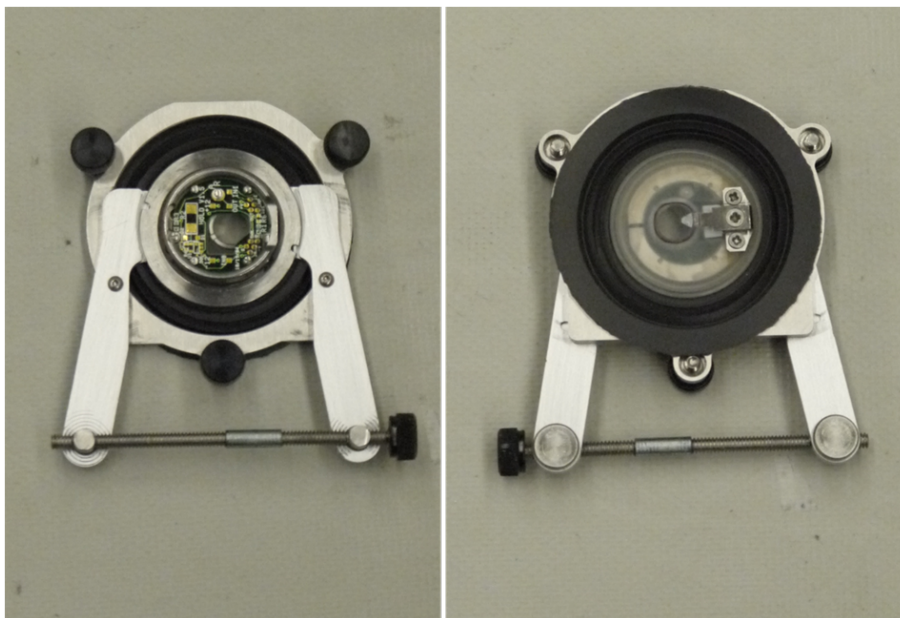


Figure A.6: Assembled top of closed cell with clamp. Here you can see the screws on the clamp that tighten the membrane over the sample holder

7. Load cell into AFM
8. Begin nitrogen flow (and open the lab door!!!) At this point, turn the N₂ flow on. Right now we are running the closed cell with the top float sitting at the top line which is 382 ml/min of N₂. **YOU MUST KEEP THE DOOR OPEN AT ALL TIMES** to prevent an asphyxiation hazard. The flow is very small, but it is best not to chance it.

A.3 Sample Testing

Hazards:

- Oxygen Deficiency Hazard (asphyxiation): from N2 flow
- Compressed Gas: N2 canister

Terminology:

- EFM Electrostatic Force Microscopy
- KPFM Kelvin Probe Force Microscopy
- Point/Time Resolved KPFM A KPFM technique where we sit at a single point on the sample as we vary the applied potential
- I-V A set up designed for taking current-voltage measurements

A.3.1 Configure Asylum software and set up cables

Since samples using the closed cell are air-sensitive, it is best to set up everything for the system and cell before taking the sample out of the nitrogen environment. Note: it usually isnt an issue, but you may need to restart the computer. Then load the Asylum software and configure it at least to the point you can tune the tip, but you should do as much as you can to minimize the samples time out of the nitrogen.

1. Under User Settings, select full or normal panels

2. Set image name and path (date and initials) in the Main tab of the Mater Panel
3. Master Channel Panel: Flatten should say saved:none in all tabs and capture and display should say both trace and retrace in height and phase tabs (z-sensor and amplitude are optional, but should at least say retrace)
4. Click camera icon on bottom of window to open
5. Set scan rate and scan size
6. Load reflective object on stage
7. Load the cell top with the tip, place the scanning head in its normal position.
 - Once the cell is closed and loaded, you will be unable to adjust the tip, so it is best to make sure the tip is loaded well and tunes well. To quickly test this, put a test sample (there is usually a gold-coated piece of silicon mounted on a slide around) on the stage; without it there wont be enough light to do a tuning.
8. Find tip with optics
9. Maximize sum when laser is close to tip point (L_x/L_y), should be around 6-7
10. Minimize deflection (pd)
11. Set target percentage at -5%

