CHARGE TRANSPORT IN MOLECULAR JUNCTIONS WITH SOFT CONTACTS

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ABSTRACT

This thesis describes a novel method to fabricate individually addressable molecular junctions of self-assembled monolayers (SAMs) and presents a series of molecular transport measurements taken with these devices. The results of these experiments are analyzed in terms of a general model applicable across a wide range of temperatures, biases and molecular species.

The molecular junctions presented in this work are the first to exhibit the desired characteristics of nanoscale resolution, high yield and low device-to-device variation. Soft conductive polymer top contacts virtually eliminate shorts associated with diffusion of metal top contacts. We improve several features of previous soft contact devices and demonstrate an order of magnitude reduction in device area. We implement an inorganic dielectric layer with features defined by e-beam lithography and dry etching. We exchange the aqueous PEDOT:PSS conductive polymer used in prior devices for Aedotron P, a low-viscosity, amphiphilic polymer, allowing incorporation of self-assembled monolayers with either hydrophobic or hydrophilic termination with the same junction geometry and materials.

We demonstrate the adaptability of this new design by presenting transport measurements on SAMs composed of alkanethiols with methyl, thiol, carboxyl, and azide terminations. We establish that the observed tunnel-barrier behavior is primarily a function of monolayer thickness, independent of the terminal group’s hydrophilicity and present a model of the device conductivity as a product of several transmission coefficients. We investigate the temperature-dependence of transport, unique to polymer-contacted molecular junctions, and show that the behavior can be explained primarily as a function of transmission through the polymer layer. Finally, we study transport through mixed and homogenous monolayers of conjugated species, revealing the limits of Aedotron P as a contact material.
ACKNOWLEDGMENTS

There are numerous people who have given me immeasurable help throughout my PhD studies. I cannot possibly thank them all or fully convey my gratitude, but I will attempt to briefly do so in this section.

Foremost, I would like to thank my advisors, David Goldhaber-Gordon and Chris Chidsey. I was fortunate during my PhD studies to work for two world-class scientists in unique disciplines.

Working with a great team of physicists in the Goldhaber-Gordon group, I learned a more rigorous way to approach experiments than was demanded of me during my undergraduate research. Whereas I was accustomed to a lot of trial and error, solving problems as they came up, and analyzing results as they came in during an experiment, David challenged me to fully think through every part of a given undertaking. I learned to anticipate what might go wrong and plan for alternate approaches if initial attempts weren’t working. I learned the importance of performing rigorous tests to dial in fabrication parameters rather than attempting to make the device in a single run and then guessing what went wrong (because something always goes wrong). Lastly, I was trained to read up on the appropriate models for the system being studied and work through simulations to predict results before they were taken. In short, David taught me how to prepare for and learn from the inevitable missteps that are part of any complicated experiment.

About a third of my PhD research was conducted in the Chidsey chemistry lab, where I benefited from Chris’s careful, enthusiastic approach to science. To put it perhaps awkwardly, I don’t know that I have ever met anyone who made me feel so lazy by comparison. If I was facing some experimental stumbling block and met with Chris to discuss it, I would leave his office with a stack of papers pulled from his archives, a few sheets of back-of-the-envelope equations, three good explanations for what I was seeing and seven different proposed methods to solve it (some number of which he suggested
trying even after the stumbling block was overcome, because he wanted to know what the result would be). I’ve never met with another professor who in mid-meeting got up, walked out of his office and into the lab, and started pulling chemicals and equipment out to start setting up the experiment he had been discussing.

I am also indebted to my two other Committee members, Professors Stacey Bent and Roger Howe, for both their time and insightful questions during my defense.

During my time in the chemistry department, I was fortunate to meet Ali Hosseini, a skilled post-doc in the Collman, Chidsey, and eventually Goldhaber-Gordon labs. Ali was happy to explain his electrochemical studies of transport through self-assembled monolayers, and patiently helped me to fill in the gaps in my spotty knowledge of organic chemistry. Later, while still working in the Chidsey lab, Ali helped me plan out and begin studying the devices in this dissertation. During the last eight months of my PhD, Ali joined the Goldhaber-Gordon lab for a short post-doc, during which he synthesized an impressive set of conjugated molecules for our transport studies.

Joey Sulpizio, a graduate student in the Goldhaber-Gordon lab, also substantially guided my experimental work. Joey was always eager to discuss physics, politics or pop-culture, while at the same time demonstrating an appreciation for and remarkable ability at the more hands-on pursuits of building setups and fixing equipment. Joey gave me my favorite saying of grad school, “Nothing is hard.” Obviously the implied notion is “…once you put in the time and effort to become good at it,” but I always loved the idea, and perhaps hubris, of believing that you can become an expert at anything if you choose to.

It was a pleasure to work with all of the other graduate students in David’s lab, in particular Adam Sciambi and Francois Amet, who helped me think through aspects of my fabrication process on multiple occasions, and Andrew Bestwick, who was kind enough to perform multiple e-beam lithography runs on Stanford’s new JEOL system. I also received guidance from David’s excellent postdocs, in particular Mike Grobis when I was just beginning my research, and Sami Amasha in more recent years.
During my time at Stanford I was also fortunate to collaborate with students in a number of other groups. Jason Bloking of the McGehee lab helped with the initial tests on the conductive polymers used in this work. Randy Lowe, Jonathan Prange, Anando Devadoss, Joshua Ratchford, and Charles McCrory of the Chidsey lab all took time to listen and offer advice at one time or another. Randy also took some important ellipsometry measurements when we were troubleshooting monolayer formation in our devices. Mike Preiner of the Melosh lab kindly answered my questions about monolayer transport measurements and helped get me pointed in the right direction at the initiation of this project. In studies prior to the present work, I was fortunate to collaborate with Frank Jäkel of the Moerner lab and Jungkyu Lee and Guihua Yu of the Bao lab.

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Finally, I thank my friends and family for their constant support. My great friend Brian Gawalt entered Berkeley’s Electrical Engineering program at the same time I started at Stanford, and he’s been an excellent source of inspiration, humor, and data presentation advice throughout the years. My girlfriend Lilly Wolfson has been a great support, helping me remember the big picture, letting me vent about frustrations at work, playing music with me, and inspiring me to put my head back down and get productive whenever we work at the same table at a cafe.
DEDICATION

This dissertation is dedicated to my uncle Benjamin Neuhausen, who passed away in the summer of 2009. Ben remained a dedicated father, a devoted community member and an enthusiastic member of his profession throughout a prolonged battle with cancer. His courage is an inspiration.
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Figure 56: Conjugated molecular species synthesized by Dr. Ali Hosseini. These include (from left to right) 11-azidoundecanethiol with and without attached ferrocene, azidophenyleneethynylenebenzylthiol $(N_3(\text{PEB})\text{SH})$ with and without attached ferrocene, azidoporphyrin thiol with and without attached ferrocene, and porphyrin-fullerene. The previously measured electron-transfer relaxation rate constants for 11-azidoundecanethiol and $N_3(\text{PEB})\text{SH}$ are presented above those species.

Figure 57: Depiction of (A) 11-azidoundecanethiol, (B) mixed 11-azidoundecanethiol and $N_3(\text{PEB})\text{SH}$, and (C) homogeneous $N_3(\text{PEB})\text{SH}$ SAMs. The images do not convey the actual monolayer packing.

Figure 58: Scatter plot of the common log of current density at 1 V bias for mixed monolayers of $N_3(\text{PEB})\text{SH}$ and 11-azidoundecanethiol, indicating no clear relationship between monolayer composition and current density. Each set is labeled by the molar concentration of $N_3(\text{PEB})\text{SH}$. The blue box delineates the upper and lower quartile, the red line is the median, and the bold symbol is the geometric mean.

Figure 59: Cu(I)-catalyzed click chemistry process by which ferrocene acetylene is attached to a terminal azide group on (A) 11-azidoundecanethiol and (B) $N_3(\text{PEB})\text{SH}$.\cite{4.131}

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Figure 61: Scatter plot of current densities at 1 V bias for azide-terminated SAMs in molecular junctions before and after click reaction with ferrocene acetylene. As in Chapter 5, the measurements have a log-normal distribution. We observe negligible change in the current for porphyrin and 11-azidoundecanethiol devices as a result of performing the click reaction. For the “Porphyrin control” sample we introduce the click conditions and catalyst without ferrocene. There is a decrease in the \( N_3(PEB)SH \) current density after clicking ferrocene, running the reaction for either 1 or 24 hours, presumably as a result of increased tunnel barrier length.

Figure 62: Observed rectification (normalized forward current minus reverse current) for azide-terminated SAMs in molecular junctions before and after click reaction with ferrocene acetylene. We observe negligible (< 1%) rectification for all species except ferrocene-terminated \( N_3(PEB)SH \) (3-4% average rectification).

Figure 63: Porphyrin synthesis.

Figure 64: Ethynyl-functionalized fullerene synthesis.

Figure 65: Scatter and box and whisker plots of measured current density at 1 V bias for 300 nm diameter molecular junctions containing thiol-porphyrin-azide and thiol-porphyrin-fullerenes. Despite the SAM of the fullerene-containing molecule being substantially thicker and possessing a different LUMO, the measured currents appear to be roughly equivalent.
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CHAPTER 1: INTRODUCTION

1.1 THE PROMISE OF MOLECULAR ELECTRONICS

In the last 50 years the world has seen exceptional advances in the field of computing. This is due primarily to the technological and economic gains made through the scaling of transistors, decreasing the cost and available complexity of computational power. Known as Moore’s Law, after Intel founder Gordon Moore, the exponential nature of this advancement was first noted in a 1965 paper. It has been summarized as the notion that the number of transistors that can be fit into a given area roughly doubles every 18 months. Since this time, the noted relationship has become self-fulfilling, as the semiconductor industry has adopted it as a research and development plan, named the International Technology Roadmap for Semiconductors (ITRS). Figure 1 illustrates this exponential increase over time, with data points representing industry-leading processors in a given year.

Figure 1: Log scale plot of the number of transistors on a commercial chip vs. year, illustrating the exponential relationship described by Moore's Law.
In practice, transistor scaling was initially accomplished in a straightforward manner, simply shrinking all of the physical dimensions (length, width and oxide thickness) and increasing the channel doping of a device by a constant factor $\kappa$ (typically equal to $\sqrt{2} = 1.41$ between successive generations), as demonstrated in Figure 2. This technique is known as “constant field scaling,” because the gate-induced field in the transistor channel remains unchanged if the gate voltage is also reduced by a factor of $\kappa$. As a result of the reduced gate voltage, even as the device density increases by a factor of $\kappa^2$, the power density of a chip remains constant, as presented in Table 1.\(^4\)

![Diagram of transistor scaling](image)

Figure 2: Demonstration of adjustment in physical device dimensions in a constant field scaling regime.\(^4\)

The primary obstacle to continued constant field scaling is the inability to indefinitely increase the channel doping concentration, as mobility and carrier velocity are reduced at high doping.\(^5\) Thus, in the mid 1980’s the industry adopted “generalized scaling,” which entails scaling with a slower doping concentration increase, $\alpha/\kappa$, at the expense of increasing power density of $\alpha^2$. This increase in power density with successive generations can be seen in Figure 3A.\(^6\)
Table 1: Device parameter changes in constant field and generalized scaling regimes. $\kappa$ and $\alpha$ are scaling parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Constant F Scaling</th>
<th>Generalized Scaling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Device dimension ($L_g$, $W$, $t_{ox}$)</td>
<td>$1/\kappa$</td>
<td>$1/\kappa$</td>
</tr>
<tr>
<td>Doping Conc.</td>
<td>$\kappa$</td>
<td>$\alpha/\kappa$</td>
</tr>
<tr>
<td>Voltage</td>
<td>$1/\kappa$</td>
<td>$\alpha/\kappa$</td>
</tr>
<tr>
<td>Carrier velocity</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Circuit Density</td>
<td>$\kappa^2$</td>
<td>$\kappa^2$</td>
</tr>
<tr>
<td>Power Density</td>
<td>1</td>
<td>$\alpha^2$</td>
</tr>
</tbody>
</table>

In the past decade, power density was further increased as a result of increasing off-state leakage. As oxide thicknesses have reached the nanometer scale, quantum tunneling of carriers through the oxide layer between the gate and channel has resulted in substantial current drain even from devices not currently in use, contributing to the overall power consumption of chips. This has been countered to an extent by the introduction of so called “high k,” or high dielectric constant, gate materials like aluminum and titanium oxide, such that the same gate-induced channel field can be achieved with a physically thicker gate.

There is a power density limit of roughly 100 W/cm$^2$ that can be maintained with an inexpensive air-cooling system. As seen in Figure 3B, this limit has come into effect in the past decade. Scaling has continued, but switching speeds are now constant between generations, with increasing computational ability achieved primarily through parallelization, as realized with multicore processors. For the foreseeable future, processor clock speeds will remain at a few GHz, and some of the benefits of each successive generation of scaling will be lost to overhead costs associated with parallelization. Power consumption has also arisen as a hurdle in the development of mobile computing devices; particularly smart phones and tablets, which operate on battery power and utilize passive cooling. As seen in Figure 3B, Intel’s Atom processor, intended for mobile applications, marked a return to much lower power density levels.
Figure 3: (A) Exponential plot of chip power density vs. year, with comparison to some well-known high power-density technologies.\textsuperscript{6} (B) Similar plot to (A) but continuing past 2005 we see that power density flat-lined with the introduction of multi-core processors.\textsuperscript{7}

To overcome the issue of power-density limitations, as well as other shortcomings of scaled silicon, many technologies have been proposed to supersede or at least complement the dominant technology, as shown in Figure 4, a projection by the ITRS from 2005.\textsuperscript{8} Considering the need for a low-power technology that can be scaled beyond the limitations of silicon, the technologies labeled “molecular” reside in a promising territory on the chart. This block refers to devices composed of individual up to dozens of organic molecules, in a field broadly known as molecular electronics. Molecular devices are anticipated to have the smallest size scale of all proposed post-silicon technologies. This is because control of individual molecular structures through synthetic chemistry is effectively the massively parallel manipulation of matter with atomic precision. In addition, it is predicted that molecular devices will be extremely cheap, both because the elements used in organic synthesis are readily abundant and because so little material is required as a result of the small scale. Finally, it is projected that molecular devices will require somewhat less power than silicon, as most proposed switching mechanisms include the mechanical reconfiguration of molecular species (but not the making and breaking of carbon bonds, which would short a device), a lower-energy process than the capacitive charging that drives CMOS switching.\textsuperscript{8}
Figure 4: Graph from ITRS Emerging Research Devices Report, presenting size, switching time, cost and energy consumption of proposed post-silicon technologies. Molecular electronics is proposed to be small, cheap, moderately low power, and slow.\textsuperscript{8}

This is the primary promise of molecular electronics – a means to achieve device dimensions smaller than those allowed by the physical limitations of semiconductor processing, potentially enabling extremely scaled logic and memory elements for use in more powerful, lower-energy-consuming computers and information storage units.\textsuperscript{9,10} These proposed advantages come from leveraging the precision of synthetic chemistry and the use of “bottom-up” fabrication techniques such as self-assembly. Numerous device designs utilizing single or few organic molecules have been proposed, ranging from simple two-terminal memory elements to complex multi-input and output logic elements.\textsuperscript{11–13}

As an aside, we note that beyond the issue of power density limitations, the continued scaling of silicon technology faces other hurdles, including lithography of ever smaller features, interconnect electromigration, and tunneling between closely spaced
interconnects. However, these issues are common to all proposed post-silicon technologies.

As will be explored in the next section, there remain many hurdles to the implementation of molecular electronics as logic devices. While not discussed in this dissertation, molecular-scale devices have already found some application in the field of chemical sensors. Nanowire- and nanotube-based devices have begun replacing assay-based sensors on microfluidic chips, achieving unprecedented detection of cells, proteins, antibodies and selected DNA sequences.

1.2 THE PITFALLS OF MOLECULAR ELECTRONICS

The primary hurdles to the development of molecular electronics include a poor understanding of the switching processes in molecular devices, the sensitivity of devices to environmental conditions, and most difficult, the domination of device characteristics by the unpredictable nature of the contacts.

While a few different active molecular devices have been demonstrated, the nature of the switching processes is often poorly understood, and whether the observed behavior is actually due to the molecule has been subject to question and later revision. For example, using single-molecules in break junctions, two groups have observed Kondo resonances that can be correlated with particular oxidation states of the molecule. The gate voltage at which the Kondo-associated zero-bias anomaly appears varies substantially from device to device, presumably because of differences in the gap structures and how the bridging molecules have assembled between the contacts. Calling into question the molecular nature of the Kondo effect seen in these experiments, Houck et. al. have shown that the Kondo effect can be observed in bare gold electromigrated break junctions without any molecules as a result of the formation of atomic-scale metal grains. Sordan et. al. have shown the presence of Coulomb blockade in bare junctions with a similar explanation.

James Heath’s group has demonstrated another active molecular switch consisting of a self-assembled monolayer (SAM) of rotaxane molecules sandwiched between polysilicon and evaporated titanium electrodes. The proposed switching occurs due to the
transversal of a ring structure in the molecule between two metastable states, changing the observed tunneling current. These results are called into question in earlier work by de Boer et al. showing that the deposition of volatile titanium as a contact material damages underlying organic layers. Piling on additional reason for skepticism, experiments by other groups after Heath’s first demonstrations showed that such switching could be observed in similar structures with arbitrary molecular species.

While it is not presently a stumbling block, the susceptibility of organic materials and interfaces to environmental factors poses potential complications for their integration into computer chips. For example, unbound thiols will oxidize and the conductivity of polymers can be affected by oxygen and water vapor upon exposure to ambient. This implies that molecular devices must be packaged, but they are still susceptible to temperature effects from downstream processing. For example, an alkanethiol SAM on gold will begin to desorb into hexadecane solvent at around 80°C. While potentially challenging, such temperature limitations aren’t hopeless. For example, the dual damascene process to deposit and pattern copper interconnects is performed at ambient temperatures.

The greatest obstacle to widespread adoption of molecular electronics technology is the difficulty in forming reliable, robust contacts to devices. Figure 5 is taken from a paper presenting a density functional theory (DFT) simulation of transmission as a function of applied bias for a single molecule between metal contacts with various atomic configurations. Figure 5A shows a series of (001) and (111) oriented surfaces, including contacts a few atoms wide (to simulate a break junction between nanoscale wires) and contacts of infinite extent. The DFT simulation results, presented in Figure 5B, show that for this ideal case of atomically perfect wires and bonding between the molecule and contacts, the adjustment of the contacts by a single atom in width causes substantial shifts in the transmission function. One should also note that there is a shift of about 1 eV for the peak transmission energies of (001) versus (111) surfaces. A similar result was found with a statistical first-principles study of bipyridine and alkanedithiol molecules between gold wire electrodes differing by a single adatom. One can extrapolate that in disordered contacts as seen in break junction devices spanned by single molecules, there are
substantial variations between devices as a result of the contact structure. In addition, molecules often prefer to bind to irregular defect sites such as adatoms, vacancies, or along the edges of terrace structures on a crystalline surface.

Figure 5: (A) Schematics of atomic structure of simulated metal-molecule-metal contact geometrics. a-c) (001) surfaces. d-f) (111) surfaces. (B) Calculated transmission coefficient vs. energy from density functional theory simulation of contacts in A. Overlaid dark lines are for infinite periodic surfaces. a) 001 surface morphology. b) 111 morphology.

Experimental studies of molecular transport yield many examples of the poor reproducibility of metal-molecule contacts. The Kondo-resonant single-molecule studies mentioned earlier in this section were performed in experiments with 10-15% yield, which is not uncommon among single-molecule junction studies. In review articles from both 2003 and 2011, the authors detail the pressing need for better studies of the interfaces between molecules and metals, and examine a multitude of research into
producing more reliable contacts. In Chapter 2 we will review the variety of techniques demonstrated in the quest to produce reliable molecular device contacts.

1.3 METHODS TO OVERCOME MOLECULE-CONTACT VARIATION

To average out the contact-induced variations discussed in the previous section, experimentalists studying molecular transport have resorted to two general strategies. The first is the measurement of statistical distributions of two-terminal single-molecules. These studies typically employ contact geometries that could not be readily integrated into a scalable architecture, but they have yielded a wealth of information about molecular transport. In addition, the simple experimental structures studied in these systems can be readily, if not necessarily accurately, simulated using a variety of theoretical techniques. The methods used for these types of experiments include scanning tunneling microscopy and conducting atomic force microscopy probing of molecules on substrates, and the measurement of molecules spanning narrow junctions formed from wires broken by electromigration or mechanical strain.

The second strategy is concerned with parallel transport through many ordered molecules in a self-assembled monolayer (SAM). In contrast to single-molecule experiments, many SAM measurements are designed with the goal of fabricating scalable devices with low variation. This is the focus of the present work, in particular, how to contact SAMs confined to nanoscale electrodes. Both sets of techniques will be reviewed in Chapter 2. Figure 6 illustrates these two general approaches.
1.4 UNIQUE CONTRIBUTIONS IN THE PRESENT WORK

This work is motivated by studying existing designs for molecular electronics devices and then seeking to improve the most promising technology. As will be detailed in Chapter 2, we conclude that polymer electrodes on top of confined SAMs on gold substrates have a strong potential to finally provide a robust contact method for molecular devices. The outstanding problem with this technique seemed to be the inability to scale such devices below a footprint of a few square microns. Thus, the key development of the present work is the scaling of polymer-contacted molecular devices to an area of less than one-tenth of a square micron, with the potential to produce even smaller devices. This is achieved through the development and implementation of several novel fabrication techniques. We develop a method to pattern nanoscale pores in a double-layer dielectric on gold. We demonstrate a novel etch process to ensure high purity of the exposed gold surface for good SAM formation. We utilize a novel low-viscosity, amphiphilic conductive polymer as the top contact material. We successfully demonstrate the scaled devices we set out to make.

We characterize our devices with a series of studies on alkanethiol SAMs, testing various molecular lengths and terminal groups at a range of temperatures. We test a
number of previously-unmeasured conjugated species in both homogeneous and mixed SAMs.

1.5 OUTLINE OF THIS DISSERTATION

In this chapter we have discussed the motivations for undertaking this work and presented a body of terminology for referring to SAMs. In the next we will present a review of ongoing molecular electronics studies – both research on transport through single molecules and attempts to build scalable devices incorporating SAMs. We will then present the specifics of the present work, beginning with a detailed explanation of the fabrication process. In Chapter 4 we will introduce two models with which to understand subsequent measurements. In the next chapters we will present transport measurements on SAMs of alkanethiols with varying lengths and terminations, taken at varying temperatures. We explain the observed data in terms of the models in Chapter 4. In Chapter 7 we present studies on additional molecular species, including conjugated molecules, mixed monolayers of conjugated molecules and alkanethiols, and ferrocene and fullerene terminated species. Finally, we will present a set of concluding remarks at the end of the main text. We will show that molecular junctions with conducting polymer contacts hold some promise for use in scaled molecular device designs. However, they are not a reliable test bed for the study of molecular transport due to confounding factors introduced by the polymer contact, particularly at low temperatures. Appendices will feature more detailed explanations of the laboratory procedures, measurement setups, and the Matlab simulation code used in this project.
CHAPTER 2: BACKGROUND

In this chapter we present a review of both historically important and ongoing molecular electronics studies. As discussed in the previous chapter, because of the difficulty of forming consistent molecular contacts, molecular electronics studies must average out variations either temporally, by taking many sequential transport measurements, or spatially, through the measurement of many molecules in parallel, typically in a SAM. This section will begin with a review of the terminology and technology of SAMs, discuss techniques to measure transport through self-assembled monolayers, and then review experiments to measure transport through single molecules.

2.1 SELF-ASSEMBLED MONOLAYERS

2.1.1 SAM COMPOSITION

A self-assembled monolayer (SAM) is a single organized layer of molecules that spontaneously align on a substrate due to intermolecular interactions and affinity between the molecular head-group and the substrate material. The structure of these formations is influenced by van der Waals forces, hydrogen bonding, and dipole-dipole interactions, each of which depends on the shape, length, functional group, and dipole moment of the assembling species. SAMs have been demonstrated on a variety of substrate materials, including noble metals and both metal and silicon oxides.

There are three key parts of a self-assembling molecule, as depicted in Figure 7A. The head group is the functional group that binds to the substrate. In the case of noble metal substrates this is typically an amine or thiol, while phosphonic acid and siloxane are popular choices for oxides. The backbone, or tail of the molecule is the generic name given to everything between the head group and termination. Backbones can range from simple alkanes and paraffinyls to more complex structures such as naphthalene, “cage” molecules such as carboranethiols, and even large, bulky species such as porphyrins, as demonstrated later in this dissertation. The termination, or functional group, of the
molecule is the end facing away from the substrate. This group is sometimes chosen to have some chemical functionality for the purpose of binding another molecule to the surface, as in the use of carboxyls for amide coupling or azides for azide-alkyne cycloaddition chemistry.\textsuperscript{40–42} Other common terminal groups are thiols and amines, chosen because they are symmetric with the head group, methyls, chosen for their hydrophobicity, and hydroxyls, chosen for their chemical functionality or hydrophilicity.

Organic thiolated monolayers have been the focus of extensive research over the last few decades.\textsuperscript{27} Thiols form strong bonds with noble metals, making these SAMs stable in a variety of solvents, temperatures and potentials. Sulfur-gold bonds have a binding energy of greater than 100 kJ/mol,\textsuperscript{43} while sulfur-silver bonds are even stronger.\textsuperscript{44} Alkanethiols are the most popular SAM-forming material because of their dense and fast assembly and the ease of preparing solutions of these molecules. An alkanethiol SAM is depicted in Figure 7B.\textsuperscript{45}

The structure of a SAM with thiol head groups is determined by a balance of the intermolecular forces with the corrugation potential of the interaction of the sulfur with the substrate.\textsuperscript{46} As a result, an average spacing of adsorption sites of 5 Å and the optimum van der Waal’s distance of 4.5 Å yields a tilt of alkanethiol hydrocarbon chains by about 30° away from the surface normal on (111) gold. Despite (111) silver having roughly the same lattice constant as gold (2.88 vs 2.89 Å), the alkane chains are oriented significantly more upright (0–15°). Explanations for this phenomenon vary, but it has been proposed that a higher surface packing density is feasible on silver, and therefore, the van der Waals interactions reach an optimum with less canted chains.

Additional considerations in the formation of SAMs are the solvent\textsuperscript{47,48} and temperature\textsuperscript{49} during the self-assembly, and the length and solvent concentration of the molecule. Weak solvation will help drive molecules to the surface and prevent desorption back into solution, provided the species is fully dissolved. Higher temperature typically results in faster monolayer formation, but can also promote unwanted side-reactions such as disulfide bonding or oxidation of exposed thiols. Longer alkanethiols demonstrate better packing due to solvation effects and stronger van der Waals bonding, but long dithiols can loop back to the surface, forming defect sites.\textsuperscript{50,51} Controlling the molecule
concentration during formation can alter the amount of looping, with a high concentration driving molecules to more quickly reach a critical surface density and translate into the “standing up” phase.

![Diagram of terms for molecular species in a SAM](image)

**Figure 7:** (A) Diagram of terms for molecular species in a SAM. (B) Illustration of a well-packed alkanethiol SAM.⁵¹

### 2.1.2 SAM FORMATION AND MORPHOLOGY

Extensive studies have been performed on the kinetics of alkanethiol SAM formation and the resulting semi-crystalline molecular structure. SAMs begin forming as soon as an appropriate substrate is immersed in a liquid or gaseous environment containing molecules that can bind to the surface. For a crystalline Au(111) surface, it has been proposed that thiols coordinate between three surface gold atoms, resulting in a so-called c(4x2) structure, as illustrated in Figure 8A.⁵² Through topographical studies performed with a scanning tunneling microscope (STM), it has been shown that SAM formation begins with alkanethiols in a “lying-down” state, with the alkane tail against the substrate. At this point, molecules can translate along the surface and form coordinated
islands, as shown in the early stages of Figure 8C and D. Once a critical density of surface-bound molecules is reached, islands of alkanes undergo a phase transition to “standing-up” phase and the alkanes orient normal to the surface. A consequence of this phase transition occurring concurrently on isolated islands is that many islands end up with different c(4x2) orientations, creating dislocations in the SAM, as illustrated in the STM image of a fully formed SAM presented in Figure 8B.

Figure 8: (A) Model illustrating the c(4x2) superlattice of alkanethiol head groups on Au(111). Light gray circles represent Au atoms, dark gray circles represent thiolate molecules. Diagonal lines indicate the projection of the plane of the all-trans hydrocarbon backbone. In the schematic, it is assumed that the sulfur binds in 3-fold hollow sites of the Au(111). (B) STM image of fully-formed SAM. (C, D) STM images and corresponding side-view illustrations demonstrating SAM formation process.
While most studies utilizing STM imaging of monolayers are performed on flame-annealed poly-crystalline Au(111) substrates, it has been shown that a well-ordered substrate is not necessary for the formation of a well-packed SAM. In particular, Chidsey et al. conducted a number of ellipsometric and electrochemical characterizations of alkanethiol and conjugated backbone SAMs on highly (111) textured, polycrystalline gold-on-titanium layers deposited through electron beam (e-beam) evaporation, and found bulk characteristics identical to those realized on Au(111) surfaces. This is partially because the dominant force in SAM organization is the van der Waal’s interactions between alkanethiols, which is independent of surface morphology, but also due to the (111) nature of evaporated gold films.

