Molecular Spintronics: Design, Fabrication, and Characterization

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ABSTRACT

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(Under the direction of Wei You)

A great deal of organic spintronics has been centered on spuncoat polymeric or thermally deposited organic materials. In contrast, few studies have focused on spin behavior through molecular layers covalently bound to electrodes such as with self-assembled monolayers (SAMs) formed on ferromagnetic metals. The reason for this is twofold; a) SAM formation methods on ferromagnetic electrodes have not been thoroughly developed, and b) forming electrical contact to molecular layers is not a trivial pursuit. The work herein is dedicated to the design, fabrication, and characterization of metal-molecule-metal (MMM) junctions for their eventual application in molecule-based spin-electronics. Firstly, SAM formation via thiol and isocyanide attachment chemistry on Ni, Co, and Fe thin films was examined under both inert and atmospheric conditions in an attempt to form pristine, oxide free monolayers. In addition, a broadly applicable electrochemical technique was developed to remove native oxides from ferromagnetic surfaces prior to the formation of high surface coverage SAMs on thin, evaporated metal films. The SAMs prepared under electroreduction conditions were found to rival those prepared under inert conditions in a glovebox. MMM junctions were fabricated by forming SAM arrays in lithographically defined wells within a photoresist followed by coating with the conductive polymer blend poly(3,4-ethylenedioxythiophene) stabilized with poly(4-styrenesulphonic acid)
(PEDOT:PSS). PEDOT:PSS protected the monolayer prior to the thermal deposition of a top metal electrode and yielded promising tunneling characteristics through alkanedithiols; however, magnetotransport was never witnessed. A soft lithographic technique called nanotransfer printing (nTP) was developed to print metal thin film electrodes (Au, Ni, and Co) directly atop molecular monolayers formed on SAM coated metal electrodes. Junctions by this technique were studied by conductive atomic force microscopy and showed scalable tunneling characteristics through alkanedithiols monolayers based on tunneling distance (i.e., molecule length) and tunneling area (i.e., printed feature size). Permanent MMM junctions by nTP were fabricated by registered lithography atop large area (≥ 50 µm) printed electrodes followed by the deposition of a top gold electrode. Tunneling characteristics were interpreted using the Simmons model.
AKNOWLEDGEMENTS

First and foremost I want to thank Wei You for giving me the opportunity to work in his lab. He has been an outstanding mentor over the past few years. I truly could not have asked for a better advisor and I will certainly miss our conversations on research and life.

So many people have helped, supported, and believed in me throughout my career. I thank my family for being a constant source of guidance over the years. I would not have made it as far as I have if it were not for your constant support. Whenever times became tough, it was comforting to know that I have a loving network of family members to help me out. Thank you to all my friends. We have had so many good times and I look forward to many more.

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TABLE OF CONTENTS

LIST OF TABLES...........................................................................................................xi
LIST OF FIGURES.........................................................................................................xii
LIST OF ABBREVIATIONS............................................................................................xv

CHAPTER

1. Towards Molecule Based Spintronics........................................................................1
   1.1. Introduction............................................................................................................2
       1.1.1. The Current State of Electronics.................................................................2
       1.1.2. Molecule-Based Electronics........................................................................4
       1.1.3. Spintronics.....................................................................................................8
       1.1.4. Molecule-Based Spin Electronics..............................................................16
   1.2. Research Overview...............................................................................................18
   1.3. References...........................................................................................................20

2. A Comprehensive Investigation of Self-Assembled Monolayer Formation on
   Ferromagnetic Thin Film Surfaces..............................................................................25
   2.1. Introduction.........................................................................................................26
   2.2. Results and Discussion.........................................................................................28
       2.2.1. SAM Formation............................................................................................28
       2.2.2. Surface Coverage.........................................................................................30
       2.2.3. Contact Angle..............................................................................................34
2.2.4. X-Ray Photoelectron Spectroscopy.................................37
2.2.5. Time Dependence on Electroreduction........................41
2.2.6. Applied Potential Dependence of Electroreduction.......43
2.2.7. Reflection-Absorption Infrared Spectroscopy...............45
2.2.8. Etching of the Surface..............................................49
2.2.9. Monolayer Stability.................................................49

2.3. Experimental...................................................................54

2.3.1. Preparation of SAMs on Ferromagnetic Surfaces........54

2.3.2. Characterization of Monolayers on Ferromagnetic Surfaces.................................................................58

2.4 References.....................................................................61

3. Protecting Fragile Molecular Layers with Poly(3,4-ethylenedioxythiophene): Poly(styrenesulfonate) (PEDOT:PSS) in Spin-Valve Assembly.................................................65

3.1. Introduction..................................................................66

3.2. Results and Discussion................................................67

3.2.1. Magnetic Properties of Thermally Deposited Ferromagnetic.................................................................67

3.2.2. Device Architecture and Fabrication..........................74

3.2.3. Magnetic Properties of PEDOT:PSS Protected Molecular Junctions.........................................................76

3.2.4. Electrical Characteristics...........................................79

3.3. Experimental..............................................................79

3.3.1. Fabrication and Characterization.................................79

3.3.2. Magneto Optic Kerr Effect Measurements..................83

3.3.3. Probe Station Current-Voltage Measurements............84
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.4</td>
<td>References</td>
<td>133</td>
</tr>
<tr>
<td>5.</td>
<td>Permanent, Individually Addressable MMM Junctions via Nanotransfer Printing</td>
<td>138</td>
</tr>
<tr>
<td>5.1</td>
<td>Introduction</td>
<td>139</td>
</tr>
<tr>
<td>5.2</td>
<td>Results and Discussion</td>
<td>140</td>
</tr>
<tr>
<td>5.2.1</td>
<td>Device Architecture and Fabrication</td>
<td>140</td>
</tr>
<tr>
<td>5.2.2</td>
<td>Electrical Characteristics</td>
<td>142</td>
</tr>
<tr>
<td>5.2.3</td>
<td>Magnetotransport in Ni/Alkanedithiol/Ni/Au Junctions</td>
<td>145</td>
</tr>
<tr>
<td>5.3</td>
<td>Experimental</td>
<td>147</td>
</tr>
<tr>
<td>5.3.1</td>
<td>Fabrication and Characterization</td>
<td>147</td>
</tr>
<tr>
<td>5.3.2</td>
<td>Probe Station Current-Voltage Measurements</td>
<td>149</td>
</tr>
<tr>
<td>5.3.3</td>
<td>Low Temperature Current-Voltage Measurements</td>
<td>150</td>
</tr>
<tr>
<td>5.3.4</td>
<td>Simmons Modeling</td>
<td>152</td>
</tr>
<tr>
<td>5.3.5</td>
<td>Magneto Optic Kerr Effect Measurements</td>
<td>152</td>
</tr>
<tr>
<td>5.4</td>
<td>References</td>
<td>154</td>
</tr>
<tr>
<td>6.</td>
<td>Summary of Conclusions and Recommendations for Future Work</td>
<td>156</td>
</tr>
<tr>
<td>6.1</td>
<td>Summary of Conclusions</td>
<td>157</td>
</tr>
<tr>
<td>6.1.1</td>
<td>Monolayer Formation on Pristine Ferromagnetic Metals</td>
<td>158</td>
</tr>
<tr>
<td>6.1.2</td>
<td>Polymer Protected Self-Assembled Monolayers in Spin-Valve Assembled</td>
<td>159</td>
</tr>
<tr>
<td>6.1.3</td>
<td>MMM Junctions by Nanotransfer Printing</td>
<td>162</td>
</tr>
<tr>
<td>6.2</td>
<td>Recommendations for Future Work</td>
<td>165</td>
</tr>
</tbody>
</table>
6.2.1. Nanotransfer Printing onto Mixed Monolayers.............165
6.2.2. Modeling MMM Tunneling Characteristics using a Multi-BARRIER Tunneling Model.....................................................169
6.2.3. Conjugated Oligomers in MMM Junctions.....................171
6.2.4. Smoother Surfaces via Template Stripping Method.................................................................174
6.2.5. Device Fabrication through Multiple nTP Steps.............177
6.3. Experimental.................................................................................................................................181
6.3.1. Template Stripping....................................................................................................................181
6.3.2. Preparation of SAMs on Si/SiOx Wafers..........................182
6.4. References..........................................................................................................................................183
LIST OF TABLES

Table

2.1. Contact angles for Ni, Co, and Fe thin films soaked in ethanol solutions of 1-hexadecanethiol or 1-hexadecaneisocyanide under three separate conditions: glovebox, after being electroreduced, and in atmosphere.................................35
### LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Moore’s law and a generic field effect transistor</td>
<td>3</td>
</tr>
<tr>
<td>1.2</td>
<td>Common metal-molecule-metal junctions</td>
<td>7</td>
</tr>
<tr>
<td>1.3</td>
<td>PEDOT:PSS protected and nTP MMM junctions</td>
<td>9</td>
</tr>
<tr>
<td>1.4</td>
<td>Energy band structure for a 3d metal</td>
<td>11</td>
</tr>
<tr>
<td>1.5</td>
<td>Magnetic hysteresis and a generic spin valve</td>
<td>14</td>
</tr>
<tr>
<td>1.6</td>
<td>Density of states representation of giant magnetoresistance</td>
<td>15</td>
</tr>
<tr>
<td>2.1</td>
<td>Three-chamber electroreduction technique</td>
<td>29</td>
</tr>
<tr>
<td>2.2</td>
<td>Cyclic voltammograms of Ni, Co, and Fe surfaces coated with Fc-(CH$_2$)$_n$-SH as prepared in glovebox, after electroreduction, and under atmospheric conditions</td>
<td>31</td>
</tr>
<tr>
<td>2.3</td>
<td>Surface coverage of SAMs on Ni, Co, and Fe surfaces</td>
<td>32</td>
</tr>
<tr>
<td>2.4</td>
<td>AFM of bare and electoreduced surfaces</td>
<td>36</td>
</tr>
<tr>
<td>2.5</td>
<td>X-Ray photoelectron spectroscopy of O 1s regions for Ni, Co, and Fe</td>
<td>38</td>
</tr>
<tr>
<td>2.6</td>
<td>X-Ray photoelectron spectroscopy scan of metal 2p regions for Ni, Co, and Fe</td>
<td>40</td>
</tr>
<tr>
<td>2.7</td>
<td>Time dependence of electroreduction on surface coverage</td>
<td>42</td>
</tr>
<tr>
<td>2.8</td>
<td>Surface coverage as a function of applied potential</td>
<td>44</td>
</tr>
<tr>
<td>2.9</td>
<td>Reflectance-absorbance infrared spectra of SAMs on metal thin film electrodes</td>
<td>46</td>
</tr>
<tr>
<td>2.10</td>
<td>Reflectance-absorbance infrared spectra for hexadecanethiol coated surfaces formed by electroreduction</td>
<td>47</td>
</tr>
<tr>
<td>2.11</td>
<td>X-ray photoelectron spectroscopy 2p metal regional scans for electroreduced surfaces</td>
<td>48</td>
</tr>
</tbody>
</table>
2.12. X-ray photoelectron spectroscopy for Ni, Co, and Fe electroreduced surfaces as a function of time..................................................................................................................................................52

2.13. X-ray photoelectron spectroscopy O 1s regional scans for hexadecanethiol on electroreduced Ni, Co, and Fe surfaces after minimal exposure to atmospheric conditions and after 5 days constant exposure to atmospheric conditions........52

2.14. X-ray photoelectron spectroscopy O 1s regional scans for hexadecanethiol SAMs on Ni, Co, and Fe prepared in the glovebox after minimal exposure to atmospheric conditions, after eight days constant exposure to atmospheric conditions, and after fifteen days constant exposure to atmospheric conditions...............................................................................................................................................................53

3.1. Coercivity as a function of film thickness for Ni thin film electrodes.............72

3.2. MOKE comparison for Ni and Co.................................................................................................................................72

3.3. PEDOT:PSS protected MMM device.........................................................................................................................75

3.4. Magnetically independent ferromagnetic layers in a Ni/HDT/PEDOT:PSS/Co junction..................................................................................................................................................................................................................77

3.5. Temperature dependence on tunneling of an Au/HDT/PEDOT:PSS/Au junction.........................................................................................................................................................................................80

4.1. General schematic for nanotransfer printing..................................................................................................................92

4.2. Atomic force microscopy images of thermally deposited Au thin films.........96

4.3. Concentration dependence on nTP........................................................................................................................................97

4.4. Possible defect formation during nTP........................................................................................................................................99

4.5. Au/SAM/Au junctions by nTP with PDMS......................................................................................................................101

4.6. Rate dependence on surface roughness for Ni and Co films........................102

4.7. Nanotransfer printed Au/Co and Au/Ni films.................................................................104

4.8. Determining the quality of Au on PDMS and PFPE stamps as well as after printing........................................................................................................................................................................................................107

4.9. A generic rectangular tunneling barrier for a MMM junction.........................110

4.10. Au/decanedithiol/Au junctions via PFPE nTP.................................................................112
4.11. Au coated silicon cantilever for conductive atomic force microscopy measurements.................................................................113
4.12. 2D conductive map of 7 µm features by c-AFM.........................................................114
4.13. I-V characteristics as a function of alkane chain length........................................116
4.15. MOKE analysis of nTP Ni films..................................................................................121
4.16. Magnetically independent layers in a Ni/SAM/Ni/Au junction as observed by MOKE..................................................................................123
5.1. Device fabrication procedure for a permanent nTP device.........................................141
5.2. Temperature dependent I-V characteristics of an Au/dodecanedithiol/Au permanent junction formed by nanotransfer printing followed by lithography..................................................................................144
5.3. Temperature dependence on tunneling for Au/tetradecanedithiol/Au junction using PEDOT:PSS prior to contacting the nTP thin film..............................................146
6.1. Mixed monolayer surfaces..........................................................................................168
6.2. Simmons model and multibarrier tunneling model................................................170
6.3. Nanotransfer printing of 20 nm films of Au onto a 4,4’-biphenyldithiol coated Au electrode via PDMS..........................................................................................173
6.4. Template stripping.....................................................................................................176
6.5. Stackable nTP............................................................................................................178
6.6. nTP + nTP device......................................................................................................180
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>ampere</td>
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<tr>
<td>Å</td>
<td>angstrom</td>
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<tr>
<td>ads</td>
<td>adsorbed</td>
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<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
</tr>
<tr>
<td>Ag</td>
<td>silver</td>
</tr>
<tr>
<td>AgCl</td>
<td>silver chloride</td>
</tr>
<tr>
<td>aq</td>
<td>aqueous</td>
</tr>
<tr>
<td>atm</td>
<td>atmosphere</td>
</tr>
<tr>
<td>Au</td>
<td>gold</td>
</tr>
<tr>
<td>EtOH</td>
<td>ethanol</td>
</tr>
<tr>
<td>eV</td>
<td>electron volt</td>
</tr>
<tr>
<td>ºC</td>
<td>degree Celsius</td>
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<tr>
<td>cAFM</td>
<td>conductive atomic force microscopy</td>
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<tr>
<td>cm</td>
<td>centimeter</td>
</tr>
<tr>
<td>Co</td>
<td>cobalt</td>
</tr>
<tr>
<td>cps</td>
<td>counts per second</td>
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<tr>
<td>CV</td>
<td>cyclic voltammetry</td>
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<tr>
<td>DDT</td>
<td>1,10-decanedithiol</td>
</tr>
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<td>DDDT</td>
<td>1,12-dodecanedithiol</td>
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<tr>
<td>EF</td>
<td>Fermi level</td>
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<tr>
<td>ER</td>
<td>electroreduced</td>
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<tr>
<td>Fe</td>
<td>iron</td>
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<td>Abbreviation</td>
<td>Definition</td>
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<tr>
<td>FET</td>
<td>field effect transistor</td>
</tr>
<tr>
<td>fwhm</td>
<td>full width at half maximum</td>
</tr>
<tr>
<td>g</td>
<td>gram</td>
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<tr>
<td>GaAs</td>
<td>gallium arsenide</td>
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<tr>
<td>GB</td>
<td>glovebox</td>
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<tr>
<td>GMR</td>
<td>giant magnetoresistance</td>
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<tr>
<td>h</td>
<td>hour</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>water</td>
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<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
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<td>HDI</td>
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<td>HMDS</td>
<td>hexamethyldisilazane</td>
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<td>I</td>
<td>current</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>ITRS</td>
<td>international technology roadmap for semiconductors</td>
</tr>
<tr>
<td>J</td>
<td>current density</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin</td>
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<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
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<tr>
<td>M</td>
<td>molar</td>
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<tr>
<td>µA</td>
<td>microampere</td>
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<tr>
<td>min</td>
<td>minute</td>
</tr>
<tr>
<td>mJ</td>
<td>milli-Joule</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
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<td>--------</td>
<td>----------------------------------------------</td>
</tr>
<tr>
<td>mL</td>
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</tr>
<tr>
<td>µL</td>
<td>microliter</td>
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<td>µm</td>
<td>micrometer</td>
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<td>mm</td>
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<td>millimolar</td>
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<td>metal-molecule-metal junction</td>
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<td>MΩ</td>
<td>mega ohm</td>
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<td>MOKE</td>
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<td>MPa</td>
<td>mega-Pascal</td>
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<td>MPTS</td>
<td>3-(mercaptopropyl)trimethoxysilane</td>
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<tr>
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<td>sodium hydroxide</td>
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<td>density of states</td>
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<td>nickel</td>
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<td>O₂</td>
<td>oxygen gas</td>
</tr>
<tr>
<td>Oe</td>
<td>Orsted</td>
</tr>
<tr>
<td>ODT</td>
<td>1,8-octanediethiol</td>
</tr>
<tr>
<td>P_deposition</td>
<td>pressure at deposition</td>
</tr>
<tr>
<td>P_initial</td>
<td>initial pressure</td>
</tr>
<tr>
<td>PDMS</td>
<td>poly(dimethylsiloxane)</td>
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</tbody>
</table>
CHAPTER 1

Towards Molecule Based Spintronics
1.1. Introduction

1.1.1. The Current State of Electronics. With much of the world relying heavily on electronic technology, research continues to focus on providing progressively more powerful data processing and data storage media at cheaper costs. Not only is future consumer electronics anticipated to be more powerful, these will be significantly smaller and consume less energy as well. This creates a curious paradigm where new computing hardware must pack additional processing components into considerably tighter spaces, while maintaining a cost of production at or below that of current gadgets on the market.

For the past four and a half decades computer technology has maintained a steady increase in electronic memory and processing power in accordance to the technology roadmap laid out by Gordon E. Moore in 1965 [1]. The most important component for the advancement of microelectronic devices is the transistor, and according to “Moore’s Law” the density of transistors that can be cost effectively achieved on an integrated circuit doubles every two years (Figure 1A). Moore’s prediction has stayed relatively consistent over time where he correctly predicted as many as 65,000 components to be on a single processing chip by 1975. In comparison, today’s chips contain several billion components per processor. Moore based his predictions on the expected advancements in miniaturization over time, largely focused on improved photolithography techniques. However, while lithography has breached the nano-regime, the technology behind the fundamental processing unit has changed relatively little over the years and has begun to reach fundamental limitations.

The modern computer is based on silicon electronics where in general, a field effect transistor (FET) is the typical component for running real-time data transitions (Figure 1B).
Figure 1.1. Moore’s law and a generic field effect transistor A) Transistors per processor versus date of introduction. Dots represent benchmark release of new processors while the dotted line represents Moore’s predicted trend [1]. B) A schematic of a generic field effect transistor.
While there are many variations of FETs, overall, FETs operate as a current switch by controlling the flow of electrons from a source electrode to a drain electrode via an induced field from a metal gate electrode. Applying a voltage to the gate electrode permits or prohibits electron flow through an induced conduction channel between the source and drain electrodes. To function properly, the gate electrode must be electrically insulated from the source and drain by a gate dielectric layer.

Sometime this year, the semiconductor industry is expected to surpass the current 45 nm node technology which is defined as a 45 nm half distance between components on a single processing chip [2]. Herein lies the problem. As the source and drain become more compact during downscaling, it is required that the gate dielectric become thinner to increase the channel conductivity for the FET to function properly. At present, the currently employed silicon dioxide dielectric is only a few silicon atoms thick (~1.2 nm). This has become increasingly problematic as electrical shorts, heat build-up, and circuit engineering issues have become evident during manufacture [3, 4]. In some recently released processors, silicon dioxide has been replaced by layers with a higher dielectric constant (κ), such as hafnium and zirconium, to minimize current leakage via quantum tunneling across the atomic scale dielectric layer [5]. While the introduction of high-κ dielectric layers have offered the semiconductor industry a temporary reprieve, future steps toward miniaturization in the coming years, namely the 32 nm node, 22 nm node, and 16 nm node technologies, predict a dielectric thickness that approaches zero. Since a zero thickness dielectric is physically impossible, a new science must arise to replace the existing technology.

1.1.2. Molecule Based Electronics. An area of great interest over the last few decades has been molecular electronics, where it is envisioned that integrated circuits,
memories, microcontrollers, and other logic systems can be produced from either a single molecule or from an array of a few molecules [6-8]. Devices with organic active layers offer several advantages given that they can be cheaply fabricated from solution, are synthetically tunable, and are ideal for flexible electronics. While applicable single molecule electronics have yet to become a reality, practical molecule based devices would almost certainly require junctions with the use of a small collection of molecules. One typical model perused by many researchers employs organic materials sandwiched between two electrodes, where the electrical properties of these junctions can be altered by synthetically tuning the conductive properties of the molecules within. There are several methods to form electrode-organic-electrode junctions. Broadly separated into two groups, the first is a bulk method where relatively thick layers ( > 20 nm) of polymers or molecules are spun-coat or drop casted onto a metal electrode [9]. Another electrode can then be deposited atop the organic layer completing the device. This method has been considerably successful in producing a wide range of devices such as organic light emitting diodes [10], organic field effect transistors [11], and molecular diodes [12]. However, at a fundamental level, molecules covalently bound to a surface and unbound polymers lying on an electrode (or between electrodes) behave very differently, especially at the metal-molecule interfaces. Furthermore, the eventual frontier of device miniaturization would be the use of single molecules as the critical component to functional devices. Therefore, the focus of the work depicted herein will be on the second method of junction formation, forming electrodes atop dense arrays of molecular wires. One common method to do this is to form electronic contact to free standing self-assembled monolayers (SAMs) covalently bound to a metal electrode [7, 13].
Intimate contact to fragile molecular monolayers is not trivial. SAMs are sensitive to most production techniques used in the fabrication of standard, solid state semiconductor electronics. A new set of techniques needed to be developed to account for the fragile nature of SAMs while forming electrical contact to molecular monolayers. Initial attempts to contact SAMs by thermal vapor deposition directly [14, 15] or onto lithographically defined nanopores [15, 16] have shown a high percentage of shorted devices as the evaporated metal atoms either penetrate into or thermally destroy the monolayer. Other methods such as molecular break junctions [17, 18], mercury-drop electrodes [19], fluid metal eutectic gallium-indium (EGaIn) drop junctions [20], crossed-wire junctions [21], and conductive atomic force microscopy (c-AFM) [22-24] have been shown to contact monolayers well, and have produced valuable information on electron transport properties through molecular layers and metal-molecule interfaces (Figure 1.2); yet, so far these methods have been limited as mostly non-permanent, analytical techniques. In addition, conductance values across these techniques are not yet in agreement. Furthermore, the fundamental movement of electrons across the electrode/molecule interface is still unclear yielding two competing transport mechanisms namely, through space tunneling and through bond tunneling [13, 25, 26].

Any method that can form a reliable, reproducible, and permanent contact to a molecular monolayer would likely be an invaluable step toward the production of applicable molecular electronics and the replacement of existing FET technology. More importantly, this method should also be integrable to existing technology. Mainly it should allow for individually addressable well defined arrays, preferably in the nano-regime. This is asking a lot from one technique and currently only two methods have been successful in forming high
Figure 1.2. Common metal-molecule-metal junctions.  A) Molecular break junction [17]. B) Conductive probe atomic force microscopy directly onto a self-assembled monolayer [27]. C) Crosswire junction [21]. D) A metal drop electrode junction [20]. Images were adapted from their respective publications.
quality metal-molecule-metal (MMM) junctions while still offering the flexibility to alter junction size, electrode composition, as well as the molecular monolayer. The first is directly integrable to existing semiconductor electronics and uses SAMs confined to lithographically defined wells atop conductive electrodes [28]. Prior to thermal evaporation of the top electrode, the SAMs in this particular system are deliberately protected by a conductive polymer blend, poly(3,4-ethylenedioxythiophene) stabilized with poly(4-styrenesulphonic acid) (PEDOT:PSS) (Figure 1.3). This fabrication technique has been rather successful in producing dependable, device applicable junctions for investigating molecular conductance [15, 29, 30]. The second method used to form dependable MMM junctions employs a soft lithography technique called nanotransfer printing (nTP). Nanotransfer printing operates by transferring metal ‘ink’ from a flexible polymeric stamp to a SAM coated metal electrode. This method is intriguing since it produces a true metal-molecule-metal array with covalently bound electrodes directly linked to the molecular monolayer (Figure 1.3) [31, 32].

1.1.3. Spintronics. It is well known that electrons contain two discrete quantum spin states, spin-up and spin-down, and an electrical current is generally composed of both spin-up and spin-down carriers. Until recently, the electron’s spin had been largely ignored in electronics. While conventional electronics rely solely on the flow of electrons, spin-based electronics (or ‘spintronics’) make use of the electron’s spin as well [33, 34]. This provides an additional degree of freedom to be exploited to produce sought-after electrical properties.

Spintronics take advantage of the flow of spin-polarized currents, which is an electric current composed of majority spin-up or spin-down electrons. The simplest way to generate a spin-polarized current is to pass current through a ferromagnetic material; therefore, to fully understand spin-based electronics, it is important to first understand the fundamentals of
Figure 1.3. PEDOT:PSS Protected and nTP MMM junctions. A) A junction with a monolayer protected with PEDOT:PSS prior to top contact formation [28]. B) nanotransfer printing [32]. Images were adapted from their respective publications.
ferromagnetic metals. Take for example the ferromagnetic metals nickel, cobalt, and iron. The origins of their magnetism lay in their 3d and 4s electrons, and as single atoms it is easy to consider their discrete atomic orbitals occupied by spin-unpaired valence electrons [35]. When considering a bulk metal it is customary to account for a vast number of atomic orbitals from a large number of atoms. This broadens the 3d and 4s energy levels into energy bands. The highest energy level occupied by electrons at 0 K is the Fermi energy ($E_F$), and the electrons very near the Fermi level are mobile and are the electrons used during transport in an electric current. Energy bands are generally not equally distributed over any particular energy range which results in a density of energy states at any given energy interval. Therefore, in solid state physics it is common to describe the energy bands using the density of states model which defines the number of energy states ($N_E$) available to be occupied within a specific energy interval. Figure 1.4A portrays the density of states for the 3d and 4s electrons of a nonmagnetic metal. Here, the 3d and 4s electrons are considered separately for the spin-up (blue) and spin-down (orange) electrons. For a nonmagnetic material the number of occupied energy states is identical for both spin states. However, for some materials (i.e., ferromagnets) it is energetically favorable to have an unbalanced number of occupied states for spin-up and spin-down electrons. This is due to the exchange interaction that states that electrons observe a reduction in their electrostatic interaction energy while their spins are aligned. Accounting for the exchange energy there is a shift in occupied states from one spin direction to the other resulting in an unequal number of occupied energy levels for spin-up versus spin-down electrons (Figure 1.4B). In a competing process, the aforementioned shift in occupied states requires the transfer of electrons from energy levels just below the Fermi level of one spin band into energy levels just above the initial Fermi level of the other spin.
Figure 1.4. Energy band structure for a 3d metal. Spin-up (blue) and spin-down (orange) electrons are considered separately with the colored areas below the Fermi energy depicting occupied energy states. A) A nonmagnetic material with equal amount of spin-up and spin-down electrons. B) A ferromagnet with spin-polarization in the up direction.
band. This results in an increase in the total energy of the system. Consequently, ferromagnetism occurs when the total energy reduction through the exchange interaction is greater than the total energy increase due to the shift in the density of states, satisfying Stoner’s criterion [36, 37]. Figure 1.4B depicts a noticeable shift in the energy band in favor of the spin-up electrons resulting in a net spin-polarization in the up direction, and an ‘up’ magnetic direction for the material. Magnetization in the opposite direction (down magnetic direction) would show a shift in favor of the spin-down electrons (not shown).