12. When just checking tip with reflective surface, do not need to lower stage,
just check angle of scanner head, should be relatively level
13. Cross point panel - lock ALL BNCout to ground as in Figure A.7

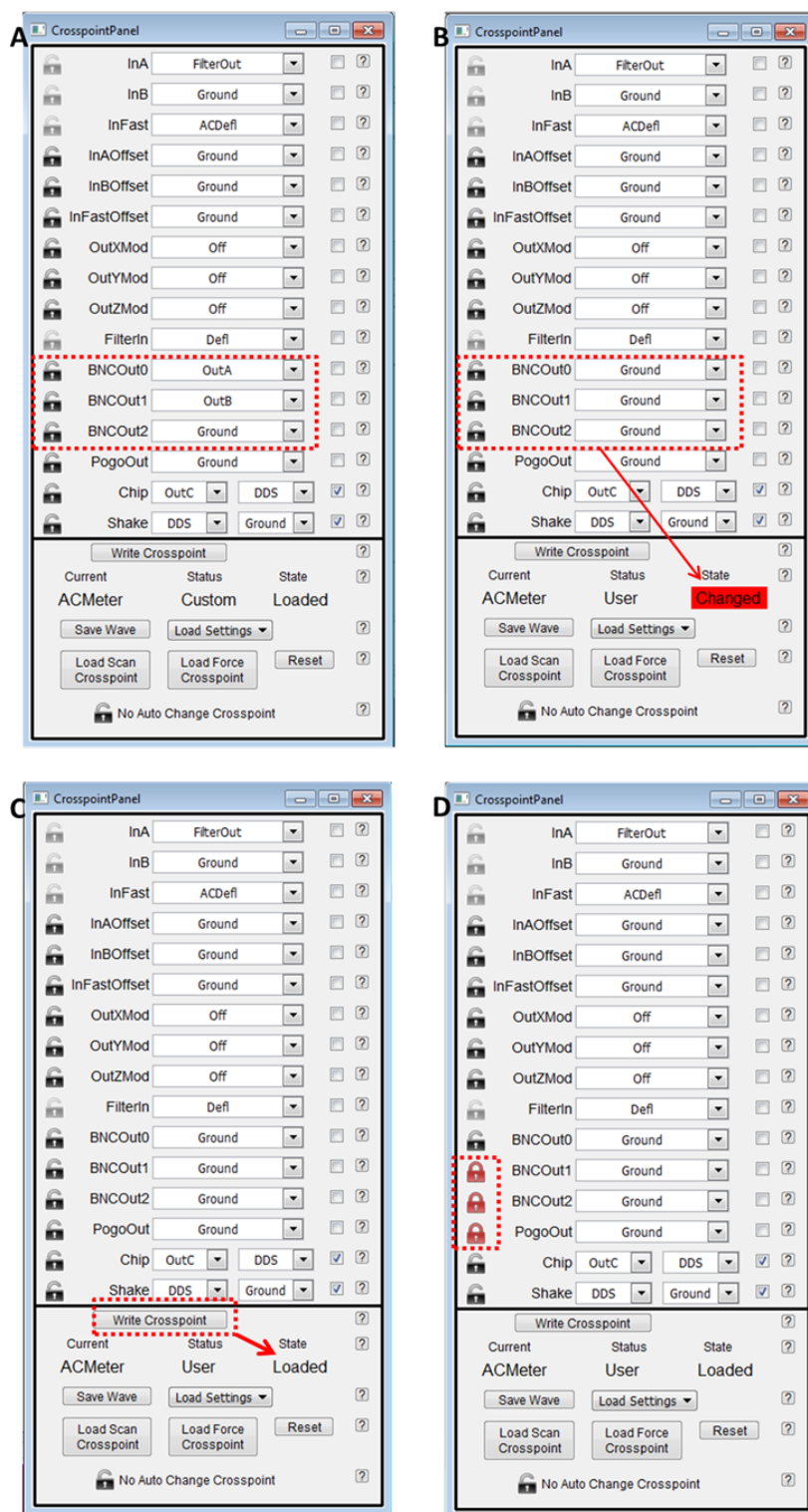


Figure A.7: Description of the oscillatory force caused by a difference in tip and sample bias.

