The Pennsylvania State University

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# CONTROLLING ADSORBATE INTERACTIONS FOR ADVANCED CHEMICAL PATTERNING

A Dissertation in

Chemistry

by

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### ABSTRACT

Molecules designed to have specific interactions were used to influence the structural, physical, and chemical properties of self-assembled monolayers. In the case of 1-adamantanethiolate monolayers, the molecular structure influences lability, enabling alkanethiol molecules in solution to displace the 1-adamantanethiolate monolayers, ultimately leading to complete molecular exchange. The similar Au-S bond environments measured for both *n*-alkanethiolate and 1-adamantanethiolate monolayers indicate that displacement is *not* a result of weakened At bond s. Instead, it was hypothesized that the density differences in the two monolayers provide a substantial enthalpic driver, aided by differences in van der Waals forces, ultimately leading to complete displacement of the 1-adamantenthiol molecules.

Additionally, it was discovered that displacement occurs via fast insertion of n-dodecanethiolate at the defects in the original 1-adamantanethiolate monolayer, which nucleates an island growth phase and is followed by slow ordering of the n-dodecanethiolate domains into a denser and more crystalline form. Langmuir-based kinetics, which describe alkanethiolate adsorption on bare Au{111}, fail to model this displacement reaction. Instead, a model of perimeter-dependent island growth yields good agreement with kinetic data over a 100-fold variation in n-dodecanethiol concentration. Rescaling the growth rate at each concentration collapses all the data onto a single universal curve, suggesting that displacement is a scale-free process.

Exploiting the knowledge gained by studying 1-adamantethiolate monolayer displacement, a reversible molecular resist was developed, in which displacement is

controlled via external stimuli. This methodology for the fabrication of controllably displaceable monolayers relies on carboxyl-functionalized self-assembled monolayers and *in-situ* Fischer esterification. Using an 11-mercaptoundecanoic acid monolayer as a model system, it was shown that *in-situ* esterification results in the creation of subtle chemical and structural defects that promote molecular exchange reactions to go to completion. The complementary hydrolysis reaction can be employed to quench the reacted monolayer, significantly hindering further displacement. The generality of reversible lability was tested by applying the *in-situ* esterification reaction to the structurally distinct carboxyl-functionalized molecule 3-mercapto-1-adamantane-carboxylic acid.

In addition to the studies of manipulating the interactions in self-assembled monolayers, materials with tunable optical and electronic properties were fabricated using atomic clusters as building blocks. It was shown that materials assembled from the same cluster motif, in this case  $As_7^{3-}$ , can result in materials with band gaps that vary predictably between 1.09 to 2.08 *eV*. The size and highest occupied molecular orbital of the alkali metal counter-cation used in the assembly was shown to affect the band gap of the cluster-assembled solids. Furthermore, the dimensionality of the cluster-cluster interactions played a crucial role in determining the resulting properties.

These results demonstrate how complex surface assemblies, or novel solid materials, can be fabricated by manipulating the interactions between the individual components within the assemblies, paving the way for the fabrication of next-generation devices and materials.

## **TABLE OF CONTENTS**

| List of Figures   | ix    |
|---|-------|
| List of Tables  | xvii  |
| List of Abbreviations   | xviii |
| Acknowledgments   | XX    |
| Chapter 1 Controlling Molecular Assemblies                                  | 1     |
| 1.1 Introduction  | 1     |
| 1.2 Background  | 4     |
| 1.2.1 Scanning Tunneling Microscopy   | 4     |
| 1.2.2 Self-Assembled Monolayers   | 6     |
| 1.2.3 Infrared Reflection Absorption Spectroscopy                           | 13    |
| 1.3 Dissertation Overview   | 16    |
| Chapter 2 Hybrid Approaches for Nanoscale Patterning                        |       |
| 2.1 Introduction  |       |
| 2.2 Conventional Techniques   |       |
| 2.2.1 Micromolding  | 19    |
| 2.2.2 Microcontact Printing   | 21    |
| 2.2.3 Area-Selective Atomic-Layer Deposition                                | 21    |
| 2.3 Hybrid Techniques   | 23    |
| 2.3.1 Microdisplacement Printing  | 23    |
| 2.3.2 Microcontact Insertion Printing                                       | 25    |
| 2.3.3 Multilayer Transfer Printing  | 27    |
| 2.3.4 Biocatalytic Microcontact Printing                                    | 29    |
| 2.3.5 Stamp Surface Chemical Functionalization                              |       |
| 2.3.6 Decal Transfer Lithography  |       |
| 2.3.7 Nanoparticle Printing   |       |
| 2.3.8 Nanotransfer Printing.  |       |
| 2.3.9  Nanoskiving  |       |
| 2.3.10 Cell Growth and Function   |       |
| 2.4 Prospects for Soft Litnography  | 40    |
| Chapter 3 Displacement of 1-Adamantanethiolate Self-Assembled<br>Monolayors | 13    |
|   |       |
| 3.1 Introduction  |       |
| 3.2 Background  |       |
| 3.2.1 Scanning Tunneling Microscopy   | 44    |

| 3.2.2 X-ray Photoelectron Spectroscopy  | 44       |
|---|----------|
| 3.2.3 Electrochemistry and Cyclic Voltammetry                                 | 46       |
| 3.2.4 Infrared Reflection Absorption Spectroscopy                             | 47       |
| 3.3 Experimental Procedures   | 47       |
| 3.3.1 Sample Preparation  | 47       |
| 3.3.2 Scanning Tunneling Microscopy   | 48       |
| 3.3.3 X-ray Photoelectron Spectroscopy  | 48       |
| 3.3.4 Cyclic Voltammetry  | 49       |
| 3.3.5 Infrared Reflection Absorption Spectroscopy                             | 49       |
| 3.4 Results and Discussion  | 50       |
| 3.4.1 Scanning Tunneling Microscopy of Displaced Self-Assembled<br>Monolayers | 50       |
| 3.4.2 X-ray Photoelectron Spectroscopy of Displaced Self-Assembled            |          |
| Monolayers  | 52       |
| 3.4.3 Cyclic Voltammetry of Displaced Self-Assembled Monolayers               | 57       |
| 3.4.4 Infrared Reflection Absorption Spectroscopy of Displaced Self-          |          |
| Assembled Monolayers  | 59       |
| 3.4.5 Driving Force for 1-Adamantanethiolate SAM Lability                     | 61       |
| 3.5 Conclusions   | 62       |
| Universal Form  | 64       |
| 4.1 Introduction  | 04       |
| 4.2 Dackground  | 05       |
| 4.2.1 Initiated Reflection Absorption Specifoscopy                            | 05       |
| 4.5 Experimental Flocedures   | 05       |
| 4.3.1 Sample reparation   | 05       |
| 4.3.3.1-Adamantanethiolate Monolaver Displacement                             | 05       |
| 4.4 Results and Discussion  | 00       |
| 4.4 Results and Discussion $\frac{1}{4}$ Adamantanethiolate Monolayers        | 00       |
| 4.4.1 Initiated Spectra of 1-Adamantanethiolate Monolayer Displacement        | 00<br>68 |
| 4.4.3 Kinetic Modeling of 1-Adamantanethiolate Monolayer Displacement         | 08<br>68 |
| 4.4.4 Concentration Dependence on the Rate Constant                           | 00       |
| 4 4 5 Model Free Analysis and Universality                                    | 75       |
| 4.4.6 Implications of 1-Adamantanethiolate Monolaver Displacement Kinetics    | 80       |
| 4 5 Conclusions   | 82       |
| Chapter 5 Reversible Lability by <i>in situ</i> Reaction of Self-Assembled    |          |
| Monolayers  | 84       |
| 5.1 Introduction  | 84       |
| 5.2 Background  | 88       |
| 5.2.1 Infrared Reflection Absorption Spectroscopy                             | 88       |
| 5.2.2 X-ray Photoelectron Spectroscopy  | 88       |
| 5.3 Experimental Procedures   | 88       |
| 5.2.1 Sample Droparation  | 88       |

| 5.3.2 Infrared Reflection Absorption Spectroscopy   | 90                         |
|---|----------------------------|
| 5.3.3 X-ray Photoelectron Spectroscopy  | 90                         |
| 5.4 Results and Discussion  | 91                         |
| 5.4.1 Characterization of 11-Mercaptoundecanoic Acid, <i>in situ</i> Esterified               |                            |
| 11-Mercaptoundecanoic Acid, and 1-Ethyl-11-Mercaptoundecanoate                                | 01                         |
| SAMS (Step 1, Figure 5.3)   | 91                         |
| 11 Mercantoundecanoic Acid 1 Ethyl 11 mercantoundecanoite and n                               |                            |
| $\Gamma$ -Mercapioundecanoic Acid, $\Gamma$ -Entry $\Gamma$ -fine capioundecanoate, and $n$ - | 07                         |
| 5.4.3 Hydrolysis of <i>in situ</i> Esterified 11-Mercantoundecanoic Acid SAMs (Sten           | )/                         |
| 3 Figure 5.1)   | 108                        |
| 5.5 Conclusions.  | 110                        |
|   |                            |
| Chapter 6 The Effect of Counter-Cations and Structure in Cluster-                             |                            |
| Assembled Materials   | 113                        |
| 6.1 Introduction  | 113                        |
| 6.2 Background  | 115                        |
| 6.2.1 Diffuse Reflectance Spectroscopy  | 115                        |
| 6.2.2 Absorption Edge of Semiconductors   | 116                        |
| 6.3 Experimental Procedures   | 118                        |
| 6.3.1 Sample Preparation  | 118                        |
| 6.3.2 Diffuse Reflectance Spectroscopy  | 121                        |
| 6.4 Results and Discussion  | 122                        |
| 6.4.1 Effects of Cationic Linker on As7-Based Cluster Assemblies                              | 122                        |
| 6.4.2 Effects of Charge Transfer and Covalent Linkers in As <sub>7</sub> Dimers               | 128                        |
| 6.4.3 Effects of Counter-Cations in Metal-Linked Cluster Assemblies                           | 131                        |
| 6.5 Conclusions   | 135                        |
| Chanter 7 Conclusions and Future Presencets   | 137                        |
| 7 1 Lability in Self-Assembled Monolayers   | 138                        |
| 7.2 Reversible Molecular Resists  | 1/0                        |
| 7.3 Cluster Assembled Materials   | 1/2                        |
| 7.4 Final Thoughts  | <u>144</u><br>1 <i>1</i> 1 |
| 7.4 Thial Thoughts  | 144                        |
| Appendix Infrared Scanning Tunneling Microscope   | 146                        |
| A.1 Introduction  | 146                        |
| A.2 Evanescent Coupling and Experimental Setup  | 147                        |
| A.3 Instrument Schematics and Assembly  | 151                        |
| A.3.1 STM Exoskeleton   |                            |
| A.3.2 STM Head  | 161                        |
| A.3.3 Coarse Approach   | 165                        |
| A.3.4 Vibration and Acoustic Isolation  | 168                        |
| A.3.5 Current Preamplifier  | 169                        |
| A.3.6 Substrates and Sample Preparation   | 178                        |
| A.3.7 Optics Setup  | 182                        |

# viii

| References                              | 196 |
|---|-----|
| A.6 Summary                             | 194 |
|   | 104 |
| A.5 Signal-to-Noise Calculation         |     |
| A.4 Infrared Source and Data Collection |     |

### **List of Figures**

- Figure 1.2. Schematic of a *n*-alkanethiol (ALK) SAM on a Au{111} substrate. (A) A side view along the nearest neighbor direction showing the 30° tilt to maximize the van der Waals interactions. (B) Top down view showing the unit cell of the Au substrate, as well as the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  unit cell and the  $c(4 \times 2)$  superlattice. Shading highlights the  $c(4 \times 2)$  structure. (C) A single surface-bound all-*trans* ALK molecule in which  $\theta, \psi$ , and  $\phi$  represent tilt, twist, and azimuth angles of the chain, respectively.
- Figure 1.4. (A) and (B) Scanning tunneling microscopy images of an **AD** SAM on a Au{111} substrate acquired with a  $V_{sample} = -1.0$  V and a  $I_{tunnel} = 5.0$  pA. Although Au substrate vacancy islands are visible in the STM images of the **AD** SAM, the images lack the protruding domain boundaries typically seen in **ALK** SAMs. (C) A side view along the nearest neighbor direction showing ~0° tilt. (D) Top-down view showing the unit cell of the Au substrate, as well as the  $(\sqrt{91} \times \sqrt{91})R5.21^{\circ}$  unit cell.

Figure 1.5. Stretching and bending vibrational modes of a methylene (-CH<sub>2</sub>-) group.... 14

- Figure 1.6. (A) Schematic of mirror dipoles generated on a metallic surface, showing how molecular dipoles parallel to the surface result in a net zero dipole moment.
  (B) and (C) Infrared reflection absorption spectroscopy (IRRAS) spectra of a C12 SAM on a Au{111} substrate, showing higher energy stretching modes (B), and lower energy bending and wagging modes (C).

- Figure 2.3. (A) Schematic and (B) and (C) field emission scanning electron micrographs of a chemical pattern fabricated by microdisplacement printing. The higher intensity

| regions   | correspond | to j | patterned  | 11- | mere | captoundenca | ic aci | d (M  | IUDA)    | and   | low  |
|-----------|------------|------|------------|-----|------|--------------|--------|-------|----------|-------|------|
| intensity | background | l co | orresponds | to  | the  | pre-existing | 1-ada  | manta | anethiol | ate ( | (AD) |
| self-asse | mbled mono | laye | er         |     |      |              |        |       |          |       | 24   |

### 

| Figure 2.6. Relief stamps (A) can suffer decreased resolution and pattern defects as a result of material failure and lateral ink diffusion. A flat stamp (B) does not encounter these issues  |
|--|
| Figure 2.7. Schematics of the two types of decal transfer lithography, (A) cohesive mechanical failure and (B) selective pattern release   |
| Figure 2.8. Schematic of the nanoskiving process   |
| Figure 2.9. Schematic of molding as used to control the size and shape of bacteria cells.  |
| Figure 3.1. Scanning tunneling microscopy images of 1-adamantanethiolate ( <b>AD</b> ) SAMs displaced by a 1.0 mM <i>n</i> -dodecanethiol ( <b>C12</b> ) solution with exposure times ranging from 0 min to 24 h. The most protruding domains correspond to <b>C12</b> , the least protruding to <b>AD</b> , and the depressed regions correspond to Au substrate vacancy islands. Image parameters: $V_{sample}=1.0$ V; $I_{tunnel}=2$ pA. Image acquisition in |

Figure 3.2. X-ray photoelectron survey spectrum of an **AD** SAM deposited from solution.

collaboration with T. J. Mullen and A. A. Dameron. 51

- Figure 3.4. Representative XPS 2p emission spectra of AD SAMs displaced by a 1.0 mM C12 solution with exposure times of (A) 0 min and (B) 40 min. (C) A representative S 2p XPS emission spectrum of a C12 SAM deposited from solution for 24 h. Spectra were fit with GL line shapes with contributions centered around 162.0 eV (*pink*) and 163.2 eV (*cyan*). Spectra collected in collaboration with A. A. Dameron and R. W. Hengstebeck. 56

- Figure 4.7. Plot of coverage versus reduced exposure time of two experimental runs at each C12 concentration (0.01, 0.03, 0.11, 0.33, 0.55, 0.77, and 1.0 mM), showing

- Figure 5.1. Reaction and patterning scheme of the chemically induced exchange reactions in 11-mercaptoundecanoic acid (MUDA) SAMs. (Step 1) Exposure to HCl and ethanol leads to the formation of a disordered ester intermediate, 1-ethyl-11mercaptoundecanoate (*in situ* esterified MUDA). (Step 2) Subsequent exposure to *n*-dodecanethiol (C12) solution enables tunable (fractional or complete) displacement of the reactive intermediate. (Step 3) Sections of the SAM containing undisplaced ethyl ester molecules can be hydrolyzed and quenched to prevent further exchange or displacement by exposure to aqueous HCl. The same patterning scheme was also applied to 3-mercapto-1-adamantanecarboxylic acid (MADCA) SAMs... 86

- Figure 5.8. Representative IRRAS spectra of an *n*-dodecanethiolate (C12) SAM (a) before displacement, (b) after exposure to similar Fischer esterification conditions used to esterify MUDA SAMs, and (c) after 1 h exposure to 1.0 mM perdeuterated *n*-dodecanethiol (C12<sub>d25</sub>) solution. The minor spectral changes after exposure to the C12 solution demonstrate that robust unfunctionalized SAMs can withstand the *in situ* esterification without leading to significant molecular exchange with further thiol exposure.

- Figure 6.2. Crystal structures of (A) the three-dimensional material As<sub>7</sub>Cs<sub>3</sub> (Compound 1), where the interactions of Cs with As<sub>7</sub> are shown; (B) twodimensional sheet of As<sub>7</sub> clusters bound by Cs, while the (K – Crypt)<sup>+</sup> separates

- Figure A.1. Evanescent wave generated by back illumination, which occurs when total internal reflection criteria are met. 149
- Figure A.3. Photograph showing the key components of the custom-built IRSTM exoskeleton. (A) Aerial view. (B) Side view without the removable side door..... 152

| Figure A.5. Schematic of the top plate. Due to the number of dimensions, the schematic was redrawn three times for clarity. A photograph of the top plate can be seen in Figure A.4C. 154   |
|---|
| Figure A.6. Schematic of the sample holder. A photograph of the sample holder can be seen in Figure A.4A  |
| FigureA.7. Schematic of the bottom plate. A photograph of the bottom plate can be seen<br>in Figure A.3.B   |
| Figure A.8. Schematic of the support rod. A photograph of the support rod can be seen in Figure A.3.B   |
| Figure A.9. Schematic of the side panel. A photograph of the side panel can be seen in Figure A.3.B   |
| Figure A.10. Schematic of the top STM 'foot'. The bottom STM 'foot' is a mirror image of the top 'foot'. A photograph of the STM 'foot' can be seen in Figure A.3 159   |
| Figure A.11. Schematic of the removable side door. For clarity, the handle is not shown in the schematic. A photograph of the removable side door can be seen in Figure A.3.A. 160  |
| Figure A.12. Photographs of (A) the custom-built IRSTM head, (B) the IRSTM head with the current wire removed for clarity, (C) the Macor base with an unglued scan tube, (D) the back of an unmounted tip assembly, showing the Ni print, and (E) the front of the tip assembly, showing the epoxy resin                    |
| Figure A.13. Schematic of the STM tip assembly. Photographs of the tip assembly can be seen in Figure A.12. 163   |
| Figure A.14. Schematic of the Macor base. A photograph of the Macor base can be seen<br>in Figure A.12.C  |
| Figure A.15. Photographs of the mounted MS5 Mirco Piezo Slides used for coarse approach. (A) The commercially available L-bracket for movement in three dimensions. The three different axes are labeled for clarity. (B) The custom-built M-bracket, which balances the weight of the STM head, enabling molecular imaging |
| Figure A.16. Schematic of the M-bracket. A photograph of the M-bracket can be seen in Figure A.15.B   |
| Figure A.17. Photographs of the alternating stack of stainless steel plates and polymers  |

used for vibrational dampening. (A) The bottom two steel plates on top of an optical jack. (B) The bottom two steel plates with the preamplifier holder inserted. (C)

- Figure A.19. Schematic of the bottom stainless steel plate used for vibrational dampening. A photograph of the bottom steel plate can be seen in Figure A.17.... 172
- Figure A.20. Schematic of the middle stainless steel plate used for vibrational dampening. A photograph of the middle steel plate can be seen in Figure A.17....173

Figure A.22. Schematic of the preamplifier holder. A photograph of the preamplifier holder can be seen in Figure A.17.
Figure A.23. Schematic of the preamplifier plate. A photograph of the preamplifier plate can be seen in Figure A.17.
176

## List of Tables

| Table 6.1.<br>materi | Molecular formulas and compound numbers of the studied cluster-assembled ials  |
|----------------------|--|
| Table 6.2.<br>based  | Experimentally measured and theoretically calculated band gaps of the <i>As</i> <sub>7</sub> -cluster-assembled materials                    |
| Table 6.3.<br>dimer  | Experimentally measured and theoretically calculated band gaps of cluster s with either Zn or Au covalently bound to $As_7$ (Compounds 8-10) |

## List of Abbreviations

| Molecules          |  |  |  |  |
|--------------------|--|--|--|--|
|                    |  |  |  |  |
| AD                 | 1-Adamantanethiol  |  |  |  |
| ALK                | Alkanethiol  |  |  |  |
| C8                 | n-Octanethiol  |  |  |  |
| C10                | n-Decanethiol  |  |  |  |
| C12                | n-Dodecanethiol  |  |  |  |
| C12 <sub>d25</sub> | Perdeuterated <i>n</i> -Dodecanethiol                      |  |  |  |
| Crypt              | 4,7,13,16,21,24-Hexaoxa-1,10-Diazabicyclo[8.8.8]Hexacosane |  |  |  |
| EMU                | 1-Ethyl-11-Mercaptoundecanoate                             |  |  |  |
| MUDA               | 11-Mercaptoundecanoic Acid                                 |  |  |  |
| MADCA              | 3-Mercapto-1-Adamantanecarboxylic Acid                     |  |  |  |
| ODTS               | Octadecyltrichlorosilane                                   |  |  |  |
| PEG                | Poly(Ethylene Glycol)                                      |  |  |  |
| PDMS               | Poly(Dimethylsiloxane)                                     |  |  |  |

# **Patterning Techniques**

- ALD Atomic Layer Deposition
- DPN Dip Pen Nanolithography
- MTP Multilayer Transfer Printing
- nTP Nanotransfer Printing
- SPL Scanning Probe Lithography
- μCIP Microcontact Insertion Printing
- μCP Microcontact Printing
- μDP Microdisplacement Printing

# **Characterization Tools**

| CV    | Cyclic Voltammetry                          |
|-------|---|
| IRRAS | Infrared Reflection Absorption Spectroscopy |
| RAIRS | Reflection Absorption Infrared Spectroscopy |
| STM   | Scanning Tunneling Microscopy               |
| XPS   | X-ray Photoelectron Spectroscopy            |

# **Other Acronyms**

| E <sub>b</sub>      | Binding Energy                              |
|---------------------|---|
| E <sub>bg</sub>     | Band Gap                                    |
| E <sub>F</sub>      | Fermi Energy Level                          |
| E <sub>k</sub>      | Kinetic Energy                              |
| E <sub>p</sub>      | Cathodic Peak Potential                     |
| FWHM                | Full-Width-at-Half-Maximum                  |
| GL                  | Gaussian-Lorentzian                         |
| НОМО                | Highest Occupied Molecular Orbital          |
| Ip                  | Cathodic Peak Current                       |
| I <sub>tunnel</sub> | Tunneling Current Set Point                 |
| JMAK                | Johnson, Mehl, Avrami, and Kolmogorov Model |
| LUMO                | Highest Unoccupied Molecular Orbital        |
| SAM                 | Self-Assembled Monolayer                    |
| UV                  | Ultraviolet                                 |
| V <sub>sample</sub> | Applied Sample Bias                         |
| θ                   | Surface Coverage                            |

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### Chapter 1

### **Controlling Molecular Assemblies**

## **1.1 Introduction**

Reducing the feature size in patterned functional materials has enabled the fabrication of high-performing and cost-effective integrated circuits, storage devices, displays, biosensors, DNA microarrays, and advanced materials. [1-22] This is particularly critical for integrated circuits, where smaller features results in increasingly higher speeds and decreasing energy consumed per computing function. Currently, the patterning of most functional materials is accomplished via photolithography, a process in which the minimum feature size scales with the wavelength of light used for exposure. While initial miniaturization resulted from scaling down the exposure wavelength, the lack of high-throughput laser sources and the lack of materials capable of performing at energies beyond 193 nm have impeded continued wavelength reduction. Therefore, a combination of immersion optics and computer-intensive resolution enhancements are currently being used to push the resolution of optical lithography beyond its current limits. [23-31] However, size limits still exist, and the exponential increases in the cost of new nanofabrication facilities offset, in part, the benefits of decreased feature sizes. If the current trends continue, it will soon become economically prohibitive to implement new technologies that rely solely on traditional semiconductor manufacturing processes. [32, 33] Fundamentally new fabrication strategies will be required in order to create

cost-effective, high-performing, and technologically feasible devices with features in the nanoscale regime (1-20 nm).

Unconventional patterning techniques present an alternative for circumventing these limitations, since they do not rely solely on focused energetic beams and thus are not wavelength-limited. These techniques, which include soft lithography and scanning-probe lithography, can be applied to a wide variety of substrates, some of which are not patternable with traditional techniques; further, they are simple enough to be used in a typical laboratory setting and do not require prohibitively expensive equipment. Although such methods are still under development and are not yet industrially competitive with conventional lithographic methods, they can supplement traditional lithographies in cases not amendable to traditional lithography — for instance, on curved substrates, in biologically compatible environments, and for the fabrication of chemical patterns. [34-36]

Soft lithography utilizes "soft" polymers to replicate and to transfer patterns onto surfaces. These techniques, which can be used on a wide variety of adsorbate and substrate systems, enable rapid, and in some cases parallel, prototyping of features down to hundreds of nanometers at a fraction of the cost of traditional lithographic strategies. Scanning-probe lithography (SPL), on the other hand, exploits the interactions between the substrate and the probe in a scanning probe microscope (such as applied forces, [37-39] potentials, [40-42] and/or electrons [43-47]) to induce physical and/or chemical reactions. The nanoscale precision and atomic resolution of SPL enables the fabrication of localized and site-specific functional structures that can be simultaneously characterized *in situ*.

Feature size limitations for these unconventional techniques are not imposed by wavelength, but instead are set by physical and chemical interactions, such as diffusion, and electrostatic intermolecular forces. [48, 49] For example, patterned clusters and small molecules often suffer from pattern degradation or dissolution due to molecular diffusion. [50, 51] Fortunately, the same set of physical phenomena that limit the resolution in unconventional top-down patterning can be used to advantage in bottom-up approaches, relying on self-assembly and electrostatic forces to create two-dimensional (2D) and three-dimensional (3D) structures with molecular precision. Unfortunately, these techniques lack the registration, interconnectability, addressability, and scalability required to make functional devices. However, when combined with one or more traditional lithographic techniques, the registration and addressability of top-down techniques can sometimes be coupled with the precise chemically and biologically active nanoscale features of a bottom-up approach. [52-57] Furthermore, unlike conventional lithographic techniques, which tend to be largely subtractive (material removal or etching), hybrid approaches can build on top of surface features, while also providing control over structure and function.

These hybrid methods can be used to fabricate structures with multiple length scales and levels of structure, in which the top-down methods define the larger-scale structures (~50 nm), while the physical, chemical, or biological interactions define the smaller structures (<1-100 nm). The resulting materials are therefore capable of being physically, chemically, and/or biologically active, thus producing patterned structures that can interact with their environment even down to the single-molecule level. [58-65] While the semiconductor industry is currently the main driving force behind

miniaturization and nanoscale patterning, patterned surface structures at the 1-100 nm scale have many potential applications, such as bioactive or catalytic surfaces. [66-83] For example, Goodman and coworkers have shown that patterned Au surface structures exhibit exceptional catalytic activity for several reactions due to the increased perimeter and the distinctive electronic and chemical properties of the structures when compared to bulk Au. [84-87]

This dissertation explores the interplay between molecular and supramolecular structure with function, in order to engineer materials and surfaces with specific properties that could be used to fabricate functional nanostructures. These surfaces were modified by exploiting bottom-up approaches such as self-assembly. The resulting chemical, physical, and optical properties of these self-assembled functional materials were thoroughly characterized with both ensemble and localized techniques. Therefore, a brief introduction of self-assembled monolayers (SAMs), as well as scanning tunneling microscopy (STM) and infrared reflection absorption spectroscopy (IRRAS), is provided.