2.2 SELF-ASSEMBLED MONOLAYER TRANSPORT MEASUREMENTS

This section will present a review of transport studies on SAMs. In addition to determining the conductance of various molecular species, some of the discussed devices represent attempts to develop functioning scaled molecular electronics. Akkerman et al. described an ideal molecular electronics device geometry as sandwiching the molecules between two electrodes and utilizing the ordered molecular domains of a SAM to ensure low variation and consistent physical properties as the device footprint is scaled. We show that a variety of fabrication methods with this geometry have been explored, each with unique advantages and drawbacks. The first three techniques discussed in this section deal with transport measurements devised for experimental settings and not envisioned for use in scalable devices. The last five techniques detail increasingly robust and high-yield molecular device designs.

2.2.1 ELECTROCHEMICAL MEASUREMENTS OF SAM TRANSPORT

Surprisingly, the earliest measurements of transport through SAMs were perhaps the most reliable. Just a few years after initial publications on alkanethiol SAM formation on gold substrates, Chidsey and collaborators used ferrocene terminations to effectively bond a single-electron charge reservoir directly onto the tail of an alkanethiol species. This molecule was then incorporated in mixed monolayers and studied via
electrochemistry, as depicted in Figure 9.\textsuperscript{60,61,56,57} After monolayer formation, the substrate is clamped in a teflon cone, which defines a working electrode area (typically ~1 cm\textsuperscript{2}). An electrolyte (1M HCIO\textsubscript{4}), counter electrode (platinum gauze), and reference electrode (Ag/AgCl/saturated KCl) are then placed in the cone. The bias between the working and reference electrode is then swept to positive and negative potentials at a constant rate, and the current through the working electrode is monitored, in a process known as cyclic voltammetry. Peaks in the forward (reverse) current evidence ferrocene oxidation (ferrocenium reduction). By examining the difference in the potential and timing of reduction and oxidation wave peaks on a cyclic voltammogram, one can extract the rate at which electrons transfer through the molecular backbones, and hence the conductance. This method of measuring transport has also been demonstrated for SAMs on silicon,\textsuperscript{62} SAMs with ruthenium redox tail groups,\textsuperscript{63} and for SAMs of conjugated molecules.\textsuperscript{58}

![Figure 9: Inferred structure of the monolayer formed by coadsorption of a ferrocene-terminated alkane thiol (highlighted with black bonds) and an unsubstituted alkane thiol on Au(111).\textsuperscript{56}](image)

Electrochemical measurements reliably yield the molecular conductance without the complications of the solid contact methods discussed in the following sections. For example, current leakage is not an issue. Charge transferred from the ferrocene supplies the measured current, so as long as the monolayer is well packed there will be negligible transport through paths other than the molecular backbone. In addition, solid top contacts often exhibit complicated transport across the interface to the molecular terminal group,
but with electrochemical measurements the ferrocene is reliably chemically bonded to the molecule.

One disadvantage of electrochemical transport measurements is that ions in the electrolyte must complete the circuit between the ferrocene and a remote electrode. The resistance to migration of the ions in the electrolyte and the capacitance of the SAM-coated electrode together limit how quickly the voltage can be swept, meaning peak splitting cannot be observed for conjugated molecules with fast transport. Robinson et. al. demonstrated the use of microelectrodes, which can be more readily accessed by ions in the electrolyte, to measure some conjugated species.64

2.2.2 **LIQUID METAL CONTACTS**

Similar to electrochemical studies, the use of liquid metal contacts is an elegant means to measure SAM transport, even if it is not directly applicable to the development of scaled devices. Due to the lack of any substrate defects and the ease with which alkanethiols can rearrange on the surface, these molecules can form well-ordered, defect-free SAMs on mercury drops. This system has primarily been investigated by the Whitesides group, first with millimeter-scale junctions between two SAM-coated mercury drops65–67 and later with SAM-coated mercury drops brought into contact with SAMs on variously prepared silver substrates.68 The presence of a monolayer on both surfaces reduces the number of defective devices, as mercury’s strong affinity for alloying with noble metals often leads to catastrophic failure. The tunneling interface between the SAM on each surface complicates the interpretation of results.

Eutectic gallium-indium (EGaIn), another room temperature metal, has been introduced as an alternate top contact material. The skin of the material consists of a few angstroms of oxidized gallium, resulting in a pliable liquid that conforms to surfaces, yet can hold its shape in filaments as small as 1 μm in diameter.69–71

2.2.3 **CROSSED WIRES**

In a number of studies, Kushmeric et. al. have demonstrated a method to repeatedly contact varying areas of a SAM in a junction between two wires.72–77,34,78–82 As shown in
Figure 10, two sets of metallic 10 µm diameter wires are mounted on a test stage in a crossed geometry. A SAM is formed on one set of wires. A perpendicular magnetic field and small current are applied the other set. The induced Lorentz force gently brings the wires together. By controlling the current, the force between the two wires can be precisely varied to change the area of the junction from a few to up to thousands of molecules. The authors claim that the curvature of the wires is negligible compared to the area of SAM measured, but this seems to conflict the ability to so precisely alter the number of molecules in the junction. By varying the metals in each set of wires, different SAM substrate materials can be tested and asymmetric junctions can be created.

![Crossed-wire molecular junction schematic](image)

Figure 10: Crossed-wire molecular junction schematic. B is the applied magnetic field, $i_{def}$ is the applied deflection current.

### 2.2.4 Evaporated Metallic Contacts

The first SAM transport measurements to employ solid top contacts used simple vapor deposition of metal contacts directly onto the monolayer surface. The SAMs are formed in pores fabricated in a thin dielectric layer, as shown in Figure 11. This technique allows fabrication of devices at a scale of tens of nanometers. However, metal filament formation in the monolayer results in poor yield when the SAM consists of any molecules other than alkanedithiols or the evaporated contact is formed from any material other than gold, as illustrated in Figure 12A. This occurs even when the substrate is cooled to liquid nitrogen temperatures and the evaporation system is back-filled with Argon to ensure scattering of the evaporated metal atoms so that they are deposited with minimal
energy. Figure 12B presents IR spectroscopy data to this effect, showing that titanium completely destroys the CH$_3$ bonds in a hexadecanethiol monolayer while gold and aluminum penetrate the monolayer. Despite these findings, some research teams have continued to produce devices with evaporated titanium top contacts, most notably the questionable rotaxane-based molecular memory elements demonstrated by Green et al.$^{22,23,87}$

![Figure 11](image1.png)

Figure 11: (A, B) Schematics of metal-SAM-metal device. (C) IV plot demonstrating unique rectification behavior in device, likely due to reaction of evaporated titanium with the monolayer rather than any intrinsic molecular behavior.$^{84}$

![Figure 12](image2.png)

Figure 12: (A) Monolayer penetration by evaporated metal. (B) Grazing-incidence Fourier transform infrared spectroscopy of monolayer surface. CH$_3$ stretch vibration peaks are at 2879 and 2937 cm$^{-1}$. These decrease after Au/Al metal evaporation due to monolayer penetration. Ti evaporation completely destroys the SAM.$^{24}$

### 2.2.5 **Atomic Layer Deposition Contacts**

A more recent method demonstrated by Preiner et al. utilizes atomic layer deposition (ALD) to deposit an initial barrier of a few nanometers of insulating aluminum oxide on SAMs of carboxyl-terminated alkanethiols, as illustrated in Figure 13.$^{88}$ Metal contacts
can then be deposited without forming shorts. The dielectric formation first proceeds slowly as initial seed islands are formed on the monolayer surface. Once an initial atomic layer has been deposited, deposition occurs at a rate of 1 atomic layer per tetramethylaluminum-water exposure cycle. Another advantage of this technique is that the oxide will preferentially deposit at defect sites, effectively plugging holes and dislocations in the monolayer. While Preiner only worked with millimeter scale devices, this method would likely translate to the nanometer scale, as ALD deposition is conformal and the reactants are introduced in the gas phase. In addition to confirming previous measurements of the length-dependence of the conductance of alkanethiols, inelastic electron tunneling spectroscopy (IETS) was used to verify the bond energies of the SAM species, and holds promise as a way to investigate the energy levels of more complicated systems such as porphyrin-metal complexes. The technique is limited to studies of molecules with hydrophilic terminations, as the water vapor used in aluminum oxide ALD will not wet a hydrophobic monolayer. Fortunately, it is relatively straightforward to attach a hydrophilic end group to any species. The key limitation of this technique is the series resistance introduced by the oxide layer, which would likely dwarf that of conjugated SAMs. In addition, any memory element developed with such contacts would need to supply a large bias to achieve any substantial current to drive switching.

Figure 13: Process flow for contact deposition in passivated metal-molecule-dielectric-metal junctions.
2.2.6 Floating Contact Deposition

Soft contact deposition entails prefabricating a top metallic contact on a substrate, floating it onto the surface of a liquid, and then gently lifting it onto patterned bottom electrodes with a preformed SAM. The technique was first demonstrated with bare metal top contacts.\textsuperscript{93} It was later shown that application of a polymer layer on top of the patterned electrodes before floating removal minimizes wrinkling and tearing and allows for the fabrication of much higher resolution top contacts, as shown in Figure 14.\textsuperscript{94} This technique is known as polymer-assisted lift-off (PALO). An appropriate solvent is chosen such that capillary forces will remove the solvent from the interface of the top electrode and the SAM. Device yields as high as 90% have been demonstrated, and the ability to fabricate many devices in a crossbar geometry allows for simple statistical measurements of many devices. Contact areas as small as 100 µm\(^2\) have been demonstrated. While the contacts could be scaled to even smaller dimensions, the imprecision in the placement of the top electrode likely rules out this method for fabricating integrated molecular devices.

Figure 14: Process flow to deposit a PALO electrode. (A) Poly(methyl methacrylate) (PMMA) is spin-cast as a hydrophobic backing layer onto metal electrodes patterned on a sacrificial substrate. (B) After a brief KOH etch, the metal–polymer layer cleanly lifts off onto the water surface upon immersion of the substrate. (C) The PMMA–metal film floats on the water surface without wrinkling owing to the surface tension of the water. (D) A device is assembled by floating the metal–polymer film onto a bottom substrate, often patterned with electrodes and/or molecular layers. The polymer film can be handled directly, allowing accurate placement and wrinkle-free deposition. (E) A completed crossbar device. (F) Definition of surface energies during metal–polymer deposition. Hydrophobic substrates and the top films result in wrinkle-free lift-on due to expulsion of water.\textsuperscript{92}
2.2.7 Nanotransfer Printing

Nanotransfer printing of top contacts involves transferring a thin metal layer onto a monolayer from an elastomeric or hard stamp. The monolayer must have a terminal group, such as a thiol, that will bond to the metal layer to aid in releasing it from the stamp. The most common stamp material is poly(dimethylsiloxane) (PDMS). The PDMS is patterned by casting and curing a layer of the material on a lithographically patterned resist layer on a silicon wafer, such that the PDMS takes on the negative image of the resist. A thin layer of metal is then evaporated onto the PDMS and transferred to the monolayer surface simply by applying moderate force (often by hand) to the stamp, as illustrated in Figure 15.

![Figure 15: Schematic of nanotransfer printing contact deposition and image of patterned contacts. Large dots are 500 μm in diameter. 300 nm wide lines have also been demonstrated.](image)

Nanotransferred contacts do not suffer from the leakage or carbon bond destruction associated with direct evaporation of metals onto monolayers. The pattern transfer can only occur if the metal film bonds to the terminal groups of the monolayer, ensuring chemical bonding at the interface of the SAM and contact. The edge resolution of PDMS stamps can be on the order of 10 nm, comparable to the grain size of the evaporated metal. Complex electrode patterns can be fabricated, allowing for potential statistical measurements on the completed devices. A potential problem in adapting this technique to production devices is the lack of barrier on the borders of the contacted monolayer to prevent interaction between the SAM and ambient environment. This could be addressed by the use of an oxygen plasma to remove the uncontacted SAM area, followed by
deposition of an oxide layer. Another limitation of the demonstrated method is the need to physically probe the fragile top contacts, which applies pressure to the monolayer underneath. Following the previous proposed improvement, once the device area is isolated by a dielectric, additional fabrication steps could be used to pattern probe pads or interconnects that are not directly above the SAM.

2.2.8 CONDUCTING POLYMER CONTACTS

A variety of devices have been fabricated in which a SAM is formed in a pore patterned in a dielectric, and a conductive polymer is spin-deposited onto the monolayer prior to the deposition of a metal contact, as shown in Figure 16. Aqueous suspensions of Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) with added fluorosurfactant have been the most popular contact material, but poly[(m-phenylenevinylene)-co-(2,5-dioctoxy-p-phenylenevinylene)] (PmPV) in chloroform has also been demonstrated. The use of soft contacts achieves high device yield and has been used to measure monolayers of alkanethiols, alkanedithiols, and paraphenyls. Thus far, the technique has only been demonstrated in the fabrication of devices of 1 μm diameter or larger due to the inability of the applied PEDOT:PSS suspensions to wet small pores. Due to the combination of high yield and potential scalability, the isolated packaging of molecules in these devices, and a substantially lower contact resistance than ALD-passivated devices, we believe that polymer-contacted devices are the most promising molecular junction design.

While polymer-contacted SAMs appear to be a particularly promising molecular device design, a number of complications have arisen which are primarily attributed to the poorly understood interface between the SAM and polymer. For example, studies using aqueous PEDOT:PSS consistently find differences in the measured conductance of alkanethiols versus dithiols, as a result of the hydrophobic alkane terminations having a higher interface resistance. Devices with varying length alkanethiols shorter than 14 carbons all exhibit similar resistance. In some experiments on alkanedithiol devices with PEDOT:PSS contacts, the reported exponential dependence of the resistance on SAM thickness has been substantially lower than the generally agreed upon value in the
literature. Finally, at low temperatures, PEDOT:PSS contacts dominate the transport characteristics of these devices. The subsequent chapters of this report will investigate and explain some of these phenomena.

Figure 16: PEDOT:PSS-contacted molecular junction fabrication. (A) Gold electrodes are vapor-deposited on a silicon wafer and a photoresist is spin-coated. (B) Holes are photolithographically defined in the photoresist. (C) An alkanedithiol SAM is sandwiched between a gold bottom electrode and the highly conductive polymer PEDOT:PSS as a top electrode. (D) The junction is completed by vapor-deposition of gold through a shadow mask, which acts as a self-aligned etching mask during reactive ion etching of the PEDOT:PSS. The dimensions for these large-area molecular diodes range from 10 to 100 μm in diameter.59

We briefly consider the molecular structure of a conducting polymer. These macromolecules have backbones of contiguous sp² hybridized carbon atoms. One valence electron on each carbon resides in a pₓ orbital, orthogonal to the other three sigma-bonds, and will form π-bonds with pₓ orbitals on adjacent carbons. The electrons in the π-bonds are weakly bound and thus easily delocalized, giving them a high mobility along the polymer backbone.¹⁰⁵

A 1D crystal with identical atomic spacing and one electron per ion, such as a conducting polymer backbone as described above, will have a single energy band. However, Peierls’ theorem indicates that 1D crystals achieve a lower energy state when adjacent atoms alternate between shorter and longer distances (ie. double and single
bonds). This splits the single band into a filled valence band (highest occupied molecular orbital or HOMO) and an empty conduction band (lowest unoccupied molecular orbital or LUMO), with a bandgap in between. This is analogous to the case of conventional 3D crystalline semiconductors, which are room temperature insulators when undoped. Through the process of adding dopants, which add (n-type) or remove (p-type) charges to the polymer, the conductivity of pristine \( \pi \)-conjugated polymers can be increased by several orders of magnitude. Unlike substitutional doping in conventional semiconductors, the dopant atomic or molecular ions are positioned interstitially between chains in \( \pi \)-conjugated polymers, and donate (accept) charges to (from) the polymer backbone. PEDOT:PSS is a unique conducting polymer, in that the conjugated PEDOT carries positive charges and the deprotonated PSS chains carry negative charges, together forming a macromolecular salt. Conducting polymers have lower mobility than their inorganic counterparts due to higher structural disorder, although this metric is the focus of intense research and has been continually improving with the development of new polymers and processing techniques.

2.3 SINGLE MOLECULE TRANSPORT MEASUREMENTS

Single molecule transport studies entail repeated measurements of single molecules between metal contacts, with the goal of assembling large statistical samples. These studies aim to provide a straightforward answer to the exact conductance of a particular molecular system. A single molecule between metal contacts can be readily simulated with DFT studies, although there is often discrepancy between theory and experiment. A key requirement of this technique is the need to verify the presence of a molecule spanning the contacts, typically using spectroscopy or analysis of the conductance of the junction as it is formed.

2.3.1 BREAK JUNCTIONS ON CHIPS

We first consider single-molecule junctions made with chip-based electromechanical break junctions. These devices are made by forming nanoscale gaps in wires on a chip immersed in a solution of the target molecule. The break is formed either through
electromigration or mechanically applying tension to the wire until it breaks. Molecules such as diamines or dithiols then span the gap by chemically bonding to the metal on either side. Chip-based electromechanical junctions allow for spectroscopy on the formed devices, and can be put into a dilution refrigerator to be studied at cryogenic temperatures.

2.3.1.1 Mechanical Break Junctions

The mechanically controllable break junction (MCBJ) was first developed in 1992 in order to study tunnel junctions between superconducting niobium electrodes. A MCBJ is formed by first lithographically fabricating an extremely thin wire, typically gold, on the order of nanometers in width at the narrowest portion, across a gap in an insulating layer such as a polymer or oxide. The chip or entire wafer is then placed into a holder, and a piezo-actuator is used to bend the substrate with micron precision, as shown in Figure 17. As the substrate bends the wire is stretched until it eventually snaps. Relaxing the pressure then reforms the junction, such that the two wire leads come back into contact, allowing for repeated measurements with a single junction. Due to the high reduction factor between the piezo position and the plane of the gold wire, the size of the junction can be controlled with sub-nanometer precision. Phosphor-bronze sheets are a commonly chosen substrate for their flexibility.

![Figure 17: Schematic depiction of a mechanically controllable break junction. The pushing rod bends the substrate with μm control. The large reduction factor between the Z-movement and the elongation in-plane allows for sub-nm control of the electrode distance.](image)

MCBJ’s can be used to perform measurements at cryogenic temperatures. The molecules spanning the two electrodes can be introduced in solution phase, either while breaking the junction or afterwards, or in the gas phase. Repeated bending of the
substrate allows for the collection of statistics from large numbers of measurements with a single junction.\textsuperscript{117–120,116}

2.3.1.2 Electromigrated Break Junctions

The other common method of forming a single-molecule junction on a chip is through electromigration, first demonstrated by McEuen and Alivisatos in 1999.\textsuperscript{121} As with a MCBJ, a thin wire is first lithographically defined. A current is run through the wire and ramped until atoms begin to electromigrate, creating a few nanometer break in the junction, as seen in Figure 18A and Figure 18B.\textsuperscript{122} Through the use of careful feedback control, the current through the wire is turned off as soon as a gap forms. Unlike with MCBJs, the substrate does not have to be flexible, meaning silicon substrates, compatible with standard CMOS processing tools, can be used.\textsuperscript{123}

The Natelson group at Rice has published numerous papers on this system.\textsuperscript{124,125,20,25,126,127,122,128–130} They have shown that the sharp metal electrodes in an electromigrated junction create intense Raman signal enhancement, similar to the bowtie systems demonstrated by the Moerner lab at Stanford. A Raman scan of a break junction system is shown in Figure 18 C-E.\textsuperscript{131}
Figure 18: (A) Full multi-bowtie structure, with seven nanoconstrictions. (B) Close-up of an individual constriction after electromigration. Note that the resulting nanoscale gap (<\~5 nm at closest separation, as inferred from closer images) is toward the right edge of the indicated red square. (C) Map of Si Raman peak (integrated from 500 to 550 cm\(^{-1}\)) in device from B, with red corresponding to high total counts. The attenuation of the Si Raman line by the Au electrodes is clear. (D) Map of pMA SERS signal for this device based on one carbon ring mode (integrated from 1050 to 1110 cm\(^{-1}\)). (E) Map of integrated low-energy background (50–300 cm\(^{-1}\)) for this device.

Despite the simple fabrication process and flexibility of electromigrated junctions, there are several prominent disadvantages as compared to mechanical junctions. Foremost, because the shape of the junction is poorly controlled, it is difficult to tell if any number between one or a few dozen molecules have assembled in the gap. Additionally, the contacts vary greatly from junction to junction and between different length molecular species. Another complication, as mentioned in the previous chapter, is that while interesting condensed matter phenomena such as Coulomb blockade and the Kondo effect have been observed in electromigrated junctions,\(^{18,19}\) these effects have also been seen in control junctions without any molecules present.\(^{20,21}\) This is due to the ragged edges of electromigrated contacts and the possible presence of metal grains in the junctions,\(^{132}\) as verified with SEM\(^{133}\) and TEM\(^{134}\) studies. Finally, because electromigrated
junctions cannot be reformed, many devices must be fabricated in order to conduct statistical studies.

2.3.2 STM Break Junctions

A mechanical break junction can also be formed between an STM tip and a metal substrate. This technique is often used for the collection of far larger statistical data sets than chip-based junctions. In these measurements, an STM tip, typically made of gold, is immersed in drop of a solution of the bridging molecule on top of a metal substrate, also typically gold. The tip is lowered until it makes contact with the substrate, forming a cold weld, and then withdrawn while a bias is applied between the tip and the substrate. As the tip is withdrawn, the differential conductance of the system drops until only a single chain of metal atoms spans the gap, measured as a single quantum of conductance, \( g_0 = \frac{2e^2}{h} \). The chain then snaps, at which point only a tunneling conductance is measured if there are no molecules present in solution. If there are molecules present which can bond between the tip and substrate, conductance steps are observed with magnitude below \( g_0 \) but higher than the tunneling conductance. By compiling hundreds thousands of conductance step measurements into a histogram, the most common junction conductance can be identified. This technique has the advantage of being readily automated for collection of massive data sets. STM junctions are only stable for a few minutes, ruling out the transfer of the junction to a cryogenic system, and thus long-term stability studies. Additionally, the break junctions are formed in solution, ruling out optical spectroscopy measurements as demonstrated in electromigrated junctions. Figure 19 depicts an artist’s rendering of a single molecule in an STM break junction.\(^{135}\)

There remains some controversy over the use of dithiols in STM break junctions. Tao and collaborators first demonstrated the technique with alkanedithiols and bipyridines in 2003 and found results that correspond with most alkanethiol transport studies.\(^{136}\) However, Venkataraman has shown that variation in the measured conductance of dithiols in these junctions gives non-conclusive statistical results.\(^{137}\) The dithiols bind so strongly to gold that after an initial randomly-placed and directed bond is formed, the molecule will not reposition itself at the terminal gold atom as the tip is withdrawn,
instead deforming the tip as it is pulled away. Diamines, with their lower bonding energy, can reorient, settling in a consistent location between the terminal gold atoms in the broken single-atom metallic chain between the tip and substrate. This allowed Venkataraman to determine conclusive conductance values for diamines, demonstrating the technique on a number of molecular species, including diaminoalkanes,\textsuperscript{138} diaminoacenes,\textsuperscript{139} diaminobiphenyls with varying angles of rotation between the two phenyl rings,\textsuperscript{37} and a number of other systems.\textsuperscript{140–143,35,144,122} In later studies, Tao revised the initial dithiol results, finding that the molecules likely bridged the STM-surface gap in either of two contact configurations, with conductance differing by a factor of 5 between the two.\textsuperscript{145}

![Figure 19: STM on gold surface break junction.](image)

**2.3.3 MICROSCOPY ON SELF-ASSEMBLED MONOLAYERS**

Transport through individual or small collections of molecules can also be measured through the use of nanoscale probes such as scanning tunneling microscopes (STMs) and conducting atomic force microscopes (AFMs) on SAMs on metal substrates. These measurements suffer from complications due to uncertainties in the probe tip size and position and the ability of individual molecules in a SAM to translate across a substrate through exchange and diffusion.

**2.3.3.1 Scanning Tunneling Microscopy**

An STM is an atomically sharp conductive tip that is scanned over a conducting surface at nanometer-scale distances while a bias is applied. As the measured tunneling current
depends exponentially on the distance between the tip and the surface, a map of the current measured while scanning over a given area yields atomically precise information about the surface morphology. Because of this precision, STMs are one of the most popular ways to study monolayer structures.\textsuperscript{146-154} A schematic of such a measurement is shown in Figure 20.\textsuperscript{99}

![Figure 20: STM Probing of SAM.](image)

As the tip is not brought into contact with the monolayer surface, a tunneling gap is measured in series with the molecule. A key limitation of STM transport measurements is the difficulty in discerning differences in surface morphology or height as opposed to changes in the molecular conductance. In densely packed SAMs it is unclear how many molecules will be measured since the exact size and morphology of the tip is unknown. Probing conducting molecules embedded in an insulating SAM matrix can circumvent this problem.\textsuperscript{155,156} However, it has been shown that inserted molecules preferentially pack at defect sites in the SAM and are capable of diffusion and exchange with nearby molecules.\textsuperscript{157} Thus, substrate morphology variation may cause anomalies in the measured conductance, and the conducting species may cluster together, meaning that even in a dilute mixed monolayer, several molecules will be measured at each conducting site.
2.3.3.2 Conducting Atomic Force Microscopy

Conducting AFM measurements differ from STMs in that a quartz AFM tip coated in a metal layer is brought directly into contact with the monolayer, as shown in Figure 21. An advantage of this approach is that the metal coating can be varied, allowing for studies of the effect of varying the work function of the AFM electrode without altering the substrate and hence the monolayer packing. The key disadvantage is that AFM tips coated in metal are much larger, rounded and microscopically rough than STM tips, creating uncertainty in the number of molecules measured. Substrate roughness may also lead to varying numbers of molecules being contacted each time the probe is lowered onto the monolayer.

![Figure 21: Conductive AFM probing of SAM.](image)

2.3.3.3 AFM Probing of Gold Nanoparticles on SAMs

A clever technique that combines the direct contact of AFM probing with the precision of STM studies is the probing of gold nanoparticles bound to isolated dithiols in an inert SAM matrix, as demonstrated in Figure 22. The relatively bulky nanoparticle prevents diffusion and translation of the target species and ensures the molecule is contacted through a chemisorbed contact. The first demonstration of this technique by the Lindsay group found anomalous results for the length dependence of the measured conductance. This was later shown to be due to the Coulomb blockade effect in small nanoparticles. The effect is alleviated for nanoparticles larger than 5 nm in diameter, however, given an alkanethiol SAM packing density of 1 molecule/5 Å², this implies the measurement of dozens of alkanes through tunneling conduction in addition...
to the through-bond measurement of the targeted dithiol. A further issue, as discussed in the section on STM measurements, is the tendency of substituted species in alkanethiol layers aggregate at defect sites, meaning even in monolayers with a low concentration of target molecules, a single nanoparticle may be bound to multiple dithiol species.

Figure 22: Probing a nanoparticle on a SAM.\textsuperscript{162}

In this section we have reviewed the terminology and technology of SAMs and discussed experiments to measure molecular transport through monolayers and single molecules.
CHAPTER 3: MOLECULAR JUNCTION FABRICATION

In this section we will first present a general outline of the device fabrication. We will next discuss complications in the fabrication process and technical innovations to overcome these hurdles. We will then present a detailed walkthrough of the fabrication process, complete with specific parameters to aid in duplicating the results in this thesis. Finally, we will present characterization data on the finished pores, indicating precise fabrication and robust monolayer formation in our devices.

3.1 GENERAL OUTLINE OF DEVICE FABRICATION

Initially, we anticipated fabrication according to the general process illustrated in Figure 23. A titanium adhesion layer is evaporated onto an undoped silicon wafer. Without breaking vacuum this is followed by a gold layer. An inorganic dielectric layer of silicon nitride or silicon oxide is then formed through plasma enhanced chemical vapor deposition (PECVD). An array of small pores is patterned in the dielectric layer using reactive ion etching (RIE) to etch those portions not covered by a lithographically defined masking layer. The wafer is then placed into a solution containing a self-assembling molecule and a SAM is allowed to form. Afterwards, the device is removed from solution, rinsed, and a layer of PEDOT:PSS is spun onto the device, followed by evaporation of a metallic top contact.
Several optimizations led to the structure demonstrated in Figure 24. Notable adjustments include the use of a triple layer of metal substrate, a double layer of dielectric material, and the use of Aedotron P, a conducting polymer suspended in nitromethane, rather than PEDOT:PSS as the layer between the SAM and top contact. The next section discusses these optimizations in detail.
Figure 24: Schematic of completed device. Image is not to scale, as monolayer thickness is ~1 nm, aluminum oxide thickness is ~20 nm and silicon nitride thickness is ~30 nm. Notable fabrication developments include the double layer dielectric, the triple layer metal substrate, and the use of Aedotron P as the conducting polymer. Note also the slight meniscus formation in the polymer, which is explained in Chapter 5.