14. Once you are satisfied it is a good tip and was loaded well, unload the cell top and can continue to the next step.
15. Once you have placed the completed closed cell into the AFM, turn the machine over onto the stage and connect the nitrogen.
16. Lower the AFM so that the closed cell body fits into the circular hole in the stage. Once this is done, release the membrane clamp by using the black and yellow screw driver to reach underneath the AFM and unscrew the clamp as in Figure A.8.

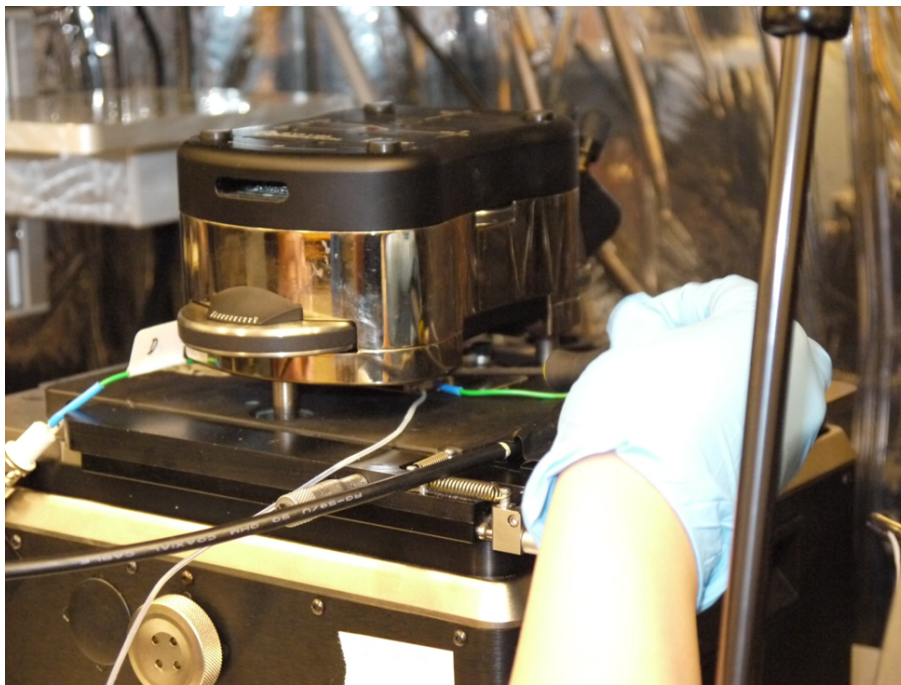


Figure A.8: Reaching under the mounted scanner head to release the clamp on the closed cell top.

17. Proceed to contact the sample gently with the tip. Watch the Z-Voltage carefully. Once the sample is contacted, you should hear a notification noise from the software if the speakers are on. Once you hear this, zero the Z.

A.3.2 IV Characteristics

We use two programs, one which performs a sweep (Voltage Sweep) and one which applies pulses (Jacob Pulse Asylum). Be sure to load and compile the proper program, in this case, the SWEEP program. Both programs use Out.A as the output and In.A as the input.

You can load the program by double clicking the file on your computer and hitting compile OR dragging and dropping the file into the Asylum software OR loading the file through the software menus.

The crosspoint panel is going to have to be set-up so that In.A is set to DDS, and Out.A is set to the electrode you want to sweep or pulse. For the other electrode, in order to apply a static voltage, set it to Out.B and use the command line command: `td_writevalue(B%Out, #)` where `#` is the voltage you want. Voltages between -9.99 and +9.99V can be applied.

Note: you will have to increase the filter on In.A. In order to do so, go into the Programming drop down menu, open the Filter panel and make In.A. up to 25kHz.

Figures A.9 and A.11 show the configuration for electronic measurements.

