# CHEMICAL BATH DEPOSITION OF MOLYBDENUM DISULFIDE AND COPPER SULFIDE THIN FILMS

by

Jenny Kleinert Orbeck



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I dedicate this dissertation to the memory of my Grandpa, Dr. Harry Jean Hedlund.

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# COPPER SULFIDE THIN FILMS

by

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# CHEMICAL BATH DEPOSITION OF MOLYBDENUM DISULFIDE AND COPPER SULFIDE THIN FILMS

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The integration of new technologies into everyday devices requires the development of reliable low-cost methods to deposit semiconductor thin-films. In this work chemical bath deposition (CBD), a solution-based technique, is investigated for the deposition of molybdenum disulfide and copper sulfide thin films on organic substrates, specifically alkanethiolate self-assembled monolayers (SAMs). SAMs serve as useful model organic layers because they are uniform organic layers on the surface and are synthetically flexible.

Using Raman spectroscopy and x-ray photoelectron spectroscopy, we demonstrate that by using CBD the deposited  $MoS_2$  polytype can be changed from semiconducting 2H  $MoS_2$  on hydrophobic –CH<sub>3</sub> and –CO<sub>2</sub>C<sub>6</sub>F<sub>5</sub> terminated self-assembled monolayers (SAMs) to semi-metallic 1T  $MoS_2$  on hydrophilic –OH and –COOH terminated SAMs. The deposition of the different polytypes is controlled by the surface energies of the substrate; high surface energy, hydrophilic substrates stabilize 1T  $MoS_2$  films while 2H  $MoS_2$ , which is the thermodynamically stable polytype, is deposited on lower surface energy substrates. Further, the studies show that the deposition occurs via the reaction of ammonium molybdate with hydrogen sulfide produced by the reaction of

hydrazine with thioacetamide. The hydrazine then reduces the thiomolybdate ions to molybdenum disulfide.

The CBD deposition of copper sulfide is strongly dependent on the bath pH and the terminal group of the SAM. Using thiourea as a sulfur source, it is shown for the first time that the copper sulfide deposit can be changed from covellite, CuS, to chalcocite, Cu<sub>2</sub>S. In contrast using thioacetamide as a sulfur source the deposited film is always CuS. The selectivity of the deposition is dependent on the SAM terminal group. At pH 9 or less, CuS is preferentially deposited on –CH<sub>3</sub> terminated SAMs. Above pH 9, CuS is preferentially deposited on –COOH terminated SAMs. This is due to three competing processes: the decomposition of the thioacetamide to form sulfide ions, the interaction of the sulfide ions with the SAM terminal groups and the formation of Cu-terminal group complexes.

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# LIST OF ABBREVIATIONS

2D: 2-Dimensional
AFM: Atomic Force Microscopy
ALD: Atomic Layer Deposition
CBD: Chemical Bath Deposition
CVD: Chemical Vapor Deposition
ESCA: Electron Spectroscopy for Chemical Analysis
HDT: Hexadecanethiol
HOPG: Highly Oriented Pyrolytic Graphite
IMFP: Inelastic Mean Free Path
MHA: Mercaptohexadecanoic Acid
MHA-PFP: Mercaptohexadecanoic Acid – Pentafluorophenol
MHL: Mercaptohexadecanol
PTFE: Polytetrafluoroethylene
PVD: Physical Vapor Deposition
SAMs: Self-Assembled Monolayers
SEM: Scanning Electron Microscopy
SIMS: Secondary Ion Mass Spectrometry
TMDs: Transition Metal Dichalcogenides
TOF SIMS: Time-of-Flight Secondary-Ion-Mass Spectrometry
UHV: Ultra-High Vacuum
UV: Ultra-Violet (referring to electromagnetic spectrum or light)

VBM: Valence Band Maximum

XPS: X-ray Photoelectron Spectroscopy

#### CHAPTER 1

#### INTRODUCTION

#### **1.1 Semiconductor Contacts to Organic Substrates**

This dissertation explores the synthesis of semiconducting thin films on organic substrates. Semiconductor contacts to organic substrates are important for the development of organic/molecular electronics,<sup>1-9</sup> photovoltaics,<sup>10-13</sup> and sensing.<sup>4</sup> Historically, many of these applications have used silicon as a semiconductor. However, there are many alternative semiconducting materials such as metal oxides,<sup>14</sup> sulfides and selenides,<sup>15, 16</sup> which offer improved physical and mechanical properties.

Creating precise contacts to organic substrates poses many practical challenges. The optimization of device performance is dependent on defect-free interaction at the interface of semiconductor/substrate.<sup>17-19</sup> At the nanoscale, manipulation of mono- or few-layered semiconductor materials can require extensive cleaning, lithographic, and post-processing steps.<sup>15,20</sup> The systematic study of the deposition of semiconducting contacts to organic substrates can be very challenging. For example, the physical and chemical properties of polymeric thin films are difficult to control or modify reliably.<sup>21</sup> In this work we address this by using self-assembled monolayers (SAMs). SAMs serve as useful organic model systems to study interactions of the semiconductor/organic interface because they have a known structure and are synthetically flexible.<sup>22, 23</sup>

There are several techniques that can be used to deposit metals and semiconductors including gas phase methods such as chemical vapor deposition (CVD),<sup>24</sup> atomic layer deposition (ALD),<sup>25</sup> and physical vapor deposition (PVD).<sup>26</sup> However, these techniques require vacuum

conditions, high temperatures, and the breakdown of complex precursors. There are also a number of solution-based deposition methods such as electrochemical/electroless deposition (ELD),<sup>27</sup> and chemical bath deposition (CBD)<sup>28, 29</sup> which can be employed to deposit semiconductors. These methods are low-cost techniques and can be employed at low temperatures which are suitable for organic thin films. Chemical bath deposition has additional advantages over electrochemical and electroless deposition because it can be used to deposit a larger number of materials and does not require a conductive substrate.<sup>29, 30</sup>

#### **1.2 Chemical Bath Deposition (CBD)**

Chemical bath deposition (CBD) is a solution phase deposition technique that can be used to deposit semiconductor materials including oxides, hydroxides, chalcogenides and halides.<sup>29</sup> Typically CBD processes are controlled ion-exchange reactions between a cationic metal and anionic species, such as a chalcogenide, to deposit thin films or nanostructures onto a substrate.<sup>29</sup> An alternate reaction pathway for CBD is via a single precursor in which a metal-complex decomposes leading to the deposition of a film.<sup>31</sup>

In general, uniform films are produced through a slow and controlled reaction of one of the precursor so that the deposits formed are strongly adhered to the substrate surface (ion-by-ion growth).<sup>29</sup> Deposition can also occur from the aggregation of particles in solution which do not adhere well to the sample (cluster-by-cluster deposition).<sup>29</sup> These reaction pathways – and the deposit morphologies – are controlled by adjusting precursor concentrations, bath temperature and bath pH and other experimental variables, such as the stirring of the deposition bath.<sup>32-34</sup>

#### 1.3 Self-Assembled Monolayers Adsorbed on Au

Self-assembled monolayers (SAMs) are model organic systems which are often used to study molecular interactions with metals and semiconductors.<sup>2, 22</sup> SAMs are highly-ordered arrays of molecular species including alkanethiols, silanes, phosphonic acids, and alkylsiloxanes.<sup>22, 23</sup> SAM formation occurs onto a solid substrate through spontaneous chemisorption in either solution or vapor phase. Once adsorbed the molecules undergo a spontaneous slow assembly and organization process to form a semicrystalline structure.