As previously mentioned, the electrons nearest the Fermi energy are the electrons that are employed in electrical conduction. From the Figure 1.4B it is obvious that there is a disparity in the density of states between spins at the Fermi level so it would be expected that there would exist a polarization of spin within the current. This makes clear why conducting a current through ferromagnetic material results in a spin-polarized current. Also a direct consequence of the disparity of the Fermi level electrons, spin-up and spin-down electrons are expected to conduct differently. A model laid out by Mott described the motion of electrons through ferromagnetic metals as being carried through separate spin-up and spin-down conduction channels [38]. In essence, ferromagnets can be thought of as having two separate electron currents dependent on electron spin. It has been shown that the mobility of electrons in ferromagnets is spin dependent and can result in a substantial difference in resistance for each spin dependent current [39]. Another contributor to resistance in ferromagnets is spin-mixing arising from spin-flip scattering where the electron’s spin is flipped to the opposite spin state. There are a few mechanisms for spin-scattering, while the most relevant to ferromagnets is electron-magnon scattering [40, 41]. (Note: this should not be confused with spin relaxation due to spin-orbit effects which will be discussed later).
The dependence of the electron’s spin to resistance in ferromagnetic metals led to the discovery of the giant magnetoresistance (GMR) in 1988 by Albert Fert and Peter Grünberg [42-44]. Their device architecture consisted of two ferromagnetic layers with dissimilar coercivities. The first layer was used to generate a spin-polarized current while the second layer was used to receive the spin polarized current. To ensure that the two magnetic layers were not magnetically coupled (in contact with one another), a trilayer system was devised such that the ferromagnetic layers were separated by a nanometer thin, nonmagnetic spacing layer. Since the ferromagnets where fabricated to have dissimilar coercivities, their magnetic directions could be switched independent from one another under an external magnetic field. Therefore, starting with the two ferromagnets layers with their magnetic poles aligned (parallel) and slowly increasing an applied external magnetic field, one layer will switch its magnetic direction before the other (Figure 1.5A). In this case, there exists a window as a function of external field where the ferromagnetic layers are magnetically anti-aligned (anti-parallel). Remarkably, it was found that when the magnetic layers were aligned, the resistance of the system was low; however, when the magnetic layers were anti-aligned the resistance was high (Figure 1.5B). This change in resistance (dubbed the giant magnetoresistance) is a direct result of the spin-dependent conduction channels in ferromagnetic metals. The first ferromagnetic layer produces a spin-polarized current and conducts those electrons through the nonmagnetic layer to the second ferromagnet. In magnetically aligned case, the electrons enter the second ferromagnet and conduct normally. In the anti-aligned case, the electrons originated from energy levels with different character and experience resistance both within the second ferromagnetic layer as well as at the nonmagnet/ferromagnet interface. A density of states model is shown in Figure 1.6.
Figure 1.5. Magnetic hysteresis and a generic spin valve. A) Switching from aligned to anti-aligned magnetic layers while scanned through an external magnetic field. B) Generic spin valve showing high (aligned) and low (anti-aligned) current states.
Figure 1.6. Density of states representation of giant magnetoresistance. In the aligned case (top), the electrons originate from a ferromagnet with the same (or similar) density of states for spin-up (blue) and spin-down (orange) electrons. In the anti-aligned case (bottom), the electrons arise from energy levels with different character than the second ferromagnetic layer and therefore experience resistance at the nonmagnet/ferromagnet interface and within the second ferromagnetic layer.
Much like the FET seen in Figure 1.1, the GMR device (spintronic device or spin-valve) can be conducting or non-conducting depending on whether the magnetic moments of the top and bottom contact are parallel or antiparallel. Compared to the standard FET, spintronic systems are expected to be easier to manufacture, have a low cost of material, improved sensitivity, faster response times, and much lower power demand [45-47]. Also, as with many magnetic based electronics, spintronic devices are non-volatile meaning the system retains its magnetic moment even after the removal of power. In theory, future spintronic computers will start up instantly at the push of a button, without having to reboot the processor or random access memory on start up. Spin-based electronics have already begun to play a key role in the next generation of computing, and are anticipated to be further utilized during the eventual replacement of field effect transistor technology. Driven by consumer demand, spin-based electronic devices went from fundamental physics to industrially available components in less than ten years [34]. They are currently used as magnetic read heads where they have enabled packing densities of up to 24 Gbits per square inch in harddrives [45]. They have also been employed as magnetic sensors, isolators, and non-volatile magnetic random access memories.

1.1.4. Molecule Based Spin Electronics. To function properly, spin based electronics require a spin-polarized current to travel through a nonmagnetic layer and arrive at a ferromagnetic layer all while maintaining its spin polarization. Therefore, the quality of the device is largely based on how well the nonmagnetic spacing layer can maintain spin polarization. The ability to maintain spin-polarization is based on the materials spin-diffusion length, or the average distance a spin polarized current can travel through a nonmagnetic material while maintaining its polarization. The discovery of the GMR effect
and subsequent research had focused heavily on solid state and inorganic spintronic materials; yet, inorganic materials are known to have very short spin diffusion lengths (on the order of a few nanometers). Surprisingly, until very recently, organic based spintronic studies were almost exclusively theoretical. Organic materials are composed of relatively light elements so they have very weak spin-orbital and hyperfine interactions. This minimizes spin-scattering and allows organic materials to have very large spin diffusion lengths (>100nm), much longer than their inorganic counterparts [48]. Therefore, the center layer in an organic spin valve can in theory be significantly larger and still maintain its spin polarization. It has already been mentioned that most organic materials can be cheaply fabricated, synthetically tuned, and processed from solution. In addition, many conjugated organic molecules are optically active, leaving the door open for studies in opto-spintronic chips [49]. However, spin injection and spin polarized transport through organic systems have been difficult to study. Inorganic spin research methods have not been found to transfer well over to organic materials. Progress has been made in the study of spin-polarized charge injection and transport in semiconducting organic layers spuncoat or thermally deposited onto ferromagnetic electrodes [50-52]. However, little progress has been made on molecule based systems for example with molecules covalently bound to a surface such as self-assembled monolayers. Theoretical calculations of charge injection and spin transport have been performed using a density of states model for dodecane dithiol and triacene [53], and a similar model showed that spin-polarized charge injection is possible through covalently bound molecular monolayers [54]. Most likely much of the holdup has to do with the fact that SAM based systems are fragile to most typical fabrication techniques and are difficult to contact electrically.
1.2. Research Overview

As a standalone research area, molecule-based electronics are fascinating. However, the successful marriage between molecular electronics and spin-based electronics would spur numerous opportunities in fundamental physics and fundamental chemistry. By replacing both metal electrodes in a molecular electronic circuit with ferromagnetic metals, it has been proposed that one could couple the promising properties of molecular electronics with those of spintronics. Unfortunately, methods to form permanent and stable ferromagnet-molecule-ferromagnet junctions have been scarce. The overarching goal of the work herein is to generate the methodology needed to form reliable, functional, and individually accessible ferromagnet-molecules-ferromagnet junctions.

The steps needed to produce a quality ferromagnet-molecule-ferromagnet junction can be split into three major groups; 1) fabrication of a self-assembled monolayer on pristine, oxide free ferromagnetic thin films, 2) formation of intimate and permanent electrical contact atop the molecular monolayer without damaging the monolayer beneath, and 3) complete electrical and magnetic characterization of the junctions and the molecules within. Chapter 2 presents a comprehensive study on the formation of self-assembled monolayers on Ni, Co, and Fe thin film electrodes using alkanethiol and alkaneisocyanide attachment chemistry. SAMs were grown from three different conditions, namely; atmospheric conditions, inert glovebox conditions, and by an electroreduction method. Alkanethiol monolayers were able to be grown on Ni, Co, and Fe thin films in surface coverages similar to that seen in gold standards. Alkaneisocyanides monolayers were grown on Ni surfaces in good coverage. SAM coated Ni and Co thin films showed little sign of surface oxidation, and therefore were expected to be possible candidates for spintronic devices. Chapter 3 replicates previous work
carried out by Akkerman, et al. [28-30] in the formation of PEDOT:PSS protected MMM junctions. Au/alkanedithiol/PEDOT:PSS/Au junctions were fabricated and electrically characterized down to 77 K. In addition, this technique was expanded to include junctions using Ni and Co thin film electrodes. Magnetic layers with dissimilar coercivities were fabricated and independent magnetic switching was found exploiting the magnetic optic Kerr effect (MOKE). Spin-valve behavior was never seen in PEDOT:PSS protected systems likely due to spin-scattering in the PEDOT:PSS layer. In addition, tunneling characteristics through alkanedithiols in this system was found to be temperature dependent suggesting a competing electron transport mechanism besides tunneling. In Chapter 4, a soft lithographic technique, nanotransfer printing, is presented for the formation of Au, Ni, and Co MMM junctions. Electrical characterization is performed by c-AFM and it was found that up to 96% of junctions yielded tunneling characteristics as expected (for 200 nm diameter Au/decanedithiol/Au junctions). Scalable tunneling characteristics were seen based on tunneling distance (i.e. molecule length) and tunneling area (i.e. junction size). Independent magnetic layers were seen for Ni/SAM/Ni systems. Chapter 5 uses nTP in the formation of permanent, individually accessible junctions. MMM junctions were printed onto thermally deposited ferromagnetic wires, and photolithography was used to register a well on top the printed feature. A permanent electrode was sputtering onto the feature and tunneling characteristics were found to be temperature independent down to 77 K, which suggests that tunneling is the only transport mechanism within the junction. Magnetotransport measurements hint at spin-valve behavior; however, the change in resistance has so far been limited to only a few percent.
1.3. References


CHAPTER 2

A Comprehensive Investigation of Self-Assembled Monolayer Formation on Ferromagnetic Thin Film Surfaces
2.1. Introduction

Self-assembled monolayers (SAMs) have been widely studied and are well understood on gold and other inert metal surfaces such as platinum, silver, and palladium [1, 2]. Covalent surface attachment in these systems is typically carried out by using alkyl or aryl thiols; however, monolayer formation has also been achieved via isocyanides, selenols, etc. [1-4]. In addition, SAMs are also known to form readily on various metal oxide surfaces such as Al$_2$O$_3$, TiO$_2$, ZrO$_2$, SiO$_2$, and Fe$_2$O$_3$, typically using carboxylate, phosphonate, hydroxamate, or silane surface attachment chemistries [5-9]. Self-assembly of alkyl or aryl thiols on pristine, oxide-free transition metal surfaces such as Ni, Co, and Fe, however, has been met with limited success mainly due to the presence of the native oxide which inhibits the formation of direct sulfur-metal linkages [10]. As a result, the majority of literature reports involving SAMs on Ni, Co, and Fe have utilized carboxylates, phosphonates, or silanes for binding to the native oxide surface while those that involve bare surfaces typically rely on gas-phase adsorption of surfactants [7, 8, 11-13]. In a few reports, the native oxide of Ni and Fe has been removed by electrochemical reduction of the oxide layer under acidic or basic aqueous conditions [10, 14-17]. Surprisingly, the electrochemical reduction of the surface followed by the transfer of the substrate to the SAM molecule solution has typically been carried out under atmospheric conditions in spite of the fact that reformation of the native oxide is known to be very rapid [10, 12, 15]. In two of these reports, the electroreduction was performed under either acidic [16, 17] or basic [14] aqueous conditions while SAM formation was carried out either in situ [14] or by pulling the substrate through a top layer of neat thiol [16, 17]. In both instances, the broad applicability of the technique is
significantly limited by the requirement that the SAM molecules be either slightly miscible [14] or completely immiscible [16, 17] with the aqueous layer.

This chapter outlines a universal method for forming high surface coverage SAMs on ferromagnetic thin ($\leq 100$ nm) films of Ni, Co, and Fe. Unlike previous reports, this technique is broadly applicable to several different SAMs and surface types, and is expected to be applicable to SAMs and surfaces beyond what is presented here. This study constitutes the first comprehensive examination of SAM formation on three different ferromagnetic surface types, using two different surface-binding chemistries (thiol and isocyanide), and three different preparation conditions: glovebox, electroreduction, and atmosphere. Previous reports have suggested that isocyanides and thiols bind well to Ni surfaces [10, 12, 15, 18, 19]. Literature reports for SAMs on Co and Fe are extremely limited but suggest that thiolated SAMs can bind to these surfaces [16, 17, 20]. For glovebox samples, the thin films are removed from a thermal deposition chamber under an inert nitrogen atmosphere ($O_2 < 0.1$ ppm) and immediately submerged into a SAM solution to avoid native oxide formation. For atmosphere samples, the thin films are removed from the glovebox and SAM formation is carried out after native oxide formation under atmospheric conditions. For electroreduction samples, the native oxide is removed electrochemically under an argon atmosphere and the thin film is then transferred to the SAM molecule solution all under an inert atmosphere. A key advancement is the ability to utilize electroreduction techniques on thin films as opposed to bulk metal samples. Thin films are a highly desirable platform for incorporating self-assembled monolayer junctions into large-scale molecular electronic devices. Moreover, the magnetic properties of thin films are of interest for spintronic devices given that the coercive fields of thin films often differ from that of the bulk ferromagnetic metal [21]. This chapter
will focus on methods employed during device fabrication to control and minimize the oxide content at the SAM-metal interface. This is of importance since the electronic structure of this interface will inevitably influence the tunneling behavior and spin scattering of the molecular junction in molecular electronic and spintronic devices [20, 22].

2.2. Results and Discussion

2.2.1. SAM Formation. Thin metal films were prepared by thermal evaporation of 50 - 100 nm of Ni, Co, or Fe onto a titanium adhesion layer (25 nm) on silicon wafers coated with a thermally grown surface oxide (1 µm thick). For consistency, a substrate with two layers of metal, titanium followed by Ni, Co, or Fe, will be denoted: Si/SiO$_x$/Ti/M (M for metal). Three different conditions for SAM formation were explored: 1) transfer of Si/SiO$_x$/Ti/M substrates into an argon-purged SAM molecule solution immediately following thermal evaporation of the thin film under glovebox conditions, 2) SAM formation following a electroreduction process, or 3) immersion of Si/SiO$_x$/Ti/M substrates into the SAM molecule solution after exposing the film to atmospheric conditions for at least 30 min. Under glovebox and electroreduction conditions, it is anticipated that minimal oxidation of the metal surface occurs prior to and during SAM formation. The major difference between these two conditions is that the electroreduced films begin with native oxides which are then removed electrochemically while the glovebox surfaces are not exposed to the atmosphere until after SAM formation. In contrast, surface oxidation is expected to occur prior to and during SAM formation for samples prepared under atmospheric conditions. The major advantage of using an electroreduction step over glovebox conditions is the ability to make devices under atmospheric conditions where one can remove the surface oxide electrochemically to allow the formation of low-defect SAMs on the ferromagnetic surface.
Figure 2.1. Three-chamber electroreduction technique. (A) electroreduction chamber; (B) rinsing chamber; (C) SAM formation chamber (left). Structures of molecules studied (right).
The electroreduction process is carried out by utilizing a custom-built, three-chamber cell that is maintained under an argon atmosphere during the entire process (Figure 2.1). In the first chamber, the native oxide is removed by electroreduction in an aqueous electrolyte by means of a three-electrode cell. The electrolyte for the electroreduction was chosen to be pH > 7 aqueous solution in order to allow for the use of thin evaporated films by avoiding extensive etching of Ni, Co, and Fe under acidic conditions [23]. Extensive etching with bulk metals is not prohibitive; however, etching is highly problematic with evaporated thin films since this can hinder SAM formation as well as greatly alter the magnetic properties of the film. The electrolyte for Ni and Fe was 0.1 M NaOH (aq) while that for Co was 0.1 M KH$_2$PO$_4$ (aq, pH = 8); Co films became visibly etched during exposure to basic aqueous conditions under both argon and atmospheric conditions. The applied potential during the electroreduction was critical for optimizing SAM surface coverages (vide infra). After electroreduction of the working electrode for 10 minutes, the substrate was immediately transferred to the second chamber for rinsing with deionized water and finally was transferred to a third chamber containing the ethanolic solution of either thiol or isocyanide molecules. The contents of each chamber were purged with argon for 1-2 hours prior to electroreduction and the cell was kept under argon during the entire duration of SAM formation in order to prevent re-oxidation of the metal surface.

2.2.2. Surface Coverage. The extent of SAM formation was probed by either cyclic voltammetry, using either (11-thiolundecyl)ferrocene (Fc-(CH$_2$)$_{11}$-SH) or (11-isocyanoundecyl)ferrocene (Fc-(CH$_2$)$_{11}$-NC). The surface coverage results from cyclic voltammetry for the ferrocene SAMs (Figure 2.2) for all three conditions are depicted graphically in Figure 2.3. For comparative purposes, surface coverage data is also provided
Figure 2.2. Cyclic voltammograms of Ni, Co, and Fe surfaces coated with Fc-(CH$_2$)$_{11}$-SH (1mM SAM solution) as prepared in a glovebox (black lines), after electroreduction (red lines), and under atmospheric conditions (blue lines). Ni and Co data was recorded at 500 mV/s while the Fe data was collected at 200 mV/s.
Figure 2.3. Surface coverage of SAMs on Ni, Co, Fe surfaces. Upper: prepared from 1 mM SAM molecule solutions. Glovebox and atmosphere samples were prepared over a two day period; electroreduction samples were soaked in the SAM molecule solution for 12-18 h. Lower: For comparison, surface coverages and contact angles for gold surfaces.
for Fc-(CH$_{2}$)$_{11}$-SH and Fc-(CH$_{2}$)$_{11}$-NC SAMs formed on freshly evaporated Au thin films (Figure 2.3). The peak current from cyclic voltammograms showed a linear dependence with scan rate over the range 0.1-1 V/s consistent with a surface-confined Faradiac process and surface-bound redox species [12]. As the data shows, surface coverages for all three metals were generally higher when Fc-(CH$_{2}$)$_{11}$-SH was used, especially for Co and Fe which showed vanishingly low surface coverages with Fc-(CH$_{2}$)$_{11}$-NC. This is consistent with literature findings that isocyanide-functionalized molecules bind appreciably well to Ni surfaces [12]. For Fc-(CH$_{2}$)$_{11}$-SH, the surface coverages for electroreduced surfaces are comparable to those prepared in the glovebox. Relative to the “gold standard,” the surface coverages for glovebox and electroreduction samples are typically less than a factor of two lower. Increasing the Fc-(CH$_{2}$)$_{11}$-SH concentration improves the surface coverage for electroreduced Co, electroreduced Fe, and glovebox Ni. Atmospheric conditions for Ni and Fe typically gave surface coverages that were lower than that for electroreduced or glovebox conditions. The exceptions are Ni (1 mM, 9 day) and Fe (10 mM, 2 day) which show higher atmospheric surface coverages than expected. Surprisingly, atmospheric conditions for Co (1 mM, 9 days) gave coverages that were an order of magnitude ($1.8 \times 10^{-9}$ mol/cm$^2$) higher than that for glovebox or electroreduction conditions. We ascribe this to unexpectedly high etching rates of CoO$_x$/Co by Fc-(CH$_{2}$)$_{11}$-SH which result in significant roughening of the surface over time as corroborated by AFM measurements [12, 13]. Interestingly, Co (atmosphere) treated with 10 mM Fc-(CH$_{2}$)$_{11}$-SH over nine days results in more typical surface coverages on the order of $10^{-10}$ mol/cm$^2$. For both Co and Fe surfaces prepared under atmospheric conditions over a nine day period in 10 mM solutions, the surfaces become visibly etched and pitted which may explain the lower-than-expected surface coverages.
2.2.3. Contact Angle. Comparisons between the three methods for SAM formation were also made with HDT and HDI using contact angle measurements (Table 2.1). High contact angles approaching or equal to that of HDT on Au (111º) were obtained for HDT on Ni and Co at both 1 mM and 10 mM SAM molecule concentrations under glovebox conditions, suggesting excellent SAM formation and alkyl chain alignment. For Fe, the contact angle for HDT was significantly lower (49º) at 1 mM concentrations but improved markedly for 10 mM concentrations (89º). Under electroreduction conditions, 10 mM HDT concentrations were required to achieve appreciably high contact angles for all three surfaces. The contact angles for HDT on e-reduced films were surprisingly low when considering the high surface coverages observed for Fc-(CH$_2$)$_{11}$-SH under identical conditions and the low surface oxide content for electroreduced films observed by XPS (vide infra). AFM studies (Figure 2.4) clearly show that the root-mean-square surface roughness ($R_{rms}$) of post-electroreduction Ni and Co films without SAMs increases relative to that for freshly evaporated thin films (Ni: 1.5 to 2.2 nm, Co: 0.89 to 1.2 nm). For Fe, the $R_{rms}$ decreases slightly after ten minutes of electroreduction from 1.7 nm to 1.6 nm; however, the lower contact angle for HDT on electroreduced films is most likely a result of higher surface oxide content according to XPS (vide infra). Hence, we attribute the lower contact angles for electroreduced Ni and Co to increased surface roughness which disturbs the long-range crystalline order of the SAM and affects the wetting behavior. For all three ferromagnetic surfaces as well as gold, HDT gave significantly higher contact angles than HDI. This is consistent with inferior crystallinity of HDI SAMs but could also be due to lower SAM densities as suggested by the ferrocene surface coverage data. It is clear that increasing the HDI solution concentration results in higher contact angles in most cases. HDI on Ni gave
Table 2.1. Contact angles for Ni, Co, and Fe thin films soaked in EtOH solutions of 1-hexadecanediithiol or 1-hexadecaneisocyanide under three separate conditions: glovebox (GB), after being electroreduced (ER), and in atmosphere (Atm). Contact angles are averaged over 4-8 samples and contact angles. Electroreductions were performed at -1.2 V versus Ag/AgCl for 10 minutes.

<table>
<thead>
<tr>
<th>SAM</th>
<th>mM</th>
<th>Ni GB</th>
<th>Ni ER</th>
<th>Ni Atm</th>
<th>Co GB</th>
<th>Co ER</th>
<th>Co Atm</th>
<th>Fe GB</th>
<th>Fe ER</th>
<th>Fe Atm</th>
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<tr>
<td>C_{16}SH</td>
<td>1</td>
<td>100.4</td>
<td>68.0</td>
<td>43.9</td>
<td>110.7</td>
<td>63.4</td>
<td>73.8–3</td>
<td>48.5</td>
<td>53.0</td>
<td>43.7</td>
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<tr>
<td></td>
<td>10</td>
<td>107.3</td>
<td>92.9</td>
<td>68.8</td>
<td>112.5</td>
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<td>74.9–4</td>
<td>89.2</td>
<td>73.3</td>
<td>76.1</td>
</tr>
<tr>
<td>C_{16}NC</td>
<td>1</td>
<td>59.1</td>
<td>48.8</td>
<td>55.6</td>
<td>57.6</td>
<td>25.5</td>
<td>43.9</td>
<td>44.3</td>
<td>64.8</td>
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<td>97.9</td>
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<td>44.4</td>
<td>57.8</td>
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</table>
Figure 2.4. AFM of bare and electroreduced surfaces. Bare nickel (A), electroreduced nickel (B), bare cobalt (C), electroreduced cobalt (D), bare iron (E), and electroreduced iron (F). Scale bar: 500 nm.
higher contact angles than the same on Co and Fe, which further corroborates the claim that isocyanides bind preferably to Ni surfaces. For Ni and Fe, HDT SAMs did not apparently form well under atmospheric conditions. Interestingly, the contact angle for HDT on Co under atmospheric conditions showed time-dependent behavior where the contact angle decreased linearly from 94° to 74° over a four day period. This is consistent with etching of the Co surface by HDT over time which leads to a rougher film. This is also evident from crystal formation on the Co surfaces over time in solution. Centrifugation followed by dissolution of the crystals in a minimal amount of THF affords a pale purple solution indicative of a Co\textsuperscript{II} complex, presumably Co(HDT)\textsubscript{x}.