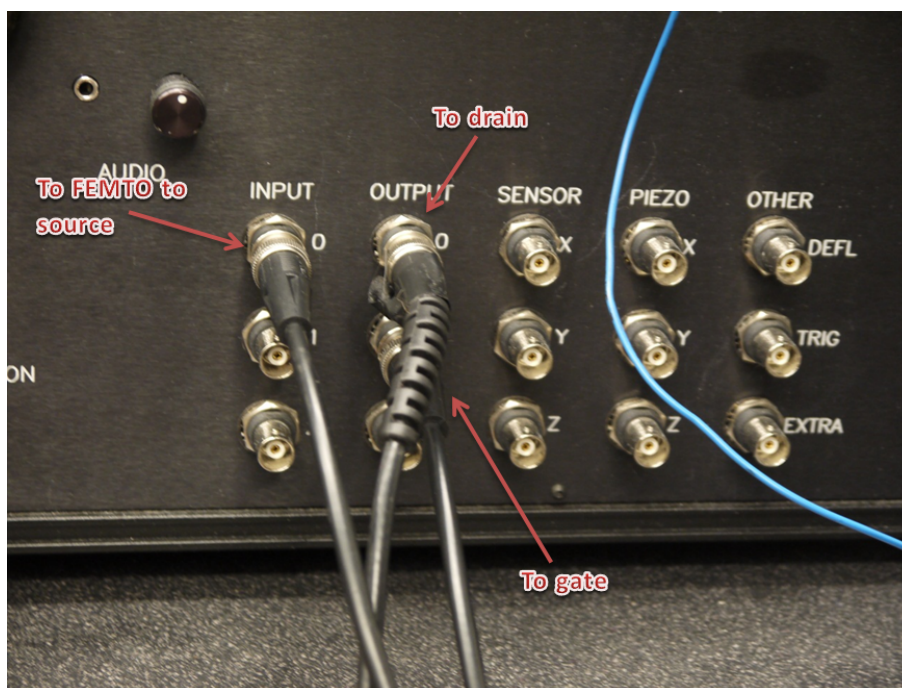


Figure A.9: BNC cables from controller box

The "source" output on the cell is connected to the "Input 0" through the FEMTO, and then the outputs 0 and 1 connect to the input on the KEPCO amplifier, with Output 0 to the 10x multiplier to the drain and Output 1 to the 5x multiplier to the gate.

Note: The ground tab for the input of the KEPCO must be inserted into the RED side to insure the proper sign of bias is being applied to the sample. There are



Figure A.10: Input with banana adapter on KEPCO

two configurations for the crosspoint panel, one for a dynamic gate and one for a dynamic drain, shown in Figure A.11.

<u>Crosspoint Panel, Dynamic Drain</u>	
<u>InA</u>	DDS
<u>InB</u>	BNCin0
BNCOut0	<u>OutA</u> , locked
BNCOut1	Ground, locked
BNCOut2	Ground, locked
<u>Crosspoint Panel, Dynamic Gate</u>	
<u>InA</u>	DDS
<u>InB</u>	BNCin0
BNCOut0	Ground, locked
BNCOut1	<u>OutA</u> , locked
BNCOut2	Ground, locked

Figure A.11: Crosspoint set up for dynamic gate or drain

Run the program using the command line. You must manually save the data. Use the "duplicate" command to save the waves. For the sweep program, the data is:

- VoltageSweepWave (the ideal output sweep)
- CurrentSweepWave (the measured response)

You'll have to save the experiment, and it is in the experiment where the duplicated waves are stored. IT IS RECOMMENDED that you save the waves outside of the experiment as well.

Be certain to plot your results to make certain things are working (e.g. it is very easy to mess up a setting in the Crosspoint).

A.3.3 KPFM

1. Open the electrical tune panel by clicking AFM Controls, Other, Electric Tune Panel, as in Figure A.12. This panel allows the user to find the resonance frequency of the probe when it is driven electrically, and more importantly, to set the phase properly for an electrically driven probe. This phase will be considerably different than that of the same probe driven mechanically with a piezo.
2. Engage on the surface in AC mode as if doing standard AC mode AFM.
3. At the top of the Electric Tune panel set the height above the surface to 1 μ m. Set the trigger to AmpVolts, and the trigger point to whatever your setpoint