3.2 NOTABLE TECHNOLOGICAL DEVELOPMENTS IN FABRICATION PROCESS

3.2.1 TRIPLE LAYER TEMPERATURE RESISTANT SUBSTRATE

When we initially used Ti/Au as the substrate electrode, we encountered problems with PECVD of dielectric films. The PECVD tool available at the Stanford Nanofabrication Facility (SNF) can only deposit high quality films at 350° C. We found that at this temperature the gold and titanium layers would diffuse into one another. Researchers have shown that titanium can diffuse into poly-crystalline gold at temperatures as low as 250° C. The PECVD would fail to deposit above spots where this occurred, resulting in pinhole shorts, as indicated in the AFM image in Figure 25.
Figure 25: (A) Optical image of PECVD shorts over Ti/Au metal layer. 500 um field. (B) AFM scan of shorts, indicating 50 nm deep pits that penetrate the entirety of the PECVD layer. 40 um field.

We find that the titanium-gold reactivity problem is solved by inserting a platinum barrier layer. This is the so-called “beam lead” process that was implemented at Bell Labs as early as 1966. The platinum layer prevents interdiffusion of the two layers during PECVD. The leads can be made even more temperature resistant by inserting TiN between the titanium and platinum layers, a step we found unnecessary for the present work.

We use an AFM to measure the roughness of the substrate just before monolayer deposition. As seen in Figure 26, we measure a roughness of a few nanometers over a distance of half a micron, caused by gold grains that are tens of nanometers in diameter. We now consider the implications of this surface roughness for the quality of our monolayer films.
Figure 26: (A) AFM scan of gold surface roughness after processing. (B) Cut along red line in A, demonstrating roughness of a few nm over 500 nm lateral distance.

We note that the literature of SAM transport measurements includes studies of monolayers on both flame-annealed gold-mica substrates and as-evaporated gold on an adhesion layer, which is not atomically flat, as shown in the STM scan and artistic depiction in Figure 27. While hydrogen flame-annealed gold-on-mica substrates exhibit several-hundred-nanometer terraces of atomically flat crystalline (111) gold, at terrace boundaries there can be trenches as deep as the film itself. As noted in Section 2.1.2, Chidsey’s seminal ellipsometry and electrochemical studies on SAMs used freshly evaporated gold substrates, and confirmed a mostly (111) orientation of the surface through through x-ray diffraction and measurements. The studies utilizing PEDOT:PSS contacts that inspired the present work were also carried out using e-beam evaporated substrates.
3.2.2 **Aluminum Oxide/Nitride Double-layer Dielectric**

We modify the fabrication process described by Akkerman *et al.*,\(^\text{59}\) by replacing the photoresist dielectric with an inorganic dielectric deposited through conformal coating methods. There are several drawbacks to a photoresist dielectric. First, organic dielectrics prevent the use of standard procedures such as oxygen plasma or piranha etching to remove adventitiously adsorbed carbon on the gold surface prior to monolayer formation. Second, the resist layer may swell or even partially dissolve in some of the common solvents used to deposit monolayers. It has been shown that photoresist dielectric layers can be baked to render them resistant to both ethanol and tetrahydrofuran.\(^\text{103}\) However, high temperature treatment may result in distortion of small features patterned in the resist layer. Finally, the photoresist layer must be deposited in an extremely clean environment, with sufficient thickness to avoid pinhole leaks and shorting from dust particles. In the present work, it was found that a resist dielectric needs to be at least several hundred nanometers thick to avoid leaks. Nanoscale-area pores in such a dielectric have high aspect ratios and suffer from poor wetting by monolayer formation solutions and conductive polymers. In contrast, a conformal inorganic dielectric deposition method such as ALD or plasma enhanced chemical vapor deposition (PECVD) can achieve a pristine dielectric layer a few nanometers thick even when deposited in a non-cleanroom environment, yielding pore structures that can be wetted more easily.
As detailed in the next section, in this work pores are formed in double-dielectric layers of ALD aluminum oxide and PECVD silicon nitride. The nitride is dry-etched using trifluoromethane and oxygen reactive ion etching with a mask of e-beam resist and thin metal, with the underlying aluminum oxide serving as an etch stop. The aluminum oxide is then wet-etched with a buffered oxide etchant, revealing a pristine gold surface for the formation of a SAM. While we are not aware of any prior work that utilizes this unique process, we would not have devised it consulting the exhaustive data on etch rates collected by Williams and Muller.\textsuperscript{168} We find that patterning a layer of silicon nitride with no underlying aluminum oxide results in poor monolayer formation, as evidenced by substantial variation between devices and poor yield due to shorting. X-ray photoelectron spectroscopy (XPS) reveals significant damage to the lower contact caused by implantation of silicon during the reactive ion etch, as envisioned in Figure 28.

![Figure 28: Illustration of silicon ions implanted into Au substrate during reactive ion etching.](image)

We used XPS to examine the surface composition of an unpatterned sample after various device fabrication steps. Figure 29-Figure 32 show the XPS signal from 0 to 1000 eV with labeled peaks, while Table 2-Table 5 present the composition in terms of atomic percentage, as determined by the area under a chosen reference peak and knowledge of the spectroscopic cross-section of each element.

Figure 29 and Table 2 present the spectra and composition of a freshly evaporated sample of a Ti/Pt/Au consisting of layers of 7, 40, and 100 nm thicknesses, respectively. We note the absence of Ti and Pt peaks indicating full gold coverage, and also the presence of 36\% atomic carbon, indicating the presence of adventitiously adsorbed carbon even on a fresh sample. For freshly e-beam-evaporated gold, it was found that
from sample to sample and at different spots on the same sample the carbon content varied by up to 15%. We have never measured any sample in the XPS tool without detecting the presence of at least a few percent elemental carbon due to adventitiously adsorbed impurities from the ambient environment around the tool.

Table 2: Atomic percentage of elements on freshly evaporated Au on Pt and Ti.

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<th>Signal</th>
<th>Corrected BE</th>
<th>Exper. Sens BE</th>
<th>Factor</th>
<th>Norm Area</th>
<th>Relative Area</th>
<th>Atom %</th>
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<td>19.04</td>
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</tbody>
</table>

Figure 29: XPS spectrum for freshly evaporated Au on Pt and Ti.
Figure 30 presents an XPS spectrum taken on a wafer after deposition of the two dielectric layers. The formation of a uniform silicon nitride layer on aluminum oxide is evidenced by the absence of Al peaks from the underlying layer. Table 3 presents the corresponding elemental composition. We note the presence of 5% atomic F as a result of impurities present in the PECVD chamber. We see an identical spectrum on a surface of PECVD silicon nitride with no underlying aluminum oxide layer.

Table 3: Atomic percentage of elements on freshly deposited PECVD silicon nitride on ALD aluminum oxide.

<table>
<thead>
<tr>
<th>Signal</th>
<th>Corrected BE</th>
<th>Exper. Sens BE</th>
<th>Factor</th>
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<tr>
<td>N1s</td>
<td>397.4</td>
<td>398.6</td>
<td>1.68</td>
<td>47910</td>
<td>28540</td>
<td>41.32</td>
</tr>
<tr>
<td>C1s</td>
<td>284.6</td>
<td>285.8</td>
<td>1.00</td>
<td>6926</td>
<td>6931</td>
<td>10.04</td>
</tr>
<tr>
<td>Si2s</td>
<td>152.6</td>
<td>153.8</td>
<td>1.03</td>
<td>24634</td>
<td>23995</td>
<td>34.74</td>
</tr>
</tbody>
</table>

![Figure 30: XPS spectrum of PECVD silicon nitride on ALD aluminum oxide.](image)
Table 4 and Figure 31 present an XPS spectrum and elemental composition of a gold surface after deposition and removal of a silicon nitride layer with no underlying layer of aluminum oxide. The trifluoromethane and oxygen reactive ion etching of the silicon nitride results in significant implantation of silicon and oxygen into the gold layer.

Table 4: Surface elemental composition after trifluoromethane and oxygen reactive ion etch of PECVD SiN on Ti/Pt/Au. Note the presence of substantial silicon and oxygen in the exposed gold layer.

<table>
<thead>
<tr>
<th>Signal</th>
<th>Corrected BE</th>
<th>Exper. Sens BE</th>
<th>Factor</th>
<th>Norm Area</th>
<th>Relative Area</th>
<th>Atom %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O 1s</td>
<td>534.2</td>
<td>533.2</td>
<td>2.49</td>
<td>78294</td>
<td>31427</td>
<td>46.02</td>
</tr>
<tr>
<td>C 1s</td>
<td>284.6</td>
<td>283.6</td>
<td>1.00</td>
<td>12054</td>
<td>12047</td>
<td>17.64</td>
</tr>
<tr>
<td>Si2p</td>
<td>104.7</td>
<td>103.7</td>
<td>0.90</td>
<td>14565</td>
<td>16161</td>
<td>23.67</td>
</tr>
<tr>
<td>Au4f</td>
<td>84.4</td>
<td>83.4</td>
<td>19.08</td>
<td>165028</td>
<td>8650</td>
<td>12.67</td>
</tr>
</tbody>
</table>

Figure 31: XPS spectrum of gold surface after trifluoromethane and oxygen reactive ion etch of PECVD SiN on Ti/Pt/Au. Note the presence of substantial silicon and oxygen in the exposed gold layer.
The introduction of an ALD aluminum oxide etch stop under the silicon nitride and a two-step etch process using RIE followed by a buffered oxide wet etch ensures a clean gold surface before monolayer formation, as shown in Table 5 and Figure 32. We note that the exposed gold layer in Table 5 is more pure than the as-evaporated gold. This is possibly a consequence of the oxide etch resulting in a reduced gold surface that adsorbs less impurities during the few minutes spent in ambient conditions before the XPS measurement is taken. The difference in purity is observed across multiple freshly evaporated and freshly etched samples.

Table 5: Gold surface atomic percentages of elements after two-step etch process.

<table>
<thead>
<tr>
<th>Signal</th>
<th>Corrected BE</th>
<th>Exper. Sens BE</th>
<th>Factor</th>
<th>Norm Area</th>
<th>Relative Area</th>
<th>Atom %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O 1s</td>
<td>531.8</td>
<td>531.4</td>
<td>2.49</td>
<td>7450</td>
<td>2987</td>
<td>3.74</td>
</tr>
<tr>
<td>C 1s</td>
<td>284.6</td>
<td>284.2</td>
<td>1.00</td>
<td>15574</td>
<td>15571</td>
<td>19.49</td>
</tr>
<tr>
<td>Au5s</td>
<td>110.8</td>
<td>110.3</td>
<td>0.53</td>
<td>32291</td>
<td>61318</td>
<td>76.77</td>
</tr>
</tbody>
</table>

Figure 32: XPS spectrum of gold surface after two-step etch process.

3.2.3 **Metal Mask Deposited by Low Angle Evaporation**

After depositing the two dielectrics, a layer of either ZEP-520A or PMMA is spun onto the sample as a resist for electron beam (e-beam) lithography. Following standard
development and exposure procedures, holes are patterned in the resist layer and the exposed silicon nitride is then reactive-ion etched, with the aluminum oxide layer acting as an etch stop. The aluminum oxide is wet-etched in a dilute HF solution with the nitride layer acting as a mask. We find that due to imperfections such as pinholes, dust and divots in the resist layer, the dielectric layer is also etched in a number of spots that aren’t exposed during the lithography process, as illustrated in Figure 33A. As a result, the exposed gold substrate after etching covers substantially more area than specified by the lithographic pattern, as confirmed by AFM characterization, transport measurements, and tests on unpatterned samples.

![Diagram of resist development and exposure]

Figure 33: (A) Dielectric shorting caused by RIE on resist-only mask. (B) Ideal defect-filling metal mask. (C) Depiction of angled evaporation and rotation process.

Shalom Wind suggested an elegant solution to this problem, demonstrated in previous work in which his group lithographically patterned 3.5 nm diameter dots. After resist development, a thin layer of RIE-resistant metal, in this case chrome and nickel, is evaporated onto the sample at a low angle while it is rotated, as depicted in Figure 33C. Due to the low angle the metal does not penetrate the pore features in the resist. The rotation ensures that no sidewalls receive an excessive amount of deposited metal and resist defects such as bumps are covered on all sides. In this manner, defects in the resist layer are effectively covered over by a much stronger mask layer, as depicted in Figure 33B. As a further advantage, this process limits the exposure of the e-beam resist layer to the RIE process. It can be exceedingly difficult to remove RIE-exposed resist, as the polymer can cross-link or break down into elemental carbon, which is not easily solvated.
3.2.4 Strongly Wetting Organic-Solvated Polymer

As demonstrated in previous work using larger pores, we initially attempted to use aqueous PEDOT:PSS as a conductive interface between the SAM and evaporated metal contact. However, we find that the polymer will not fill pores with diameters smaller than a few microns, even with the addition of surfactants. Better results are found with Aedotron P, a commercially available conductive polymer dispersed in organic solvent. The particular Aedotron blend used in the present work is a block copolymer of PEDOT and polyethylene glycol solvated in nitromethane and doped with p-toluene sulfonate. We find that the low viscosity and superior wetting of nitromethane allows the deposition of the polymer into pores as small as 100 nanometers in diameter and 50 nanometers deep. Other blends of Aedotron were also considered. Mixtures using propylene carbonate solvent fail to penetrate submicron pores. Aedotron C3, a highly conductive blend of polymer in nitromethane, results in shorted devices, presumably because the lauryl-terminated polymer backbone is able to penetrate and break up the alkanethiol SAMs.

A key tradeoff in the use of Aedotron P in place of PEDOT:PSS is the higher resistivity of the new polymer. At room temperature, the specific contact resistance of polymer-only devices (SAM omitted) is 6 mΩ-cm², or 800 kΩ for a 1 μm diameter pore, a resistance on the order of the shortest alkanethiol molecular junctions investigated in this study. At room temperature, the polymer exhibits ohmic behavior and the device transport behavior resembles that seen in other molecular tunnel barriers, albeit with higher contact resistance. At lower temperatures, the polymer layer transport dominates the device behavior. The high contact resistance could potentially be alleviated with the use of a more conductive blend of Aedotron beyond those tested in this study. For example, Aedotron C is 3-4 orders of magnitude more conductive than Aedotron P, has a similar molecular structure, and comes solvated in nitromethane.

Jason Bloking of the McGehee lab at Stanford has given us access to his unpublished measurements of the work function of films of Aedotron P spun onto glass slides. While the work function is reported as 4.19 eV in the product literature, he measures it to be 5.0 eV using photoelectron spectroscopy in air. The measurement is taken with a with a
Riken Keiki AC-2 Photoelectron Spectrometer. Photoelectron spectroscopy is a common technique for measuring the work function of a surface and has been used in previous studies of PEDOT:PSS.\textsuperscript{171,172} The surface of a material is bombarded by increasingly energetic electrons while a detector counts the number that are ejected from the surface. Linear extrapolation of the cube root of the number of counts indicates the excitation energy at which electrons begin to be ejected from the polymer. This corresponds to the work function. The data is presented in Figure 34.

![Figure 34](image.png)

Figure 34: Photoelectron spectroscopy measurement in air to establish the work function of Aedotron P. Data taken by Jason Bloking of the McGehee lab with a Riken Keiki AC-2 Photoelectron Spectrometer. Linear extrapolation of the cube root of the number of counts indicates the work function (5.0 eV), measured as the excitation energy at which electrons begin to be ejected from the polymer.

### 3.3 DETAILED FABRICATION PROCESS

In this section we presented a detailed description of the fabrication process for a typical molecular junction. Appendix A presents similar material in even more detail.

#### 3.3.1 PORE FABRICATION

The device fabrication begins with the deposition of 7, 30 and 150 nanometers of titanium, platinum and gold, respectively, onto an undoped silicon wafer. Each layer is evaporated a rate of 1 Å/s in an e-beam evaporator evacuated to $3 \times 10^{-7}$ torr. The platinum
layer is be essential in preventing diffusion of the titanium and gold layers during the 350° C nitride deposition process, which otherwise results in dielectric pitting and shorting. The gold layer root mean square roughness is 1.2 nm (Figure 26) measured with an Asylum Research Molecular Force Probe 3D AFM. Next, 20 nm of aluminum oxide (200 cycles) is deposited by ALD in a Cambridge Nanotech system followed by 40 nm of silicon nitride deposited by PECVD for 4.5 minutes in an STS PECVD system.

A layer of ZEP-520A or a bilayer of PMMA/MMA e-beam resist is then spun onto the wafer. The resist is applied with a 5 ml syringe with a 0.2 um particle filter. The spin speed is chosen such that the resist thickness is roughly equivalent to the desired diameter of the pores. For the fabrication of 300 nanometer devices, undiluted ZEP-520A is spun at 5000 rpm. For the fabrication of 1 µm devices, a layers of Microchem EL 11 MMA copolymer followed by PMMA 950 A5 are spun at 3000 rpm for each layer. After each layer of resist is applied, the sample is baked at 180° C (PMMA/MMA) or 200° C (ZEP) on a hotplate in ambient for 2 minutes. The resist is exposed in a Philips XL30 SFEG field-emission scanning electron microscope controlled by a Nabity Nanometer Pattern Generation System, at a dose of 400 µC/cm². Wafers containing dozens of devices with exposed resist are stored under nitrogen. Over several months of experiments, chips are cleaved from the wafer as needed, and the proceeding steps are performed on batches of a few to a dozen chips.

The resist is developed for 40 seconds at room temperature in 3:1 isopropanol:methyl isobutyl ketone (PMMA/MMA) or for 1 minute in ZED-N50 developer (ZEP), and then cured for 10 minutes on a hot plate at 110° C. To ensure the integrity of the etch mask, a low angle metal mask evaporation technique has been adapted from previous work.169 2 nm chrome and 5 nm nickel are evaporated at an angle of 14° from the plane of the surface while rotating the sample, such that the resist surface is covered with a thin layer of metal while preventing the penetration of metal into the patterned pores.

The nitride layer is then etched for 70 seconds in an MRC reactive ion etcher at a rate of ~0.8 nm/sec using 18 sccm of CHF₃ and 2 sccm of O₂ at 10 mTorr with 100 Watts power. It is found that this etch compacts the revealed aluminum oxide layer, reducing it to a thickness of a few nanometers, but never penetrates the aluminum oxide, even after
several minutes of etching. The residual few nanometers of aluminum oxide are removed with a 10 second wet etch in 20:1 dilute buffered oxide etch (BOE), revealing gold that is uncontaminated by any ion residue, as confirmed by XPS (Figure 32). In devices in which the aluminum oxide buffer layer is not used and nitride on gold is simply dry etched, the gold is invariably contaminated by implanted silicon from the nitride layer, which results in poor monolayer formation.

The steps in the pore fabrication are illustrated in Figure 35. SEM and AFM images of a completed pore before monolayer formation are presented in Figure 36.
Figure 35: Pore fabrication process.
3.3.2 **Monolayer Formation**

Prior to monolayer formation, the chips are exposed to O₂ plasma for 5 minutes. This oxidizes the exposed gold surface at the bottom of each pore and removes any adventitiously adsorbed carbon. The chips are then immersed in 200 proof ethanol (Acros) for 20 minutes to reduce the oxidized gold layer. They are then transferred to a 50 mM solution of the appropriate molecule in solvent and left for 48 hours under inert atmosphere. Alkanethiols are dissolved in ethanol, while the conjugated species discussed
in Chapter 7 are typically dissolved in chloroform. After monolayer formation, the devices are rinsed in 200 proof ethanol and CMOS grade isopropanol and water, and then dried with nitrogen.

3.3.3 CONTACT DEPOSITION

Immediately after rinsing, the devices are reintroduced into a nitrogen-filled glovebox. Aedotron P (1% Poly(3,4-ethylenedioxythiophene)-block-poly(ethylene glycol) solution in nitromethane with sulfonate p-toluene as a dopant is deposited onto each chip and then spun at 1000 rpm for 15 seconds before acceleration to 2000 rpm for another 30 seconds. This results in a 90 nm thick polymer layer. The devices are then dried under vacuum for 4 hours. Top gold contacts (100 nm) are evaporated onto the devices through shadow masks and the residual polymer is removed using oxygen plasma for one minute. The monolayer formation and contact deposition steps are illustrated in Figure 37.

![Figure 37: Self-assembled monolayer formation and application of top contact (not to scale – aluminum oxide is 20 nm thick compared to 1 nm thickness of monolayer, top gold contact is 100 nm thick)](image-url)
3.4 ELECTROCHEMICAL CHARACTERIZATION OF SAM FORMATION

The formation of densely packed monolayers is verified by electrochemical reduction of ferricyanide using an array of pores as the working electrode.\textsuperscript{41,62,64} Similar to the electrochemical monolayer transport experiments described in Chapter 2, a Teflon cone with a 1 cm diameter hole drilled through it is clamped against the chip. An electrolyte solution of 10 mM K₄Fe(CN)₆ in 100 mM KCl is added to the cone and the reference and counter electrodes are placed in the solution. As the voltage is swept negative, ferricyanide is reduced to ferrocyanide. Figure 38A illustrates the experimental setup.

A chip with an array of several hundred 1 µm pores was measured before and after SAM deposition. The formation of a dense SAM slows the electron transfer to the gold layer, evidenced by a significant reduction in the oxidative current, as seen in Figure 38B. We note that the bare gold surface in 38B is not a typical cyclic voltammogram curve, as the 1 µm pores experience extremely fast diffusion such that the electrolyte is never depleted near the working electrode.

![Experimental setup for electrochemical testing of SAM formation. (B) Cyclic voltammetry of 10 mM K₄Fe(CN)₆ in 100 mM KCl prior to (dashed blue line) and after (solid red line) formation of SAM in an array of 1 µm pores (scan rate 50 mV/sec). The formation of a dense SAM in the pores slows the electron transfer, evidenced by a significant reduction in the redox current.](image-url)
In this chapter, we presented a detailed discussion of the device fabrication process, focusing on complications and the technical innovations employed to overcome these hurdles.
CHAPTER 4: TRANSPORT AND CONTACT RESISTANCE MODELS

In this chapter we consider two different models of SAM molecular junctions. The first, known as the Simmons model, considers the SAM as a rectangular potential barrier between two contacts. While the model provides a good fit to our measured data, the calculated device parameters are unphysical. Further, the Simmons model assumes metallic contacts, which is inaccurate in the case of our conducting polymer devices. The second, more general model conceptualizes the device as a series of transmission barriers, appropriate to the complex electronic structure of the gold-monolayer-polymer interface. Future work, not contained in this thesis, will focus on combining this transmission model with a series element appropriate for transport through the overlying polymer. This chapter concludes with a short discussion of transport in disordered conductors such as the polymer layer used in our contacts.

4.1 SIMMONS MODEL OF TRANSPORT

4.1.1 SIMPLE MODEL

The current density as a function of voltage can be modeled by considering the SAM as a rectangular tunnel barrier between two metallic contacts, with the barrier height defined by the lowest unoccupied molecular orbital (LUMO) of the monolayer. For alkanethiol SAMs, this is the vacuum energy. We assume that coherent tunneling through the barrier is the only transport process. As described in the previous chapter, we measured the work function of Aedotron P to be 5.0 eV. The work function of gold is 5.1 eV. As we apply only 1 V bias to the devices in our measurements and our barrier is ~5 eV, we can be assured that Fowler-Nordheim tunneling does not occur. As our model only considers the average barrier height independent of shape, a slight mismatch of the contact work functions does not affect our analysis below. Simmons has shown that the current measured across a tunnel barrier with mismatched contacts should be slightly asymmetric at finite temperature, with increased current when the electrode with a
smaller work function is negatively biased. Figure 39 depicts the band diagram of an Au-Aedotron-monolayer-Au device. The polymer has numerous intraband trap states, making it an ohmic conductor, although they are only illustrated at the interface with the SAM. The work functions of gold and Aedotron P are precise and the SAM band gap is drawn to scale. The energy levels of the polymer bands are conjecture. The physical dimensions (left to right) are not to all to scale, as in reality the polymer layer is roughly 100 times thicker than the monolayer.

Figure 39: Band diagrams of Au-Aedotron P-SAM-Au sections in (A) equilibrium, (B) forward bias, and (C) reverse bias, where the right Au contact is considered ground. The polymer has numerous intraband trap states, making it an ohmic conductor, although they are only illustrated at the interface with the SAM. The work functions of gold and Aedotron P are precise and the SAM band gap is drawn to scale. The energy levels of the polymer bands are conjecture. The physical dimensions (left to right) are not to scale.

The derivation of the Simmons model relies on a few important assumptions. First, the WKB approximation for the electron tunneling probability through an arbitrary potential barrier must apply, as it does for energy barriers that are substantially larger than the thermal energy, $kT$. Second, the Drude-Sommerfeld free-electron model must describe the electrons in the metal contacts. These electrons will have isotropically distributed momentum and only those carriers traveling towards the barrier will have a probability of tunneling. The tunneling current $J$ through a rectangular tunnel barrier of average height $\Phi$ and width $d$ at biases $V < \Phi/e$ can be described by the following equation:
\[ J = J_0 \left( \frac{eV}{2} \right) e^{-A \alpha \sqrt{\frac{\phi - eV}{2}}} \left( \Phi + \frac{eV}{2} \right) e^{-A \alpha \sqrt{\frac{\phi + eV}{2}}} \]

(4.1)

where

\[ J_0 = \frac{e}{2\pi \hbar d^2} \]

(4.2)

and

\[ A = \frac{4\pi d}{h} \sqrt{2m_e} \]

(4.3)

where \( m_e \) is the bare electron mass, and \( h \) is the Planck constant. \( \alpha \) is a fit parameter. The physical nature of \( \alpha \) is not completely understood, but it is generally thought to account for the non-rectangularity of the barrier or the effective mass of electrons traversing the SAM. We determine the barrier thickness, \( d \), from Chidsey’s ellipsometry measurements of alkanethiol SAMs on e-beam evaporated gold.\(^{55}\) In the next chapter we will find the values of \( \alpha \) and \( \Phi \) that achieve the best least squares fit for a given data set.

### 4.1.2 Accounting for Image Charge

The image charge arises as electrons transiting the dielectric layer induce an opposite charge on the surface of the nearby contacts. This charge then attracts the transiting electron, effectively reducing the barrier height at that point in the monolayer. The effective barrier height with image charge taken into account (scale normalized for barrier thickness and dielectric constant) is presented in Figure 39. Image A is in equilibrium while B is under bias.
In both our own work (Chapter 5) and in prior studies by other groups, the simple Simmons model reliably produces curves that fit the measured data for molecular junctions. However, in most cases the best fit is found by setting $\Phi = 1$-$2$ eV.\textsuperscript{85,145} This result is unphysical, as the barrier height of alkanethiols should be $\sim 5$ eV. In addition, these groups could only achieve good fits by applying the model to two separate bias regimes, above and below $0.3$ V, finding different $\alpha$ and $\Phi$ values in each. Akkerman \textit{et. al.} explicitly account for the image charge in their junction modeling.\textsuperscript{100} They find values of $\Phi$ ranging from $3.6$ eV for 14-carbon alkanethiols up to $5.6$ eV for octanethiol with a single fit for the range between 0 and 1 V.

The Simmons model can be adjusted to take the image potential into account by solving for the effective average height of the barrier. We no longer consider the fit parameter $\alpha$ and instead fit the effective mass, $m^*_e$, in addition to the barrier height $\Phi$.

At a distance $x$ from the left electrode, the image potential, $V_i$, can be approximated by:\textsuperscript{100,176,177}
\[ V_i = -1.15\lambda \frac{d^2}{x(d-x)} \] 

(4.4)

where

\[ \lambda = \frac{e^2 \ln 2}{8\pi \epsilon_0 \epsilon_r d}. \]

(4.5)

We define the dielectric constant \( \epsilon_r = 2.1 \), as measured in previous work.\(^{100}\) The barrier height at a distance \( x \) from the left electrode is given by:

\[ \varphi(x) = \varphi_0 - eV \frac{x}{d} - 1.15\lambda \frac{d^2}{x(d-x)}. \]

(4.6)

The mean value of the barrier is calculated by integrating (4.6) to find:

\[ \bar{\varphi} = \varphi_0 - eV \frac{d_2 - d_1}{2d} - \left[ 1.15\lambda \frac{d}{d_2 - d_1} \right] \times \ln \frac{d_2(d-d_1)}{d_1(d-d_2)}. \]

(4.7)

The tunneling current can be expressed in the same form as (4.1), given by:

\[ J = J_0 \left( \bar{\varphi} e^{-A\sqrt{\bar{\varphi}}} - (\bar{\varphi} - eV) e^{-A\sqrt{\bar{\varphi} - eV}} \right) \]

(4.8)

where \( A \) is given by (4.3), with the bare electron mass \( m_e \) replaced by the effective mass, \( m_e^* \).

### 4.1.3 Limitations of Simmons Model

The primary drawback of applying the Simmons model to the devices in this project is that we must assume the polymer contact is metallic in nature. While the material is ohmic and typically of much lower resistance than the monolayer, the band structure assumptions in the Simmons model don’t apply with a polymer contact. The Sommerfeld model of the contacts as three-dimensional, flat-bottomed, potential wells containing free electrons\(^{175}\) is not consistent with the band structure of a conducting polymer.\(^{178}\) We could consider an adjustment of the Simmons model by placing an ohmic resistance in series
with the source electrode, but this does nothing to improve the faulty assumption of the polymer contact band structure. One could derive a Simmons-like model to account for the non-metallic band structure of the conducting polymer, but various necessary modeling parameters such as the density and energies of the trap states are unknown.