#### **1.2 Background**

#### **1.2.1 Scanning Tunneling Microscopy**

The drive to understand the atomic-scale world has led to the development of numerous techniques that characterize the molecular and atomic arrangement of surfaces. Scanning tunneling microscopy, developed by Binnig and Roher, [88, 89] measures the electronic properties and the atomic structures of surfaces by rastering an atomically sharp tip across flat conducting (or semiconducting) substrates and measuring the tunneling current. Since its invention, STM has been employed to study and to

understand surface structures, molecular assemblies, catalysis, and even reactions of single molecules. [90-98]

STM measurements begin by bringing an atomically sharp metallic tip within 3-10 Å of a substrate using a piezoelectric transducer for placement and motion. At these distances, electrons have a non-zero probability of quantum mechanically tunneling through the classically forbidden potential barrier that separates the tip and sample. A one-dimensional energy level diagram of this process is depicted in Figure 1.1A. Applying a positive voltage across the tip-sample gap offsets the Fermi levels ( $E_F$ ) of the tip and sample, enabling electrons to tunnel from the occupied states of the tip into unoccupied states within the sample, resulting in a net current. Reversing the bias polarity reverses the current flow, causing electrons to tunnel from filled levels in the sample to the empty states in the tip. As a convention, the polarity of the bias is typically reported with respect to the sample ( $V_{sample}$ ).

The wavefunction  $(\psi)$  of an electron in a one-dimensional tunneling junction with a rectangular potential barrier is defined by:

$$\psi(z) = \psi(0)e^{-\kappa z},\tag{1.1}$$

where

$$\kappa = \frac{\sqrt{2m(V_{Barrier} - E)}}{\hbar},$$
(1.2)

*z* is the tip-sample separation, *m* is the mass of an electron,  $V_{Barrier}$  is the barrier potential, *E* is the energy of the tunneling electron, and  $\hbar$  is Planck's constant. The probability that an electron at  $z_0$  (left edge of barrier) can be found at *z* (right edge of barrier) is proportional to the wavefunction squared, yielding a non-zero tunneling probability and thus a predicted tunneling current ( $I_{tunnel}$ )

$$I_{tunnel}(z) \propto |\psi(z)|^2 \propto e^{-2\kappa z}.$$
(1.3)

The exponential current decay is about an order of magnitude per Å change in z, resulting in high sensitivity (tenths to thousands of Å) to both lateral and vertical changes in topography. [99-101]

The probe tip is typically rastered across the surface in one of two modes: constant current or constant height. In constant-current mode, a feedback loop maintains a constant tunneling current by adjusting the tip height in response to changes in topography (Figure 1.1B). The resulting topographic image is a convolution of the geometric structure and the local density of states of the tip or sample. In constant-height mode, the tip is rastered across the surface at a constant height while recording the resulting  $I_{tunnel}$ . The simplicity of constant height imaging enables faster measurements and image acquisition; constant-current mode is slower, a result of the required mechanical manipulation of the piezoelectric scanner that also enables high-precision imaging (atomic resolution or better).

#### **1.2.2 Self-Assembled Monolayers**

Adventitious organic materials adsorb readily onto bare surfaces, since adsorbates can lower the free energy of the interface. [102] Adsorbates also alter the interfacial properties of the substrate, including the physical, chemical, and/or biological properties. However, adventitious adsorbates do not result in the reproducible physical properties (*i.e.*, wettability and conductivity) and long-range order required to tailor surfaces.



Figure 1.1. (A) A one-dimensional metal-vacuum-metal tunneling junction, where an applied voltage offsets the Fermi levels of the tip and sample. (B) Schematic of a STM tip rastering across a SAM functionalized surface, where a feedback loop extends and retracts the tip to maintain a constant tunneling current.

Self-assembled monolayers, on the other hand, provide a simple route to engineer the surface properties of metals and semiconductors. Such organic assemblies form spontaneously, directed by the chemical and physical properties of the molecules. Molecules that form SAMs typically have a chemically functionalized headgroup with a high affinity for the substrate that enables them to displace adsorbed adventitious materials. Numerous headgroup/surface combinations exists, such as ROH/Si, RCOOH/Ni, and R(PO<sub>4</sub>)<sup>2-</sup>/TiO<sub>2</sub>. [102] However, the most studied system is the adsorption of alkanethiols (**ALK**) onto Au{111}, due to the strong gold-sulfur bond (44 kcal/mol), and the stabilizing van der Waals forces (~1 kcal/mol per methylene) between the adjacent alkyl chains, both of which contribute to the formation of highly ordered and stable SAMs.

The specific details and mechanism of self-assembly remain incomplete, although the process is understood to involve the subtle interplay between the energetics of the chemisorbed headgroup and the energetics of the noncovalent lateral intermolecular interactions among the organic tails. Kinetically, self-assembly occurs via a two-step process. During the first and fastest step, the chemisorption of the headgroup leads to 80-90% surface coverage within seconds to minutes, and sometimes faster, depending on concentration. During the next several hours, or even days, the hydrocarbon chains undergo a transition from having high degrees of gauche defects to having fully extended nearly all-*trans* configurations. This slow reordering process increases the crystallinity and molecular order within the SAM, while enabling the adsorption of additional molecules so that nearly 100% coverage can be achieved. Figure 1.2B shows a schematic of the lattice and superlattice of an *n*-dodecanethiolate (C12) SAM on a Au{111}



Figure 1.2. Schematic of a *n*-alkanethiol (ALK) SAM on a Au{111} substrate. (A) A side view along the nearest neighbor direction showing the 30° tilt to maximize the van der Waals interactions. (B) Top down view showing the unit cell of the Au substrate, as well as the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  unit cell and the  $c(4 \times 2)$  superlattice. Shading highlights the  $c(4 \times 2)$  structure. (C) A single surface-bound all-*trans* ALK molecule in which  $\theta, \psi$ , and  $\phi$  represent tilt, twist, and azimuth angles of the chain, respectively.

substrate. It is generally understood that the sulfur-gold interactions drive the assembly of the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  lattice in short chain **ALK**. However, in longer chains (>10 C) assembly is more complicated, since the energy balance between the intermolecular and the sulfur-gold interactions can be constantly changing, leading to the coexistence of an additional  $c(4 \times 2)$  superlattice. [103-106] In order to maximize the hydrocarbon tail interactions, the molecules tilt ( $\theta$ ) ~33° with respect to the Au surface normal (Figure 1.2C). [104, 105, 107-111] This resulting molecular tilt is determined by the interplay between the packing density of the thiol headgroups and the optimization between the hydrocarbon tails. For example, **ALK** SAMs on Ag substrates order with less molecular tilt (~15°), compared to **ALK** SAMs on Au.

Even highly ordered SAMs have defects, and Figure 1.3 shows representative STM images of a C12 SAM deposited on Au{111} from a 1.0 mM C12 ethanolic solution, where arrows highlight the characteristic defects of ALK SAMs. The red arrows point to Au substrate step edges, the boundaries between adjacent terraces that are different in height by one Au atom. The purple arrows point to Au substrate vacancy islands, one-atom-deep substrate defects resulting from lifting the  $(22 \times \sqrt{3})$  surface reconstruction of the bare Au{111} surface. Finally, the green arrows show domain boundaries formed in places where domains with similar tilt ( $\theta$ ) but different azimuthal angles ( $\phi$ ) converge. [112-115]

A representative STM image of an 1-adamantanethiol (**AD**) SAM is shown in Figure 1.4A, since a considerable portion of this dissertation focuses on **AD** SAMs. Similar to **ALK** SAMs, the topography of the **AD** SAM shows depressions with sizes on



**Figure 1.3.** Scanning tunneling microscopy images of a C12 SAM on a Au{111} substrate acquired with a  $V_{sample} = -1.0$  V and a  $I_{tunnel} = 1.0$  pA. The *red*, *yellow*, and *orange* arrows highlight Au substrate step edges, Au substrate vacancy islands, and molecular domain boundaries, respectively. The circular protrusions correspond to single C12 molecules.



Figure 1.4. (A) and (B) Scanning tunneling microscopy images of an AD SAM on a Au{111} substrate acquired with a  $V_{sample} = -1.0$  V and a  $I_{tunnel} = 5.0$  pA. Although Au substrate vacancy islands are visible in the STM images of the AD SAM, the images lack the protruding domain boundaries typically seen in ALK SAMs. (C) A side view along the nearest neighbor direction showing  $\sim 0^{\circ}$  tilt. (D) Top-down view showing the unit cell of the Au substrate, as well as the  $(\sqrt{91} \times \sqrt{91})R5.21^{\circ}$  unit cell.

the order of a single Au atom, consistent with substrate vacancy islands. However, the **AD** SAM lacks the protruding domain boundaries that are typical in **ALK** SAMs. High-resolution images, such as the one in Figure 1.6B, reveal a  $(\sqrt{91} \times \sqrt{91})R5.21^{\circ}$  overlayer with a 6.9 Å nearest neighbor-distance (Figure 1.6D), which is larger than the 5.0 Å nearest neighbor distance in the  $(\sqrt{3} \times \sqrt{3})R30^{\circ}$  lattice of an **ALK** SAM.

### **1.2.3 Infrared Reflection Absorption Spectroscopy**

Infrared spectroscopy is one of the primary tools for characterizing the bonding and chemical interactions of molecules on surfaces, in solutions, or in the gas phase. Even the simplest organic molecules give rise to complex IR spectra, since a molecule consisting of *n* atoms has a total of 3*n* degrees of freedom, corresponding to the Cartesian coordinates of each atom in the molecule. Five or six of these degrees of freedom correspond to rotational and translational modes, and therefore, the number of fundamental vibrations for linear and nonlinear molecules are (3n - 5) and (3n - 6), respectively. A small molecule such as propane  $(C_3H_8)$  has 27 fundamental vibrations. Figure 1.5 illustrates the fundamental vibrations of methylene  $(-CH_2 -)$ , an important organic group that is used repeatedly throughout this dissertation. The (3n - 6) rule does not apply to methylene, since it is only represents a portion of an entire molecule.

In infrared reflection absorption spectroscopy (IRRAS), also known as reflection absorption spectroscopy (RAIRS), the infrared radiation is incident on the substrate at a grazing angle to maximize the light-sample interaction. Unlike solution- or gas-phase measurements, IRRAS on metallic films, such as Au, excites only vibrational modes with non-zero components normal to the surface. This surface selection rule is a result of the



Figure 1.5. Stretching and bending vibrational modes of a methylene (-*CH*<sub>2</sub>-) group.


Figure 1.6. (A) Schematic of mirror dipoles generated on a metallic surface, showing how molecular dipoles parallel to the surface result in a net zero dipole moment. (B) and (C) Infrared reflection absorption spectroscopy (IRRAS) spectra of a C12 SAM on a Au{111} substrate, showing higher energy stretching modes (B), and lower energy bending and wagging modes (C).

mirror dipoles that cancel the component of the dipole moment parallel to the surface, as shown in Figure 1.6A.

Figures 1.6B and 1.6C show representative IRRAS spectra of the high and low energy regions of a C12 SAM on a Au{111} substrate, respectively. The 2800-3000 cm<sup>-1</sup> region shows the methylene ( $-CH_2 -$ ) and methyl ( $-CH_3$ ) stretching vibrations, while the 1200-1600 cm<sup>-1</sup> region shows the lower energy methylene and methyl bending and wagging modes. The peak at 2919 cm<sup>-1</sup>, corresponding to the CH<sub>2</sub> asymmetric stretch, can be used to determine the average order and crystallinity of an **ALK** SAM. If the **ALK** molecules are arranged in an all-*trans* configuration, the vibrational frequency will be similar to that of crystalline **ALK** (2916 cm<sup>-1</sup>). However, if the SAM has a significant number of gauche defects, the vibration will shift to values as high as 2926 cm<sup>-1</sup>, the absorption frequency for disordered liquid **ALK** molecules. [108] The average molecular tilt of a SAM can also be determined, by combining the surface selection rules with rigorous calculations of vibrational peak intensities as a function of tiltl angle. [109, 116, 117]

## **1.3 Dissertation Overview**

This dissertation explores the effects of molecular structure on the chemical, physical, and optical properties of SAMs and cluster assemblies. Chapter **2** provides an overview of soft-lithographic patterning techniques and hybrid approaches that exploit self-assembly and other bottom-up strategies to increase the resolution and sophistication of molecularly patterned features.

In Chapter **3**, the solution-phase displacement of **AD** SAMs by **C12** molecules is discussed. The structures of partially displaced SAMs are thoroughly characterized with both ensemble (XPS, CV, and IRRAS) and local (STM) techniques, revealing the thermodynamic driving forces for **AD** SAM displacement.

Chapter 4 discusses the kinetics of AD SAM displacement by C12 solutions of varying concentrations. Numerous SAM growth models are used to describe the observed uptake curves. A model based on nucleation and island growth is the only model to adequately describe the observed kinetics, which, along with modeling provides general rules regarding kinetically hindered displacement in monolayers.

In Chapter 5, concepts from Chapters 3 and 4 are used to design a new labile monolayer. These labile monolayers are similar to a photoresist, since they inhibit displacement until exposure, at which time they can readily undergo exchange. Unlike photoresists, these labile monolayers can be regenerated, making the monolayer once again resist displacement. This new labile monolayer was thoroughly characterized with IRRAS and XPS during all stages of exposure and displacement.

Chapter **6** introduces the concept of cluster-assembled materials, in which solids are assembled out of atomic cluster building blocks in order to control the resulting electronic and optical properties (band gap). To study the role of structure on function, building blocks were used to create several cluster-assemblies, providing us with general protocols on how to design new materials with tunable properties.

Finally, the preceding chapters are summarized in Chapter 7, and future prospects are discussed. These areas are specifically highlighted: self-assembly, soft-lithographic strategies, and cluster-assembled materials.

### Chapter 2

## Hybrid Approaches for Nanoscale Patterning

## **2.1 Introduction**

In soft lithography, soft and flexible materials are used to transfer patterns onto substrates without the need for energetic beams (*i.e.*, photons, electrons, or ions). [118-123] Since its introduction by Whitesides and coworkers, [124] numerous studies have demonstrated the versatility of this family of techniques in fabricating microscale and nanoscale architectures with a wide range of adsorbates and substrates. [66] Originally intended as an alternative to photolithography, its pattern resolution is not diffractionlimited, but is instead controlled by molecular dynamics and intermolecular interactions from molecular through micron length scales. [125] Unfortunately, in-plane registration is difficult to maintain through multiple stamping steps, resulting in difficulties in creating complex functional devices. Thus, soft lithography does not typically compete directly with conventional lithographic techniques. Instead, soft lithography has been employed in areas where conventional lithography cannot be applied, such as to curved [126, 127] and biologically compatible [81, 128-131] surfaces with feature sizes down to hundreds of nanometers. Its simplicity and low cost have brought lithography into new disciplines that traditionally do not have access to nanofabrication facilities, such as biology and pharmacology. In these disciplines, the ability to engineer surfaces with molecular-level precision enables high-throughput assays and detection of biologically relevant compounds, critical for both pathogen sensing and drug development. Soft lithography can be used to pattern self-assembled monolayers (SAMs) with the desired surface properties and functionality, while maintaining patterning costs far below those of traditional methods. This section will discuss recent work in two broad categories of soft lithography – contact printing and molding – and illustrate how they have been coupled with assembly and deposition to create precise surface structures at micron, supramolecular (1-100 nm), and molecular scales.

## 2.2 Conventional Techniques

## 2.2.1 Micromolding

Micromolding uses soft materials to replicate and to cast features onto substrates, offering a simple and economical method for fabricating features over large areas. [118, 132, 133] In replica molding, the simplest form of micromolding, a prepolymer is cast over a rigid master, cured for a set amount of time, and excised from the master. [134-136] Poly(dimethylsiloxane) (PDMS) is one of the most common polymers employed for replica molding, due to its excellent mechanical, physical, and chemical properties. [137-139] It is important to note that micromolding is the initial step for many soft-lithographic techniques (Figure 8), notably microcontact printing. Flexible PDMS molds enable conformal contact with flat, rough, or even curved surfaces. More complicated molding techniques, such as micromolding in capillaries [140-142] or solvent-assisted micromolding, utilize PDMS molds as templates to fabricate surface structures from other materials. There have been number of excellent detailed reviews of these and other micromolding-related techniques. [118, 132, 143, 144]



Figure 2.1. Microcontact printing is the basis for many hybrid patterning schemes, through control of substrate and adsorbate interactions.

#### **2.2.2 Microcontact Printing**

Microcontact printing ( $\mu$ CP, Figure 2.1A) is an inexpensive and straightforward "top-down" method of creating features with high spatial resolution (<100 nm) over large areas (>10 cm). [132, 143, 145-148] An elastomeric stamp is first created by casting a pre-polymer (typically PDMS) over a master pattern. Once the polymer is cured, the elastomeric stamp is excised from the master and cleaned with hexanes and ethanol to remove any uncured and low-molecular-weight polymers. [136] Subsequently, an adsorbate solution is dropcast onto the elastomeric stamp, allowed to adsorb, and then dried. The coated elastomeric stamp is brought into conformal contact with the substrate, transferring the adsorbate in areas where the stamp and substrate are in contact. Fidelity and quality of the patterned features vary with several parameters, including: stamp deformation, adsorbate concentration, stamping time, and applied back-pressure. [49, 149-157] Although the resolution of  $\mu$ CP is limited to the dimensions and the structural rigidity of the elastomeric stamp, simple sub-50-nm features (circles and lines) have been achieved with the use of specific inks and stamp geometries. [158-160]

#### 2.2.3 Area-Selective Atomic-Layer Deposition

The combination of  $\mu$ CP with atomic layer deposition (ALD) enables 3D nanoscale structures to be created via area-selective ALD. [161] Here, the sequential self-limiting steps of ALD enable precise control over film thickness, composition, and uniformity. [162] Bent and coworkers have utilized area-selective ALD to pattern metal and metal-oxide films commonly used in metal-oxide-semiconductor field-effect transistors. [163] Figure 2.2 shows a schematic of selective-area ALD, in which a



Figure 2.2. Schematic of area-selective atomic-layer-deposition.

patterned elastomeric stamp coated with octadecyltrichlorosilane (ODTS) molecules is brought into contact with the substrate. A monolayer of ODTS forms in the regions of contact, and ALD films are then selectively deposited onto areas not protected by the ODTS monolayer. Subsequent removal of the ODTS monolayer exposes the underlying substrate. Auger elemental maps of the substrates have shown that the Pt films selectively grow only on the unpatterned regions, showing how the patterned ODTS monolayers block the reactive functional groups on the surface.

### 2.3 Hybrid Techniques

Soft lithography is typically used to fabricate features on bare surfaces; however, it can also be applied to a variety of pre-treated or pre-patterned surfaces, as shown in Figures 2.1B-2.1F. For example, if a self-assembled monolayer is deposited onto the substrate prior to  $\mu$ CP, the resulting surface will be a (controlled) mixture of the patterned molecules and the pre-existing monolayer. Therefore, by determining the interplay between placement and competitive adsorption, the rational design of complex molecular surface structures is possible. Here, we first discuss a number of approaches based on  $\mu$ CP.

### 2.3.1 Microdisplacement Printing

In microdisplacement printing ( $\mu$ DP, Figure 2.1) the substrate is first coated with a labile monolayer, such as 1-adamantanethiolate (**AD**), which is susceptible to molecular exchange. The stamp is then inked with a molecule such as an alkanethiol that can displace the labile SAM via competitive adsorption in the areas of stamp contact, as



Figure 2.3. (A) Schematic and (B) and (C) field emission scanning electron micrographs of a chemical pattern fabricated by microdisplacement printing. The higher intensity regions correspond to patterned 11-mercaptoundencaic acid (MUDA) and low intensity background corresponds to the pre-existing 1-adamantanethiolate (AD) self-assembled monolayer.

shown in Figure 2.3A. [51, 164-168] Figure 2.3B and 2.3C show a field emission scanning electron micrographs of a patterned gold substrates fabricated by  $\mu$ DP. [169]

There are several advantages of  $\mu$ DP relative to conventional  $\mu$ CP. First, the labile SAM prevents lateral diffusion of patterned molecules. This is especially important for molecules with weak intermolecular interactions and low molecular weights, which have high surface mobilities. [48] Such diffusion can be directly related to line-edge roughness in lithographic methods, with the further issue that if left unchecked, the line-edge roughness, due to diffusion, increases with time. Therefore,  $\mu$ CP often requires exposure to solvated molecules that "backfill" the exposed unpatterned regions of the substrate, in order to minimize pattern degradation over time. [48, 49, 66, 147, 156, 165] However, the precision and fidelity of the chemical pattern degrades during backfilling, due to the molecular exchange between patterned and solvated molecules. With  $\mu$ DP, backfilling is not required because the labile monolayer remains in uncontacted regions, preventing pattern degradation and dissolution. Furthermore, due to hindered molecular diffusion, multiple stamping steps can be used to pattern proximal structures without pattern degradation between fabrication steps.

## 2.3.2 Microcontact Insertion Printing

In microcontact insertion printing ( $\mu$ CIP, Figure 2.1C), a molecule-inked elastomeric stamp is brought into contact with a substrate coated with a monolayer that is *not* easily displaced. [165] Therefore, molecules on the stamp insert only into defect sites of the pre-existing monolayer, such as domain boundaries and substrate vacancy islands, and only in places where the stamp and substrate are in contact (Figure 2.4A). [66, 170]



Figure 2.4. (A) Schematic, (B) field-emission scanning electron microscopy image, and (C) scanning tunneling microscopy image of a chemical pattern created by microcontact insertion printing. The higher intensity regions of the FESEM image correspond to patterned 11-mercaptoundecanoic acid (MUDA), and the lower intensity background corresponds to the preexisting 1-octanethiolate monolayer (C8). The more protruding features in the STM image correspond to the stamped 1-dodecanethiolate (C12), and the less protruding lattice corresponds to the pre-existing monolayer of C8. The most depressed features are substrate vacancy islands formed during the initial monolayer deposition.

Figures 2.4B and 2.4C show FESEM and STM images, respectively, of a chemical pattern fabricated by  $\mu$ CIP. By tuning the degree of molecular insertion and exchange between the patterned molecules and the preexisting SAM, the resulting molecular composition in the chemical pattern can be controlled (from isolated single molecules to bundles of molecules). Similar to  $\mu$ DP, the pre-existing monolayer limits the lateral diffusion of the patterned molecules, thereby maintaining the dilution and isolation of molecules within the background SAM. [170-172]

Isolated target molecules diluted in a matrix (Figure 2.4A) interact more readily with binding partners in solution, and  $\mu$ CIP offers a straightforward strategy for creating such chemical patterns. In particular, the spatially isolated molecules can be longer than the matrix used for dilution, enabling the protruding functionality to capture target analytes. [65, 173, 174] For example,  $\mu$ CIP is currently being utilized to fabricate films with patterned small-molecule probes that mimic neurotransmitters and other small biomolecules. Spatial isolation is critical for enabling the specific binding of large proteins (>5 nm) in competitive environments and to minimize nonspecific binding. [65, 83, 174]

### 2.3.3 Multilayer Transfer Printing

Rather than pre-patterning a substrate, Hammond and coworkers have employed layer-by-layer growth to assemble multilayer films of molecular inks on PDMS stamps *prior* to stamping, through a process known as multilayer transfer printing (MTP). [175-177] Figure 2.5A shows a schematic of MTP, in which polyelectrolyte multilayers are assembled on PDMS by alternating adsorption of polyanion and polycation pairs.



Figure 2.5. Schematic of the multilayer transfer printing process.

Once the desired thickness of the multilayer is achieved, the stamp is brought into contact with the substrate and the multilayer is transferred in areas of contact. The charge on the substrate must be complementary to the charge on the topmost layer on the PDMS for pattern transfer to occur.

Multilayer films are completely and selectively transferred to the substrate in the contact regions, remaining intact throughout the transfer. Fluorescent micrographs of fluorescently labeled multilayer patterns on glass substrates via MTP show how the multilayers transfer from the stamp to the substrate only in regions of contact. Multilevel and multicomponent patterned surface structures and composites can be fabricated by sequentially printing onto, or next to, previously stamped multilayer patterns. [177]

### 2.3.4 Biocatalytic Microcontact Printing

Instead of patterning adsorbates onto a substrate, Toone and coworkers have used enzymes immobilized on a polymeric stamp to induce chemical reactions on a surface, in a process called biocatalytic  $\mu$ CP. [69] Elastomeric stamps, coated with the immobilized enzyme exonuclease I digest the ssDNA-functionalized substrate in contact areas. In these regions, the enzymes digest the ssDNA, releasing the surface-bound fluorophores. Therefore, the background corresponds to regions of unaltered and fluorescent ssDNA. A key advantage of biocatalytic  $\mu$ CP is the inkless nature of the technique, since no adsorbates are transferred from the stamp to the substrate. As a result, the lateral resolution of fabricated features is controlled by the length and flexibility of the tether (<2 nm), as opposed to the diffusion of patterned molecules (>100 nm).

## 2.3.5 Stamp Surface Chemical Functionalization

Despite the chemical and physical benefits of using PDMS in soft lithography, the polymer limits both resolution and ink selection. Nonpolar methyl groups in the polymer are more compatible with nonpolar inks and solvents, limiting the use of polar inks and solvents that neither wet nor adsorb onto the surface of the PDMS stamps. Development of techniques and methodologies that expand soft lithography to polar inks will be critical for patterning new classes of molecules and functionalities, particularly biological molecules. Many efforts have focused on the development of hydrophilic polymer stamps. However, to date, such materials have lacked the mechanical properties that would provide conformal contact during patterning. [178-181] Therefore, researchers have also investigated strategies for functionalizing PDMS stamps to create polar surfaces, since inks need only adhere to the stamp surface. These functionalized surfaces improve not only ink selection but also resolution of  $\mu$ CP and related techniques.

Up to now, stamp surface functionalization has been achieved by two means: SAM formation in pre-curing stages [182] and the oxidation and silanation of the surface. [183-186] Oxidation has emerged as the dominant method, due to its simplicity and versatility. The surface is typically oxidized by a short, intense burst (*e.g.*, 10 s at 10 W) of oxygen plasma, yielding a transient thin layer of dangling Si bonds, which is exposed to silanated compounds that react to form surface layers. [187] Formation of a thin layer is essential, since thicker layers result in brittle surfaces that crack and have a higher rate of surface hydrophobicity recovery. [188, 189] Amine- and poly(ethylene-oxide)functionalized layers have been used successfully with polar inks, while fluorinated layers can repel both polar and non-polar inks. [188] Delamarche *et al.* employed various



Figure 2.6. Relief stamps (A) can suffer decreased resolution and pattern defects as a result of material failure and lateral ink diffusion. A flat stamp (B) does not encounter these issues.

polyethylene oxide derivatives for the soft lithographic patterning of proteins and Pd/Sn colloids. [183] These surfaces can last longer than one month, without the need for storing them under water, in contrast to unsilanated surfaces that recover their hydrophobicity within hours. [188, 190, 191]

Stamp surface functionalization enables the use of flat, rather than relief (textured) stamps. This is achieved by oxidizing only certain areas of the stamp so that when ink is introduced, it only wets certain regions of the surface prior to the printing Change from a relief or textured stamp to a flat stamp greatly increases the step. resolution of contact printing techniques, since the sources of many errors in soft lithographic patterning, such as stamp deformation (roof collapses, bent posts, and lateral diffusion), can be reduced or eliminated, as shown in Figure 2.6. [192, 193] Bv selectively oxidizing the stamp surface through a mask, Huskens and coworkers have fabricated flat surfaces with positively charged amine regions capable of retaining polar inks, and fluorinated regions that repel polar inks. [188] The chemically patterned flat stamps were created with masks containing 2-µm and 350-nm holes and were used to print poly(propylene imine) dendrimer dialkyl sulfides on Au. Mirkin and coworkers have further increased the resolution of bifunctional flat stamps by patterning the stamp surface via dip pen nanolithography (DPN). [194] In this case, a polyethylene glycol (PEG) mask is created on the surface via dip pen nanolithography. Subsequent oxidizing and silanizing steps functionalize the exposed areas not protected by the PEG monolayer, making those areas compatible with the desired ink (dependent on functionalization). Although DPN masks have been used to create patterns with sub-50-nm features, the high resolution comes at the expense of fabrication time, which is considerably increased by the serial nature of DPN.