2.2.4. X-Ray Photoelectron Spectroscopy. X-Ray Photoelectron Spectroscopy (XPS) was used to determine the extent of oxide formation before and after hexadecanethiol SAM formation for glovebox and electroreduction conditions. Samples prepared under atmospheric conditions were studied by XPS to a lesser extent because of inferior surface coverage and contact angle data. Bare Ni, Co, and Fe surfaces were analyzed as references. Bare Ni showed a broad (full width at half max (fwhm) = 2.1) O 1s peak at 531.8 eV, (% Area = 64.4%), a narrower peak (fwhm = 1.0) at 529.6 eV (% Area = 30.1%), and a broad peak at 532.8 eV (% Area = 5.5%) (Figure 2.5). These peaks are assigned to Ni\textsuperscript{2+}(OH)\textsubscript{2}, NiO, and surface contaminants (H\textsubscript{2}O, C-O containing organics, and CO\textsubscript{2}), respectively [24, 25]. Bare Co showed similar peaks with the same binding energies and assignments with similar distributions. Bare Fe showed a broad (fwhm = 2.0) O 1s peak at 531.7 eV, (% Area = 50.1%) along with a narrower peak (fwhm = 1.1) at 530.2 eV (% Area = 49.9%) assigned as Fe\textsuperscript{2+}(OH)\textsubscript{2} and Fe\textsubscript{3}O\textsubscript{4}, respectively [26]. The metal 2p\textsubscript{3/2} spectral regions for all three bare ferromagnetic films showed evidence of a highly oxidized surface especially in the case of Fe.
Figure 2.5. X-Ray photoelectron spectroscopy of O 1s regions for Ni, Co, and Fe. Bare surfaces (black line), bare surfaces after 10 minute *in situ* Ar ion sputter treatment (black dashed line), 10 mM hexadecanethiol SAMs prepared in the glovebox (red line), and 10 mM hexadecanethiol SAMs prepared after 10 minute electroreduction (blue line).
as indicated by the presence of intense peaks at slightly higher binding energy than the pristine metal 2p\textsubscript{3/2} peaks at 852.7 eV (Ni), 778.3 eV (Co), and 707 eV (Fe) (Figure 2.6) [26]. After these samples were Ar ion sputtered for 10 minutes in situ, the intensities of the O 1s band decreased significantly by a factor of \(~7.5\) and the metal 2p\textsubscript{3/2} spectral regions were consistent with pristine, non-oxidized metal surfaces. The O 1s and metal 2p\textsubscript{3/2} spectral regions for hexadecanethiol (10 mM) glovebox and electroreduction samples were then compared to that of bare and sputtered metal surfaces. *The intensities of the O 1s bands for Ni and Co glovebox and electroreduction samples were comparable to that of the sputtered bare surfaces indicating that these films have very low surface oxygen content.* The oxygen content of glovebox and electroreduced Fe surfaces was significantly higher and only showed slightly lower oxygen levels than the bare surface with native oxide. Interestingly, the electroreduced Fe sample showed lower amounts of Fe\textsubscript{3}O\textsubscript{4} than glovebox and bare surfaces but greater amounts of Fe\textsuperscript{2+} (OH)\textsubscript{2}. The metal 2p\textsubscript{3/2} spectral regions corroborate the findings from the O 1s data: electroreduced Ni and Co show high intensity pristine metal 2p\textsubscript{3/2} peaks with low intensity peaks at 856.0 and 781.5 eV, respectively; glovebox Ni and Co show signs of shoulders at slightly higher binding energies than the pristine metal 2p\textsubscript{3/2} peaks; the metal 2p\textsubscript{3/2} spectra for glovebox and electroreduced Fe are practically superimposable with that of bare Fe. Importantly, the XPS data clearly shows that the electroreduction process effectively removes oxide/hydroxide from a surface that has been exposed to atmospheric conditions. This supports our claim that electroreduction can be utilized as a process step during the construction of molecular electronic devices under atmospheric conditions. Low surface oxide/hydroxide content at the SAM/ferromagnetic surface is expected to play a crucial role in charge transport in metal-molecule-metal device architectures.
Figure 2.6. X-Ray photoelectron spectroscopy scan of metal 2p regions for Ni, Co, and Fe. Upper plots: Bare surfaces (black line) and bare surfaces after 10 minute in situ Ar ion sputter treatment (red line). Lower plots: Surfaces prepared via 10 mM hexadecanethiol SAMs as prepared in the glovebox (red line), and 10 mM hexadecanethiol SAMs as prepared after a 10 minute electroreduction (black line).
2.2.5. Time Dependence on Electroreduction. The aforementioned XPS data was obtained after 10 minutes of electroreduction at the minimum potential that could maintain the current at > 1 mA for the entire duration. Atomic force microscopy performed on Ni and Co freshly evaporated surfaces and electroreduced surfaces without SAMs showed that electroreduction causes a ~40% increase in surface roughness. The increased roughness is attributed to etching of the surface during the electroreduction process. It is important to control surface roughening during the electroreduction process to ensure good SAM coverage. To this end, the electroreduction as a function of time was analyzed. First, surface coverage of Fc-(CH$_2$)$_{11}$-SH was examined as a function of electroreduction time (Figure 2.7, upper). For Ni, the surface coverage increases sharply at $t > 30$ sec and then increases less dramatically up to 10 min. For Fe, the surface coverage remains fairly constant as a function of electroreduction time. Surface coverages for Co appear to abide by a sigmoidal function showing a rapid increase in surface coverage between 5 and 10 minutes. Since the surface roughness from AFM only increases by ~40% for Ni and Co between $t = 0$ and $t = 10$ min and actually decreases slightly for Fe, the surface coverage improvement at longer electroreduction times is most likely a result of more complete surface oxide removal. The surface coverage data is consistent with O 1s and metal 2p$_{3/2}$ XPS data performed as a function of electroreduction time (Figure 2.7, lower). For Ni, maximum oxide/hydroxide removal from the surface occurs after five minutes of electroreduction. For Co, ten minutes of electroreduction appears to be necessary to achieve minimal surface oxygen content. For Fe, the lowest oxygen/oxidized Fe levels occurs at 1 minute of electroreduction and increases slightly for longer electroreduction times which is consistent with the low variance of the time-dependent surface coverage data.
Figure 2.7. Time dependence of electroreduction on surface coverage. Upper: surface coverages of Fc-(CH$_2$)$_{11}$-SH as a function of the duration of electroreduction at -1200 mV vs. Ag/AgCl reference electrode for nickel (black line), cobalt (red line), and iron (blue line). Lower: 1 Os XPS scans for Ni, Co, and Fe as a function of time. 1 min ER (black line), 5 min ER (red line), 10 min ER (blue line).
2.2.6. Applied Potential Dependence of Electroreduction. The optimal applied potential used during the 10 minute electroreduction was also studied for Ni, Co, and Fe systems by determining the surface coverage of Fc-(CH$_2$)$_{11}$-SH after submersion of the electroreduced sample in a 1 mM ethanolic solution (Figure 2.8). A clear plateau in surface coverage is reached beyond -1.0 V vs. Ag/AgCl for both Ni and Co. In the case of Fe, the surface coverage reaches a maximum at -1.2 V vs Ag/AgCl and then dramatically plummets. The critical potential appears to coincide with prevalent hydrogen evolution at the working electrode; below this potential, bubble formation does not occur to a large extent. It is known from the literature that hydrogen atoms are facile surface oxide etchants [27-30]. Thus, we propose that the surface oxide is removed by electroreduction via one or both of the following mechanisms:

**Proposed Mechanism 1**

\[
\text{NiO/Ni + H}_2\text{O} + e^- \rightarrow \text{Ni/NiO/\text{H(ad)s} + OH}^- \\
\text{Ni/NiO/2H(ad)s} \rightarrow \text{H}_2\text{O} + \text{Ni/Ni}^0
\]

**Proposed Mechanism 2**

\[
\text{Ni/Ni(OH)$_2$ + 2H}_2\text{O} + 2e^- \rightarrow \text{Ni/Ni(OH)$_2$/2H(ad)s} + 2 \text{OH}^- \\
\text{Ni/Ni(OH)$_2$/2H(ad)s} \rightarrow 2\text{H}_2\text{O} + \text{Ni/Ni}^0
\]

Beyond -1.2 V, the surface coverage on Fe dramatically plummets to $\sim 1 \times 10^{-11}$ mol/cm$^2$. The cause of this may be due to the fact that at -1.4 V, O$_2$ evolution at the Pt counterelectrode becomes increasingly rapid. Thus, the solution O$_2$ concentration increases allowing for surface reoxidation either during electroreduction or immediately after the applied potential
Figure 2.8. Surface coverage as a function of the applied potential. After electroreduction on nickel (black line), cobalt (red line), and iron (blue line) surfaces with Fe-(CH$_2$)$_{11}$-SH SAMs.
is removed. Iron oxidation is known to be quite facile. The results are consistent with Fe being more susceptible to reoxidation than both Ni and Co. One way to avoid reoxidation of the electroreduced surface is to purge the solution rapidly with argon during the electroreduction process. When this is performed in the case of -1.4 V for Fe for 10 minutes, the surface coverage dramatically improves to $1.4 \times 10^{-10}$ mol/cm$^2$.

### 2.2.7. Reflection-Absorption Infrared Spectroscopy.

Hexadecanethiol SAM formation on Ni, Co, and Fe under glovebox and electroreduction conditions was studied using Reflectance-Absorbance Infrared Spectroscopy (RAIRS). Figure 2.9C shows the IR spectra for electroreduction samples of hexadecanethiol on Ni, Co, and Fe overlaid with hexadecanethiol on evaporated Au. For HDT on Ni, Co, Fe and Au, three peaks were observed at 2961, 2925, and 2853 cm$^{-1}$ assigned as the $\nu_{as}(CH_3)$, $\nu_{as}(CH_2)$, and $\nu_s(CH_2)$ stretching modes, respectively [31]. For atmospheric and glovebox conditions, nearly identical spectra with similar absorbances were attained for surface-bound hexadecanethiol (Figure 2.9A and 2.9B). For electroreduction samples, however, the absorbances were sample dependent (Figure 2.10). For Ni, the absorbance is greatest after 10 minutes, consistent with XPS and Fc-(CH$_2$)$_{11}$-SH surface coverage data. For Fe, the highest absorbance was observed with the 1 minute electroreduction sample, which is consistent with XPS data which shows lower surface hydroxide/oxide content for the 1 minute sample. For Co, the absorbance decreased considerably as the electroreduction time was increased from 1 min, to 5 min, to 10 min (Figure 2.11). This observation may be due to extensive etching of Co during electroreduction which results in thinner films and signal attenuation.
Figure 2.9. Reflectance-absorbance infrared spectra of SAMs on metal thin film electrodes. Surfaces of hexadecanethiol prepared (A) under atmosphere conditions and (B) under glovebox conditions on nickel (black line), cobalt (red line), and iron (blue line). (C) Surfaces of hexadecanethiol prepared by electroreduction method on nickel (black line), cobalt (red line), iron (blue line), and on thermally deposited gold (green line).
**Figure 2.10.** Reflectance-absorbance infrared spectra for hexadecanethiol coated surfaces (from 10 mM solution) formed by electroreduction. Prepared by electroreduction conditions at $V_{\text{app}} = -1.2$ V vs Ag/AgCl as a function of electroreduction time for (A) Ni, (B) Co, and (C) Fe: 1 min (black line), 5 min, (red line), and 10 min (blue line).
Figure 2.11. X-ray photoelectron spectroscopy 2p metal regional scans for electroreduced surfaces. For hexadecanethiol on electroreduced A) Ni, B) Co, and C) Fe after minimal exposure to atmospheric conditions as a function of electroreduction time: 1 min (black line), 5 min (red line), and 10 min (blue line).
2.2.8. Etching of the Surface. Several observations suggest that etching of the surface occurs in the cases and Co and Fe but is undetectable in the case of Ni. First, crystals form over time on the surface and in solution when Co and Fe surfaces are submerged in 10 mM solutions of HDT or Fc-(CH$_2$)$_{11}$-SH under atmospheric conditions. Second, the entire ferromagnetic surface becomes visibly etched over long periods of time (> 2 weeks) under these conditions leaving behind only the titanium adhesion layer. The etching rates appear to be faster for HDT than Fc-(CH$_2$)$_{11}$-SH perhaps due to lower solubility of the metal-HDT adducts. Third, the Fc-(CH$_2$)$_{11}$-SH surface coverage data abides by predictable trends in the case of Ni but not for Co and Fe which suggests that etching/surface roughening is playing a role in the latter cases. It is interesting to note that Nuzzo and coworkers observed discoloration and pitting when forming short-chain SAMs ($n \leq 3$) on Cu and Ag surfaces and that prolonged exposure resulted in dissolution of the metal [32].

2.2.9. Monolayer Stability. The stability of SAMs on ferromagnetic surfaces upon extended exposure to atmospheric conditions is an important consideration for implementation of these molecular monolayers into real devices. XPS was used to examine the stability of hexadecanethiol (10 mM) SAMs prepared under glovebox and electroreduction conditions over the course of several days to weeks. For glovebox and electroreduction samples exposed to atmospheric conditions on the 1-2 hour timescale, the XPS data shows a S 2p peak at ~ 162 eV consistent with a metal-bound thiolate species (Figure 2.12, top row) [32]. Over time, the sulfur atom becomes increasingly oxidized to a S=O containing species (e.g. sulfonate, sulfinate, sulfone) as shown by the appearance of a S 2p peak at ~ 169 eV [32]. After five days, the Ni and Co electroreduced samples contain both oxidized and non-oxidized sulfur with the latter predominating. After eight days,
glovebox Ni and Fe samples contain a mixture of oxidized and non-oxidized sulfur atoms while the Co sample’s sulfur atoms have become almost entirely oxidized.

By focusing on the metal 2p spectral regions, the kinetics of oxidation of the surface metal atoms in the presence of a SAM overlayer can be attained (Figure 2.12). Electroreduced Co appears to re-oxidize more rapidly than electroreduced Ni over a five day period as observed by the attenuation of the pristine Co peak at 778.3 eV and growth of an equally intense broad peak at 782 eV (attributed to oxidized Co, or Co(ox)) (Figure 2.12, middle row). For Ni, surface oxidation appears to occur more slowly as is evident from only a slight increase in the intensity of the Ni(ox) peak at 856.3 eV. In fact, the intensity ratio for the pristine Ni peak at 852.7 eV to the Ni(ox) peak at 856.3 eV only decreases from 1.5 to 1.3 over a five day period. For electroreduced Fe, the 1 h and 5 day spectra are nearly superimposable indicating only a minor change in the oxidation of the Fe surface atoms.

Oxidation of Ni and Co surfaces under appears to occur more slowly for samples prepared in the glovebox than those prepared by electroreduction by comparing the relative intensities of the pristine and M(ox) peaks over time (Figure 2.12, bottom row). For glovebox Co, the intensity ratio decreases to 1.2 over 8 days while that for Ni decreases to 1.4. For glovebox Fe, the surface at \( t = 1 \text{ h} \) is noticeably less oxidized than the related electroreduced sample (intensity ratio 0.75 vs. 0.61, respectively). As a result, the surface of the glovebox Fe sample showed signs of oxidation over time.

Additional insights into the oxidation of the surfaces over time were attained by analyzing the XPS O 1s spectral region and fitting the curves to the sum of three Lorentzian-Gaussian functions centralized at \(-\sim 533, ~ 531.5, \text{ and } 529.5\text{ eV} \) (Ni and Co, 530.1 eV for Fe) (Figures 2.13 and 2.14). The peaks at \(-\sim 530\text{ eV}\) were attributed to \(O^2-\)-containing species,
Figure 2.12. X-ray photoelectron spectroscopy for Ni, Co, and Fe electroreduced surfaces as a function of time. Top row: XPS S 2p regional scans for hexadecanethiol on electroreduced surfaces after minimal exposure to atmospheric conditions (black line) and after 5 days constant exposure to atmospheric conditions (red line). Middle row: metal 2p regional scans for hexadecanethiol on electroreduced surfaces after minimal exposure to atmospheric conditions (black line) and after five days constant exposure to atmospheric conditions (red line). Bottom row: Metal 2p regional scans for hexadecanethiol SAMs surfaces prepared in the glovebox after minimal exposure to atmospheric conditions (black line), after eight days constant exposure to atmospheric conditions (red line), and after fifteen days constant exposure to atmospheric conditions (blue line).
Figure 2.13. XPS O 1s regional scans for hexadecanethiol on electroreduced Ni, Co, and Fe surfaces after minimal exposure to atmospheric conditions (black line) and after 5 days constant exposure to atmospheric conditions (red line).
Figure 2.14. XPS O 1s regional scans for hexadecanethiol SAMs on Ni, Co, and Fe prepared in the glovebox after minimal exposure to atmospheric conditions (black line), after eight days constant exposure to atmospheric conditions (red line), and after fifteen days constant exposure to atmospheric conditions (blue line).
NiO, CoO, or Fe$_3$O$_4$, while the broader peak at 533 eV was attributed to the adsorption of H$_2$O, C-O containing organics, and/or CO$_2$ to the surface [24, 25]. The intensities of both of these peaks remain fairly constant over extended periods on time in the ambient. The ~531.5 eV species were assigned to the presence of M$^{2+}$(OH)$_2$ species as previously mentioned. Both glovebox Ni and Co exhibit a marked increase (~ by a factor of 3) in the intensity of the ~531.5 eV peak over time. Meanwhile, electroreduced Ni and Fe show negligible changes in intensity of the ~531.5 eV peak while glovebox Fe and electroreduced Co show noticeable but relatively minute intensity increases at this binding energy over time. Since the O 1s peak intensities at ~531.5 eV increase over time while those at ~530 eV remain constant for Ni and Co, we attribute the increases in intensity of the metal 2p$_{3/2}$ spectral region at ~856.0 and ~781.5 eV, respectively, to oxidation of surface atoms to M$^{2+}$(OH)$_2$ species for both glovebox and electroreduction cases.

2.3. Experimental

2.3.1. Preparation of SAMs on Ferromagnetic Surfaces. Nickel, iron and cobalt metal films (50 or 100 nm) were prepared by thermal evaporation ($P_{\text{initial}} = 2-4 \times 10^{-6}$ mbar; $P_{\text{deposition}} = 2-8 \times 10^{-6}$ mbar) on top of a 25 nm titanium adhesion layer (2 Å/s) on a Si/SiO$_x$ wafer (Si <100>, 1 micron thick thermally grown oxide, Addison Engineering). Ni, Fe, and Co were deposited at 1-1.5 Å/s. The evaporation boats were purchased from RD Mathis; the specific boat for Ni, Co, and Fe evaporation was an alumina-coated tungsten boat (Type S1AO-W to avoid alloying of the metals with tungsten) while that for Ti and Au were tungsten boats (Type S4-015 W and S42-015W, respectively). Gold (99.999%), nickel (99.98%), cobalt (99.95%), and iron (99.95%) pellets (1/8”x1/8”) were purchased from Kurt J. Lesker, Inc. Titanium slugs (99.995%, 3.175 mm x 3.175 mm) were purchased from Alfa
Aesar. Thermal evaporations were performed with an MBraun evaporator contained within an MBraun nitrogen glovebox such that freshly evaporated thin films could be removed from the evaporator chamber under a nitrogen atmosphere. Thicknesses of films were determined using a quartz crystal microbalance located just below the substrate holder in the evaporator. Tooling factors were determined by measuring the true thicknesses of films with a profilometer; the films were deposited through a TEM grid (Ted Pella, Item No. 1GC50, 50 square mesh) shadow mask that was secured to the surface with Kapton tape. X-Ray diffraction spectra were obtained for the Si/SiO$_x$/Ti/M thin films (100 nm for Ni, Co, and Fe; 50 nm for Au; 25 nm Ti for all cases) using a Rigaku Multiplex Powder Diffractometer with Ni-filtered Cu Ka radiation (1.5418 Å) over the range 2θ = 10-85°. The evaporated metal films were observed to grow with either a <111> texture (Au, Ni, and Co) or <110> texture (Fe) [33]. The grain sizes for the thin films were deduced from the X-Ray diffraction data using the Scherer equation: Ni (7.0 Å), Co (5.1 Å), Fe (8.6 Å), and Au (9.3 Å).

For SAMs prepared in the glovebox, a 1 or 10 mM SAM solution in ethanol (100%, Pharmco) was placed in a vial with septum screw cap, purged with Argon for 1 h, then brought into the glovebox (O$_2$ levels ≤ 0.1 ppm). The freshly evaporated Si/SiO$_x$/Ti/M film was immediately submerged in the SAM solution and allowed to react inside of the glovebox (time was typically for 24-48 h). For SAMs prepared under atmospheric conditions, the Si/SiO$_x$/Ti/M film was removed from the glovebox and exposed to atmospheric conditions for 30 minutes prior to submersion in the SAM solution and stored under atmospheric conditions.

For SAMs prepared via electroreduction, the Si/SiO$_x$/Ti/M film was removed from the glovebox and secured to a glass microscope slide (typically substrate size = 1.5 × 2.5 cm)
using UV-epoxy (Epotek #OG116-31). UV irradiation was carried out by exposing both sides of the sample for ~10 minutes; through-glass irradiation was performed by placing the substrate on a small, clean plastic Petri dish at an angle of ~15°. The purpose of the UV-epoxy is to ensure that the applied potential during the electroreduction step is provided to the exposed metal surface and not to the underlying sides and bottom of the silicon substrate; lower SAM surface coverages were observed when the Si/SiOₓ/Ti/M sample was not secured to glass with UV-epoxy especially in the cases of Co and Fe. A custom-built (Quark Glass, Inc.), three-chambered piece of glassware was used to perform the electroreduction procedure under an argon atmosphere (Figure 2.1). The SAM solution (20 mL) was prepared and placed in the right-most chamber, deionized water (30 mL) was placed in the central chamber, and aqueous electrolyte was placed in the left-most chamber (20 mL). Rubber septa were used to seal the openings of the three chambers. For the left-most chamber, a wire soldered to an alligator clip was inserted through the rubber septum to make electrical connection to the reference electrode. An alligator clip was soldered to a PTFE-coated stainless steel rod (1/16 inch diameter, McMaster-Carr) for electrical connection to the platinum gauze counter electrode. A bent (~30°), PTFE-coated stainless steel rod (1/16 inch diameter) was inserted through the rubber septum located at the central chamber opening to make electrical connection to the working glass/epoxy/Si/SiOₓ/Ti/M electrode via a series of alligator clips. The chambers were purged with Argon for 1-2 h prior to the electroreduction step by using three 10” stainless steel needles that penetrate through the rubber septa and are submerged in the solution within each chamber; a short needle was placed in one of the septa to avoid pressure build-up. During electroreduction, purging was continued only at the SAM solution chamber. During the entire purging process, the glass/epoxy/Si/SiOₓ/Ti/M electrode
was submerged in the central chamber’s deionized water in order to discourage exposure to semi-volatile SAMs like hexadecanethiol. This process was used to avoid gas-phase hexadecanethiol from depositing on the metal surface prior to electroreduction. Following electroreduction and working electrode transfer into the SAM solution, purging was continued for the entire duration of the SAM formation.

The applied potential during the electroreduction was provided by a Bioanalytical Systems (BAS) Epsilon potentiostat and currents were measured as a function of time in the controlled electrolysis mode. The applied potential was increased until the initial current reached 2-3 mA. For Ni and Fe, the electrolyte was 0.1 M NaOH and the applied potential was typically -1.0 - (-1.1) V and -1.2 - (-1.3) V, respectively, versus a BAS Ag/AgCl (3 M NaCl) reference electrode. For Co, the electrolyte was chosen to be 0.1 M KH$_2$PO$_4$ (pH=8, adjusted with NaOH (aq)) and the applied potential was typically -0.95 - (-1.0 V) vs. Ag/AgCl. Significant etching of the Co film was evident when 0.1 M NaOH (aq) was used as the electrolyte; etching was not apparent by eye with 0.1 M KH$_2$PO$_4$ (pH=8). The electroreduction time was typically 10 minutes. After electroreduction, the working electrode was transferred to the middle chamber for rinsing of the electrode using the rigid, PTFE-coated stainless steel rod and then transferred to the SAM solution for SAM formation.

At the completion of SAM formation, the working electrode was rinsed. All samples (i.e. glovebox, electroreduction, and atmospheric samples) were rinsed with ethanol followed by acetone, sonicated for 30 seconds in THF, and then rinsed again with acetone and ethanol and then dried in a nitrogen stream. After characterization by CV and/or contact angle measurements, SAM samples were stored in a nitrogen atmosphere glovebox (< 0.1 ppm O$_2$) in a parafilm-encapsulated plastic Petri dish.
2.3.2. Characterization of Monolayers on Ferromagnetic Surfaces. Surface coverage measurements were made by performing cyclic voltammetry in a three-electrode cell with Fc-(CH$_2$)$_{11}$-SH or Fc-(CH$_2$)$_{11}$-NC derivatized Si/SiO$_x$/Ti/M as the working electrode. The electro-active area of the working electrode was defined by a viton o-ring (7 mm outer diameter) placed in a 7 mm hole of a 1 mm thick Delrin spacer. A 1” inner diameter viton o-ring was then placed about the Delrin hole followed by a glass joint (Chemglass, Part # CG-124-05). The entire arrangement was held together by a clamp (Chemglass, Part # CG 150-06). The electrolyte solution (0.1 M tetrabutylammonium hexafluorophosphate in dry, distilled tetrahydrofuran) was then placed inside the glass joint along with a platinum gauze counterelectrode and a BAS non-aqueous reference electrode (Ag wire in 0.01 M AgNO$_3$/0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile). External electrical contact to the working electrode was made via an alligator clip. The dryness of the THF electrolyte was critical for attaining good CV data with Co films and was less critical for Ni and Fe. As a result, all components of the apparatus were dried with a heat gun prior to CV experiments performed on Co films. Cyclic voltammograms were attained by scanning the potential from -0.2 V to 0.4 V and back at a particular scan rate (typically 0.2 or 0.5 V/s). Integration of the area under the redox waves was performed after subtracting away the baseline current that results from non-faradaic processes.

Contact angle measurements were performed using a CAM 200 Optical Contact Angle Meter (KSV Instruments, Ltd.). A 5 µL drop of deionized water was placed atop the SAM/surface. The contact angle data reported are averages of 4-8 contact angles; standard deviations fall within the range ± 0.5-2.0.
X-Ray Photoelectron Spectroscopy (XPS) measurements were carried out at the Chapel Hill Analytical and Nanofabrication Laboratory (CHANL) at UNC using a Kratos Analytical Axis Ultra spectrometer with monochromatized X-Ray Al Kα radiation (1486.6 eV). Survey scans were performed with a step size of 1 eV and a pass energy of 80 eV while region scans were performed with a step size of 0.1 eV and a pass energy of 20 eV. The peaks of region scans were fit with a Gaussian-Lorentzian product function that was weighted 30% Lorentzian. The binding energies of the O 1s, C 1s, and S 2p XPS peaks were referenced to metal 2p\textsubscript{3/2} photoelectron peaks at 852.7 (Ni), 778.3 (Co), and 707 eV (Fe) for oxide-free metal surfaces [26]. Surfaces functionalized with hexadecanethiol (10 mM SAM molecule solution concentration) were prepared under glovebox, electroreduction, and atmosphere conditions. The stability of the SAM and the surface beneath the SAM was studied as a function of exposure time to the ambient. The first data point was attained by removing the samples from their storage conditions and transporting the samples to the XPS location (total loading time ~ 30 min – 1 h). Electroreduction and glovebox samples were stored under a nitrogen atmosphere in a glovebox. Atmospheric samples were removed from their SAM molecule solutions and rinsed with solvent an hour prior to XPS analysis.

AFM images were collected using a Multimode IIIa Atomic Force Microscope (Veeco Metrology Group). The microscope was operated in tapping mode at ambient conditions (T = 21°C, RH = 45%), using silicon cantilevers (Mikromasch, Part No. NSC14/no Al) with resonance frequencies of approximately 160 kHz and tip radii less than 10 nm. To ensure accuracy, multiple images were taken of the same sample but in different areas.
Reflection-absorption infrared spectroscopy (RAIRS) was conducted at the Nanochemistry Laser and Vibrational Spectroscopy Laboratory located at North Carolina State University in the Department of Chemistry. Spectra were recorded using a Bio-Rad-Digilab FTS-3000 Fourier transform infrared (FT-IR) spectrometer using a Varian Universal variable grazing angle reflectance attachment with a ZnSe polarizer having a normal spectral window of 650 to 7500 cm\(^{-1}\). The infrared light was focused onto the photodiode of a liquid nitrogen-cooled, narrow band mercury-cadmium-telluride (MCT) detector with a normal spectral response of 650 to 7000 cm\(^{-1}\). The angle of incidence used was 70° with respect to the surface normal. An infrared polarizer was used to obtain p-polarized light. The spectrometer and attachment where purged with dry compressed air to reduce the possibility of atmospheric water or CO\(_2\) contamination of the spectra and samples. The spectra presented are an average of 256 scans. All spectra were recorded at room temperature, approximately 23° ± 0.5° C with a resolution of 2 cm\(^{-1}\).