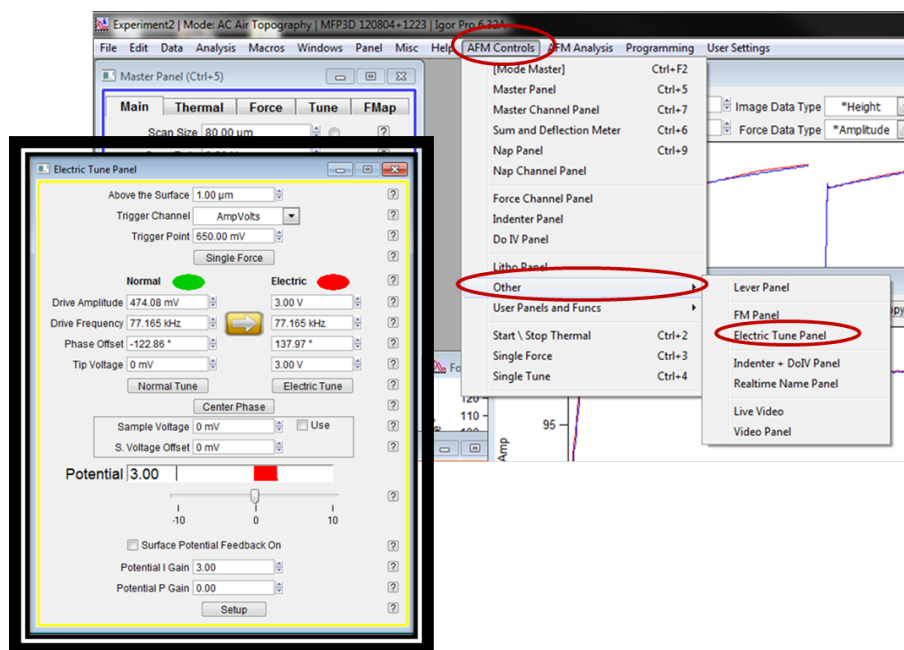


Figure A.12: How to find the Electric Tune Panel

is (typically 600-800 mV). Then click the button marked Single Force, the result should look like Figure A.13. When the force curve is done the tip will be hovering just above the surface.

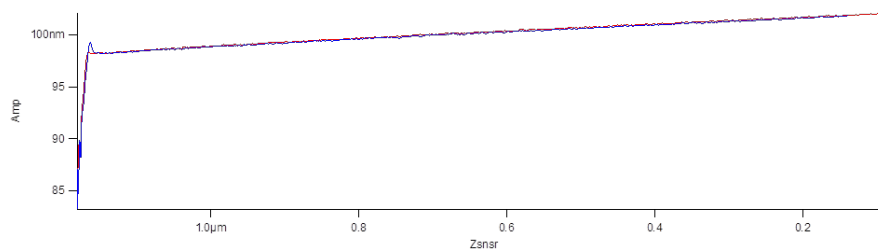


Figure A.13: A typical, good looking force curve.

4. Click on the right arrow button to copy the drive frequency over to the

electric tune frequency. Then click the Electrical Tune. This will sweep an AC bias to the probe and show the response in the tune graph. The resonance frequency will be very close to that of the electric tune. Be sure that the tip voltage field under the Electric column reads 3.0V and that you have at least 500mV in the drive amplitude under the Electric column. If the scan looks bad, you can try raising the drive amplitude higher, I frequently use 3V.

5. Now click Center Phase. The software will set the phase properly so that the feedback loop can function properly.

- Note: The AFM software assumes that the tip is at a positive potential relative to the sample. For samples with very high potential offsets, it may be necessary to set the tip voltage higher than 3V. The easiest way to see if the sample has too high a voltage is to tune everything as described here, then collect an image. normally, if the tip is at too high a potential, the Nap surface potential channel will be railed either at positive or negative 8-10 V (depending on the drive voltage). If this happens set the tip bias to a higher voltage and try again. Repeat if necessary.

6. Open AFM Controls, Nap Channel Panel.
7. Select Potential as a data channel in the Master Channel Panel as in Figure A.14. Selecting this automatically turns the potential feedback loop whenever the scanner is imaging.