As will be seen in Chapter 6, an additional indication that the Simmons model is a poor choice for polymer-contacted devices is its poor applicability at low temperature. The Simmons model predicts a conductance change of a few percent between 0 K and room temperature. Both our work and that of Kronemeijer et. al. find changes of a few orders of magnitude cooling from 300 to 25 K. Additionally, although the polymer contacts may exhibit a resistance several orders of magnitude less than the SAM, one observes temperature-dependent behavior dominated by the contact to the polymer layer, indicating clear non-metallic contact behavior. It is remarkable that over the course of several papers and years of study Akkerman et. al. observed no relationship between temperature and transport for PEDOT:PSS contacted devices. This oversight was corrected once Kronemeijer inherited the project, and in more recent papers the group has described their work using a transmission coefficients model, similar to that presented in this thesis.

4.2 TRANSMISSION COEFFICIENTS MODEL

We consider a model of molecular junction conductance as a product of transmission coefficients associated with each interval and interface traversed by a charge carrier. This is consistent with the WKB approximation of tunneling used in the Simmons model as well as more complex density-functional theory simulations, while allowing for arbitrary contact behavior.

The device conductance is described by the equation:

\[
\sigma = \frac{2e^2}{h} \cdot N \cdot T_{\text{Au-poly}} \cdot T_{\text{poly}} \cdot T_{\text{poly-end}} \cdot T_{\text{alkane}} \cdot T_{\text{thiol-Au}}
\]

(4.9)
where $\sigma$ is the device conductivity, $2e^2/h$ is a quantum of conductance, $N$ is the number of transport channels, and $T_{\text{Au-poly}}$, $T_{\text{poly}}$, $T_{\text{poly-end}}$, $T_{\text{alkane}}$, and $T_{\text{thiol-Au}}$ are the transmission probabilities of the gold-polymer interface, the polymer layer, the polymer-molecule termination interface, the alkane backbone of the molecule, and the molecule-substrate (thiol-gold) interface, respectively. For simplicity in discussion, we introduce the terms:

$$T_{\text{poly}} = T_{\text{Au-poly}} \cdot T_{\text{poly}}.$$  

(4.10)

and

$$T_{\text{SAM}} = T_{\text{poly-end}} \cdot T_{\text{alkane}} \cdot T_{\text{thiol-Au}}.$$  

(4.11)

such that

$$\sigma = \frac{2e^2}{h} \cdot N \cdot T_{\text{poly}} \cdot T_{\text{SAM}}.$$  

(4.12)

Figure 41 presents a schematic illustrating the terms in (4.9) overlaid on a sketch of the device, laid out horizontally. The top contact is on the left, the substrate is on the right.

Figure 41: Schematic illustrating transport barriers and associated transmission coefficients in device. The top contact is on the left, the substrate is on the right.
4.3 TRANSPORT IN DISORDERED MATERIALS

We now discuss the unique mechanisms of transport in disordered materials such as conductive polymers like PEDOT:PSS and Aedotron P. We will show in Chapter 6 that the transport through the polymer dominates the electrical characteristics of our devices at low temperature.

In a disordered material, localized trap states exist from the bottom of the conduction band up to a critical energy $E_c$, called the mobility edge. The distance between the mobility edge and the conduction band is referred to by the energy term $\Delta E$. An illustration of the density of states and a depiction of the mobility edge are shown in Figure 42.

![Figure 42: The density of states in the conduction band of a non-crystalline material, showing the mobility edge $E_c$ separated by an energy $\Delta E$ from the band edge.](image)

Charge transport between localized trap states occurs via thermally activated carrier hopping, a process known as variable-range hopping because the typical hops become longer with decreasing temperature. For a three-dimensional material, variable-range hopping gives a conductivity varying as an exponential function of $T^{-1/4}$. Above the mobility edge, states become non-localized or extended, and transport is equivalent to carrier drift seen in single-crystal semiconductors, with carriers freely accelerating under the applied field before reaching a constant average velocity due to collisions with charge
impurities and phonons. Combining the contribution from the two kinds of states, the conductivity of Aedotron P can be described by the equation:

\[
\sigma(T) = \sigma_1 e^{-\Delta E/kT} + \sigma_2 e^{-\left(\frac{T_0}{T}\right)^{1/\alpha}},
\]

(4.13)

where \(\sigma_1\) and \(\sigma_2\) are prefactors dependent on the applied field, \(\Delta E\) is the energy difference between the Fermi level and the mobility edge, \(k\) is the Boltzmann constant, \(T\) is the temperature, and \(T_0\) is a term dependent on the radial extension of the carrier wavefunction and the density of states in the material. Figure 43 presents a qualitative illustration of the drift mobility \(\mu_0\), and the log of the conductivity \(\sigma\), of a disordered material. In Chapter 6 we will look at a quantitative measurement of the polymer transport and show that it dominates the molecular junction device behavior.

Figure 43: The drift mobility \(\mu_0\), and the log of the conductivity \(\sigma\), of a material where the conduction band is as in Figure 42.
In this chapter we have presented models to describe the transport in a molecular junction and in a disordered conductor such as Aedotron P, the top contact material used in this project. We first described molecular junction transport with the Simmons model of electron tunneling through a dielectric material between two metal contacts, with and without quantitative accounting for image charge in the contacts. We then discussed a more general model of molecular junction transport as a series of transmission coefficients. Finally, we considered transport through disordered materials such as the conducting polymers used as soft contacts for molecular junctions. In Chapters 5 and 6 we will apply these models to interpret the transport behavior of our molecular junctions.
CHAPTER 5: ROOM TEMPERATURE TRANSPORT IN ALKANETHIOL SAMS

The polymer-contacted molecular junctions are first studied by measuring transport through a series of alkanethiol SAMs of varying length and termination in pores of 1 µm and 300 nm diameter.

5.1 MEASUREMENT SETUP

The devices are measured under vacuum using a Desert Cryogenics (now LakeShore) flow cryostat probe station and a Keithley 2400 Source Meter. The gold substrate is grounded, and we refer to the bias on the polymer contact as the voltage across the device. See Appendix B for a diagram of this setup.

The conductance of Aedotron P varies significantly as a function of duration under vacuum, although the effect saturates after a few hours. Thus, each device is maintained under vacuum for four hours prior to measurement. Devices that are not dried under vacuum demonstrate substantially asymmetric JV curves, with higher current observed under reverse bias. These devices often show substantial hysteresis.

5.2 ALKANETHIOL TRANSPORT DATA

Figure 44 presents a representative IV curve taken for a 300 nm pore with a SAM of dodecanethiol, a 12-carbon alkane with thiol termination. With the substrate grounded, the sweep goes from 0 to +1 V bias, shown in red, from +1 V to -1 V, shown in black, and then back to 0, shown in red. There is negligible hysteresis in this device. This was the case with over 80% of the measured devices, provided we dried the polymer for a few hours under vacuum before measurement. Examining the shape of the curve, one sees that at low bias the current is linearly dependent on voltage and then transitions into an exponential relationship, as described by the limits of the Simmons model in Chapter 4.
Figure 44: Representative IV trace of a 300 nm diameter dodecanethiol device from 0 -> +1V -> -1V -> 0 on a linear scale.

Figure 46 presents a large log-scale dataset of measurements on devices like the one in Figure 44, covering a series of alkanethiols including octanethiol (M8), decanethiol (M10), dodecanethiol (M12) and tetradecanethiol (M14). These molecular species are illustrated in Figure 45. The M8-M14 abbreviations are used as labels in figures throughout the rest of the document.

Figure 45: Chemical structure and labels of measured alkanethiol species. The abbreviations in parenthesis are used as labels in figures throughout the rest of the document.

To collect the data for Figure 46, 34 devices are fabricated per chip, with one chip per molecule/pore size combination, with a yield ranging from 70 to 100%. Failed devices
are typically shorts or exhibit orders of magnitude higher conductivity than a typical device. The failures are due to defects in the resist layer, which are then transferred to the mask, resulting in shorts or excessive device area. This is evidenced by the improvement yield when the resist is filtered before application. Each data point in Figure 46 represents the geometric mean of at least 20 devices out of the possible 34 on a single chip. Before calculating the geometric mean, shorted devices are discarded from the data set. Outlying devices from each set are then removed by eliminating the most and least conductive 1/6 of the remaining devices. Error bars corresponding to one standard deviation are displayed for every other point.

There are a number of notable features in Figure 46. The current density for a given molecular species is the same for both pore sizes, if one accounts for an 18 nm rim of uncontacted area as illustrated in the device schematic in Figure 24. This effectively reduces the device diameters to 0.96 μm and 264 nm. This could be due to either incomplete filling of the pores due to meniscus formation, or slight shrinking of the polymer “plug” during vacuum drying after deposition. Every curve in Figure 46 is qualitatively similar, with a curved portion corresponding to a linear dependence on voltage at bias below 0.3 V, and a straight portion corresponding to an exponential dependence on voltage above 0.3 V. Each set of curves corresponding to a given molecular species has a roughly constant offset. As the data is plotted on a log scale, this indicates that increasing (decreasing) the alkanethiol length by 2 carbons results in a roughly constant multiplication (reduction) of the current density. The JV curves correspond roughly to those reported for larger-area devices with PEDOT:PSS top contacts.59
Figure 46: Alkanethiol SAM current densities in 1 μm and 300 nm diameter pores measured at room temperature under vacuum. The M8-M14 abbreviations correspond to the molecules in Figure 45.

The conductance of working devices on a given chip varies with a lognormal distribution. The measured current density at 1 V bias of every device analyzed in Figure 46 is presented as a scatter plot in Figure 47. The median current density for a given set of devices (horizontal red line in each box) is typically close to the geometric mean (enlarged data point in each set), indicating a lognormal distribution in the measured current densities. Given that the conductance of a tunnel barrier varies as an exponential function of barrier thickness, we hypothesize that the lognormal distribution is due to a normal distribution in the effective barrier thicknesses. It is unclear why this distribution doesn’t average out over the area of a given device.
Figure 47: Scatter plot overlaid on box and whiskers plot of the common logarithm of the measured current density at 1 V bias for 8, 10, 12, and 14 carbon alkanethiols in 1 μm diameter (left) and 300 nm (right) devices, as presented in Figure 46. Red horizontal line in each box is the median, top and bottom of box correspond to first and third quartiles, and dashed lines stretch to the furthest outliers for each set. Measurements were taken at room temperature under vacuum. The plot demonstrates the lognormal distribution for each set of devices and the exponential decay of current density as a function of increasing molecule length.

5.3 SIMMONS MODEL ANALYSIS

As discussed in Chapter 4, while Simmons model assumptions about the nature of the contacts are not valid for polymer-contacted devices and fail to model the temperature dependence, we do find that the model provides nice empirical fits to our data and produces plausible molecular barrier height values.

Using the Simmons model without accounting for the image charge as in (4.1), the data presented in Figure 46 can be modeled with barrier heights, \( \Phi \), between 1.39 and 2.09 eV and \( \alpha \) between 0.68 and 0.88. The accuracy of the model is demonstrated in
Figure 48, with calculated fit lines overlaid on the experimental data at positive bias voltages. The calculated fit parameters are presented in Table 6. In general, the calculated $\Phi$ decreases as the molecule length increases, possibly because the SAM thickness is systematically miscalculated due to a gap at the polymer-molecule interface. The values derived for the devices in the present work are consistent with those reported using the same model for alkanedithiols between gold electrodes measured up to 1 V bias, either as single molecules in a break junction between an STM tip and a gold surface ($\alpha = 0.61$, $\Phi = 1.83$ eV)\textsuperscript{145} or as SAMs in junctions tens of nanometers in diameter with evaporated gold contacts ($\alpha = 0.65$, $\Phi = 1.39$ eV).\textsuperscript{85} As discussed in Chapter 4, these findings are not consistent with the expected ~5 eV barrier height of alkanethiols, likely because they fail to explicitly account for the image charge in the contacts.

Table 7 presents the calculated fit parameters using the Simmons model with an accounting for the image charge, as described by (4.8). The described fit lines match the data roughly as well as those in Figure 48. The calculated barrier heights, $\Phi$, now range from 2.3 to 4 eV, which is a more physically reasonable estimate. However, the calculated effective mass, $m_e^*$, averages around 0.55 $m_e$. This is troubling, as Akkerman et. al. found $m_e^* = 0.28 m_e$ using the same model for a series of alkanedithiol SAMs with the same number of carbons and PEDOT:PSS top contacts.\textsuperscript{100} $m_e^* = 0.28 m_e$ has also been theoretically predicted using a complex band structure calculation for n-alkanes of infinite length.\textsuperscript{180} It is unclear why the simple Simmons model yields fit parameters roughly matching those found in the literature (although they are physically untenable), but the model accounting for image charge yields a much larger effective mass than expected. The next section will show that there are additional disagreements between the alkanethiol transport data and the behavior typically reported in the literature.
Figure 48: Alkanethiol current density values measured under positive bias from Figure 2 in the text, overlaid on curves derived from the rectangular potential barrier model as described by (4.1). The calculated barrier heights and fit parameter alpha are presented Table 6.

Table 6: Calculated barrier height $\Phi$, and fit parameter $\alpha$ for various length alkanethiol molecular junction devices as determined by (4.1).

<table>
<thead>
<tr>
<th>Device</th>
<th>$\alpha$</th>
<th>$\Phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAM</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M8</td>
<td>$1 \ \mu$m</td>
<td>0.88</td>
</tr>
<tr>
<td>M10</td>
<td>$1 \ \mu$m</td>
<td>0.73</td>
</tr>
<tr>
<td>M12</td>
<td>$1 \ \mu$m</td>
<td>0.68</td>
</tr>
<tr>
<td>M14</td>
<td>$1 \ \mu$m</td>
<td>0.71</td>
</tr>
<tr>
<td>M8</td>
<td>300 nm</td>
<td>0.79</td>
</tr>
<tr>
<td>M10</td>
<td>300 nm</td>
<td>0.77</td>
</tr>
<tr>
<td>M12</td>
<td>300 nm</td>
<td>0.75</td>
</tr>
<tr>
<td>M14</td>
<td>300 nm</td>
<td>0.69</td>
</tr>
</tbody>
</table>
Table 7: Fit parameters calculated using the Simmons model, accounting for image charge.

<table>
<thead>
<tr>
<th>Device</th>
<th>Pore size</th>
<th>$m_e^*$ ($m_e$)</th>
<th>$\Phi_{\text{image}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAM</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M8</td>
<td>1 µm</td>
<td>0.54</td>
<td>3.92</td>
</tr>
<tr>
<td>M10</td>
<td>1 µm</td>
<td>0.57</td>
<td>3.00</td>
</tr>
<tr>
<td>M12</td>
<td>1 µm</td>
<td>0.47</td>
<td>2.78</td>
</tr>
<tr>
<td>M14</td>
<td>1 µm</td>
<td>0.57</td>
<td>2.16</td>
</tr>
<tr>
<td>M8</td>
<td>300 nm</td>
<td>0.52</td>
<td>3.99</td>
</tr>
<tr>
<td>M10</td>
<td>300 nm</td>
<td>0.68</td>
<td>2.72</td>
</tr>
<tr>
<td>M12</td>
<td>300 nm</td>
<td>0.52</td>
<td>2.63</td>
</tr>
<tr>
<td>M14</td>
<td>300 nm</td>
<td>0.51</td>
<td>2.29</td>
</tr>
</tbody>
</table>

5.4 ANALYSIS OF LENGTH-DEPENDENT CURRENT DECAY

Numerous experimental and theoretical studies have found that non-resonant, through
bond tunneling is the transport mechanism through an alkanethiol SAM in a molecular
junction. Thus, we anticipate that the alkane transmission coefficient, $T_{\text{alkane}}$, the device
conductivity, $\sigma$, and the measured current density $J$, are all exponentially dependent on
the SAM thickness, which can be represented by the number of carbons in the molecular
species.\textsuperscript{55} Figure 49 presents the current density as a function of the number of carbons in
the alkanethiol species at 0.1, 0.3 and 0.5 V biases. The fit is described by the equation:

$$J = A \exp(-\beta_e n),$$  \hspace{1cm} (5.1)

where $J$ is the current density, $A$ is an arbitrary constant, $\beta_e$ is the decay parameter, and $n$
is the number of carbons in the alkane chain. We note the decrease of $\beta_e$ with increasing
bias, in accordance with the Simmons model and other theoretical calculations of
transport through a tunnel barrier.\textsuperscript{36}
Figure 49: Current density and exponential fit of data from as a function of number of carbons in the alkanethiol tail at 0.1, 0.3 and 0.5 V bias.

We find $\beta_c$ values of 0.55, 0.51 and 0.45 per carbon at a bias of 0.1, 0.3 and 0.5 V, respectively. $\beta_c$ for alkane transport at low bias is typically found to be $\sim$1, in both solid-state\textsuperscript{86,99,160} and electrochemical measurements\textsuperscript{62} as well as in theoretical simulations\textsuperscript{181}. We are aware of only three prior experimental reports of $\beta_c < 0.8$ out of dozens of studies in the literature (Note that all experiments discussed in this section are also described in some detail in Chapter 2). One of those reports, based on AFM probing of gold nanoparticles deposited on alkanedithiol SAMs, initially found $\beta_c = 0.58$\textsuperscript{162} In a subsequent study, the authors attributed their findings to Coloumb blockade effects and revised the figure to $\beta_c = 0.95$.\textsuperscript{163} Another low value ($\beta_c = 0.52$) was reported for measurements of single dithiols using an STM tip above a gold surface in solution\textsuperscript{182}. The reason for this anomalous result is unclear, but it is in disagreement with several similar studies of both dithiol and diamine alkanes in STM break-junctions\textsuperscript{99}. Most relevant to the current study, Akkerman \textit{et. al.} found $\beta_c = 0.66$ at 0.1 V for alkanedithiols with PEDOT:PSS top contacts in a device geometry similar to that of the present work\textsuperscript{59}. The same research team later reported $\beta_c = 0.9$ for alkanethiol monolayers, but noted that the
relationship only held for alkanethiols with more than 14 carbons, with $\beta_c$ effectively equal to 0 below this length.$^{101}$

We theorize that in both the present work and Akkerman’s studies of alkanethiols, the polymer contact may be penetrating into the monolayer at defect sites, as depicted in Figure 50. Whitesides et al. have previously shown that the presence of even a small area percentage of “thin-area” defects, typically present at grain boundaries and raised vacancy islands, can substantially affect the current measured through a monolayer junction.$^{68}$ The penetration could be a result of measures taken to ensure good wetting of the monolayer surface, such as the addition of surfactants to aqueous PEDOT:PSS by Akkerman et al., and the use of nitromethane as the solvent for Aedotron P in the present work. We note that such penetration does not happen in all experiments that use polymer contacts, as Milani et al. found $\beta_c = 1.13$ for devices with undoped polyphenylenevinylene spin-coated from a dispersion in chloroform onto 8-16 carbon alkanethiols.$^{104}$ Monolayer defect penetration appears to be unique to the application of strongly wetting polymer contacts to SAMs shorter than 16 carbons.

![Conducting Polymer](image_url)

Figure 50: Depiction of conducting polymer layer penetrating defect sites in SAM, leading to less-than-expected dependence of current density on molecule length.
To quantify our theory of SAM penetration by the polymer, we reapply the image charge Simmons model, this time assuming the expected barrier height (~5 eV), effective mass (0.28 \( m_e \)), and \( \beta_c \) (~1) values while adjusting the monolayer thickness as a fit parameter. We find good fits if the monolayers formed from M8, M10, M12 and M14 are treated as 6, 7, 8 and 9 carbons long, respectively. Figure 51 replots the current density as a function of molecule length, with the actual number of carbons in each molecule on the top x-axis. The bottom x-axis shows the number of carbons presumed in order to calculate an accurate fit line (i.e., the effective number of carbons). Table 8 and

Table 9 present the calculated fit parameters. This modeling indicates that the alkanethiol SAMs are well-packed near the surface and prevent shorting penetration by the polymer, but for every two carbon increase in alkane length, the disorder and defects result in an effective increase of a single carbon. This physical interpretation explains both the observed low barrier height and \( \beta_c \) values.

Figure 51: Measured current density as a function of SAM species length for 1μm and 300 nm pores at various voltages. Top x-axis is the actual number of carbons in each species. Bottom x-axis is the number of carbons presumed in order to produce an accurate fit line with the expected barrier height, effective mass, and \( \beta_c \) values.

As a caveat, we have several times noted that the assumptions in the Simmons model are not valid for polymer top contacts, so we should not expect these findings to be
quantitatively predictive. The mechanism proposed here is simply consistent with the observed anomalies in our data set.
Table 8: $\beta_i$ values corresponding to the bottom x-axis in Figure 51.

<table>
<thead>
<tr>
<th>Bias</th>
<th>Beta</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.87</td>
</tr>
<tr>
<td>0.3</td>
<td>0.91</td>
</tr>
<tr>
<td>0.1</td>
<td>1.09</td>
</tr>
</tbody>
</table>

Table 9: Calculated fit parameters assuming the effective number of carbons for molecule length.

<table>
<thead>
<tr>
<th>Device</th>
<th>$m^*$ ($m_e$)</th>
<th>$\Phi_{\text{image}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAM M8</td>
<td>1 $\mu$m</td>
<td>0.56</td>
</tr>
<tr>
<td>SAM M10</td>
<td>1 $\mu$m</td>
<td>0.54</td>
</tr>
<tr>
<td>SAM M12</td>
<td>1 $\mu$m</td>
<td>0.53</td>
</tr>
<tr>
<td>SAM M14</td>
<td>1 $\mu$m</td>
<td>0.51</td>
</tr>
<tr>
<td>SAM M8</td>
<td>300 nm</td>
<td>0.53</td>
</tr>
<tr>
<td>SAM M10</td>
<td>300 nm</td>
<td>0.51</td>
</tr>
<tr>
<td>SAM M12</td>
<td>300 nm</td>
<td>0.51</td>
</tr>
<tr>
<td>SAM M14</td>
<td>300 nm</td>
<td>0.54</td>
</tr>
</tbody>
</table>

5.5 STUDY OF ALKANETHIOL TRANSPORT WITH VARYING TERMINAL GROUPS

A positive aspect of the superior wetting of Aedotron P is the material’s compatibility with any SAM termination as a result of the amphiphilic nature of the nitromethane solvent. Figure 52 presents the current density measured at 1 V bias for devices containing 8- and 12- carbon alkanethiols terminated with methyl (M8, M12), thiol (T8, T12), and carboxyl (C8, C12) groups, as well as azidoundecanethiol (A11). The methyl, carboxyl and azide-terminated molecules all display similar current density for a given monolayer thickness, while the dithiols, particularly octanedithiol, are somewhat more conductive. This may be due to the ability of alkanedithiols to fold over with both terminal thiols bound to the gold surface, resulting in an effectively shorter monolayer. While previous work has shown that SAM formation with concentrations of greater than 30 mM minimizes this tendency, it is not clear that it can ever be completely eliminated.\textsuperscript{20}
Figure 52: (A) Box and whiskers plots showing medians, quartiles and outliers overlaid on scatterplots of current density at 1 V bias for octanedithiol, octanethiol, octanoic acid, dodecanedithiol, dodecanethiol, dodecanoic acid and azidoundecanethiol. Measurements are taken at room temperature under vacuum. The large data point for each scatterplot set indicates the geometric mean. (B) Measured alkane species.

In this chapter we have presented room temperature transport studies on a variety of alkanethiol SAMs with varying backbone lengths and terminal groups. We have modeled the data using the methods presented in Chapter 4. We have found that the barrier height, electron effective mass, and molecular length-dependent current decay all vary from previously reported values reported in the literature for alkanethiols. We have shown that
these results can be qualitatively explained with a model of polymer penetration at defect sites in the SAM, effectively reducing the tunnel barrier thickness. Finally, we have shown that with contacts formed from Aedotron P suspended in nitromethane the molecular termination has little impact on the measured transport, in contrast to junctions with PEDOT:PSS top contacts.
CHAPTER 6: LOW TEMPERATURE TRANSPORT IN ALKANETHIOLS

To better understand the role of the polymer top contact in transport, and to establish another comparison between Aedotron P and PEDOT:PSS-contacted devices, a subset of devices is characterized across a range of temperatures. As described in Chapter 4, according to the Simmons model description of transport between two metallic contacts through a tunnel barrier in a low bias regime, the current density should only vary by a few percent as the device is cooled from room temperature to 0 K. In contrast, we find that the current density varies by orders of magnitude as the device is cooled below room temperature. This is in agreement with measurements of junctions with PEDOT:PSS top contacts by Kronemeijer et al., but contrasts with earlier reports by the same researchers. We find that the temperature-dependent behavior of a device can be explained primarily by changes in transport through the polymer layer as the device is cooled. The measured data can be simulated both with a model of the device as a series of transmission coefficients, as in Chapter 5, and with a model of dissipative tunneling. We find the dissipative tunneling model less intuitive and question some of the assumptions upon which it is based, but acknowledge that it produces fit lines that match the data both in our work and for devices with PEDOT:PSS contacts.

6.1 AEDOTRON P TEMPERATURE-DEPENDENT TRANSPORT

As in Chapter 5, the devices are measured under vacuum using a Desert Cryogenics (now LakeShore) flow cryostat probe station and a Keithley 2400 Source Meter. The gold substrate is grounded, and we refer to the bias on the polymer contact as the voltage across the device. The chips are pumped under vacuum for 4 hours and then cooled to 25 Kelvin over 30 minutes as liquid helium is pumped through the cryostat. Using a heating element inside the cryostat stage, the devices are then warmed to room temperature over a period of a few hours, with measurements taken at each temperature reported in the figures below.
We first study the temperature-dependent transport of the isolated polymer layer with no SAM. Recalling from Section 4.3, we anticipate that for devices containing only a polymer layer the conductivity is described by the equation:

$$\sigma_{poly} = 2e^2/h \cdot N \cdot T_{poly} = \sigma_1 e^{-\Delta E/kT} + \sigma_2 e^{-(T_0/T)^{1/4}},$$

(6.1)

where $2e^2/h$ is a universal quantum of conductance, $N$ is the number of transport channels, $T_{poly}$ is the transmission probability through the polymer layer, $\sigma_1$ and $\sigma_2$ are constant fit parameters, $T$ is the temperature, $\Delta E$ is the energy difference between the mobility edge and Fermi energy, and $T_0$ is the temperature associated with the variable-range hopping process.

Figure 53A presents the current density as a function of voltage at various temperatures in a representative 30 μm diameter device containing only a polymer layer and no SAM. As the device is cooled its conductivity decreases and transport becomes non-ohmic. Figure 53B presents selected datapoints from Figure 53A on an Arrhenius plot, showing the measured specific contact conductance as a function of inverse temperature at various biases. Fit lines as described by (6.1) are overlaid on the measured data. The bias values Figure 53B are chosen such that the current in the polymer-only devices is roughly equivalent to the current through devices containing dodecanethiol at 0.1, 0.3, 0.5 and 1 V bias.
Figure 53: (A) Current density as a function of bias for 30 um diameter polymer-only device at various temperatures. For visibility, 25K and 12K traces have been multiplied by a factor of 40. Below 200K, Aedotron P demonstrates increasingly non-ohmic transport behavior. (B) Arrhenius plot of selected data points from (A), with overlaid fit lines.

### 6.2 SAM TEMPERATURE-DEPENDENT TRANSPORT

We next measure the temperature dependence of a set of dodecanethiol devices. Figure 54A presents an Arrhenius plot of the average specific contact conductance of a set of three 300 nm diameter devices containing a dodecanethiol SAM at 0.1, 0.3, 0.5 and 1.0 V
bias. Due to the substantially lower current measured in the 300 nm diameter devices, at low temperature and low bias the signal cannot be isolated from the background noise and those data points are not included in the plot. A least-squares fit line defined by a curve of the form described in (6.1) is overlaid on the data at each bias voltage. Figure 54B presents an Arrhenius plot of the 1 V, 0.5 V, 0.3 V, and 0.1 V dodecanethiol device traces in Figure 54A divided by the 100 mV, 50 mV, 30 mV and 10 mV Aedotron-only traces in Figure 53B, in effect isolating the term $T_{SAM}$, as defined in (4.11).

For all biases, $T_{SAM}$ is constant for temperatures below 100 K, indicating that the SAM-containing device conductance is dominated by polymer transmission at these temperatures. Prior experiments$^{83}$ and theory$^{174,176,177}$ indicate that $T_{SAM}$ should be roughly constant for all temperatures. Above 100 K there may be additional factors affecting the conductivity of the molecular junctions as a function of temperature, for example, a change in the dielectric constant of the SAM, a change in the polymer wetting of the pore, or a temperature-dependent change in $T_{poly-SAM}^*$, the transmission between the polymer and SAM.