Great care was taken to ensure that the SAMs being characterized were chemisorbed and not physisorbed species. Physisorbed molecules were removed by 30 seconds of sonication in THF. For glovebox and electroreduction samples, sonication did not result in a lowering of the surface coverage and/or contact angle, suggesting a prevalence of chemisorbed SAMs. For SAMs prepared under atmospheric conditions, however, sonication typically resulted in a significant lowering of the surface coverage and/or contact angle. For example, the contact angle for HDT/Co(ox) was ~120° prior to sonication and decreased to 70-90° after sonication. Presumably, hydrogen-bonded/physisorbed molecules are removed during sonication in THF.
2.4. References


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CHAPTER 3

Protecting Fragile Molecular Layers with Poly(3,4-ethylenedioxythiophene) Poly(styrenesulfonate) (PEDOT:PSS) in Spin-Valve Assembly
3.1. Introduction

After monolayer formation on ferromagnetic electrodes (Chapter 2), a permanent contact needs to be formed atop the self-assembled monolayer. As previously stated, forming intimate contact to self-assembled monolayers is an arduous task. To resolve the issues involved, a dependable junction needs to be engineered such that a top electrode can be formed reproducibly and repeatedly while maintaining permanent, strong contact to the molecular layer. Also, the ideal junction should be scalable to the sub micron regime as well as being integrable into existing electronics as permanent, individually addressable molecular junctions. One technique that has shown to fulfill all the requirements begins by forming SAM arrays in lithographically defined wells in a photoresist [1, 2]. Prior to thermal evaporation of the top electrode, the SAM in this particular system is deliberately protected by a conductive polymer blend, poly(3,4-ethylenedioxythiophene) stabilized with poly(4-styrenesulphonic acid) (PEDOT:PSS). This fabrication technique has been rather successful in producing dependable, device applicable junctions for investigating molecular conductance [2, 3]. It also provides a promising step toward replacing silicon based circuits with durable molecular electronic devices.

Up until now, SAM formation on ferromagnetic electrodes has been difficult. Therefore, previous work in PEDOT:PSS protected junctions was limited to studying only well behaved Au electrode molecular electronic systems, and had not yet been expanded to included ferromagnetic electrodes in an attempt to form spintronic devices. This chapter will discuss the formation and characterization of both Au electrode junctions as well as the formation of spintronic devices using Ni and Co ferromagnetic electrodes.
3.2. Results and Discussion

3.2.1. Magnetic Properties of Thermally Deposited Ferromagnetic Thin Films.

Dense SAM coverage was seen on Ni, Co, and Fe metal thin film electrodes under the electrophoretic and glovebox processing conditions covered in Chapter 2. However, in those studies Fe surfaces were found to still contain a substantial degree of oxidation by XPS analysis. Transition metal oxides are known to be strongly paramagnetic and have been shown to readily scatter spin polarized currents in previously studied ferromagnet-insulator-ferromagnet junctions [4]. Therefore, iron metal thin films were ruled out as a bottom electrode and the work here focused on Ni and Co thin film electrodes.

The magnetic properties of the bottom ferromagnetic electrodes needed to be well defined and easily controlled before attempting to fabricate a spin valve. Magnetic characteristics of ferromagnetic films are known to vary by metal [5], film thickness [6], surface variations [7, 8], and purity. Magnetism depends not only on the fundamental properties of the element but on the crystalline structure and microscopic arrangement. In fact, magnetism on the surface does not necessarily extend the same properties as those viewed in the material’s bulk [7-9]. As a result, surface characteristics are of the utmost importance while controlling the coercivity in ferromagnetic thin films. Surface roughness plays a significant role since surface variations can change on the order of a nanometer or more. Rougher surfaces tend to create additional surface domains apart from the standard bulk domains seen in thicker layers. As a ferromagnetic film becomes thinner (or laterally confined for that matter), these domains play a larger role in the material’s hysteresis due to the fact that they compose a greater percentage of the overall film.
Surface functionalization by various materials can also lead to changes in the magnetic properties given that magnetic domains and spin arrangement may be disrupted by surface bonding [9]. As previously mentioned, it is well known that transition metals Fe, Co, and Ni form a native oxide layer rapidly under atmospheric conditions. It is expected, but not yet known whether this oxide layer plays a role in the overall coercivity of thin ferromagnetic films. Regardless, limiting surface oxidation and controlling surface characteristics is expected to make it easier to control the coercivity of the final material.

The magnetic properties of thermally deposited Ni and Co metal thin films were studied as a function of film thickness, surface roughness (i.e. after being electroreduced), surface oxidation, and after being coated with self-assembled monolayer. Films with various thicknesses were fabricated by first depositing a 10 nm thick Ti adhesion layer on a silicon wafer followed by 20, 50, or 100 nm of Co or Ni. A magnetic standard was made for each thickness by depositing 20, 50, and 100 nm Ni and Co films followed by a 3 nm layer of Au. The Au film was deposited immediately following Ni or Co deposition without breaking vacuum to the deposition chamber to protect the ferromagnetic layer from surface oxidation. The Au standard surfaces were measured via MOKE immediately following fabrication to minimize any possibilities of surface changes. Other MOKE measurements were made for bare Ni and Co surfaces for each thickness after a series of conditions, namely; 1) after exposure to atmospheric conditions (24 h) to allow the formation of surface oxide, 2) electroreduced at – 1.0 V for 10 minutes using the technique outlined in section 2.2.1 of Chapter 2, and 3) after SAM formation using the glovebox conditions outlined in section 2.2.1 of Chapter 2. Two electroreduced surfaces were fabricated. The first was electroreduced followed by soaking in an ethanolic solution of the self-assembled monolayer
hexadecanethiol (HDT). The second electroreduced sample was not coated with a SAM, but was left bare and allowed to oxide in atmosphere (24 h) after the electroreduction step prior to MOKE measurement.

For Ni thin films, the Si/Ti/Ni/Au standard gives a linear increase in coercivity with respect to film thickness (Figure 3.1A). The general trend in coercivity for surface oxidized, SAM coated, and electroreduced surfaces are a reduced coercivity (compared to the standard) as the surface thickness increases. This implies that surface irregularities tend to reduce the overall coercivity of the film. This would make sense particularly for the oxidized surfaces which were also shown to have a linear coercivity with respect to film thickness albeit with a smaller slope. One notable result was the relatively small change in coercivity for the 20 nm thick films. It would be expected that the 20 nm thick Ni film would see the largest change in coercivity since any change in the surface structure would constitute a larger percentage change of the entire film. However, this was not the case. It was found that the 20 nm film had the smallest overall change in coercivity for each system with the one exception being the electroreduced films which saw a large spike in the coercivity for the 20 and 50 nm films.

The electroreduced films are known to be considerably rougher than regularly deposited films. This was seen in Chapter 2 where the roughness was found to increase from 1.5 nm $R_{\text{rms}}$ for deposited Ni films to 2.2 nm $R_{\text{rms}}$ for electroreduced Ni films. Since it was impossible in our current experimental setup to create an Au coated standard with ~ 2.2 nm $R_{\text{rms}}$, electroreduced surfaces were coated with HDT and compared to non-SAM coated electroreduced samples (Figure 3.1B). The results show both surfaces containing a large spike in coercivity for the thinnest Ni film. This implies surface roughness to be a
Figure 3.1. Coercivity as a function of film thickness for Ni thin film electrodes. A) Electroreduced, HDT coated, and surface oxidized Ni thin films compared to the Au coated standard. B) Electroreduced Ni films with and without HDT. C) Films with HDT monolayers formed by glovebox conditions and then allowed to sit for 3 days and 14 days in atmosphere or in the glovebox.
dominating factor in determining the coercivity as the film thickness becomes smaller. This is sensible given that an $R_{rms}$ of 2.2 nm is roughly 10% of the 20 nm film’s total thickness. A useful future study would be to vary the film thickness from 5 nm upward (in reasonably small intervals) and find the point at which surface roughness is no longer a contributing factor to the film’s overall coercivity.

Monolayer coated thin films were fabricated to test the stability of the monolayer coated ferromagnetic film in atmosphere and under inert glovebox conditions. Nickel thin films (20, 50, and 100 nm) were coated with HDT under inert conditions according to the glovebox SAM preparation conditions laid out in section 2.2.1 of Chapter 2. The coercivities remained roughly unchanged after allowing the surfaces to sit for 3 and 14 days in atmosphere and under inert glovebox conditions (Figure 3.1C). An interesting discovery was that of the non-linearity with respect to film thickness for HDT coated nickel thin films. The 20 and 50 nm thick Ni films possess near identical coercivities for each sample. As suggested in literature, this result implies that thiol attachment at the surface contributes a great deal to the electronic structure of the metal film [9]. As an additional note, surfaces coated with decanedithiol produced the same results as those seen by HDT.

Cobalt surfaces were not studied as extensively as Ni surfaces. Unlike Ni surfaces, Co surfaces showed a strong anisotropy with respect to the angle at which the substrate was facing during MOKE measurement. An example can be seen in Figure 3.2A where a 60 nm Co film was examined by MOKE at 0 degree and at 90 degrees. A clear variation in coercivity is seen at these two angles. Similar variation was observed at subsequent angles between 0 and 90. It is believed that the Co films align with the lattice plane of the silicon wafer beneath. This has been reported in other studies, yet it is generally uncommon for
Figure 3.2. MOKE comparison for Ni and Co.  A) Anisotropy of a typical Co thin film (60 nm) seen during MOKE measurements at 0 deg and at 90 deg.  B) Corresponding Ni thin film (50 nm) at 0 and 90 degree.  C) Coercivities versus film thickness for some Co thin films.
thick layers (> 10 Å) and for surfaces that contain an adhesion layer [10]. Depositing Ti/Co thin films onto silicon while taking note of the wafer direction confirmed that interfacial alignment with the silicon wafer may be the case as the 0 deg coercivities and 90 deg coercivities were in perfect agreement from sample to sample. However, interestingly enough, the same effect was not seen with deposited Ni surfaces (Figure 3.2B).

The anisotropy seen above should not affect a spin-valve’s functionality as long as the substrate direction is noted while acquiring the MOKE data. Therefore, a few Co systems were examined as a function of Co film thickness such as Au coated Co, bare Co that has been exposed to atmosphere (24 h), and HDT coated Co thin films (Figure 3.2C). The Co films see a distinct reduction in coercivity as the films become thicker for all three systems. Surprisingly, the HDT coated films are remarkably similar to the Co standard suggesting that the HDT monolayer is able to protect the surface from oxidation in atmosphere. Stability measurements in atmosphere were never gathered for HDT surfaces, although it would be interesting to see if the coercivities of the HDT coated Co thin films merge with the bare oxidized surfaces over time.

Electroreduced Co thin films were not studied in depth by MOKE due to the fact electroreduced Co surfaces become inherently rough during the electroreduction process (see Chapter 2). In addition, noticeable etching and pitting was seen for Co surfaces while soaking in the ethanolic alkanethiol solution after electroreduction [11]. For these reasons, electroreduced Co thin films yielded sporadic and uncontrolled coercivities. For this reason, and the display of anisotropy, Co was ruled out as a bottom contact for these experiments and the remainder of the study focused on Ni thin film bottom electrodes. Although it should be
noted that cobalt (and iron) should not been ruled out as an alternatives to Ni bottom electrodes and could be useful in future studies.

3.2.2. Device Architecture and Fabrication. Gold electrode devices were fabricated according to previous literature reports [2, 3]. Briefly, a 3 nm titanium adhesion layer was thermally deposited onto a silicon wafer through a metal shadow mask followed by the deposition of 60 nm of Au. Photoresist (MaN-140, 1 µm thick) was spuncoat onto the Au electrode and lithographic wells were opened using standard photolithography practices. The photoresist was then hard-baked at 200 °C for 2 hours to remove remaining residual solvent and to ensure complete cross-linking of the resist molecules. The substrate was then exposed to oxygen plasma treatment (80 W, 30 s) to ensure that the wells were clean and ready for molecular self-assembly. Following O₂ cleaning, the substrate was soaked in a SAM molecule solution for 24 hours. The substrate was removed from the SAM solution, rinsed thoroughly with ethanol, and a layer of PEDOT:PSS was spuncoat over the entire substrate (~ 100 nm thick). A top electrode was thermally deposited through a shadow mask. Finally, the substrate was subjected to another round of oxygen plasma cleaning (100 W, 2 min) to remove PEDOT:PSS from between the devices to prevent each device from being shorted to one another. An example of a device can be seen in Figure 3.3 along with an illustration of a generic device architecture.

Junctions formed with Ni electrodes had to be fabricated slightly differently than those from literature since Ni forms an unwanted surface oxide in air. Following the deposition of a Ti adhesion layer onto a Si/SiOₓ wafer, 100 nm of Ni was deposited through a shadow mask. Photoresist (MaN-140, 1 µm thick) was spuncoat onto the Ni substrate and wells were opened by standard photolithography methods. The substrate was hard-baked at
Figure 3.3. PEDOT:PSS protected MMM device. SEM image of a well opened on a Ni thin film electrode (top left). Illustration of a generic PEDOT:PSS protected junction (middle). Optical micrograph of completed device (front middle).
200 °C for 2 hours to remove residual solvent. The oxygen plasma cleaning procedure could be skipped for Ni electrode since it is expected that O$_2$ cleaning would only further oxidize the surface. To remove the existing oxide, the Ni electrode was electroreduced using the electroreduction conditions outlined in Chapter 2 followed by soaking in alkanethiol or alkanedithiol. Following electroreduction and SAM formation, the substrate was coated with PEDOT:PSS (~ 100 nm) and a top electrode (Ni or Co) was thermally deposited through a shadow mask followed by the deposition of 100 nm of Au to ensure quality electrical contact could be made. To finish the device, the substrate was subjected to oxygen plasma cleaning (100 W, 2 min) to remove residual PEDOT:PSS from between the devices.

3.2.3. Magnetic Properties of PEDOT:PSS Protected Molecular Junctions. Ni/SAM/PEDOT:PSS/Ni and Ni/SAM/PEDOT:PSS/Co devices were fabricated by the method outlined above and their magnetic properties were determined by MOKE. The thicknesses of the ferromagnetic electrodes were chosen based on the coercivities found by MOKE in section 3.2.1 of this chapter. The ferromagnetic thin films from both Co and Ni device architectures were shown to switch their magnetic directions independently from one another when exposed to an external magnetic field. An example of independent switching is shown for a Ni/HDT/PEDOT:PSS/Co device in Figure 3.4. For the example shown, a 60 nm Ni thin film was used for a bottom electrode and a 20 nm Co metal thin film was used for the top electrode.

The hysteresis curve for the bottom electrode was obtained by directing the MOKE light source through the photoresist to the back contact between devices (Figure 3.4, red arrow). This yielded a 45 Orsted coercivity which is what one would expect for a HDT coated 60 nm thick nickel film according to what was found previously. However, for an
Figure 3.4. Magnetically independent ferromagnetic layers in a Ni/HDT/PEDOT:PSS/Co junction. A) 60 nm Ni thin film, bottom electrode. B) Additive magnetic signal from bottom Ni (60 nm) and top Co (20 nm) electrodes. C) Superposition of top Co (20 nm) and bottom Ni (60 nm) electrode.
electroreduced nickel (60 nm) surface, 45 Oe is much smaller than what would be expected. The disparity between the two values likely arises from the difference in working electrode area during electroreduction. By masking off most the working electrode with photoresist, the working electrode area is confined to be only the area that has been exposed by photolithography. The current density within the wells is in all undoubtedly higher than that of bare, uncoated surfaces during electroreduction. Surface roughness arguments were ruled out by performing AFM within the well after the photolithography step. The root mean square roughness within the well after electroreduction was comparative to a bare electroreduced surface. To attain the coercivity of the top electrode, the MOKE laser was directed at the top Co metal thin film electrode within the well (Figure 3.4B, blue arrows). However, the laser penetrates both the Co layer and the Ni layer; therefore, the odd shape of the hysteresis is due to the superposition of two separate hysteresis loops, one for cobalt and one for nickel. The Kerr rotation of nickel’s hysteresis loop is subtracted from the overall signal when combining the two metal films due to a 180° phase shift as the light passes through the PEDOT:PSS layer. This causes a reduction in overall signal when the bottom nickel electrode switches its magnetic direction, which is portrayed by the two spikes in the hysteresis loop of Figure 3.4C. It is these two intense spikes indicate a switch in the Ni bottom electrode as the field is increased while the top Co electrode stays magnetically independent. Had they switched at the same time, the hysteresis curve would be a single smooth curve. By superimposing the bottom Ni electrode’s hysteresis on the top Co electrode’s hysteresis, it becomes obvious that the nickel and cobalt thin films switch their magnetic directions independently.
3.2.4. Electrical Characteristics. Current-voltage characteristics were gathered on both the Au electrode junctions and the ferromagnetic junctions. Combined, over a hundred junctions were tested. Nonresonant tunneling is the expected electron transport mechanism across alkanethiols since alkanes are intrinsically insulating and have shown little to no temperature dependence on electron transport in prior studies [1, 12]. Tunneling characteristics were observed in a number of junctions; however, the number of operational devices was less than ideal (< 15 %), and the resulting sigmoidal I-V curve was highly temperature dependent down to 77 K. This suggests the existence of a competing electron transport mechanism in addition to quantum tunneling (Figure 3.5). Temperature dependence on quantum tunneling could arise from pinhole defects at the device level, impurities within the junction, or residual water remaining in the PEDOT:PSS layer. In addition, the range of zero-crossing resistances was large (25 Ohm to several thousand Ohm). Despite frequent attempts, the temperature dependence was always evident. In addition, spin-valve behavior was never observed in the ferromagnet junctions even though independent magnetic switching was observed. It is likely that the electron spin polarization was not maintained as it traveled through the PEDOT:PSS layer given that it contains several heavier atoms and has a thickness on the order of the spin diffusion length (~ 100 nm) found in other organic materials [13, 14]. In the ideal case, the top ferromagnetic layer would be attached directly to the molecular layer, ruling out any interference to the electrical properties of junction by the PEDOT:PSS layer.

3.3. Experimental

3.3.1. Fabrication and Characterization. Devices were characterized by optical microscopy, scanning electron microscopy, and atomic force microscopy.
Figure 3.5. Temperature dependence on tunneling of a Au/HDT/PEDOT:PSS/Au junction.
Optical micrographs were gathered using a Zeiss Imager.D1m with an AxioCam MRm camera using AxioVision 40 V4.7.1.0 software. Scanning electron micrographs (SEM) were obtained using the electron beam capabilities on a FEI Helios 600 Nanolab Dual Beam System (accelerating voltage 15 kV, beam current 20 nA). AFM images for $R_{\text{rms}}$ roughness were collected using an Asylum Atomic Force Microscope (Asylum MFP-3D, Asylum Research). The microscope was operated in tapping mode at ambient conditions ($T = 21^\circ \text{C}, RH = 45\%$), using silicon cantilevers (BudgetSensors, Tap300Al) with resonance frequencies of approximately 300 kHz, a force constant of $\sim 40 \text{ N/m}$, and tip radii less than 10 nm.

Co, Ni, and Au metal thin films were prepared by thermal evaporation onto a Si/SiOx wafer. Prior to thermal evaporation, silicon wafers (Si/SiOx - 1 micron thick surface oxide on one side, Addison Engineering) were cleaned in a solution of DI water, ammonium hydroxide (14.8 M, Fisher Scientific), and hydrogen peroxide (ACS certified 30%, Fisher Scientific) in a 2:1:1 ratio for 15 minutes. The wafers were removed from this solution, rinsed thoroughly with water and ethanol (100%, Pharmco), and dried with a stream of dry nitrogen. Additional UV ozone cleaning (Bioforce Nanosciences ProCleaner™) was performed on the wafers for 20 minutes. Au metal thin films were prepared by thermal vapor deposition on top of a 3 nm titanium adhesion layer (2 Å/s) on Si/SiOx. Au deposition started at 1 Å/s for the first 10 Å and then was quickly increased to 15 Å/s for the duration of the vapor deposition. Nickel and cobalt metal films were prepared by thermal evaporation ($P_{\text{initial}} = 2 \sim 4 \times 10^{-6} \text{ mbar}; P_{\text{deposition}} = 2 \sim 8 \times 10^{-6} \text{ mbar}$) on top of a 3 nm titanium adhesion layer (2 Å/s) on a SiOx/Si wafer. Ni and Co were deposited at 1 Å/s for the first 10 Å then the rate was increased to 8 Å/s until the final thickness was achieved. The evaporation boats were purchased from R.D. Mathis; the specific boat for Ni and Co
evaporation was an alumina-coated tungsten boat (Type S1AO-W to avoid alloying of the metals with tungsten) while that for Ti and Au were tungsten boats (Type S4-015 W and S42-015W, respectively). Gold (99.999%), nickel (99.98%), and cobalt (99.95%) pellets (1/8” × 1/8”) were purchased from Kurt J. Lesker, Inc. Titanium slugs (99.995%, 3.175 mm × 3.175 mm) were purchased from Alfa Aesar. Thermal evaporations were performed with an MBraun evaporator contained within an MBraun nitrogen glovebox such that freshly evaporated thin films could be removed from the evaporator chamber under a nitrogen atmosphere. Thicknesses of films were determined using a quartz crystal microbalance located just below the substrate holder in the evaporator. Tooling factors were determined by measuring the true thicknesses of films with a profilometer. X-Ray diffraction spectra were obtained for the Si/SiO₂/Ti/M thin films (100 nm for Ni, Co, and Fe; 50 nm for Au; 25 nm Ti for all cases) using a Rigaku Multiplex Powder Diffractometer with Ni-filtered Cu Kα radiation (1.5418 Å) over the range 20 = 10-85°. The evaporated metal films were observed to grow with either a <111> texture (Au, Ni, and Co) or <110> texture (Fe) [15]. The grain sizes for the thin films were deduced from the X-Ray diffraction data using the Scherer equation: Ni (7.0 Å), Co (5.1 Å), Fe (8.6 Å), and Au (9.3 Å).

Photolithography was performed at CHANL (Chapel Hill Analytical and Nanofabrication Laboratory). MaN-1410 photoresist (Micro Resist Technology) was spuncoat at 3000 RPM using a Chemat Technology (KW-4A) spincoater. Exposure and mask alignment was performed using a Karl Suss MA6/BA6 mask aligner (350 W lamp, 365 nm) for 45 s. Development was done in MaD 533 (Micro Resist Technology) for 45 s. The PEDOT:PSS used was PH 500 (Clevios, H.C. Stark) and was mixed with DMSO (5 %, w/w).
to increase conductivity. PEDOT only devices yielded shorted devices with resistances less than 100 Ohm.

Oxygen plasma cleaning was done with an AutoGlow O₂ plasma system (Glow Research).

3.3.2. Magneto Optic Kerr Effect Measurements. Magnetization studies were carried out using an experimental set-up that measures the Magneto-Optic Kerr Effect, and is designed to operate as described by Sato [16]. In the experiments here, a birefringent photoelastic modulator (PEM) modulated the reflected laser beam, in order to separate the polarization components of rotation and ellipticity in the reflected beam. This was done using lock-in techniques since both components are proportional to the magnetization in the sample. In the conventional set-up, the laser output from a diode laser (K-Space Associates) at a wavelength of 664 nm passes through a focusing lens and then through a Glan-Thompson prism polarizer set at 0° to polarize the laser light (p-polarization). The laser beam reflects off of the sample mounted perpendicular to the plane of incidence in the vacuum chamber between the poles of an electromagnet. The reflected beam passes through the birefringent photoelastic modulator (or PEM) (Hinds Instruments model PEM-90, modulation frequency 50 kHz and set to λ/2), an analyzer, and finally a Glan-Thompson prism (45° rotation from the polarizer). The light is focused through a lens onto a photodiode.

The signal from the photodiode is passed to two lock-in amplifiers, one using a reference source supplied from the PEM controller at 1× the PEM modulation frequency (1 ω = 50 kHz) and a second using a reference source from the PEM controller at 2× the PEM modulation frequency (2 ω = 100 kHz). The two signals are de-convoluted by the lock-in
amplifiers. They correspond to the change in ellipticity (1\(\omega\)) and rotation (2\(\omega\)) undergone by the incident polarized light as a result of the MOKE effect. The analysis here focused primarily on the 2\(\omega\) Kerr rotation signal.

The magnet is driven by a Kepco Power Supply ATE 100-10M. The DC signal from the photodiode is input into a Hewlett-Packard 3456A Digital Voltmeter. The entire experiment is operated by a Labview program. The main function of the program is sweeping of the magnetic field by increasing or decreasing the output of the power supply which controls the current through the electromagnet. Positioning is also controlled on the sample surface via two stepper motors that change the horizontal and/or vertical location of the sample. Positioning onto the individual device or region of interest was aided with the use of a CCD camera (Adimec MX12P).

### 3.3.3. Probe Station Current-Voltage Measurements.

Devices were measured on an Alessi Industries probe station using four probes for a four-terminal measurement. Of the four probes, two were Alessi Industries probes and two were Signatone Model S-600 probes. The circuit for the I-V measurement included a DC source and an AC function generator for measurement of the instantaneous conductance with a lock-in amplifier. The DC source was a Keithley 230 Programmable Voltage Source, and the AC function generator was a Wavetek Model 270 12MHz Programmable Function Generator. The function generator was connected across the primary windings of a conventional transformer to step down the input voltage (usually set to 300 mV unless otherwise noted) in order to output a 24.64 mV peak sine wave at the secondary winding. The DC source was connected in series to this secondary winding on the transformer, followed by connection to one side of the top electrode crossbar on the SAM device via the probe. Next a probe was connected to the back
(bottom) electrode on the sample wafer, and this leg of the circuit then went to an op-amp based current converter/amplifier hard-wired to convert the input current into a voltage signal at a magnitude of 100× that input current. The output voltage signal from the current amplifier was branched to a Keithley 2182A Nanovoltmeter, to read the voltage-converted DC current signal, and, on the other side of the branch, to a Stanford Model SR830 Lock-In Amplifier to read the modulated current signal occurring at the specific DC voltage. The DC voltage across on the other two terminals (top electrode to bottom electrode) was recorded by a Keithley 6514 Electrometer. A labview program ran the various meters and recorded the data for the I-V and conductance measurements.