### **2.3.6 Decal Transfer Lithography**

In decal transfer lithography (DTL), portions of a patterned PDMS stamp are transferred to the substrate by controlled fracture of the stamp. Stamps are treated with UV/ozone prior to stamping in order to ionize the stamp surface. Contact between stamp and substrate then results in irreversible binding. [195-199] Figure 2.7 shows a schematic of the two methodologies that have been developed: cohesive mechanical failure and selective pattern release. In cohesive mechanical failure DTL, the features of the surface-bound PDMS stamp are sheared away when the stamp is separated from the substrate. In contrast, selective pattern release DTL uses a thin film support layer fabricated into the PDMS, which serves as a delamination plane within the stamp, leaving a pattern "decal" on the substrate when the stamp is peeled away. The lack of mechanical deformation in selective pattern release DTL is a significant advantage when compared to cohesive mechanical failure DTL for micron or larger sized features. However, selective pattern release DTL stamps are hard to create, due to the difficulty in releasing them from the masters without inducing delamination or other mechanical failures. Both approaches can be used to create resists or templates for a range of materials, complementing other soft- and conventional lithographic techniques. [200, 2011 Specifically, DTL excels in fabrication of high-aspect-ratio or 3D polymeric structures on planar and non-planar substrates, with micron-scale and larger features. [200]



Figure 2.7. Schematics of the two types of decal transfer lithography, (A) cohesive mechanical failure and (B) selective pattern release.

## **2.3.7 Nanoparticle Printing**

In addition to varying stamp and surface properties, the range and variety of molecular inks for soft lithography is also expanding. Metallic and semiconducting nanoparticles are excellent candidates for inks, due to their interesting and tunable optical and electronic properties, as well as their ability to be annealed into solid features or assemblies. [202-207] By exploiting the geometry of a polymeric stamp, Wolf and coworkers not only directed the placement of nanoparticles in a pattern, but also controlled the arrangement and number of particles on the substrate. [208, 209] Lines, arrays, and bitmaps of nanoparticles created in this manner preserve the catalytic and optical activity of the individual particles. [123] Nanoparticles are typically transferred to the substrate when polymeric stamps are brought into conformal contact with the substrate. A key advantage of nanoparticle inks in comparison to small molecules is that adhesive forces prevent their diffusion. Nanoparticle printing is also compatible with different particle and substrate systems including metals, polymers, semiconductors (Figure 18B), and oxides, making them suitable for some device applications. [208, 209]

#### 2.3.8 Nanotransfer Printing.

A further example of non-traditional inks is nanotransfer printing (nTP), a  $\mu$ CP variant that patterns thin layers of solid material. [195, 210-218] A thin metallic layer is evaporated onto a high-resolution stamp, and then brought into conformal contact with the substrate. This substrate is typically coated with a reactive surface, such as a terminally functionalized SAM, so that contact results in a strong bond between metal and substrate. After the binding reaction, the stamp is removed and the metal is

transferred within the contact areas, since the metal only weakly adheres to the stamp. Controlling the intermolecular interactions between the solid ink and the substrate is critical to ensure that the solid ink is efficiently transferred to the substrate over large areas. The solid ink must adhere strongly to the surface, and only weakly to the stamp, in order for large areas to be transferred. The ability of nTP to pattern with multiple dimensions and relief heights is a particular strength compared to other lithographic methodologies. For example, through additive processes, this technique enables the fabrication of complex and 3D structures, such as closed channels and suspended beams. [211]

#### 2.3.9 Nanoskiving

Whitesides and coworkers have fabricated complex metallic nanostructures by sectioning polymeric molds embedded with a thin metal film, in a process called nanoskiving (Figure 2.8). [219-221] A metallic film is first embedded into an epoxy mold created via replica molding. Microtoming removes thin slabs or sections of the epoxy-embedded metal nanostructures that are transferred onto a substrate. Finally, the epoxy is removed by oxygen plasma, leaving metallic nanostructures arranged on the substrate. The topography of the initial mold (50 nm) and the thickness of the evaporated metal ( $\geq 20$  nm) determine the lateral dimensions of the metallic nanostructure. The thickness of the metallic nanostructures is determined by the slicing operation of the microtome, which can be controlled from 50-1000 nm. Continuous 3D metallic structures have been created using 1000 nm sections of an epoxy master patterned with 1 µm lines, 2 µm pitches, and 100 nm of Au. Nanoskiving enables the



Figure 2.8. Schematic of the nanoskiving process.

fabrication of metallic nanosctructure arrays over large areas on both planar and curved surfaces, and at dimensions that are difficult to attain with traditional lithographic techniques.

#### 2.3.10 Cell Growth and Function

Soft lithography lends itself to microbiology because of its simplicity, low cost, and applicability in patterning biocompatible surfaces. [82, 144, 222] For example, micromolding enables individual cells and their extracellular environment to be addressed, manipulated, and studied through microfluidic channels and microchambers. Whitesides and coworkers have utilized molding to mediate and to control the sizes and shapes of cells confined within microchambers. [223] Figure 2.9 shows a schematic of how molding can be used to exploit physical confinement and to engineer the sizes and shapes of bacterial cells. Employing replica molding, microchambers composed of an agarose growth medium were fabricated, and E. coli bacterial cells were seeded into the microchambers and subsequently sealed with a thin PDMS layer. In the presence of the antibiotic cephalexin, the *E. coli* cells could not divide and thus filamented, adopting the shapes of the microchambers. The cells retained their shapes after being released from the microchambers. This straightforward strategy to control the sizes and shapes of cells through confinement enables the exploration and elucidation of how mechanical stress affects cellular function and movement. More specifically, it provides a new way of engineering the growth of biological materials, aiding in areas such as tissue engineering and implant biocompatibility. [224] Tools similar to the ones described in this section enable the manipulation of individual cells and their extracellular environment in order to



Figure 2.9. Schematic of molding as used to control the size and shape of bacteria cells.

study microbial physiology, behavior, differentiation, and evolution. For example, reactive surfaces have been fabricated that provide enclosures that trap *E. coli* cells and/or other pathogenic organisms. [225] With similar structures, the binding strength of *E. coli* to antibodies has been measured. [226, 227] The merger of microfabrication with microbiology is opening a new field, primarily focused on studying biological structure and function of organisms, rather than new approaches for nanolithography. Further discussion of this topic can be found in the recent reviews and perspectives by Whitesides and coworkers. [144, 228-230]

### 2.4 Prospects for Soft Lithography

Soft lithography is a versatile method of replicating features onto surfaces in a rapid, straightforward, and economical manner. The soft materials used enable the fabrication of patterns as small as <50 nm on a variety of surfaces (*e.g.*, curved, uneven, or biologically active) without specialized and expensive facilities. Conventional soft-lithography methods, such as  $\mu$ CP (Figure 2.1A), rely on polymeric (PDMS) stamps to deliver a molecular ink to the substrate, with features typically at 100-nm and larger scales. However, combining basic concepts of soft lithography with self-assembling systems (1-10 nm) enables the fabrication of molecularly precise nanoscale structures that are defined by the self-assembly and placement of the patterned material. These hybrid approaches typically stamp on pre-patterned or pre-assembled layers (Figures 2.1B-2.1F), resulting in features that are a convolution between the adsorbates and the existing monolayer. Therefore, by tuning the interactions of the molecular ink

with the surface layer or with other molecular inks, the rational design of previously unattainable and precise molecular structures is possible. For example, the patterning of delicate biological matter provides a new way of controlling the properties of surfaces and facilitates the creation of new, miniaturized, and high-throughput biochemical and cell-based assays and biosensors. [128, 230-236]

Originally, the driving force for developing hybrid and unconventional lithographies was to continue patterning semiconductor devices beyond the predicted resolution limits of photolithography. Yet, photolithography has continued to advance, using physics and diffraction itself to reduce feature size. This has temporarily alleviated the imperative for alternatives such as hybrid methods for wafer-scale microelectronic fabrication, albeit at increasingly high complexity and cost of lithographic tools. [31] However, these hybrid methods have opened unexplored frontiers in patterning, exploiting and probing the physical, chemical, and biological properties of nanoscale features. These methods are finding applications in fields beyond traditional lithography, such as in biological recognition and material assembly.

Several issues must be addressed in order to bring these technologies from laboratories to commercial settings. In soft lithography, spatial registration of multiple steps is often difficult, and therefore, precise alignment tools similar to those used in traditional lithographies are required. On the other hand, while SPL offers significant advances over traditional and next-generation lithographies, in terms of simplicity, registration, and especially resolution (<10 nm), throughput requires significant improvement. The chemical and physical properties of nano- and molecular-scale features differ from those of bulk and macro-scale materials. This is a result of feature size and not a consequence of the particular technique used for patterning. Many hybrid strategies offer high precision by taking advantage of these nanoscale phenomena, but as a result are sensitive to environmental parameters that impact self-assembly and other nanoscale processes. In some cases, the relevant phenomena are not well understood, and slight modifications can lead to significant changes in pattern formation and quality. This high sensitivity can be an advantage, since it may offer, in turn, precise control over the size, shape and assembly of the patterned features. Ongoing efforts seek to develop independent control of such parameters.

Most hybrid techniques are currently used in a realm outside of microelectronics. Hybrid approaches such as the molecular-ruler method and the use of block copolymers, may further extend the use of current methods since they can reduce the cost, extend the lifetime, and broaden the capabilities of existing tools. [55, 237-242]

## Chapter 3

# Displacement of 1-Adamantanethiolate Self-Assembled Monolayers

## **3.1 Introduction**

The patterning and functionalization of surfaces with self-assembled monolayers facilitate the creation of complex well-ordered structures for biosensors, [243] biomimetics, [174, 244] molecular electronics, [67, 245] lithography, [48, 51, 55, 66, 246-249] and other applications. [64] However, surface diffusion and contamination hinder the creation of high-quality structures, especially for soft-lithographic techniques that require multiple deposition steps. Protective layers can assist in controlling deposition, if they can be easily removed when desired but otherwise remain impermeable during the fabrication of surface-bound nanoscale assemblies.

It has been demonstrated that 1-adamantanethiolate (**AD**) SAMs are labile and can be displaced even by short-chain *n*-alkanethiolates. [168] Although such displacement or exchange reactions are not unique to **AD** SAMs, the complete and rapid displacement of one SAM by another under gentle thermal conditions (room temperature) and dilute concentrations (millimolar) is unusual and useful. [250-253] For example, Schlenoff *et al.* have shown that exposing 1-octadecanethiolate SAMs to a 1.0 mM radiolabled ( $^{35}$ S) 1-octadecanethiol solution results in only ~60% displacement after 50 h. [253] Similar results have been observed with 1-eicosanethiol SAMs, which after 30 h of exposure results in ~50% displacement. [254] The lability of **AD** SAMs enables microdisplacement printing ( $\mu DP$ ), a technique similar to microcontact printing ( $\mu CP$ ) but wherein the patterned molecules displace an existing SAM only in contacted regions, while the remaining SAM acts as both a placeholder and a diffusion barrier. [48, 168] These diffusion barriers not only create sharper, higher quality patterns than  $\mu CP$  but also extend the library of patternable molecules to those otherwise too mobile to retain surface patterns. In particular, molecules that do not form robust, well-ordered SAMs but have desirable electrical or sensing properties can be patterned using this technique. The same methodology can be used to improve other chemical patterning techniques, such as dip-pen nanolithography, [255] for which the applications range from lithographic resists [256] to biologically compatible surfaces [59] and proteomics. [257] Here, we use scanning tunneling microscopy, X-ray photoelectron spectroscopy (XPS), cyclic voltammetry (CV), and IRRAS to determine the extent, driving forces, and pathways of **AD** SAM displacement.

#### **3.2 Background**

### **3.2.1 Scanning Tunneling Microscopy**

See Chapter 1 for an introduction to STM.

## **3.2.2 X-ray Photoelectron Spectroscopy**

X-ray photoelectron spectroscopy is a quantitative technique that measures the identity, chemical state, and chemical environment of elements present on a surface. [258-261] In XPS, spectra are obtained by irradiating a material with monochromatic X-rays to eject core level electrons from surface and near-surface atoms, while simultaneously measuring the kinetic energies of the photoelectrons emitted. These core electrons reside in inner electron quantum shells that do not participate in chemical bonding. For every element, there is a characteristic electron binding energy ( $E_b$ ) that is associated with each inner shell orbital. When the energy of an incoming X-ray (hv) is larger than  $E_b$ , the excess energy is converted to kinetic energy in the resulting photoelectron. This kinetic energy ( $E_k$ ) is typically measured with respect to a metal standard, and thus the  $E_b$  of a material can be determined by:

$$E_b = hv - E_k - \Phi, \tag{3.1}$$

where  $\Phi$  is the work function of the metal standard. By measuring the  $E_k$  of all emitted photoelectrons, the elemental composition of a surface can be determined. The precise  $E_b$ , and thus precise  $E_k$ , depends on the chemical (bonding) environment of the atom, since charge transfer leaves atoms with partial positive charges that increase the Coulombic attraction between the nucleus and core electrons. An increase in the effective oxidation state an atom results in an increased attraction that leads to a downfield shift in the observed  $E_k$  of the resulting photoelectrons.

Only core electrons originating within tens of Ångstroms of the surface can be ejected into vacuum and measured, since electrons generated deeper in the material are typically scattered before reaching the detector. Each material has a characteristic distance that an electron can travel before being inelastically scattered (inelastic mean free path,  $\lambda$ ). The probability of an electron scattering while traveling through a film of thickness t is determined by:

$$P = e^{(-t/\lambda)}.$$
(3.2)

Furthermore, at larger incident angles the surface cross-section increases, localizing the analyzed region closer to the surface. This angular sensitivity also enables the determination of the depths of specific elements within a film or surface.

#### **3.2.3 Electrochemistry and Cyclic Voltammetry**

Electrochemistry is the study of chemical reactions at a conducting or semiconducting interface (working electrode); for example, understanding oxidation and reduction reactions driven by an externally applied voltage. [262, 263] Typically, the working electrode is complemented with counter and reference electrodes, all of which are submerged in a supporting electrolyte. The counter electrode is used to make an electrical connection to the electrolyte so that current can be applied to the working electrode, while the reference electrode accurately monitors the applied potential.

In cyclic voltammetry, one of the most common electrochemical techniques, the working electrode is scanned from an initial to a final potential at a constant scan rate, while the resulting current is measured. For SAMs, these measurements can determine surface coverage, SAM crystallinity, and relative intermolecular interactions strengths. In a SAM-functionalized gold electrode, an applied cathodic potential causes the one-electron reductive desorption of thiols as described by Equation 3.3.

$$[RS - Au] + e^- \longrightarrow RS^- + Au_o \tag{3.3}$$

The relative intermolecular interactions strengths in a SAM are inversely related to the full-width-at-half-maximum (FWHM) of the resulting cathodic peak (*i.e.*, the smaller the FWHM, the stronger the interactions), since the width of the peak is proportional to the permeability of the solvent into the SAM. Another indication of intermolecular interactions strengths within the SAM is the potential of the cathodic peak  $(E_p)$ , where more negative potentials indicate relatively higher intermolecular interaction strengths. For example, Porter and coworkers have shown a linear relationship between the  $E_p$  and chain length in alkanethiolate SAMs. [264-266] They attribute the trend to the higher potential gradients required to establish an ion flux through the longer monolayers.

### **3.2.4 Infrared Reflection Absorption Spectroscopy**

See Chapter 1 for an introduction to IRRAS.

#### **3.3 Experimental Procedures**

#### 3.3.1 Sample Preparation

*n*-Dodecanethiol and 1-adamantanethiol were purchased from Sigma-Aldrich (St. Louis, MO) and used as received. Ethanol (200-proof) from Pharmaco (Brookfield, CT) was used as received. Monolayers were fabricated by immersing flame-annealed Au{111} on mica substrates (Agilent Technologies, Santa Clara, CA) into ethanolic solutions of the desired thiol molecule. The **C12** SAMs were prepared from 1.0 mM solutions, while **AD** SAMs were prepared from 10 mM solutions. After 24-h deposition from solution, Au substrates were removed, rinsed with 200-proof ethanol, and dried under a stream of nitrogen. All **AD** SAMs were used immediately after preparation and characterized with STM, XPS, and CV.

Solution-displaced **AD** SAMs were created by fabricating an **AD** SAM, confirming the presence of a well-ordered lattice using STM, and then immersing the sample into a 1.0 mM **C12** solution for the specified exposure time. To achieve full

displacement, samples were placed in a C12 solution overnight to enable slow reordering and annealing. For XPS studies, to minimize water content in the SAMs, assembly steps including displacement were also performed in an oxygen-free glovebox using anhydrous hexanes as a solvent.

## **3.3.2 Scanning Tunneling Microscopy**

All STM measurements were performed under ambient conditions using a custom-built beetle-style STM. [267, 268] Images were recorded in constant-current mode with high tunneling gap impedances  $(10^{12} \Omega)$  to ensure large tip-sample separation for minimal contact between the probe tip and the monolayer. [269] Lattice parameters were determined by imaging SAMs with known lattices (*i.e.*, C12 SAM) to calibrate the piezoelectric scanners prior to imaging samples (AD SAMs). In multicomponent SAMs, lattice parameters were also determined by internally calibrating with ALK domains within the SAMs. Lattice values were determined from the Fourier transforms of the STM images, while corrugation, or height, was calibrated by using monoatomic Au{111} steps.

### **3.3.3 X-ray Photoelectron Spectroscopy**

X-ray photoelectron spectra were acquired using an Axis Ultra spectrometer (Kratos, Chestnut Ridge, NY) with a monochromatic Al K $\alpha$  source (20 mA, 1.4 keV), a base pressure of 1 x 10<sup>-9</sup> Torr, and a spot size of 300  $\mu$ m x 700  $\mu$ m. Survey spectra were acquired at a pass energy of 80 eV, while high-resolution spectra of the O 1s, C 1s, S 2p and Au 4f regions were collected at a pass energy of 20 eV. The binding energies (E<sub>b</sub>) were referenced to the Au 4f<sub>7/2</sub> peak at 83.98 eV. All of the peaks from the spectra were

fit using Gaussian-Lorentzian (GL) line shapes using a Shirley-type background. The Au 4f peaks were fit with a fixed energy separation of 3.68 eV and a fixed-area ratio of 3:4. The S  $2p_{3/2,1/2}$  doublet peaks were fit using a fixed-energy separation of 1.18 eV, and a fixed-area ratio of 1:2.

## **3.3.4 Cyclic Voltammetry**

All cyclic voltammograms were acquired using a three-electrode BAS Epsilon potentiotat (BASi, West Lafayette, IN) with a custom-built electrochemical cell (detailed schematics can be found elsewhere [270]). The Au{111} substrates served as the working electrode, with an area of ~0.1 cm<sup>2</sup>. The potential was referenced to a Ag/AgCl saturated KCl electrode (BASi, West Lafayette, IN), while a Pt wire was used as a counter electrode. The supporting electrolyte was a 0.5 M KOH solution (99.99%, Sigma-Aldrich, St. Louis, MO), which was sparged with ultra-high-purity nitrogen prior to all electrochemical experiments. The CVs were baseline corrected for solution resistance and the sample-electrode contact resistance using a straight line subtraction in the first 0.100 V of the sweep, where faradic processes are assumed to be negligible.

# 3.3.5 Infrared Reflection Absorption Spectroscopy

Infrared spectra were acquired using a Nicolet 6700 FTIR spectrometer (Thermo Electron Corporation, Waltham, MA), equipped with a liquid-nitrogen-cooled mercurycadmium-telluride detector and a Seagull variable angle reflection accessory (Harrick Scientific Inc., Ossining, NY). The spectrometer and its accessory were purged with dry and CO<sub>2</sub>-free air produced from a FTIR Purge Gas Generator (Parker-Balston, Cleveland, OH). The data were collected at grazing incidence reflection (86° relative to the surface normal) with *p*-polarized light, a mirror speed of 1.8988 cm/s, with a resolution of 2 cm<sup>-1</sup>, averaged over 1024 scans, and transformed using N-B medium apodization. All SAM spectra were normalized with data recorded from  $C12_{d25}$  monolayers Au{111} substrates.

#### **3.4 Results and Discussion**

## 3.4.1 Scanning Tunneling Microscopy of Displaced Self-Assembled Monolayers

Figure 3.1 shows STM images of AD SAMs exposed to a 1.0 mM C12 solution for exposure times ranging from 10 min to 24 h. An initial AD SAM, with an exposure time of 0 min is also shown as a reference. In these images, domains with two distinct lattices and two distinct apparent heights are observed, both of which were used to differentiate between the two molecules. The most protruding lattice with a spacing of  $\sim 5.0$  Å is attributed to C12 domains, while the less protruding lattice with a spacing of ~6.9 Å is attributed to AD domains. The AD SAM exposed for 10 min showed single and small clusters of C12 molecules inserting at defect sites of the original AD SAM, such as Au substrate step edges and vacancy islands. After a 20-min exposure, the single and small clusters of C12 molecules grew into islands, while more C12 molecules inserted at the remaining defect sites in the AD lattice. Few singly inserted C12 molecules were observed after 30 min of exposure, and further displacement occurred via rapid island growth. Nucleation was not observed at 45 min and 80 min exposure times, although images showed C12 domains rapidly expanding and coalescing. After 120 min, changes in surface coverage were no longer observed, but the crystallinity and the size of the C12 domains increased, thereby reducing the number of defect sites.


**Figure 3.1.** Scanning tunneling microscopy images of 1-adamantanethiolate (**AD**) SAMs displaced by a 1.0 mM *n*-dodecanethiol (**C12**) solution with exposure times ranging from 0 min to 24 h. The most protruding domains correspond to **C12**, the least protruding to **AD**, and the depressed regions correspond to Au substrate vacancy islands. Image parameters:  $V_{sample}=1.0$  V;  $I_{tunnel}=2$  pA. Image acquisition in collaboration with T. J. Mullen and A. A. Dameron.

However, even after a 24-h displacement time, the average domain size was significantly smaller when compared to a C12 SAM fabricated on a clean Au{111} substrate. These smaller domains result in increased numbers of domain boundaries, a type of SAM defect. A similar phenomenon has been observed for monolayers grown on bare Au substrates, where domains in the SAMs deposited from solution were smaller than in the SAMs deposited from the gas phase. [271] In the displaced SAMs, it is hypothesized that the smaller domain sizes are a product of the varied domain orientations that result from numerous nucleation sites. Therefore, when two distinct domains with different orientations meet, the domains are kinetically trapped and do not possess the activation energy required to change the orientation of an entire domain to match the orientation of another.

#### **3.4.2 X-ray Photoelectron Spectroscopy of Displaced Self-Assembled Monolayers**

Figure 3.2 shows a representative XPS survey spectrum of an **AD** SAM, revealing the relative elemental composition of the substrate. The most intense peaks correspond to the Au{111} substrate, with C, O, and S as minor components. Ideally, oxygen should not be present in these SAMs, and therefore its presence must be carefully considered. The O 1s peak was present in all SAMs, although its intensity was greatly reduced when samples were fabricated with anhydrous hexanes and in an oxygen-free environment. Therefore, this peak at  $E_b$ =532.8 eV was attributed to water, in agreement with literature values of 533 eV. [272, 273] The O 1s emission of a gold oxide would result in a peak with an energy of ~530 eV, while also broadening and shifting the Au 4f peaks to higher energies. The lack of broadening, along with the lack of peak shifts in these emissions,



Figure 3.2. X-ray photoelectron survey spectrum of an AD SAM deposited from solution.

indicates that there is no surface oxide, thus eliminating surface oxides as a contributing factor for **AD** SAM displacement.

Figure 3.3A shows the XPS C 1s emission spectrum of an **AD** SAM deposited from solution for 24 h, showing a single asymmetric peak with a wider tail on the higher  $E_b$  side. Therefore, the peak was fit with two GL line shapes, where the larger peak  $(E_b=284.4 \text{ eV})$  and the smaller peak  $(E_b=285.1 \text{ eV})$  had an area ratio of ~9:1. This energy splitting is attributed to the varying electron distribution throughout the **AD** cage, where the S atom changes the electron configuration of the  $\alpha$ -carbon.

The C 1s emission of a C12 SAM deposited from solution for 24 h is shown in Figure 3.3E. The single symmetric emission can be fit to a single GL line shape centered at 284.9 eV, attributed to the hydrocarbon tail of the C12 molecules and is in agreement with literature values. [104, 274-276] These peaks are shifted to higher  $E_b$ , when compared to the AD C 1s peaks, a result of the increased C–C bonding in the adamantane cage (as compared to *n*-alkyl chains). This 2 eV shift is similar to the C 1s  $E_b$  observed in highly ordered pyrolitic graphite ( $E_b$ =284.4 eV) and diamond ( $E_b$ =284.0 eV). [273] Figures 3.3B-D show the C 1s XPS spectra of AD SAMs displaced by a 1.0 mM C12 solution, with exposure times of 20, 40, and 120 min. The observed emission in these samples is wider than either Figure 3.3A or E, since these samples contain contributions from both molecules. Therefore, the peaks were fit using 3 GL line shapes, two for the **AD** cage and one for the **C12** alkyl backbone (*vide supra*). The area ratios of the line shapes, used to estimate the extent of displacement, revealed that longer displacement solution exposure times resulted in higher degrees of displacement; for example, 20 min of exposure resulted in ~30% displacement and 40 min resulted in ~50% displacement.



Figure 3.3. (A)-(D) Representative XPS C 1s emission spectra of AD SAMs displaced by a 1.0 mM C12 solution with exposure times of 0, 20, 40, and 120 min. (E) A representative C 1s XPS emission spectrum of a C12 SAM deposited from solution for 24 h. Spectra were fit with GL line shapes with contributions centered around 284.3 eV (*green*), 284.9 eV (*blue*), and 285.2 eV (*red*). Spectra are offset for clarity. Spectra collected in collaboration with A. A. Dameron and R. W. Hengstebeck.



Figure 3.4. Representative XPS 2p emission spectra of AD SAMs displaced by a 1.0 mM C12 solution with exposure times of (A) 0 min and (B) 40 min. (C) A representative S 2p XPS emission spectrum of a C12 SAM deposited from solution for 24 h. Spectra were fit with GL line shapes with contributions centered around 162.0 eV (*pink*) and 163.2 eV (*cyan*). Spectra collected in collaboration with A. A. Dameron and R. W. Hengstebeck.

The XPS S 2p emission spectra of **AD** SAMs displaced by **C12** molecules with varying exposure times are shown in Figure 3.4, as well as a spectrum of a **C12** SAM deposited from solution as a reference. The S 2p:Au 4f peak area ratios of the **AD** SAM exposed to displacement solution for 40 min were higher in intensity than the SAM exposed for 0 min, attributed to the higher S concentration in the more compact **C12** lattice. However, shifts in the  $E_b$  for the S 2p emissions were never observed, even when comparing these **AD** SAMs to the spectrum of a **C12** SAM deposited from solution (Figure 3.4C). This indicates that **AD** SAMs and **C12** SAMs have similar chemical environments around the Au-S bond. The  $E_b$  values of these peaks were also too low to account for the presence of sulfinates, sulfonates, disulfides, or unbound thiols. [277-284]

## 3.4.3 Cyclic Voltammetry of Displaced Self-Assembled Monolayers

Figure 3.5A and D show representative CV sweeps of AD and C12 SAMs adsorbed on Au{111} working electrodes, respectively. The cathodic peak potential  $(E_p)$  of the AD SAM at -990 mV represents the reductive desorption of thiolate molecules from the surface electrode. In the C12 SAM this  $E_p$  shifted to -1113 mV, indicating that it takes more energy to remove this SAM from the surface, compared to the AD SAM. This is again a result of the increased intermolecular interactions in C12 SAMs, compared to those in AD SAMs. Since desorption is a one-electron process, the smaller cathodic peak current  $(I_p)$  and peak area of the AD SAM sweep, compared to those of the C12 SAM, indicate lower surface coverage in the AD SAMs, in agreement with previously acquired STM images (Chapter 1).



Figure 3.5. (A)-(C) Representative cyclic voltammograms of AD SAMs displaced by a 1.0 mM C12 solution for 0 min, 30 min, and 60 min. (D) A representative voltammogram of a C12 SAM deposited from solution. Spectra are offset for clarity. Voltammograms acquired by T. J. Mullen.