As an alternative to the transmission coefficients model, one might consider the polymer layer as a series resistance that could be subtracted to isolate the contribution from the SAM. However, similar to the results of Kronemeijer et. al.$^{103}$ we find that a series resistor model fails to explain the observed temperature-dependence. For all devices in Kronemeijer et. al. and for the dodecanethiol devices considered here, the resistivity of the polymer layer is substantially smaller than the resistance of devices containing SAMs, indicating that as a series resistance the polymer should have a negligible impact on the overall device conductance. However, a simple visual analysis of the polymer-only and dodecanethiol Arrhenius plots in Figure 53B and Figure 54A, respectively, indicates a relationship of the form described in (4.12), wherein the molecular junction conductance is the product of the polymer layer conductance and $T_{SAM}$. This relationship is further evidenced by the constant value of $T_{SAM}$ for temperatures below 100 K, as seen in Figure 54B.
Figure 54: (A) Arrhenius plot of 300 nm diameter dodecanedithiol device conductivity as a function of temperature at various biases. Overlaid solid lines are fits in the form of (6.1). (B) Result of dividing 1 V, 0.5 V, 0.3 V, and 0.1 V traces in A by 100 mV, 50 mV, 30 mV and 10 mV traces in Figure 53B, respectively, removing the temperature-dependent effects of the polymer layer to derive $T_{SAM}$, as described in (4.11).

Table 10 compares the derived $\Delta E$ and $T_\theta$ values for the polymer layer and the average of the dodecanedithiol devices. Calculated values of $T_\theta$ vary substantially for both kinds of devices, as the exponential $1/4$ term in (6.1) allows for considerable play in $T_\theta$ while still producing similar low temperature curves in Figure 53B and Figure 54A.
$\Delta E$ is somewhat higher for devices containing dodecanethiol than those with only polymer, as evidenced in the steeper high-temperature slopes in Figure 54A and the residual slope above 100 K for $T_{\text{SAM}}$ in Figure 54B.

Table 10: Calculated parameters for Arrhenius plot fit lines in Figure 53B and Figure 54A.

<table>
<thead>
<tr>
<th>Poly Bias</th>
<th>Poly - $\Delta E$</th>
<th>Poly - $T_0$</th>
<th>SAM Bias</th>
<th>Dodecanethiol - $\Delta E$</th>
<th>Dodecanethiol - $T_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 mV</td>
<td>62.5 meV</td>
<td>3897 K</td>
<td>0.1 V</td>
<td>100 meV</td>
<td>4000 K</td>
</tr>
<tr>
<td>30 mV</td>
<td>61 meV</td>
<td>2136 K</td>
<td>0.3 V</td>
<td>89 meV</td>
<td>3997 K</td>
</tr>
<tr>
<td>50 mV</td>
<td>63 meV</td>
<td>1703 K</td>
<td>0.5 V</td>
<td>76 meV</td>
<td>1314 K</td>
</tr>
<tr>
<td>100 mV</td>
<td>64 meV</td>
<td>1285 K</td>
<td>1.0 V</td>
<td>76 meV</td>
<td>3511 K</td>
</tr>
</tbody>
</table>

**6.3 DISSIPATIVE QUANTUM TUNNELING MODEL**

The observed temperature-dependent transport can also be described with a model of dissipative quantum tunneling through a potential barrier, as previously demonstrated by Kronemeijer et al.\textsuperscript{102,103} In this conceptualization, the transport is characterized by a power-law dependence on both bias and temperature. This model was previously employed to describe transport in one-dimensional Luttinger liquids such as carbon nanotubes.\textsuperscript{183} While the model was originally thought to apply to polymer systems only if they consisted of long one-dimensional chains, such as PBTTT,\textsuperscript{184} further studies have shown that the model also describes transport in polymers consisting of distinct microscopic grains such as PEDOT:PSS,\textsuperscript{102} as well as molecular junctions of the kind described in the present work.\textsuperscript{103} It is unclear why a model of a one-dimensional system describes transport through a disordered three-dimensional series of grains in a conductive polymer. The physical nature of the dissipation mechanism in this model is also ambiguous. Furthermore, it is uncertain whether the potential barrier being described is the SAM or gaps between localized sites in the polymer. With these caveats in mind, this model does produce curves that accurately fit the data, and we find utility in comparing the extracted fit parameters with those published for PEDOT:PSS contacted devices.

The dissipative tunneling model defines the tunneling current density $J$ as:\textsuperscript{185,186}
\[ J = J_0 T^{1+\sigma} \sinh \left( \frac{eV}{kT} \right) \Gamma \left( 1 + \frac{\sigma}{2} + i \frac{eV}{\pi kT} \right), \]

(6.2)

where \( \sigma \) is derived from measurements, \( J_0 \) and \( \Upsilon \) are fit parameters, \( V \) is the applied bias, \( e \) is the elementary charge, \( k \) is the Boltzmann constant, and \( \Gamma \) is the Gamma function. \( \sigma \) can be considered as a relative measure of the effect of temperature on transport. It has been demonstrated that \( J_0 \) varies substantially as a function of the length and barrier height of the SAM. In the case of Luttinger liquid transport, \( \Upsilon \) describes the distribution of potential across the tunnel barriers between the contacts and the one-dimensional transport channel,\(^{183}\) however, the appropriate physical interpretation is not clear for a molecular junction with a polymer contact. Temperature-dependent measurements of larger molecular junctions containing a variety of paraphenylthiol and alkanethiol molecules under PEDOT:PSS top contacts yielded values of \( \sigma = 2 \) to 3, \( J_0 = 2 \times 10^6 \) to 1 A/m\(^2\), and \( \Upsilon = 0.02 \) to 0.03.\(^{103}\)

Figure 55A plots the current density of a representative dodecanethiol SAM device at 0.1, 0.3 and 0.5 V bias versus temperature on a log-log scale. Data at each bias can be fit by a straight line, indicating that the observed temperature dependence also fits a power law. The slope increases as a function of decreasing bias. By extrapolating the fit lines to a bias of 0 V, (6.2) reduces to \( J = J_0 T^{1+\sigma} \), yielding \( \sigma = 5.0 \). In Figure 55B we use this derived value of \( \sigma \) to scale the current density across all measured temperatures and observe that JV data taken at various temperatures collapses onto a single curve. The y-axis, defined by \( J/T^{1+\sigma} \), spans 6 orders of magnitude. The x-axis, defined with the dimensionless parameter \( eV/kT \), spans 2.5 orders of magnitude. Fitting a line described by (6.2) to the data, we extract the parameters \( \Upsilon = 0.048 \) and \( J_0 = 4 \times 10^{-11} \) A/m\(^2\). Data points corresponding to current density less than 0.05 A/cm\(^2\) have been removed because they fall below the noise limit of the measurement. While the emergence of a universal curve and the precision of the determined fit are not as unambiguous as previous results, we find utility in comparing this device’s extracted parameters with those found for larger-area junctions.
Figure 55: (A) Current density as a function of temperature for a given bias plotted on a double logarithmic scale. (B) Scaled current density presented on a double logarithmic scale as a function of \( eV/kT \). The solid curve is calculated with (6.2) using \( \sigma = 5.0, \gamma = 0.048, \) and \( J_0 = 4 \times 10^{-11} \text{A/m}^2 \).

The value obtained for \( \sigma \) is substantially higher than that reported for PEDOT:PSS devices, indicating that transport in Aedotron P devices is substantially more dependent on temperature. This may be due to the fact that Aedotron P is more resistive than PEDOT:PSS, and thus variation in the polymer resistance is more noticeable in our devices. \( J_0 \) in the present devices is several orders of magnitude lower than values reported for PEDOT:PSS. As \( J_0 \) simply positions the fit curve vertically along \( J/T^{1+\gamma} \) axis, the difference is explained by the exponential dependence of \( J_0 \) on \( \gamma \). Finally, the extracted value of \( \gamma \) in this series is roughly double that reported for paraphenylthiol and alkanethiol devices with PEDOT:PSS contacts. As noted previously, it’s not clear how to physically interpret this parameter.

In this chapter, we have considered the influence of temperature on transport in Aedotron P contacted molecular junctions. We have shown that both a transmission coefficients model and a dissipative tunneling model can adequately fit the data, but determined that the latter does not have a clear physical interpretation.
CHAPTER 7: TRANSPORT IN CONJUGATED MOLECULES

After discussing alkanethiol molecular junctions in the previous two chapters, we now consider devices with SAMs containing conjugated molecules. Dr. Ali Hosseini provided his invaluable expertise for this part of the project, synthesizing a number of molecules that had never before been studied in molecular junctions. The molecular structures of these species are presented in Figure 56. Most of the species are azide-terminated, to allow for straightforward attachment of ferrocene acetylene through copper(I)-catalyzed azide-alkyne cycloaddition chemistry, a process that will be described later in this chapter.

Figure 56: Conjugated molecular species synthesized by Dr. Ali Hosseini. These include (from left to right) 11-azidoundecanethiol with and without attached ferrocene, azidophenyleneethynebenzylthiol (N₃(PEB)SH) with and without attached ferrocene, azidoporphyrinthiol with and without attached ferrocene, and porphyrin-fullerene. The previously measured electron-transfer relaxation rate constants for 11-azidoundecanethiol and N₃(PEB)SH are presented above those species.⁴¹
11-azidoundecanethiol is used as a diluent and baseline comparison with the various conjugated species.\textsuperscript{187,188} Azidophenyleneethynylenebenzylthiol (N$_3$(PEB)SH) is synthesized to serve as a simple conjugated species. Previous work has shown that N$_3$(PEB)SH will self-assemble on a gold surface both with and without diluent 11-azidoundecanethiol, and that the two species are of roughly similar length.\textsuperscript{41} Azidoporphyrin-thiol is synthesized for multiple uses. We anticipated comparing this conjugated species with the simpler, denser packing N$_3$(PEB)SH, we intended to study the effect of swapping out different metal centers, with the knowledge that this shifts the HOMO and LUMO levels, and hoped to see some effect on transport from porphyrin’s photoactivity in the UV-visible spectrum.\textsuperscript{189,190} Porphyrin-fullerene is developed to further explore Dr. Hosseini’s previous spectroscopy studies of porphyrin-fullerene host-guest complexes.\textsuperscript{191–193} In host-guest systems the porphyrin cups the fullerene, with the former acting as a donor species and the latter as an acceptor. While the molecule synthesized here has the two units connected via a conjugated 1,2,3-triazole linkage, we hope to observe some measure of rectification and perhaps photodiode-like behavior.

Before presenting the details of each experiment, we note here that none of these studies is particularly successful. Every species yields nearly identical transport behavior in the measured molecular junctions. The only hint of unique transport behavior is in the case of slight rectification after attaching ferrocene to the N$_3$(PEB)SH SAM. We hypothesize that defect sites dominate the transport, with the result that every SAM looks like a tunnel barrier and exotic transport phenomena are hidden.

### 7.1 TRANSPORT IN MIXED MONOLAYERS WITH SOFT CONTACTS

We first studied mixed and homogeneous SAMs of N$_3$(PEB)SH and 11-azidoundecanethiol. Figure 57 presents a simplified cartoon of these monolayers. The herringbone packing of N$_3$(PEB)SH is not shown.\textsuperscript{194} The rate at which electrons transit these monolayers has previously been studied in electrochemical measurements. In those experiments, a potential step is applied across the monolayer and the exponential decay of the resulting current transient is measured. This “electron-transfer relaxation rate
constant” is much higher for $N_3$(PEB)SH than 11-azidoundecanethiol ($> 60,000 \text{k}_q(E^0)/\text{s}^{-1}$ vs. $500 \text{k}_q(E^0)/\text{s}^{-1}$), leading us to expect a higher conductance in these monolayers.\textsuperscript{41}

Figure 57: Depiction of (A) 11-azidoundecanethiol, (B) mixed 11-azidoundecanethiol and $N_3$(PEB)SH, and (C) homogeneous $N_3$(PEB)SH SAMs. The images do not convey the actual monolayer packing.

Figure 58 presents the common logarithm of the current at 1 V forward bias for a set of devices containing mixed monolayers of $N_3$(PEB)SH and 11-undecanethiol, formed from a 50 mM solution of the two species in chloroform. Each set of devices exhibits the same log-normal distribution behavior as noted for alkanethiols in Chapter 5. The molar fraction of $N_3$(PEB)SH in each SAM formation solution is labeled, from 0% to 100%. The blue box delineates the upper and lower quartiles, the red line delineates the median, and the bold symbol indicates the geometric mean. We see that contrary to our expectations there is no increase in the measured current density as a function of $N_3$(PEB)SH concentration in the monolayer formation solution.
Figure 58: Scatter plot of the common log of current density at 1 V bias for mixed monolayers of \( \text{N}_3(\text{PEB})\text{SH} \) and 11-azidoundecanethiol, indicating no clear relationship between monolayer composition and current density. Each set is labeled by the molar concentration of \( \text{N}_3(\text{PEB})\text{SH} \). The blue box delineates the upper and lower quartile, the red line is the median, and the bold symbol is the geometric mean.

Given that the electron transfer rate of the conjugated molecule should be at least 100 times greater than the alkane, the lack of any significant relationship is puzzling. One factor could be that the much “thinner” 11-undecanethiol molecules pack with a higher surface density than \( \text{N}_3(\text{PEB})\text{SH} \), meaning there are less electron transport pathways available as the monolayer becomes more conjugated. However, this alone shouldn’t offset the much higher conductivity. The IV curves of the devices with conjugated molecules are indistinguishable from those of the alkanethiols, indicating that coherent tunneling is still the dominant transport mechanism. Despite the presence of delocalized pi bonds, the LUMO level still appears to reside 2-4 eV above the Fermi level of the contacts according to the image charge accounting Simmons model.
7.2 RECTIFICATION IN FERROCENE-TERMINATED SPECIES

For each azide-terminated molecule in Figure 56, we study how transport is affected after attaching a ferrocene group using a copper(I)-catalyzed azide-alkyne cycloaddition reaction. In this section we will refer to this as a “click” reaction. “Click chemistry” is a general term introduced by K. Barry Sharpless of the Scripps Research Institute in 2001. This is a general term for modular, high-yield, simple reactions with large thermodynamic driving forces that can be performed in benign solvents and generate only inoffensive byproducts, mimicking many processes that occur in nature. The technique of “clicking” ferrocene acetylene onto a SAM with dilute azide-terminated molecules is common in electrochemical transport studies, as it allows for monolayer formation with a less bulky molecular structure before attaching the ferrocene “electrode.”

7.2.1 SAM FORMATION

Figure 59 demonstrates the process by which ferrocene acetylene is clicked onto a SAM with azide functionality. The figure shows the click process on mixed monolayers of decanethiol with 11-azidoundecanethiol and N$_3$(PEB)SH, as demonstrated in the work of Devaraj et. al. The process can also be performed on a homogeneous azide-terminated SAM, although only ~60% of azide terminations can participate in the reaction due to steric hindrance between binding sites.

The azide-terminated monolayer is first formed by immersing a chip with an open set of pores into a 50 mM ethanol (11-undecanethiol) or chloroform (N$_3$(PEB)SH) solution of the appropriate molecule under nitrogen. An appropriate amount of diluent molecule is added to the solution if so desired. The chip is left in solution for 48 hours, and then rinsed in clean solvent (ethanol or chloroform), isopropanol, and water. As described by Collman et. al., the chip is next completely submerged in a 1mM ferrocene acetylene solution (solvent 2:1 water:DMSO). 15 mol% of ascorbic acid is added, followed by 1 mol% of copper(I) tris-(benzyltriazolylmethyl)amine tetrafluoroboride (Cu(TBTA)BF$_4$). The addition of the copper catalyst results in substantially higher yield and a faster reaction. The presence of the ascorbic acid ensures that the catalyst is in the active Cu(I)
oxidation state. Typically less than 3 hours is required to reach full reaction yield. We allow each reaction to run for 24 hours. The reaction chamber is covered in foil and stored inside a drawer for the duration of the reaction in order to prevent photo-oxidation of the monolayer. After reaction, the chips are rinsed with copious amounts of ethanol, water, chloroform, and then water again to ensure that any physisorbed ferrocene is washed off.  

Before being used to form devices, all of the click reactions in this chapter are verified for bulk samples using Fourier transform infrared spectroscopy on a Nicolet spectrometer. Azide-terminated SAMs have a distinct, large peak at 2100 cm$^{-1}$, which disappears upon full reaction with an ethynyl-terminated species.

![Cu(I) catalyzed click](image)

Figure 59: Cu(I)-catalyzed click chemistry process by which ferrocene acetylene is attached to a terminal azide group on (A) 11-azidoundecanethiol and (B) N$_3$(PEB)SH.$^{413}$

7.2.2 **Theoretical Prediction of Rectification**

We anticipated that clicking ferrocene onto the SAM surface would result in current rectification, as previously observed in SAM transport experiments using eutectic-GaIn as a top contact material.$^{71,201}$ The energy level diagrams in Figure 60 illustrate the Fermi
levels of the gold and Aedotron P contacts (5.1 and 5.0 eV respectively) and the HOMO of ferrocene (5.4 eV) as measured by photoemission spectroscopy,\textsuperscript{202} at positive and negative 1 V bias. In the figure it is assumed that ferrocene is in contact with the polymer electrode and the entire voltage drop in the device is across the alkane. The HOMO of clicked ferrocene acetylene is possibly different from that of pure ferrocene, which may invalidate the predicted behavior. Nijhuis \textit{et. al.} have reported a HOMO of 5.0 eV for SAMs in which ferrocene is bound directly to 11-undecanethiol, with no triazole linkage. Their measurements are taken with electrochemistry, a less precise method than photoemission spectroscopy.

![Figure 60: Band diagrams indicating Fermi energies of gold and Aedotron P contacts, HOMO level of ferrocene, and length of ferrocene group and alkane backbone. (A) Under forward bias, electrons tunnel from the gold electrode to the Aedotron P. The HOMO of the ferrocene remains filled so that electrons must tunnel the entire distance between the electrodes. (B) Under reverse bias, the ferrocene HOMO is now between the Fermi levels of the two contacts. Electrons can hop onto the ferrocene before tunneling to the gold electrode. As the effective tunnel barrier is now shorter, we anticipate a higher magnitude of current in the reverse bias case.](image)

Assuming that the HOMO of ferrocene is 5.4 eV below the vacuum energy, we expect different transport behavior under forward and reverse bias, as depicted in Figure 60. Under forward bias, electrons tunnel from the gold electrode to the Aedotron P. The HOMO of the ferrocene remains filled so that electrons must tunnel the entire 20 Å distance between the electrodes. Under reverse bias, the ferrocene HOMO level moves between the Fermi levels of the two contacts. Electrons can hop onto the ferrocene before tunneling to the gold electrode. As the effective tunnel barrier is now shorter (13 Å), we
anticipate a higher magnitude of current under reverse bias, similar to that observed with no clicked ferrocene.

7.2.3 Clicked Ferrocene Results

The effect of clicking ferrocene is studied by measuring transport through dozens of devices on chips as described in Chapter 5. Control devices are immersed in 2:1 water:DMSO for 24 hours, but no ferrocene acetylene or catalyst is added, to mimic the incubation conditions for clicked monolayers. As an additional test, we also reproduce the click reaction conditions (addition of 15 mol% of ascorbic acid followed by 1 mol% of Cu(TBTA)BF$_4$) for 11-azidoundecanethiol, leaving out the ferrocene acetylene. We verify that 24 hours is more than sufficient time to attain full yield by also running the click reaction for a single hour. Figure 61 presents the measured current densities at 1 V forward bias for each set of devices. For both 11-azidoundecanethiol and porphyrin we observe negligible difference between clicked and control samples, while for N$_3$(PEB)SH we observe a substantial decrease in the forward bias current for a device with clicked-ferrocene as opposed to the control. The N$_3$(PEB)SH behavior is consistent with the theory that the HOMO of the ferrocene is filled during forward bias transport, such that electrons must tunnel the full distance between contacts. We also observe that for 11-azidoundecanethiol, exposing the monolayer to the click reaction conditions in the absence of ferrocene acetylene has no impact on the measured current. We see that the change in the N$_3$(PEB)SH is observable after 1 hour of reaction time, indicating that 24 hours is a sufficient reaction time for the other samples.

Surprisingly, the data in this experiment show that N$_3$(PEB)SH appears to be somewhat more resistive than 11-azidoundecanethiol. In the previous experiment, the median current density for N$_3$(PEB)SH devices at 1 V forward bias is ~30 A/cm$^2$, similar to 11-azidoundecanethiol. It has now dropped to ~10 A/cm$^2$. The experiments are performed about a week apart using the same equipment and techniques. One notable difference is that in the present experiment the control monolayers are immersed in 2:1 water:DMSO to mimic the click reaction conditions. It is unclear why this would increase the resistivity of just the N$_3$(PEB)SH devices and not the other species.

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We also note that porphyrin is the most conductive molecular species of the set considered in this chapter. There are too many variables (molecular structure, HOMO and LUMO levels, SAM packing) to reliably speculate why porphyrin monolayers are more conductive than N₃(PEB)SH. The cause may not even be attributable to the monolayer transport, as the bulky porphyrins could form a more leaky monolayer, which is more easily penetrated by the Aedotron P polymer.

Figure 61: Scatter plot of current densities at 1 V bias for for azide-terminated SAMs in molecular junctions before and after click reaction with ferrocene acetylene. As in Chapter 5, the measurements have a log-normal distribution. We observe negligible change in the current for porphyrin and 11-azidoundecanethiol devices as a result of performing the click reaction. For the “Porphyrin control” sample we introduce the click conditions and catalyst without ferrocene. There is a decrease in the N₃(PEB)SH current density after clicking ferrocene, running the reaction for either 1 or 24 hours, presumably as a result of increased tunnel barrier length.

We define the rectification $R$, of each measurement with the following equation:
\[ R = \left( J(+1\ V) - |J(-1\ V)| \right) / J(+1\ V), \]

(7.1)

where \( J(V) \) is the current density at a given bias. In other words, \( R \) is the difference between the reverse current at -1 V bias and the forward current at +1 V bias, normalized by dividing by the forward current at +1 V bias. Figure 62 shows that we observe a 3-4% percent change in the rectification of the \( N_3(PEB)SH \) molecule after clicking ferrocene for 1 hour and 24 hours, but do not see a significant change after performing the reaction on porphyrin or 11-azidoundecanethiol monolayers. We note that for all molecules there is a slight (< 1%) reverse rectification, likely due to differences in the work functions of Aedotron P and gold as discussed in Chapter 4.

![Figure 62: Observed rectification (normalized forward current minus reverse current) for azide-terminated SAMs in molecular junctions before and after click reaction with ferrocene acetylene. We observe negligible (< 1%) rectification for all species except ferrocene-terminated \( N_3(PEB)SH \) (3-4 % average rectification).](image)

We hypothesize that the observed rectification is smaller than expected because defect sites where the polymer has penetrated into the monolayer dominate the measured
current. Thus, we see little impact from electrons hopping onto the ferrocene molecule before tunneling across the alkanethiol.

7.3 PORPHYRINS, PORPHYRIN-FULLERENE SAMS

As a final study in our survey of exotic molecules in molecular junctions, we examine the use of click chemistry to attach ethynyl functionalized fullerenes to azide-terminated porphyrin monolayers. Concurrent with our own studies, a different research team synthesized triazole-linked porphyrin fullerenes and simulated the molecular orbitals and energy levels of these species. Also concurrent with our work, a third, unrelated group developed a conjugated porphyrin-fullerene and measured rectifying and photosensitive transport in these molecules in STM break junctions. Before these single molecule studies, transport through SAMs containing similar molecules had been measured in large-area solid-state junctions. Unfortunately, in the present work we see no effect from clicking fullerenes onto azide-terminated porphyrin SAMs.

7.3.1 PORPHYRIN-FULLERENE SYNTHESIS

The porphyrin synthesis is presented in Figure 63. Tetra-alkyl-dipyromethanes are chosen as the starting material because they are known as versatile precursors for the formation of trans-disubstituted porphyrins. They react with a variety of aldehydes to give porphyrins in a relatively high yield. Utilizing tetra-alkyl-dipyrromethane in a condensation reaction prevents scrambling, a process that can occur when using aromatic-dipyrromethane.

Bis-(4-methyl-3-propyl-2-pyrrole)methane (1) is synthesized from acetyl acetone in five steps according to previously reported procedures. The condensation of 1 with 4-(hydroxymethyl)-benzaldehyde and para-acetamidobenzaldehyde in dry dichloromethane is carried out using catalytic amounts of trifluoracetic acid under an atmosphere of N₂. This results in the formation of a statistical mixture of porphyrinogen that is oxidized to porphyrin using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in air. The desired amido-porphyrin (2) is separated from the statistical mixture to give 26% yield. Hydrolysis of the amide (2) in 6 M HCl gives amino-porphyrin (3). The diazotation of the
amine group followed by nucleophilic substitution with NaN₃ gives the azido-porphyrin (4). The conversion of benzyl alcohol to thioacetate (5) is accomplished by modification of a previously reported procedure. Deprotecting the thiol group in MeOH gives the desired 5-thiolmethylphenyl,15-azidophenyl-porphyrin (6).

Figure 63: Porphyrin synthesis.

In parallel to the synthesis of the azide-terminated porphyrin, we prepare two ethynyl-functionalized C₆₀ molecules as shown in Figure 64. The “bent” fullerene derivative (8) is synthesized according to a previously reported procedure. Here, the simple reaction of n-methylglycine and 4-ethynylbenzaldehyde with C₆₀ in refluxing toluene results in the desired ethynyl-pyrrolidinofullerene (8) in good yield after purification. The synthesis of the “linear” fullerene derivative (11) is initiated by the coupling of 4-ethynyl
aniline (9) and ethylbromoacetate to give ethyl 2-(4-ethynylphenylamino)acetate. This is followed by hydrolysis of the ester group in basic ethanol to give 2-(4-ethynylphenylamino)acetic acid (10). The reaction of C$_{60}$ with carboxylic acid (10) and para-formaldehyde yields ethynyl-pyrrolidinofullerene (11) in moderate yield after purification via flash column chromatography.

![Chemical structures and reaction scheme](image)

Figure 64: Ethynyl-functionalized fullerene synthesis

### 7.3.1 PORPHYRIN-FULLERENE TRANSPORT MEASUREMENTS

We see no impact on the measured current as a result of clicking ethynyl-functionalized ferrocene onto azide-terminated porphyrin layers, as shown in Figure 65. This is likely because there is substantial space between adjacent fullerenes and the Aedotron P layer simply fills in these areas, effectively shorting any contribution to transport from the fullerenes. We similarly see no change in current rectification or evidence of photosensitivity from the donor-acceptor system.
Figure 65: Scatter and box and whisker plots of measured current density at 1 V bias for 300 nm diameter molecular junctions containing thiol-porphyrin-azide and thiol-porphyrin-fullerenes. Despite the SAM of the fullerene-containing molecule being substantially thicker and possessing a different LUMO, the measured currents appear to be roughly equivalent.

In this chapter we have presented transport measurements of polymer-contacted molecular junctions with SAMs containing conjugated molecules. We synthesized and tested $N_3$(PEB)SH and thiol-azide-porphyrin molecules in both homogeneous monolayers and mixed with 11-azidoundecanethiol. We also demonstrated the ability to use azide-alkyne cycloaddition chemistry to attach functionalized fullerenes to the SAM surface.

None of the experiments yielded encouraging results, as we observed negligible difference in the transport behavior between conjugated and saturated SAMs and minimal rectification as a result of adding ferrocene or fullerene terminations. There are likely two factors impeding our work. First, as noted in Section 7.1, we see little difference between the transport behavior of conjugated and saturated molecules. This may be because the contact resistance at the polymer-molecule interface dominates the transport. Akkerman et. al. noted orders of magnitude difference in the reported conductance of alkanethiol SAMs depending on if the experiment utilized chemisorbed versus adsorbed contacts.\cite{99} This indicates that there may be limited utility in contacts made of conducting polymers unless they can be functionalized to directly bond to the molecule of interest. Second, as
noted in Chapter 5, Aedotron P seems to readily penetrate defect sites in the monolayer. This means that the addition of bulky terminal groups like ferrocenes and fullerenes likely has no impact on the transport as the polymer seeps into the spaces between these functional groups, effectively shorting them. Thus, the transport remains more or less unchanged after performing click chemistry, as seen in sections 2 and 3 of this chapter. In future experiments this problem may be avoided by selecting a polymer layer that less aggressively wets defect sites in the polymer and through the use of longer diluent alkanethiols to fill in the spaces between bulky terminal groups.
CHAPTER 8: CONCLUDING REMARKS

8.1 SUMMARY

We have demonstrated a nanoscale molecular electronics device with high yield and unprecedented flexibility to incorporate any SAM species. We have modeled the length and temperature-dependent transport of alkanethiols as coherent tunneling through a rectangular potential barrier and as a series of transmission coefficients. We have considered the low decay of current as a function of SAM thickness for our own and previous studies with polymer contacts, presenting a quantitative analysis that indicates the polymer may be penetrating the SAM at defect sites. We have explored the conductivity of alkanethiols with a variety of terminations, and examined the temperature dependence of our devices, finding that the polymer contact plays a dominant role in transport at low temperatures. The device structure demonstrated in this work resolves scaling and monolayer compatibility issues seen with previous conducting polymer molecular junctions while maintaining high yield.