3.3.4. Low Temperature Current-Voltage Measurements. To put a sample into the vacuum chamber, a small portable vacuum chamber was used (approx. 5″ × 3″ × 2″). This was necessary to create leads going from the electrodes of the sample to soldered connections on a feed-through in the walls of the vacuum chamber to perform measurements using the same measurement equipment above as was used on the probe station. To make electrical connections into the vacuum chamber, the sample wafer was first affixed to a separate wafer with a 1 micron silicon oxide layer. Photolithographic gold pads were formed on the Si/SiO$_x$ wafer for wire-bonding and soldering, since soldering directly to the device could easily over heat and short the device. Larger wires were soldered onto the pads of the photolithographic pattern so that they could make a continuous contact to the 0.010″ diameter aluminum wires wire-bonded onto the opposite end of each pad. The wire-bonding was performed on a Kulicke and Soffa model No. 1413 wire-bonder. The vacuum chamber is an MMR (MicroMiniature Technologies) vacuum chamber that is capable of cooling the sample down to liquid nitrogen temperature (77 K). The design makes use of small capillaries for the flow
of gas inside a glass sample mounting arm. When the gas reaches the sample mounting location, the capillary expands out into a small expansion chamber (also inside the glass), allowing cooling of high-pressure nitrogen gas by the Joule-Thompson effect. The gas used was a high purity nitrogen (99.999%) compressed gas cylinder (National Welders). A silicon diode affixed to the gold sample mounting pad inside the MMR chamber at the cooling point (gas expansion point) is used to monitor the sample temperature. To reach a specific set point temperature, a Lakeshore 330 Temperature Controller monitors the temperature using the diode, and increases or decreases the voltage output to a heater circuit also located underneath the gold sample mounting pad. The heater is capable of heating against the cooling effect and can bring the sample temperature rapidly from 77 K to room temperature, for example, if desired. The sample holder wafer with the sample mounted onto it is mounted onto the sample mounting pad using Dow-Corning 340 silicone heat sink compound (a type of thermal grease).

A turbo pump system consisting of a Varian DS102 roughing pump and a Varian Turbo-V 70D Macro Torr turbo pump controlled by a Varian Turbo V-70 controller was used to pull vacuum (~ 5 × 10⁻⁶ Torr) prior to low temperature measurement. A Granville-Phillips 270 Gauge Controller was used to determine the pressure by reading either an MKS ion gauge or a Duniway Stockroom DST-06M thermocouple mounted inside the vacuum system. A 3/8” inside diameter rubber tube connected the vacuum pump system to the vacuum chamber. The chamber is small enough so that it can also be placed between the poles of an electromagnet in order to perform magnetic field measurements on the sample. Control of the magnet is done using a Labview program (as described in the MOKE section), and electrical measurements are performed at different applied fields.
3.4. References


CHAPTER 4

Metal-Molecule-Metal Junctions via Nanotransfer Printing (nTP) onto Self-Assembled Monolayers
4.1. Introduction

The soft lithographic method, nanotransfer printing (nTP), has been shown to form permanent and stable metal electrodes on molecular layers without damaging the SAM beneath. In theory, metal thin films thermally deposited onto elastomeric soft polymer stamps with defined recessed features can be transferred to any surface as long as the metal thin film has a higher affinity for the receiving substrate than that of the stamp. Often this requires covalent binding between the metal to be transferred and the substrate to achieve high quality transfer. Most nTP studies use elastomeric poly(dimethylsiloxane) (PDMS) as a patterned stamp since PDMS is cheap, flexible, and easy to fabricate on a variety of surfaces and in a variety of shapes. Work in this area has been quite successful yielding high quality patterns of metal thin films covalently bound to SAMs formed on near atomically smooth surfaces such as silicon [1], glass [2], and n+ doped GaAs [3, 4]. However, on rough surfaces via thermal vapor deposition, production of practical Au/SAM/Au [5] and Co/SAM/Co [6] MMM junctions via nTP has been limited due to inadequate metal film transfer.

Recently, perfluoropolyether (PFPE) stamps were used to transfer Au thin films onto silicon substrates [7]. Since the surface energy of PFPE (~ 15 mJ/m²) is significantly lower than that of PDMS (22-25 mJ/m²), using PFPE eliminated the need for surface functionalization of the receiving surface prior to transfer. This finding suggested that PFPE could be useful for transferring other materials that have thus far been unable to be transferred by PDMS. In addition, PFPE has a higher modulus (~ 4 MPa) than PDMS (~ 1.5 MPa) and is less prone to lateral feature collapse during transfer which is important for transferring nanometer sized, tightly compact arrays. Despite these attractive properties, prior to this work, nTP by PFPE had yet to be thoroughly studied.
This chapter focuses on a simple, reliable method to fabricate MMM junctions by PDMS and PFPE based nTP. A variety of MMM junctions were fabricated via nTP by printing Au, Co, and Ni thin films onto SAM coated Au, Co, and Ni electrodes. Au/alkanedithiol/Au junctions were studied in depth through electrical studies by conductive probe atomic force microscopy (c-AFM). The SAMs used were variable length alkanedithiols. Nonresonant tunneling is the customary electron transport mechanism across alkanedithiol systems since alkanes are intrinsically insulating and have shown little to no temperature dependence on electron transport in prior studies [8, 9]. Scalable tunneling characteristics were observed based on tunneling area (i.e. printed feature size) and tunneling distance (i.e. molecule length), and the electrical characteristics were interpreted by means of the classical tunneling model through a thin film insulator as laid out by Simmons [10]. Ferromagnetic MMM junctions were formed using nTP with Ni and Co thin films and are appealing for molecular spintronics. The magnetic properties of nanotransfer printed and thermally deposited films were probed by using the Magneto Optic Kerr Effect (MOKE).

4.2. Results and Discussion

4.2.1. General Printing Procedure. Figure 4.1 shows the general schematic for nanotransfer printing used in several systems in literature [1-7, 11]. For the work illustrated here, the process is as follows: 1) Si/SiO$_x$/Metal/SAM substrates are fabricated as described using the glovebox SAM formation conditions outlined in Chapter 2. Briefly, a metal thin film deposited on a Si/SiO$_x$ substrate by thermal evaporation is immediately immersed in an ethanolic SAM molecule solution under a nitrogen atmosphere in a glovebox. This solution is allowed to soak for 24 to 48 hours within the glovebox to ensure complete SAM formation at the metal surface. 2) The substrate is removed from the SAM solution, rinsed by ethanol,
Figure 4.1. General schematic for nanotransfer printing. A) A SAM coated metal thin film substrate is brought into contact with a polymeric stamp coated with a metal thin film and allowed to interact for > 1 min. The metal on the stamp covalently binds to the exposed monolayer. B) The stamp is slowly peeled away from the substrate revealing a well defined array of metal-molecule-metal junctions (shown in C).
sonicated in tetrahydrofuran (THF) for 30 seconds to remove residual physisorbed molecules, dried with a stream of N₂ gas, and further dried in a vacuum chamber (1 mbar) for an hour.  
3) Separately yet simultaneously, an elastomeric stamp with a preset relief pattern is coated with a metal thin film (10 – 30 nm) by thermal vapor deposition.  
4) The dry metal/SAM substrate is removed from the vacuum chamber while the stamp is removed from the vacuum deposition chamber and the two are immediately (< 5 min) brought into intimate contact under N₂ inside a glovebox.  
5) After a sufficient amount of contact time (> 10 min) to ensure adequate covalent binding between the metal film and the functionalized SAM, the stamp is peeled from the substrate leaving behind the mirror image of the stamp’s raised pattern.

4.2.2. Perfecting nTP on Au/SAM Substrates using PDMS Stamps. Since Au/thiol chemistry is well behaved and Au does not quickly form unwanted surface oxides, initial investigations were focused on constructing simple Au/SAM/Au junctions with octane, decane, dodecane, and tetradecane dithiols. This was done to optimize the parameters needed to obtain reproducible high quality transfer for Au/alkanedithiol/Au systems and to reassign the knowledge gained from these studies to be used in systems with other more complex SAM molecules and/or while printing other metal thin films.

Initial attempts to apply the standard PDMS based nTP protocol described above to Au/alkanedithiol systems produced little to no transfer, even while applying external pressure to the stamp to force Au/SAM interaction. It was assumed that un-cleaned, crude PDMS stamps would hinder transfer; therefore, PDMS stamps were cleaned by UV ozone, oxygen plasma etching, and Soxhlet extraction in ethyl acetate but yet again yielded the same results. In contrast, gold thin films (20 – 30 nm thick) have been transferred with PDMS stamps onto atomically smooth GaAs/SAM and SiOx/SAM layers relatively easily, in high resolution,
and without externally applied pressure [3, 4, 12-14]. The only variation in the Au/SAM/Au structure presented here is the bottom Au contact; therefore, it was suspected that the lack of transfer depended on discrepancies at the bottom Au electrode such as on the surface roughness of the Au electrode or the density of the molecular monolayer.

There have been numerous studies on monolayers formed from alkane(mono)thiols and it is generally accepted that alkanethiolates form ordered (√3 × √3)R30° domains on Au(111) films with the alkyl tails oriented 26 - 31° from normal to maximize van der Waals interactions [15-19]. It is also well known that local surface conditions such as surface roughness, surface defects, and grain boundaries can directly determine the SAM density and tilt angle in any given region [15, 20]. Therefore, in order to maximize the terminal thiols available for covalent attachment during nanotransfer printing, it is expected that the surface roughness be minimized. Similar to alkane(mono)thiols, alkane(di)thiols (longer than hexanediithiol) have been shown to orient themselves vertically from metal surfaces in free standing arrays with only one thiol attached to the surface [21-23]. However, monolayers from alkanedithiol solutions have a greater dependence on concentration and soak time than their monothiol counterparts due to the fact that both thiol ends are active to the Au surface. In the case of relatively long alkanedithiols (> 1 nm), as is the case with decanediithiol and longer, it has been suggested that the molecule can loop back on itself allowing both thiols to attach to the Au surface [24, 25]. In addition to minimizing surface roughness, the SAM density should be maximized during SAM formation to expose more terminal thiols for covalent attachment during nTP.

Lowering surface roughness was the initial objective. Literature suggests that the technique by which the a metal is deposited onto a substrate can greatly dictate the overall
root mean square (R_{rms}) roughness and quality of the resulting film [26]. Following the deposition of a 3 nm titanium adhesion layer onto a Si/SiO_x wafer, 60 nm of Au was deposited two different ways: 1) at a constant rate of 1 Å/s, or 2) at a rate of 1 Å/s for the initial 10 Å followed by an increase to 15 Å/s until the final thickness (60 nm) was achieved. The resulting surfaces were analyzed by atomic force microscopy and it was seen that the average R_{rms} roughnesses dropped dramatically from 1.163 nm to 0.605 nm (Figure 4.2).

Since the SAM molecules used are short (~ 1 – 2 nm), this substantial change in R_{rms} is expected to greatly affect the number of exposed thiol groups available for binding to the top electrode during nTP. It was found that when the bottom contact was deposited by method 2, nTP was successful albeit sporadic and mediocre quality.

Further investigation looked to the concentration of the SAM solution required to adequately self-assemble the monolayer to allow enough active thiol groups for quality nTP. To do this, separate bottom Au electrodes were individually soaked in 1 mM, 5 mM, 10 mM, and 30 mM SAM solutions for 24 hours. They were then removed from their respective solutions, sonicated in THF for 60 seconds to removed physisorbed molecules, dried by a stream of N_2, and placed in a vacuum chamber (1 mbar) for 1 hour to remove residual solvent. Using PDMS stamps formed simultaneously from the same master, 20 nm thick Au films were nanotransfer printed concurrently to each surface and allowed to contact the surface for the same length of time. No transfer was observed on the 1 mM surface, while the 5 mM and the 10 mM surfaces showed only partial transfer. The 30 mM surface yielded complete Au transfer to the bottom electrode (Figure 4.3). Electrodes soaked in more concentrated solutions showed equal quality transfer to the 30 mM surface while allowing the electrodes to soak for 3 days and 7 days neither improved nor hindered the transfer.
Figure 4.2. Atomic force microscopy images of thermally deposited Au thin films. A 60 nm Au surface deposited at a constant rate of 1 Å/s (top) and a 60 nm Au surface deposited at 1 Å/s for the initial 10 Å followed by an increase to 15 Å/s for the final thickness of the film (bottom).
Figure 4.3. Concentration dependence on nTP. Surfaces soaked in 5 mM and 10 mM SAM solutions show partial, fragmented transfer while soaking in 30 mM SAM solutions yielded complete transfer of the features.
process with Au surfaces.

Once $R_{\text{rms}}$ was minimized and SAM density was maximized, complete features were able to be transfer printed; still, it was often the case that regional defects occurred during transfer. One recurring defect seen on nearly all nanotransfer printed substrates was a defect where the feature contained a void in the middle of the printed feature while the remainder of the feature printed fine. Also, features had a tendency to crack at the edges, which can be seen in the 30 mM features of Figure 4.3. Optical and AFM images of the Au coated stamps prior to nTP showed smooth, flat surfaces (Figure 4.4A, 4.4B), ruling out an issue with the stamp prior to printing; therefore, the problem had to come from the printing process itself. Given the appearance of the ‘void’ defect (Figure 4.4C), it seemed as though some material was trapped under the feature during transfer. The substance could come from a variety of sources such as trapped air under the feature while making contact to the Au/SAM substrate or residual remaining surface bound solvent or water. Additionally, the fate of the hydrogen from the thiol group is still relatively unknown during chemisorption of the thiolated SAM to the printed Au film. It has been suggested that removal of the hydrogen atoms results in either $H_2$ evolution driven by entropy gain or water through oxidative conversion (employing surface bound solvents) [16]; in any case, removal of this material is required. If it is assumed that any of the three postulates could be correct, air, surface bound solvent/water, and $H_2$/water formation could easily be removed under vacuum. In practice, Au coated PDMS stamps and the Au/SAM surfaces were brought into intimate contact. The whole setup was placed in a vacuum system and was evacuated to $1 \times 10^{-6}$ mbar for 1 hour. Once removed from the vacuum, the PDMS stamp was peeled from the substrate revealing clean, consistent, high quality nanotransfer printing over the whole substrate (Figure 4.4D).
Figure 4.4. Possible defect formation during nTP. A) Optical micrograph of a PDMS stamp after being coated with 20 nm of Au. B) Atomic force micrograph and cross section of a PDMS stamp coated with Au. C) SEM image of reoccurring defect seen following nTP. D) Optical micrograph of nTP after pulling a vacuum. Inset shows an SEM image of a single feature.
After perfecting Au nanotransfer printing using PDMS stamps onto Au/SAM substrates, a series of interesting designs and features were printed, including but not limited to: printing various size (and shaped) features from 5 µm up to 5 mm, printing reverse ‘honeycomb’ patterns, and printing ordered and well spaced features onto SAM coated, thermally deposited thin wires. Examples of printed features can be seen in Figure 4.5.

**4.2.3. Nanotransfer Printing Ferromagnetic Thin Films.** For spintronic devices, ferromagnetic thin films would need to be transfer printed to form ferromagnet/SAM/ferromagnet junctions. Mimicking the Au/SAM/Au study, it was expected that R_{rms} of each surface would be reduced dramatically as the deposition rate of Ni and Co thin films increased. Following the deposition of a 3 nm Ti adhesion layer, Ni and Co were deposited via two different ways: 1) at a constant rate of 1 Å/s, or 2) at a rate of 1 Å/s for the initial 10Å followed by an increase to 8 Å/s until the final thickness (60 nm) was achieved. As expected, Ni R_{rms} roughness decreased from 1.242 nm to 0.470 nm and Co surface R_{rms} decreased from 1.139 nm to 0.387 nm (Figure 4.6).

Since Ni and Co are known to form unwanted surface oxides readily in atmosphere, every processing step in the fabrication of Ni/SAM/Ni and Co/SAM/Co molecular junctions needed to be performed under inert N₂ glovebox conditions. All solvents used while processing Ni and Co films were dry and purged with N₂ prior to use. As a benchmark, Au/SAM/Au junctions were formed in tandem with the Ni and Co junctions. Co/SAM, Ni/SAM, and Au/SAM surfaces were fabricated according to the glovebox conditions laid out in Chapter 2 using 30 mM N₂ purged, ethanolic solutions of alkanedithiols. For Au nTP, 20 nm of Au was thermally deposited onto PDMS stamps at 1 Å/s for the first 10 Å followed by 15 Å/s for the final thickness of the film. For Ni nTP, 10 nm of Au was first deposited on
Figure 4.5. Au/SAM/Au junctions by nTP with PDMS. Each feature was printed using PDMS stamps coated with 20 nm of Au. A) Inverse ‘honeycomb’ pattern printed on 30 mM surface soaked in decanedithiol SAM solution. B) 100 µm features printed on a decanedithiol coated thermally deposited Au thin film wire. C) Tar Heels printed on 30 mM a tetradecanethiol surface. D) 420 µm and 50 µm Au features printed on octanethiol surfaces.
Figure 4.6. Rate dependence on surface roughness for Ni and Co films. AFM of Ni films deposited at 1 Å/s (top left) and Ni films deposited at 8 Å/s (top right). AFM of Co films deposited at 1 Å/s (bottom left) and Co films deposited at 8 Å/s (bottom right).
the PDMS stamp (at 1 Å/s for 10 Å then 15 Å/s), followed by 10 nm of Ni at 2 Å/s. Similarly, for Co nTP, 10 nm of Au was first deposited on the PDMS stamp (at 1 Å/s for 10 Å then 15 Å/s), followed by 10 nm of Co at 2 Å/s. Cobalt is expected to have a higher affinity for thiol than even that of gold [27] so it was anticipated that Co thin films should print very easily. This was indeed the case as the Au/Co thin films printed very rapidly onto Au/SAM, Ni/SAM, and Co/SAM surfaces, in mere seconds, and without the need of vacuum. A general observation seen was that the interaction between Au/Co coated stamps and dithiols surfaces was noticeably stronger than printing Au thin films. Examples of Co/SAM/Co junctions are shown in Figure 4.7A.

Nanotransfer printing of nickel films behaved differently than expected. Thiols on nickel have been calculated to have a higher absorption energy than on Au [19] and in contrast to thermodynamic calculations [28], the Ni-thiol bond has been observed in practice to be stronger than the Au-thiol bond in a number of cases [29, 30]. Therefore, nTP of Au/Ni thin films was expected occur fairly easily. However, while it should be noted that nTP with Au/Ni is able to be carried out using PDMS and an example of quality Ni/SAM/Ni junctions can be seen in Figure 4.7B, most transfer was sporadic, fractured, and typically required external force to promote covalent attachment from the thiol surface to the printed Au/Ni thin film. Stamps with thermally deposited Au (10 nm) and Ni (10 nm) seemed to be more rigid than their Au and Au/Co counterparts which could explain the difficulties seen while transfer printing Au/Ni thin films as the stiffness of the stamp/Au/Ni could hinder complete contact between the stamp and the surface functionalized monolayer. However, attempts to elucidate the differences in modulus between the three systems by nanoindentation were inconclusive. In addition to being difficult to print complete substrates, many features that were printed
Figure 4.7. Nanotransfer printed Au/Co and Au/Ni films. A) Co/alkanedithiol/Co/Au, B) Co/alkanedithiol/Ni/Au, and C) an example of a typical brittle-like defect seen while printing Au/Ni to form a Ni/tetradecanedithiols/Ni/Au junction.
with Au/Ni were cracked, suggesting thermally deposited nickel thin films to be fairly brittle. Evidence of the brittle nature of Ni can be seen in the example in Figure 4.7C showing a representative feature of Au/Ni as printed by PDMS.

4.2.4. Nanotransfer Printing using PFPE Stamps. Though PDMS based nTP successfully demonstrated the construction of MMM junctions on the micrometer scale, several issues were encountered when attempting to transfer smaller features (≤ 1 µm). Replication of submicron masters using PDMS deemed difficult, and when master replication was possible, partial transfer or lateral stamp collapse was often observed. Although micron scale metal-molecule-metal junctions are interesting in the formation of permanent large scale molecular electronic and molecular spintronic devices, the ultimate miniaturization of MMM junctions exists in the nano-regime. Furthermore, the electronic properties of nanoscale MMM junctions could be easily probed via conductive probe atomic force microscopy. These issues prompted pursuit of other elastomeric soft polymer stamps. One such candidate is, perfluoropolyether (PFPE). It is known from literature that liquid PFPE can be molded from silicon masters with features much smaller than a micron. In a similar process, liquid PFPE can be replicated from PFPE molds with submicron features [31]. In addition, PFPE has a higher modulus than PDMS and boasts a surface energy of ~ 15 mJ/m², significantly lower than that of PDMS (22-25 mJ/m²). The elevated modulus of PFPE makes it a promising candidate for submicron nTP since it is more rigid and less prone to lateral stamp collapse while printing tightly compacted, nano arrays. The low surface energy has been shown to eliminate the need for surface functionalization of the receiving surface prior to transfer in some cases [7]. This suggests that PFPE could be useful in transferring materials that are difficult to transfer by PDMS such as Au/Ni.
Nanotransfer printing Au, Au/Ni, and Co/Ni thin films onto Au/SAM, Ni/SAM, and Co/SAM surfaces using PFPE stamps was very successful. Using the same processing procedure as printing by PDMS, it was found that a large range of features could be successfully and reproducibly printed ranging from as small as 200 nm to as large as 200 µm. Furthermore, the many of the problems experienced with Au/Ni nTP using PDMS stamps went away upon employing PFPE stamps.

4.2.5. Morphological Considerations in PDMS and PFPE nTP. It was shown already that surface roughness of the bottom thin film electrode plays a crucial role in the final quality of nTP (section 4.2.2). This implies that nTP is a highly surface sensitive technique. For that reason it would also be expected that the surface roughness and morphology of the thin films, as deposited on the polymer stamps, would be significant in determining the outcome of nTP. Furthermore, it is appealing to compare the printed features as a function of the polymer stamp used to print the features (PDMS vs PFPE) and as a function of the film morphology as deposited on the stamp. AFM and SEM were used to characterize the features and determine the $R_{\text{rms}}$ of the features after transfer printing. In addition, AFM was used to determine $R_{\text{rms}}$ of the films as deposited on the stamps.

Using flat stamps replicated from a cleaned, near-atomically smooth silicon wafer, 20 nm of Au was deposited on both PFPE and PDMS side-by-side starting at 1 Å/s for the first 10 Å, followed by 15 Å/s for the final thickness. The $R_{\text{rms}}$ roughness of the Au film on PFPE (0.586 nm) stamps was lower than that on PDMS (1.014 nm) stamps (Figure 4.8A). It has already been proven that nTP is a surface sensitive process given that the alkanedithiols used for surface functionalization are relatively short. Based on the elevated surface roughness of the Au on PDMS, it would be expected that the resulting nTP features would be better via
Figure 4.8. Determining the quality of Au on PDMS and PFPE stamps as well as after printing. A) AFM images of 10 nm of Au deposited on flat PDMS (left) and PFPE (right) stamps. B) AFM and SEM of 10 nm Au features printed on Au/decanedithiol with PDMS (left) and PFPE (right)
PFPE transfer printing. Gold coated PFPE and PDMS stamps from the same thermal deposition were used to nTP onto Au/decanedithiol substrates. The resulting features were analyzed by AFM and SEM. As expected, the features printed by PFPE gave a surface roughness of 1.539 nm and appeared smooth and relatively crack free by SEM. The surfaces printed using PDMS gave a slightly higher $R_{\text{rms}}$ (1.871 nm) and appeared to have a much different surface topology with a hint of surface cracking (Figure 4.8B). Similar results were seen for Ni and Co films. Au/Ni film $R_{\text{rms}}$ plummet from 1.121 nm when thermally deposited on PDMS to 0.454 nm when deposited on PFPE. Likewise, Au/Co films’ $R_{\text{rms}}$ dropped from 0.998 nm to 0.617 nm for PDMS and PFPE respectively.

4.2.6. Conductive Properties of Metal-Molecule-Metal Junctions via c-AFM. The process of nanotransfer printing outlined above has offered the unparalleled ability to easily form MMM junctions of varied size and electrode composition. However, before practical and permanent molecular electronic devices can be realized it is important to understand the fundamental electrical properties of the junctions themselves. Conductive atomic force microscopy (c-AFM) is a well established technique, and it can be used to prove the capabilities of nTP as a viable process to produce stable and reproducible MMM junctions. It can also be used to study the electrical integrity of transfer printed MMM junctions as well as reveal intricate details about the nTP process itself.

The study presented within this section will focus primarily on Au/alkanedithiol/Au junctions since c-AFM is performed under atmospheric conditions and Ni and Co are known to readily form oxides in atmosphere. Oxide formation in Ni and Co systems would provide extra tunneling barrier at both metal/thiol interfaces. Since nickel and cobalt oxides are well known insulators, it would be expected that the electrical properties in Ni and Co systems
would vary over time and in turn be unreliable. This was indeed the case in preliminary studies where 200 nm Ni/decanedithiol/Ni/Au and Co/decanedithiol/Co/Au were analyzed by c-AFM [11]. Those studies showed that c-AFM results for Ni and Co MMM junctions were irregular yielding a wide range of junction resistances.

Nonresonant tunneling is the customary electron transport mechanism across generic alkanedithiols since alkanes are intrinsically insulating and have shown little to no temperature dependence on electron transport in prior studies [8, 9]. More specifically, tunneling is expected to be the transport mechanism in Au/alkanedithiol/Au junctions given that gold’s Fermi level is more or less centrally located between alkanedithiols’ large (8 – 10 eV) highest occupied molecular orbital – lowest unoccupied molecular orbital (HOMO-LUMO) gap. Moreover, previous studies using Au electrodes have followed nicely with the Simmons equation [8, 21, 32] for tunneling current through thin film insulators which assumes a simple square rectangular tunneling barrier (Figure 4.9) and is defined by the equation [10]:

\[
I = \left(\frac{qA}{4\pi^2\hbar d^2}\right) \left\{ \left(\Phi_B - \frac{qV}{2}\right) \cdot \exp \left[ -\frac{2(2m)^{1/2}}{\hbar} \alpha \left(\Phi_B - \frac{qV}{2}\right) \frac{d}{\alpha} \right] \right. \\
- \left(\Phi_B + \frac{qV}{2}\right) \cdot \exp \left[ -\frac{2(2m)^{1/2}}{\hbar} \alpha \left(\Phi_B + \frac{qV}{2}\right) \frac{d}{\alpha} \right] \right\}
\]

(1)

where \(A\) is the tunneling junction area, \(m\) is the electron mass, \(d\) is the tunneling barrier distance (in this case, molecule length), \(\Phi_B\) is the barrier height, \(V\) is the applied bias, and \(\alpha\) is a unitless adjustable parameter that has been introduced to modify the rectangular barrier. At low-bias, we expect direct tunneling and use the approximation:

\[
I \approx \left(\frac{(2m\Phi_B)^{1/2}}{\hbar^2 d} \left(\frac{\alpha}{q^2}\right)\right) A V \cdot \exp \left[ -\frac{2(2m)^{1/2}}{\hbar} \alpha (\Phi_B)^{1/2} \frac{d}{\alpha} \right]
\]

(2)
Figure 4.9. A generic rectangular tunneling barrier for a MMM junction. Represented with a spacing distance, $d$, for an alkanedithiol. The two metal’s Fermi level is represented by the blue dotted line ($E_F$).
where the low bias resistance can be expressed as:

$$R = \left( \frac{4\pi^2\hbar^2d}{A(2m\Phi_B)^{1/2}q^2\alpha} \right) \cdot \exp\left[ \frac{2(2m)^{1/2}}{h}\alpha(\Phi_B)^{1/2}d \right]$$  \hspace{1cm} (3)

According to equation 1, Au/alkanedithiol/Au junctions should be sensitive to both tunneling area (i.e., printed feature size) and tunneling distance (i.e., molecule length). To test the transfer printed MMM junctions, four different alkanedithiols were employed and current-voltage curves were collected on 200 nm diameter junctions containing octanedithiol (ODT), decanedithiol (DDT), dodecanedithiol (DDDT), and tetradecanethiol (TDDT). Variable sized junctions were also printed on Au/decanedithiol. The printed feature sizes were 200 nm diameter circles, 3 \( \mu \)m squares, 5 \( \mu \)m squares, and 7 \( \mu \)m diameter circles (Figure 4.10). In an effort to minimize contact resistance between the conductive tip and printed features during c-AFM measurement, substantially large area AFM cantilevers (80 - 110 nm in diameter) were custom manufactured. The tips were fabricated from standard silicon cantilevers which were coated via sputter deposition by 25 nm of Ti adhesion layer followed by 200 nm of Au (Figure 4.11).