**Figure 1.1** Schematic illustrating the components of an alkanethiol SAM on gold. Reprinted with permission from *Chemical Reviews* **2005**, *105*, 1103-1169. Copyright 2005 American Chemical Society.<sup>23</sup>

In these studies, alkanethiolate SAMs adsorbed on Au are employed. Alkanethiolate SAMs are comprised of three main components; a head group, a hydrocarbon chain, and a terminal functional group. SAM formation is primarily driven by the stability of the Au-S bond and the lateral interactions between the methylene chains. At the beginning of alkanethiol SAM formation, the thiol head-group chemisorbs onto the substrate surface leading to the formation of a Au-S bond. The methylene chain, or backbone, of the SAM molecule rearranges to maximize lateral

interactions and are further stabilized by van der Waals interactions. As a result, ordered alkanethiol SAMs are tilted  $\sim 30^{\circ}$  from the surface normal.<sup>22</sup>

#### **1.4 Molybdenum Disulfide**

Molybdenum disulfide (MoS<sub>2</sub>) is a transition metal dichalcogenide (TMD). TMDs have a unique set of properties that can be varied from metallic, semiconducting to insulating and even superconducting based on selection of transition metal and chalcogenide.<sup>16, 19, 35</sup> TMDs have a layered, sandwich structure X-M-X where X is the chalcogenide and M is the transition metal.<sup>16</sup> MoS<sub>2</sub> is an attractive material to study due to its tunable bandgap and flexible mechanical properties.<sup>16, 36</sup> MoS<sub>2</sub> is known to exist in two polytype forms, thesemi-metallic 1T (octahedral coordination geometry) and semiconducting 2H (trigonal prismatic coordination geometry) form.<sup>16, 37</sup> One of the challenges of incorporating MoS<sub>2</sub> materials into device design is the ability to precisely place MoS<sub>2</sub> in the desired polytype into a device.

#### **1.5 Copper Sulfide**

Copper sulfide is a material used in several important applications including biology,<sup>38</sup> photovoltaics,<sup>39</sup> and sensors.<sup>40</sup> Copper sulfide is a particularly attractive material due to its earth abundance<sup>41</sup> and non-toxic properties<sup>42, 43</sup> making it a safe low-cost material. One of the reasons that copper sulfide has many applications is that its stoichiometry can easily be varied from  $1 \le Cu/S \le 2$  which allows the electrical and other material properties to be controlled. Copper sulfides are generally semiconductors but can act as a metallic conductor.<sup>44</sup> Covellite (CuS) and chalcocite (Cu<sub>2</sub>S) are the two stoichiometric forms of copper sulfide but many other non-stoichiometric copper sulfides are naturally occurring, including digenite (Cu<sub>1.8</sub>S) and geerite (Cu<sub>1.6</sub>S).<sup>45</sup>

#### **1.6 Research Objectives**

In this dissertation, chemical bath deposition of semiconducting thin films on organic substrates are investigated. The reaction pathways and material properties are characterized in detail. Deposition of large-area thin films and area-selective deposition of films are demonstrated.

The chapters of this dissertation are organized as follows. Chapter 2 introduces the characterization techniques employed in this work. Techniques include time-of-flight secondary ion mass spectrometry (TOF SIMS), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM), and attenuated total reflection infrared (ATR-IR) spectroscopy. The basic principles, instrumentation, and applications are described.

Chapter 3 describes the CBD of molybdenum disulfide thin films on surfaces with differing surface energies and how the surface energy leads to the deposition of different MoS<sub>2</sub> polytypes. Deposition is carried out on SAMs with four different chemical functional groups. The chemistries of these functional groups also have different known surface energies. On low surface energy surfaces, 2H MoS<sub>2</sub> is deposited while on high energy surfaces 1T MoS<sub>2</sub> is deposited. To demonstrate that this effect is general, deposition was also carried out on other substrates which are known to have different surface energies. The MoS<sub>2</sub> polytype is determined by Raman spectroscopy and XPS measurements, and the thin films are further characterized by AFM, valence band XPS, and optical microscopy.

Chapter 4 explores the reaction pathways of the  $MoS_2$  CBD which is investigated using XPS, Raman spectroscopy, ATR-IR, SEM, optical microscopy and TOF SIMS. A reaction pathway is proposed consistent with the identified intermediates, by-products and products.

Chapter 5 demonstrates the area selective of  $MoS_2$  deposition on micropatterned SAMs as well as the interaction of the deposited film with the gold substrate. Using Raman mapping measurements, the identified polytype across a micro-patterned surface is shown.

Chapter 6 describes a CBD method by which to deposit copper sulfide thin films and its dependence on the deposition bath pH using thiourea as a sulfur source. The deposition is carried out on  $-CH_3$ , -COOH, and -OH terminated SAMs. Using XPS analysis, the stoichiometry of the  $Cu_xS$  film is demonstrated to be dependent on both the bath pH and the chemical identity of the SAM terminal group. Further characterization of the film deposit using TOF SIMS shows changes in the surface coverage with changing bath pH.

Chapter 7 demonstrates a comparison of the deposition of CuS with a different thiol precursor, thioacetamide. CuS deposition is done on  $-CH_3$ , -OH, and -COOH terminated SAMs at pH 6, 9, and 12. We show that the deposition selectivity is dependent on the interaction of the bath components with the SAM terminal group.

Chapter 8 provides a summary and conclusion of the work described in this dissertation and discusses future research directions.

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#### CHAPTER 2

#### CHARACTERIZATION TECHNIQUES

In this work a variety of analytical techniques were employed including time-of-flight secondary ion mass spectrometry (TOF SIMS), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM) and attenuated total reflection infrared (ATR-IR) spectroscopy. The following sections give descriptions of these techniques.

#### 2.1 TOF SIMS

#### **2.1.1 Introduction**

Secondary ion mass spectrometry (SIMS) is a surface sensitive technique which is used to characterize samples with ppb sensitivity ~100 nm lateral resolution and ~0.5 nm depth resolution.<sup>1</sup> SIMS is employed in a wide variety of fields including in the analysis of organic thin films, <sup>2,3</sup> semiconductors,<sup>4,5</sup> polymers,<sup>6,7</sup> and biochemistry.<sup>8-10</sup> In a SIMS measurement the sample surface is bombarded by a highly energetic beam of primary ions.<sup>1, 11</sup> This causes a collision cascade leading to the desorption of secondary species, which are positive ions, negative ions, neutrals and electrons (Figure 2.1). Only 1 to 5 % of the desorbed species are ions which can be positively or negatively charged, while the rest are neutrals (95-99%).<sup>1</sup>



**Figure 2.1** Schematic representing SIMS ion bombardment on a self-assembled monolayer on gold. Reprinted by permission from Springer Nature Customer Service Centre GmbH: Nature<sup>12</sup>, Copyright 2003.

The secondary ion current produced is given by:

$$I_m^{\pm} = I_p \times Y_m \times \eta^{\pm} \times \alpha^{\pm} \times \theta_m \tag{2.1}$$

where  $I_m$  is the intensity of the secondary ion of a species m,  $I_p$  is the primary ion beam current,  $Y_m$  is the sputtering yield,  $\eta$  is the ion transmission efficiency for a positive or negative ion,  $\alpha$  is the ionization probability of the sputtered species, and  $\theta_m$  is the surface concentration, or coverage, of species m in the analyzed area. After bombardment the secondary ions are measured using a mass analyzer.