8.2 PROPOSED IMPROVEMENTS

The primary limitation of our device design stems from the use of Aedotron P as the top contact material. The material has an undesirable propensity to penetrate the SAM at defect sites. This seems to be a result of the excellent amphiphilic wetting properties of nitromethane. Diluting or exchanging the solvent could likely address the issue. At the far extreme of hydrophilic solvents, water-based polymers such as PEDOT:PSS are incapable of wetting submicron pores even with the addition of fluoro surfactants. There is hopefully a middle ground in which small pores can be wetted without filling in SAM defects. The effect could also be reduced by minimizing the number of SAM defects through the use of flame-annealed gold-on-mica substrates, as discussed in Chapter 3.

A second drawback, seemingly common among devices with conductive polymer contacts, is a high contact resistance and the seeming inability to access the delocalized
LUMO levels of conjugated molecules, as seen in Chapter 7. This has also been reported by Kronemeijer et. al. using PEDOT:PSS contacts. Akkerman et. al. previously theorized that high contact resistance is common to all molecular junctions with an adsorbed top contact. (Akkerman & de Boer, 2008) While not an obstacle to simple alkanedithiol characterization, this high contact resistance will limit the implementation and study of molecular junctions with conjugated, rectifying or bi-stable transport. In the future, other self-assembling contact methods may supersede the use of conducting polymers. For example, researchers have shown the ability to reduce gold from solution onto the surface of a dithiol SAM, resulting in a covalently bound metal top contact. However, many technical difficulties remain to be solved to avoid shorts with this method.

8.3 OUTLOOK

If the difficulties discussed in this chapter are overcome, it is likely that future research will produce reliable nanoscale molecular junctions utilizing soft contacts, marking an impressive achievement in the advancement of molecular electronics. It is unlikely that molecular devices will ever form an entire computational architecture, but we envision a day when molecular electronics is integrated alongside other post-Moore’s Law technologies to push forward the boundaries of computational hardware.
APPENDIX A: TECHNICAL PROTOCOLS

The work for this project was carried out in a number of labs, utilizing a range of chemical synthesis, cleanroom fabrication, measurement, and characterization tools. This section gives a detailed description of the procedures, equipment, and protocols used, with the goal of aiding the reproduction of our experimental devices and results. The techniques discussed in A.1-3 are also described in less detail in Chapter 3. The synthesis procedures in A.4 are described in less detail in Chapter 7.

A.1 FABRICATION

The device fabrication begins with blank silicon wafers, the doping of which is unimportant. These wafers are cleaned with the RCA process at the Stanford Nanofabrication Facility (SNF) and 100 nm of oxide is grown using a standard wet thermal oxidation process immediately after cleaning. 25 wafers are cleaned at a time and they are stored in an airtight container for up to a year before use.

The device fabrication begins with the deposition of 7, 30 and 150 nanometers of titanium, platinum and gold, respectively, onto an undoped silicon wafer. Each layer is evaporated a rate of 1 Å/s in an e-beam evaporator evacuated to 3×10⁻⁷ torr. The platinum layer is essential in preventing diffusion of the titanium and gold layers during the 350°C nitride PECVD process, which otherwise results in dielectric pitting and shorting. Platinum is prone to spitting as impurities boil out of the molten material, so we let it evaporate for a few minutes before opening the shutter to expose the sample surface. The gold layer root mean square roughness (ie. the roughness of the metal stack) is 1.2 nm (Figure 26) measured with an Asylum Research Molecular Force Probe 3D AFM. The e-beam evaporator is a custom Lesker system, jointly owned by the Goldhaber-Gordon and Moler labs at Stanford. The AFM is owned by the Golhaber-Gordon lab.

Next, 20 nm of aluminum oxide (200 cycles) is deposited by atomic layer deposition (ALD) in a Cambridge Nanotech system owned by the Goldhaber-Gordon lab. We follow the system’s standard recipe. The sample is kept at 100°C while the chamber walls are
maintained at 120° C. Both the water and tetramethylaluminum valves open for 0.025 seconds on each cycle and there is 10 seconds of pumping between each valve opening. The system is maintained at roughly 0.5 torr during the deposition process.

The ALD process is followed by the deposition of 40 nm of silicon nitride using the STS PECVD system in the SNF for 4.5 minutes. The sample is maintained at 350° C for the entire process. We find that we achieve a better film quality if we first season the system by running our deposition recipe with no samples in the machine.

A layer of ZEP-520A or bilayer of PMMA/MMA e-beam resist is then spun onto the wafer. The resist is applied with a 5 ml syringe with a 0.2 um particle filter. If the resist is not filtered, shorts due to dust and impurities disrupting the etch mask at later steps can be an issue. The spin speed is chosen such that the resist thickness is roughly equivalent to the desired diameter of the pores. For the fabrication of 300 nanometer devices, undiluted ZEP-520A is spun at 5000 rpm. For the fabrication of 1 μm devices, a bilayer of Microchem EL 11 MMA copolymer under PMMA 950 A5 is spun at 3000 rpm for each layer. After each layer of resist is applied, the sample is baked at 180° C (PMMA/MMA) or 200° C (ZEP) on a hotplate in ambient for 2 minutes. This is done in the Ginzton Flexible Cleanroom at Stanford.

The resist is exposed in a Philips XL30 SFEG field-emission scanning electron microscope controlled by a Nabity Nanometer Pattern Generation System, at a dose of 400 μC/cm². This is a custom system owned jointly by the Goldhaber-Gordon, Cui, and Melosh labs. Some of the exposures are also performed on the 100 kV JEOL system in the Stanford Nano Center. For these exposures a dose of only 150 μC/cm² is required.

A typical chip consists of an array of 7x7 1 μm or 300 nm diameter pores with a pitch of 867 μm, as illustrated in Figure 66. This pitch is chosen because it matches that of the wire mesh used as a shadow mask during the top electrode evaporation. At this pitch and resolution, it is impossible to observe the patterned pores with an optical microscope. To aid in later shadow mask placement, two large (~100 μm) crosses are patterned over the bottom left and top right pores. We know that if both crosses are later visible through diagonally aligned openings in the shadow mask, then every pore will be centered under an evaporated contact. The 7x7 grid on each chip takes up a square of roughly 5.2 mm.
To allow for some tolerance in cleaving the chips before SAM formation, the chip patterns (5.2 mm wide) have a pitch of 8 mm. An entire 100 mm wafer can be patterned with hundreds of devices at this step. In practice, to allow for subsequent fabrication optimizations we typically pattern 10-12 devices in a single row on a cleaved slice of a wafer. To allow for easy inspection of downstream steps we also pattern a small 4x4 dose array on the corner of each chip area. Once the process is well characterized we process entire wafers, which are then stored in a dry box filled with nitrogen. Over several months of experiments, chips are cleaved from the wafer as needed, and the proceeding steps are performed on batches of a few to a dozen chips.

Figure 66: Not-to-scale sketch of the pattern of a typical chip. Pores have a pitch of 867 µm and are only 1 µm or 300 nm in diameter.

When we are ready to proceed with SAM formation, we cleave a section of wafer containing the desired number of chips and processing continues. The resist is developed for 40 seconds in 3:1 isopropanol:methyl isobutyl ketone (PMMA/MMA) or for 1 minute in ZED-N50 developer (ZEP 520-A), and then cured for 10 minutes on a hot plate at 110° C. This is performed in the Ginzton Flexible Cleanroom.
To ensure the integrity of the etch mask, a low angle metal mask evaporation technique has been adapted from previous work. (Schvartzman & Wind, 2009) 2 nm chrome and 5 nm nickel are evaporated at an angle of 14° from the plane of the surface while rotating the sample such that the resist surface is covered with a thin layer of metal while preventing the penetration of metal into the patterned pores. This is done in the Goldhaber-Gordon lab evaporator.

The exposed nitride layer is then etched for 70 seconds in an MRC reactive ion etcher. The resist and thin layer of evaporated metal serve as an etch mask. The etch takes place at a rate of ~0.8 nm/sec using 18 sccm of CHF₃ and 2 sccm of O₂ at 10 mTorr with 100 Watts power. Via AFM inspection, it is found that this etch compacts the revealed aluminum oxide layer, reducing it to a thickness of a few nanometers, but never penetrates the aluminum oxide, even after several minutes of etching. This step is performed in the SNF. Before the etch is performed, the machine is cleaned of any residual gases by running a high power oxygen etch for 10 minutes. The chamber is then seasoned by running our etch recipe with the chamber empty for 10 minutes each. It is critically important to use the available few mm thick quartz plate to cover the bottom metal electrode in the machine. This prevents sputtering of the bottom electrode during the etch, which has been shown to deposit iron onto the samples of unsuspecting users. The samples to be etched are placed on top of this plate. The plate can get extremely hot during long etches, but this is not an issue during our 70 second process.

The etch mask is then removed in hot (120° C) CMOS-grade n-methyl-2-pyrrolidone (NMP). Sometimes light sonication is needed because the metal etch mask prevents the resist from being easily dissolved. This step is performed in the Golhaber-Gordon lab fume hood. As the silicon nitride has already been patterned and the underlying gold is protected by aluminum oxide, this particular step doesn’t have to be performed in a clean environment.

The silicon nitride layer now serves as an etch mask. The residual few nanometers of aluminum oxide in each pore is removed with a 10 second wet etch in 20:1 dilute buffered oxide etch (BOE). This reveals gold that is uncontaminated by any ion residue, as confirmed by XPS (Figure 32). In devices in which the aluminum oxide buffer layer is
not used and silicon nitride on gold is simply dry etched, the gold is invariably contaminated by implanted silicon from the nitride layer, which results in poor monolayer formation. This etch is performed in the Ginzton Flexible Cleanroom. While we are not aware of any work in the literature that utilizes this unique process, we would not have come up with it without the exhaustive data on etch rates collected by Williams and Muller.168

A.2 SAM FORMATION

Prior to monolayer formation, the chips are exposed to O$_2$ plasma for 5 minutes. This oxidizes the exposed gold surface at the bottom of each pore and removes any adventitiously adsorbed carbon.173 The chips are then immersed in 200-proof ethanol (Acros) for 20 minutes to reduce the oxidized gold layer. It is important to go through the reduction step before introducing the thiols, otherwise oxidized areas of the surface will disrupt the monolayer formation.

At this point, the processing diverges for every chip, because each one incubates in a different vial with a unique SAM-forming solution. If it has not already been done, (and usually we wait until this step) the individual chips, each containing a 7x7 array of pores, are cleaved from a larger piece containing several patterns. The chips are then loaded into a nitrogen glovebox. This process is performed in the Collman lab at Stanford, where we have access to a little-used glovebox. Once inside, the chips are transferred to scintillation vials with a few ml of 50 mM solution of the appropriate molecule in solvent. Each chip is put face-up into its own vial to avoid scratching the surface. The chips are left at room temperature for 48 hours.

The SAM solutions are made fresh inside the glovebox from solvents that are also stored inside the box, and the mixtures are used immediately. The alkanethiols are typically dissolved in ethanol. Conjugated species are dissolved in chloroform. We found that hexadecanethiol as well as dithiols and carboxyl-terminated alkanethiols longer than 12 carbons will not dissolve in pure ethanol, even with substantial sonication and stirring. In these cases 30% THF was added to the ethanol solvent.
After SAM formation, the devices are removed from the glovebox and rinsed in 200 proof ethanol, CMOS grade isopropanol, and then water. Conjugated SAMs are initially rinsed in chloroform, followed by ethanol, isopropanol and water.

## A.3 POLYMER APPLICATION

Immediately after rinsing the SAMs, the devices are reintroduced into a nitrogen-filled glovebox. Aedotron P (1% Poly(3,4-ethylenedioxythiophene)-block-poly(ethylene glycol) solution in nitromethane with sulfonate p-toluene as a dopant is deposited onto each chip and then spun at 1000 rpm for 15 seconds before acceleration to 2000 rpm for another 30 seconds. This results in a 90 nm thick polymer layer. This step is performed in the McGehee lab nitrogen glovebox at Stanford. It is important to vigorously shake and ideally sonicate the polymer before use. We experimented with filtering the polymer before application but found that submicron filter pores removed a substantial amount of material from the Aedotron P solution. We tested the effect of pressing the polymer through cheesecloth as a large-pore filtering technique, but found that this didn’t change the deposited film. After the polymer is applied, the devices are dried under vacuum for 4 hours.

Top gold contacts (100 nm) are evaporated onto the devices through shadow masks using the Goldhaber-Gordon lab e-beam evaporator. We use a simple piece of wire mesh with wires about 0.3 mm thick and a spacing of 0.6 mm between wires (exact pitch of 867 μm). As mentioned in the earlier section describing the e-beam lithography, the pores have been patterned in an array with a matching pitch. The shadow mask is aligned to the large crosses that serve as alignment marks. We use tweezers to manipulate the mask while observing things under a long working distance microscope. Once in place, a few μL drop of PMMA in anisole is applied to opposite corners of the mask. After about 20 minutes it dries and will hold the mask in place during the subsequent evaporation. After evaporation the mask is easily pulled off the surface.

Finally, the residual polymer (the area not covered by gold contacts) is removed using a tabletop SPI Plasma-Prep II oxygen plasma etcher. The machine is run for 1 minute at
100 Watts at a pressure of 50 mTorr. Until this step, all of the top contacts are shorted together. The system we use is located in the Stanford Nanocharacterization Laboratory.

A.4 CHEMICAL SYNTHESIS

All chemical synthesis in this project was performed in the Collman lab at Stanford. With the exception of 11-azidoundecenathiol, all of the alkanethiols studied in this project were purchased from Sigma-Aldrich. Here we detail the synthesis of the molecules studied in Chapter 7, primarily through excerpts from the original literature.

11-AZIDOUNDECANETHIOL

This excerpt is taken from the supporting information in a paper by Collman et. al.\textsuperscript{188}. The procedure is adapted from a technique published by Shon et. al.\textsuperscript{210}

To 150mL of DMF, 10g of Br(CH\(_2\))\(_{11}\)OH and 2.86g of NaN\(_3\) were added. The flask containing the mixture was evacuated, refilled with N\(_2\), and refluxed under N\(_2\) for 24 hours. After cooling to room temperature, 150mL of H\(_2\)O was added after which the mixture was extracted three times with diethyl ether. The organic phase was washed with water three times and dried over MgSO\(_4\). Rotary Evaporation yielded a pale yellow oil. 87% Yield. \(\text{\textsuperscript{1}H}NMR\) (CDCl\(_3\), 400MHz): 3.63, (q, 2H); 3.24 (t, 2H); 1.57 (m, 4H); 1.22-1.4 (m 14H).

Synthesis of 1-Azidoundecan-11-methylsulfonate

To 1g of N\(_3\)(CH\(_2\))\(_{11}\)OH 35mL of THF (from still) and 1mL of methanesulfonyl chloride were added. In a separate vial, 1.27g of triethylamine was dissolved in 5mL THF. The triethylamine solution was slowly added to the stirring N\(_3\)(CH\(_2\))\(_{11}\)OH solution over 5 minutes. The reaction progressed at room temperature for 2 hours. 35mL of ice-cold water was added, and the organic phase was separated from the aqueous phase. The aqueous phase was extracted twice with diethyl ether (2x35mL). The combined organic phases were then combined and washed with 1M HCl, H\(_2\)O, NaHCO\(_3\), and H\(_2\)O. After drying over MgSO\(_4\), the solvent was removed via rotary evaporation yielding a pale yellow oil. 87% Yield. \(\text{\textsuperscript{1}H}NMR\) (CDCl\(_3\), 400MHz): 4.21, (t, 2H); 3.24 (t, 2H); 2.99 (s, 3H); 1.74 (m, 2H); 1.59 (m, 2H); 1.22-1.42 (m, 14H);
Synthesis of 1-Azidoundecan-11-thioacetate

1g of N₃(CH₂)₁₀OSO₂C and 0.775g of potassium thioacetate was dissolved in 30mL of methanol. The solution was degassed and refluxed under N₂ for three hours. After cooling to room temperature, excess methanol was removed via rotary evaporation and ice cold water (30mL) was added. The mixture was extracted 3 times with diethyl ether (30mL) and washed three times with water (3x30mL). The solution was dried over MgSO₄ and the solvent removed by rotary evaporation yielding a yellow oil. ¹HNMR (CDCl₃, 400MHz): 3.24 (t, 2H); 2.85 (t, 2H); 2.31 (s, 3H); 1.5-1.61 (m, 4H); 1.22-1.4 (m, 14H).

Synthesis of 1-Azidoundecane-11-thiol (1):

To 300mg of N₃(CH₂)₁₀SCOCH₃, 20mL of methanol was added. The solution was degassed thoroughly and backfilled with N₂. 1 mL conc HCl was added, and the entire mixture was refluxed for 5hrs. The reaction mixture was quenched with water and extracted twice with diethyl ether. The organic phase was washed twice with water (2x20mL) and dried over MgSO₄. Rotary evaporation yielded a yellow oil. 80% Yield ¹HNMR (CDCl₃, 400MHz): 3.24 (t, 2H); 2.51 (q, 2H); 1.59 (m, 4H); 1.22-1.41 (m, 14H).

FERROCEN ACETYLENE

This synthesis is derived in Rosenblum et. al.¹¹¹

AZIDOPHENYLETHYNYLNEBENZYLTHIOL (N₃(PEB)SH)

The synthesis was adapted from a previously reported procedure.¹¹² A suspension of 4-iodoaniline (3.02 g, 13.8 mmol) in water (30 mL) and concentrated hydrochloric acid (30 mL) was cooled in an ice/salt bath. To the suspension was slowly added a solution of sodium nitrite (1.5 g, 20.7 mmol) in ice cold water (10 mL) under vigorous stirring. After being stirred for 15 min, the diazonium solution was slowly added to a solution of diethylamine (2.52 g, 35 mmol) in water (30 mL), in an ice bath. Potassium carbonate was added until CO₂ evolution ceased. The mixture was stirred for 1 h at room temperature, extracted with CH₂Cl₂, and washed with brine. The organic phase was dried with anhydrous MgSO₄ and the solvent was evaporated. Column chromatography (silica,
hexane/CH$_2$Cl$_2$, 1:1 v/v) of the residue yielded a reddish brown oil (3.94 g, 94%). $^1$H NMR (CDCl$_3$, 200 MHz) $\delta$ 7.59 (d, 2H), 7.14 (d, 2H), 3.73 (q, 4H), 1.24 (t, 6H).

**AZIDO-PORPHYRIN-THIOL**

The porphyrin synthesis is presented in Figure 67. Trans-substituted octaalkylporphyrins are simple building blocks for the synthesis of donor-acceptor systems. Tetra-alkydipyromethanes are chosen as the starting material because of their use as versatile precursors for the formation of trans-disubstituted porphyrins. They react with a variety of aldehydes to give porphyrins in a relatively high yield. Utilizing tetra-alkydipyrrromethane in a condensation reaction prevents scrambling, a process that can occur when using aromatic-dipyrmethane.

Bis-(4-methyl-3-propyl-2-pyrrole)methane (1) is synthesized from acetyl acetone in five steps according to previously reported procedures.$^{206}$ The condensation of 1 with 4-(hydroxymethyl)-benzaldehyde and para-acetamidobenzaldehyde in dry dichloromethane is carried out using catalytic amounts of trifluoracetic acid under an atmosphere of N$_2$. This results in the formation of a statistical mixture of porphyrinogen that is oxidized to porphyrin using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in air. The desired amido-porphyrin (2) is separated from the statistical mixture to give 26% yield. Hydrolysis of the amide 2 in 6 M HCl gives amino-porphyrin (3). The diazotation of the amine group followed by nucleophilic substitution with NaN$_3$ gives the azido-porphyrin (4). The conversion of benzyl alcohol to thioacetate (5) is accomplished by modification of a previously reported procedure.$^{207}$ Deprotecting the thiol group in MeOH gives the desired 5-thiolmethylphenyl,15-azidophenyl-porphyrin (6).
Figure 67: Porphyrin synthesis.

**ETHynyL-**FUNCTIONALIZED FULLERENE

In parallel to the synthesis of the azide-terminated porphyrin, we prepare two ethynyl-functionalized C$_{60}$ molecules as shown in Figure 64. The “bent” fullerene derivative (8) is synthesized according to a previously reported procedure.$^{208}$ Here, the simple reaction of n-methylglycine and 4-ethynylanilide with C$_{60}$ in refluxing toluene results in the desired ethynyl-pyrrolidinofullerene (8) in good yield after purification. The synthesis of the “linear” fullerene derivative (11) is initiated by the coupling of 4-ethynylaniline (9) and ethylbromoacetate to give ethyl 2-(4-ethynylphenylamino)acetate. This is followed by hydrolysis of the ester group in basic ethanol to give 2-(4-ethynylphenylamino)acetic acid (10). The reaction of C$_{60}$ with carboxylic acid (10) and
para-formadehyde yields the ethynyl-pyrrolidinofullerene (11) in moderate yield after purification via flash column chromatography.

![Chemical structure diagram](image)

Figure 68: Ethynyl-functionalized fullerene synthesis

**Copper(I)-Catalyzed Azide-Alkyne Cycloaddition Reaction**

We first form a mixed or homogeneous azide-terminated SAM in a set of open molecular junctions. As described by Collman et. al., the monolayer is completely submerged in a 1mM ferrocene acetylene solution (solvent 2:1 water DMSO). 15 mol% of ascorbic acid is added, followed by 1 mol% of copper(I) tris-(benzyltriazolylmethyl)amine tetrafluoroboride (Cu(TBTA)BF$_4$). The addition of the copper catalyst results in substantially higher yield and faster reaction times. The presence of the ascorbic acid ensures that the catalyst is in the active Cu(I) oxidation state. Typically less than 3 hours is required to reach full reaction yield. We allow each reaction to run for 24 hours. The reaction chamber is covered in foil and stored inside a drawer for the duration of the reaction in order to prevent photo-oxidation of the monolayer. After reaction, the chips are rinsed with copious amounts of ethanol, water, chloroform, and then water again to ensure that any physisorbed ferrocenes are washed off.

40,188

Before being used to form devices, all of the click reactions in this chapter are verified for bulk samples using Fourier transform infrared spectroscopy on a Nicolet
spectrometer, located in the basement of the Stauffer 2 Chemistry building at Stanford. Azide-terminated SAMs have a distinct, large peak at 2100 cm$^{-1}$, which disappears upon full reaction with an ethynyl-terminated species.
This section presents diagrams of the two measurement setups used for device characterization in this work. All of the data presented in chapters 5-7 was taken with Setup 1. Setup 2 is used in lock-in measurements in which extremely small bias is applied to control samples consisting of Aedotron P and no monolayer, verifying the ohmic behavior of these films at room temperature.

All transport measurements were performed under vacuum in a Desert Cryogenics (now LakeShore) probe station. The substrate (ground) is probed by scraping a probe needle along a corner of the chip so that it ruptures the dielectric layer. The top contact of each device must be probed very gently to avoid breaking the dielectric and shorting the device. A thin, 50 µm diameter wire-bonding wire is soldered onto one of the probe station needles and this is maneuvered into contact with the top contact of each device.

Figure 69 shows that the output of a Keithley 2400 Source Meter is simply hooked to two probe station lines. The Keithley is controlled via GPIB connection with a computer.

**Figure 69:** Measurement Setup 1. Simple DC measurement using LakeShore probe station and GPIB-controlled Keithley 2400.

Figure 70 shows a diagram of the setup and circuit used for lock-in measurements. As in the previous setup, a thin gold wire is soldered to one of the probe station needles to
contact the top electrode of each device. Conductance traces are measured using a PAR 124A lock-in amplifier. The oscillator output of the lock-in, a 17 Hz, 10 μV excitation, is added to the output of a Yokogawa 7651 using a passive resistive adder with low-pass filter to apply source-drain bias along with AC excitation to the molecular junction under study. The current output of the junction is fed into an Ithaco 1211 current preamplifier, and its output is connected to the lock-in input. For lower noise measurements, the preamplifier can be powered with a deep cycle marine battery, but this is not used in our studies. As the lock-in used is analog, an Agilent 34401 DMM is used to measure its output. Data acquisition is automated by controlling the Yokogawa DC source and the DMM with a computer via GPIB.

Figure 70: Measurement Setup 2. Lock-in measurements using LakeShore probe station, Multimeter, Yokogawa.
APPENDIX C: MATLAB ANALYSIS CODE

This appendix presents some of the Matlab code used to produce the figures and fits in the main body of this document, particularly Chapters 5 and 6.

C.1 DC IV SWEEPS

K2400IVSD – COLLECT AND PLOT DATA

function k2400ivsdalex(fname,n,vstart,vend,nosteps,delay,numscans)

% pp is a switch to toggle dynamic plotting (1= plotting, 0= no plotting)
% Factor.
pp = 1;

%assemble plot info to send to sweep function
plotinfo = pp;

% Directory for saving things.
directory = 'C:\Documents and Settings\Alex\Desktop\alex\alexdata\101211_drytek_C12\1um\';
newpath = [directory fname];

% Open file if previously used and load data structure for writing.
if n==1
    create(fname,directory);
else
    load(newpath);
end

global gkeithsourcedrain;

% Save parameters to variable arus.
arus(n).delay = delay; arus(n).vstart = vstart; arus(n).vend = vend;

% Taking data. Columns are voltage out, lockin 'current' back, leakage signal.
arus(n).starttime = datestr(now);
tic; arus(n).ivsd1 = k2400sweepalex(0, vstart, nosteps/2, delay,gkeithsourcedrain, numscans, plotinfo); toc;
arus(n).endtime = datestr(now);

arus(n).ivsd2 = k2400sweepalex(vstart, vend, nosteps, delay, gkeithsourcedrain, numscans, plotinfo);
arus(n).ivsd3 = k2400sweepalex(vend, 0, nosteps/2, delay, 
gkeithsourcedrain, numscans, plotinfo); 
save(newpath,'arus','-append')
% else
%end

% Save the current data.
%save(newpath,'arus','-append')

% Plot everything together.
figure;
axis tight; grid on;

if repeat==1
plot(arus(n).ivsd1(:,1),arus(n).ivsd1(:,2),'ro',arus(n).ivsd2(:,1),arus 
(n).ivsd2(:,2),'ko',arus(n).ivsd3(:,1),arus(n).ivsd3(:,2),'ro');
else
  plot(arus(n).ivsd1(:,1),arus(n).ivsd1(:,2));
end

xlabel('Drain-Source Voltage (V)');
ylabel('Drain-Source Current (A)')
title(['Device: ' fname num2str(n)])
zerovoltages;

set(gcf, 'WindowStyle', 'docked')
saveas(gcf,[newpath,num2str(n),'.fig'])
disp(datestr(now))

%Alarm
numalarms = 1;
for nn = 1:numalarms
  load chirp; y1 = y/6; Fs1 = Fs; wavplay(y1,Fs1,'sync');
  %load gong;
  %y1 = y;
  %Fs1 = Fs;
  %wavplay(y1,Fs1,'sync');
end

K2400Sweepalex — Voltage Sweep Code to Perform Measurement

function DATA  = k2400sweepalex(vs, ve, nosteps, delay, 
gkeithsourcedrain, numscans, plotinfo)

vrange = ve-vs; % Output voltage range.
voltout = vs*1.0 + [0:nosteps]*(vrange/nosteps); % Vector of output
voltages.