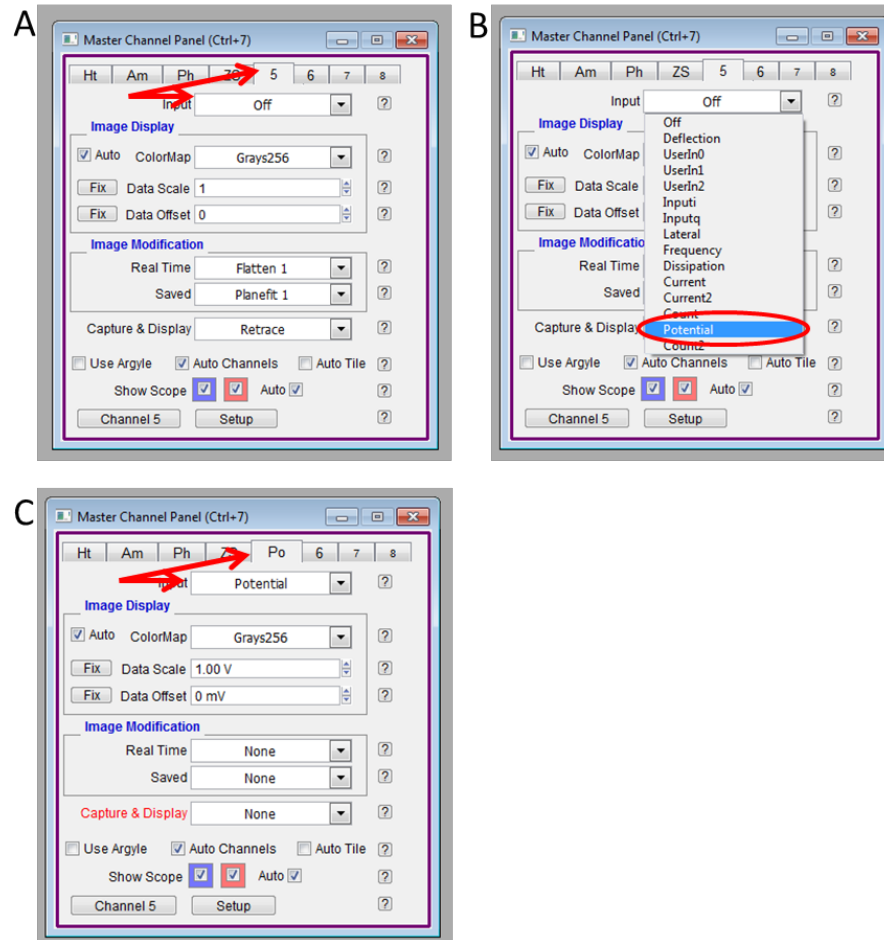


Figure A.14: Master Channel Panel potential tab set up

8. Configure the Nap Channel Panel so that the potential channel is saved without flattening, and that the other Nap channels aren't saved.

Potential is only measured during the NAP phase, so turn it off in the Master Channel Panel and record both trace and retrace in the Nap Channel Panel. You can turn everything else off in the Nap Channel Panel, but height can

be useful to make sure things are working properly.

9. Open AFM Controls, Nap Panel. Select Drive amplitude, Drive Frequency, and Phase Offset under the Params column.
10. Set the Nap Mode to Nap.
11. Our default Delta Height is 50nm. This can be lowered later if you want to try to get better lateral resolution. Because the reference height is based on the zero point of the cantilever oscillations, and because the potential feedback loop will keep the amplitude at zero during the potential scan, it is actually possible to enter a value lower than 0 nm as a delta height. If too low a value is entered, the tip will strike the surface, and significant, obvious scan line errors will occur. If you are imaging a sticky sample, Nap Start Height might need to be raised to get the tip off of the surface for the nap scan.
 - Crosspoint Panel Functionality: You should always perform your first SPM scans with the whole system grounded. In order to insure this, we will need to use the Crosspoint Panel. Make certain for the neutral scan BNCOut0, BNCOut1 and BNCOut2 are all set to ground. Be aware that these can change by changing modes, clicking or unclicking items or performing functions like Single Force. In order to prevent this from happening, you can lock the items on the Crosspoint Panel, but this can prevent them from changing when they need to.

- When the neutral scans are finished, it is time to apply biases. By convention, hook the system up so BNCOut0 is the drain, BNCOut1 is the gate.
- If you have already done your grounded scans and are ready to apply voltages.
- To control the gate and drain voltages it is best to use the Nap Panel. User 0 Voltage and User 1 Voltage set the outputs to the BNCOut0 (drain) and BNCOut1 (source). Verify that BNCOut0 and BNCOut1 are not locked in the Crosspoint panel, then click the User 0 and User 1 voltages on both columns. Setting the number on the left means that voltage is applied during the normal AC pass, and the number on the right is the voltage applied on the NAP phase. Using this, we can take height scans with the voltage off, but NAP with the voltage on.