The primary ion dose determines if the SIMS measurement is static or dynamic. Static SIMS employs an ion dose of  $<1x10^{13}$  ions/cm<sup>2</sup> and offers several advantages including minimal surface damage, and high surface sensitivity (ppb).<sup>11</sup> Dynamic SIMS uses a higher primary ion dose leading to the erosion of the sample surface. Dynamic SIMS is generally employed for obtaining mass spectra as a function of depth ("depth profiling") and the analysis of bulk materials.<sup>11</sup>

#### 2.1.2 Time-of-flight secondary ion mass spectrometry (TOF SIMS)

Time-of-flight mass (TOF) analyzers provide several advantages over magnetic sector and quadrupole mass analyzers. These advantages include the collection of all mass-to-charge (m/z) ratios simultaneously and a high secondary ion transmission efficiency.

All TOF SIMS data collected in this work were obtained using an ION TOF IV instrument (ION TOF Inc., Chestnut Hill, NY) equipped with a  $Bi_m^{n+}$  (m = 1-7, n = 1-2) liquid metal ion gun (LMIG). An overview of the main components of the ION TOF IV instrument are described in the next sections.

#### 2.1.3 Vacuum System

An ultra-high vacuum (uhv) system is required for TOF SIMS data collection to ensure ejected secondary ions can travel to the detector without interacting with any other gaseous species. Furthermore, low pressure environments significantly reduce the adsorption of gas phase species onto a sample. The ION TOF vacuum system is comprised of three chambers: the airlock (or the loadlock), the preparation chamber, and the analysis chamber each separated by gate valves. Samples are first introduced into the system in the airlock chamber which is pumped down from atmosphere. After the loadlock has reached a vacuum pressure, typically  $\leq 10^{-6}$  mbar, the sample is transferred to the preparation chamber to provide further outgassing so that the sample can be introduced into the uhv analysis chamber. After a short time, the samples are transferred to the main chamber. The pressure of the main chamber is  $<5 \times 10^{-9}$  mbar.

#### 2.1.4 Liquid metal ion gun (LMIG)

The primary ion beam used in these experiments is 20 keV Bi<sup>+</sup> which is produced using a liquid metal ion gun (LMIG). The LMIG produces a high energy ion beam that is focused to a small spot

size for sample bombardment. In a LMIG a reservoir containing bismuth is heated and a large electric field is applied to the tip of the LMIG emitter, causing a liquid droplet to form. If a sufficiently large electric field is applied, the droplet becomes elongated, forming a Taylor cone and the primary ion beam

The ion beam is then focused by lenses and apertures onto the sample. To provide a start time for the mass analyzer, the ion beam is pulsed using a combination of a beam blanker, which makes ion packets of  $\sim$ 20 ns duration, and a buncher. The "buncher" further shortens the ion packets to make make ion pulses of  $\sim$ 600 ps in length.

#### 2.1.5 Time of flight analyzer

Secondary ions produced by the LMIG are measured using a time-of-flight analyzer which measures the mass-to-charge ratio (m/z) of the secondary ions produced. After a primary ion pulse bombards the surface, secondary ions are extracted and accelerated by an electric field. All secondary ions have unique mass-to-charge ratios and therefore different velocities as described by the following equation:

$$zeV = \frac{1}{2}mv^2$$

where z is the charge, m is mass, v is velocity, and V is the electric field used to accelerate the ions through the analyzer. The secondary ions then travel through a field-free region of length, L, and arrive at the detector at different travel times (t). The travel time through the analyzer is expressed as:

$$t = \frac{L}{v} = L \left(\frac{m}{2eVz}\right)^{\frac{1}{2}}$$
 2.3

However, when secondary ions are ejected from the sample surface there is a small distribution in their kinetic energies which is due uncertainties in the time and position of each created ion. Therefore, ions with the same m/z may arrive at the detector at different times. To compensate for this small kinetic energy spread, a reflectron is employed.<sup>13</sup>

#### 2.2 XPS

#### 2.2.1 Introduction

X-ray photoelectron spectroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA), is a popular surface analysis technique that provides elemental information as well as information about chemical environments in the top 1-12 nm of materials.<sup>14</sup> This technique can provide both qualitative and quantitative information. XPS is used to investigate materials including rare-earth compounds,<sup>15</sup> metal oxides,<sup>16</sup> polymers,<sup>17, 18</sup> and semiconductors.<sup>19</sup>

#### 2.2.2 Principles of XPS

In XPS, x-rays irradiate a sample surface which results in the ejection of photoelectrons generated from a core energy level (Figure 2.2a). After emission of the photoelectron secondary processes can occur. The excited atom can either relax via the emission of an x-ray (x-ray fluorescence) or the emission of an eltron (Auger electron) (Figure 2.2b).


Figure 2.2 Schematic diagram of a) the X-ray photoelectron and b) the Auger photoelectron.

In general, XPS measures the kinetic energy of a generated photoelectron which is dependent on the binding energy (BE) of the electron in the atom, the X-ray energy used and the material's work function as described in Equation 2.4:

$$E_{KE} = hv - BE - \varphi \tag{2.4}$$

where  $E_{KE}$  is the kinetic energy of the photoelectron, *h* is Planck's constant, *v* is the frequency of the X-ray and  $\varphi$  is the work function of the material.

# 2.2.3 Photoelectron Spectra

Typical XPS spectra are generally shown as intensity in counts per second (cps) versus binding energy with units of eV. A spectrum is typically dominated by the photoelectron peaks but Auger electron peaks can also be detected.



**Figure 2.3** XPS spectrum of the Sb 3d region in  $Pr_2Fe_{4-x}Co_xSb_5$  (1 < x < 2.5). Adapted with permission from *Inorganic Chemistry*, 55 (4), 1946-1951. Copyright 2016 American Chemical Society.<sup>15</sup>

The binding energy is used to identify elements present in the sample while the chemical shifts  $(\Delta E_B)$  ascertain their chemical environment. For example, Figure 2.3 shows the Sb 3d photoelectron spectra of a Pr<sub>2</sub>Fe<sub>4-x</sub>Co<sub>x</sub>Sb<sub>5</sub> (x ~1 and x ~2) crystals.<sup>15</sup> In this example there are two distinct Sb 3d peaks due to different bonding environments. Note that the 3d peaks are further split by spin orbit coupling into  $3d_{5/2}$  and  $3d_{3/2}$  binding energies. The Sb  $3d_{5/2}$  peaks are at ~ 530.5 eV and 528 eV and assigned to Sb<sup>3+</sup> and Sb<sup>0</sup>, respectively. The corresponding Sb  $3d_{3/2}$  peaks appear at ~ 540 eV and 537.5 eV. At lower concentrations of cobalt (x ~ 1) Sb is primarily present in the 3+ oxidation state. When the crystal is rich in cobalt (x ~ 2) there is a mix of Sb in the Sb<sup>0</sup> and Sb<sup>3+</sup> as indicated by the increase in the intensity of the photoelectron peaks at ~530.5 eV.

## 2.2.4 Valence Band XPS

Using XPS the valence band (BE  $\leq$  20 eV), or highest occupied molecular orbitals, of materials can also be analyzed. Such data provides information about the Fermi level density of states, and the work function of the material.

# 2.2.5 X-ray Photoelectron Instrument

In this work a PHI VersaProbe II (Physical Electronics Inc.) equipped with an Al K $\alpha$  source was used for all *ex-situ* XPS measurements. The main components of an XPS instrument are the X-ray source, the concentric hemispherical analyzer, and detector (Fig. 2.4).



**Figure 2.4** Schematic diagram showing the main components of an X-ray photoelectron spectrometer. Figure used with permission from *Surface Analysis - The Principle Techniques*, Second Ed., Copyright 2009 John Wiley & Sons.<sup>1</sup>

The most common sources are Al K $\alpha$  or Mg K $\alpha$  which have energies of 1486.6 eV and 1253.6 eV, respectively. The X-rays are diffracted and focused onto the sample using a crystal x-ray monochromator (typically graphite). Photoelectrons generated from the surface travel through an electron lens and concentric hemispherical analyzer (CHA) before being detected by a multi-channel detector.