The CV sweeps of **AD** SAMs displaced by **C12** solutions with varying exposure times are shown in Figure 3.5A-C. The two distinct  $E_p$  values confirm the presence of two distinct lattice types, in agreement with STM images (Figure 3.1). [285-287] The more negative  $E_p$  corresponds to the **C12** SAM, while the less negative  $E_p$  corresponds to the **AD** SAM. Both  $E_p$  measurements were shifted to less negative values when compared to their single-component counterparts, revealing a more facile ion flux through these partially displaced SAMs. This is a result of disrupted intermolecular interactions within both lattices, which is likely to be more prominent at the domain boundaries between the different lattices. [288, 289] As the exposure time increased, the **C12**  $E_p$  shifted to more negative values, attributed to the ordering and annealing of the **C12** molecules as the **C12** domains grew, also in agreement with STM measurements (Figure 3.1).

# 3.4.4 Infrared Reflection Absorption Spectroscopy of Displaced Self-Assembled Monolayers

To complement the STM, XPS, and CV measurements, IRRAS was employed to investigate the displacement of **AD** SAMs. To determine the complete displacement of **AD** SAMs, the perdeuterated **C12** analogue (**C12**<sub>d25</sub>) was used, since deuterium atoms in the **C12**<sub>d25</sub> molecules shift the C-H vibrational modes to the 2000-2300 cm<sup>-1</sup> region. This shift avoids spectral overlap between the two molecules that would otherwise impede measurements that quantify the disappearance of **AD** molecules. [98] Figure 3.6 shows the disappearance of the **AD** molecules with increasing **C12**<sub>d25</sub> exposure times of 0, 20, 40, and 60 min. The 0 min **AD** spectrum is an **AD** SAM deposited from solution



Figure 3.6. Representative IRRAS of AD SAMs displaced by a 1.0 mM  $C12_{d25}$  solution with exposure times of (A) 0 min, (B) 20 min, (C) 40 min, and (D) 60 min. Spectra are offset for clarity.

for 24 h that was not exposed to the  $C12_{d25}$  solution, serving as a starting reference point. In this spectrum, the peaks at 2850, 2911, and 2934 cm<sup>-1</sup> are attributed to the methylene symmetric stretching mode, the methylene asymmetric stretching mode, and the methine (CH) stretching mode, respectively. [103, 109-111] Upon a 20 min exposure to the  $C12_{d25}$  solution, the strongest peak (2911 cm<sup>-1</sup>), associated with the methine stretching mode, was approximately half its original intensity. After a 40 min exposure, this peak is significantly diminished, causing it to broaden and to blend with the neighboring shoulder peak. The vibrational modes of the AD molecules were no longer evident after 60 min exposure, confirming the complete displacement of the AD SAM. Due to the similarities between the C12 and C12<sub>d25</sub> molecules, the same results are expected when AD SAMs are displaced by C12 solutions.

#### 3.4.5 Driving Force for 1-Adamantanethiolate SAM Lability

The covalent Au-S bond has a bond enthalpy of 44 kcal/mol. [271] Therefore, the ~80% increase in molecular packing density observed by STM and CV in C12 SAMs, when compared to AD SAMs, provides an energy gain of ~35 kcal/mol. However, as the CV results indicate, the AD molecules with the larger nearest-neighbor distances result in poor molecular overlap and thus lower stabilization energies. The magnitude of this stabilization energy remains unknown, although all measurements indicate that AD SAMs have relatively weaker intermolecular interactions. Using the previously measured interaction energy of ~22 kcal/mol in C12 SAMs, [290-292] the exchange of an AD SAM by C12 molecules could result in an energy gain maximum of 40 kcal/mol (22 kcal/mol × 1.8). Therefore, the total energy gain for displacement, considering both

enthalpic contributions from the increased Au–S bond density and the stronger intermolecular interactions, can be as high as 75 kcal/mol.

These enthalpic contributions thermodynamically account for *why* C12 molecules displace AD SAMs, and why the reverse reaction does not occur. However, self-assembling systems with similar driving forces, such as carboranethiols or mercaptobiphenyls, do not undergo the complete molecular exchange observed for AD SAMs. [251, 293, 294] Considering these thermodynamic driving forces, the displacement of other SAMs must be kinetically hindered (Chapter 4).

# **3.5 Conclusions**

Localized (STM) and ensemble (XPS, CV, and FTIR) measurements were used to elucidate the origins and the driving force of **AD** SAM displacement. X-ray photoelectron spectroscopy has shown that **AD** and *n*-alkanethiolate SAMs have similar 2p sulfur chemical environments, so the displacement is not due to differences in Au-S bond strengths. Scanning tunneling microscopy (STM) has shown that *n*-alkanethiolate SAMs are 1.8 times as densely packed as **AD** SAMs. This packing density difference provides a substantial enthalpic driver (~35 kcal/mol), aided by differences in van der Waals forces ( $\leq$  40 kcal/mol), to displace the **AD** SAMs completely. Imaging with STM reveals that displacement begins with a rapid nucleation phase, in which *n*-dodecanethiolate (**C12**) molecules insert at defect sites of the **AD** SAM, followed by radial growth into domains that coalesce and eventually fully displace the original monolayer. Defects consist of both randomly distributed single-atom-deep vacancy islands in the gold substrate (from lifting the Au{111} surface reconstruction during selfassembly) and rotational/tilt domain boundaries in the original SAM. Other selfassembling systems can result in similar thermodynamic driving forces, since SAMs can be fabricated with relatively less dense lattices and decreased intermolecular interactions, suggesting that displacement could be observed in other self-assembling systems.

# Chapter 4

# 1-Adamantanethiolate Monolayer Displacement Kinetics Follow a Universal Form

# 4.1 Introduction

Taking advantage of **AD** SAM displacement or similar monolayers will require precise control of the displacement process, specifically in nanofabrication applications where reliability and nanoscale precision over patterning are crucial. In this sense, **AD** SAMs are interesting, since they enable a wider range of displacement and molecular exchange behavior. Understanding this process a molecular level is one of the first steps in achieving the control necessary for nanofabrication applications. The ability to correlate molecular structure with displacement behavior may also enable new molecules and SAMs to be engineered for specific electronic or biotechnological applications.

The previous chapter explored the thermodynamic driving forces for displacement, raising questions as to why conventionally studied SAMs do not yield fully-displaced homogenous SAMs upon exposure to other thiols. Here, IRRAS is used to study the quantitative kinetics of the solution-phase displacement of **AD** SAMs by **C12** on Au{111}, where the fast insertion of **C12** molecules at the defects in the original **AD** SAM nucleates a fast island growth phase, followed by the slow ordering of **C12** domains into a denser and more crystalline form. Langmuir-based kinetics, which describe **ALK** adsorption on bare Au{111}, fail to model this displacement reaction. Instead, a Johnson-Mehl-Avrami-Kolmogorov model of perimeter-dependent island growth yields good agreement with kinetic data obtained by IRRAS over 100-fold

variation in C12 concentration. Rescaling the growth rate at each concentration collapses all the data onto a single universal curve, suggesting that displacement is a scale-free process. These kinetics, along with modeling of AD-C12 domain boundaries, give insight to the complete displacement of AD SAMs and why the same is not observed for other SAMs.

## 4.2 Background

## 4.2.1 Infrared Reflection Absorption Spectroscopy

See Chapter 1 for an introduction to IRRAS.

### **4.3 Experimental Procedures**

# 4.3.1 Sample Preparation

Perdeuterated *n*-dodecanethiol  $(C12_{d25})$  was synthesized by methods previously described. [276] See Chapter 3 for sample and monolayer preparations already discussed.

# 4.3.2 Infrared Reflection Absorption Spectroscopy

The data were collected at grazing incidence reflection (84° relative to the surface normal) with *p*-polarized light, a mirror speed of 1.27 cm/s, and a resolution of 2 cm<sup>-1</sup>. The first and last spectra, 0 min and 24 h, were averaged over 1024 scans, while all spectra for the kinetic measurements were averaged over 400 scans. All SAM spectra were transformed using N–B medium apodization and normalized with data recorded for C12<sub>d25</sub> monolayers on Au{111}.

# 4.3.3 1-Adamantanethiolate Monolayer Displacement

Prior to displacement, FTIR spectra were acquired for each **AD** SAM to verify the absence of impurity-related features and the presence of the  $CH_2$  stretch at 2911 ± 1 cm<sup>-1</sup>, both indicative of a well-ordered **AD** SAM. [295, 296] The samples were then placed in ethanolic **C12** solutions of the specified concentration to achieve displacement. Every 6 min, the SAMs were rinsed with ethanol and dried with nitrogen. An IRRAS spectrum was then recorded and the sample returned to the **C12** solution for the next incremental exposure. Once the signals plateaued, displacements were no longer incrementally monitored. However, in order to achieve saturation coverage, the samples were placed in a **C12** solution overnight to enable slow reordering and annealing. Subsequently, a final spectrum was recorded for each sample.

#### 4.4 Results and Discussion

### 4.4.1 Infrared Spectra of 1-Adamantanethiolate Monolayers

Infrared spectra of adsorbed species were obtained from 400 to 4000 cm<sup>-1</sup>. The region from 2800 to 3000 cm<sup>-1</sup> contains the CH<sub>2</sub> and CH<sub>3</sub> stretch modes of the aliphatic and carbon-cage tails of the thiolated molecules. Figure 4.1 shows typical spectra of an **AD** SAM (blue) and a **C12** SAM (red), both recorded after 24 h solution deposition. Several absorption peaks overlap in this region: CH<sub>2</sub> symmetric stretches (2850 cm<sup>-1</sup> for both **AD** and **C12** SAMs) and CH<sub>2</sub> asymmetric stretches (2911 cm<sup>-1</sup> for **AD** SAMs and 2919 cm<sup>-1</sup> for **C12** SAMs). [296] The peaks that do not overlap correspond to the CH<sub>3</sub> symmetric and asymmetric stretching modes of the **C12** SAM, at 2877 and 2963 cm<sup>-1</sup>, respectively. [104]



Figure 4.1. Infrared spectra of the C-H stretch region of a AD SAM (*blue*) and a C12 SAM (*red*), showing their spectral overlap (see text for mode assignments).

#### 4.4.2 Kinetic Plots of 1-Adamantanethiolate Monolayer Displacement

The spectra in Figure 4.2A provide peak intensities and positions as a function of immersion time and solution concentration, displaying four spectra obtained at increasing immersion times in a 0.11 mM C12 solution. Each spectrum is a sum of contributions from both AD and C12. Figure 4.2B plots the integrated 2877 cm<sup>-1</sup> peak intensity as a function of exposure time. Molecular orientation and lattice crystallinity affect the spectrum; for example, shifts in the CH<sub>2</sub> asymmetric mode track monolayer order and crystallinity, while relative peak intensities can track monolayer tilt. However, the symmetric and asymmetric CH<sub>3</sub> stretching modes are not sensitive to the orientation of the C12 molecule, because of the tetrahedral coordination of the three relevant hydrogens. Therefore, the strength of the symmetric  $CH_3$  mode directly measures the C12 surface coverage. [104] Initially, this mode is very weak, but after about 18 min of exposure to 0.11 mM C12, the intensity of the 2877 cm<sup>-1</sup> peak increases rapidly and eventually dominates the spectrum. After 36 min, no signal from AD molecules can be detected by IRRAS, and the spectrum is nearly identical to that of a pure C12 SAM. Displacement becomes very slow at around 92% of the final saturation intensity and approaches final saturation only after 24 h in solution. A similar but faster time evolution is observed at higher displacement solution concentrations.

# 4.4.3 Kinetic Modeling of 1-Adamantanethiolate Monolayer Displacement

Ellipsometry, [297] surface acoustic wave devices, [298] second harmonic generation, [299, 300] and quartz crystal microbalance [301] measurements have established that the growth rates of **ALK** monolayers on bare Au{111} surfaces are



**Figure 4.2.** (A) Representative FTIR spectra of a 0.11 mM C12 solution displacing an AD SAM. The 2877 cm<sup>-1</sup> peak, corresponding to the  $CH_3$  symmetric mode, is highlighted. (B) Kinetic curve derived from the FTIR spectra by plotting the integrated C12  $CH_3$  symmetric mode peak versus deposition exposure time. The open squares represent the integrated absorbance for each of the four spectra shown above.

proportional to the number of unoccupied adsorption sites on the surface, *i.e.*, follow Langmuir kinetics. We consider seven kinetic models for C12/AD displacement kinetics: a model based on pure diffusion, four variants of simple Langmuir kinetics, and two models based on island growth (analysis performed with C. M. Barbu).

For diffusion-controlled adsorption, the time-dependent coverage ( $\theta$ ) follows from the solution of the diffusion equations for a semi-infinite medium: [253, 302]

$$\theta(t) = \sqrt{\kappa_D t} , \qquad (4.1)$$

where

$$\kappa_D = \frac{4D}{\pi B_{ml}^2} \,, \tag{4.2}$$

D is the diffusion constant, and  $B_{ml}$  is the number of molecules per unit area in the full monolayer. The rate of adsorption is then proportional to the flux of molecules to the surface. Since this model does not account for saturation or the depletion of adsorption sites, it could only apply to the initial stages of growth.

First-order Langmuir kinetics assume an irreversible random process with a rate proportional to the number of unoccupied adsorption sites: [303]

$$\theta(t) = 1 - e^{-\kappa t},\tag{4.3}$$

where  $\theta$  is the surface coverage and  $\kappa$  is the rate constant. In this model, the adsorption rate is uniform across the entire available surface, since the model assumes equivalent surface sites and no interactions with pre-adsorbed or solvent molecules.

Despite their simplicity, first-order Langmuir kinetics describe monolayer uptake curves on bare gold surfaces fairly well. They have also been used to model the molecular exchange of *n*-octadecanethiolate SAMs by radiolabeled *n*-octadecanethiol molecules, although the reaction took 50 h and reached only  $\sim 60\%$  completion. [253] If the onset of growth is delayed, then a time offset can be introduced: [304, 305]

$$\theta(t) = 1 - e^{-\kappa(t - t_c)}. \tag{4.4}$$

First-order Langmuir kinetics have been extended to account for diffusion-limited kinetics,[306] second-order processes, [250, 306] and intermolecular interactions. [299] When growth is limited by the diffusion of molecules from the bulk solution to the surface, one obtains the square-root time dependence associated with diffusive random walks:

$$\theta(t) = 1 - e^{-\sqrt{\kappa t}},\tag{4.5}$$

The diffusion-limited Langmuir model successfully describes the adsorption kinetics of alkanethiol molecules on bare gold surfaces from very dilute solutions ( $<100 \ \mu$ M). [307] If the rate of adsorption is second-order in the thiol concentration, one obtains:

$$\theta(t) = 1 - \frac{1}{1 + \kappa t}.$$
(4.6)

Second-order Langmuir adsorption kinetics have been used to describe ligandexchange reactions on ligand-stabilized nanoparticles, in which the rate of the reaction is taken to depend on the concentration of the exchanging thiol both in solution and on the surface. [250]

The kinetics of nucleation and island growth were first modeled by Johnson, Mehl, Avrami, and Kolmogorov (JMAK) in the 1940s to describe metal alloy phase transformations. [308-311] The model has since been extended to address heterogeneous nucleation, [312] non-uniform island growth rates, [313, 314] and boundary constraints [315-317] across a variety of physical systems including oxidizing metal surfaces, [318, 319] graphite-diamond transformations, [320] and the crystallization of thin films [321] or proteins. [322] In this model, the rate of adsorption is proportional to the summed perimeter of all islands, yielding:

$$\theta(t) = 1 - e^{-(\kappa t)^n},\tag{4.7}$$

where  $\kappa$  is a rate constant. [308-310] The Avrami exponent *n* reflects the dimensionality of the system and the time dependence of the nucleation: n = 2 for a two-dimensional film, wherein nucleation proceeds rapidly to completion (site-saturated nucleation, JMAK2), and n = 3 in two dimensions if the nucleation rate is constant in time (constantrate nucleation, JMAK3). In JMAK3, more nucleation sites become available as the transformation proceeds, such as in certain glass ceramics. [323] The exponentiation accounts for overlap between idealized non-interacting islands, whose growth curve is proportional to  $(\kappa t)^n$ .

Figure 4.3 shows least-squares fits of each kinetic model to the C12 coverage versus exposure time for a 0.01 mM C12 displacement solution. Only JMAK2 (equation 4.7 with n = 2) fits the data. A similar conclusion applies across the full range of all C12 concentrations studied, from 0.01 to 1.0 mM, as shown in Figure 4.4.

The failure of the diffusion-limited models is, in fact, expected. Although such behavior is seen for **ALK** growth from very dilute solutions onto bare gold surfaces, [297] adsorption in our system is much slower (minutes as opposed to seconds), and the solution concentrations are much higher (millimolar as opposed to micromolar). The failure of Langmuir-based models, wherein adsorption is equally probable at all unoccupied sites, is consistent with the STM observation that adsorption begins at defect sites (*i.e.*, not within the interiors of **AD** domains) and then proceeds at the **AD–C12** 



**Figure 4.3.** Representative 0.01 mM **C12** uptake curve with least-squares fits to pure diffusion (*green*), first-order Langmuir (*purple*), first-order Langmuir with an onset of growth at 23 min (*orange*), diffusion-limited Langmuir (*gray*), second-order Langmuir (*black*), site-saturated nucleation JMAK2 (*red*), and constant-rate nucleation JMAK3 (*blue*) models.



**Figure 4.4.** *n*-Dodecanethiolate monolayer formation by the displacement of an **AD** SAM as a function of concentration. Solid lines are least-squares fits based on the site-saturated nucleation model JMAK2 (eq. 4.7 with n = 2).

domain boundaries (Figure 4.5). [295] Rapid nucleation across these pre-existing active sites would then account for the success of JMAK2 over JMAK3. Although several elaborations upon JMAK2 (incorporating boundary effects or non-uniform growth rates) could be derived, such subtle distinctions are not resolved by the data.

# 4.4.4 Concentration Dependence on the Rate Constant

The fits to JMAK2 also provide a measure of the displacement rate constant  $\kappa$  for each **C12** concentration. Figure 4.6 plots the log of  $\kappa$  for all experimental trials against the log of the **C12** solution concentration. The slope of 0.50 ± 0.05 suggests that the displacement rate is proportional to the square-root of the **C12** solution concentration, assuming that the density of nucleation sites is roughly constant across all samples. This result is surprising, since insertion/displacement is expected to be a unimolecular process and a bimolecular process would yield a slope of 2, not 1/2. Half-order kinetics can arise, for example, when the displacement of *Y* by *X* actually proceeds by the decomposition of a predominant bimolecular state  $X_2$  that generates *X*.

#### 4.4.5 Model Free Analysis and Universality

In addition to drawing specific conclusions regarding the relative quality of fits to different kinetic models, one can also analyze the displacement curves on a model-free basis to extract general conclusions regarding the number and character of any component subprocesses. Consider a general physical process as a composition of multiple subprocesses, each having a unique characteristic time scale or length scale, such as the growth of a tree across diurnal and annual cycles from a narrow smoothskinned sapling to a wider mature state with regular cracks in its bark. When observing



Figure 4.5. (A) Schematic of displacement process showing how adsorption is limited to defects and domain boundaries between the AD and C12 domains. (B) A three-dimensional rendered STM image of an AD SAM partially displaced by C12.



Figure 4.6. Displacement rate constant versus C12 concentration on a logarithmic scale. The slope of  $0.50\pm0.05$  implies that the rate constant is proportional to the square-root of the C12 concentration.

only a time-lapse movie of the tree's growth, one can immediately determine the frame rate and zoom factor: the faster cycle can be used as a clock to pace the slower process, and the finer details can be used to measure out the coarser features (tree analogy by V. H. Crespi). However, if a physical process is governed by a single time scale (*i.e.*, one rate constant) and a single length scale (*i.e.*, a density of nucleation sites), then the physical system, considered in isolation, has no intrinsic clocks or rulers. By simply viewing a movie of ideal island nucleation and growth, one can determine neither the frame rate nor the zoom setting. In mathematical terms, the curves describing the kinetics of a scale-free process can be collapsed onto a *single universal curve* by a simple rescaling of the time and space (in this case, areal coverage) axes. In physical terms, from just the shape of a C12 displacement curve, one can surmise nothing about the density of nucleation sites nor the rate of displacement. In chemical terms, displacement is dominated solely by the rate of insertion at the island edge—were any other insertion processes to be active, with different dependences on solution concentration, then the displacement curves would have different shapes at different concentrations.

Figure 4.7 demonstrates, on a model-free basis, that the displacement of **AD** by **C12** is, to a good approximation, a scale-free process, governed by a single rate constant and a single characteristic length scale. Upon rescaling the time and coverage axes, the data across a 100-fold range of **C12** concentration collapse onto a single universal curve. For convenience, this rescaling uses the JMAK2 rate constants, but as mentioned above, this scale-free universal behavior is model-independent. The scale-free universal behavior suggests that the displacement of **AD** is dominated by a single physical process, edge insertion, across a 100-fold variation in solution concentration.



**Figure 4.7.** Plot of coverage versus reduced exposure time of two experimental runs at each C12 concentration (0.01, 0.03, 0.11, 0.33, 0.55, 0.77, and 1.0 mM), showing collapse onto a universal curve. The time axis rescaling factor that results in reduced time was determined by  $\kappa_x/\kappa_{0.01mM}$ , where  $\kappa_x$  is the rate constant at concentration x, and  $\kappa_{0.01mM}$  is the rate constant at a 0.01 mM C12 concentration.

#### 4.4.6 Implications of 1-Adamantanethiolate Monolayer Displacement Kinetics

The importance of island growth in controlling the shape of the kinetic curves reflects the fact that displacement, adsorption, and desorption kinetics, more generally, are affected by the spatial structure of the growing phase. For example, desorption of small molecules from surfaces (*e.g.*, alkanes from MgO [324, 325]) is purely first-order if all molecules remaining on the surface are desorbed with equal probability, but there may be an island growth component if molecules desorb preferentially from the edges of patches. These effects could be especially important if subtle features in desorption curves are used to fit detailed kinetic models with, *e.g.*, temperature-dependent entropic contributions to pre-exponential factors in the Polanyi–Wigner equation. [324]

Why is it that **AD** SAMs are displaced fully by alkanethiols, but shorter-chain alkanethiols are only partially displaced by longer-chain alkanethiols? Does this distinction have larger relevance to the relation between lattice structure and kinetics for nucleation and growth of one phase within another? Generally, when one solid phase consumes another, whether by a structural phase transformation in an alloy or by a reaction such as oxidation at a surface or elsewhere, the lattices of the two phases are incompatible, meaning that lattice regularity is disrupted at the interface between the phases. This disruption tends to lower kinetic barriers against growth of the new phase at the interface. However, in SAMs, it is the solid substrate underneath that defines the lattice: for alkanethiol/alkanethiolate displacement on gold, the lattices of the two phases are *identical*: this situation is highly unusual in material phase transformations. In this regard, having two spatial dimensions is special: in three dimensions there is no orthogonal direction by which to define a consistent lattice externally, and in one



Figure 4.8. Schematic showing 1-adamantanethioltae (AD), *n*-decanethilate (C10), and *n*-dodecanethilate (C12) SAM structures on Au $\{111\}$ . (*Top*) A side view along the nearest neighbor direction. (*Bottom*) A top down view showing the unit cells of the two different unit cells. The boundaries between the alkathilate lattices (C10) and (C12) can be seamless, while the alkathilate-adamantanethilate boundaries have significant room that provides access to the surface.

dimension long-range order is strongly suppressed. The interface between long- and short-chain alkanethiol SAMs can then be seamless, with no gaps to facilitate insertion of new longer-chain alkanethiols (at least after any pre-existing defect sites are filled), as shown in Figure 4.8 (right side). The free energy gain of enhanced cohesion in the new phase (due, in the SAM, to the greater length of the new alkyl chains) is then not sufficient to drive the reaction: the displacement of one thiol by another also requires ready access to the surface, [252] which is possible only if the two SAM lattices are incompatible. Adamantanethiolates, with a  $(7 \times 7)$  unit cell, are incompatible with the alkanethiolate  $(\sqrt{3} \times \sqrt{3})R30^\circ$  unit cell; in this case, the interface is disrupted and available for transverse attack by alkanethiols into the AD domain (Figure 4.8). This mechanism should apply more generally: phase transitions in systems wherein initial and final phases share an identical lattice can be kinetically hindered by the coherence of the interface between phases. In cases where lattice disruption at the interface is essential for overcoming kinetic barriers, universal island growth kinetics, as described here, are expected to occur.

#### **4.5 Conclusions**

Our IRRAS studies of the displacement of **AD** SAMs by **C12** on Au{111} demonstrate that displacement proceeds by site-saturation island nucleation and growth, not Langmuir kinetics nor any other model that has been previously used to describe the formation, exchange, or displacement of SAMs. It is believed that the rapid and full displacement of **AD** SAMs is not unique and probably arises from a lattice mismatch with the C12 domains, rationalizing why slow and incomplete displacement occurs in systems with similar packing structures. The kinetic curves collapse onto a universal curve upon rescaling, suggesting that the displacement process is purely geometrical.

# Chapter 5

# Reversible Lability by in situ Reaction of Self-Assembled Monolayers

# 5.1 Introduction

Chapter 2 described some examples of how AD SAMs can be used to enhance existing microcontact printing techniques, since they provide labile monolayers that undergo complete molecular exchange in the contact areas while the remaining AD SAM domains in the uncontacted areas act as barriers to lateral diffusion. [48] The labile nature of this monolayer enables the preparation of sharp, high-quality microscale features, while extending the library of patternable molecules to include those that would not otherwise retain their patterned structures. [51] The AD SAMs not only control the deposition rate and minimize surface contamination, but also maintain the integrity of the patterned features. [326] However, in order for AD SAMs to be widely used as molecular resists for chemical and soft lithography, they would need to withstand a variety of fabrication steps; unfortunately, the highly labile nature of the SAM, while necessary for the desired exchange to occur, results in a SAM that rapidly exchanges with virtually any ALK or related molecule in contact with its surface. [166, 167, 295] This limits AD SAMs to patterning strategies that expose thiols only to the specific areas of the SAM that would result in the desired pattern and also hinder subsequent fabrication steps.

In order to obtain more precise control over a single functionality, molecule, or patterned feature on a surface, a methodology similar to resist exposure in photolithography needs to be developed to make robust SAMs that are resistant to molecular exchange, and undergo rapid and switchable displacement when desired. Previous studies have shown that molecular exchange in well-ordered SAMs other than **AD** undergo an inhomogeneous process, where rapid exchange (minutes to hours) occurs at grain boundaries, defects, and other disordered regions while occurring slowly in the crystalline domains, taking from days to weeks to reach steady state, but often incomplete, displacement ( $3\theta60\%$ ). [250-253] Therefore, in order to achieve more homogeneous and controlled displacement over a selected region of a SAM, the degree of order in these crystalline regions needs to be tuned after the self-assembly process but prior to the desired fabrication step.