12. Scan!

13. Advanced: Look at the surface potential data. If the trace and retrace do not match, but seem to be tracking roughly, raise the potential I gain and potential P gain on the electrical tune panel. If the potential data is unstable or very chaotic, try lowering the gains quite a bit. A good starting value is around 1 for integral and 0.5 for proportional. To improve lateral resolution slightly, try lowering the delta height. It might even be possible for this number to be negative, since the zero point is based on AC mode imaging, where the cantilever is oscillating.

A.3.4 Time Resolved KPFM

Point KPFM is where we configure the AFM so the tip hovers at a given point above the surface with the feedback loop on while we pulse or sweep voltages on one of the electrodes.

First, you will need a good topography scan at the location of interest. Once you have completed the scan, in the Master Panel, go to the Force tab. Then click on the Go There tab. This tab allows you to define places in the scan and send the tip there.

1. Click Show Markers to begin. Dragging the cursor around allows you to choose a place. Once you have chosen a point, click on Pick Point (which becomes Thats It!). Spot Number is which spot is currently selected. To go to the point, make sure it is in Spot Number and then click on Go There. Be certain to take a screen capture of your points, because it doesnt save by default.
2. Choose a position, then go through the steps in the KPFM section to electric tune the system. Once the system is tuned, you have to decide what kind of scan you are going to perform.
3. We use two programs, one which applied a single bias to the gate and one which incrementally increases and decreases the bias to the gate. The details of the programs will not be included here, but be sure to load and compile the proper program. Both programs use Out.A as the output and In.A as the input.

4. The crosspoint panel is going to have to be set-up so that In.A is set to DDS, and Out.A is set to the electrode you want to pulse. For the other electrode, in order to apply a static voltage, set it to Out.B and use the command line command: `td.writevalue(B%Out, #)` where `#` is the voltage you want. Voltages between -9.99 and +9.99V can be applied.
5. Always check the crosspoint panel to be set up correctly before you start the scan.
6. Finally, click the checkbox on the Electric Tune panel to turn on the feedback loop.

Note: With the current software it is necessary to increase the filter on In.A. In order to do so, go into the Programming & Filter panel and make In.A up to 25kHz.

7. Run the program using the command line. Both versions of the program require you to manually save the data. I usually use the duplicate command to save the waves. For the pulse program the output is saved as:

- `root:pulse:pulse` (the ideal output pulse)
- `root:pulse:responsea` (the measured surface potential response)
- `root:pulse:responseb` (the measured current response)

You'll have to save the experiment, and it is in the experiment where the duplicated waves are stored. IT IS RECOMMENDED that you also save

the waves outside of the experiment. Be certain to plot your results to make certain things are working (it is very easy to mess up a setting in the Crosspoint or forget to turn on the Potential Feedback loop).

A.4 Data Analysis and automation

As of May 2016, the Aidala lab is developing programs to automate data analysis and is in the process of revising the approach to the extracted data. Please consult your adviser for the most up to date information regarding data analysis.

Appendix B: Materials

- Asylum Research MFP-3D Atomic Force Microscope
- FEMTO current to voltage converter
- KEPCO voltage amplifier
- poly(3-hexylthiophene-2,5-diyl) (96+% regioregular, 32k Mw, Rieke Metals)
- chloroform (anhydrous, Sigma Aldrich)
- octadecyl-trichlorosilane (Acros Organics)
- toluene (anhydrous 99.9%, Sigma Aldrich)
- PTFE dish
- .2um syringe filter, VWR
- 3:1 DI water:Micro-90
- DI water
- acetone (Sigma Aldrich)
- Isopropanol (Sigma Aldrich)

- Substrates are n-type (Sb-doped) low resistivity (0.008-0.020 $\Omega\cdot\text{cm}$) silicon with a 200nm thermally grown oxide layer
- Source and drain electrodes were photolithographically patterned using a dual-layer of Shipley 1313 photoresist over Futurrex LOR5A. The electrodes are 50nm of gold with a 3nm titanium adhesion underlayer, deposited by e-beam evaporation.