#### 2.2.6 Vacuum System

Similar to TOF SIMS, XPS requires collection under ultra-high vacuum (UHV) conditions. UHV minimizes elastic and inelastic scattering of photoelectrons with gas molecules present at high pressures. Scattering of photoelectrons produced after X-ray irradiation results in loss in intensity and energy resulting in noisy spectra. Samples are introduced into the UHV system through a preparation chamber that can be pumped down from atmosphere and then transferred to the main analysis chamber through a gate valve. The pressure was  $\leq 5 \times 10^{-10}$  mbar in the main analysis chamber for collection of all spectra in this work.

# 2.3 Raman spectroscopy

# **2.3.1 Introduction**

Raman spectroscopy was first discovered by scientist C.V. Raman in 1928 when he discovered that visible wavelengths of light will cause some molecules to inelastically scatter light as opposed to absorbing it (as in IR) or elastically scattering.<sup>20</sup> Raman is a fast and easy method to measure solids, liquids, and gases and can provide information about the crystallinity and bonding environments in a sample.

# 2.3.2 Principles of Raman Spectroscopy

Upon irradiation with a quantum of light,  $hv_{ex}$ , one of three scattering outcomes is possible: elastic (Rayleigh) scattering, Stokes scattering, and anti-Stokes scattering. Figure 2.5 shows the energy level diagram for these processes.



Figure 2.5 Diagram showing Raman scattering processes.

In Rayleigh scattering, the light elastically scatters from the molecule or substrate:

$$E_{in} = E_{out} = h\nu 2.5$$

where *h* is Planck's constant, v is the frequency of the light source and *E* is the energy of the light source. The subscripts in and out refer to the light incident on the sample and the light emitted by the sample, respectively.

In Stokes scattering, upon absorption of light, the molecule, or material, will exhibit a transition from the ground state to a "virtual" state. Upon de-excitation, the molecule becomes vibrationally excited and a photon is emitted with lower energy than the excitation radiation:

$$E_{out} = h\nu - h\nu_m \tag{2.6}$$

where  $v_m$  is the frequency of the vibration or phonon mode that is excited. In Anti-Stokes scattering, the opposite effect occurs. A vibrationally excited molecule, or material, absorbs the radiation and upon de-excitation, it returns to its ground state leading to the ejection of photons with higher energy:

$$E_{out} = h\nu + h\nu_m \tag{2.7}$$

# 2.3.3 Raman Spectroscopy Instrumentation

Typically, lasers of short wavelength of light are selected for Raman analysis because the scattering intensity is larger at such wavelengths. In this work a Thermo Scientific DXR Raman microscope with a 532 nm laser and a  $50 \times$  objective lens was employed. The laser is focused on the sample using an objective lens with a high numerical aperture. The scattered light from the sample is recollected by the lens and is detected at a 90° angle (in order to minimize interference from Rayleigh scattering) and also filtered through a laser-blocking filter before reaching the spectrometer.

# 2.4 Attenuated total internal reflection infrared (ATR-IR) spectroscopy

#### **2.4.1 Introduction**

Attenuated total internal reflection infrared (ATR-IR) spectroscopy is a method by which to study solids and liquids under ambient atmospheric conditions.<sup>21</sup> Its main advantage is that no sample preparation is required and so the characteristics of the sample are unchanged prior to investigation.

# 2.4.2 Principles of ATR-IR

When radiation passes from a high-density medium to a low-density medium reflection occurs. The amount of reflection will increase as the angle of incidence becomes larger and beyond a certain critical angle reflection is achieved. This reflection process has been shown to penetrate a small distance into the less dense medium before reflection occurs. The radiation which penetrates into the sample is called an evanescent wave, which decays exponentially with distance from the reflecting surface. The radiation's depth of penetration ( $d_p$ ) is given by:<sup>20</sup>

$$d_p = \frac{\lambda_c}{2\pi [\sin^2\theta - (n_s/n_c)^2]^{\frac{1}{2}}}$$
 2.8

where  $\lambda_c$  is the wavelength in the crystal,  $n_s$  and  $n_c$  are the refractive indices of the sample and crystal, and  $\theta$  is the angle of incidence.

IR spectroscopy measures absorption of radiation by a sample with frequency (usually, wavenumber cm<sup>-1</sup>) and is reported as either transmittance or absorbance. For ATR-IR the data is measured as absorbance versus wavenumber, cm<sup>-1</sup>. Absorbance is defined by the Beer-Lambert Law:

$$A = -\log\left(\frac{l_0}{l}\right) = \mathcal{E} \cdot l \cdot c \tag{2.9}$$

where *A* is absorbance  $I_0$  is the intensity of light incident on the sample *I* is the intensity of the transmitted (collected) light,  $\varepsilon$  is absorptivity, *l* is path length and *c* is concentration.

# 2.4.3 ATR-IR Instrumentation

In this work a Thermo Scientific Nicolet iS50 FT-IR was used. This instrument employs an ATR with a horizontal sampling accessory geometry (Fig. 2.6).



**Figure 2.6** Components of an ATR-IR sampling accessory. Reprinted from *Advances in Colloid and Interface Science*, Vol. 93, Hind, A.R.; Bhargava, S.K.; Mckinnon, A., At the solid/liquid interface: FITR/ATR – the tool of choice, 91-114, Copyright 2001, with permission from Elsevier.<sup>21</sup>

The sample is placed in close contact with an internal reflection element (IRE), typically a crystal made of silver chloride, germanium, diamond, silicon or thallium bromoiodide. In these studies, a diamond crystal was employed. The incident radiation (*I*) passes through the IRE at angle  $\theta$ . In the case of solid samples an additional attachment is sometimes used to apply a measured amount of force to place the sample in close contact with the crystal. Reflected radiation (*R*) is measured by a detector.

# 2.5 Scanning electron microscopy (SEM)

# **2.5.1 Introduction**

Scanning electron microscopy (SEM) employs electrons to form images and is widely used to characterize pure and mixed organic, inorganic, and semiconducting materials.<sup>22</sup> Lateral resolution of ~1nm can be achieved using SEM, but more typically the lateral resolution is 2-5 nm. SEM images in this work were collected using a Supra-40 Scanning Electron Microscope (Zeiss), equipped with a field emission electron gun.

# 2.5.2 SEM Instrumentation

SEM instruments consist of an electron gun, a series of focusing optics including lenses and apertures and a detector.

#### **2.5.3 Electron-Sample Interactions and Signal Detection**

Figure 2.7 illustrates the various interactions and penetration volumes of a primary electron beam with a sample surface.<sup>23</sup> When high energy electrons interact with a surface, the electrons can either elastically or inelastically scatter. Secondary electrons are produced via inelastic scattering of the electrons with the substrate; the primary electrons to transfer kinetic energy to the substrate which leads to the ejection of secondary electrons.



**Figure 2.7** Interaction of primary electrons with a sample surface in SEM. Figure used with permission from *Materials Characterization: Introduction to Microscopic and Spectroscopic Methods*. Copyright 2008 John Wiley & Sons.<sup>24</sup>

Secondary electrons produced in the outermost 5-50 nm will escape from the sample surface, and so topographic images are obtained. The primary electrons can also undergo elastic scattering in the top 50-300nm of a sample surface which leads to the ejection of backscattered electrons.

Backscattered electrons are employed for compositional imaging and the images have a reduced lateral resolution.