%unpack plot info
pp = plotinfo;

gkeithsweep = gkeithsourcedrain;

  %go to starting voltage
k2400 goto2(.05, vs, 0, gkeithsweep);
pause(2);

% loop through voltage output
for i = 1:length(voltout)

voltnow = voltout(i);
amplitude = [ 'SOUR:VOLT:LEV:IMM:AMPL ' num2str(voltnow)];
fprintf(gkeithsweep, amplitude);
pause(delay)

% read currents from keithley
toaverage = 0;
for aa = 1:numscans

fprintf(gkeithsourcedrain, 'INIT')
fprintf(gkeithsourcedrain, 'FETC?')
kdata = str2num(fscanf(gkeithsourcedrain));

toaverage = kdata(2) + toaverage;
end
imeasured = toaverage/numscans;
DATA(i,:) = [voltnow imeasured];

% plotting
if pp == 1

    if i==1
        if exist('tempplot') == 0
            tempplot4 = figure; set(tempplot4, 'WindowStyle',
            'docked');
        else
            end
    end

    thisline1 = line(DATA(i,1),DATA(i,2));
    set(thisline1, 'Color', 'k', 'LineStyle', '-'
    , 'Marker', '.', 'MarkerSize', 2, 'MarkerEdgeColor', 'r');
    xlim([min(vs,ve) max(vs,ve)]); %ylim([0 12]);
    xlabel('Drain-Source Voltage (V)');
    ylabel('Drain-Source Current (A)');
    drawnow; hold on;
    else
        figure(tempplot4)
        set(thisline1,'XData',DATA(:,1),'YData',DATA(:,2));
        drawnow;
    end
else
    end
end
close(tempplot4)
C.2 SCATTER PLOT OF CURRENTS FOR A GIVEN BIAS, BETA CALCULATION

Scatter Plots

%plot current values at 1 V bias (ie. index 51) to look at distribution
sample_index = 51;
figure;

% Make the box and whisker plots
G = vertcat(1*ones(size(currentsT8(:,sample_index))),
2*ones(size(currentsM8(:,sample_index))),
3*ones(size(currentsC8(:,sample_index))),
4*ones(size(currentsT12(:,sample_index))),
5*ones(size(currentsM12(:,sample_index))),
6*ones(size(currentsC12(:,sample_index))),
7*ones(size(currentsA11(:,sample_index)))));

boxplot1 = boxplot(vertcat(log10(currentsT8(:,sample_index)),
log10(currentsM8(:,sample_index)), log10(currentsC8(:,sample_index)),
log10(currentsT12(:,sample_index)), log10(currentsM12(:,sample_index)),
log10(currentsC12(:,sample_index)),
log10(currentsA11(:,sample_index))), G);

% Plot the scatter
hold on
grid on
scatterplot1 = scatter(1*ones(size(currentsT8(:,sample_index))),
log10(currentsT8(:,sample_index)), 'ks');
scatterplot2 = scatter(2*ones(size(currentsM8(:,sample_index))),
log10(currentsM8(:,sample_index)), 'co');
scatterplot3 = scatter(3*ones(size(currentsC8(:,sample_index))),
log10(currentsC8(:,sample_index)), 'mx');
scatterplot4 = scatter(4*ones(size(currentsT12(:,sample_index))),
log10(currentsT12(:,sample_index)), 'ks');
scatterplot5 = scatter(5*ones(size(currentsM12(:,sample_index))),
log10(currentsM12(:,sample_index)), 'co');
scatterplot6 = scatter(6*ones(size(currentsC12(:,sample_index))),
log10(currentsC12(:,sample_index)), 'mx');
scatterplot7 = scatter(7*ones(size(currentsA11(:,sample_index))),
log10(currentsA11(:,sample_index)), 'g*');

% Plot the mean with a large shape
scatterplot1m = scatter(1, log10(meancurrentT8(sample_index)),
'ks', 'LineWidth', 5);
scatterplot2m = scatter(2, log10(meancurrentM8(sample_index)),
'co', 'LineWidth', 5);
scatterplot3m = scatter(3, log10(meancurrentC8(sample_index)),
'mx', 'LineWidth', 5);
scatterplot4m = scatter(4, log10(meancurrentT12(sample_index)),
'ks', 'LineWidth', 5);
scatterplot5m = scatter(5, log10(meancurrentM12(sample_index)), 'co', 'LineWidth', 5);
scatterplot6m = scatter(6, log10(meancurrentC12(sample_index)), 'mx', 'LineWidth', 5);
scatterplot7m = scatter(7, log10(meancurrentA11(sample_index)), 'g*', 'LineWidth', 5);
axis tight;
ylabel('Current Density at 1V Bias [A/m^2]');
title('Scatter and Box and Whisker Plots of Alkanethiol Species');
legend([scatterplot1m, scatterplot2m, scatterplot3m, scatterplot4m, scatterplot5m, scatterplot6m, scatterplot7m], 'Octanedithiol (T8)', 'Octanethiol (M8)', 'Octanoic Acid (C8)', 'Dodecanedithiol (T12)', 'Dodecanethiol (M12)', 'Dodecanoic Acid (C12)', 'Azidoundecanethiol (A11)', 'Location', 'SouthWest');
hold off

**Beta Calculation**

```matlab
function cc = beta_calc(A,B,d)

cc = log(A*exp(-d*B));
```
C.3 SIMMONS MODEL FITTING

%Units: d is in nm, phi is in ev, output is in nA
function cc = simmons_model(alpha,d,phi,vv)

hbar = 1.054e-34;
 ee = 1.602e-19;
 mm = 9.109e-31;

phi = phi*1.6022e-19;
d = d*1e-9;

dsquare = d.*d;

%Straight-forward application of the Simmons Model for tunneling

K = ee./(4*pi*pi*hbar*dsquare);
phidiff = phi-(ee*vv/2);
phisum = phi+(ee*vv/2);
 M = -2*alpha*d*((2*mm)^(1/2))/hbar;

cc = log(K.*(phidiff.*exp(M*phidiff.^(1/2)) -
phisum.*exp(M*phisum.^(1/2)))); %output current in nanoamps
C.4 IMAGE CHARGE SIMMONS MODEL FITTING

%Units: d is in nm, phi is in ev, output is in nA
function cc = samcurrent_image(mstar,d,phi,vv)

hbar = 1.054e-34;
h = hbar*2*pi;
ee = 1.6022e-19;
mm = 9.109e-31;

phi0 = phi*ee;
s = (d*1.5 + 3.8)*1e-10;
e0 = 8.85e-12;
er = 2.1;

dsquare = d.*d;
mestar = mstar*mm;
lambda = ee^2*log(2)/(8*pi*e0*er*s);

xvals = 0:1:1000;

% calculate potential barrier height at 1000 evenly spaced points. % Determine s1 and s2 values along the way. % s1 and s2 are where the top of the barrier intersects the Fermi energy of the % contacts, ie. s2 - s1 is the actual barrier thickness % because very close to the contacts the barrier is actually lower than % the Fermi energy due to the image charge effect.

% We need to figure this out for every measured bias value, thus the loop % from 1 to length(vv) where vv is an array of applied biases

snorm = 1000;

for n=1:length(vv)
    s1(n) = 3;
s2(n) = snorm-3;
    for x=1:snorm-1
        phivals(n,x) = phi0 - ee*vv(n)*x/snorm - 1.15*lambda*(snorm/x)*(snorm/(snorm-x));
        if x > 1
            if phivals(n,x-1) < 0 && phivals(n,x) >= 0
                s1(n) = x;
            elseif phivals(n,x-1) > 0 && phivals(n,x) <= 0
                s2(n) = x;
            end
        end
    end
end
% determine phiavg values, i.e. what's the average barrier height
% for a given bias, using a
% parabolic approximation

for n=1:length(vv)
    phiavg(n) = phi0 - ee*vv(n)*(s2(n)-s1(n))/(2*snorm) - (1.15*lambda*snorm/(s2(n)-s1(n)))*log((s2(n)*(snorm-s1(n)))/(s1(n)*(snorm-s2(n))));
    deltas(n) = (s2(n) - s1(n))*s/snorm;
    A(n) = 4*pi*deltas(n)*sqrt(2*mestar)/h;
    J0(n) = ee/(2*pi*h*deltas(n)^2);
end

% Now that we know the average barrier height we can apply the WKB
% approximation to calculate the expected current

for n=1:length(vv)
    base1(n) = phiavg(n);
    expl1(n) = -A(n)*sqrt(phiavg(n));
    base2(n) = phiavg(n) + ee*vv(n);
    exp2(n) = -A(n)*sqrt(phiavg(n)+ee*vv(n));
end

cc = log(J0.*(base1.*exp(expl1) - base2.*exp(exp2)))';
C.5  TEMPERATURE DEPENDENCE

C.5.1.  FUNCTION TO FIT ARRHENIUS DATA

```matlab
function cc = temppowerlawArr(A,B,C,D,t)
    temp = t./1000;
    cc = log(A*exp(-B*temp) + C*exp(-(D*temp).^0.25));
```

C.5.2  IV AND ARRHENIUS PLOTS OF TEMPERATURE DEPENDENT TRANSPORT

```matlab
data = 18;
data = pi*((150-edge)*1e-9)^2; %put in terms of A/m^2
data2 = pi*(15*1e-6)^2; %measured 30 um diameter polymer-only device

% open directories, get number of files, load up voltage, current arrays,
filenames = dir('/Users/alexneuhausen/Stanford/alexdata/110613 M12 from 110610 temp dep/62 data clean/warmup');
load(['/Users/alexneuhausen/Stanford/alexdata/110613 M12 from 110610 temp dep/62 data clean/warmup/ filenames(4).name']);
volt = arus.ivsd1(:,1);
for j=4:length(filenames)
    load(['/Users/alexneuhausen/Stanford/alexdata/110613 M12 from 110610 temp dep/62 data clean/warmup/ filenames(j).name']);
    currentsfull(j-3,:) = arus(1).ivsd1(:,2) - arus(1).ivsd1(1,2) + yoffset; %current in nA
end
currents = sort(currentsfull);
datasize = size(currentsfull);
x=1;
for j=1:datasize
    currents(x,:) = currents(j,:);
x=x+1;
end
meancurrent = mean(abs(currents));
stdcurrent = std(abs(currents));

% AEDOTRON CTRL DEVICES
% PLOT IV TRACE AT EACH TEMPERATURE
load(['/Users/alexneuhausen/Stanford/alexdata/111026 aedotron temp dep/large area/vertical-rt-hf.mat']);
polycurrent295(1,:) = (arus(1).ivsd1(:,2) - arus(1).ivsd1(1,2))/data2; %current in nA
polyvolts = arus.ivsd1(:,1);
load(['/Users/alexneuhausen/Stanford/alexdata/111026 aedotron temp dep/large area/vertical-1250k-hf.mat']);
polycurrent250(1,:) = (arus(1).ivsd1(:,2) - arus(1).ivsd1(1,2))/data2; %current in nA
```

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load('/Users/alexneuhausen/Stanford/alexdata/111026 aedotron temp dep/large area/vertical-200k-hf.mat');
polycurrent200k(1,:) = (arus(1).ivsd1(:,2) - arus(1).ivsd1(1,2))/area2;
% current in nA

load('/Users/alexneuhausen/Stanford/alexdata/111026 aedotron temp dep/large area/vertical-150k-hf.mat');
polycurrent150k(1,:) = (arus(1).ivsd1(:,2) - arus(1).ivsd1(1,2))/area2;
% current in nA

load('/Users/alexneuhausen/Stanford/alexdata/111026 aedotron temp dep/large area/vertical-100k-hf.mat');
polycurrent100k(1,:) = (arus(1).ivsd1(:,2) - arus(1).ivsd1(1,2))/area2;
% current in nA

load('/Users/alexneuhausen/Stanford/alexdata/111026 aedotron temp dep/large area/vertical-75k-hf.mat');
polycurrent75k(1,:) = (arus(1).ivsd1(:,2) - arus(1).ivsd1(1,2))/area2;
% current in nA

load('/Users/alexneuhausen/Stanford/alexdata/111026 aedotron temp dep/large area/vertical-50k-hf.mat');
polycurrent50k(1,:) = (arus(1).ivsd1(:,2) - arus(1).ivsd1(1,2))/area2;
% current in nA

load('/Users/alexneuhausen/Stanford/alexdata/111026 aedotron temp dep/large area/vertical-25k-hf.mat');
polycurrent25k(1,:) = (arus(1).ivsd1(:,2) - arus(1).ivsd1(1,2))/area2;
% current in nA

load('/Users/alexneuhausen/Stanford/alexdata/111026 aedotron temp dep/large area/vertical-13k-hf.mat');
polycurrent13k(1,:) = (arus(1).ivsd1(:,2) - arus(1).ivsd1(1,2))/area2;
% current in nA

load('/Users/alexneuhausen/Stanford/alexdata/111026 aedotron temp dep/large area/vertical-12k-hf.mat');
polycurrent12k(1,:) = (arus(1).ivsd1(:,2) - arus(1).ivsd1(1,2))/area2;
% current in nA

% PLOT IV TRACES

figure;
plot(polyvolts, polycurrent295k, 'r', 'LineWidth',2);
hold on
plot(polyvolts, polycurrent250k, 'm', 'LineWidth',2);
plot(polyvolts, polycurrent200k, 'y', 'LineWidth',2);
plot(polyvolts, polycurrent150k, 'g', 'LineWidth',2);
plot(polyvolts, polycurrent100k, 'c', 'LineWidth',2);
plot(polyvolts, polycurrent75k, 'b', 'LineWidth',2);
plot(polyvolts, polycurrent50k, 'k', 'LineWidth',2);
plot(polyvolts, polycurrent25k*40, 'r--', 'LineWidth',2);
plot(polyvolts, polycurrent12k*40, 'm--', 'LineWidth',2);
hold off

xlabel('Bias Voltage [V]');
ylabel('Current Density [A/m^2]');
title('Current Density vs. Voltage for Poly Only, Varying Temp');
legend('295K', '250K', '200K', '150K', '100K', '75K', '50K', '25K x 40', '12K x 40', 'Location', 'NorthWest');

% Define some limit variables for these plots to throw out the noisy parts
% of the traces.
% Most of these don't get used.
vlowerlimit = 0.3;
vupperlimit = 1.0;
poslower = find(diff(volts>vlowerlimit));
posupper = find(diff(volts>=vupperlimit)) + 1;
vlowerlimit2 = 0.0;
vupperlimit2 = 1.0;
poslower2 = find(diff(volts>vlowerlimit2));
posupper2 = find(diff(volts>=vupperlimit2)) + 1;
vlowerlimit3 = 0.2;
vupperlimit4 = 0.5;
poslower3 = find(diff(volts>vlowerlimit3));
vupperlimit3 = 0.0;
poslower4 = find(diff(volts>vlowerlimit4));
vupperlimit6 = 0.4;
poslower5 = find(diff(volts>vlowerlimit5));
vupperlimit5 = 1.0;
poslower6 = find(diff(volts>vlowerlimit6)) + 1;
figure;

% NOW LOAD DATA FOR 3 DODECANETHIOL DEVICES
% open directories, get number of files, load up voltage, current arrays,
%load individual files and plot each
load(['/Users/alexneuhausen/Stanford/alexdata/110613 M12 from 110610 temp dep/62 data clean/warmup/295k.mat']);
current295k62(1,:) = (arus(1).ivsd1(:,2) - arus(1).ivsd1(1,2))/area;
% in nA
load(['/Users/alexneuhausen/Stanford/alexdata/110613 M12 from 110610 temp dep/64 data clean/warmup/295k.mat']);
current295k64(1,:) = (arus(1).ivsd1(:,2) - arus(1).ivsd1(1,2))/area;
% in nA
load(['/Users/alexneuhausen/Stanford/alexdata/110613 M12 from 110610 temp dep/65 data clean/warmup/295k.mat']);
current295k65(1,:) = (arus(1).ivsd1(:,2) - arus(1).ivsd1(1,2))/area;
% in nA
current295k = (current295k62 + current295k64 + current295k65)/3;
semilogy(volts(poslower5:posupper5), abs(current295k(poslower5:posupper5)), 'ro', 'LineWidth', 2);
hold on
grid on
load('/Users/alexneuhausen/Stanford/alexdata/110613 M12 from 110610 temp dep/62 data clean/warmup/250k.mat');
current250k62(1,:) = (arus(1).ivsd1(:,2) - arus(1).ivsd1(1,2))/area;
%current in nA
load('/Users/alexneuhausen/Stanford/alexdata/110613 M12 from 110610 temp dep/64 data clean/warmup/250k.mat');
current250k64(1,:) = (arus(1).ivsd1(:,2) - arus(1).ivsd1(1,2))/area;
%current in nA
load('/Users/alexneuhausen/Stanford/alexdata/110613 M12 from 110610 temp dep/65 data clean/warmup/250k.mat');
current250k65(1,:) = (arus(1).ivsd1(:,2) - arus(1).ivsd1(1,2))/area;
%current in nA
current250k = (current250k62 + current250k64 + current250k65)/3;

load('/Users/alexneuhausen/Stanford/alexdata/110613 M12 from 110610 temp dep/62 data clean/warmup/200k.mat');
current200k62(1,:) = (arus(1).ivsd1(:,2) - arus(1).ivsd1(1,2))/area;
%current in nA
load('/Users/alexneuhausen/Stanford/alexdata/110613 M12 from 110610 temp dep/64 data clean/warmup/200k.mat');
current200k64(1,:) = (arus(1).ivsd1(:,2) - arus(1).ivsd1(1,2))/area;
%current in nA
load('/Users/alexneuhausen/Stanford/alexdata/110613 M12 from 110610 temp dep/65 data clean/warmup/200k.mat');
current200k65(1,:) = (arus(1).ivsd1(:,2) - arus(1).ivsd1(1,2))/area;
%current in nA
current200k = (current200k62 + current200k64 + current200k65)/3;

load('/Users/alexneuhausen/Stanford/alexdata/110613 M12 from 110610 temp dep/62 data clean/warmup/150k.mat');
current150k62(1,:) = (arus(1).ivsd1(:,2) - arus(1).ivsd1(1,2))/area;
%current in nA
load('/Users/alexneuhausen/Stanford/alexdata/110613 M12 from 110610 temp dep/64 data clean/warmup/150k.mat');
current150k64(1,:) = (arus(1).ivsd1(:,2) - arus(1).ivsd1(1,2))/area;
%current in nA
load('/Users/alexneuhausen/Stanford/alexdata/110613 M12 from 110610 temp dep/65 data clean/warmup/150k.mat');
current150k65(1,:) = (arus(1).ivsd1(:,2) - arus(1).ivsd1(1,2))/area;
%current in nA
current150k = (current150k62 + current150k64 + current150k65)/3;

load('/Users/alexneuhausen/Stanford/alexdata/110613 M12 from 110610 temp dep/62 data clean/warmup/100k.mat');
current100k62(1,:) = (arus(1).ivsd1(:,2) - arus(1).ivsd1(1,2))/area;
%current in nA
load('/Users/alexneuhausen/Stanford/alexdata/110613 M12 from 110610 temp dep/64 data clean/warmup/100k.mat');
current100k64(1,:) = (arus(1).ivsd1(:,2) - arus(1).ivsd1(1,2))/area;
%current in nA
load('/Users/alexneuhausen/Stanford/alexdata/110613 M12 from 110610 temp dep/65 data clean/warmup/100k.mat');
current100k65(1,:) = (arus(1).ivsd1(:,2) - arus(1).ivsd1(1,2))/area;
%current in nA
current100k = (current100k62 + current100k64 + current100k65)/3;
load(['/Users/alexneuhausen/Stanford/alexdata/110613 M12 from 110610 temp dep/62 data clean/warmup/75k.mat']);
current75k62(1,:) = (arus(1).ivsd1(:,2) - arus(1).ivsd1(1,2))/area;
%current in nA
load(['/Users/alexneuhausen/Stanford/alexdata/110613 M12 from 110610 temp dep/64 data clean/warmup/75k.mat']);
current75k64(1,:) = (arus(1).ivsd1(:,2) - arus(1).ivsd1(1,2))/area;
%current in nA
current75k = (current75k62 + current75k64 + current75k65)/3;

load(['/Users/alexneuhausen/Stanford/alexdata/110613 M12 from 110610 temp dep/62 data clean/warmup/50k.mat']);
current50k62(1,:) = (arus(1).ivsd1(:,2) - arus(1).ivsd1(1,2))/area;
%current in nA
load(['/Users/alexneuhausen/Stanford/alexdata/110613 M12 from 110610 temp dep/64 data clean/warmup/50k.mat']);
current50k64(1,:) = (arus(1).ivsd1(:,2) - arus(1).ivsd1(1,2))/area;
%current in nA
load(['/Users/alexneuhausen/Stanford/alexdata/110613 M12 from 110610 temp dep/65 data clean/warmup/50k.mat']);
current50k65(1,:) = (arus(1).ivsd1(:,2) - arus(1).ivsd1(1,2))/area;
%current in nA
current50k = (current50k62 + current50k64 + current50k65)/3;

load(['/Users/alexneuhausen/Stanford/alexdata/110613 M12 from 110610 temp dep/62 data clean/warmup/25k.mat']);
current25k62(1,:) = (arus(1).ivsd1(:,2) - arus(1).ivsd1(1,2))/area;
%current in nA
load(['/Users/alexneuhausen/Stanford/alexdata/110613 M12 from 110610 temp dep/64 data clean/warmup/25k.mat']);
current25k64(1,:) = (arus(1).ivsd1(:,2) - arus(1).ivsd1(1,2))/area;
%current in nA
load(['/Users/alexneuhausen/Stanford/alexdata/110613 M12 from 110610 temp dep/65 data clean/warmup/25k.mat']);
current25k65(1,:) = (arus(1).ivsd1(:,2) - arus(1).ivsd1(1,2))/area;
%current in nA

current25k = (current25k62 + current25k64 + current25k65)/3;

load(['/Users/alexneuhausen/Stanford/alexdata/110613 M12 from 110610 temp dep/62 data clean/warmup/25k.mat']);
current25k62(1,:) = (arus(1).ivsd1(:,2) - arus(1).ivsd1(1,2))/area;
%current in nA
load(['/Users/alexneuhausen/Stanford/alexdata/110613 M12 from 110610 temp dep/64 data clean/warmup/25k.mat']);
current25k64(1,:) = (arus(1).ivsd1(:,2) - arus(1).ivsd1(1,2))/area;
%current in nA
load(['/Users/alexneuhausen/Stanford/alexdata/110613 M12 from 110610 temp dep/65 data clean/warmup/25k.mat']);
current25k65(1,:) = (arus(1).ivsd1(:,2) - arus(1).ivsd1(1,2))/area;
%current in nA
current25k = (current25k62 + current25k64 + current25k65)/3;

semilogy(volts(poslower3:posupper5),
abs(current75k(poslower3:posupper5)), 'cd', 'LineWidth', 2);

load(['/Users/alexneuhausen/Stanford/alexdata/110613 M12 from 110610 temp dep/62 data clean/warmup/50k.mat']);
current50k62(1,:) = (arus(1).ivsd1(:,2) - arus(1).ivsd1(1,2))/area;
%current in nA
load(['/Users/alexneuhausen/Stanford/alexdata/110613 M12 from 110610 temp dep/64 data clean/warmup/50k.mat']);
current50k64(1,:) = (arus(1).ivsd1(:,2) - arus(1).ivsd1(1,2))/area;
%current in nA
load(['/Users/alexneuhausen/Stanford/alexdata/110613 M12 from 110610 temp dep/65 data clean/warmup/50k.mat']);
current50k65(1,:) = (arus(1).ivsd1(:,2) - arus(1).ivsd1(1,2))/area;
%current in nA

current50k = (current50k62 + current50k64 + current50k65)/3;

semilogy(volts(poslower:posupper5),
abs(current50k(poslower:posupper5)), 'k^', 'LineWidth', 2);

semilogy(volts(poslower:posupper5),
abs(current25k(poslower:posupper5)), 'b^', 'LineWidth', 2);

semilogy(xlabel('Bias Voltage [V]'),
ylabel('Current Density [A/m^2]'),
title('Current Density vs. Voltage for Dodecanethiol in 300nm Pores, Varying Temp'),
legend('295K','200K','150K','77K','50K','Location','NorthWest');

%%% ARRHENIUS PLOT OF AVERAGE CURRENT DENSITY FOR 3 DODECANETHIOL DEVICES
%% AT 100, 300, 500, 1000 mV BIAS
b = -1;
cuttemps1 = 1000*[295^b, 250^b, 200^b, 150^b, 100^b];
cuttemps1disp = 1000*[295^b, 250^b, 200^b, 150^b, 100^b];
cuttemps3 = 1000*[295^b, 250^b, 200^b, 150^b, 100^b, 75^b];
cuttemps5 = 1000*[295^b, 250^b, 200^b, 150^b, 100^b, 75^b, 50^b, 25^b];
cuttemps10 = 1000*[295^b, 250^b, 200^b, 150^b, 100^b, 75^b, 50^b, 25^b];
cut1 = [current295k(6) current250k(6) current200k(6) current150k(6)
current100k(6)];
cut3 = [current295k(16) current250k(16) current200k(16) current150k(16)
current100k(16) current75k(16)];
cut5 = [current295k(26) current250k(26) current200k(26) current150k(26)
current100k(26) current75k(26) current50k(26) current25k(26)];
cut10 = [current295k(51) current250k(51) current200k(51) current150k(51)
current100k(51) current75k(51) current50k(51) current25k(51)];
f10x = 3.3:0.1:85;
figure;
cut10dataplot = semilogy(cuttemps10, cut10, '^r', 'LineWidth', 2);
hold on;
grid on
cut5dataplot = semilogy(cuttemps5, cut5, 'dg', 'LineWidth', 2);
cut3dataplot = semilogy(cuttemps3, cut3, 'sb', 'LineWidth', 2);
cut1dataplot = semilogy(cuttemps1, cut1, 'ok', 'LineWidth', 2);
currentoptions = fitoptions('Method', 'NonlinearLeastSquares');
% nonlinear least squares
currentoptions.MaxIter = 1000000; % maximum number of iterations
currentoptions.MaxFunEvals = 1000000; % maximum number of function evaluations
currentoptions.StartPoint = [4e5 1500 3e2 700]; % fit starting point!!!!
currentoptions.Upper = [4e8 5000 1e5 3000]; % fit starting point!!!!
currentoptions.Lower = [0 0 0 0]; % fit starting point!!!!
currentproblem = {}; % fit function values to remain constant (these values are specified, not fit)
currenttype = fittype(\texttt{temppowerlawArrVRH(A,B,C,D,t)'},'independent', 't', 'problem', currentproblem, 'options', currentoptions);
currentproblemvalues = {}; % create string array of constants (values that are specified, not fit)

% 100 mV bias
[cut1fit, cut1gof] = fit(cuttemps1, log(cut1), currenttype, 'problem', currentproblemvalues);
% do fit!
cut1coefts = coeffvalues(cut1fit); % extract fit parameters
cut1confint = confint(cut1fit); % extract confidence intervals of fit parameters
cut1Afit = cut1coefts(1);
cut1Bfit = cut1coefts(2);
cut1Cfit = cut1coefts(3);
cut1Dfit = cut1coefts(4);
trans1 = 55;
cut1fitplot = semilogy(fitx,exp(temppowerlawArrVRH(cut1Afit,cut1Bfit,cut1Cfit,cut1Dfit,fitx)), 'k', 'LineWidth', 2);

% 300 mV bias
currentoptions.StartPoint = [2.0e6 1.3e3 8e2 1e3];
currentproblem = {};
currenttype = fittype('temppowerlawArrVRH(A,B,C,D,t)', 'independent', 't', 'problem', currentproblem, 'options', currentoptions);
currentproblemvalues = {};
cut3fit, cut3gof = fit(cuttemps3', log(cut3'), currenttype, 'problem', currentproblemvalues);
% do fit!
cut3coeffs = coeffvalues(cut3fit); % extract fit parameters
cut3confint = confint(cut3fit); % extract confidence intervals of fit parameters
cut3Afit = cut3coeffs(1);
cut3Bfit = cut3coeffs(2);
cut3Cfit = cut3coeffs(3);
cut3Dfit = cut3coeffs(4);
trans3 = 55;
cut3fitplot = semilogy(fitx, exp(temppowerlawArrVRH(cut3Afit, cut3Bfit, cut3Cfit, cut3Dfit, fitx)), 'b', 'LineWidth', 2);

% 500 mV bias
currentoptions.StartPoint = [2.5e6 1.1e3 2.0e3 1e3];
currentproblem = {};
currenttype = fittype('temppowerlawArrVRH(A,B,C,D,t)', 'independent', 't', 'problem', currentproblem, 'options', currentoptions);
currentproblemvalues = {};
cut5fit, cut5gof = fit(cuttemps5', log(cut5'), currenttype, 'problem', currentproblemvalues);
% do fit!
cut5coeffs = coeffvalues(cut5fit); % extract fit parameters
cut5confint = confint(cut5fit); % extract confidence intervals of fit parameters
cut5Afit = cut5coeffs(1);
cut5Bfit = cut5coeffs(2);
cut5Cfit = cut5coeffs(3);
cut5Dfit = cut5coeffs(4);
trans5 = 55;
cut5fitplot = semilogy(fitx, exp(temppowerlawArrVRH(cut5Afit, cut5Bfit, cut5Cfit, cut5Dfit, fitx)), 'g', 'LineWidth', 2);

% 1 Volt
currentoptions.StartPoint = [2.5e6 1.1e3 8.0e4 1e3];
currentproblem = {}; % fit function values to remain constant (these values are specified, not fit)
currenttype = fittype('temppowerlawArrVRH(A,B,C,D,t)', 'independent', 't', 'problem', currentproblem, 'options', currentoptions);
currentproblemvalues = {}; % create string array of constants (values that are specified, not fit)

[cut10fit, cut10gof] = fit(cuttemps10', log(cut10'), currenttype, 'problem', currentproblemvalues); % do fit!
cut10coeffs = coeffvalues(cut10fit); % extract fit parameters
cut10confint = confint(cut10fit); % extract confidence intervals of fit parameters
cut10Afit = cut10coeffs(1);
cut10Bfit = cut10coeffs(2);
cut10Cfit = cut10coeffs(3);
cut10Dfit = cut10coeffs(4);
trans10 = 55;
cut10fitplot = semilogy(fitx, exp(temppowerlawArrVRH(cut10Afit, cut10Bfit, cut10Cfit, cut10Dfit, fitx)), 'r', 'LineWidth', 2);