Previously, Bumm *et al.* applied thermal processing to modify SAMs after their self-assembly. [174, 268] By heating an **ALK** SAM in the presence of excess thiol in solution, the densities of structural domain boundaries and Au substrate vacancy islands were decreased dramatically. The elevated temperatures led to Ostwald ripening of the SAM domains, assisted by an increase in surface diffusion and by acceleration in alkanethiolate desorption/adsorption. [327-333] In this way, the crystalline domain sizes were limited by the terrace size of the underlying Au substrate. Along these lines, Cyganic *et al.* annealed 2-(aryl)ethane thiolate SAMs under a nitrogen atmosphere, leading to a phase transition that dramatically improved the film stability (demonstrated by exchange experiments). [294]

However, in order to fabricate complex chemical patterns, a complementary approach is required, in which SAMs are purposefully disrupted to enable molecular exchange. To this end, ultraviolet (UV) and low-energy electron irradiation have been



Figure 5.1. Reaction and patterning scheme of the chemically induced exchange reactions in 11-mercaptoundecanoic acid (MUDA) SAMs. (*Step 1*) Exposure to HCl and ethanol leads to the formation of a disordered ester intermediate, 1-ethyl-11-mercaptoundecanoate (*in situ* esterified MUDA). (*Step 2*) Subsequent exposure to *n*-dodecanethiol (C12) solution enables tunable (fractional or complete) displacement of the reactive intermediate. (*Step 3*) Sections of the SAM containing undisplaced ethyl ester molecules can be hydrolyzed and quenched to prevent further exchange or displacement by exposure to aqueous HCl. The same patterning scheme was also applied to 3-mercapto-1-adamantanecarboxylic acid (MADCA) SAMs.
used to create chemical and structural defects in ALK SAMs to promote molecular exchange. [55, 334-339] Using such techniques, Ballav et al. successfully increased exchange rates by an order of magnitude while tuning the degree of exchange from 10% to 100%. However, this type of irradiation irreversibly damages the exposed regions, whether via oxidation of the thiol headgroup or by dehydrogenation of the SAM. This damage prevents self-assembly and its intermolecular interactions from aiding the resulting feature size, thus limiting the technique to the resolution and capabilities of topdown lithographic approaches. Exploiting the chemistry of the molecules enables the independent manipulation of a single functionality in the film, thereby allowing precise patterning and/or modification of molecules while tailoring the surface reactivity of the resulting film at the supramolecular-100 nm scale without the need for expensive nanofabrication facilities. [340-342] Here, we employ a simple chemical reaction, Fischer esterification (Equation 5.1), to create subtle chemical and structural defects in carboxylic-acid-terminated SAMs, thereby promoting the partial or complete molecular exchange of a robust, well-ordered SAM.

$$\begin{array}{c} O \\ R_1 \\ OH \end{array} \xrightarrow{\text{ROH / HCl}} O \\ H_2O/HCl \\ R_1 \\ OR \end{array}$$
 (5.1)

We also utilize the complementary hydrolysis reaction to regain the carboxylic acid termini, thus quenching further molecular exchange, as illustrated in Figure 5.1. These chemical and structural changes were measured with IRRAS and XPS, to monitor the properties and composition of the resulting film, demonstrating that well-ordered and otherwise stable monolayers can be controllably exchanged with molecules in solution using these step-by-step reactions.

#### 5.2 Background

# 5.2.1 Infrared Reflection Absorption Spectroscopy

See Chapter 1 for an introduction to IRRAS.

# **5.2.2 X-ray Photoelectron Spectroscopy**

See Chapter 3 for an introduction to XPS.

# **5.3 Experimental Procedures**

# 5.3.1 Sample Preparation

Gold substrates, 1000 Å thick (99.999%, Kurt J. Lesker, Clairton, PA), were prepared with an electron-beam evaporator using 4 in. polished silicon {100} wafers (Silicon Quest Int., Santa Clara, CA) with a 100 Å chromium adhesion layer (99.998%, Kurt J. Lesker, Clairton, PA). Monolayers were fabricated by immersing freshly prepared, hydrogen-flame-annealed gold substrates into ethanolic solutions of the desired thiol molecule. *n*-Dodecanethiolate (C12), perdeuterated *n*-dodecanethiolate (C12<sub>d25</sub>), and 1-ethyl-11-mercaptoundecanoate (EMU) [343] SAMs were prepared from 1.0 mM solutions, while 11-mercaptoundecanoic acid (MUDA) (Sigma-Aldrich, St. Louis, MO) and 3-mercapto-1-adamantanecarboxylic acid (MADCA) (Matrix Scientific, Columbia, SC) SAMs were prepared from 1.0 mM solutions containing 10% acetic acid (Figure 5.2). [344, 345] After deposition for 24 h, the gold substrates were removed, rinsed with ethanol, and dried under a stream of nitrogen. All SAMs were used immediately after preparation.



3-mercapto-1-adamantanecarboxylic acid

Figure 5.2. Structures, names, and abbreviations of the different molecules used.

# 5.3.2 Infrared Reflection Absorption Spectroscopy

IRRAS instrumentation is described in Chapter 3. Spectra were collected at grazing incidence reflection (84° relative to the surface normal) with *p*-polarized light and a mirror speed of 1.27 cm/s, with a resolution of 2 cm<sup>-1</sup>. Spectra were transformedusing Norton–Beer (N–B) medium apodization, averaged over 1024 scans, and normalized with data recorded from C12<sub>d25</sub> SAMs.

# **5.3.3 X-ray Photoelectron Spectroscopy**

X-ray photoelectron spectra were acquired using a Kratos Axis Ultra spectrometer (Chestnut Ridge, NY) with a monochromatic Al K $\alpha$  source (20 mA, 1.4 keV), a base pressure of 1 × 10<sup>-9</sup> Torr, and a spot size of 300 µm 700 µm. Survey spectra were acquired at a pass energy of 80 eV, while high-resolution spectra of the O 1s, C 1s, S 2p, and Au 4f regions were collected at a pass energy of 20 eV. The binding energies ( $E_b$ 's) were referenced to the Au 4f<sub>7/2</sub> peak at 83.98 eV. All of the peaks from the spectra were fit using Gaussian-Lorentzian (GL) line shapes using a Shirley -type background. The Au 4f peaks were fit with a fixed energy separation of 3.68 eV and a fixed-area ratio of 3:4. The S 2p<sub>3/2,1/2</sub> doublet peaks were fit using a fixed-energy separation of 1.18 eV, and a fixed-area ratio of 1:2.

### 5.4 Results and Discussion

# 5.4.1 Characterization of 11-Mercaptoundecanoic Acid, *in situ* Esterified 11-Mercaptoundecanoic Acid, and 1-Ethyl-11-Mercaptoundecanoate SAMs (Step 1, Figure 5.3)

IRRAS and XPS were used to provide detailed, quantitative information on film structure and composition. Grazing incidence IRRAS spectra of SAMs were obtained from 800 to 4000 cm<sup>-1</sup>. Figure 5.3A (red) shows a typical spectrum of a pristine **MUDA** SAM. The 2800–3100 cm<sup>-1</sup> region in the **MUDA** SAM spectrum is dominated by the characteristic stretching bands of methylene groups, in which the positions of the symmetric and asymmetric stretching modes are located at ~2850 and ~2920 cm<sup>-1</sup>, respectively. [103, 110, 111, 113, 276] These are in agreement with the literature values of 2850 and 2919 cm<sup>-1</sup>, which are indicative of crystalline-like packing of the alkyl chains. [108, 338, 346, 347] These features suggest a predominantly all-*trans* configuration of the alkyl chains, with few gauche defects. The broad 1740 and 1404 cm<sup>-1</sup> absorption bands in the 1100 to 1800 cm<sup>-1</sup> region correspond to the carboxyl and carboxylate C=O stretches. The broad carboxyl C=O absorption can be attributed to the free and hydrogen-bonded forms observed in **MUDA** SAMs, which occur between 1700 and 1740 cm<sup>-1</sup>. [344]

The spectrum of the **MUDA** SAM (Figure 5.3A, red) after 24 h exposure to 0.62 M ethanolic HCl solution (*in situ* esterified **MUDA**, Figure 5.3B, green) shows a shift in the asymmetric methylene absorption band (2921 cm<sup>-1</sup>), indicating lower conformational and orientational order in the SAM. The position of this absorption is highly sensitive to the conformational order of the alkyl chains and varied among samples from 2921 to 2923 cm<sup>-1</sup>, in which the upper value is characteristic of liquid-like



Figure 5.3. Representative IRRAS spectra of a 11-mercaptoundecanoic acid (MUDA) SAM (a) before and (b) after *in situ* esterification, which consists of 24-h exposure to ethanolic 0.6 M HCl. The spectrum after Fischer esterification shows the characteristic absorptions of an ester. (c) Spectrum of a 1-ethyl-11-mercaptoundecanoate (EMU) SAM deposited from 1.0 mM EMU solution. The inset shows the structure of MUDA and EMU molecules.

disorder. Additional bands in the aliphatic C–H stretch region were also observed. These bands, 2879 and 2983 cm<sup>-1</sup>, are characteristic of methyl symmetric and asymmetric stretching modes. Variations are also observed in the carbonyl stretching absorption, which becomes considerably sharper and stronger while shifting to  $1742 \text{ cm}^{-1}$ , characteristic of a predominantly non-hydrogen-bonded carbonyl stretch. [344] However, the largest variations are observed in the 1100–1400 cm<sup>-1</sup> region, where multiple sharp and well-defined absorption bands are now present. These bands have been observed previously, and are characteristic of alkyl esters. [344] The 1383 and  $1192 \text{ cm}^{-1}$  absorption bands correspond to a C–O stretch and a methyl rocking mode, respectively.

The C 1s XPS spectra of a pristine **MUDA** SAM and an *in situ* esterified **MUDA** SAM are shown in Figure 5.4. For the **MUDA** SAM (Figure 5.4A), the C 1s emission can be fit to two GL lineshapes: a low intensity peak centered at 289.5 eV and a much higher intensity peak centered at 284.8 eV. The more intense, lower-energy peak is attributed to the hydrocarbon backbone of the **MUDA** molecules, while the low intensity peak is attributed to the carbonyl carbon. Both of these features are in agreement with literature values. [104, 274-276] The **MUDA** aliphatic chain XPS C 1s emission with  $E_b = 284.8$  eV is in agreement with the literature values for C12 SAMs ( $E_b = 284.9$  eV), indicating a densely packed and contamination-free SAM. The S 2p XPS spectrum (data not shown, similar spectra in Figure 3.4) exhibits a single S  $2p_{3/2,1/2}$  doublet ( $E_b = 162.1$ , 163.2 eV), corresponding to the Au–thiolate bond.

The XPS C 1s spectrum of the **MUDA** SAM changed upon *in situ* esterification (Figure 5.4B). The C 1s aliphatic chain emission shifted to a lower energy (284.1 eV)



Figure 5.4. X-ray photoelectron spectra of the C 1s region of MUDA SAMs (a) before and (b) after *in situ* esterification. Each spectrum was fit with Gaussian-Lorentzian line shapes, revealing contributions from the carbonyl carbon (*blue*), the ethoxy methylene (*red*), the methyl of the ethoxy (*yellow*), and the alkyl methylenes (*green*). The C 1s spectrum of the Fischer esterification product reveals characteristic peaks of ethyl esters, and the resulting 1:1:1 area ratio between the carbonyl carbon, ethoxy methylene, and the terminal methyl of the ethoxy indicates that the reaction proceeds to near completion.

and slightly decreased in intensity (5  $\pm$  1%) with respect to that of the **MUDA** SAM. The slight decrease in intensity indicates partial desorption of the initial **MUDA** SAM, while the peak shift reflects structural and/or chemical changes in the film consistent with the disorder observed with IRRAS. The aliphatic chain peak was also found to be asymmetric, with a wider tail and a shoulder on the high  $E_b$  side. The C 1s spectrum was therefore fit with four GL line shapes. The two additional features, centered at 286.4 and 285.2 eV, have an area ratio of approximately 1:1. These features have been previously observed in XPS spectra of alkyl esters, and were attributed to the carbon backbone of the alkoxy portion of the molecule. [273] The higher energy peak corresponds to the rest of the carbon backbone in the alkoxy group. It is important to note that neither shifts nor broadening of the Au  $4f_{7/2}$  peaks were observed, which would have indicated the presence of gold oxide. [348-351]

Both IRRAS and XPS spectra show the appearance of methyl groups in the *in situ* esterified **MUDA** SAM, indicating chemical and structural changes in the film. Further evidence is provided by the sharp carbonyl stretch, which is no longer broadened by hydrogen bonding. However, the appearance of the multiple bands in the 1100–1400 cm<sup>-1</sup> region of the IRRAS spectrum sheds light on the chemical identity of the resulting SAM, specifically the 1192 cm<sup>-1</sup> band of the C–O stretch, which suggests the formation of an ester. Ethanol is the only alcohol present for reaction via Fischer esterification, which indicates the formation of an ethyl ester. Furthermore, direct evidence of ethyl ester formation is observed in the XPS spectra, with a 1:1 area ratio between the two features corresponding to the alkoxy portion of the ester. This ratio

relates the carbon bonded to the ester functionality and the remaining carbons of the alkoxy backbone. The 1:1 area ratio indicates an alkoxy backbone that is only two carbons long, which suggests the formation of 1-ethyl-11-mercaptoundecanoate. Furthermore, the spectrum also shows a 1:1 area ratio between the carbonyl carbon emission and the emission from the carbon closest to the ester functionality on the alkoxy portion ( $^{-}OCH_2CH_3$ ) of the ester. This indicates that the film is completely esterified, since in a partially esterified film the ratio would favor the carbonyl carbon.

To complement the characterization of the products resulting from in situ esterification, the corresponding ester thiol, 1-ethyl-11-mercaptoundecanoate (EMU), was synthesized and purified in order to investigate pristine and unreacted EMU SAMs. Figure 5.3C shows a representative IRRAS spectrum of an EMU SAM deposited from a 1.0 mM EMU solution, which exhibits similarities to spectra of *in situ* esterified MUDA The vibrational absorptions occur at the same positions, although there are SAMs. variations in peak intensities. In the 2800–3100 cm<sup>-1</sup> region of the EMU SAM spectrum, the asymmetric methyl stretch absorption (2983  $\text{cm}^{-1}$ ) is considerably weaker and barely visible, while the symmetric methyl stretch absorption (2879  $\text{cm}^{-1}$ ) is stronger and better defined, when compared to those of in situ esterified MUDA SAMs. However, the largest variations in the EMU SAM spectrum are observed in the 1100-1400 cm<sup>-1</sup> region, where the multiple absorption bands characteristic of esters are roughly twice as intense, as compared to the *in situ* esterified **MUDA** SAM spectrum. These intensity differences, which are due to the surface selection rules of IRRAS, indicate differences in the packing and in the conformational order of the terminal chains, which are the reacted portions of the molecules in the *in situ* esterified SAM. [109, 116, 117] It is assumed that the **EMU** SAM deposited from solution has greater conformational order at the tail termini, since packing is better optimized during the self-assembly process.

# 5.4.2 Displacement of 11-Mercaptoundecanoic Acid, *in situ* Esterified 11-Mercaptoundecanoic Acid, 1-Ethyl-11-mercaptoundecanoate, and *n*-Dodecanethiolate SAMs (Step 2, Figure 5.1)

Previous work has shown that molecules with stronger intermolecular interactions can exchange into SAMs, displacing adsorbates that interact more weakly. [352-356] It is important to note that currently only a handful of monolayers, such as AD with its tailored intermolecular interactions and lower packing density, form labile layers that readily and completely exchange with other thiols. For other SAMs, only partial exchange is typically achieved, reaching a fractional value even after several days of thiol exposure. [102, 250-253, 271] Figure 5.5A and 5.5 B show representative IRRAS spectra of MUDA SAMs before and after 1 h exposure to a 1.0 mM C12 solution, respectively. After exposure, the SAM showed symmetric and asymmetric methyl stretch absorptions. Due to the chemical composition of the unreacted MUDA SAM, only bands corresponding to the methylene stretches should be observed, in the absence of exchange with C12 molecules. The appearance of both methyl bands, and subsequent increases in intensity with further exposure, suggest molecular insertion and exchange of the **MUDA** SAM with the **C12** solution. [166] The low intensity of the methyl absorptions, and thus the limited extent of molecular exchange, indicate a high-quality and densely packed SAM that is not particularly susceptible to displacement. [102] A higher degree of molecular exchange was achieved after 71 h exposure to 1.0 mM C12 solution (Figure 5.5C), resulting in spectra with contributions from both molecules, with



Figure 5.5. (a) Representative IRRAS spectra of an 11-mercaptoundecanoic acid (MUDA) SAM before displacement, and the resulting spectra after (b) 1 h and (c) 72 h exposure to 1.0 mM *n*-dodecanethiol (C12) solution. These spectra indicate that limited displacement is observed in untreated MUDA SAMs.

peaks at 2879 and 2966 cm<sup>-1</sup>. However, the integrated areas of these peaks relative to those of a pristine C12 SAM reveal that only  $29 \pm 4\%$  of the MUDA SAM was exchanged, in agreement with literature values. [64]

Greater impact on molecular exchange kinetics can be achieved by treating the MUDA SAM with an ethanolic HCl solution, leading to the formation of the corresponding ethyl ester. Figure 5.6 shows representative IRRAS spectra of an *in situ* esterified MUDA SAM before and after 12 min and 1 h exposures to 1.0 mM C12 solution. The 1 h spectrum has sharp and well-defined absorption peaks at 2878 and 2985 cm<sup>-1</sup>, as well as a shoulder at 2937 cm<sup>-1</sup>, corresponding to the C12 methyl stretch modes. Furthermore, the FWHM of the asymmetric methylene peak narrowed from 25 to 17 cm<sup>-1</sup>, while shifting from 2921 to 2919 cm<sup>-1</sup>, indicating the presence of a well-ordered ALK SAM in a predominantly all-trans configuration, also supported by the disappearance of the carbonyl stretch at  $1742 \text{ cm}^{-1}$ . The spectrum was therefore nearly identical to the spectrum of a single-component C12 SAM fabricated on a bare gold substrate, indicating that the fractional in situ esterified MUDA coverage has been significantly diminished. It is important to note that although the resulting spectrum is almost identical to that of a pristine C12 SAM, slight variations are evident even after 24 h exposure to the displacing solution (data not shown). For example, the integrated area and intensity of the methyl stretch modes were somewhat smaller than those of a pristine C12 SAM, indicating lower molecular density in the resultant SAM. Furthermore, the intensity ratios between all the methyl and methylene stretch modes were slightly different, and indicated a larger number of defects in the resultant SAM. [103, 104, 107, 110, 111, 276, 338, 341, 346, 347] These IRRAS spectral differences



Figure 5.6. (a) Representative IRRAS spectra of an *in situ* esterified 11mercaptoundecanoic acid (MUDA) SAM before displacement, and the resulting spectra after (b) 12 min and (c) 1 h exposures to 1.0 mM *n*-dodecanethiol (C12) solution. The disappearance of the carbonyl stretch after 1 h exposure indicates the lack of MUDA molecules, showing that *in situ* esterification promotes complete molecular exchange.

have been previously observed in C12 SAMs formed by the displacement of pre-existing AD SAMs. [295] Scanning tunneling microscopy images of the resulting C12 SAM revealed smaller-sized domains and, thus, increased numbers of boundaries and defects, as shown in Figure 3.1. These differences in domain size can be attributed to the nucleation-induced displacement of AD molecules, which kinetically traps molecular domains to their specific tilts, since they lack sufficient thermal energy to change the orientations of entire domains to match the orientations of neighboring molecules, as discussed in Chapter 3.

The exchange reaction is likely promoted by the formation of defects and disorder in the SAM that result from *in situ* esterification, as described above in the characterization of the *in situ* esterified SAMs. This disorder is likely a consequence of the steric hindrance of the new terminal functionalities, which may be augmented by the reaction exothermicity. [66, 268] Similar effects were observed by Mirkin and co-workers, who showed that electrochemical reactions on inserted azobenzene moieties disrupted the surrounding SAM. [357, 358]

The degree of molecular exchange in **EMU** SAMs was also determined, as described below. Figure 5.7 shows the IRRAS spectra of an **EMU** SAM deposited from a 1.0 mM **EMU** solution before and after 1 h exposure to 1.0 mM **C12** solution. The symmetric and asymmetric methyl absorptions at 2960 and 2877 cm<sup>-1</sup>, respectively, slightly increased in intensity  $(13 \pm 1\%)$ , while the carbonyl and ester bands decreased slightly in intensity  $(9 \pm 1\%)$ . This indicates a limited degree of molecular exchange, since increases in the methyl absorptions are mostly due to molecular insertion at defect sites, as previously observed in alkanethiolate SAMs. [170, 172, 269, 359, 360]



**Figure 5.7. (a)** Representative IRRAS spectrum of 1-ethyl-11-mercaptoundecanoate (**EMU**) SAM formed from 1.0 mM **EMU** solution. (**b**) The resulting spectrum after 1 h exposure to 1.0 mM *n*-dodecanethiol (**C12**) solution. Small intensity changes, such as the decrease in the carbonyl group absorption and the increase in the symmetric methyl mode absorption, indicate small amounts of molecular exchange even though the SAM is chemically identical at the molecular level of each molecule to the *in situ* esterified **MUDA** SAM. This suggests that differences in the degree of disorder, and in the assembly, play important roles.

Therefore, the stability of the **EMU** SAM, and its ability to undergo molecular exchange, is similar to alkanethiolate SAMs. The stability differences between the **EMU** and *in situ* esterified **MUDA** SAMs can be explained by their spectral differences, which indicate greater disorder in the latter SAM, as described above.

To create a complex chemically patterned surface, it will be necessary to react specific molecules or patterns in a SAM selectively without disturbing the surrounding matrix. In order to determine the stability of an unfunctionalized SAM that could serve as a surrounding matrix, a pristine C12 SAM was exposed to *in situ* esterification conditions. Figure 5.8A shows the IRRAS spectrum of a pristine C12 SAM, which is dominated by the characteristic stretching bands of methyl and methylene groups (vide supra). The position of the asymmetric methylene stretch was found to be 2919 cm<sup>-1</sup>, which is again in agreement with literature values for crystalline-like films with predominantly all-trans configurations. This absorption is also sharper, with a FWHM of 16  $cm^{-1}$ , as compared to the 26 cm<sup>-1</sup> FWHM of the pristine **MUDA** SAM, reflecting higher conformational and orientational order, in agreement with previous experiments. [361] After exposing the SAMs to the *in situ* esterification reaction for 24 h, only minor changes in the spectra were observed (Figure 5.8B). The symmetric and asymmetric methyl absorptions at 2967 and 2877 cm<sup>-1</sup>, respectively, decreased in intensity  $(19 \pm 2\%)$ . Similar results, but smaller effects (8  $\pm$  3%), were observed when a pristine C12 SAM was exposed to neat ethanol for 24 h. This indicates slight degradation, not due to reaction, of the C12 SAM when exposed to neat ethanol, in agreement with previous experiments showing limited alkanethiolate disorption as disulfides occurs. [114, 362-364] The rate and extent of desorption are highly dependent on the solvent; even small changes in the solvent



Figure 5.8. Representative IRRAS spectra of an *n*-dodecanethiolate (C12) SAM (a) before displacement, (b) after exposure to similar Fischer esterification conditions used to esterify MUDA SAMs, and (c) after 1 h exposure to 1.0 mM perdeuterated *n*-dodecanethiol (C12<sub>d25</sub>) solution. The minor spectral changes after exposure to the C12 solution demonstrate that robust unfunctionalized SAMs can withstand the *in situ* esterification without leading to significant molecular exchange with further thiol exposure.

composition (e.g., the addition of 5% dimethylformamide to water) influences desorption rates. [362] Thus, it is not surprising that the extent of desorption into the acid/ethanol mixture is somewhat different than that for neat ethanol. Therefore, though in situ esterification reaction conditions result in some C12 SAM degradation, due to the prolonged ethanolic HCl exposure, we conclude that the reaction selectively catalyzes the reaction of MUDA molecules without significantly disturbing unfunctionalized molecules. The slight degradation observed could be decreased by optimizing the *in situ* esterification reaction conditions, minimizing the time required to react the MUDA SAM. In turn, this would minimize the amount of time any SAM would need to be exposed to ethanolic solution, and thus reduce the degradation of unfunctionalized portions of the film. A 24 h reaction is not necessary to esterify a MUDA SAM; this length of exposure was chosen in order to give ample time for the reaction to reach completion. Furthermore, catalysts that promote esterification could be used to reduce the amount of time required to esterify the SAM fully. [365-367] For example, Naik and co-workers [367] were able to esterify, within 15 min, various carboxylic acids with ~93% efficiency using catalytic amounts of tetrabutylammonium tribromide. Both efficiency and kinetics could be further improved by using a dehydrating agent, or other special techniques for the removal of water, which under these conditions hydrolyze the ester.

To establish the susceptibility of unfunctionalized SAMs to molecular exchange caused by *in situ* esterification, both pristine and treated C12 SAMs were exposed to C12<sub>d25</sub> solutions. Displacement by C12<sub>d25</sub> molecules would cause a decrease in the intensity of the C-H absorptions in the IRRAS spectra and a corresponding increase in

C-D absorption intensity. Figure 5.8C shows the IRRAS spectrum of the previously treated C12 SAM from Figure 5.8B after exposure to 1.0 mM C12<sub>d25</sub> solution. The symmetric and asymmetric methyl absorptions at 2965 and 2878 cm<sup>-1</sup>, respectively, further decreased in intensity (4  $\pm$  1%) upon exposure to the solution. Once again, similar results were obtained when a pristine untreated C12 SAM was exposed to the 1.0 mM C12<sub>d25</sub> solution. These results show that *in situ* esterification does *not* promote molecular exchange reactions in unfunctionalized molecules, and that the observed molecular exchange is similar to that of an untreated C12 SAM.

**MADCA** SAMs, carboxylfunctionaled versions of **AD**, were displaced using a similar methodology, since *in situ* esterification is by no means unique to **MUDA** SAMs. Since MADCA is structurally different from MUDA (Figure 5.2), the ability to apply this methodology to both molecules indicates that our approach is generalizable. Figure 5.9A (light blue) shows a typical IRRAS spectrum of a pristine MADCA SAM, which has two strong absorptions, at 2926 and 2860  $\text{cm}^{-1}$ , attributed to the symmetric and asymmetric methylene stretch modes, respectively. The broad peak at 2926  $\text{cm}^{-1}$  is asymmetric, with a longer tail on the low energy side, due to the absorption of the two methine groups (C-H) in the carbon cage (which in AD SAMs appears around 2934 cm<sup>-1</sup>). [166, 295] After further 1 h exposure to 1.0 mM C12 solution, the MADCA SAM spectrum (Figure 5.9B, blue) showed a slight increase in the symmetric and asymmetric methylene stretch mode intensities. However, the lack of absorption in the methyl regions indicates a lack of molecular exchange. A 72 h exposure to the C12 solution (Figure 5.9, purple) resulted in spectra with contributions from both molecules, with peaks at 2879 and 2964  $\text{cm}^{-1}$ . However, even after 72 h total exposure to the C12



Figure 5.9. (a) Representative IRRAS spectrum of 3-mercapto-1-adamantanecarboxylic acid (MADCA) SAM. The resulting spectra after (b) 1 h and (c) 72 h exposure to 1.0 mM *n*-dodecanethiol (C12) solution. (d) The spectrum of an *in situ* esterified MADCA SAM after 1 h exposure to 1.0 mM C12 solution. The disappearance of the carbonyl stretches in the *in situ* esterified MADCA SAM spectrum after the 12 min exposure indicates that complete molecular exchange was achieved

solution, little molecular exchange was observed. Comparing the integrated absorption peak areas of the symmetric methyl stretch with that of a pristine C12 SAM indicates that only  $6 \pm 2\%$  of the MADCA SAM was exchanged. This low degree of molecular exchange relative to MADCA's unfunctionalized counterpart, AD, which readily undergoes complete and rapid molecular exchange, highlights the importance of intermolecular interactions in stabilizing SAMs. [166, 167, 295]

In contrast, *in situ* esterified **MADCA** SAMs are much more susceptible to displacement. Figure 5.9D (red) shows a representative IRRAS spectrum of an *in situ* esterified **MADCA** SAM after 12 min of exposure to 1.0 mM **C12** solution. The spectrum does not contain a carbonyl absorption and has sharp, well-defined absorption peaks corresponding to a well-ordered alkanethiolate SAM (*vide supra*). Although determining the detailed displacement kinetics of the process is beyond the scope of this chapter, a larger degree of displacement was observed for the *in situ* esterified **MADCA** SAMs (86  $\pm$  2%), each after 12 min of exposure to **C12** solutions. The ability to switch the reactivity of both **MUDA** and **MADCA** SAMs demonstrates that the reaction technique can be made general and can be applied to a range of SAMs that contain carboxyl groups.

# 5.4.3 Hydrolysis of *in situ* Esterified 11-Mercaptoundecanoic Acid SAMs (Step 3, Figure 5.1)

Esterified SAMs can also be hydrolyzed, returning the switchable surface nearly to its original state. In a complex patterning application, these hydrolyzed molecules could once again serve as controllable sacrificial layers in subsequent patterning steps or modifications. Figure 5.10A and 5.10B shows the spectra of an *in situ* esterified **MUDA** 



Figure 5.10. (a) Representative IRRAS spectrum of an *in situ* esterified 11-mercaptoundecanoic acid (MUDA) SAM. (b) The resulting spectrum after hydrolysis, which consists of 24 h exposure to aqueous 5.0 M HCl. (c) The spectrum after 1 h exposure to 1.0 mM *n*-dodecanethiol (C12) solution, showing small amounts of displacement after hydrolysis.