Prior to static contact mode measurements on individual junctions, two dimensional conductive mapping of the printed surfaces was obtained under a 1.0 V surface bias and a grounded conductive tip. In Figure 4.12, a 2D conductive map was superimposed over the corresponding height map (gathered simultaneously) and shows definitive contrast in the junction’s current on and off the transfer printed feature.

In the case that tunneling characteristics are observed, the results can interpreted using the simplified Simmons equation which describes classical tunneling through an insulating thin film [10]. Adjusting fit parameters such as tunneling barrier height (\( \Phi \)),

111
Figure 4.10. Au/decanedithiol/Au junctions via PFPE nTP. A) 200 nm diameter junctions. B) 3 µm squares. C) 5 µm squares. D) Three dimensional AFM of 7 µm diameter junctions.
Figure 4.11. Au coated silicon cantilever for conductive atomic force microscopy measurements.
Figure 4.12. 2D conductive map of 7 µm features by c-AFM. The inset graph shows I-V characteristics gathered in contact mode from atop 200 nm features from the same sample after 1 day (black) and after 7 days in atmosphere (red).
junction area (A), tunneling distance (d), and alpha (α), a nonlinear least-squares best fit can be used to fit the Simmons equation to the raw data.

For the molecule length dependent study, I-V characteristics were gathered from 25 individual 200 nm junctions for each molecule length. Junction resistance values were collected from the linear, zero-crossing low bias regime and can be seen in Figure 4.13A. As expected, the current was scalable as a function of molecule length (Figure 4.13A - inset) and the resistance was found to increase as the tunneling distance became larger (i.e., increase in molecule length). By performing Simmons fitting with three free floating parameters (barrier height, alpha, and tunneling distance) it was found that the nTP junctions yielded barrier heights of 2.79, 3.19, 3.64, and 3.88 eV for octane, decane, dodecane, and tetradecane dithiols respectively (Figure 4.13B). These values are significantly closer to the predicted theoretical value (~ 3.0 – 5.0 eV) for alkanedithiols [33] when compared to the barrier heights for the same molecules found by other analytical techniques [8, 21, 34, 35]. While the reason for this is still relatively unknown, one possible explanation for the large barrier height is that an nTP junction forms direct and permanent covalent linkage atop the self-assembled monolayer, providing a more stable and reliable test bed when compared to other methods. A well defined, covalently bound top electrode is significant since the metal/molecule interfaces and the molecules’ local environment are considered critically important to the tunneling mechanism across MMM junctions [36-38]. For example, covalent attachment to gold electrodes was found to alter the tunneling current density of MMM junctions by three orders of magnitude when directly comparing junctions with and without PEDOT:PSS [39]. Even so, PEDOT:PSS protected junctions, conductive probe techniques, break junctions, and others have all obtained barrier height values well below
Figure 4.13. I-V characteristics as a function of alkane chain length. Results for octane (C8), decane (C10), dodecane (C12), and tetradecane (C14) dithiols. A) Average resistance as a function of chain-length. Absolute value of I-V curves (inset). B) Barrier height as a function of chain length. C) Tunneling distance (d) as a function of chain length. D) Tunneling distance (d) versus book values.
2.5 eV [21, 34, 40, 41]. The inherent surface roughness of the printed top electrode that arises during the printing process may have the largest effect on the final tunneling. However, a rougher electrode should increase the effective tunneling area as a rough surface should have a significantly larger effective area. This would likely lower the fitted tunneling barrier since the fitting performed here fixed the area during the fitting process to the expected area for the 200 nm diameter features.

As expected, tunneling distance increased as a function of molecule length (Figure 4.13C). Plotting fitted tunneling distances versus book values for SAM monolayer length [16] gives a linear plot with a negligible y-intercept (Figure 4.13D). This suggests that the printing technique and the Simmons fitting were successful.

For the tunneling area experiments, more than 50 individual I-V curves were gathered for each of the four sized features printed by nTP as mentioned earlier (all were printed on Au/decanedithiol). The I-V curves were averaged and the results can be seen in Figure 4.14B (absolute value of current is shown). An interesting artifact noticed for each of the area dependent I-V curves is that they are asymmetric with respect to bias. In Figure 4.14A, the 200 nm Au/decanedithiol/Au is shown with the absolute value of both current and bias. The positive bias regime shows a higher current, suggestive of an asymmetric junction. In theory, the MMM junction is symmetric with two gold electrodes and a dithiol tunneling barrier; yet, the Au electrodes are fabricated in vastly different fashions. The difference in current in the positive and negative regime points to the fact that the bottom electrode is more conductive than the printed feature. This is expected given the rough nature of the printed electrode.

Strangely, the tunneling distance varied with printed feature size (Figure 4.14C).
Figure 4.14. I-V characteristics of various printed feature sizes. A) Example of asymmetry seen in current-voltage curves (absolute value of current and voltage shown for positive and negative bias). B) Current-Voltage for different feature sizes (absolute value of the current is shown) C) Tunneling distance (d) dependence on printed feature size.
The reason for this is unclear, and future studies will be aimed at determining the cause for this abrupt change. One possible explanation would be the formation of air pockets or larger tunneling gaps under features as the printed junction becomes larger. This would be anticipated since forming conformal contact to the bottom electrode would be increasingly more difficult as the printed feature becomes larger.

4.2.7. Magnetic Properties of Printed Ferromagnetic Metal Thin Films.

Ferromagnetic thin films have proven difficult to nanotransfer print in most systems with successful transfer printing being detailed in only a limited number of reports [6, 42]. Yet to date, no one has reported the magnetic properties of nanotransfer printed ferromagnetic films. As with thermally deposited ferromagnetic bottom electrodes, the magnetic properties of printed ferromagnetic films need to be well defined and easily controlled before producing a spin-valve.

Au/Co and Au/Ni thin films (100 µm square pads) were nanotransfer printed onto Au/decanedithiol surfaces and the printed features were analyzed by MOKE. It was anticipated that similar results would be seen for nanotransfer printed films as those seen for thermally deposited films, keeping in mind that nTP films would be inherently rougher and should present slightly higher coercivities. Furthermore, it was expected that varying the film thickness should allow for tuning of the films’ coercive field. However, nanotransfer printing of nickel films is difficult for Ni films thicker than 10 nm due to the fact that the Ni film becomes noticeably stiff and will not conform to the bottom SAM coated electrode during the printing process. Similarly, Co cannot be printed for film thickness above 30 nm. For cobalt, 5 nm, 10 nm, 20 nm, and 30 nm thin films were printed onto Au/alkanedithiol substrates. For Ni, only 10 nm films were transfer printed onto Au/decanedithiol substrates.
under the assumption that a thicker layer would be better for producing ferromagnetic behavior while limiting surface roughness contributions. Astonishingly, nanotransfer printed cobalt thin films showed no ferromagnetic behavior for any of the printed films. Initially it was thought that the lack of ferromagnetic properties arose from morphological differences while thermally deposited on PDMS and PFPE; however, cobalt films as deposited on PDMS and PFPE showed normal ferromagnetic behavior. The possibility of electrical coupling to the Au bottom electrode was ruled out by printing Co thin films onto Si/SiO$_x$ surfaces coated with a 3-mercapto)trimethoxysilane monolayer. These features were also magnetically dead. Two other explanations lie in the crystal orientation of Co thin films after nTP and SAM – Co surface interactions. Nanotransfer printing is a relatively abrasive technique and it is likely that the crystal orientation of Co after nTP is highly disturbed after printing. Though SEM and AFM analysis show the films to be relatively smooth and defect free, nanoscale variations within the film would definitely hinder magnetic domain formation and limit the ferromagnetic properties. Cobalt has also been suggested to be etched by alkanethiols in solution [43]. Surface etching of thin Co films could also contribute to the magnetic problems seen in printed Co films.

The fate of spin-valve assembly via nTP lay in the magnetic properties of transfer printed Au/Ni thin films. Luckily, printed Ni films responded as expected after nanotransfer printing yielding clean coercive fields (Figure 4.15B). A 2D MOKE image of an array 10 nm thin Ni films printed onto an Au electrode can be seen in Figure 4.15A. Two types of nTP Ni films were studied. Both were fabricated under inert conditions inside a glovebox according to the printing techniques defined in sections 4.2.3 and 4.2.4 of this chapter. The first type of film was fabricated under inert conditions, and then was brought into atmosphere...
Figure 4.15. MOKE analysis of nTP Ni films. A) A 2D MOKE image of an array of printed nickel pads. B) A representative hysteresis loop of a printed nickel feature (10 nm Ni). C) Comparison of photoresist-sealed (red) versus non-sealed (black) nTP features (10 nm) and thermally deposited bottom contacts (60 nm).
for 24 hours before being analyzed by MOKE. The second printed Au/Ni film was printed in the glovebox then coated with a photoresist (MaN-1410) and placed in a turbo vacuum (~ $1 \times 10^{-6}$ mbar) for an hour to remove residual solvent. Once removed from the vacuum, the surface was allowed to sit in atmosphere for 24 h prior to MOKE analysis. It was hoped that the Au layer on top the printed Ni film (recall Ni is printed as an Au/Ni bilayer) would protect it from atmospheric conditions. This seems to be the case since it was found that printed Ni films exposed to atmosphere and those sealed with photoresist contained very similar coercivities; although, the non-sealed Ni films tended toward lower coercivity (Figure 4.15C). This is presumably due to slight oxidation at the Ni surface which corresponds to what was seen in thermally deposited Ni thin films from section 3.2.1 of Chapter 3. Conversely, a severe increase in coercivity was seen from the thermally deposited bottom Ni contacts (60 nm) when exposed to atmosphere versus photoresist-sealed substrates. In all probability, the thermally deposited film undergoes chemical changes when exposed to atmospheric conditions.

Nickel substrates (usually as an Au(10 nm)/Ni(10 nm) bilayer) were printed onto Co/decanedithiol and Ni/decanedithiol substrates. For the third time, cobalt films yielded no useable magnetic results as only one hysteresis curve was witnessed for the Co/SAM/Ni/Au junction even while attempting a wide range of thicknesses of bottom Co thin films. Yet again, the fate of a successful nTP spin-valve depended on Ni bottom electrodes. Fortunately, Ni(60 nm)/decanedithiol/Ni(10 nm)/Au(10 nm) yielded independent magnetic switching for the sandwich complex. The results are shown in Figure 4.16 where it can clearly be seen in the hysteresis curve that layers switch independently.
Figure 4.16. Magnetically independent layers in a Ni/SAM/Ni/Au junction as observed by MOKE. A) MOKE on a 10 nm Ni printed feature (shows both top and bottom magnetic layers). B) Bottom 60 nm Ni electrode formed by thermal vapor deposition. C) Superposition of the two hysteresis curves.
4.3. Experimental

4.3.1. Silicon Master Formation for Stamp Replication. Silicon masters formed by photolithography were used for PDMS and PFPE stamp replication for features 10 µm and larger. For features smaller than 10 µm, stamps were replicated from PFPE based molds (*Liquidia Technologies*). For silicon master fabrication, silicon wafers (*Addison Engineering*) were cleaned in a solution of DI water, ammonium hydroxide (14.8 M, *Fisher Scientific*), and hydrogen peroxide (ACS certified 30%, *Fisher Scientific*) in a 2:1:1 ratio for 15 minutes. The wafers were removed from this solution, rinsed thoroughly with water and ethanol (100%, *Pharmco*), and dried with a stream of dry nitrogen. Additional UV ozone cleaning (*Bioforce Nanosciences ProCleaner™*) was performed on the wafers for 30 minutes. Following cleaning, a 10:1 (w:w) Su-8 50 (*MicroChem*) : γ-butyrolactone (*Alfa Aesar*) solution was spuncoat onto the wafer at 3000 RPM using a Chemat Technology (KW-4A) spincoater. This resulted in a 7 µm thick Su-8 as seen by profilometry. The Si/Su-8 substrate was cured on a hotplate at 90°C for 3 min, allowed to cool for 10 minutes, and exposed using a Karl Suss MA6/BA6 mask aligner (350 W lamp, 365 nm) for 6 s. The Si/Su-8 substrate was again heated on a hotplate for 2 minutes and allowed to cool for 10 min. The substrate was developed in Su-8 developer (MicroChem) for 4.5 min, rinsed with isopropyl alcohol, dried with a N₂ stream, and cured in a vacuum oven for 2 h at 200°C.

4.3.2. Stamp Formation and Preparation. For PDMS stamp replication, silicon masters fabricated according to the procedure above were fixed to a Petri dish using cyanoacrylate glue. Liquid PDMS prepolymer (*Dow Corning, Sylgard® 184 silicone elastomeric*) and cross-linking compound mixed in a 10:1 (w:w) ratio, was poured into the Petri dish covering the master. Only enough liquid PDMS was used to cover the master
resulting in a layer less than 1 mm thick. The Petri dish was placed under vacuum at 1 mbar for 20 min to remove residual air pockets and to ensure complete filling of the master. Once removed from the vacuum, the material was cured at 70°C overnight. The cured stamp was removed from the master by tweezers and cut to size with a razor blade.

PFPE stamps can be replicated from silicon masters or from previously formed PFPE molds as shown in literature [31]. For stamps with features smaller than 10 µm, PFPE molds with preset feature sizes were obtained from Liquidia Technologies. To replicate, the mold or master was placed in a Petri dish and liquid PFPE (Liquidia Technologies Fluorocur® Brand Resin, batch OMU-01) was dropped via pipette onto the master or mold. The liquid PFPE was spread onto the master or mold so that the resulting stamp after cure would be ≤ 1 mm. The liquid PFPE/PPFE mold or PFPE/silicon master was then placed in a photo-cure chamber, purged with dry nitrogen for 4 minutes, then cured under UV irradiation (Electro-Lite Corporation - Electro Cure 4001: Lamp 82011 - 125mW/cm²) for 4 minutes. The resulting stamp/mold was separated by tweezers revealing a negative stamp of the initial mold or master. This process could then be repeated on the initial PFPE mold master or on the newly made PFPE stamp. Attempts to replicate PDMS stamps from submicron PFPE molds were unsuccessful presumably due to the fact the PDMS’s inability to fully fill the mold.

The newly formed PDMS and PFPE stamps were cut to size with a razor blade (1 cm × 1 cm) and taped to a glass slide using double sided tape with the features exposed, directed away from the glass slide. This was done simply for ease of handling during vapor deposition. After securing the stamp to a slide, the stamp was placed in the evaporator and a metal thin film was deposited using the same thermal vapor deposition equipment detailed
above. For Au nTP, 20 nm of Au was thermally deposited starting at 1 Å/s for the first 10 Å of thickness then was increased to 15 Å/s for the final duration of the deposition. Gold needed to be deposited for a longer period of time and at an elevated rate to see accumulation of metal on PPFE stamps. This is due to low particle adsorption and high particle migration on low surface energy PFPE. For Ni and Co nTP, Au/Ni and Au/Co was deposited on the stamps. For Au/Ni and Au/Co deposition, 10 nm of Au was thermally deposited starting at 1 Å/s for the first 10 Å of thickness then was increased to 15 Å/s for the final duration of the deposition. This was followed by Ni or Co deposition at a constant 2 Å/s.

4.3.3. Substrate Preparation: Metal Thin Film Deposition and SAM Formation.

Prior to thermal evaporation, silicon wafers (Si/SiOx - 1 micron thick surface oxide on one side, Addison Engineering) were cleaned in a solution of DI water, ammonium hydroxide (14.8M, Fisher Scientific), and hydrogen peroxide (ACS certified 30%, Fisher Scientific) in a 2:1:1 ratio for 15 minutes. The wafers were removed from this solution, rinsed thoroughly with water and ethanol (100%, Pharmco), and dried with a stream of dry nitrogen. Additional UV ozone cleaning (Bioforce Nanosciences ProCleaner™) was performed on the wafers for 20 minutes. Au metal thin films were prepared by thermal vapor deposition on top of a 3 nm titanium adhesion layer (2 Å/s) on Si/SiOx. Au deposition started at 1 Å/s for the first 10 Å and then was quickly increased to 15 Å/s for the duration of the vapor deposition. Nickel and cobalt metal films were prepared by thermal evaporation (P_{initial} = 2 ~ 4 \times 10^{-6} \text{ mbar}; P_{deposition} = 2 ~ 8 \times 10^{-6} \text{ mbar}) on top of a 3 nm titanium adhesion layer (2 Å/s) on a SiOx/Si wafer. Ni and Co were deposited at 1 Å/s for the first 10 Å then the rate was increased to 8 Å/s until the final thickness was achieved. The evaporation boats were purchased from R. D. Mathis; the specific boat for Ni and Co evaporation was an alumina-
coated tungsten boat (Type S1AO-W to avoid alloying of the metals with tungsten) while that for Ti and Au were tungsten boats (Type S4-015 W and S42-015W, respectively). Gold (99.999%), nickel (99.98%), and cobalt (99.95%) pellets (1/8” × 1/8”) were purchased from Kurt J. Lesker, Inc. Titanium slugs (99.995%, 3.175 mm × 3.175 mm) were purchased from Alfa Aesar. Thermal evaporations were performed with an MBraun evaporator contained within an MBraun nitrogen glovebox such that freshly evaporated thin films could be removed from the evaporator chamber under a nitrogen atmosphere. Thicknesses of films were determined using a quartz crystal microbalance located just below the substrate holder in the evaporator. Tooling factors were determined by measuring the true thicknesses of films with a profilometer. X-Ray diffraction spectra were obtained for the Si/SiO\textsubscript{x}/Ti/M thin films (100 nm for Ni, Co, and Fe; 50 nm for Au; 25 nm Ti for all cases) using a Rigaku Multiplex Powder Diffractometer with Ni-filtered Cu Kα radiation (1.5418 Å) over the range 2θ = 10° - 85°. The evaporated metal films were observed to grow with either a <111> texture (Au, Ni, and Co) or <110> texture (Fe) [44]. The grain sizes for the thin films were deduced from the X-Ray diffraction data using the Scherer equation: Ni (7.0 Å), Co (5.1 Å), Fe (8.6 Å), and Au (9.3 Å).

For SAMs prepared in the glovebox, a SAM solution in ethanol (100%, Pharmco) was placed in a vial with septum-containing screw cap, purged with Argon for 1 h, and then brought into the glovebox (O\textsubscript{2} levels ≤ 0.1 ppm). The freshly evaporated Si/SiO\textsubscript{x}/Ti/M film was immediately submerged in the SAM solution and allowed to react inside of the glovebox (time was typically for 24 - 48 h). Octanedithiol and decanedithiol were purchased from Alfa Aesar and were used as received. Dodecanedithiol and tetradecanedithiol were synthesized using previously reported synthetic procedures [9]. After soaking in the SAM solution, each
sample was removed from the solution, sonicated in dry THF for 30 seconds to remove any physisorbed SAM units in a vial containing a screw cap that was sealed with para-film. Following sonication the sealed vial was returned to the glovebox, the substrates were removed from the THF, rinsed with N\textsubscript{2} purged 200 proof ethanol, dried with a dry N\textsubscript{2} stream, and further dried under vacuum (~ 1 mbar) for 1 h.

4.3.4. Characterization of MMM Junctions. MMM junctions were characterized by optical microscopy, scanning electron microscopy, and atomic force microscopy. Optical micrographs were gathered using a Zeiss Imager.D1m with an AxioCam MRm camera using Axiovision 40 V4.7.1.0 software. Scanning electron micrographs (SEM) were obtained using the electron beam capabilities on a FEI Helios 600 Nanolab Dual Beam System (accelerating voltage 15 kV, beam current 20 nA). AFM images for R\textsubscript{rms} roughness were collected using a Multimode IIIa Atomic Force Microscope (Veeco Metrology Group). The microscope was operated in tapping mode at ambient conditions (T = 21°C, RH = 45%), using silicon cantilevers (Mikromasch, Part No. NSC14/no Al) with resonance frequencies of approximately 160 kHz and tip radii less than 10 nm. R\textsubscript{rms} values were obtained over a 2\textmu m x 2\textmu m scan area and averaged over 5 scans from a minimum of three independently deposited surfaces for each metal. Other AFM images for step height and feature characterization were collected using an Asylum Atomic Force Microscope (Asylum MFP-3D, Asylum Research). The microscope was operated in tapping mode at ambient conditions (T = 21°C, RH = 45%), using silicon cantilevers (BudgetSensors, Tap300Al) with resonance frequencies of approximately 300 kHz, a force constant of ~ 40 N/m, and tip radii less than 10 nm.
4.3.5. Conductive Atomic Force Microscopy. Conductive atomic force microscopy measurements were carried out using an Asylum atomic force microscope (Asylum MFP-3D, Asylum Research) with an Orca dual gain cantilever holder and customized Ti/Au coated silicon cantilevers (BudgetSensors, Tap300Al). In an effort to minimize contact resistance between the conductive tip and printed feature, substantially large area AFM cantilevers ($\geq$ 80 nm diameter) were manufactured. Custom coating of the cantilevers was performed using a Kurt J. Lesker PVD 75 magnetron sputtering system. The cantilevers were mounted onto a glass slide using double sided tape with the tip exposed. 25 nm of Ti was sputtered onto the tips followed by 200 nm of Au (substrate temperature $\sim$ 30°). The spring constant of the newly formed tips was calculated to be $\sim$ 73 N/m. The tip diameter was confirmed by SEM.

For contact mode I-V measurements, a survey height map was first gathered in tapping mode to define the position of each feature. The tip was then brought to direct contact with each individual feature in contact mode using $\sim$ 10 nN of compressive force to ensure complete contact while minimizing contact-based resistance. Each junction was scanned through a bias range while detecting current. A single I-V curve was gathered for each junction before moving to the next junction. Depending on the sample, this process was repeated on 20 – 150 features per substrate. Conductive measurements were obtained in contact mode using a loading force of $\sim$ 5 - 10 nN. Loading with forces $\geq$ 20 nN resulted in shorted devices while the AFM tip forced the transfer printed electrode into direct contact with the bottom electrode. Disengaging the tip and then re-loading with $\sim$ 5 - 10 nN again resulted in a functional device. As a control, bare gold surfaces were contacted with a custom conductive AFM tip which included a 1 MΩ resistor in series. This experiment was done to ensure that both the applied force of the tip and the area of the tip were sufficient
enough to produce reliable results while contacting the surface. The surface was contacted as before with ~ 5 - 10 nN of tip force using three separate custom coated AFM tips. Ten separate scans were taken on two independently prepared bare Au surfaces producing a resistance of $1.016 \pm 0.009 \, \text{M}\Omega$ (average ± standard deviation). Conductive data for MMM junctions was worked up using OriginLab, Minitab (version 16.0), and Igor Pro (version 6.05).

Conductive mapping of the features was gathered in tapping mode under a 1.0 V surface bias and a grounded conductive tip. The 2D conductive map was superimposed over the corresponding height map (gathered simultaneously) to show a contrast in the junction’s current on and off the transfer printed feature using. Superposition of the 2D conductive map and height map, data flattening, and 3D image rendering was performed using the Argyle Light software (Asylum Research.).

**4.3.6. Simmons Modeling.** Each individual tunneling curve was fit using the Simmons tunneling model [10] as discussed by Wang et al. [8] to determine the unique properties of the tunneling barrier. Prior work employing the Simmons fitting has fit data to two parameters; namely, barrier height ($\Phi$) and the fitting parameter ($\alpha$). Here, three fitting parameters, barrier height, alpha (a dimensionless parameter to account for a non-rectangular barrier and effective mass), and spacer distance ($d$) were allowed to be free during the fit. A least squares fit was used to fit the experimental data. A program was developed in Igor Pro version 6.05 for this purpose.

**4.3.7. Magneto Optic Kerr Effect Measurements.** Magnetization studies were carried out using an experimental set-up that measures the Magneto-Optic Kerr Effect, and is designed to operate as described by Sato [45]. In the experiments here, a birefringent
photoelastic modulator (PEM) modulated the reflected laser beam, in order to separate the polarization components of rotation and ellipticity in the reflected beam. This was done using lock-in techniques since both components are proportional to the magnetization in the sample. In the conventional set-up, the laser output from a diode laser (K-Space Associates) at a wavelength of 664 nm passes through a focusing lens and then through a Glan-Thompson prism polarizer set at 0° to polarize the laser light (p-polarization). The laser beam reflects off of the sample mounted perpendicular to the plane of incidence in the vacuum chamber between the poles of an electromagnet. The reflected beam passes through the birefringent photoelastic modulator (or PEM) (Hinds Instruments model PEM-90, modulation frequency 50 kHz and set to $\lambda/2$), an analyzer, and finally a Glan-Thompson prism (45° rotation from the polarizer). The light is focused through a lens onto a photodiode.

The signal from the photodiode is passed to two lock-in amplifiers, one using a reference source supplied from the PEM controller at 1x the PEM modulation frequency ($1 \omega = 50$ kHz) and a second using a reference source from the PEM controller at 2x the PEM modulation frequency ($2 \omega = 100$ kHz). The two signals are de-convoluted by the lock-in amplifiers. They correspond to the change in ellipticity ($1 \omega$) and rotation ($2 \omega$) undergone by the incident polarized light as a result of the MOKE effect. The analysis here focused primarily on the $2 \omega$ Kerr rotation signal.

The magnet is driven by a Kepco Power Supply ATE 100-10M. The DC signal from the photodiode is input into a Hewlett-Packard 3456A Digital Voltmeter. The entire experiment is operated by a Labview program. The main function of the program is sweeping of the magnetic field by increasing or decreasing the output of the power supply.
which controls the current through the electromagnet. Positioning is also controlled on the sample surface via two stepper motors that change the horizontal and/or vertical location of the sample. Positioning onto the individual device or region of interest was aided with the use of a CCD camera (Adimec MX12P).
4.5. References


CHAPTER 5

Permanent, Individually Addressable MMM Junctions via Nanotransfer Printing
5.1. Introduction

Nanotransfer printing is an easy, fast, and reproducible method to generate permanent, covalently bound metal thin film electrodes atop self-assembled monolayers formed on conductive metal thin film electrodes [1, 2]. In many instances, conductive probe atomic force microscopy has been employed as a means to study the electrical properties of the molecular monolayer within (Chapter 4). Without question, c-AFM is a valuable technique to acquire conductive properties of nanotransfer printed metal-molecule-metal junctions without destroying the junction itself. All the same, c-AFM is limited in that it is a two probe measurement (both probes sense voltage and current in tandem) and is generally only useful as an analytical method. Ideally, a device architecture would be designed such that the MMM junction could be analyzed by the more sensitive four point probe measurement [3] (four probes, two for each of current and voltage), and at lower temperatures. Moreover, the ideal molecular junction would be scalable to the sub micron regime as well as being integrable into existing electronics as a permanent, individually addressable molecular junction. A junction such as this would not only be inspiring as a fundamental analytical test bed to study molecule-based spin valve assemblies, but would be a step toward industrially viable molecule-based spin electronics.