# 2.6 Atomic force microscopy

Atomic force microscopy (AFM)uses the interactions between a sharp tip and a sample surface to produce atomic scale resolution images.<sup>25</sup> AFM is widely used to characterize sample topography under a variety of sample conditions including ambient air, vacuum, low temperature and in liquid media. <sup>26-28</sup> Generally, a vertical resolution of 0.01 nm can be easily achieved but the lateral resolution is much larger, 3 nm or above.<sup>29</sup>

# 2.6.1 AFM Instrumentation

In this work two AFM instruments were employed. For data collected on the highly oriented pyrolytic graphite (HOPG), a Nanoscope Dimension 3100 microscope (Veeco Instruments) was used. For other analyses, a Veeco Dimension 5000 SPM was employed (Veeco Instruments).

An AFM instrument is equipped with a sharp tip connected to a flexible cantilever, a detection system, a positioning system and a data system. The tip is typically made of silicon nitride.



Figure 2.8 Diagram showing the main components of an atomic force microscope.<sup>30</sup>

A laser photodiode is focused on the back of the cantilever. The reflected light from the cantilever is detected by a position sensitive split photodiode detector. The weak interactions of the AFM tip with the sample surface causes small shifts in the cantilever position and/or frequency which is recorded by the position-sensitive photodetector. The shifts are converted into an analog signal and a topographic image is recorded.

# 2.6.2 Operational Modes in AFM

# **Contact Mode**

Contact mode is often selected for the analysis of hard materials. In this mode the tip scans in contact with the surface and is dragged across the sample surface with a constant force. However, this can lead to sample damage. Additionally, image artifacts are observed due to the presence of gas molecules on the substrate and electrostatic forces between the tip and sample.<sup>23</sup>

#### **Non-Contact Mode**

To minimize sample damage non-contact mode may be used. The tip is positioned 50-150 Å above the sample surface and is oscillated at a constant resonant frequency while rastering across the surface. The tip-to-sample distance is then measured, and a surface topographical image is created. Non-contact mode is usually selected for analysis of soft materials such as organic materials or biological samples, where the sample surface can easily be damaged.<sup>23</sup> However, artifacts are often detected due to adsorption of fluid or gas species on the surface.

# **Tapping mode**

Tapping mode was used to collect all AFM images in this work. This mode combines the advantages of contact and non-contact modes.<sup>23</sup> In tapping mode, the tip is oscillated at a resonant frequency. However, unlike non-contact mode the Z motion is controlled by the vibration of the cantilever. The Z scanner in tapping mode keeps the tip amplitude constant when the tip is displaced. The tip is moved toward the surface and taps it lightly. As the tip comes into contact with surface the oscillation is dampened. The amplitude of the oscillation is typically > 20 nm in order to overcome capillary and other attractive forces.

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#### CHAPTER 3

# POLYTYPE CONTROL OF MOLYBDENUM DISULFIDE USING CHEMICAL BATH DEPOSITION

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#### **3.1 Abstract**

Molybdenum disulfide (MoS<sub>2</sub>) has a wide range of applications from electronics to catalysis. While the properties of single- and multi- layer MoS<sub>2</sub> films are well understood, controlling the deposited MoS<sub>2</sub> polytype remains a significant challenge. In this work we employ chemical bath deposition (CBD), an aqueous deposition technique, to deposit large area MoS<sub>2</sub> thin films. Using Raman spectroscopy and x-ray photoelectron spectroscopy we demonstrate that the deposited MoS<sub>2</sub> polytype can be changed from semiconducting 2H MoS<sub>2</sub> on hydrophobic –CH<sub>3</sub> and –CO<sub>2</sub>C<sub>6</sub>F<sub>5</sub> terminated self-assembled monolayers (SAMs) to semi-metallic 1T MoS<sub>2</sub> on hydrophilic –OH and –COOH terminated SAMs. The deposition of the different polytypes is controlled by the surface energies of the substrate; high surface energy, hydrophilic substrates stabilize 1T MoS<sub>2</sub> films while 2H MoS<sub>2</sub>, which is the thermodynamically stable polytype, is deposited on lower surface energy substrates. This effect appears to be general enabling the controlled deposition of MoS<sub>2</sub> polytypes further broadens the applications of MoS<sub>2</sub> in catalysis, electronics, sensing, energy storage and optoelectronics.

## **3.2 Introduction**

Transition metal dichalcogenides (TMDs) have varied and unusual physical, electronic and chemical properties<sup>1-6</sup> and consequently have applications in energy,<sup>2, 3, 7</sup> sensors,<sup>3, 8</sup> catalysis, <sup>2,3,6</sup>

biomedicine,<sup>3</sup> optoelectronics<sup>6, 8</sup> and nanoelectronics.<sup>1, 9-11</sup> The large number of potential applications can be attributed to the chemical identity of the chalcogenide (S, Se, Te), and the d-electron count and co-ordination of the transition metal.<sup>2, 4, 12, 13</sup> TMDs are X-M-X sandwich structures where M is the transition metal and X is the chalcogenide.<sup>2, 12, 13</sup> The metal atom either has octahedral co-ordination (ABC stacking) leading to tetragonal symmetry (1T) or trigonal co-ordination (ABA stacking) with either hexagonal (2H, 4H<sub>c</sub>) or rhombohedral symmetries (3R). Mixed co-ordination structures (4H<sub>b</sub>, 6R) are also possible.

Molybdenum disulfide is one of the most widely studied TMDs<sup>6, 8, 14-25</sup> and has applications from lubrication<sup>15, 18, 19</sup> to catalysis.<sup>14, 15, 20</sup> Most recently there has been increasing interest in the use of MoS<sub>2</sub> in electronics<sup>14, 16, 17, 21, 26, 27</sup> and as photodetectors.<sup>6, 8</sup> Single-layer MoS<sub>2</sub> transistors with high on-off ratios (~10<sup>8</sup>) and negligible off current have been demonstrated.<sup>14</sup> Photoresponsitivities reaching 880 A W<sup>-1</sup> at 561 nm have been reported for single-layer MoS<sub>2</sub> devices suggesting that MoS<sub>2</sub> also has applications in optoelectronics and biomedical imaging.<sup>8</sup> These applications rely on the direct bandgap of ~1.8 eV of single-layer 2H MoS<sub>2</sub>, which is the thermodynamically stable polytype.<sup>14, 28</sup> However the bandgap of semiconducting 2H MoS<sub>2</sub> varies with the number of layers in the material; for bulk 2H MoS<sub>2</sub> the bandgap is indirect and is ~1.2 eV.<sup>15</sup> Molybdenum disulfide can also be synthesized as a metastable octahedral phase (1T) which is semi-metallic.<sup>29</sup> The unique indirect to direct bandgap transition of 2H MoS<sub>2</sub> and semi-metallic nature of 1T MoS<sub>2</sub> enables the tuning of the material properties, and so further broadens the applications of MoS<sub>2</sub>.