SAM before and after 24 h *in situ* hydrolysis with 5.0 M HCl aqueous solution, respectively. The hydrolysis reaction results in a spectrum that is similar to that of a **MUDA** SAM, with two peaks corresponding to the symmetric and asymmetric methylene stretches and no evidence of peaks corresponding to the methyl modes. A 1 h exposure to 1.0 mM C12 solution results in spectra with contributions from both **MUDA** and C12 molecules (Figure 5.10C), in which the weak methyl absorptions correspond to  $7 \pm 5\%$  exchange. *In situ* hydrolysis thus substantially neutralizes the promoted exchange observed for *in situ* esterified **MUDA** SAMs. However, the *in situ* esterification, followed by the hydrolysis reaction, slightly decreases the quality of the original **MUDA** SAM and results in more molecular exchange ( $7 \pm 5\%$  as compared to  $2 \pm 1\%$ ). Nevertheless, exchange was limited, leaving ~93% of the hydrolyzed molecules in the film.

# 5.5 Conclusions

A straightforward and robust strategy for preparing switchable monolayers for use in complex surface patterning applications has been demonstrated. The IRRAS and XPS data presented illustrate the effects of *in situ* esterification on the extent of exchange reactions with carboxyl-functionalized **ALK** in SAMs. Using **MUDA** and **MADCA** SAMs as model systems, with **C12** molecules as the exchanging species, *in situ* esterification promoted the molecular exchange reaction (to completion). Without reaction, only very limited molecular exchange  $(2 \pm 1\%)$  took place within the same time frame; this increased somewhat  $(29 \pm 4\%)$  with longer exposures (72 h). The data reveal that *in situ* esterification induces chemical and structural defects that result in partial desorption and increased conformational disorder of the SAMs. Previous studies have shown that the rate and extent of molecular exchange depend on the quality of the SAM, and are both larger for disordered films. [64, 252, 253, 334, 337, 368] Here, film disorder also appears to play a key role, since well-ordered **EMU** SAMs deposited from 1.0 mM **EMU** solutions do *not* show significant molecular exchange, even though they are identical at the molecular level to the *in situ* esterified **MUDA** SAMs. Thus, the order and defects of the SAM are critical to its stability and properties.

The data also show that the complementary hydrolysis reaction can be employed to quench a partially displaced or patterned surface. Versatile molecular resists for chemical patterning, including soft lithography, need to withstand subsequent chemical and/or physical fabrication steps. Displacement experiments on the pristine MUDA and MADCA SAMs, along with experiments on the hydrolyzed SAMs, show the stability of these films and their applicability as versatile molecular resists when exposed to thiol solutions for relatively short times. The remaining hydrolyzed molecules in the film could act as lateral diffusion barriers to protect the integrity of the patterned features and/or to serve as sacrificial layers for subsequent patterning steps. Typically, resists used in traditional lithographies are sacrificial structures that are used to transfer patterns to the substrate, where exposure to electrons, photons, or ions causes irreversible changes to the film. However, the use of molecules or monolayers as resists, with simple and reversible chemical reactions as the resist exposure mechanism, provides the capability of cycling the resist between its exposed and unexposed states. This may enable the fabrication of complex features with multiple length scales by limiting molecular

exchange and/or patterning to different areas of the surface during different patterning steps. Furthermore, by returning the resist to its unexposed state, the resist can serve a dual role, or could even be used to *repair* errors in the functional surface.

This approach should not be limited to carboxyl-terminated SAMs, and could likely be extended to target different functional groups, employing chemical reactions analogous to those used here. [369] The extent of molecular exchange of a single functionality in a multiplexed or multifunctionalized SAM can then be tuned meticulously utilizing this methodology, enabling the patterning of SAMs with precisely tailored compositions and reactivity. Furthermore, this methodology can be used for advanced chemical patterning of functional surfaces that can chemically and biologically interact with their environment at the single-molecule level. These patterned functional surfaces. this methodology, have potential applications ranging and from bioactive/biocompatible surfaces to molecular-sized sensors and electronic components. For example, sensors can be manufactured for small molecules such as neurotransmitters, or surfaces could be functionalized to detect biological agents such as viruses, toxins and bacteria quickly and cost effectively.

# Chapter 6

# The Effect of Counter-Cations and Structure in Cluster-Assembled Materials

# **6.1 Introduction**

Atomic clusters, nanoparticles, and quantum dots have tunable and sizedependent magnetic, optical, and electronic properties due to quantum confinement. [202, 205, 370, 371] Particularly, in the case of clusters, the addition or removal of a single atom can have significant effects on the resulting physical properties. Clusters can also be assembled into solid functional materials, where the individual clusters serve as building blocks, analogous to the assembly of ionic salts. [207, 372-375]

The tunability of counter-cation, lattice spacing, and coupling between clusters in the assemblies provides a means to tailor solid materials with unique combinations of properties. Therefore, numerous structural assemblies can be fabricated from the same structural sub-unit, yet result in materials that differ in optical and electronic properties. These materials would also serve as a link between the properties of the bulk materials and the size-dependent properties observed at the nanoscale, enabling the hierarchical assembly of designer materials that retain the properties of the individual clusters.

Zintl phases are one of the classes of cluster assemblies that provide a means to study comprehensively the effects of structure and function in cluster-assembled materials. A zintl cluster is composed of heavy post-transition metals and electropositive elements, such as the alkali metals. [376-381] The electropositive alkali or alkaline earth element donates its electrons to the electronegative metal, thereby forming the necessary number of homoatomic bonds so that both the element and cluster have complete octets. These Zintl compounds vary electronically between insulator and intermetallic phases, and in some cases can exhibit "locally" delocalized electrons. [382] An example is the  $As_7^{3-}$ -based Zintl phase, where the anionic As cluster is surrounded by alkali metal ions (Cs, K, Rb, etc.), forming compact and crystalline cluster assemblies. [207, 373, 383, 384]

The flexibility of these Zintl phases enable the ability to alter the counter-cations synthetically, providing ideal test cases for determining the parameters that control and determine the optical and electronic properties of the resulting functional materials. Ultimately, such control will lead to recipes for fabricating new materials with specifically tailored properties. In this chapter, numerous Zintl-based cluster subunits and assemblies are characterized, showing how counter-cations affect the degree of charge transfer to the cluster and thus impact the resulting properties. Furthermore, it is shown that the extent of electronic coupling between clusters can be controlled by modifying the lattice parameters of the functional material via changes of the counter cation and the use of different polycyclic ligands.

This work was a collaborative effort between The Pennsylvania State University and Virginia Commonwealth University, with contributions from four research groups (Profs. A.W. Castleman, A. Sen, P.S. Weiss, and S. Khanna). The cluster-assembled materials were synthesized by Dr. Nirmalya K. Chaki and Dr. Sukhendu Mandal, density functional theory was performed by Meichun Qian and Dr. Arthur C. Reber, while I measured the diffuse reflectance spectra and determined the band gaps of the assemblies.

#### 6.2 Background

## **6.2.1 Diffuse Reflectance Spectroscopy**

In transmission spectroscopy, non-absorbing solvents provide a means to measure the absorption of the dissolved substances as a function of wavelength. [385] However, difficulties arise when studying turbid or colloidal systems, in which light-scattering results in substantial energy losses. [386] Furthermore, the technique becomes unsuitable when measuring the absorption spectra of surfaces, powders, or crystalline materials.

Diffuse reflectance spectroscopy is a technique in which scattered light from fine particles, powders, or rough surfaces is collected and analyzed. Reflections from these materials consist of a specular component and a diffuse component. [386] The former arises from regular reflection occurring at the surface, while the latter results from radiation that penetrates and reappears at the surface following partial absorption and multiple scattering events within the system.

Diffuse reflection and the transmission of light-scattering layers were first adequately described by the Kubelka and Munk. [387-389] For an infinitely thick layer, experimentally achieved with a thickness of only a few mm, the Kubelka-Munk theory states that:

$$F(R_{\infty}) \equiv \frac{(1-R_{\infty})^2}{2R_{\infty}} = \frac{k}{s},$$
 (6.1)

where  $R_{\infty}$  is the diffuse reflectance of the layer relative to a non-absorbing standard (such as MgO), *k* is the molar absorption coefficient, and *s* is the scattering coefficient. When the sample is diluted with a non- or low-absorbing powder, the absorption coefficient, *k*, can be replaced with 2.303  $\epsilon c$ , where  $\epsilon$  is the extinction coefficient and *c* is molar concentration. [386] Since  $F(R_{\infty})$  is proportional to the molar concentration under constant experimental conditions, the Kubelka-Munk equation in this form is comparable to the Beer-Lambert law of transmission spectroscopy, in which

$$A = \varepsilon_{\lambda} b c , \qquad (6.2)$$

where *A* is the measured absorbance,  $\varepsilon_{\lambda}$  is the wavelength-dependent molar absorptivity, *b* is the path length, and *c* is the analyte concentration. [385]

The non-penetrating specular reflection component needs to be minimized or eliminated in diffuse reflectance spectroscopy, since it results in deviations from the Kubelka-Munk theory, while also changing band shapes, band intensities, and in some cases results in complete band inversions. [386-389] Diluting the sample with a non-absorbing matrix minimizes the specular component of reflection, while also ensuring deeper penetration of the incident beam into the sample that results in increased scattering. Reducing particle size of the samples also results in increased scattering. For sufficient scattering, the particle size for both the sample and the diluting matrix should be  $\leq 50 \ \mu m$ .

#### 6.2.2 Absorption Edge of Semiconductors

Optical absorption is widely used to characterize the electronic properties of materials, since it determines the parameters that describe electronic transitions, such as: band gap, valence band tails, and the lifetime of the excited states. Electronic transitions between the valence and conduction bands start at the absorption edge, corresponding to the minimum energy difference ( $E_{bg}$ , band gap) between the lowest minimum in the conduction band and the highest maxima in the valence band. When these extrema lie at

the same point in k-space, the transitions are called direct. However, if the extrema lie at different points in k-space, the transitions are possible only when assisted by a phonon or occurring at a lattice defect, in a process known as indirect transitions. In this case, the creation or annihilation of a phonon provides a means to conserve quasimomentum during the transition. [387, 390-394]

For a direct transition, conservation of energy requires that the final states obey

$$\hbar\omega = \frac{\hbar^2 \kappa^2}{2m^*} + E_{bg} , \qquad (6.3)$$

where  $m^*$  is the electron reduced mass,  $E_{bg}$  is the band gap, and  $\hbar^2 \kappa^2 / 2m^*$  is the conduction band energy. Thus,  $\frac{dE}{dk} = h^2 \kappa / m^*$ . Writing the density of states as  $\frac{dN}{d\kappa} \times \left(\frac{dE}{d\kappa}\right)^{-1}$ , and assuming the three-dimensional form of  $\frac{dN}{d\kappa}$ , the density of states just above the band gap is proportional to  $(\hbar \omega - E_{bg})^{1/2}$ . This leads to dependence of  $\epsilon_2$  on the photon energy just above the band gap of:

$$\omega^2 \epsilon_2 \sim \left(\hbar\omega - E_{bg}\right)^{1/2}.\tag{6.4}$$

However, for an indirect transition, a phonon is also either created or annihilated, so the quantum mechanical expression for absorption becomes a double sum. [391, 392, 394] Thus, the final density of states becomes proportional to  $(\hbar\omega - E_{bg})^{1/2} \times E_V^{1/2}$ , where  $E_V$  is the valence band energy (relative to the top of the valence band). Performing a double integration over the valence and conduction band states leads to the "indirect" absorption band edge scaling of

$$\omega^2 \epsilon_2 \sim \left(\hbar\omega - E_{bg}\right)^2. \tag{6.5}$$

Therefore, the optical band gaps of semiconductors and cluster-assembled materials can be measured using diffuse reflectance spectroscopy, and the Kubelka-Munk model. [395-399] The two-flux model, which considers only diffuse light, is used to determine the absorption coefficients from a surface that both scatters and absorbs incident radiation. For a crystalline solid with a band gap  $(E_{bg})$ , the frequency  $(\omega)$  dependence of the absorption coefficient ( $\alpha$ ) can be approximated as:

$$\alpha(\omega) = \frac{B_T (\hbar \omega - E_{bg})^n}{\hbar \omega},\tag{6.6}$$

where  $B_T$  is a constant derived from the square of the averaged dipolar momentum matrix element, and *n* is equal to 0.5 and 2 for *direct* and *indirect* band gap transitions, respectively. [390-392, 394] Using the above equation, the band gap of a material can be obtained by extrapolating to zero with the linear fit to a plot of  $(\alpha \hbar \omega)^{1/n}$  vs.  $\hbar \omega$ .

### **6.3 Experimental Procedures**

#### **6.3.1 Sample Preparation**

All reagents were commercially available and used without further purification. 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (Crypt), Zn(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> and anhydrous ethylenediamine (99.5%) were purchased from Aldrich. Au(PPh<sub>3</sub>)Cl, As powder (-70 mesh, 99.99%), K (99.95%, ampouled under Argon), Cs (99.98%, vacuum sealed in break-sealed ampoules) and Rb (99.8%, vacuum sealed in break-sealed ampoules) were purchased from Alfa Aesar. Toluene and tetrahydrofuran were dried by passing each through an activated alumina column followed by deoxygenating with a

| COMPOUND                                      | MOLECULAR FORMULA                           |
|---|---|
| As <sub>7</sub> <sup>3–</sup> Building Block  |   |
| 1   | As <sub>7</sub> Cs <sub>3</sub>             |
| 2   | As <sub>7</sub> Cs <sub>2</sub> (K – Crypt) |
| 3   | $As_7Cs_{1.5}(K - Crypt)_{1.5}$             |
| 4   | $As_7Cs_{1.5}(Rb - Crypt)_{1.5}$            |
| MAs <sub>7</sub> <sup>3–</sup> Building Block |   |
| 5   | $Zn(As_7)_2(K - Crypt)_4$                   |
| 6   | $Au_2(As_7)_2(K - Crypt)_4$                 |
| 7   | $Au_2(As_7)_2K_2(K - Crypt)_2$              |
| 8   | $Au_2(As_7)_2Cs_2(K - Crypt)_2$             |
| 9   | $Au_2(As_7)_2Cs_2(Rb - Crypt)_2$            |
| 10  | $Au_2(As_7)_2Rb_2(Rb - Crypt)_2$            |

**Table 6.1.** Molecular formulas and compound numbers of the studied cluster-assembled materials.



**Figure 6.1.** Building motifs for As<sub>7</sub>-based cluster-assembled materials. **(A)** Cryptated-K cation  $[(K - Crypt)^+]$ . **(B)** Naked  $As_7^{3-}$ . **(C)** and **(D)** Zn- and Au-linked dimers. As atoms are shown in red, C in gray, O in green, H in white, Zn in blue, and Au in gold. Molecular structures drawn by N. K. Chaki.

copper catalyst. All glassware (oven dried), reactants, and solvents were stored in a glove box filled with argon.

The precursor  $As_7K_3$  was synthesized in bulk from the corresponding elements in ethylenediamine (Compound 1). [392] The  $[M_x(As_7)_2]^{4-}$  [M=Au, Zn, Cr] building blocks were synthesized by reacting the  $As_7K_3$  precursor with Au(PPh\_3)Cl at room temperature. All cluster assemblies were crystallized from precursor solutions in the presence of the polycyclic ligand Crypt (Figure 6.1A) and any additional alkali metals. Crypt was used as a cation sequestering agent, since it selectively sequesters K<sup>+</sup> and Rb<sup>+</sup> over Cs<sup>+</sup>. [400, 401] This selectivity enables the integration of two different cations in the assembly, a sequestered and "naked" cation. Additional synthetic procedures are described elsewhere in detail. [384, 402, 403]

# 6.3.2 Diffuse Reflectance Spectroscopy

Diffuse reflectance measurements were collected at room temperature using a Lambda 950 UV-vis-NIR spectrophotometer (Perkin Elmer, Waltham, MA), equipped with a Praying Mantis diffuse reflectance accessory (Harrick Scientific, Ossining, NY). A photomultiplier tube was used for detection in the 320-860 nm range, while a lead sulfide detector was used for the 860-2300 nm range. A dry and finely ground magnesium oxide (MgO) powder was used as a reflectance reference material. Prior to any measurements, all cluster-assembled materials were finely ground and diluted with MgO to 30% by weight.

#### 6.4 Results and Discussion

#### 6.4.1 Effects of Cationic Linker on As<sub>7</sub>-Based Cluster Assemblies

Clusters composed of post-transition metals can be used to form Zintl phases. [376, 379-381] For example,  $As_7^{3-}$  (Figure 6.1B) forms Zintl phases, and can therefore be used as a building block in cluster-assembled materials. [207, 372-375, 378, 383, 384, 402, 403] Figure 6.1B shows the additional building blocks discussed in this chapter. The  $As_7^{3-}$  cluster, requiring three additional electrons to complete its electronic shell, forms compact crystalline assemblies when combined with alkali metals. Using Cs as the electropositive element results in  $As_7Cs_3$  motifs that arrange in compact, directly-linked three-dimensional structures ( $As_7Cs_3$ , Compound 1), as shown in Figure 6.2A. The corresponding Tauc plot of Compound 1 is shown in Figure 6.3A (blue), revealing  $E_{bg} = 1.09 \pm 0.05$  eV.

Replacing one of the Cs atoms in each unit of the assembly with a cryptated species, in this case cryptated K [(K – Crypt)<sup>+</sup>], facilitates the fabrication of ionic phases through charge transfer. The resulting solid,  $As_7Cs_2(K - Crypt)$  (Compound 2), consists of  $As_7$  clusters assembled into two-dimensional sheets of slightly distorted hexagonally-arranged clusters, where the vertices of each cluster are joined by shared Cs atoms. Adjacent two-dimensional sheets are separated from each other by the cryptated species, as shown in Figure 6.2B. The Tauc plot for Compound 2 is shown in Figure 6.3A (green), revealing a  $E_{bg} = 2.04 \pm 0.12$  eV.

Further increasing the stoichiometric ratio of the  $(K - Crypt)^+$  species during crystallization, relative to Cs, leads to the formation of a third structure with a molecular


**Figure 6.2.** Crystal structures of (**A**) the three-dimensional material  $As_7Cs_3$  (Compound 1), where the interactions of Cs with  $As_7$  are shown; (**B**) two-dimensional sheet of  $As_7$  clusters bound by Cs, while the  $(K - Crypt)^+$  separates these layers in  $As_7Cs_2(K - Crypt)$  (Compound 2); (**C**) two-dimensional sheet of  $As_7$  clusters bound by Cs, while the  $(K - Crypt)^+$  separates these layers in  $As_7Cs_{1.5}(K - Crypt)_{1.5}$  (Compound 3); (**D**) two-dimensional sheet of  $As_7$  clusters bound by Cs, while the  $(Rb - Crypt)_{1.5}$  (Compound 3); (**D**) two-dimensional sheet of  $As_7$  clusters bound by Cs, while the  $(Rb - Crypt)_{1.5}$  (Compound 4). As atoms shown in red, Cs in purple, K in blue, Rb in brown, Au in gold,  $(K - Crypt)^+$  and  $(Rb - Crypt)^+$  are indicated as isolated K<sup>+</sup> and Rb<sup>+</sup>, respectively, for clarity. Crystal structures drawn by N. K. Chaki.

formula of  $As_7Cs_{1.5}(K - Crypt)_{1.5}$  (Compound 3). The resulting structure is again a two-dimensional sheet, although in this case the hexagonally-arranged two-dimensional structure is not distorted. Furthermore, the  $As_7$  motifs are now linked via a single Cs atom at each of the three vertices, although the two-dimensional sheets are still separated and charge stabilized by the  $(K - Crypt)^+$ . The  $Cs_{1.5}$  stoichiometry results from the Cs atoms shared by the adjacent rings in the extended structure, where the cryptated species occupy cavities within the adjacent two-dimensional sheets in the three-dimensional structure. Figure 6.3A (black) shows the Tauc plot of Compound 3, revealing a  $E_{bg} = 2.08 \pm 0.05$  eV.

Cluster-assembled material properties can be further tuned by utilizing a different cryptated species, such as cryptated Rb [Rb – Crypt]<sup>+</sup>, resulting in a molecular formula of As<sub>7</sub>Cs<sub>1.5</sub>(Rb – Crypt)<sub>1.5</sub> (Compound 4). This change does not result in a different structural arrangement, but changes the electron transfer between adjacent layers. This chemical change lead to a band gap of  $E_{bg} = 1.77 \pm 0.02$  eV, as observed in the Tauc plot of Compound 4 (Figure 6.3A, purple).

As mentioned above, variations in the architectures and compositions of the cluster assemblies leads to different electronic, optical, and other properties. Diffuse reflectance spectroscopy and the Tauc relation were used to determine the corresponding band gaps of the different cluster-assembled materials. Significant variations were observed in the band gaps of the structurally and chemically distinct assemblies prepared from the same  $As_7^{3-}$  cluster building block. Compound 1 has a  $E_{bg} = 1.09 \pm 0.05$  eV, while Compound 4 has a  $E_{bg} = 2.04 \pm 0.12$  eV. These results were used to determine



**Figure 6.3.** Tauc plots showing the band gaps determined from the optical absorption spectra (see text) of: (A) alkali-metal-linked As<sub>7</sub> cluster assemblies (Compounds 1-4) and (B) cluster dimers with either Zn or Au covalently bound to As<sub>7</sub> (Compounds 8-10).

| As <sub>7</sub> <sup>3–</sup> Building Block |                                  |                                   |                             |  |
|--|----------------------------------|-----------------------------------|-----------------------------|--|
| Compound                                     | Formula                          | Experimental E <sub>bg</sub> (eV) | Theoretical E <sub>bg</sub> |  |
| 1  | As <sub>7</sub> Cs <sub>3</sub>  | 1.09±0.052                        | 1.19                        |  |
| 2  | $As_7Cs_2(K - Crypt)$            | 2.04±0.12                         | 1.98                        |  |
| 3  | $As_7Cs_{1.5}(K - Crypt)_{1.5}$  | 2.08±0.05                         | 1.84                        |  |
| 4  | $As_7Cs_{1.5}(Rb - Crypt)_{1.5}$ | 1.77±0.021                        | 1.80                        |  |

**Table 6.2.** Experimentally measured and theoretically calculated band gaps of the  $As_7$ -based clusterassembled materials. Density functional theory values obtained from ref. [402]. general trends in the band gaps of the cluster assemblies. For example, the twodimensional sheets of Compound 2 and Compound 4 both had larger band gaps,  $E_{bg} =$ 2.08 and 2.04 eV, respectively. Consequently, the three-dimensional structure of Compound 1, which enables larger orbital overlap, had a lower  $E_{bg} = 1.09 \pm 0.05$  eV. One would expect cluster assemblies composed of the same motif to be isoelectronic, yet  $E_{bg}$  almost doubled when replacing Cs<sup>+</sup> with (K – Crypt)<sup>+</sup>.

The  $As_7^{3-}$  motifs are separated from each other by the alkali cation and therefore do not interact directly. As a result, the energy bands are expected to have low dispersion. This  $As_7^{3-}$  motif is a closed-shell species stabilized by charge transfer from the alkali atoms, the latter thereby also acquiring closed-shell configurations. Therefore, the resulting solid is a semiconductor (as the valence band is completely full and separated from the conduction band). The three-dimensional structure of Compound 1 has the lowest  $E_{bg}$  (1.09  $\pm$  0.05 eV), attributed to the large degree of interaction between adjacent clusters in the compact structure. However, when the same cluster motif is arranged in a two-dimensional sheet, with the aid of  $(K - Crypt)^+$  (as in Compound 2), there is a net decrease in connectivity since the adjacent sheets are separated by the cryptated species. It is important to note that cryptated species do interact with the cluster subunits. However, theoretical calculations by Qian et al. have shown that the energy levels resulting from these interactions are high enough that the interactions do not significantly affect the band gap of the solid. [402] Nevertheless, the decrease in cluster connectivity leads to an increase in the  $E_{bg}$  of the material to 2.08 ± 0.05 eV. The addition of more  $(K - Crypt)^+$  during crystallization (Compound 3), does not lead to

significant structural rearrangements of the individual As<sub>7</sub> cluster subunits. In fact, neighboring clusters are still bound via similar Cs<sup>+</sup> linkers, and therefore does not lead to a significant variation in the  $E_{bg}$ . However, if the cryptated species is changed to  $(Rb - Crypt)^+$ , while maintaining the same structural arrangement, the  $E_{bg}$  of the material decreases to a value of  $1.77 \pm 0.02$  eV, indicating a increase in the electronic coupling between the adjacent two-dimensional sheets.

Density functional theory calculations by Khanna and coworkers have shown that the electronic states of a single cluster subunit are only mildly broadened by assembly, and shifted by the clusters' varying local environment. [402] These results show that the highest occupied molecular orbital (HOMO) of the assembly is composed mainly of contributions from the As atoms, while the lowest unoccupied molecular orbital (LUMO) is mainly localized on the alkali metal cations. This indicates that the orbital on the counter-cation, and not the electronic structure of the As cluster, primarily controls the energy level of the LUMO. Therefore, the LUMO of the material is derived from the absolute position of the HOMO of the neutral alkali metal atom. It is expected that the upper limit of the material's  $E_{bg}$  is the HOMO-LUMO gap of the cluster, in this case  $As_7^{3-}$ , which has a theoretical HOMO-LUMO gap of ~2.5 eV.

## 6.4.2 Effects of Charge Transfer and Covalent Linkers in As<sub>7</sub> Dimers

The incorporation of metallic atoms during material assembly leads to the formation of metal-linked dimers, as shown in Figure 6.1C and 6.1D. This type of linker provides an additional method of directing cluster assembly, while inducing additional electronic and geometric properties. Dimers, where two individual Zintl clusters are

joined by transition metals, provide a means of studying the effects of charge transfer within cluster-assembled materials. However, to compare the effects of charge transfer directly, cluster assemblies of similar structure, but with varying metal linkers, are required. These types of assemblies can be synthesized by reacting the  $As_7K_3$  precursor with  $Zn(C_6H_5)_2$  and  $Au(C_6H_5)_2Cl.$  [402, 403]

The reaction of the As<sub>7</sub>K<sub>3</sub> precursor with Zn(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> leads to the formation of the Zn-linked As<sub>7</sub> dimer [As<sub>7</sub>ZnAs<sub>7</sub>]<sup>4-</sup>, which crystallizes into Zn(As<sub>7</sub>)<sub>2</sub>(K – Crypt)<sub>4</sub> (Compound 5) in the presence of excess (K – Crypt)<sup>+</sup>. The formation of a stable Zn(As<sub>7</sub>)<sub>2</sub>(K – Crypt)<sub>4</sub> solid is quite interesting, since the ionization potential for Zn is 9.39 eV, compared to 4.34 eV for K, and is therefore not expected to result in the same donation of charge. The resulting crystal, shown in Figure 6.4A, shows two crystallographically independent [Zn(As<sub>7</sub>)<sub>2</sub>]<sup>4-</sup> cluster anions with different orientations. The cluster anion consists of two seven-atom As clusters, one bound on each side of a Zn atom; each cluster dimer is separated by four (K – Crypt)<sup>+</sup>, as shown in Figure 6.4B. This structure and cluster motif results in a  $E_{bg} = 1.69 \pm 0.01$  eV, as shown in Figure 6.3B (blue).

On the other hand, when the As<sub>7</sub>K<sub>3</sub> precursor is reacted with Au(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Cl, the Au-linked As<sub>7</sub> dimer [As<sub>7</sub>Au<sub>2</sub>As<sub>7</sub>]<sup>4-</sup> is formed, which crystallizes into Au<sub>2</sub>(As<sub>7</sub>)<sub>2</sub>(K – Crypt)<sub>4</sub> (Compound 6). In this case, the same basic crystal structure is preserved, with the exception that within the cluster motif the single divalent Zn atom is replaced by two Au atoms. Although the crystal structures of Compound 5 and Compound 6 are similar, the substitution of Zn by Au<sub>2</sub> decreases the E<sub>bg</sub> from  $1.99 \pm 0.05$  to  $1.69 \pm 0.02$  eV.