Direct mechanical attachment to an nTP film by a conductive electrode is virtually impossible without destroying the film itself. Therefore, a more noninvasive electrical attachment needs to be developed. Direct contact to fragile monolayers has been attempted by physical vapor deposition techniques directly onto self-assembled monolayers [4-6]. These methods have shown a high percentage of shorted devices as the evaporated metal atoms either penetrate into or thermally destroy the monolayer. However, deposition onto
nanotransfer printed metal thin films has not yet been attempted. It is expected that nTP films will adequately protect the monolayer from the harsh deposition conditions. Herein, metal-molecule-metal junctions are formed using the nanotransfer printing methodology outlined in Chapter 4. Following junction formation, the MMM junctions are coated with a photoresist and wells are opened atop each featured via registered lithography. Subsequently, a permanent top electrode can then be deposited into the photolithographically defined well.

5.2. Results and Discussion

5.2.1. Device Architecture and Fabrication. The fabrication method can be seen in Figure 5.1. A clean, dry Si/SiO$_x$ wafer was further cleaned by UV ozone for 20 minutes and then treated with neat hexamethyldisilazane (HMDS) which will later assist in the adhesion of a photoresist. Subsequently, a 3 nm Ti adhesion layer was thermally deposited through a shadow mask followed by 60 nm of either Ni or Au. The Ni and Au were deposited following the elevated rate deposition described in Chapter 4 to ensure smooth surfaces for high quality nTP. For the work described here, the bottom electrode was deposited in the shape of a 3 centimeter long, 380 micron wide wire. Immediately following thermal deposition of the bottom wire electrode, an alkanedithiol SAM was formed using inert glovebox processing conditions as described in section 2.2.1 of Chapter 2. For the Ni/SAM substrate, a Au(10 nm)/Ni(10 nm) thin film was nanotransfer printed onto the Ni wire electrode to form a Ni/SAM/Ni/Au junctions. Similarly, for the Au/SAM substrate, 20 nm of Au was transfer printed onto a gold wire substrate (Figure 5.1A). The size of the printed features was 50 micron squares. Immediately following nTP, the MMM junctions were spuncoat with photoresist (MaN-1410) all while remaining inside the glovebox under inert
Figure 5.1. Device fabrication procedure for a permanent nTP device. A) Ni or Au thin films are printed onto a wire thin film electrode. B) Photoresist is spuncoat onto the features and wells are opened on each individual feature. C) A top electrode is sputter deposited to finish the device.
solvent. Preheating concentrates the photo-active crosslinkers within the photoresist film conditions. Generally at this point during the photolithography process, the substrate would be pre-heated to ~ 100 °C before exposure to remove residual solvent. Preheating concentrates the photo-active crosslinkers within the photoresist film resulting in a more compact layer following UV exposure. It was not certain how the SAM layers would respond to heat since previous studies have revealed temperature dependence on MMM junction stability [7]. Therefore, vacuum was used in place of heat to remove residual solvent. The substrate was placed under vacuum (1 × 10^{-6} mbar) for two hours to remove residual solvent from the resist in preparation for photolithography. A ten micron wells in the middle of each printed feature was defined by photolithography (Figure 5.1B). After developing the wells, the substrates were thoroughly rinsed with water, dried with an N₂ stream, and further dried under vacuum (1 × 10^{-6} mbar) for two hours. After drying, a permanent top Au electrode (~ 200 nm) was deposited through a shadow mask by sputter deposition (Figure 5.1C).

Oxidation of the MMM junctions was a general concern for the Ni thin films, since the photolithography steps were carried out in atmosphere. It was anticipated that the Au on top of the nickel printed film would protect the nTP nickel layer while the photoresist was expected to protect the bottom Ni thin film electrode. By MOKE analysis, the printed nickel surfaces yielded coercivities around 25 Oe while the bottom Ni electrodes yielded coercivities around 50 Oe. These values match nicely with those seen in the resist coated Ni/SAM/Ni junction from MOKE studies in section 4.2.7 of Chapter 4. More importantly, independent magnetic layers were seen in completed devices.
5.2.2. Electrical Characteristics. Electrical studies on permanent, individually accessible MMM junctions by nTP plus lithography are currently still in progress. Highlighted here are the preliminary results from electrical characterization of printed permanent junctions. Future work will focus on mimicking c-AFM studies from Chapter 4 for permanent junctions with the addition of low temperature analysis.

Electrical characteristics were carried out using four point probe techniques by probe station and by means of permanently soldered contacts under high vacuum at variable temperature. Out of over two hundred individually fabricated MMM junctions, just under 10% of the junctions yielded tunneling characteristics while the majority of the rest of the devices were shorted. Although the success rate was low, the functional junctions yielded very clean, temperature independent tunneling characteristics down to 77 K (Figure 5.2). The zero-crossing resistance values are in good agreement with literature; for example, 50 µm squares of printed Au/dodecanedithiol/Au and Ni/tetradecanedithiol/Ni/Au junctions were found to have resistances of 2000 Ω and 1200 Ω respectively.

Since the majority of the MMM junctions were shorted out by this fabrication technique, it was thought that pinhole defects in the printed film caused shorting as the sputtered top contact penetrated into the monolayer. An astonishing example of how readily vapor phase deposition techniques penetrate a monolayer can be seen in work by Song and coworkers, where 50 nm diameter Au/octanedithiol/Au junctions formed by direct thermal vapor deposition onto the monolayer yielded only ~ 7% functional devices [8]. Increasing the device area to 2 µm diameter yields an astoundingly low 1.75% functional junctions [9]. By this logic, if there exists a defect that spans through the nanotransfer printed film to the monolayer (on the order of 50 nm in diameter), the permanent junction formed by the
Figure 5.2. Temperature dependent I-V characteristics of an Au/dodecanedithiol/Au permanent junction formed by nanotransfer printing followed by lithography.
techniques outlined here only has a 7% chance of not being shorted. Since it was seen in SEM images after printing films that surfaces can become slightly cracked (section 4.2.4, Chapter 4), it is assumed that the shorting issue must have to do with nanoscale defects in the printed film. Therefore, after the wells were opened on the nTP films in the process outlined above, a 100 nm film of PEDOT:PSS (PH 500) was spuncoat onto the substrate prior to sputter coating of the top electrode. This greatly improved the success rate for device fabrication. Out of more than 50 devices fabricated by this method, a little over 60% of the junctions were functional yielding clean, temperature independent tunneling characteristics. Interestingly, by probe station measurements, the junctions tended to show hysteresc in the tunneling curve under atmospheric conditions. However, up placing the junction under vacuum, the hysteresis went away and clean tunneling results were seen. All the functional devices were temperature independent as expected (Figure 5.3). The zero-crossing resistance values were as in line with the non-PEDOT:PSS permanent junctions. For example, Au/tetradecanedithiol/Au junctions were found to have resistances between 4300-6000 Ω while Ni/tetradecanedithiol/Ni/Au junctions were found to have resistances around 3700 Ω. Simmons fitting was performed on Au/tetradecanedithiol/Au junctions and the barrier height was found to be 3.43 ± 0.40 eV. In comparison, the barrier height for 200 nm diameter Au/tetradecanedithiol/Au junctions found by c-AFM studies in Chapter 4 was 3.90 ± 1.03 eV. More data needs to be gathered to form any conclusive interpretation. Studies currently in progress are focused on the fabrication of junctions with variable length molecules, junctions with different printed feature size, and junctions formed on conjugated organic semiconductors.

5.2.3. Magnetotransport in Ni/Alkanedithiol/Ni/Au Junctions. Similar to the
Figure 5.3. Temperature dependence on tunneling for Au/tetradecanedithiol/Au junction using PEDOT:PSS prior to contacting the nTP thin film.
electrical characterization, magnetotransport measurements are ongoing. Nevertheless, preliminary findings are presented here.

As previously stated, non-magnetically coupled films were observed after printing 10 nm thin Ni films onto SAM coated Ni electrodes (60 nm). Therefore, determination of a junction’s magnetotransport properties (i.e. spin-valve capabilities) is as easy as placing the junction under an external magnetic field while continuously gathering I-V characteristics. For example, maintaining a junction at a constant tunneling current (i.e. constant bias) while scanning through an external magnetic field, we would expect to see a change in the tunneling current as the ferromagnetic thin films change from magnetically aligned to anti-aligned (as described in detail in Chapter 1). This is indeed the case for Ni/alkanedithiol/Ni junctions; however, the change in resistance has been tremendously small (on the order of 0.2 percent). Current work is focused on probing, understanding, and increasing the spin-valve effect.

5.3. Experimental

5.3.1. Fabrication and Characterization. Devices were characterized by optical microscopy, scanning electron microscopy, and atomic force microscopy.

Optical micrographs were gathered using a Zeiss ImagerD1m with an AxioCam MRm camera using AxioVision 40 V4.7.1.0 software. Scanning electron micrographs (SEM) were obtained using the electron beam capabilities on a FEI Helios 600 Nanolab Dual Beam System (accelerating voltage 15 kV, beam current 20 nA).

Ni and Au metal thin films (bottom electrodes) were prepared by thermal evaporation onto a Si/SiOx wafer. Prior to thermal evaporation, silicon wafers (Si/SiOx - 1 micron thick surface oxide on one side, Addison Engineering) were cleaned in a solution of DI water,
ammonium hydroxide (14.8 M, *Fisher Scientific*), and hydrogen peroxide (ACS certified 30%, *Fisher Scientific*) in a 2:1:1 ratio for 15 minutes. The wafers were removed from this solution, rinsed thoroughly with water and ethanol (100%, *Pharmco*), and dried with a stream of dry nitrogen. Additional UV ozone cleaning (*Bioforce Nanosciences ProCleaner™*) was performed on the wafers for 20 minutes. Au metal thin films were prepared by thermal vapor deposition on top of a 3 nm titanium adhesion layer (2 Å/s) on Si/SiOx. Au deposition started at 1 Å/s for the first 10 Å and then was quickly increased to 15 Å/s for the duration of the vapor deposition. Nickel and cobalt metal films were prepared by thermal evaporation ($P_{\text{initial}} = 2 \sim 4 \times 10^{-6}$ mbar; $P_{\text{deposition}} = 2 \sim 8 \times 10^{-6}$ mbar) on top of a 3 nm titanium adhesion layer (2 Å/s) on a SiOx/Si wafer. Ni and Co were deposited at 1 Å/s for the first 10 Å then the rate was increased to 8 Å/s until the final thickness was achieved. The evaporation boats were purchased from RD Mathis; the specific boat for Ni and Co evaporation was an alumina-coated tungsten boat (Type S1AO-W to avoid alloying of the metals with tungsten) while that for Ti and Au were tungsten boats (Type S4-015 W and S42-015W, respectively). Gold (99.999%), nickel (99.98%), and cobalt (99.95%) pellets (1/8” x 1/8”) were purchased from Kurt J. Lesker, Inc. Titanium slugs (99.995%, 3.175 mm x 3.175 mm) were purchased from Alfa Aesar. Thermal evaporations were performed with an MBraun evaporator contained within an MBraun nitrogen glovebox such that freshly evaporated thin films could be removed from the evaporator chamber under a nitrogen atmosphere. Thicknesses of films were determined using a quartz crystal microbalance located just below the substrate holder in the evaporator. Tooling factors were determined by measuring the true thicknesses of films with a profilometer. X-Ray diffraction spectra were obtained for the M/Ti/SiOx/Si thin films (100 nm for Ni, Co, and Fe; 50 nm for Au; 25 nm Ti for all cases) using a Rigaku
Multiplex Powder Diffractometer with Ni-filtered Cu Kα radiation (1.5418 Å) over the range 2θ = 10 - 85°. The evaporated metal films were observed to grow with either a <111> texture (Au, Ni, and Co) or <110> texture (Fe) [10]. The grain sizes for the thin films were deduced from the X-Ray diffraction data using the Scherer equation: Ni (7.0 Å), Co (5.1 Å), Fe (8.6 Å), and Au (9.3 Å).

Photolithography was performed at CHANL (Chapel Hill Analytical and Nanofabrication Laboratory). MaN-1410 photoresist (Micro Resist Technology) was spuncoat at 3000 RPM using a Chemat Technology (KW-4A) spincoater. Exposure and mask alignment was performed using a Karl Suss MA6/BA6 mask aligner (350 W lamp, 365 nm) for 45 s. Development was done in MaD 533 (Micro Resist Technology) for 45 s. The PEDOT:PSS used was PH 500 (Clevios, H.C. Stark) and was mixed with DMSO (5 %, w/w) to increase conductivity (300 S/cm). PEDOT only devices yielded shorted devices (resistances less than 50 Ohm).

Oxygen plasma cleaning was done with an AutoGlow O2 plasma system (Glow Research).

5.3.2. Probe Station Current-Voltage Measurements. Devices were measured on an Alessi Industries probe station using four probes for a four-terminal measurement. Of the four probes, two were Alessi Industries probes and two Signatone Model S-600 probes. The circuit for the I-V measurement included a DC source and an AC function generator for measurement of the instantaneous conductance with a lock-in amplifier. The DC source was a Keithley 230 Programmable Voltage Source, and the AC function generator was a Wavetek Model 270 12 MHz Programmable Function Generator. The function generator was connected across the primary windings of a conventional transformer to step down the input
voltage (usually set to 300 mV unless otherwise noted) in order to output a 24.64 mV peak sine wave at the secondary winding. The DC source was connected in series to this secondary winding on the transformer, followed by connection to one side of the top electrode crossbar on the SAM device via the probe. Next a probe was connected to the back (bottom) electrode on the sample wafer, and this leg of the circuit then went to an op-amp based current converter/amplifier hard-wired to convert the input current into a voltage signal at a magnitude of 100× that input current. The output voltage signal from the current amplifier was branched to a Keithley 2182A Nanovoltmeter, to read the voltage-converted DC current signal, and, on the other side of the branch, to a Stanford Model SR830 Lock-In Amplifier to read the modulated current signal occurring at the specific DC voltage. The DC voltage across on the other two terminals (top electrode to bottom electrode) was recorded by a Keithley 6514 Electrometer. A labview program ran the various meters and recorded the data for the I-V and conductance measurements.

5.3.3. Low Temperature Current-Voltage Measurements. To put a sample into the vacuum chamber, a small portable vacuum chamber was used (approx. 5” × 3” × 2”). This was necessary to create leads going from the electrodes of the sample to soldered connections on a feed-through in the walls of the vacuum chamber to perform measurements using the same measurement equipment above as was used on the probe station. To make electrical connections into the vacuum chamber, the sample wafer was first affixed to a separate wafer with 1 micron silicon oxide layer. Gold pads were formed on the Si/SiOₓ wafer by deposition through a shadow mask and were used for wire-bonding and soldering given that soldering directly to the device could easily overheat and short the device. Larger wires were soldered onto the pads of the photolithographic pattern so that they could make a continuous
contact to the 0.010" diameter aluminum wires wire-bonded onto the opposite end of each pad. The wire-bonding was performed on a wire-bonder (Kulicke and Soffa model No. 1413). The vacuum chamber is an MMR (MicroMiniature Technologies) vacuum chamber that is capable of cooling the sample down to liquid nitrogen temperature (77 K). The design makes use of small capillaries for the flow of gas inside a glass sample mounting arm. When the gas reaches the sample mounting location, the capillary expands out into a small expansion chamber (also inside the glass), allowing cooling of high-pressure nitrogen gas by the Joule-Thompson effect. The gas used was a high purity nitrogen (99.999%) compressed gas cylinder (National Welders). A silicon diode affixed to the gold sample mounting pad inside the MMR chamber at the cooling point (gas expansion point) is used to monitor the sample temperature. To reach a specific set point temperature, a Lakeshore 330 Temperature Controller monitors the temperature using the diode, and increases or decreases the voltage output to a heater circuit also located underneath the gold sample mounting pad. The heater is capable of heating against the cooling effect and can bring the sample temperature rapidly from 77 K to room temperature, for example, if desired. The sample holder wafer with the sample mounted onto it is mounted onto the sample mounting pad using Dow-Corning 340 silicone heat sink compound (a type of thermal grease).

A turbo pump system consisting of a Varian DS102 roughing pump and a Varian Turbo-V 70D Macro Torr turbo pump controlled by a Varian Turbo V-70 controller was used to pull vacuum (~ 5 × 10⁻⁶ Torr) prior to low temperature measurement. A Granville-Phillips 270 Gauge Controller was used to determine the pressure by reading either an MKS ion gauge or a Duniway Stockroom DST-06M thermocouple mounted inside the vacuum system. A 3/8" inside diameter rubber tube connected the vacuum pump system to the
vacuum chamber. The chamber is small enough so that it can also be placed between the poles of an electromagnet in order to perform magnetic field measurements on the sample. Control of the magnet is done using a *Labview* program (as described in the MOKE section), and electrical measurements are performed at different applied fields.

**5.3.4. Simmons Modeling.** Each individual tunneling curve was fit using the Simmons tunneling model [11] as discussed by Wang et al. [5] to determine the unique properties of the tunneling barrier. Prior work employing the Simmons fitting has fit data to two parameters; namely, barrier height ($\Phi$) and the fitting parameter ($\alpha$). Here, three fitting parameters, barrier height, alpha (a dimensionless parameter to account for a non-rectangular barrier and effective mass), and spacer distance ($d$) were allowed to be free during the fit. A least squares fit was used to fit the experimental data. A program was developed in Igor Pro version 6.05 for this purpose.

**5.3.5. Magneto Optic Kerr Effect Measurements.** Magnetization studies were carried out using an experimental set-up that measures the Magneto-Optic Kerr Effect, and is designed to operate as described by Sato [12]. In the experiments here, a birefringent photoelastic modulator (PEM) modulated the reflected laser beam, in order to separate the polarization components of rotation and ellipticity in the reflected beam. This done using lock-in techniques since both components are proportional to the magnetization in the sample. In the conventional set-up, the laser output from a diode laser (*K-Space Associates*) at a wavelength of 664 nm passes through a focusing lens and then through a Glan-Thompson prism polarizer set at $0^\circ$ to polarize the laser light (P-polarization). The laser beam reflects off of the sample mounted perpendicular to the plane of incidence in the vacuum chamber between the poles of an electromagnet. The reflected beam passes through
the birefringent photoelastic modulator (or PEM) (*Hinds Instruments* model PEM-90, modulation frequency 50 kHz and set to $\lambda/2$), an analyzer, and finally a Glan-Thompson prism (45° rotation from the polarizer). The light is focused through a lens onto a photodiode.

The signal from the photodiode is passed to two lock-in amplifiers, one using a reference source supplied from the PEM controller at 1× the PEM modulation frequency (1$\omega$ = 50 kHz) and a second using a reference source from the PEM controller at 2× the PEM modulation frequency (2$\omega$ = 100 kHz). The two signals are de-convoluted by the lock-in amplifiers. They correspond to the change in ellipticity (1$\omega$) and rotation (2$\omega$) undergone by the incident polarized light as a result of the MOKE effect. The analysis here focused primarily on the 2$\omega$ Kerr rotation signal.

The magnet is driven by a *Kepco* Power Supply ATE 100-10M. The DC signal from the photodiode is input into a *Hewlett-Packard* 3456A Digital Voltmeter. The entire experiment is operated by a *Labview* program. The main function of the program is sweeping of the magnetic field by increasing or decreasing the output of the power supply which controls the current through the electromagnet. Positioning is also controlled on the sample surface via two stepper motors that change the horizontal and/or vertical location of the sample. Positioning onto the individual device or region of interest was aided with the use of a CCD camera (*Adimec MX12P*).
5.4. References


CHAPTER 6

Summary of Conclusions and Recommendations for Future Work
6.1. Summary of Conclusions

As computer components continually become smaller, silicon-based electronics (the building block for the modern computer) are expected to become obsolete due to fundamental size limitations. One exciting alternative to existing technology is the emerging field of spin-based electronics, or spintronics. Typical electronics, for example an integrated circuit, rely solely on the manipulation of the flow of electrons (i.e. electrical current) to perform logic operations. Spintronic systems on the other hand utilize the intrinsic spin of the electron as well as electron flow [1-3]. This provides an additional degree of freedom to be exploited to produce sought-after electrical properties.

The conventional model for a spintronic device is a three level system consisting of two ferromagnetic layers separated by a nanometer thin, nonmagnetic ‘spacer layer’. Spacer layers produced from inorganic materials have been thoroughly studied in literature and have gained considerable recognition. Organic molecules on the other hand offer the advantage of being significantly cheaper to process and are often active to external stimuli such as light or an electric field. Include the fact that organic materials contain incredibly large spin diffusion lengths and that the structure and function of an organic molecule can be easily synthetically tuned to fit a specific need, and it is clear to see that organic based spintronics are a promising substitute for their inorganic counterparts. However, molecule based spintronics have not been thoroughly explored. Therefore, the focus in this work has been on the formation of ferromagnet-molecule-ferromagnet junctions based on organic molecule as spacer layers.

While applicable single molecule electronics have yet to become a reality, abundant research has been dedicated to studying the electrical properties of small collections of
molecules under the principle that larger area molecular electronics could be easily produced and would be rather inexpensive. In general, electrical studies are performed by sandwiching molecules between two independent electrodes, often by forming electrical contact to self-assembled monolayers (SAM) formed on conductive electrodes [4-11]. However, intimate contact to fragile molecular monolayers is not a trivial pursuit.

Initially, the methodology to form pristine molecule layers on ferromagnetic electrodes needed to be developed; subsequently, methods needed to be shaped to form intimate electrical contact atop these molecular layers with ferromagnetic metals. Once fabricated, the ferromagnet-molecule-ferromagnet junctions could then be studied for their magnetic and electrical properties. Preferably, the methods used to form the junctions would be reliable, permanent, and produce individually accessible junctions.

6.1.1. Monolayer Formation on Pristine Ferromagnetic Metals. Self-assembled monolayer formation on Au surfaces has been thoroughly studied and is well understood [12-14]; conversely, reports of SAM formation on pristine, oxide free ferromagnetic Ni, Co, and Fe surfaces had been sparse [14]. Since Ni, Co, and Fe are known to form surface oxides readily in air, most studies form monolayers on Ni, Co, and Fe systems via carboxylate, phosphonate, or silane surface attachment chemistry [15-19]. However, for molecular electronic and spintronic devices, the ferromagnetic surface should be oxide free given that oxides are known to create additional quantum tunneling barriers and tend to scatter electron spin [20-23]. SAM formation via thiol and isocyanide attachment chemistry on Ni, Co, and Fe thin films was examined under both inert and atmospheric conditions in an attempt to form pristine, oxide free monolayers. It was found that isocyanides form decent SAMs on Ni while thiols form high-quality monolayers on all three surfaces especially for Ni and Co [24].
In addition, a broadly applicable electrochemical technique was developed to remove native oxides from ferromagnetic surfaces facilitating the formation of high surface coverage SAMs on thin, evaporated metal films that have been pre-exposed to atmospheric conditions. The SAMs prepared under electroreduction conditions rival those prepared under inert conditions in a glovebox prior to exposure to the ambient. For all three fabrication methods it was found that the Fe surfaces tended to maintain a sizeable amount of surface oxidation while the Ni and Co systems were relatively oxide free under the electroreduction and inert processing conditions.

6.1.2. Polymer Protected Self-Assembled Monolayers in Spin-Valve Assembly.

One way to form intimate electrical contact atop self-assembled monolayers is to first protect the monolayer with a conductive organic material. Poly(3,4-ethylenedioxythiophene)–poly(styrenesulfonic) acid (PEDOT:PSS), a highly conducting polymer, has been utilized as an interlayer between the self-assembled monolayer and the top contact [8, 25]. In this system, well ordered SAM arrays are first formed in lithographically defined wells within a photoresist and are then coated with PEDOT:PSS. The PEDOT:PSS protects the molecular layer from shorting or being thermally damaged during thermal vapor deposition of the top metallic contact. Up until now, SAM formation on ferromagnetic electrodes has been difficult; therefore, previous work in this area has been limited to studying only well behaved Au electrode junctions and had not yet been expanded to included ferromagnetic electrodes in an attempt to form spintronic devices. Now that SAM formation on ferromagnetic materials is possible, this device architecture provides the possibility of incorporating ferromagnetic electrodes into the device to study molecule based spintronic devices.
Metal/molecule/PEDOT:PSS/metal junctions were fabricated with Au, Ni, and Co metal thin film electrodes. The Au electrode junctions were fabricated as outlined in literature [8, 25], but with only intermittent success. Over a 50 junctions were fabricated by this method, and tunneling characteristics were observed in a number of successful junctions. However, the number of operational devices was less than ideal (~ 15 %), and the resulting sigmoidal I-V curve was highly temperature dependent which suggests the existence of competing electron transport mechanisms in addition to quantum tunneling. The temperature dependence could arise from pinhole defects at the device, impurities in the junction, or residual water remaining in the PEDOT:PSS layer.

The magnetic properties of Ni and Co metal thin films were studied as a function of film thickness and surface roughness. Magnetism is an effect that depends not only on the fundamental properties of the element but on the crystalline structure and microscopic arrangement of the atoms as well. Magnetic properties at the surface do not necessarily extend the same properties as those viewed in the material’s bulk [26, 27], and rougher surfaces tend to impart separate surface domains in addition to the standard bulk domains. As the ferromagnetic film becomes thinner (or laterally confined), these domains play a larger role in the material’s hysteresis due to the fact that they compose a greater percentage of the overall layer.

It was found that the coercivity of thermally deposited Ni and Co films could be tuned from only a few Orsted up to several hundred Orsted depending on composition and film thickness. Nickel and cobalt surfaces were studied under a series of circumstances: a) Ni and Co films as a function of film thickness, b) with a native oxide grown under atmospheric conditions, c) with a monolayer grown by inert glovebox conditions or by
electroreduction, and d) freshly deposited and protected from surface oxidation by a photoresist coating. Thermally deposited Ni films were well behaved yielding coercivities that could be control reliably from condition to condition. In addition, their coercivity stayed constant while testing at different incident light angles during MOKE studies. Electroreduced Ni films were inherently rougher and showed a slight increase in coercivity, yet stayed within a small range (± 30 Oe) overall. Cobalt on the other hand yielded more interesting results. Thickness dependence saw increased coercivity until a maximum around 20 nm of film thickness where then a sharp decline continued through larger film thicknesses (up to 100 nm). It was also seen that deposited films aligned with the crystal structure of the silicon wafer (or the titanium adhesion layer) producing anisotropic, directional dependence on the final hysteresis curves as seen by MOKE. Furthermore, electroreduced surfaces produced a wide range of coercivities, the source of which is likely to arise from surface roughness produced during the electroreduction process.