While the variation in polytype properties is advantageous for potential technological applications such as self-aligned gate structures, it is a large problem for the controlled synthesis

and precise *in situ* placement of these materials. In current methods, such as chemical vapor deposition (CVD),<sup>2, 3, 14, 17, 23, 25</sup> atomic layer deposition (ALD),<sup>24, 30</sup> hydrothermal synthesis,<sup>6, 20, 31</sup> electrodeposition<sup>32</sup> and micromechanical<sup>14, 33</sup> and chemical<sup>14, 34, 35</sup> exfoliation there is little, or no, control of the deposited MoS<sub>2</sub> polytype. The transition temperature of metastable 1T MoS<sub>2</sub> to 2H MoS<sub>2</sub> is relatively low, 95.7 °C,<sup>29, 33</sup> and so high temperature deposition of 2H MoS<sub>2</sub>. Upon chemical exfoliation using lithium compounds (Li intercalation),<sup>14, 15, 34, 35</sup> 2H MoS<sub>2</sub> undergoes a transition to 1T MoS<sub>2</sub>.<sup>34, 35</sup> However, the transition to 1T MoS<sub>2</sub> film to single polytype films of 2H MoS<sub>2</sub>.<sup>34, 36</sup> Additionally, the high temperatures used in the synthesis and annealing of MoS<sub>2</sub> are generally incompatible with organic thin films which are used in flexible electronics.<sup>37</sup>

Given these observations, a low temperature deposition technique is required to control the deposition of 1T and 2H MoS<sub>2</sub>. Chemical bath deposition (CBD) is a solution-based method which employs a controlled ion-exchange precipitation reaction to deposit thin films,<sup>38</sup> and can be performed at low temperatures ( $\leq 50$  °C). It is attractive for large area synthesis because it is inexpensive since no vacuum equipment is required. Lead sulfide was the first material to be deposited by CBD in the late 1800s,<sup>38</sup> and today it is employed to deposit a wide range of semiconductors including sulfides (e.g. PbS, CuS), selenides (e.g. CdSe, NiS), tellurides (e.g. CdTe), halides (e.g. AgBr) and oxides (e.g. ZnO).<sup>38, 39</sup> Generally, the CBD reaction is controlled by both the concentration of the cation and the anion.<sup>38</sup> To control the concentration of the "free" metal ions in solution, metal ions are complexed with species such as nitriloacetate.<sup>40</sup> The anion concentration (e.g. S<sup>2-</sup>) is controlled via the slow decomposition of a precursor such as thiourea or

thioacetamide.<sup>38, 40-42</sup> While most CBD films are reported for group 7 to 10 transition metals, <sup>38, 39</sup> there have been several studies of CBD films using group 4 to 6 transition metals, e.g. Mo,<sup>38, 39, 43</sup> W,<sup>44</sup> Hf,<sup>45</sup> Ti<sup>39</sup> and Zr.<sup>46</sup>

The second requirement for the controlled deposition of 1T and 2H MoS<sub>2</sub> is a means by which to preferentially stabilize 1T MoS<sub>2</sub>. The energy difference between few layer-1T and 2H films of MoS<sub>2</sub> is likely to be very small for two reasons. First, the transition temperature of metastable 1T MoS<sub>2</sub> to 2H MoS<sub>2</sub> is relatively low, 95.7 °C.<sup>29, 33</sup> Using the differential scanning calorimetry data of Yu and coworkers,<sup>33</sup> we estimate that the energy difference between the 1T and 2H polytypes of MoS<sub>2</sub> is ~21.5 kJ mol<sup>-1</sup>. Second 2H MoS<sub>2</sub> undergoes a transition to 1T MoS<sub>2</sub> upon the intercalation of small ions, such as Li, which can easily be reversed either by heating or aging.<sup>15, 35, 47, 48</sup> On metals, such as Pt, it is well known that the energy difference between two structural phases of the surface (often called the "reconstructed" and "unreconstructed" surface) is very small,<sup>49</sup> and substrates can undergo reconstruction upon adsorption of small molecules.<sup>49, 50</sup> For example, Pt  $\{100\}$  has two surface structures: a metastable, unreconstructed  $(1 \times 1)$  phase and a thermodynamically stable hexagonal phase. Upon adsorption of CO the hexagonal Pt {100} surface converts to the  $(1 \times 1)$  phase while the  $(1 \times 1)$  metastable phase does not reconstruct. King and co-workers<sup>49</sup> determined the energy difference between these two Pt  $\{100\}$  phases to be  $12\pm 2$ kJ Pt<sub>s</sub>·mol<sup>-1</sup> where Pt<sub>s</sub> is the number density of surface Pt atoms.<sup>49</sup> Thus one possible route to the synthesis 1T MoS<sub>2</sub> films is to exploit the surface energy of the substrate in a similar way to small adsorbate molecules "lifting' the surface reconstructions of Pt and other substrates.<sup>50</sup>

Initially MoS<sub>2</sub> CBD was investigated on functionalized alkanethiolate self-assembled monolayer (SAM) substrates. Functionalized SAMs were chosen because they are ideal model systems; they are synthetically flexible, are well-ordered, have a known number of terminal functional groups and so their surface energy can be controlled.<sup>51</sup> In this paper, we employ –OH and –COOH terminated SAMs which are hydrophilic and have high surface energy. We also use methyl- (–CH<sub>3</sub>) and pentafluorophenol ester- (–CO<sub>2</sub>C<sub>6</sub>H<sub>5</sub>) terminated SAMs which are hydrophobic and have a low surface energy. Our results show that 2H MoS<sub>2</sub> is deposited on the low energy SAM surfaces while 1T MoS<sub>2</sub> is stable on the higher energy SAM surfaces. This effect appears to be quite general: 1T MoS<sub>2</sub> deposits on hydrophilic surfaces, such as soda lime glass, while 2H MoS<sub>2</sub> deposits on lower energy, hydrophobic surfaces such as polytetrafluoroethylene (PTFE) tape.



#### 3.3 Results and Discussion

**Figure 3.1** Bright field optical images of the bare gold substrate, and after MoS<sub>2</sub> is deposited on MHA, MHL, MHA-PFP and HDT substrates. Deposition time: 24 h.

After MoS<sub>2</sub> CBD for 24 hours, all four SAM substrates show a color change from gold (yellow) to green indicating that a film has deposited (Figure 3.1). The color change is consistent with the deposition of MoS<sub>2</sub> multilayers, which are blue deposits, atop the gold (yellow) substrate.<sup>16, 31</sup> Atomic force microscopy (AFM) (Figure 3.2) and scanning electron microscopy (SEM) (data not shown) images indicate that the deposited layers have different morphologies which are dependent on the SAM terminal group chemistry. The data show that for –COOH (MHA) and –CH<sub>3</sub> (HDT) terminated SAMs, the deposited films are relatively smooth, polycrystalline films with a grain size of ~100 nm. We note that similar grain sizes have been observed for multilayer MoS<sub>2</sub> films grown by CVD.<sup>28</sup> The films also appear to be conformal to the underlying substrate; the RMS roughness of the deposited films is very similar to the underlying –COOH and –CH<sub>3</sub> SAM substrates (Table 3.1).



**Figure 3.2** AFM images of the deposited MoS<sub>2</sub> film on MHA, MHL, MHA-PFP and HDT substrates. Deposition time: 24 h.

In contrast, MoS<sub>2</sub> films deposited on  $-CO_2C_6F_5$  terminated SAM (MHA-PFP) substrates exhibit a different morphology than on MHA and HDT substrates. The film appears to be incomplete; there are a number of "holes" in the film and the grain size is difficult to determine (Figure 3.2), which is likely due to the interaction of the aqueous deposition solution with the very hydrophobic MHA-PFP SAM substrate. The RMS roughness of the MoS<sub>2</sub> film is similar to the underlying  $-CO_2C_6F_5$  terminated SAM substrate within the deposited layer areas, but the overall roughness of the film is larger than the MHA-PFP SAM substrate (Table 3.1). At first glance, on -OH terminated SAMs (MHL) the morphology of the deposited MoS<sub>2</sub> film appears to be similar to those deposited on MHA and HDT substrates; the films are polycrystalline with a grain size of ~100 nm (Figure 3.2). However, the films are very rough; the rms roughness of the deposit is ~10× that of the underlying MHL SAM (Table 3.1).