**Figure 6.4. (a)** The arrangement of the cluster anion  $[Au_2(As_7)_2]^{4-}$  and  $(K - Crpt)^+$  in Compound 6 as viewed through *b* axis. (b) The structure  $[Au_2(As_7)_2]^{4-}$  as two seven atom arsenic clusters *A* (left) and *B* (right) linked through a gold-dimer. (c) Naked K<sup>+</sup> mediated one-dimensional arrangement of  $[Au_2(As_7)_2]^{4-}$  in Compound 7 as viewed through *b* axis and (d) interaction of two different naked K<sup>+</sup> cations with  $[Au_2(As_7)_2]^{4-}$  in Compound 8 as viewed through *a* axis and (f) interaction of naked Cs<sup>+</sup> cations with  $[Au_2(As_7)_2]^{4-}$  in Compound 8. Arsenic atoms are shown in red, cesium in purple, potassium in blue and gold in gold, while (K - Crypt)<sup>+</sup> are indicated only as isolated K<sup>+</sup> in (**a**,**c** and **e**) for clarity. Crystal structures drawn by N. K. Chaki.

Using the Pauling scale, the electronegativity of Zn is 1.65 eV, while the electronegativity of Au is 2.54 eV. [404-406] Therefore, an increase in the electronegativity of the metallic linker results in a decrease of  $E_{bg}$  of the assembled solid.

Replacing two of the  $(K - Crypt)^+$  cations in Compound 6 with two K<sup>+</sup> ions leads to formation of Au<sub>2</sub>(As<sub>7</sub>)<sub>2</sub>K<sub>2</sub>(K - Crypt)<sub>2</sub> (Compound 7). Each of the two K<sup>+</sup> cations per motif interact differently with the two As<sup>3-</sup><sub>7</sub> clusters, where one of the K<sup>+</sup> ions (K<sub>1</sub> in Figure 6.4F) interacts directly with the terminal tetragonal faces of the As<sub>7</sub> units to form a one-dimensional chain, while the other K<sup>+</sup> ion (K<sub>2</sub> in Figure 6.4F) forms a triangle with the Au-dimer within the motif (Figures 6.4E and 6.4F). This results in a decrease of E<sub>bg</sub> from ~1.69 eV to  $1.46 \pm 0.02$  eV due to counter-cation effects, as previously discussed, where the smaller K<sup>+</sup> cations enable stronger interactions with adjacent clusters in one dimension. Although  $K_1^+$  increases connectivity between adjacent dimer motifs,  $K_2^+$  changes the connectivity within each motif, making it difficult to make any additional direct comparisons between Compound 6 and Compound 7.

## 6.4.3 Effects of Counter-Cations in Metal-Linked Cluster Assemblies

The effects of counter-cations in metal-linked cluster assemblies can be studied systematically if the geometries of all the compounds are similar, and only differ in the cation used for charge transfer. Compounds 8-10 all have the same crystal structure, where two Cs<sup>+</sup>or Rb<sup>+</sup> ions link the cluster subunits in two dimensions, while the additional charge is stabilized by a cryptated species. Therefore, the resulting solid consist of  $[As_7Au_2As_7]^{4-}$  cluster motifs assembled in two-dimensional sheets, where the vertices of each subunit are joined by shared Cs<sup>+</sup>or Rb<sup>+</sup> ions. The adjacent two-



**Figure 6.5.** Tauc plots showing the band gaps determined from the optical absorption spectra (see text) of: **(A)** cluster dimers with either Zn or Au covalently bound to  $As_7$  (Compounds 5 and 7) and **(B)** cluster dimers with Au covalently bound to  $As_7$  with similar two-dimensional structures (Compounds 8-10).

| MAs <sub>7</sub> <sup>3–</sup> Building Block |                                  |                              |                           |  |
|---|----------------------------------|------------------------------|---------------------------|--|
| Compound                                      | Formula                          | Experimental E <sub>bg</sub> | Theoretical $E_{bg}$ (eV) |  |
| 5   | $Zn(As_7)_2(K-Crypt)_4$          | 1.99 <u>+</u> 0.05           | 1.97                      |  |
| 6   | $Au_2(As_7)_2(K - Crypt)_4$      | $1.69 \pm 0.02$              | 1.68                      |  |
| 7   | $Au_2(As_7)_2K_2(K-Crypt)_2$     | $1.46 \pm 0.02$              | 1.43                      |  |
| 8   | $Au_2(As_7)_2Cs_2(K - Crypt)_2$  | $1.97 \pm 0.01$              | 2.06                      |  |
| 9   | $Au_2(As_7)_2Cs_2(Rb - Crypt)_2$ | 1.98 ± 0.05                  | 2.00                      |  |
| 10  | $Au_2(As_7)_2Rb_2(Rb - Crypt)_2$ | 1.87 <u>+</u> 0.05           | 2.09                      |  |

**Table 6.3.** Experimentally measured and theoretically calculated band gaps of cluster dimers with either Zn or Au covalently bound to  $As_7$  (Compounds 8-10). Density functional theory values obtained from ref. [403].

dimensional sheets are separated by a cryptated species, as shown in Figure 6.4G. It is important to note that although Compounds 8-10 all have the same stoichiometry as Compound 5, a different crystal structure was observed for Compound 5, and it was therefore not used in this analysis.

The Au<sub>2</sub>(As<sub>7</sub>)<sub>2</sub>Cs<sub>2</sub>(K – Crypt)<sub>2</sub> cluster-assembled material (Compound 8) has  $E_{bg}$  of  $1.97 \pm 0.01 \text{ eV}$ , as shown in Figure 6.5B (purple) and in Table 6.3. Replacing the two (K – Crypt)<sup>+</sup> in Compound 8 with two (Rb – Crypt)<sup>+</sup> cations results in a Au<sub>2</sub>(As<sub>7</sub>)<sub>2</sub>Cs<sub>2</sub>(Rb – Crypt)<sub>2</sub> cluster-assembled material (Compound 9). As mentioned above, this exchange does not lead to different structural arrangements of the cluster motifs, but could reduce the extent of electron transfer and the degree of electronic coupling between the adjacent layers. This change in the cryptated species, from (K – Crypt)<sup>+</sup> to (Rb – Crypt)<sup>+</sup>, leads to an indistinguishable decrease in the  $E_{bg}$  from ~2.00 eV to  $1.98 \pm 0.05$  eV.

Finally, the Cs<sup>+</sup> linkers in the cluster dimer of Compound 9 were replaced by Rb<sup>+</sup> ions, resulting in a cluster-assembled material with a molecular formula of  $Au_2(As_7)_2Rb_2(Rb - Crypt)_2$  (Compound 10). Again, this exchange does not lead to different crystal structures, but could result in reduced electron transfer within the twodimensional sheet. These two materials with similar structures can be used to compare directly the effects of counter-cations that link individual dimer motifs. Compounds 9 and 10 have very similar band gaps, ~1.98 and ~1.87 eV, respectively. Therefore, these measurements suggest that unlike the materials assembled from single  $As_7$  clsuters, the materials assembled from metal-linked  $As_7$  dimers do *not* vary significantly with changes in the counter-cations that link the individual motifs. In fact, the band gaps of the dimers remain relatively constant with changes to the counter-cations, the cryptated species, or even the structures of the assemblies. While band gaps of  $As_7$  cluster assemblies (Compounds 1-4) varied by ~1 eV, the  $As_7$  dimer assemblies with the same structural motifs (Compounds 8-10) vary by only ~10 meV. This suggests that the covalent metal linker predominantly determines the HOMO and LUMO, resulting in band gaps robust with respect to cation and structural changes.

# **6.5 Conclusions**

From these results we can begin to elucidate how the properties of clusters evolve into the properties of cluster-assembled materials. First, the band gap of the solid depends on the intrinsic band gap of the cluster and the counter cation. If using alkali metal counter cations, Li, the smallest element, should have the smallest band gap, while Cs with its larger radius will have the largest gap. It is also evident that the HOMO of the alkali metal counter-cation and the degree of charge transfer play important roles in determining the band gaps of these cluster-assembled solids. However, if using cryptated species, the cryptated cation state is high enough that the gap of the solid becomes roughly that of the intrinsic cluster. In covalently linked dimer clusters, the metallic linker stabilizes the electronic structure of the cluster, resulting in minimal effects to the band gap with varying counter cations.

Fabricating such materials has its challenges. Currently, only a limited library of cluster motifs have been fabricated and significantly characterized. Furthermore, the

rules that govern the assembly and the resultant properties of the material remain inadequately understood. Developing new polyvalent anions with varying valence configurations through covalent binding of existing clusters with other elements offer additional methods for controlling the  $E_{bg}$  of cluster assemblies. Therefore, it is expected that new clusters with novel assembly methods will be studied, paving the way for materials that are tailored for specific applications.

## Chapter 7

# **Conclusions and Future Prospects**

This dissertation focuses on understanding and exploiting the interplay between molecular or supramolecular structure and function, where molecules were engineered with specific interactions at the 1-50 nm scale. Variations in the supramolecular structure, intermolecular interactions, and hydrogen-bonding enabled the fabrication of tailored surfaces and materials. Chapter 2 provided an overview of the capabilities and advantages of hybrid soft-lithographic approaches in fabricating nanoscale features. A more detailed description, spanning other areas of soft lithography, including traditional energetic beam and scanning probe methods, was given in the review article:

H. M. Saavedra, T. J. Mullen, P. Zhang, D. C. Dewey, S. A. Claridge, and P.S. Weiss. *Hybrid strategies in nanolithography*. Reports on Progress in Physics **73**, *in press* (2010).

In Chapters 3 and 4, monolayers that improve the sophistication and resolution of hybrid soft-lithographic techniques were rigorously characterized in order to elucidate the origins, mechanisms, and kinetics of labile monolayers. In Chapter 5, the knowledge gathered in Chapters 3 and 4 was used to develop a new class of molecular resists that hinder or enhance molecular exchange during patterning. In Chapter 6, novel cluster-based assemblies were developed and characterized to determine the role of structure and function in tailored materials, which have tunable optical and electronic properties.

#### 7.1 Lability in Self-Assembled Monolayers

In Chapter 3, the influence of molecular structure and intermolecular interactions strengths in affecting the resulting properties of SAMs was investigated. Results showed that by manipulating the intermolecular distance, and thus the degree of intermolecular forces, the stability and the lability of SAMs can be controlled. The bulky tail group of the AD molecules had sufficient intermolecular interactions to form well-ordered monolayers, but these were weak enough to make AD SAMs susceptible to molecular exchange with other thiolated species. In fact, the interactions were weak enough to enable complete molecular exchange upon exposure to ALK molecules. At the time, AD SAMs were the only monolayers that could be completely exchanged under gentle conditions (room temperature and millimolar concentrations). Thorough characterization, using numerous techniques (IRRAS, XPS, STM and CV), revealed that solution displacement of AD SAMs followed a nucleation and island growth phase that starts with insertion at the defect sites of the original AD SAM. XPS measurements revealed similar Au-S bond environments for both AD and C12 molecules, indicating that displacement was not caused by a weakened Au-S bond. However, considerable thermodynamic contributions, resulting from the higher density of Au-S bonds and increased intermolecular interactions, were attributed to the liability of the monolayer.

The work characterizing **AD** SAMs and elucidating the origins and dynamics of **AD** SAM displacement resulted in the following publications:

T. J. Mullen, A. A. Dameron, H. M. Saavedra, and P. S. Weiss. *Dynamics of displacement in 1-adamantanethiolate self-assembled monolayers*. Journal of Physical Chemistry C **111**, 6740 (2007).

A. A. Dameron, T. J. Mullen, R. W. Hengstebeck, H. M. Saavedra, and P. S. Weiss. *Origins of displacement in 1-adamantanethiolate self-assembled monolayers*. Journal of Physical Chemistry C **111**, 6747 (2007).

H. M. Saavedra, C. M. Barbu, A. A. Dameron, T. J. Mullen, V. H. Crespi and P. S. Weiss. *1-Adamanatanethiolate monolayer displacement kinetics follow a universal form.* Journal of the American Chemical Society **129**, 10741 (2007).

Ongoing experiments by M. H. Kim focus on investigating the structural and electronic properties of adamantanethiolate SAMs that have the thiol functional groups in different positions throughout the cage. For example, 2-adamantanethiol has the mercapto group at one of the vertices that would otherwise have two hydrogen atoms, resulting in molecules with reduced symmetries that, when adsorbed on a surface, could result in domains of either left or right chirality. [407] Each of these chiralities could have their own electronic and labile properties, which could potentially be exploited for patterning or molecular electronics. Furthermore, J. N. Hohman is studying the assembly of other thiolated cage molecules, such as carboranethiol, a cage composed of both carbon and boron atoms. [293] These molecules enable the fabrication of surfaces with ordered molecular dipoles in which structural modifications to the adsorbing thiolate results in different dipole directions.

Future experiments should include other structural modifications, such as the addition of functional groups that either increase or decrease intermolecular interactions, thus tuning the lability of the SAM. The **AD** cage is extremely versatile, since it has numerous positions for functionalization, all of which could lead to novel structural assemblies. For example, functionalizing the three C-H vertices on the top of the **AD** cage with hydrogen bonding groups could drive the molecular assembly of the molecules

into a graphene-like monolayer. The energetic contributions of these hydrogen bonds could drive such assembly to form a nearly defect-free, highly stable SAM.

Finally, the influences of other structural parameters need to be investigated, such as the effects of the solvent or the chain length in the displacing molecules. Preliminary results, not presented in this dissertation, show that the rate constant for displacement is not altered significantly when increasing the length of the alkyl chain from six to 16 carbons. However, there could be a slight variation in the rate constants between molecules with odd and even numbers of carbon atoms. In order to achieve these goals, the instrumentation needs to be redesigned to collect *in situ* measurements, preferably in vacuum, providing the necessary temporal resolution in the uptake curves.

## 7.2 Reversible Molecular Resists

Building on the mechanisms and kinetics observed in **AD** SAM displacement, a straightforward and robust strategy for preparing switchably displaceable monolayers was developed. Prior to exposure, these molecular resists hinder molecular exchange. However, when exposed to an activating solution, composed of hydrochloric acid and ethanol, molecular exchange is promoted to completion. This change in lability is a side effect of a surface chemical reaction, which transforms the carboxylic acid terminal groups of the SAM into an ethyl ester. This reaction results in structural and chemical defects that increase the conformational disorder of the SAM, thereby promoting molecular exchange. Each step of the reaction, including displacement, was characterized with IRRAS and XPS, confirming the roles of defects and disorder in

displacement. Usually, resists used in traditional lithographies are sacrificial structures that cannot be unexposed. However, using functionalized molecules as the resist and simple chemical reactions as the exposure mechanism enables the cycling of the resists between exposed and unexposed states in a multi-step fabrication process.

The methodology for reversibly labile monolayers, along with their characterization, resulted in the following publication:

H. M. Saavedra, C. M. Thompson, J. N. Hohman, V. H. Crespi and P. S. Weiss. *Reversible lability by in situ reaction of self-assembled monolayers*. The Journal of the American Chemical Society **131**, 2252 (2009).

The fact that the same methodology was applied to structurally different molecules with carboxylic acid functionalities suggests that the technique could be extended to target different functional groups. Therefore, future experiments should focus on determining the different groups that can be selectively reacted with analogous reactions that also result in reversible lability. Having multiple reactions that target specific molecules would enable the selective removal of molecules in a patterned multiplexed SAM. A promising system involves amine-terminated alkanethiolates, which, when exposed to an acid chloride, will react to form the corresponding amide. Numerous analogous combinations should be possible, facilitating the hierarchical assembly of complex surface structures. It would also be interesting to determine if these reversible layers could be used with traditional nanofabrication methods such as reactive ion etching. Finally, experiments should also focus on determining the sharpness of the different molecular boundaries in the patterned features, since tailored resists could aid in further minimizing diffusion, pushing the resolution limits of  $\mu CP$  and  $\mu DP$ .

#### 7.3 Cluster-Assembled Materials

Clusters, with their unique properties, can serve as building blocks in assembled solid materials. The individual clusters can be tuned to have specific magnetic, optical, and electronic properties due to quantum confinement, where the addition or removal of a single atom can have significant effects. However, further tunability is achieved when assembling these individual clusters into a solid, providing a link between the bulk properties of the material and the size-dependent properties of clusters. In Chapter 6, we have shown how Zintl phases can be used to study comprehensively the effects of structure and function in cluster-assembled materials. For example, modifying the lattice spacing, as well as the counter cations in  $As_7$  cluster solids, leads to a change in the band gap of the material from 1.09 to 2.09 eV, even though the same cluster motifs were used. This change in lattice spacing is in some ways analogous to the addition or removal of an atom in a single cluster, since decreasing the spacing results in larger interactions and charge transfers between neighboring molecules or atoms. It is important to note that the HOMO of the counter cation also plays a crucial role in determining the band gap of the material. However, this only applies to bare As<sub>7</sub> cluster building blocks, since the As<sub>7</sub> dimer building blocks, linked via transition metals (As<sub>7</sub>Au<sub>2</sub>As<sub>7</sub>), are not affected strongly by the counter cations nor the degree of charge transfer. These results begin to elucidate how the properties of clusters evolve into the properties of cluster-assembled materials.

The work characterizing these cluster assemblies and determining the factors that contribute to the resultant properties have led to the following publications:

M. Qian, A. C. Reber, A. Ugrinov, N. K. Chaki, S. Mandal, H. M. Saavedra, S. N. Khanna, A. Sen, and P. S. Weiss. *Cluster Assemblies: Towards Nano-Materials with Precise Control over Properties* ACS Nano *in press*.

S. Mandal, N. K. Chaki, M. Qian, A. C. Reber, H. M. Saavedra, X. Ke, P. Schiffer, S. N. Khanna, P. S. Weiss, and A. Sen. *The Zintl Ion [As7]2-: A Rare Example of an Electron-Deficient As7 Cluster* Angewandte Chemie, *submitted*.

N. K. Chaki, S. Mandal, M. Qian, A. C. Reber, H. M. Saavedra, A. Sen, S. N. Khanna, and P. S. Weiss. *Controlling band gaps in cluster-assembled ionic solids through internal electric fields*. Nature Chemistry, *submitted*.

S. Mandal, N. K. Chaki, M. Qian, A. C. Reber, H. M. Saavedra, A. Sen, S. N. Khanna, and P. S. Weiss. *Tunning the Bang Gap of the Cluster Assembled Materials: Role of Inter-Chain Distance and Structural Arrangement* (in preparation for *Chemical Communications*).

Pertinent future experiments should focus on the synthesis of cluster assemblies with smaller counter cations, such as lithium, which should increase significantly the interactions between clusters, thus lowering the band gap. Furthermore, new synthetic strategies need to be developed that do not involve the use of the crypt crystallizing agent. Additionally, the use of different macromolecules will enable the degree of interaction between adjacent sheets in the two-dimensional materials to be studied further. Developing new polyvalent anions that covalently bind to the clusters with varying electron configurations would also enable an additional method of varying the electronic properties of the assemblies.

Further study is also encouraged in the dimer cluster assemblies. The study of dimers, linked via different metals, would provide insight as to why these cluster assemblies are only affected slightly by the degree of charge transfer. However, in order to understand fully the electronic stability of these individual clusters in the assembly, rigorous theoretical calculations are also required.

Assemblies based on  $As_7$  clusters are easy to fabricate, making them ideal candidates for fundamental studies. However, their sensitivity to air, which results in oxidation when exposed to atmosphere, makes them unsuitable for device fabrication. Therefore, it is important to develop air-stable cluster motifs that can be assembled into functional materials. A promising candidate is the  $Al_{13}^-$  cluster, in which the 13 aluminum atoms have an extra electron and do not appear to react with oxygen when it is introduced in the same gas stream. These clusters, which have properties similar to noble metals, would enable the fabrication of stable assemblies, providing tailored surfaces for microelectronics, optoelectronics, sensors, and photovoltaics.

## 7.4 Final Thoughts

Smaller tends be faster, more efficient, and more cost effective, especially when dealing with integrated circuits. This drive has progressed to a point where small features can be fabricated cost effectively and, more importantly, functionalized, opening patterning to areas such as chemistry, biology, and medicine. The numerous patterning strategies, some of which are described in Chapter 2, all have their set of benefits and drawbacks, providing numerous methods of generating surface features for different applications. Therefore, it is important to understand the current limitations of each technique in order to circumvent or to eliminate them. Furthermore, it is important to understand the roles that structure and size play in determining the properties of fabricated features. That is why these studies emphasize the significance of molecular and supramolecular structure with function in both SAMs and cluster-assembled materials. In SAMs, manipulating the structure, interaction strengths, and electronic properties of the molecules results in changes to the lability and the reactivity of the monolayer. This, in turn, can help the hierarchical assembly of advanced devices and sensors. In cluster-assembled materials, structure also plays a crucial role, determining the degree of interaction with neighboring clusters, thereby affecting the optical and electronic properties of the material. This provides a means to tailor the properties of a solid material to fit specific applications. Overall, these fundamental studies extend our knowledge and the sophistication of nanoscale assemblies, providing insight required to pattern surfaces or to fabricate materials intelligently.

# Appendix

# **Infrared Scanning Tunneling Microscope**

# A.1 Introduction

Although the invention of the STM has opened a window into the nanoscale world by providing real-space atomic-resolution images, it is limited by its inability to provide unequivocal chemical assignments of adsorbates. [408] Therefore, it is typically difficult to distinguish one adsorbate from the other unambiguously. Further, vibrational spectroscopy of single adsorbates would give key information on bonding of each molecule given its local environment.

Specialized STM-based spectroscopic techniques, such as inelastic electron tunneling spectroscopy (IETS), provide limited chemical assignments of adsorbates. [97, 409-413] These limitations are a result of undetermined selection rules, and the small number of vibrational modes that can be measured. Furthermore, these techniques require ultra-stable, ultrahigh vacuum STMs that operate at low temperatures (4K). [412]

Infrared spectroscopy, on the other hand, can distinguish and identify surface adsorbates, but is thus far incapable of doing so with the atomic resolution of STM. [408] Combination of this technique with STM would enable chemical identification of adsorbates at the molecular scale. Here, we present schematics and experimental considerations for building an infrared scanning tunneling microscope (IRSTM) that provides this capability. Direct illumination of the tunneling junction, first proposed by Walle *et al.* in 1987, typically results in undesirable heating and thermal expansion of the tip. [408, 414-417] In the IRSTM, tip heating is minimized by avoiding direct illumination using the Kretschmann-Raether attenuated total internal reflection (ATR) geometry for sample construction and excitation (Figure A.1). [418]

## A.2 Evanescent Coupling and Experimental Setup

The instrument and experimental design must take into account two key considerations: coupling light into the tunneling junction with minimal heating, and fast acquisition of spectral data to minimize probe drift. For the latter, the implementation of Fourier transform techniques enables rapid spectral collection (<1 s). Changes in the tunneling current due to excitations [419-422] can be recorded and then be converted into the frequency domain. The former, dealing with tip heating, is a direct result of the means by which light is coupled into the tunneling junction.

A schematic of the experimental setup is shown in Figure A.2, where evanescent illumination of the tunneling junction is achieved using the Kretshmann-Raether ATR geometry. In this geometry, molecules are excited by an evanescent wave generated at the dielectric interface when the angle of incident light ( $\theta$ ) exceeds the critical angle ( $\theta_c$ ), thus satisfying total internal reflection criteria (Figure A.1). [418, 423, 424] The evanescent field produced in the second medium decays exponentially, following the equation:

$$I = I_0 e^{(-\gamma Z)},\tag{A.1}$$

where

$$\gamma = \frac{2\pi}{\lambda} \sqrt{n_0^2 \sin \theta - n_2^2},\tag{A.2}$$

I is the intensity of the evanescent wave,  $I_0$  is the intensity of the incident wave,  $\lambda$  is the wavelength of incident light, Z is the distance from the interface, and *n* is the refractive index.



Figure A.1. Evanescent wave generated by back illumination, which occurs when total internal reflection criteria are met.



# Tip and Preamp

**Figure A.2.** Infrared excitation scanning tunneling microscope schematic design, where illumination is provided by a commercial FTIR microscope.

#### A.3 Instrument Schematics and Assembly

#### A.3.1 STM Exoskeleton

The exoskeleton of the STM, which is mounted on a 'foot' mount, serves as a Faraday cage and housing for all the critical components of the STM, including the coarse approach mechanism, the STM head, and the sample. Photographs of the assembled exoskeleton are shown in Figure A.3, while schematics for all the parts are shown in Figures A.5-A.11.

The assembly of the STM exoskeleton is straightforward, requiring only assembly of the parts shown in Figure A.3. The assembly of the sample holder (Figure A.4A), and its integration to the top plate, is more delicate. This sample holder must provide: a means to mount the sample securely, an electrical connection to the sample, and reproducible positioning to facilitate optical alignment. The main body of the sample holder is made of nonconductive Delrin (Dupont, Wilmington, DE), the black material (also available in white) shown in Figure A.4A. Typical substrates (*vide infra*) are Au films deposited on Si or sapphire prisms. In order to achieve an electrical connection between the sample holder. A single strand coaxial cable (MDC, Hayward, CA) is inserted through the small opening (left side of Figure A.4B), where it can then be soldered. The assembled sample holder is inserted and secured into the top plate with 4-40 screws. Silicone rubber (red material in Figure A.4C) secures the coaxial bias connection and prevents vibrations from traveling through the cable.



Figure A.3. Photograph showing the key components of the custom-built IRSTM exoskeleton. (A) Aerial view. (B) Side view without the removable side door.



Figure A.4. Photographs of the top plate and the sample holder. (A) Unmounted sample holder. (B) Close-up of sample holder, showing the solder joint between the bias cable and the Au foil. (C) Top plate with mounted sample holder.



**Figure A.5.** Schematic of the top plate. Due to the number of dimensions, the schematic was redrawn three times for clarity. A photograph of the top plate can be seen in Figure A.4C.



Sample Holder (derlin).dwg Hector M. Saavedra Material: Derlin Tol. 0.001

2/9/2005

**Figure A.6.** Schematic of the sample holder. A photograph of the sample holder can be seen in Figure A.4A.



**FigureA.7.** Schematic of the bottom plate. A photograph of the bottom plate can be seen in Figure A.3.B.





Figure A.8. Schematic of the support rod. A photograph of the support rod can be seen in Figure A.3.B.



**Figure A.9.** Schematic of the side panel. A photograph of the side panel can be seen in Figure A.3.B.


Back

**Figure A.10.** Schematic of the top STM 'foot'. The bottom STM 'foot' is a mirror image of the top 'foot'. A photograph of the STM 'foot' can be seen in Figure A.3.



**Figure A.11.** Schematic of the removable side door. For clarity, the handle is not shown in the schematic. A photograph of the removable side door can be seen in Figure A.3.A.

### A.3.2 STM Head

The STM head comprises the Macor base (Corning Inc., Corning, NY), piezoelectric scan tube (EBL Products, East Hartford, CT), and tip assembly (Figures A.12A and A.12B). All of these components are bonded together using superglue (Krazy Glue, Columbus, OH). The Macor base provides the mount for the piezoelectric scan tube of the STM head (Figure A.12C). The scan tube enables 3D motion of the probe tip, while also supporting the tip assembly. The tip assembly is a custom-built, rigid, coaxial, hollow conductor comprised of two stainless steel syringe tubes, similar to others developed in our laboratory. [425] A photograph and a schematic of the tip assembly are shown in Figures A.12D and A.13, respectively. The inner tube is a 23-gauge extra thin wall syringe tube (Small Parts, Miramar, FL) with an inner diameter large enough to allow the tip wire (Pt/Ir 90:10 wire, 0.25 mm diameter, Alfa Aesar, Ward Hill, MA) to be inserted snuggly. This inner syringe tube is inserted into a 22-gauge Teflon tube (Small Parts, Miramar, FL) to act as an electrical insulator. The inner syringe tube and Teflon tube are inserted into an 18-gauge syringe tube outer conductor (Small Parts, Miramar, FL). The outer syringe tube is electrically connected to the ground plane via Nickel Print (GC Waldom, Rockford, IL) and glued to a piezoelectric cap. The inner tube is secured in place by using an epoxy resin (Torr Seal, Varian Vacuum Technologies, Lexington, MA). The bias signal is applied via coaxial cable inserted into the outer tube, so that the grounding mesh of the coaxial cable contacts the outer tube, while the conductor is inserted into the inner tube. The coaxial tip assembly and grounding plane are required to shield the bias signal, which would otherwise capacitively couple to the changing voltages applied to the piezoelectric scan tube.