% PLOT RESULTS...
cut1Aerror = (cut1confint(2,1) - cut1confint(1,1))/2;
cut1Berror = (cut1confint(2,2) - cut1confint(1,2))/2;
dispstring1 = ['Fitted B 0.1 V = ' num2str(cut1Bfit) ' +/- ' num2str(cut1Aerror) ' (95% confidence) ']; % display the fit parameters
disp(dispstring1);
dispstring2 = ['Fitted D 0.1 V = ' num2str(cut1Dfit) ' +/- ' num2str(cut1Berror) ' (95% confidence) '];
disp(dispstring2);

cut3Aerror = (cut3confint(2,1) - cut3confint(1,1))/2;
cut3Berror = (cut3confint(2,2) - cut3confint(1,2))/2;
dispstring1 = ['Fitted B 0.3 V = ' num2str(cut3Bfit) ' +/- ' num2str(cut3Aerror) ' (95% confidence) ']; % display the fit parameters
disp(dispstring1);
dispstring2 = ['Fitted D 0.3 V = ' num2str(cut3Dfit) ' +/- ' num2str(cut3Berror) ' (95% confidence) '];
disp(dispstring2);

cut5Aerror = (cut5confint(2,1) - cut5confint(1,1))/2;
cut5Berror = (cut5confint(2,2) - cut5confint(1,2))/2;
dispstring1 = ['Fitted B 0.5 V = ' num2str(cut5Bfit) ' +/- ' num2str(cut5Aerror) ' (95% confidence) ']; % display the fit parameters
disp(dispstring1);
dispstring2 = ['Fitted D 0.5 V = ' num2str(cut5Dfit) ' +/- ' num2str(cut5Berror) ' (95% confidence) '];
disp(dispstring2);

cut1Aerror = (cut10confint(2,1) - cut10confint(1,1))/2;
cut1Berror = (cut10confint(2,2) - cut10confint(1,2))/2;
dispstring1 = ['Fitted B 1.0 V = ' num2str(cut10Bfit) ' +/- ' num2str(cut10Aerror) ' (95% confidence) ']; % display the fit parameters
disp(dispstring1);
dispstring2 = ['Fitted D 1.0 V = ' num2str(cut10Dfit) ' +/- ' num2str(cut10Berror) ' (95% confidence) '];
disp(dispstring2);
disp(dispstring1);
dispstring2 = ['Fitted D 1.0 V = ' num2str(cut10Dfit) ' +/- ' num2str(cut10Berror) ' (95% confidence)'];
disp(dispstring2);

xlabel('1000/(T/K)');
ylabel('Current [A/m^2]');
title('Current vs. Temperature^-1 for Dodecanethiol in 300nm Pores, Varying Voltage');
legend('1.0 V','0.5 V','0.3 V','0.1 V','Location','NorthEast');
hold off

%%%% ARRHENIUS PLOT OF AVERAGE CONDUCTANCE OF THE DODECANETHIOL DEVICES
% Divide the measured current by the bias for each trace

b = -1;
cутtemps1 = 1000*[295^b, 250^b, 200^b, 150^b, 100^b];
cутtemps1disp = 1000*[295^b, 250^b, 200^b, 150^b, 100^b];
cутtemps3 = 1000*[295^b, 250^b, 200^b, 150^b, 100^b, 75^b];
cутtemps5 = 1000*[295^b, 250^b, 200^b, 150^b, 100^b, 75^b, 50^b, 25^b];
cутtemps10 = 1000*[295^b, 250^b, 200^b, 150^b, 100^b, 75^b, 50^b, 25^b];
cut1 = [current295k(6) current250k(6) current200k(6) current150k(6) current100k(6)]/0.1;
cut3 = [current295k(16) current250k(16) current200k(16) current150k(16) current100k(16) current75k(16)]/0.3;
cut5 = [current295k(26) current250k(26) current200k(26) current150k(26) current100k(26) current75k(26) current50k(26) current25k(26)]/0.5;
cut10 = [current295k(51) current250k(51) current200k(51) current150k(51) current100k(51) current75k(51) current50k(51) current25k(51)]/1.0;
fitx = 3.3:0.1:85;

figure;
cut10dataplot = semilogy(cuttemps10, cut10, '^r', 'LineWidth',2);
hold on;
cut5dataplot = semilogy(cuttemps5, cut5, 'dg', 'LineWidth',2);
cut3dataplot = semilogy(cuttemps3, cut3, 'sb', 'LineWidth',2);
cut1dataplot = semilogy(cuttemps1, cut1, 'ok', 'LineWidth',2);

currentoptions = fitoptions('Method','NonlinearLeastSquares');

% Create string array of constants (values that are specified, not fit)
currenttype = fittype('temppowerlawArrVRH(A,B,C,D,t)', 'independent', 't', 'problem', 'currentproblem', 'options', currentoptions);
currentproblemvalues = {};
% 100 mV bias
[cut1fit,cut1gof] = 
fit(cuttemps1',log(cut1'),currenttype,'problem',currentproblemvalues);
% do fit!
cut1coeffs = coeffvalues(cut1fit); % extract fit parameters
cut1confint = confint(cut1fit); % extract confidence intervals of fit parameters
cut1Afit = cut1coeffs(1);
cut1Bfit = cut1coeffs(2);
cut1Cfit = cut1coeffs(3);
cut1Dfit = cut1coeffs(4);
trans1 = 55;
cut1fitplot = 
semilogy(fitx,exp(temppowerlawArrVRH(cut1Afit,cut1Bfit,cut1Cfit,cut1Dfit,fitx)),'k','LineWidth',2);

% 300 mV bias
currentoptions.StartPoint = [6.0e6 1.3e3 8e2 1e3];
currentproblem = {}; % fit function values to remain constant (these values are specified, not fit)
currenttype = 
fittype('temppowerlawArrVRH(A,B,C,D,t)','independent','t','problem',currentproblem,'options',currentoptions);
currentproblemvalues = {}; % create string array of constants (values that are specified, not fit)
[cut3fit,cut3gof] = 
fit(cuttemps3',log(cut3'),currenttype,'problem',currentproblemvalues);
% do fit!
cut3coeffs = coeffvalues(cut3fit); % extract fit parameters
cut3confint = confint(cut3fit); % extract confidence intervals of fit parameters
cut3Afit = cut3coeffs(1);
cut3Bfit = cut3coeffs(2);
cut3Cfit = cut3coeffs(3);
cut3Dfit = cut3coeffs(4);
trans3 = 55;
cut3fitplot = 
semilogy(fitx,exp(temppowerlawArrVRH(cut3Afit,cut3Bfit,cut3Cfit,cut3Dfit,fitx)),'b','LineWidth',2);

% 500 mV bias
currentoptions.StartPoint = [5.0e6 1.1e3 2.0e3 1e3];
currentproblem = {}; % fit function values to remain constant (these values are specified, not fit)
currenttype = 
fittype('temppowerlawArrVRH(A,B,C,D,t)','independent','t','problem',currentproblem,'options',currentoptions);
currentproblemvalues = {}; % create string array of constants (values that are specified, not fit)
[cut5fit,cut5gof] = 
fit(cuttemps5',log(cut5'),currenttype,'problem',currentproblemvalues);
% do fit!
cut5coeffs = coeffvalues(cut5fit); % extract fit parameters
cut5confint = confint(cut5fit); % extract confidence intervals of fit parameters
parameters
cut5Afit = cut5coeffs(1);
cut5Bfit = cut5coeffs(2);
cut5Cfit = cut5coeffs(3);
cut5Dfit = cut5coeffs(4);
trans5 = 55;
cut5fitplot = semilogy(fitx,exp(temppowerlawArrVRH(cut5Afit,cut5Bfit,cut5Cfit,cut5Dfit,fitx)),'g','LineWidth',2);

% 1 Volt
currentoptions.StartPoint = [2.5e6 1.1e3 8.0e4 1e3];
currentproblem = {}; %fit function values to remain constant (these values are specified, not fit)
currenttype = fittype('temppowerlawArrVRH(A,B,C,D,t)','independent','t','problem',currentproblem,'options',currentoptions);
currentproblemvalues = {}; %create string array of constants (values that are specified, not fit)
[cut10fit,cut10gof] = fit(cuttemps10',log(cut10'),currenttype,'problem',currentproblemvalues);
% do fit!
cut10coeffs = coeffvalues(cut10fit); %extract fit parameters
cut10confint = confint(cut10fit); %extract confidence intervals of fit parameters
cut10Afit = cut10coeffs(1);
cut10Bfit = cut10coeffs(2);
cut10Cfit = cut10coeffs(3);
cut10Dfit = cut10coeffs(4);
trans10 = 55;
cut10fitplot = semilogy(fitx,exp(temppowerlawArrVRH(cut10Afit,cut10Bfit,cut10Cfit,cut10Dfit,fitx)),'r','LineWidth',2);

%plot results...
cut1Aerror = (cut1confint(2,1) - cut1confint(1,1))/2;
cut1Berror = (cut1confint(2,2) - cut1confint(1,2))/2;
dispstring1 = ['Fitted B 0.1 V = ' num2str(cut1Bfit) ' +/- ' num2str(cut1Aerror) ' (95% confidence)'];
disp(dispstring1);
dispstring2 = ['Fitted D 0.1 V = ' num2str(cut1Dfit) ' +/- ' num2str(cut1Berror) ' (95% confidence)'];
disp(dispstring2);

cut3Aerror = (cut3confint(2,1) - cut3confint(1,1))/2;
cut3Berror = (cut3confint(2,2) - cut3confint(1,2))/2;
dispstring1 = ['Fitted B 0.3 V = ' num2str(cut3Bfit) ' +/- ' num2str(cut3Aerror) ' (95% confidence)'];
disp(dispstring1);
dispstring2 = ['Fitted D 0.3 V = ' num2str(cut3Dfit) ' +/- ' num2str(cut3Berror) ' (95% confidence)'];
disp(dispstring2);

cut5Aerror = (cut5confint(2,1) - cut5confint(1,1))/2;
cut5Berror = (cut5confint(2,2) - cut5confint(1,2))/2;

dispstring1 = ['Fitted B 0.5 V = num2str(cut5Bfit) ' +'/-' num2str(cut5Aerror) ' (95% confidence)']; %display the fit parameters
disp(dispstring1);
dispstring2 = ['Fitted D 0.5 V = num2str(cut5Dfit) ' +'/-' num2str(cut5Berror) ' (95% confidence)'];
disp(dispstring2);
cut10Aerror = (cut10confint(2,1) - cut10confint(1,1))/2;
cut10Berror = (cut10confint(2,2) - cut10confint(1,2))/2;
dispstring1 = ['Fitted B 1.0 V = num2str(cut10Bfit) ' +'/-' num2str(cut10Aerror) ' (95% confidence)']; %display the fit parameters
disp(dispstring1);
dispstring2 = ['Fitted D 1.0 V = num2str(cut10Dfit) ' +'/-' num2str(cut10Berror) ' (95% confidence)'];
disp(dispstring2);
xlabel('1000/(T/K)');
ylabel('Conductance [A/m^2]');
title('Conductance vs. Temperature^-1 for Dodecanethiol in 300nm Pores,
Varying Voltage');
legend('1.0 V','0.5 V','0.3 V','0.1 V','Location','NorthEast');
hold off

% AEDOTRON CTRL DEVICE ARRHENIUS PLOT
cuttempsaedotron = 1000*[295^-1, 250^-1, 200^-1, 150^-1, 100^-1, 75^-1, 50^-1, 20^-1, 13^-1, 12^-1]; %
cut1 = [polycurrent295k(6) polycurrent250k(6) polycurrent200k(6)
polycurrent150k(6) polycurrent100k(6) polycurrent75k(6)
polycurrent50k(6) polycurrent25k(6) polycurrent13k(6)
polycurrent12k(6)];
cut3 = [polycurrent295k(16) polycurrent250k(16) polycurrent200k(16)
polycurrent150k(16) polycurrent100k(16) polycurrent75k(16)
polycurrent50k(16) polycurrent25k(16) polycurrent13k(16)
polycurrent12k(16)];
cut5 = [polycurrent295k(26) polycurrent250k(26) polycurrent200k(26)
polycurrent150k(26) polycurrent100k(26) polycurrent75k(26)
polycurrent50k(26) polycurrent25k(26) polycurrent13k(26)
polycurrent12k(26)];
cut10 = [polycurrent295k(51) polycurrent250k(51) polycurrent200k(51)
polycurrent150k(51) polycurrent100k(51) polycurrent75k(51)
polycurrent50k(51) polycurrent25k(51) polycurrent13k(51)
polycurrent12k(51)];
fitx = 3.3:0.1:85;

% First plot the data points
figure;
cut1dataplot = semilogy(cuttempsaedotron, cut1, 'ok', 'LineWidth',2);
hold on;
grid on

cut3dataplot = semilogy(cuttempsaedotron, cut3, 'sb', 'LineWidth',2);
cut5dataplot = semilogy(cuttempsaedotron, cut5, 'dg', 'LineWidth',2);
cut10dataplot = semilogy(cuttempsaedotron, cut10, '^r', 'LineWidth',2);

% 100 mV bias
currentoptions = fitoptions('Method','NonlinearLeastSquares');
%nonlinear least squares

currentoptions.MaxIter = 10000000;  %maximum number if iterations
currentoptions.MaxFunEvals = 10000000;  %maximum number of function evaluations

currentoptions.StartPoint = [1e3 1.3e3 2e1 3];  %fit starting point!!!!
currentoptions.Lower = [0 0 0 0];  %fit starting point!!!!
currentproblem = {};  %fit function values to remain constant (these values are specified, not fit)
currenttype = fittype('temppowerlawArrVRH(A,B,C,D,t)', 'independent', 't', 'problem', currentproblem, 'options', currentoptions);
currentproblemvalues = {};  %create string array of constants (values that are specified, not fit)

cut1fitplot = semilogy(fitx, exp(temppowerlawArrVRH(polycut1Afit, polycut1Bfit, polycut1Cfit, polycut1Dfit, fitx)));

% 300 mV bias

currentoptions.StartPoint = [3.0e5 1.3e3 4e4 3];  %fit function values to remain constant (these values are specified, not fit)
currenttype = fittype('temppowerlawArrVRH(A,B,C,D,t)', 'independent', 't', 'problem', currentproblem, 'options', currentoptions);
currentproblemvalues = {};  %create string array of constants (values that are specified, not fit)

cut3fitplot = semilogy(fitx, exp(temppowerlawArrVRH(polycut3Afit, polycut3Bfit, polycut3Cfit, polycut3Dfit, fitx)));

% 500 mV bias

currentoptions.StartPoint = [7.0e5 1.1e3 5e3 3];  %fit function values to remain constant (these
values are specified, not fit)
currenttype = fittype('temppowerlawArrVRH(A,B,C,D,t)', 'independent', 't', 'problem', currentproblem, 'options', currentoptions);
currentproblemvalues = {}; %create string array of constants (values that are specified, not fit)
[cut5fit,cut5gof] = fit(cuttempsaedotron',log(cut5'),currenttype, 'problem', currentproblemvalues); %do fit!
cut5coeffs = coeffvalues(cut5fit); %extract fit parameters
cut5confint = confint(cut5fit); %extract confidence intervals of fit parameters
polycut5Afit = cut5coeffs(1);
polycut5Bfit = cut5coeffs(2);
polycut5Cfit = cut5coeffs(3);
polycut5Dfit = cut5coeffs(4);
trans5 = 55;
cut5fitplot = semilogy(fitx,exp(temppowerlawArrVRH(polycut5Afit,polycut5Bfit,polycut5Cfit,polycut5Dfit,fitx)),'g','LineWidth',2);

% 1 Volt
currentoptions.StartPoint = [15.0e5 1.1e3 3.0e4 3];
currentproblem = {}; %fit function values to remain constant (these values are specified, not fit)
currenttype = fittype('temppowerlawArrVRH(A,B,C,D,t)', 'independent', 't', 'problem', currentproblem, 'options', currentoptions);
currentproblemvalues = {}; %create string array of constants (values that are specified, not fit)
[cut10fit,cut10gof] = fit(cuttempsaedotron',log(cut10'),currenttype, 'problem', currentproblemvalues); %do fit!
cut10coeffs = coeffvalues(cut10fit); %extract fit parameters
cut10confint = confint(cut10fit); %extract confidence intervals of fit parameters
polycut10Afit = cut10coeffs(1);
polycut10Bfit = cut10coeffs(2);
polycut10Cfit = cut10coeffs(3);
polycut10Dfit = cut10coeffs(4);
trans10 = 55;
cut10fitplot = semilogy(fitx,exp(temppowerlawArrVRH(polycut10Afit,polycut10Bfit,polycut10Cfit,polycut10Dfit,fitx)),'r','LineWidth',2);

%plot the fit lines...
cut1Aerror = (cut1confint(2,1) - cut1confint(1,1))/2;
cut1Berror = (cut1confint(2,2) - cut1confint(1,2))/2;
dispstring1 = num2str(cut1Bfit) + '/' - num2str(cut1Aerror) '(95% confidence)'; %display the fit parameters
disp(dispstring1);
dispstring2 = num2str(cut1Dfit) + '/' - num2str(cut1Berror) '(95% confidence)';
disp(dispstring2);
cut3Aerror = (cut3confint(2,1) - cut3confint(1,1))/2;
cut3Berror = (cut3confint(2,2) - cut3confint(1,2))/2;
dispstring1 = ['Fitted B 0.3 V = ' num2str(cut3Bfit) ' +/- '
num2str(cut3Aerror) ' (95% confidence)'];
disp(dispstring1);
dispstring2 = ['Fitted D 0.3 V = ' num2str(cut3Dfit) ' +/- '
num2str(cut3Berror) ' (95% confidence)'];
disp(dispstring2);

cut5Aerror = (cut5confint(2,1) - cut5confint(1,1))/2;
cut5Berror = (cut5confint(2,2) - cut5confint(1,2))/2;
dispstring1 = ['Fitted B 0.5 V = ' num2str(cut5Bfit) ' +/- '
num2str(cut5Aerror) ' (95% confidence)'];
disp(dispstring1);
dispstring2 = ['Fitted D 0.5 V = ' num2str(cut5Dfit) ' +/- '
num2str(cut5Berror) ' (95% confidence)'];
disp(dispstring2);

cut10Aerror = (cut10confint(2,1) - cut10confint(1,1))/2;
cut10Berror = (cut10confint(2,2) - cut10confint(1,2))/2;
dispstring1 = ['Fitted B 1.0 V = ' num2str(cut10Bfit) ' +/- '
num2str(cut10Aerror) ' (95% confidence)'];
disp(dispstring1);
dispstring2 = ['Fitted D 1.0 V = ' num2str(cut10Dfit) ' +/- '
num2str(cut10Berror) ' (95% confidence)'];
disp(dispstring2);

xlabel('1000/(T/K)');
ylabel('Current Density [A/m^2]');
title('Current Density vs. 1/T for Aedotron Ctrl Devices in 30um Pore, Varying Voltage');
legend('100 mV','50 mV','30 mV','10 mV','Location','NorthEast');
hold off

% AEDOTRON CTRL DEVICES ARRHENIUS CONDUCTIVITY PLOT
% Simply divide the measured current by the bias
% First plot the data
cuttempsaedotron = 1000*[295^-1, 250^-1, 200^-1, 150^-1, 100^-1, 75^-1, 50^-1, 20^-1, 13^-1, 12^-1];

% AEDOTRON CTRL DEVICES ARRHENIUS CONDUCTIVITY PLOT
% Simply divide the measured current by the bias
% First plot the data
cuttempsaedotron = 1000*[295^-1, 250^-1, 200^-1, 150^-1, 100^-1, 75^-1, 50^-1, 20^-1, 13^-1, 12^-1];
cut1 = [polycurrent295k(6) polycurrent250k(6) polycurrent200k(6) polycurrent150k(6) polycurrent100k(6) polycurrent75k(6) polycurrent50k(6) polycurrent25k(6) polycurrent13k(6) polycurrent12k(6)]/(0.01);
cut3 = [polycurrent295k(16) polycurrent250k(16) polycurrent200k(16) polycurrent150k(16) polycurrent100k(16) polycurrent75k(16) polycurrent50k(16) polycurrent25k(16) polycurrent13k(16) polycurrent12k(16)]/(0.03);
cut5 = [polycurrent295k(26) polycurrent250k(26) polycurrent200k(26) polycurrent150k(26) polycurrent100k(26) polycurrent75k(26) polycurrent50k(26) polycurrent25k(26) polycurrent13k(26) polycurrent12k(26)]/(0.05);
cut10 = [polycurrent295k(51) polycurrent250k(51) polycurrent200k(51)
% Now determine fits
figure;
cut10dataplot = semilogy(cuttempsaedotron, cut10, '^r', 'LineWidth',2);
hold on;
grid on
cut5dataplot = semilogy(cuttempsaedotron, cut5, 'dg', 'LineWidth',2);
cut3dataplot = semilogy(cuttempsaedotron, cut3, 'sb', 'LineWidth',2);
cut1dataplot = semilogy(cuttempsaedotron, cut1, 'ok', 'LineWidth',2);

% 100 mV bias

currentoptions = fitoptions('Method','NonlinearLeastSquares');
% nonlinear least squares

currentoptions.MaxIter = 10000000; % maximum number of iterations

currentoptions.MaxFunEvals = 10000000; % maximum number of function evaluations

currentoptions.StartPoint = [12.0e6 1.3e3 60e4 3]; % fit starting point!!!

currentoptions.Lower = [0 0 0 0]; % fit starting point!!!

currentproblem = {}; % fit function values to remain constant (these values are specified, not fit)

currenttype = fittype('temppowerlawArrVRH(A,B,C,D,t)', 'independent', 't', 'problem', 'currentproblem', 'options', currentoptions);
currentproblemvalues = {}; % create string array of constants (values that are specified, not fit)
[cut1fit, cut1gof] = fit(cuttempsaedotron', log(cut1'), currenttype, 'problem', currentproblemvalues); % do fit!
cut1coeffs = coeffvalues(cut1fit); % extract fit parameters
cut1confint = confint(cut1fit); % extract confidence intervals of fit parameters
polycut1Afit = cut1coeffs(1);
polycut1Bfit = cut1coeffs(2);
polycut1Cfit = cut1coeffs(3);
polycut1Dfit = cut1coeffs(4);
transl = 55;
cut1fitplot = semilogy(fitx, exp(temppowerlawArrVRH(polycut1Afit, polycut1Bfit, polycut1Cfit, polycut1Dfit, fitx)), 'k', 'LineWidth',2);

% 300 mV bias

currentoptions.StartPoint = [12.0e6 1.3e3 60e4 3];
currentproblem = {}; % fit function values to remain constant (these values are specified, not fit)

currenttype = fittype('temppowerlawArrVRH(A,B,C,D,t)', 'independent', 't', 'problem', 'currentproblem', 'options', currentoptions);
currentproblemvalues = {}; % create string array of constants (values that are specified, not fit)
[cut3fit, cut3gof] =
fit(cuttempsaedotron',log(cut3'),currenttype,'problem',currentproblemvalues); % do fit!
cut3coeffs = coeffvalues(cut3fit); %extract fit parameters
cut3confint = confint(cut3fit); %extract confidence intervals of fit parameters
polycut3Afit = cut3coeffs(1);
polycut3Bfit = cut3coeffs(2);
polycut3Cfit = cut3coeffs(3);
polycut3Dfit = cut3coeffs(4);
trans3 = 55;
cut3fitplot = semilogy(fitx,exp(temppowerlawArrVRH(polycut3Afit,polycut3Bfit,polycut3Cfit,polycut3Dfit,fitx)),'b','LineWidth',2);

% 500 mV bias
currentoptions.StartPoint = [12.0e6 1.1e3 60e4 3];
currentproblem = {}; %fit function values to remain constant (these values are specified, not fit)
currenttype = fittype('temppowerlawArrVRH(A,B,C,D,t)', 'independent', 't', 'problem', currentproblem, 'options', currentoptions);
currentproblemvalues = {}; %create string array of constants (values that are specified, not fit)
[cut5fit,cut5gof] = fit(cuttempsaedotron',log(cut5'),currenttype,'problem',currentproblemvalues); %do fit!
cut5coeffs = coeffvalues(cut5fit); %extract fit parameters
cut5confint = confint(cut5fit); %extract confidence intervals of fit parameters
polycut5Afit = cut5coeffs(1);
polycut5Bfit = cut5coeffs(2);
polycut5Cfit = cut5coeffs(3);
polycut5Dfit = cut5coeffs(4);
trans5 = 55;
cut5fitplot = semilogy(fitx,exp(temppowerlawArrVRH(polycut5Afit,polycut5Bfit,polycut5Cfit,polycut5Dfit,fitx)),'g','LineWidth',2);

% 1 Volt
currentoptions.StartPoint = [12.0e6 1.1e3 9.0e5 3];
currentproblem = {}; %fit function values to remain constant (these values are specified, not fit)
currenttype = fittype('temppowerlawArrVRH(A,B,C,D,t)', 'independent', 't', 'problem', currentproblem, 'options', currentoptions);
currentproblemvalues = {}; %create string array of constants (values that are specified, not fit)
[cut10fit,cut10gof] = fit(cuttempsaedotron',log(cut10'),currenttype,'problem',currentproblemvalues); %do fit!
cut10coeffs = coeffvalues(cut10fit); %extract fit parameters
cut10confint = confint(cut10fit); %extract confidence intervals of fit parameters
polycut10Afit = cut10coeffs(1);
polycut10Bfit = cut10coeffs(2);
polycut10Cfit = cut10coeffs(3);
polycut10Dfit = cut10coeffs(4); 
trans10 = 55; 
cut10fitplot = semilogy(fitx,exp(temppowerlawArrVRH(polycut10Afit,polycut10Bfit,polycut10Cfit,polycut10Dfit,fitx)),'r','LineWidth',2);

%plot results...
cut10Aerror = (cut10confint(2,1) - cut10confint(1,1))/2;
cut10Berror = (cut10confint(2,2) - cut10confint(1,2))/2;
dispstring1 = ['Fitted B 100mV = ' num2str(polycut10Bfit) ' +/- ' num2str(cut10Aerror) ' (95% confidence)']; disp(dispstring1);
dispstring2 = ['Fitted D 100 mV = ' num2str(polycut10Dfit) ' +/- ' num2str(cut10Berror) ' (95% confidence)']; disp(dispstring2);

cut5Aerror = (cut5confint(2,1) - cut5confint(1,1))/2;
cut5Berror = (cut5confint(2,2) - cut5confint(1,2))/2;
dispstring1 = ['Fitted B 50 mV = ' num2str(polycut5Bfit) ' +/- ' num2str(cut5Aerror) ' (95% confidence)']; disp(dispstring1);
dispstring2 = ['Fitted D 50 mV = ' num2str(polycut5Dfit) ' +/- ' num2str(cut5Berror) ' (95% confidence)']; disp(dispstring2);

cut3Aerror = (cut3confint(2,1) - cut3confint(1,1))/2;
cut3Berror = (cut3confint(2,2) - cut3confint(1,2))/2;
dispstring1 = ['Fitted B 30 mV = ' num2str(polycut3Bfit) ' +/- ' num2str(cut3Aerror) ' (95% confidence)']; disp(dispstring1);
dispstring2 = ['Fitted D 30 mV = ' num2str(polycut3Dfit) ' +/- ' num2str(cut3Berror) ' (95% confidence)']; disp(dispstring2);

cut1Aerror = (cut1confint(2,1) - cut1confint(1,1))/2;
cut1Berror = (cut1confint(2,2) - cut1confint(1,2))/2;
dispstring1 = ['Fitted B 10 mV = ' num2str(polycut1Bfit) ' +/- ' num2str(cut1Aerror) ' (95% confidence)']; disp(dispstring1);
dispstring2 = ['Fitted D 10 mV = ' num2str(polycut1Dfit) ' +/- ' num2str(cut1Berror) ' (95% confidence)']; disp(dispstring2);

xlabel('1000/(T/K)');
ylabel('Current Density [A/m^2]');
title('Conductance vs. 1/T for Aedotron Ctrl Devices in 30um Pore, Varying Voltage');
legend('100 mV','50 mV','30 mV','2 mV','Location','NorthEast');
hold off

%%% PLOT DEVICE CONDUCTIVITY / POLY ONLY CONDUCTIVITY TO WORK OUT TRANSFER
%%% FUNCTION OF MONOLAYER
figure;
% 1 Volt
cut10fitplot = 
semilogy(fitx,exp(temppowerlawArrVRH(cut10Afit,cut10Bfit,cut10Cfit,cut10Dfit,fitx))./exp(temppowerlawArrVRH(polycut10Afit,polycut10Bfit,polycut10Cfit,polycut10Dfit,fitx)), 'r','LineWidth',2);
hold on;
% 500 mV
cut5fitplot = 
semilogy(fitx,exp(temppowerlawArrVRH(cut5Afit,cut5Bfit,cut5Cfit,cut5Dfit,fitx))./exp(temppowerlawArrVRH(polycut5Afit,polycut5Bfit,polycut5Cfit,polycut5Dfit,fitx)), 'g','LineWidth',2);
% 300 mV
cut3fitplot = 
semilogy(fitx,exp(temppowerlawArrVRH(cut3Afit,cut3Bfit,cut3Cfit,cut3Dfit,fitx))./exp(temppowerlawArrVRH(polycut3Afit,polycut3Bfit,polycut3Cfit,polycut3Dfit,fitx)), 'b','LineWidth',2);
% 100 mV
cut1fitplot = 
semilogy(fitx,exp(temppowerlawArrVRH(cut1Afit,cut1Bfit,cut1Cfit,cut1Dfit,fitx))./exp(temppowerlawArrVRH(polycut1Afit,polycut1Bfit,polycut1Cfit,polycut1Dfit,fitx)), 'k','LineWidth',2);

% plot results...
xlabel('1000/(T/K)');
ylabel('Transfer Function of Monolayer');
title('Dodecanethiol Conductance/Poly Conductance at 100 mV');
axis([0 90 0.001 0.4]);
hold off
BIBLIOGRAPHY

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