SAM terminal group	RMS roughness (nm)	
	Before Deposition	After MoS <sub>2</sub> Deposition
$-CO_2C_6F_5$	2.53	2.05 within deposited area;
		4.42 overall
CH3	1.33	1.58
-OH	1.30	11.62
-СООН	1.44	1.69

Table 3.1 RMS roughness of the samples before and after MoS<sub>2</sub> CBD.

The above data indicate that the morphology of the  $MoS_2$  film is dependent on the terminal group chemistry of the SAM substrate. A possible reason for these observations is that different

MoS<sub>2</sub> polytypes are deposited. Due to the differences in their symmetry, 2H and 1T MoS<sub>2</sub> films can be distinguished in both x-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. Since it is well known that the presence of a gold layer or nanoparticles affects the Raman shifts and XPS photoelectron binding energies,<sup>21, 28</sup> the MoS<sub>2</sub> films were mechanically exfoliated from the SAM substrates for analysis. Figure 3.3 displays the Mo 3d and S 2s photoelectron spectra of the deposited MoS<sub>2</sub> films. Between 224 eV and 236 eV, three peaks are observed. For MoS<sub>2</sub> films deposited on HDT and MHA-PFP SAMs the peak binding energies are at 229.8 eV, 232.7 eV and 226.6 eV which correspond to the Mo 3d<sub>5/2</sub>, Mo 3d<sub>3/2</sub> and S 2s peaks of 2H MoS<sub>2</sub>.<sup>34</sup> In contrast, for MoS<sub>2</sub> films deposited on MHA and MHL SAMs these peaks shift to lower binding energies by ~0.9 eV indicating that 1T MoS<sub>2</sub> has deposited.<sup>34</sup> Further, the photoelectron peaks can be fit to a single Gaussian-Lorentzian peak indicating that for each MoS<sub>2</sub> film there is only one polytype present. Consistent with the Mo 3d and S 2s peaks, the S 2p<sub>3/2</sub> binding energy decreases from 161.9 eV to ~161 eV for films deposited on HDT and MHA-PFP, and MHL and MHA SAMs respectively (Appendix figure A3.1).



**Figure 3.3** Mo 3d and S 2s photoelectron spectra of mechanically exfoliated MoS<sub>2</sub> films deposited on MHA, MHL, HDT and MHA-PFP SAMs. Deposition time: 24 h.

Since 2H- and 1T- MoS<sub>2</sub> are semiconducting and semi-metallic, respectively, the valence band (VB) XPS data can also be employed to distinguish between MoS<sub>2</sub> polytypes (Appendix A3.2). For MoS<sub>2</sub> deposited on –COOH terminated SAMs (MHA), there is photoelectron intensity from the Mo 4d band (VB) even at a binding energy of 0 eV which is the Fermi level of the system ( $E_F$ ). These observations indicate that the MoS<sub>2</sub> layer is metallic and is consistent with deposition of 1T MoS<sub>2</sub>. On –OH terminated SAMs (MHL) a small bandgap of 0.8 eV is observed which is also consistent with the deposition of semi-metallic 1T MoS<sub>2</sub>.<sup>52</sup> In contrast, for MoS<sub>2</sub> deposited on –CO<sub>2</sub>C<sub>6</sub>F<sub>5</sub> (MHA-PFP) terminated SAMs, the valence band maximum (VBM) is at higher binding energies than 0 eV indicating the deposit is semiconducting, ie. 2H MoS<sub>2</sub>. For MoS<sub>2</sub> deposited on HDT the VBM is at 1.30 eV which is consistent with the bandgap typically observed for multilayer 2H MoS<sub>2</sub>.<sup>28</sup> On MHA-PFP SAMs the measured VBM, 1.0 eV, is lower than expected for semiconducting 2H MoS<sub>2</sub> (Appendix figure A3.2). However, we note that for this sample, photoelectron peaks due to Au exfoliated with the sample were also observed, and the

measured VBM is likely lower due to the presence of Au under the  $MoS_2$  film. For HDT, MHL and MHA-PFP, we note that the VB spectra also show that there is a small tail in front of the valence band edge (Appendix figure A3.1) which likely arise from defect-induced gap states.<sup>28</sup>

Raman spectroscopic studies of the exfoliated MoS<sub>2</sub> films are consistent with the XPS data (Figure 3.4). There are two prominent first-order Raman active modes which correspond to the  $E_{2g}^1$  and  $A_{1g}$  modes.<sup>19, 53</sup> The in-plane  $E_{2g}^1$  mode is due to the vibration of the Mo and S atoms in opposite directions while the out-of-plane  $A_{1g}$  mode results from the symmetric vibration of S atoms along the c-axis. Additionally, in the spectra of the MoS<sub>2</sub> deposited on –COOH (MHA) and –OH (MHL) SAM substrates, there are additional weak modes in the lower frequency range suggesting the presence of 1T MoS<sub>2</sub>. These additional broad peaks centered at ~160 cm<sup>-1</sup>, ~225 cm<sup>-1</sup> and ~338 cm<sup>-1</sup> correspond to the J<sub>1</sub>, J<sub>2</sub> and J<sub>3</sub> modes which are active in 1T MoS<sub>2</sub> and not in 2H MoS<sub>2</sub>.<sup>6, 53</sup> We note that as the deposition time increases the J<sub>1</sub>, J<sub>2</sub> and J<sub>3</sub> modes become stronger in intensity (Appendix figure A3.3).



**Figure 3.4** Raman spectra of mechanically exfoliated MoS<sub>2</sub> films which were deposited on MHA, MHL, HDT and MHA-PFP SAMs. Deposition time: 24 h.

Additionally, for the –OH terminated SAMs we observe that there are some areas which are more characteristic of 2H  $MoS_2$  (data not shown). In testing sixteen areas on four different samples, which were synthesized on different days, four spots appeared to have Raman spectra characteristic of 2H  $MoS_2$  while the other areas were composed of 1T  $MoS_2$  (ie. 25% were 2H  $MoS_2$ ).

SAM terminal	$E_{2g}^1$	$A_{1g}$	$\Delta$ (cm <sup>-1</sup> )
group	(cm <sup>-1</sup> )	(cm <sup>-1</sup> )	
-CO <sub>2</sub> C <sub>6</sub> F <sub>5</sub>	381	405	24
-CH <sub>3</sub>	380	405	25
-OH	381	405	24
-СООН	381	405	24

**Table 3.2** Frequencies observed for  $E_{2g}^1$ , and  $A_{1g}$  modes, and the difference in frequency between  $E_{2g}^1$  and  $A_{1g}$  modes ( $\Delta$ ).