As mentioned above, metal/molecule/PEDOT:PSS/metal junctions were fabricated using Ni and Co metal thin film electrodes. After photolithography, the electrocution SAM formation process was used to form pristine monolayers as outlined in Chapter 2. Electroreduction was shown to produce significantly rougher metal thin films than freshly deposited films. Magnetically, Co thin films did not respond well to electroreduction and surface roughness issues, therefore Co was ruled out as a possible bottom contact in this device architecture. Nickel responded well and maintained a clear, stable cohesive curve before and after electroreduction. Ni/alkanedithiol/PEDOT:PSS/Co devices were fabricated. It was found by MOKE that the bottom Ni and top Co thin films were uncoupled magnetic layers with dissimilar coercivities. Therefore, under an external magnetic field, the top and
bottom ferromagnetic electrodes could be switched independently. Current-voltage results were similar to those found in Au junctions where roughly 10% of devices showed tunneling-like characteristics at room temperature (all others were shorted), with the conducting current showing temperature dependence. Under an external magnetic field, the top and bottom electrodes exchanged magnetic directions independently at different field strengths, yet the junctions showed no sign of resistance change in the expected magnetic region of interest, even down to 77 K. It is likely that the electron spin polarization was not maintained as it traveled through the PEDOT:PSS layer given that it contains several heavier atoms and has a thickness on the order of the spin diffusion length found in other organic materials [28, 29]. In the ideal case, the top ferromagnetic layer would be attached directly to the molecular layer, ruling out any interference to the electrical properties of junction by the PEDOT:PSS layer.

6.1.3. MMM Junctions by Nanotransfer Printing. Nanotransfer printing offers an easy method to form covalently attached electrical contacts to molecular layers without ruining the fragile monolayer beneath. It operates on the principle that metal thin films can be transferred from a flexible polymeric stamp to a substrate if the metal has a higher affinity for the receiving substrate than that of the stamp. Nanotransfer printing has proved successful on a variety of surfaces [7, 30, 31]. However, until recently printing onto SAM coated metal electrodes had been met with little success. This work set out to determine the steps needed to reproducibly and reliably transfer print onto SAM coated metal electrodes. This was followed by a thorough electrical and magnetic characterization of the junctions.

Nanotransfer printing was demonstrated to be a highly surface sensitive technique. Surface roughness was dependent on the rate of deposition for Au, Ni, and Co thin films with
faster deposition rates ($\geq 8 \text{ Å/s}$) yielding smoother surfaces. SAM density for alkanedithiols is heavily dependent on the molecule concentration during SAM formation and it was found that 30 mM SAM molecule solution produced the densest monolayers. This occurs since both ends of the molecule are active to the surface and the molecule can loop back on itself. Using polydimethylsiloxane stamps, $R_{rms}$ needed to be minimized ($\sim 0.60 \text{ nm or less}$) and the SAM density needed to be maximized for nTP to be successful. Gold, nickel, and cobalt thin films were transfer printed with great success particularly in the case of Au and Co thin films. Nickel transfer printing via PDMS stamps could be carried out, but the printed features were frequently cracked or incomplete.

Perfluoropolyether stamps were employed for nTP. PFPE has a lower surface energy and a higher modulus than PDMS so it was expected that PFPE would release the metal film to the receiving substrate with less effort. It was also expected to be better suited for printing tightly compact, nanometer arrays since PFPE is more rigid than PDMS and less prone to lateral stamp collapse. It was found that PFPE could easily print Au, Co, and Ni films to SAM coated Au, Ni, and Co electrodes without difficulty [32].

Alkanedithiols were used as the molecular monolayer for nTP studies. Therefore, tunneling was the expected mode of electron transport in the printed MMM junctions given that Au, Co, and Ni’s Fermi levels are more or less centrally located between alkanedithiols’ large (8 – 10 eV) HOMO-LUMO gap. As expected, scalable tunneling characteristics were observed based on tunneling area (i.e., printed feature size) and tunneling distance (i.e., molecule length), and the results were interpreted using the simplified Simmons equation which describes classical tunneling through an insulating thin film [33]. By Simmons
modeling, the tunneling barrier height and tunneling distance of the tunneling junction were found to increase with increasing chain length as expected.

For low temperature I-V characteristics, each printed feature needed to be contacted with an external electrode. Mechanically attaching an electrode to an nTP film is virtually impossible without destroying the film itself. Therefore, and external electrode was formed by opening lithographic wells within a photoresist atop each feature, followed by the sputtering of a top electrode. This method was successful in creating permanent junctions, yet the rate of success was dreadfully low with ~ 10 % of devices showing tunneling characteristics while the majority of the junctions were shorted. Further inspection by SEM showed that nearly all the nTP films contain nanoscale cracks that penetrate through the entire film due to the harsh nature of nTP. This problem is unavoidable with the current technology, and the nano-cracks made it possible to short the devices through the fragile monolayer during sputter deposition. To circumvent this issue, after opening the wells on the nTP features, PEDOT:PSS was spun coat over the substrate to protect the feature prior to sputtering of the top electrode. This improved the shorting issue yielding 60 % of the devices functional. More importantly, the tunneling junctions by this method were completely temperature independent suggesting that the main mode of electrical transport is tunneling.

Ferromagnetic materials were printed onto SAM coated Au, Ni, and Co electrodes. Cobalt films ranging from 5 nm up to 30 nm were printed onto Au/SAM, Ni/SAM, and Co/SAM surfaces yet the printed Co film was found to be magnetically unresponsive by MOKE measurements. As previously mentioned, ferromagnetism is dependent on crystal structure and microscopic arrangement in addition to chemical make-up. Cobalt films as
deposited on PDMS and PFPE showed normal ferromagnetic behavior, so it is likely that the crystal orientation of Co after nTP is highly disturbed. Nickel on the other hand yielded clean, reproducible hysteresis curves after printing on Au/SAM and Ni/SAM surfaces. Independent magnetic layers were seen when printing Ni (10 nm) onto alkanedithiol coated Ni (60 nm) films. I-V characteristics show tunneling similar to that seen in the Au/alkanedithiol/Au system and were temperature independent down to 87 K. Current-voltage characteristics under an external magnetic field are still in progress, however, initial results show a change in resistance within the coercive regions of interest.

6.2. Recommendations for Future Work

6.2.1. Nanotransfer Printing onto Mixed Monolayers. The covalent bond at the metal/molecule interface is thought to have a significant effect on the overall tunneling mechanism (and current) in a MMM junction [34-36]. This has been corroborated by experimental data [37-42]; however, the experimental data spans a number of techniques, making it difficult to directly compare the results. In addition, there are two competing mechanisms for tunneling transport in MMM systems, namely through bond and through space tunneling [34]. While it is quite possible for tunneling in alkanethiol and alkanedithiol systems to be a combination of both through bond and through space tunneling, the primary conduction mechanisms for chemically bound and unbound alkanes are still up in the air. Diffusive tunneling (electron ‘hopping’) is not expected to occur in the manner in which it is understood in conjugated organic materials and DNA systems since alkanes have a relatively inaccessible conduction band throughout their entire carbon backbone [43, 44]. Hopping into or through the metal/molecule interface is an option, and altering the chemical bonds from thiols to isocyanides has been shown to produce dissimilar tunneling currents [41, 45]. Yet
the variation seen in these systems could just as easily be due to competing mechanisms such as: small mechanical changes due to electrostriction [40]; changes in surface bound image potential and/or work function at the SAM/metal interface [25, 35, 45-47]; or by increased (or reduced) flexibility, length, or orientation at the surface bond [35]. In addition to the uncertainty already attributed to the metal/molecule interface, the molecular junctions formed by nTP were shown to yield considerably higher barrier heights than those obtained by other methods (Chapters 4 and 5). One way to help elucidate the influence of the metal/molecule interface in transfer printed MMM junctions would be to change the chemical attachment at the metal. Nanotransfer printing onto diisocyanides has not yet been studied and would be an interesting addition to the studies already performed. A second way to probe the metal/molecule interface would be to change the extent of the covalent attachment at the metal/molecule interface. This could be easily done by nanotransfer printing onto surfaces prepared from mixed dithiol/monothiol, diisocyanide/minoisocyanide, or dithiol/diisocyanide solutions.

It is known that mixed monolayer surfaces can be formed from mixed SAM molecule solutions [12]. Therefore, preliminary experiments focused on preparing mixed monolayer surfaces from decanedithiol/decanethiol solutions. Two separate solutions were made; a 30 mM solution of decanedithiol (DDT) in absolute ethanol and a 30 mM solution of decanethiol (DT) in absolute ethanol. The solutions were combined in varying ratios using graduated pipettes. The solutions were purged with N₂, brought into the glovebox, and freshly evaporated gold surfaces were soaked in the mixed monolayer solutions for 24 hours according to the glovebox conditions outlined in section 2.2.1 of Chapter 2. Three surfaces of each DT:DDT ratio were fabricated simultaneously, one each for contact angle
measurement, XPS, and for nTP. The surfaces were removed from their respective solutions, sonicated for 30 s in THF to remove any physisorbed molecules, and dried with a N\textsubscript{2} stream. The XPS and contact angles were gathered immediately after drying and the results can be seen in Figure 6.1A. As expected, the contact angle increases dramatically as the surface becomes more aliphatic with a larger percentage of decanethiol on the surface (black line). Similarly it can be seen that the ratio of total sulfur versus total gold goes down with the reduction of the number of terminal thiols (red line). These results imply that the exposed thiols for covalent binding during nanotransfer printing are reduced as the ratio of decanethiol increases. They also show that the spaces that do not have decanedithiol are filled with decanethiol, hence the increase in contact angle.

The remaining surfaces were used for creating MMM junctions via nTP. 200 nm diameter circles of Au (20 nm thick) were printed onto each surface using a PFPE mold as outlined in section 4.2.4 of Chapter 4. Only surfaces soaked in solutions with \( \geq 25\% \) decanedithiol contained enough terminal thiols for successful nTP. Conductive atomic force microscopy was performed on these features for each surface and the resulting I-V characteristics were interpreted using the Simmons model. The barrier heights are shown in Figure 6.1B and show a significant reduction in the barrier height as the amount of decanedithiol increases. This suggests that covalent attachment at the top metal electrode plays a significant role in the tunneling mechanism in nTP formed MMM junctions by reducing the tunneling barrier. Many situations would make this occur such as if the covalent thiol/metal bond pulls the electrode closer to the molecule and shortens the tunneling gap, if surfaces image potential is altered [25, 35, 47], or if there is a substantial difference between a metal/thiol and a metal/terminal methyl contact barrier. The later effect
Figure 6.1. Mixed monolayer surfaces. A) Contact angle (black) and XPS (red) of mixed dithiols/monothiol surfaces. B) Barrier height versus percent decanedithiol as found using the Simmons model.
has been witnessed in previous work [42].

Regardless the reason for the reduction in the barrier height, additional work needs to be performed in this area before any solid hypotheses can be formed. Forming similar junctions with different chemical attachment is required such as with terminal cyano and/or nitro groups. In addition, permanent junctions should be fabricated as outlined in Chapter 5 so the junctions could be studied under higher bias and at lower temperatures.

6.2.2. Modeling MMM Tunneling Characteristics using a Multi-Barrier Tunneling Model. It would be wonderful if tunneling current occurred by simply one mechanism or through only one distinct tunneling barrier height (or shape for that matter) in MMM junctions; however, this is virtually never the case since surface roughness, pinhole defects, molecule orientation, molecule/metal interface, and regional lattice fluctuations can alter the barrier height and shape of the tunneling barrier [34, 36, 40, 45, 47]. The Simmons equation is a great model to estimate barrier height and decay coefficients of MMM junctions. Yet, the Simmons equation was formulated as an approximation to model a symmetrical, rectangular square tunneling barrier (under zero bias) with the insulator’s band gap centrally located with respect to the two electrodes Fermi levels (Figure 6.2A) [33]. This is more or less correct given a perfect Au/alkane/Au junction, but with alkanedithiols, metal/molecule barriers exist at each electrode. In addition, it can be expected that junctions formed by nTP would have two significantly different Au electrodes since one is thermally deposited and the other is transfer printed. For example, it was shown in section 4.2.5 of Chapter 4 that the morphology and surface roughness of metal thin films thermally deposited on PFPE and PDMS stamps is much different than that of thermally deposited thin films on Si/SiOₓ wafers. One could anticipate a drastic difference in Au/thiol bond formation with
Figure 6.2. Simmons model and multibarrier tunneling model. A) Quantum tunneling model laid out by Simmons. Designates one rectangular tunneling barrier to define the entire system (grey). B) Multibarrier tunneling model with three distinct tunneling barriers (green, orange, and blue). Adapted from reference [42]. $E_F$ represents the Fermi level of the metal electrodes.

$$\beta_0 = \frac{\beta_1 d_1 + \beta_{\text{body}} d_{\text{body}} + \beta_2 d_2}{d_1 + d_{\text{body}} + d_2}$$
SAMs formed on the bottom electrode from ethanolic solution versus Au/thiol attachment during the nTP process. In any case, both Au/thiol bonds (to the bottom electrode and to the nTP film) would be likely to contribute to the charge transport mechanism, and a more accurate model would need to account for multiple different barriers.

Multibarrier models are not new; indeed, a useful model has been proposed to include the influence on electron tunneling at the metal/molecule interfaces [42, 48]. This model divides the tunneling barrier into three parts; 1) the alkane backbone, 2) the bottom electrode’s metal/molecule interface, and 3) the top electrode’s metal/molecule interface (Figure 6.2B). The overall decay coefficient (\( \beta_o \)) can be designated as a combination of the two metal/molecule interfaces and the carbon backbone, each with their own beta decay and tunneling distance (d). This model, and perhaps an expanded model that accounts for regional defects or air gaps that occur during nTP, should be used to fully interpret the electrical characteristics of MMM junctions formed by nTP.

6.2.3. Conjugated Oligomers in MMM Junctions. Quantum tunneling is a fascinating quantum mechanical phenomenon. It is the primary mode of current transport in molecular tunneling junctions (barring defects), and is important for spintronic devices based on tunneling magnetoresistance. However, in metal/insulator/metal junctions the electron does not reside within the molecule for any tangible amount of time. This may seem trivial but the ramifications are not. Since the electron does not exist within the molecule it cannot be manipulated as it traverses the tunneling barrier. Stated more directly, a tunneling junction cannot be manipulated by external stimuli. By definition, semiconductors contain a narrower HOMO–LUMO gap than insulators. Therefore, while applying a bias to a metal-semiconductor-metal junction, it is possible for the electrons to access the conduction band.
while they travel across the semiconducting layer. During that time, they can be manipulated by external sources such as light or electric field depending on the semiconducting material. This gives an extra mode of control over the junction that can be used to modulate the current. The next step in MMM junctions by nTP would be to incorporate organic semiconductors as the active molecule layer.

Semiconducting properties have been seen in small molecule, oligomer, and polymer organic materials [49-51]. The most interesting for molecule based electronics from a metal-molecule-metal standpoint would be \( \pi \)-conjugated oligomers since they can be easily self-assembled on conductive electrodes. Some possible oligomers include, but are not limited to: para-phenylene, oligothiophene, oligoacenes (anthracene, pentacene, etc.), and other synthetic derivations. Electron injection from metal electrodes into covalently bound conjugated materials and charge transport along conjugated organic backbones has been studied rigorously for the last couple decades [52-54], although no applicable molecular electronic MMM device has yet to hit the market.

As a proof of concept, Au metal thin films were printed onto a 4,4’-biphenyldithiol coated Au electrode using the printing method outlined in section 4.2.2 of Chapter 4. Though printing was successful (Figure 6.3), electrical characteristics have not yet been obtained.

Even more intriguing would be the use of semiconducting organic molecules in molecular spintronic devices. Semiconducting molecules present many advantages to spintronic systems. Organic materials are known to have large spin diffusion lengths (> 100 nm), much longer than their inorganic counterparts [29]. This occurs since organics contain relatively light elements with small nuclei and therefore have weak spin-orbital coupling and
Figure 6.3. Nanotransfer printing of 20 nm films of Au onto a 4,4’-biphenyldithiol coated Au electrode via PDMS.
weak hyperfine interactions [55, 56]. Because of this, the molecule layer in an organic spin valve could theoretically be fairly large while still maintaining its spin polarization. Since organic semiconductors are optically active, semiconducting active layers are good candidates for new types of magneto-optoelectronic device [29]. Moreover, organic semiconductors offer the ability to manufacture a system where spins can be controlled in molecules down to a single spin [28]. In preparation of molecular spintronics, the spin polarized current within molecular semiconductors has been studied theoretically and experimentally, and it has been found that the spin polarization is maintained as it travels along the molecules’ backbone [20, 28]. This proves that semiconducting organic molecules could be successfully employed in molecule based spintronics; however, a successful device has not yet been realized.

6.2.4. Smoother Surfaces via Template Stripping Method. As discussed previously (section 4.2.2), the surface roughness of the bottom metal thin film electrode significantly impacts the packing of a molecular monolayer. More notably, a roughened surface would expose fewer thiol groups for binding to the top metal thin films during nTP, leading to either partial transfer or transfer failure. Even with successful printing, the surface roughness of the bottom metal thin film will affect the number of thiols that ultimately bind to the top printed electrode. It is easy to imagine that this may translate into a noticeable variation in the measured tunneling resistance of each device. More importantly, the coupling of inherent roughness to tunneling current might explain: a) why a 100% success rate has not yet been achieved while measuring the tunneling current of printed nano devices (only 94% successful junctions per substrate thus far); and b) the standard deviation of measured resistance values was not negligible in measured devices.
One approach to fabricate an ultra smooth film is template stripping [57-59]. Schematically shown in Figure 6.4, this method replicates the surface of an ultra flat substrate by first slowly depositing a metal thin film onto that surface. When deposited at a constant, slow rate (< 1 Å/s), the metal atoms are given ample time to organize and evenly coat the entirety of the surface. Therefore, at the interface, the freshly deposited film should be an ultra smooth mirror image of the initial surface. A second rigid substrate is then glued onto the freshly deposited film, the glue is cured, and the rigid substrate is mechanically cleaved from the initial surface. The result is a rigid substrate/glue/thin film surface that replicates the ultra smooth surface of the original material.

Initial attempts to replicate smooth Si/SiO$x$ substrates (starting $R_{rms} = 0.134$ nm) by this method produced relatively smooth Au thin films. Starting with a clean, dry Si/SiO$x$ wafer, 100 nm of Au was deposited (~0.5 Å/s) directly onto the surface (note: without a titanium adhesion layer). A glass slide was super-glued (Super Glue Gel, 3M) to the surface and allowed to cure for 24 hours. The glass slide was pulled from the Si/SiO$x$ substrate, taking with it the deposited Au film. The resulting surface was analyzed by AFM. It was found that the $R_{rms}$ was low (0.560 nm), but there exist obvious surface anomalies visible in the AFM image (Figure 6.4), most likely due to the rough nature of the mechanical stripping step during the removal of the film. In contrast, prior work has shown template stripping to produce very smooth (~0.20 nm), defect free surfaces over a relatively large areas from Si/SiO$x$ surfaces [57] and from freshly cleaved mica [59]. Future optimization of template stripped films should afford near atomically smooth metal thin film surfaces which would be expected to improve the quality of nanotransfer printing. Furthermore it should ensure that nearly every terminal thiol is covalently bound to the top electrode to result in a near perfect
Figure 6.4. Template stripping. A) A metal thin film is deposited onto an ultra smooth substrate. B) An adhesive is applied. C) A rigid substrate is pressed onto the adhesive and cured. D) The rigid substrate is mechanically cleaved from the substrate. An AFM of a template stripped Au surface on a glass slide.
6.2.5. Device Fabrication through Multiple nTP Steps. Nanotransfer printing offers the unprecedented opportunity to bring molecular electronics and molecular spintronics directly from a fundamental research level to new areas of device architecture and application. Transfer printing is an additive approach, which begs the question can nTP be used to build three dimensional structures, and if so, will these three dimensional structures respond as expected? Three dimensional structures of alternating ferromagnetic metals would be incredibly attractive for spintronic devices since it is known that the magnetoresistance effect is increased with additional layers in series [3, 60]. In principle, the ideal structure would alternate ferromagnetic layers with dissimilar coercivities.

As a proof of concept, stacked metal thin film structures were attempted. After forming an Au/decanedithiol/Au junction via nTP (100 µm square) by the same method outlined in section 4.2.2 of Chapter 4, the entire substrate was soaked into a decanedithiol solution to form a SAM layer atop the printed metal electrode. A second nTP step was carried out to transfer another thin Au film (20 nm) with smaller lateral size (50 µm square) onto the SAM coated nTP feature. The result was an Au/decanedithiol/Au/decanedithiol/Au junction. Although feature alignment can be an issue (alignment was performed by hand under a microscope), it is noticed that a stacked structure can be obtained by applying a second nTP process (Figure 6.5). The whole process can be optimized to obtain better alignment/registration where it is imagined that both series and parallel devices can be formed by this method. From a printing point of view, the surface roughness on top of the first printed feature should be minimized to ensure that the second printing step occurs without any issues. Root mean square roughness values have been gathered from features
Figure 6.5. Stackable nTP. Proof of concept of an Au/decanedithiol/Au/decanedithiol/Au junction.
printed by both PDMS and PFPE (Chapter 4). The roughness of the features printed by PFPE ($R_{rms} = 1.539$ nm) is considerably less than that printed by PDMS ($R_{rms} = 1.871$ nm) although the roughness is larger than ideal. Improving the printing technique further by employing different polymeric stamps, using removable sacrificial layers on the stamp, or improving bottom substrate surface roughness should produce higher quality nTP. Smoother, well defined nTP features should in turn make the fabrication of three dimensional structures by nTP much easier.

The current model for nTP uses thermally deposited metal thin film bottom electrodes, yet it is easy to imagine that the bottom electrode could be formed by nTP as well. Realizing that stackable nTP is possible, it was thought that a thin metal wire could be printed onto an insulating substrate. The printed substrate could then be soaked in a SAM solution and a thin wire could be printed perpendicular to the initial contact to complete a crosswire-like device (Figure 6.6).

Firstly, a bottom contact needed to be fabricated on an insulating substrate. Transfer printing has been carried out on Si/SiOH [30] and SAM coated Si/SiO$_x$ [61] surfaces in other work. Exploiting well known silane chemistry, 3-(mercaptopropyl)trimethoxysilane (MPTES) was used to form a thiol terminated SAM on Si/SiO$_x$. Nanotransfer printing of 20 nm thick, gold was carried out on the MPTES surfaces using PDMS stamps as laid out in section 4.2.2 of Chapter 4. This surface was then immediately immersed into a 30 mM decanedithiol solution for 24 h to form a monolayer atop the printed film. A second nTP formed a crosswire structure affording a MMM junction at the two wires’ interface. A proof of concept device can be seen in Figure 6.6E where a 100 $\mu$m wire was printed onto a Si/SiO$_x$ wafer followed by printing a series of 100 $\mu$m wires across the initial wire. A four point
Figure 6.6. nTP + nTP device. A) A bottom contact is printed onto a SAM coated Si/SiO$_x$ wafer. B) After forming a SAM on the bottom contact, a second nTP step forms the top contacts. C) MMM junctions. D) Current-Voltage characteristics of nTP + nTP junctions. E) Optical microscope images of representative junctions.
probe conductive measurement was carried out on these junctions using a probe station, and the results can be seen in Figure 6.6D. The barrier height of this junction was found to be 2.57 by Simmons fitting.

Future work in this area should focus on improving the transfer printing while forming this style of junction. Of the 45 MMM junctions fabricated by this technique, only 6 gave clean tunneling-like behavior while a grand majority of the devices (33) were shorted. Moreover, the tunneling current of the devices that worked was sporadic with resistances ranging from a few hundred Ohms to tens of thousands of Ohms. The printed bottom contact was 20 nm thick; therefore, it protrudes off of the Si/SiO\textsubscript{x} wafer and forces the top electrode to stretch over the top. It is assumed that most often the shorting occurs due to flexing at the point where the top contact first intersects at the edge of the bottom electrode. Other future work should focus on the formation of spintronic devices through multiple nTP steps by replacing the Au electrodes with ferromagnetic metals. Of course all ferromagnetic work would need to be done under inert atmosphere.

6.3. Experimental

6.3.1. Template Stripping. Prior to thermal evaporation, silicon wafers (Si/SiO\textsubscript{x} - 1 micron thick surface oxide on one side, Addison Engineering) were cleaned in a solution of DI water, ammonium hydroxide (14.8M, Fisher Scientific), and hydrogen peroxide (ACS certified 30%, Fisher Scientific) in a 2:1:1 ratio for 15 minutes. The wafers were removed from this solution, rinsed thoroughly with water and ethanol (100%, Pharmco), and dried with a stream of dry nitrogen. Additional UV ozone cleaning (Bioforce Nanosciences ProCleaner\textsuperscript{TM}) was performed on the wafers for 20 minutes. 100 nm of Au was deposited (~0.5 Å/s) directly onto the wafer. A glass slide was super-glued (Super Glue Gel, 3M) to the
surface and allowed to cure for 24 hours. The glass slide was pulled from the Si/SiO\textsubscript{x} substrate with a pair of tweezers, taking with it the deposited Au film. The evaporation boats were purchased from RD Mathis (tungsten, S42-015W). Gold (99.999) was purchased from Kurt J. Lesker, Inc. Thermal evaporations were performed with an MBraun evaporator contained within an MBraun nitrogen glovebox such that freshly evaporated thin films could be removed from the evaporator chamber under a nitrogen atmosphere. Thicknesses of films were determined using a quartz crystal microbalance located just below the substrate holder in the evaporator. Tooling factors were determined by measuring the true thicknesses of films with a profilometer.

AFM was collected using an Asylum Atomic Force Microscope (Asylum MFP-3D, Asylum Research). The microscope was operated in tapping mode at ambient conditions (T = 21°C, RH = 45%), using silicon cantilevers (BudgetSensors, Tap300Al) with resonance frequencies of approximately 300 kHz, a force constant of ~ 40 N/m, and tip radii less than 10 nm.

6.3.2. Preparation of SAMs on Si/SiO\textsubscript{x} Wafers. Si/SiO\textsubscript{x} substrates were prepared by cleaning in a 2:1:1 solution of water, hydrogen peroxide, and ammonium hydroxide for 15 minutes. These substrates were rinsed by water and ethanol, dried with a N\textsubscript{2} stream, and cleaned via UV ozone treatment for 1 hr. Following UV ozone, the Si/SiO\textsubscript{x} wafers were immediately submerged in a 5 % solution (v/v) of MPTES in hexanes. Acetic acid was added (~ 0.1 % (v/v) with respect to MPTES) to catalyze the surface reaction. After 24 h, the substrates were removed from the solution, sonicated for 30 s in THF, rinsed with ethanol, and dried by an N\textsubscript{2} stream.
6.4. References