**Figure A.12.** Photographs of **(A)** the custom-built IRSTM head, **(B)** the IRSTM head with the current wire removed for clarity, **(C)** the Macor base with an unglued scan tube, **(D)** the back of an unmounted tip assembly, showing the Ni print, and **(E)** the front of the tip assembly, showing the epoxy resin.



**Figure A.13.** Schematic of the STM tip assembly. Photographs of the tip assembly can be seen in Figure A.12.



**Figure A.14.** Schematic of the Macor base. A photograph of the Macor base can be seen in Figure A.12.C.

### A.3.3 Coarse Approach

In order to achieve the small (~1.0 nm) tip-sample separations required for electron tunneling, a coarse approach mechanism is required to bring the sample into close proximity with the tip without allowing physical contact. The IRSTM utilizes MS 5 Micro Piezo Slides (Omicron NanoTechnology GmbH, Taunusstein, Germany) for coarse approach, which are piezo-electrically driven linear stepper motors. The step size of these units can be varied between 40-400 nm, with a maximum travel length of 5 mm. The load-bearing capacities for horizontal and vertical positioning are 300 g and 50 g, respectively.

In the IRSTM, the tip is required to have independent movement in all x, y, and z directions, since the z-axis enables the coarse approach while the x- and y-axes enable alignment of the probe tip with the focused IR beam. Therefore, three MS5 Micro Piezo Slides were combined, each providing movement along a different axis, as pictured in Figure A.15. The commercially available z-axis mounting L-bracket (Figure A.15A) was not used in the final design, since the weight of the STM head results in a seesaw mechanical vibrational mode that increases noise, thus hindering molecular resolution. This seesaw mode is a result of unbalanced weight on top of the x and y MS5 Micro Piezo Slides, which cause instability in the magnetic forces that hold together the two stainless steel plates in each slide. Therefore, in order to achieve molecular resolution, a custom-built z-axis bracket was implemented, pictured in Figure A.15B and schematically shown in Figure A.16. This bracket, along with the attached lead weight (~40 g), balances the weight of the tip assembly, reducing the seesaw vibrational mode.





Figure A.15. Photographs of the mounted MS5 Mirco Piezo Slides used for coarse approach. (A) The commercially available L-bracket for movement in three dimensions. The three different axes are labeled for clarity. (B) The custom-built M-bracket, which balances the weight of the STM head, enabling molecular imaging.



Figure A.16. Schematic of the M-bracket. A photograph of the M-bracket can be seen in Figure A.15.B.

### A.3.4 Vibration and Acoustic Isolation

The STM is designed to operate with extremely small tunneling currents (<1.0 pA) and with sub-Ångstrom motion, making it susceptible to external noise sources. Therefore, the design of the STM and the environment of the instrument must be controlled carefully. Common noise sources include: building vibrations, acoustic coupling, and interference from electromagnetic radiation.

To isolate the instrument from building vibrations, the instrument is placed on an optical table with Gimbal Piston Isolators (TMC, Peabody, MA). Additionally, the STM exoskeleton is mounted on an alternating stack of stainless steel plates with layers of varying elastic moduli, such as PDMS or Viton O-rings, that dampen vibrations in the system. Pictures of the alternating stainless steel plates are shown in Figure A.17, while schematics of the individual parts are shown in Figures A.19-A.23.

Acoustic noise can couple into the STM head or the preamplifier wire, inducing mechanical vibrations that result in noise. To minimize this type of coupling, the STM is placed in an acoustic isolation box comprised of hard plastics and acoustic foam, as pictured in Figure A.18. Interference from electromagnetic radiation is minimized via the grounded STM exoskeleton.

Infrared radiation is absorbed readily by ambient water and carbon dioxide, reducing optical throughput when operated under ambient conditions. Therefore, to increase optical throughput, the IRSTM is housed inside a custom-built glove box that is purged with dry and CO<sub>2</sub>-free air provided by a FTIR Purge Gas Generator (Parker-Balston, Cleveland, OH). The glove box also has a small load-lock chamber that allows samples and other small objects to be introduced to the main chamber without exposing it

to atmosphere. Pictures of the glove box can be seen in Figure A.18, while the schematic is displayed in Figure A.24.

# A.3.5 Current Preamplifier

A high-gain transresistance (current to voltage) amplifier, referred to as the preamplifier, is used to measure the small tunneling currents. The IRSTM utilizes the IVP-300 (RHK Technology, Troy, MI), which provides a  $10^9$  V/A gain. In order to shield the sensitive preamplifier from vibrations and electromagnetic radiation, it is housed in a case that resides within the alternating stacks of stainless steel vibration isolation plates. Pictures of the case are shown in Figure A.17B-A.17D; schematics are shown in Figure A.22 and A.23.



Figure A.17. Photographs of the alternating stack of stainless steel plates and polymers used for vibrational dampening. (A) The bottom two steel plates on top of an optical jack. (B) The bottom two steel plates with the preamplifier holder inserted. (C) Preamplifier attached to the preamplifier plate. (D) The bottom two steel plates with the inserted preamplifier holder, preamplifier, and preamplifier plate. Four Viton O-rings serve as the elastomer in this layer. (E) All three steel plates stacked on top of the optical jack. (F) The fully assembled unit (excluding optics), showing the lab jack, steel plates, STM exoskeleton, and STM head.



**Figure A.18.** Photographs of the different environmental enclosures. The outer box is lined with acoustic foam in order to decrease sound waves, which would otherwise mechanically couple into the tunneling current. The inner Plexiglas box provides an inert atmosphere, minimizing IR atmospheric absorptions and maximizing optical throughput.



Steel disk (bottom).dwg

Hector M. Saavedra

Material, Stainless Steel

Tol. 0.001

#### 1/19/05

**Figure A.19.** Schematic of the bottom stainless steel plate used for vibrational dampening. A photograph of the bottom steel plate can be seen in Figure A.17.



**Figure A.20.** Schematic of the middle stainless steel plate used for vibrational dampening. A photograph of the middle steel plate can be seen in Figure A.17.



Steel Disk (top).dwg

Hector M. Saavedra

Material Stainless Steel

Tol. 0.001

1/19/05

**Figure A.21.** Schematic of the top stainless steel plate used for vibrational dampening. A photograph of the top steel plate can be seen in Figure A.17.



**Figure A.22.** Schematic of the preamplifier holder. A photograph of the preamplifier holder can be seen in Figure A.17.



Preamp Plate.dwg Hector M. Saavedra Material: Al

# 1/19/05

**Figure A.23.** Schematic of the preamplifier plate. A photograph of the preamplifier plate can be seen in Figure A.17.



**Figure A.24.** Schematic of the custom-built glove box. A photograph of the glove box can be seen in Figure A.18.

### A.3.6 Substrates and Sample Preparation

In ATR, the evanescent wave resulting from total internal reflection is used to measure the vibrational spectrum of the sample. Here, the electromagnetic wave passes from a higher refractive index material to a lower refractive index material, so that the electric field of the light wave penetrates the material with the lower refractive index. As previously mentioned, total internal reflection only occurs when the angle of incident light is greater than the critical angle. The critical angle is determined by:

$$\theta_c = \sin^{-1}\left(\frac{n_2}{n_1}\right),\tag{A.3}$$

where  $n_1$  is the refractive index of the denser medium, and  $n_2$  is the refractive index of the less dense medium. [418]

Therefore, in order to excite molecules in the tunneling junction of the IRSTM, a prism with a higher refractive index than the sample is required. Furthermore, the prism needs to have a wide spectral range such that it does not absorb light in the regions of interest. Silicon and germanium prisms are widely used in ATR spectroscopy, since they have refractive indices of 3.4 and 4.0, and long wavelength cutoffs of 1500 and 780 cm<sup>-1</sup>, respectively. Therefore, Si prisms were used as the substrates for initial testing of the IRSTM.

A schematic of the custom-ordered hemispherical Si prisms is shown in Figure A.25. Gold substrates, 1000 Å thick (99.999%, Kurt J. Lesker, Clairton, PA), were prepared with an electron-beam evaporator using the 20-mm hemispherical Si{100} prisms (Crystal Techno, Moscow, Russia) with a 100-Å chromium (99.998%, Kurt J. Lesker, Clairton, PA) adhesion layer. A schematic of the custom-built sample holder for metal evaporation is shown in Figure A.26. However, the evaporated Au is polycrystalline, preventing molecular resolution imaging with an STM. Alternative substrate systems, which allow epitaxial growth of Au $\{111\}$  and also meet the previously mentioned requirements, are necessary. Sapphire prisms could provide a temporary solution, since they can support flat Au $\{111\}$  films that are grown epitaxially. [426] Unfortunately, their spectral range is limited, with poor transmission at frequencies below 2000 cm<sup>-1</sup>.



Figure A.25. Top view schematic of the hemispherical substrates.



Figure A.26. Schematic of the enclosure used to hold the substrates during a metal evaporation. (A) Base plate. (B) Lid.

# A.3.7 Optics Setup

Most FTIR instruments use off-axis parabolic mirrors for collimating and focusing infrared light, since mirrors do not have dispersion and do not suffer from chromatic aberrations. Therefore, the focal point stays at the same place for any given wavelength. These mirrors are usually Au-coated to maintain polarization and provide ~98% reflectivity in the IR range. Figure A.27 shows a picture of the optics setup in the IRSTM, while Figure A.28 shows the light-path schematic.

In the IRSTM an interferometer (Nicolet 6700, Thermo Electron Corporation, Waltham, MA) provides a 2 in. collimated IR beam. The first right angle mirror (RA 1, NT47-308, Edmund Optics, Barrington, NJ) reflects the beam towards a set of flat mirrors (F 1 and F 2, PF20-03-M01, Thor Labs, Newton, NJ) that elevate and reflect the beam towards the first parabolic mirror (P1, NT47-106, Edmund Optics, Barrington, NJ). The P1 mirror focuses the IR light onto the sample, exciting the molecules in the tunneling junction located on the other side of the hemispherical Si prism evanescently. The light reflected off the sample is collimated by the second parabolic mirror (P2) and reflected onto a set of flat mirrors (F3 and F4) that lower the beam towards RA2. Finally, the last parabolic mirror (P3) focuses the beam onto a mercury-cadmium-telluride detector (Thermo Electron Corporation, Waltham, MA). Note that the light reflected off the sample is not required for data collection, since the tunneling current serves as the detector. However, the additional optics and detector past the sample facilitate beam alignment.



Figure A.27. (A) Photographs of the optics setup used in the IRSTM. In (B) the optic path is illuminated with a 532 nm laser.



**Figure A.28.** Schematic of optics setup. Each mirror is individually labeled (RA# = right angle mirror, F# = flat mirror, P# = parabolic focusing mirror).

#### A.4 Infrared Source and Data Collection

The IRSTM requires a broadband light source that is intense enough to result in a high probability of exciting a single molecule in the tunneling junction. Furthermore, spectral collection must be achieved within 1-2 s, since in atmosphere an STM tip will drift significantly within that timeframe. Therefore, a Nicolet 6700 FTIR spectrometer (Thermo Electron Corporation, Waltham, MA) was used as a source and modulator. The use of interferometers enables half of the full power of the source to reach the sample, as slits and gratings are not required. Importantly, spectral collection can be achieved in less than 0.5 second.

Although the use of an interferometer is beneficial, data collection must be obtained at discrete mirror modulation intervals. In an interferometer, a moving mirror causes the individual wavelengths of the broadband source to interfere constructively and destructively. As a result, each wavelength contributes to the interferogram; the signal output of an interferometer as a function of path length difference ( $\Delta \ell$ ). Mathematically, the spectrum can be recovered from the interferogram by taking the Fourier transform. Therefore, any spectrum collected with the IRSTM is recorded in terms of path length  $(i.e., "i vs \Delta \ell$ " and *not* "i vs t").

To collect  $i vs \Delta \ell$ , data acquisition needs to be synchronized with mirror modulation in two different ways. First, data must begin at the zero path difference (ZPD,  $\Delta \ell = 0$ ), the beginning of a new mirror sweep. Second, subsequent data collection must occur with evenly spaced  $\Delta \ell$  intervals, enabling the fast Fourier transform to recover the frequency domain spectrum. In most FTIR spectrometers, this is achieved via an internal HeNe laser, since interferrometric modulation of a monochromatic source results in a sine wave in which the separation between each zero point crossing corresponds to a 316 nm mirror retardation (half the HeNe wavelength). In the IRSTM, the same signals are used to synchronize data collection with mirror modulation. Most research grade FTIR spectrometers provide access to these signals. In the Nicolet 6700, a remote signal accessory (Thermo Electron Corporation, Waltham, MA) is required, in which the signals labeled "TAKE DATA" and "SAMPLE CLOCK" can be used to determine the ZPD and zero point crossing, respectively.

The software and electronics used to control the IRSTM is similar to others used in our lab, and is described elsewhere. [267] Listing A.1 shows a modification to the WinSTM software that automates this synchronization. The code uses a circular buffering scheme to handle the large number of data points collected. The function of this code is straightforward: when the STM tip stops to collect a spectrum at the userdefined spot, it waits for a start signal to begin data collection. Once the signal is received, data collection occurs at each zero point crossing of the HeNe signal, thereby serving as an external sampling clock. The result of this data collection is an *i* vs  $\Delta \ell$ spectrum, which can be mathematically converted to a traditional IR spectrum (frequency domain) using a fast Fourier transform. Listing A.2 shows the Matlab (Mathworks, Natick, MA) code used to perform this operation.

#### **Listing A.1.** Acquisition of "*i* vs $\Delta \ell$ " Spectra

```
// Acquire an X vs. time (or mirror retardation) plot
void CSpectroscopy::AcquireIT(CInstrument::struct SpecData *data)
{
      // OK lots to do
      // first, SpecData struct uses long as data type - seemed like a
good idea at the time disk space is cheap right?
      // so, what we have to do is acquire the data as type short - and
convert
      // each and every number to long on a discrete basis
      // so we need to get the extra ram
      // also don't do the conversion (short->long) until the end -
some fast acquisitions may run too quickly
      // to finish the conversion in time
      // don't forget to fill in the X data :)
      //% \left( for those of you not in the know here is how real time \right)
sampling works (aka double buffering = db)
      // there are 2 buffers (hence the double part...) the full
buffer can be though of as circular
      // the ADC card fills up the buffer until it hits the end, then
starts over at the beginning
      // we query the card to see when half of the buffer is full and
copy the half that is not being filled
     // by the ADC card. if you don't ask often enough it will
overwrite!!
     short *fullbuffer;
                                          // size of the half buffer
                                           // pointer to full data
struct
      short *halfbuffer;
                                          // pointer to half data
struct (the buffer)
      //short *databuffer; // data buffer
short *predatabuffer; // data buffer, not re-size
long count = 0; // how many data points we
                                          // data buffer, not re-sized
have collected
      long offset = 0;
      long TotalPts = 0;
      int
                 SweepNum = 0;
      long RealTotalPts = 0;
                 ResetPts = 0;
      int
      // this will round nPts to the nearest binary multiple and div by
4 (should give us the Ivst in 4 shots
      buffersize = pow(2, round(log(data->nPts)/log(2)))/4;
      // make sure buffer size is reasonable
      while(buffersize > 8192)
            buffersize /= 2;
      fullbuffer = new short[buffersize*2];
      halfbuffer = new short[buffersize];
```

```
int predatasize = round(ceil((double)data->nPts /
buffersize))*buffersize;
      predatabuffer = new short[predatasize];
      //databuffer = new short[round(ceil((double)data->nPts /
buffersize))*buffersize];
      ResetPts = data->nPts;
      while (!theInst->m Flags.Halt && SweepNum < m SpecParam-
>It Sweeps)
      {
            //data->nPts = ResetPts;
            // check if we need to change gap conditions
            if(!m SpecParam->GapImage)
            {
                  // if you are here, we are not using image conditions
so set spec gap
                 theInst->DCBiasSet(m SpecParam-
>Gap Bias, DCBIASRAMP STEP);
                 theInst->CurrentSet(m SpecParam->Gap Current);
                  // setteling time
                 theInst->m Clock->Sleep(theInst-
>m Spec Delay.FBLStabalize);
            // check if we are to blank FBL
            if(m SpecParam->It FBLBlank)
                 theInst->FBLBlank(true);
            // ZDrift Corr setup
            // setup ZDrift Corr
             int64 Blank
                                   = theInst->m Clock-
                             // get the current time
>StartStopWatch();
            double gain
                             = 1.0/theInst->m Piezo.ZGain *
1.0/theInst->m Digi Flags.ZHoldGain;
            double DriftRate = theInst->m Spec Param.ZDriftRate;
           bool ZCorr
                                 = theInst->m Spec Param.ZDriftCorr;
            double ZHoldV
                                   = theInst->m Digi Flags.ZHoldVolts;
            // here we go
            theInst->ADCdbRead(m SpecParam->ChanArray[0],m SpecParam-
>It SampleRate,
                                    buffersize*2,fullbuffer,halfbuffer,
m SpecParam->It ExtTrigger, m SpecParam->It ExtClock);
            bool cont = true;
            short iDAQstopped = 0;
           unsigned long ulPtsTfr = 0;
           offset = 0;
            TotalPts = 0;
            count = 0;
            while(!theInst->m Flags.Halt && cont && (iDAQstopped == 0))
            {
                  if(theInst->ADCdbInquire2(halfbuffer, ulPtsTfr,
iDAQstopped))
                  {
```

```
//ok we have the half buffer - copy it to data
      memcpy(&predatabuffer[offset], halfbuffer, sizeof(short) *
ulPtsTfr);
                        // bump the offset
                        offset += ulPtsTfr;
                        TotalPts += ulPtsTfr;
                        // bump our # of collected data points
                        count += ulPtsTfr;
                        // test if we are done
                        if(count > data->nPts)
                              cont = false;
                  }// end if Inquire
                  if(ZCorr)
                  {
                        double Vout = ZHoldV - theInst->m Clock-
>HowLong(Blank) * DriftRate * gain;
                        theInst->DACwrite(theInst-
>m_DAC_Chan.ZHoldDev,theInst->m DAC Chan.ZHoldChan,Vout);
            }// end while
            if(m SpecParam->It ExtTrigger)
            {
                  if(theInst->ADCdbInquireFinal(halfbuffer, ulPtsTfr))
                  {
      memcpy(&predatabuffer[offset], halfbuffer, sizeof(short) *
ulPtsTfr);
                        TotalPts += ulPtsTfr;
                        //data->nPts = int (TotalPts);
                        //buffersize = pow(2, round(log(data-
>nPts)/log(2)))/4;
            }// end if trigger
            //short *databuffer;
            //databuffer = new short[round(ceil((double)data->nPts /
buffersize))*buffersize];
            //memcpy(&databuffer[0],predatabuffer,sizeof(short) *
TotalPts);
            theInst->ADCdbStop();
            // ok data collection done - now for data conversion
            float timestep = 1.0/m SpecParam->It SampleRate;
            for(long index = 0; index < data->nPts; index++)
            {
                  data->XData.Data[RealTotalPts + index] = index *
timestep;
                  data->Buff[0].Data[RealTotalPts + index] =
(long)predatabuffer[index];
            }
```

```
if(!m SpecParam->GapImage)
            {
                  // reset to image bias and current
                  theInst->DCBiasSet(m_SpecParam-
>Image Bias, DCBIASRAMP STEP);
                  theInst->CurrentSet(m SpecParam->Image Current);
                  // do we want to delay here to stabilize?
                  theInst->m Clock->Sleep(theInst-
>m Spec Delay.FBLStabalize);
            }
            // check if we need to release the FBL
            if(m SpecParam->It FBLBlank)
                  theInst->FBLBlank(false);
            SweepNum ++;
            RealTotalPts += data->nPts;
            //delete [] databuffer;
            ZeroMemory(predatabuffer, sizeof(short) * predatasize);
      }// end sweep while loop
      // clean up RAM
      delete [] fullbuffer;
      delete [] halfbuffer;
      //delete [] databuffer;
      delete [] predatabuffer;
}
void CSpectroscopy::SpecDataAcq(long *data[8], int point, int
conversions)
{
      short ADCin[8];
      // m ChanArray contains the chan numbers to record
      for(int i = 0; i < conversions; i++)</pre>
      {
            // Read all of the ADCs
            theInst->ADCread(m nChan,m ChanArray,ADCin);
            // start the convolution delay
            theInst->m Clock->Start Event(theInst->m Spec Delay.conv);
            //copy data to linedata array
            for(int j = 0; j < m nChan; j++)</pre>
            {
                  data[j][point] += ADCin[j];
            }
            theInst->m Clock->Wait();
      }
}
```

Listing A.2. Open IRSTM spectra and apply a fast Fourier transfrom

```
% usage: openir(specin, freq)
%specin is the winSTM spectra file (must openwinstm to get this)
%%%%HMS 11/09/05
%%%%% this file is to open spectra taken as I vs t (really pathlength).
curves with the IRSTM
%%%%% signals
function openir(specin, pow) %%pass in winSTM spec file (specNf####)
\% plot on = 1 ; plot off = 0
ploti = 0; %creates IV curve
plotn = ploti; %tells how many plots are being made
%define data channels
xchan = 1;
ichan = 2;
sz = size(specin);
if (length(sz)==3)
    specin = spectralshift(specin);
    specin = averagespec(specin);
end
scrsz=get(0, 'ScreenSize');
figure('Position',[0 1200 scrsz(3)*.8 scrsz(4)*.5]);
%plotindex = 1;
ydat=specin(ichan,:);
\dim = 2^{pow}
hf = dim/2
Y = fft(ydat, dim);
Pyy = Y.*conj(Y)/dim;
xdat = 31595.58*(0:hf)/dim;
plot(xdat, Pyy(1:(hf+1)))
axis([750 7000 0 1])
axis autoy
xlabel('Wavenumbers (cm-1)')
ylabel('Intensity (a.u.)')
title(sprintf('Infrared STM Spectra %s','string'));
```

```
if ploti==1;
%subplot(plotn,1,plotindex);
plot(xdat,specin(ichan,:)); hold on;
xlabel(sprintf('Mirror Position (cm) at %.2f cm intervals',freq));
ylabel('DC Current (pA)');
plotindex = plotindex+1;
end
```

### A.5 Signal-to-Noise Calculation

Considering a two-level system, the evolution of the population is dependent on three effects:

absorption 
$$W_{1\to 2}N_1 = \frac{\sigma l}{\hbar\omega}N_1$$
 (A.4)

stimulated emission 
$$W_{2\to 1}N_2 = \frac{\sigma I}{\hbar\omega}N_2$$
 (A.5)

spontaneous decay 
$$\gamma_{21}N_2 = (\gamma_{rad} + \gamma_{nr})N_2$$
 (A.6)

where,  $W_{1\rightarrow 2}$  is the probability of absorption,  $W_{2\rightarrow 1}$  the probability of stimulated emission,  $\gamma_{21}$  the probability of spontaneous decay,  $N_1$  ground state population,  $N_2$  the excited state population,  $\sigma$  the excitation cross section, and I the intensity of the source.

Differential equations describe the population:

$$\frac{dN_2}{dt} = W_{1\to 2}N_1 - W_{2\to 1}N_2 - \gamma_{21}N_2 \tag{A.7}$$

$$\frac{dN_1}{dt} = -W_{1\to 2}N_1 + W_{2\to 1}N_2 + \gamma_{21}N_2 \tag{A.8}$$

Taking the difference results in

$$\frac{d\Delta N_{21}}{dt} = 2W_{1\to 2}N_1 - 2W_{2\to 1}N_2 - 2\gamma_{21}N_2 = \frac{2\sigma I}{\hbar\omega}\Delta N_{21} - 2\gamma_{21}N_2$$
(A.9)

for total population

$$N_0 = N_1 + N_2 \Longrightarrow \Delta N_{21} = 2N_2 - N_0$$
 (A.10)

where  $N_0$  is the thermal equilibrium population.

At steady state,  $d'_{dt} = 0$ ,  $-\left(\frac{2\sigma}{\hbar\omega} + \gamma_{21}\right)\Delta N_{21} - \gamma_{21}N_0 = 0$  $\Delta N_{21}(I) = \frac{\gamma_{21}N_0}{(2\sigma I/\hbar\omega) + \gamma_{21}} = -N_0 \frac{1}{1 + (2\sigma/\hbar\omega\gamma_{21})I}$ 

(A.11)

Therefore, for a carbonyl adsorbed on a surface, the number of irradiated molecules in the excited state is only 0.0000315% (using a  $0.1 W/cm^2$  single wavelength source, a  $\sigma$  of  $1 \times 10^{-16} cm^2$ , a  $\gamma_{21}$  of  $1 \times 10^{12} s^{-1}$ , and a  $\omega$  of  $3.0 \times 10^{14} cm^2$ ). However, surface and field enhancements that range from  $10^2$  to  $10^6$  could increase the excited state population to 0.315% and 31.5%, respectively. Assuming tunneling current intensity changes similar to those observed in IETS (4-8%) and a  $10^6$  enhancement, the tunneling current should change ~2-5% upon excitation of a surface bound carbonyl. Typical tunneling currents range from 1 to 10 pA, meaning that projected changes in the tunneling current would be on the order of 0.05 to 0.5 pA. It is important to note that a single spectrum obtained with the IRSTM contains information about many excitations of the same molecule, since the lifetime of the excited state is in the order of  $10^{-12} s$ , while the preamplifier collects data at only ~5 ×  $10^3 s^{-1}$ .

# A.6 Summary

The design and operation of the infrared scanning tunneling microscope, which combines the chemical identification of IR spectroscopy with the atomic resolution of STM, have been discussed in this appendix. The schematics for all appropriate parts, as well as the programming code and control software, have been included or referenced.

Although the IRSTM is fully capable of molecular resolution, there is room for improvement. For example, the coaxial cable that connects the STM tip assembly to the preamplifier (Figures A.12A and A.15.B) is too long and too flexible. Shortening and
stiffening this connection would reduce the noise floor of the instrument, enabling the detection of weaker signals. However, this might require a re-design of the STM head assembly and should be carefully considered. Furthermore, the pocket of the sample holder (Figure A.4A) can be reduced in size to provide a tighter fit, facilitating the alignment of the IR beam between consecutive experimental runs. These modifications, along with custom software changes that automate alignment procedures, would enable new techniques that can identify adsorbates while also determining the interactions between neighboring molecules.

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### VITA

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#### **Education**

Ph.D. in Chemistry, The Pennsylvania State University University Park, Pennsylvania, May 2010 Advisor: Distinguished Professor Paul S. Weiss Dissertation Title: Controlling Adsorbate Interactions for Advanced Chemical Patterning

B.A. in Chemistry (ACS-certified), University of Pittsburgh
Pittsburgh, Pennsylvania, August 2002
Advisor: Professor Stephen Weber
Thesis Title: The Effects of Protonation and Deprotonation in SAMs Containing a Tethered Redox Couple (Ferrocene) on Redox Potentials

# **Professional Experience**

- 2003-2009 Graduate Research Assistant, The Pennsylvania State University Advisor: Prof. Paul S. Weiss
- 2004 **Teaching Assistant**, The Pennsylvania State University Electrochemistry and Chromatography
- 2001-2002 Undergraduate Research Assistant, University of Pittsburgh Advisor: Stephen Weber

### **Honors and Awards**

| 2009-2010 | Apple Fellowship, The Pennsylvania State University             |
|-----------|---|
| 2009      | Penn State Graduate Exhibition (3 <sup>rd</sup> place)          |
| 2007      | Dalalian Graduate Fellowship, The Pennsylvania State University |
| 2007      | Dorothy M. and Earl S. Hoffman Travel Grant, AVS                |
| 2006      | PSU Chemistry Travel Award, The Pennsylvania State University   |
| 2002-2004 | Bunton-Waller Fellowship, The Pennsylvania State University     |

# **Professional Affiliations**

American Chemical Society American Vacuum Society Materials Research Society