The frequencies observed for the  $E_{2g}^1$  and  $A_{1g}$  modes are lower than those generally reported for bulk 2H MoS<sub>2</sub> ( $E_{2g}^1 \sim 383$ cm<sup>-1</sup>and  $A_{1g} \sim 408$  cm<sup>-1</sup>) (Table 3.2). There are often slight differences in the frequencies of Raman lines due to differences in temperature, pressure, crystal size, polytype, and the number of layers in the sample.<sup>19, 53-55</sup> In agreement with the AFM data, the observed Raman shifts suggest that the films are composed of small crystallites or platelets.<sup>55</sup> We also note that the full-width-half-maximum (FWHM) of the Raman peaks are relatively broad, 8-9 cm<sup>-1</sup>, compared to other mechanically exfoliated samples.<sup>34</sup> This is also consistent with a film composed of small crystallites or platelets. The frequencies of the  $E_{2g}^1$  and  $A_{1g}$  modes can be additionally employed to estimate the thickness of the MoS<sub>2</sub> deposit. Li *et al*<sup>54</sup> reported that for mechanically exfoliated MoS<sub>2</sub> that the  $A_{1g}$  peak frequency increases from 403 cm<sup>-1</sup> for a monolayer to 407 cm<sup>-1</sup> for bulk material while the  $E_{2g}^1$  peak frequency decreases from 384 cm<sup>-1</sup> to 382 cm<sup>-1</sup>. This effect was attributed to changes in the MoS<sub>2</sub> interlayer coupling. For the deposited MoS<sub>2</sub> films the difference in the  $E_{2g}^1$  and  $A_{1g}$  peak frequencies is ~24 cm<sup>-1</sup> (Table 3.2) suggesting that the deposit is approximately 5 layers thick (~3.25 nm).<sup>14, 54</sup> In the XPS spectra for the unexfoliated MoS<sub>2</sub> samples clear signals are observed from the Au substrate, and so we can determine the maximum thickness of the MoS<sub>2</sub> films in the following way. According to the uniform overlayer model:

$$I_{Au}^{x} = I_{Au}^{0} exp\left(-\frac{x}{\cos\theta \times L_{Au}}\right)$$
3.1

where  $I_{Au}^0$  and  $I_{Au}^x$  are the Au 4f<sub>7/2</sub> peak intensities (peak areas) before and after MoS<sub>2</sub> deposition, respectively; *x* is the thickness of MoS<sub>2</sub> film;  $\theta$  is the photoelectron take-off angle with respect to the sample surface normal; and  $L_{Au}$  is the average practical effective attenuation length of Au 4f<sub>7/2</sub> photoelectrons in the MoS<sub>2</sub> overlayer. The value of  $L_{Au}$  was calculated using the TPP-2M predictive inelastic mean free path (IMFP) equation in the NIST Standard Reference Database 82<sup>56</sup> to be between 2.557 nm (bulk MoS<sub>2</sub> E<sub>g</sub> = 1.23 eV) and 2.565 nm (monolayer MoS<sub>2</sub> E<sub>g</sub> = 1.80 eV). The following values were used during calculation: electron kinetic energy = 1402.6 eV, asymmetry parameter ( $\beta$ ) = 1.04, number of valence electrons per molecule (N<sub>v</sub>) = 18,<sup>57</sup> and density = 5.06 g/cm<sup>3</sup>. After MoS<sub>2</sub> deposition, for unexfoliated samples the intensity of the Au 4f<sub>7/2</sub> photoelectron peak is ~10 % of the bare SAM samples. Assuming that the deposited MoS<sub>2</sub> forms a complete overlayer, we calculate that the films are ~4.0 nm thick (~6 layers<sup>14</sup>) which is consistent with the Raman spectroscopic data.

The data clearly show that the deposited  $MoS_2$  polytype is dependent on the chemistry of the SAM terminal group. There are two possible reasons for this behavior. First, the interaction of the precursors with the SAM terminal groups leads to the nucleation and growth of different  $MoS_2$ polytypes. Pramanik and Bhattacharya<sup>43</sup> proposed that  $MoS_2$  CBD occurs via the following reaction pathway:

$$MoO_4^{2-} + NH_2NH_2 + S^{2-} \rightarrow MoS_2 + H_2O + N_2$$

$$3.2$$

In this deposition, S<sup>2-</sup> ions are formed by the slow decomposition of thioacetamide:<sup>38</sup>

$$C_2H_5NS + OH^- \rightarrow CH_3COO^- + NH_3 + HS^-$$
3.3

$$HS^- + OH^- \rightarrow S^{2-} + H_2O \tag{3.4}$$

The above reaction suggests that molybdate ions,  $MOQ_4^{2-}$ , are reduced by hydrazine to  $Mo^{4+}$  which then react to form  $MoS_2$ . In deposition of PbS,<sup>41</sup> CdSe,<sup>40</sup> ZnO<sup>58</sup> and ZnS,<sup>42</sup> Walker and co-workers showed that the CBD reaction pathways were dependent on the terminal functional group chemistry of SAMs. On –OH and –CH<sub>3</sub> terminated SAMs deposition occurs via a cluster-by-cluster mechanism. In contrast on –COOH terminated SAMs the film growth occurs via an ion-by-ion reaction. At the typical deposition bath pHs (pH~11) the –COOH terminal functional groups are almost fully deprotonated and so the deposits nucleate at metal ion-carboxylate surface complexes.<sup>40-42, 58</sup> However, the formation of metal ion-terminal group complexes cannot explain the observed differences in the MoS<sub>2</sub> film growth. On –OH and –COOH terminated SAMs, the metastable 1T MoS<sub>2</sub> polytype deposits. While the –COOH terminal groups can deprotonate at the bath pH employed (pH~11), the –OH terminal groups do not deprotonate. The pK<sub>a</sub> of hexadecanol

is 16.2,<sup>59</sup> and surface  $pK_{\frac{1}{2}}$  values are typically 2-5 units higher than the bulk  $pK_a$  value.<sup>60</sup> Thus, the –OH terminal groups do not deprotonate and there are no metal ion-terminal group complexes present to act as the nucleation sites for deposition. Further, on MHA-PFP and HDT substrates, which also do not deprotonate and form metal-terminal group complexes, the thermodynamically stable 2H MoS<sub>2</sub> is deposited. It is therefore unlikely that the interaction of metal ions with the SAM surface leads to the deposition selectivity of the MoS<sub>2</sub> polytype.

A second reason for the observed behavior is that the surface energy of the SAMs stabilizes the metastable 1T MoS<sub>2</sub>. Small differences in surface energies are well known to drive surface reconstructions and change surface properties of metallic and semiconducting surfaces.<sup>50</sup> These changes are often caused by the adsorption, or reaction with, the surface. For MoS<sub>2</sub>, it has been shown that lithium intercalation of 2H MoS<sub>2</sub> films leads to the formation of 1T MoS<sub>2</sub>. The mechanism is believed to involve charge transfer between the Li and MoS<sub>2</sub> substrate. Voiry *et al*<sup>36</sup> demonstrated that covalent functionalization of 1T MoS<sub>2</sub> by groups such as  $-CH_3$  and  $-CH_2ONH_2$ altered its properties such that the MoS<sub>2</sub> film changed from metallic to semiconducting and exhibited photoluminescence. More recently Tang and Jiang<sup>52</sup> predicted that 1T MoS<sub>2</sub> is more stable than 2H MoS<sub>2</sub> after functionalizing the surface with ~25 % of a monolayer of small functional groups, such as H, CH<sub>3</sub>, CF<sub>3</sub>, OCH<sub>3</sub> and NH<sub>2</sub> groups. Further the bandgap of the 1T MoS<sub>2</sub> layer could be adjusted from 0 eV to 1 eV depending on the functional group chemistry.

Acid-terminated and hydroxyl-terminated alkanethiol SAMs have low water contact angles,  $\sim 0^{\circ 61}$  and  $\sim 20^{\circ 61-63}$  respectively, indicating that they are hydrophilic and have a relatively high surface energy. In contrast,  $-CH_3$  and  $-CO_2C_6H_5$  terminated SAMs have a large water contact angle,  $\sim 120^{\circ}$ ,  $^{61-63}$  and so are hydrophobic and have a lower surface energy. Our data indicates that

the more thermodynamically stable 2H  $MoS_2$  polytype is deposited on the surfaces with lower energy, ie.  $-CH_3$  and  $-CO_2C_6H_5$  terminated SAMs, while 1T  $MoS_2$  is deposited on the higher surface energy -COOH and -OH terminated SAMs suggesting that the extra surface energy stabilizes the metastable 1T  $MoS_2$  film.

To test the hypothesis that the surface energy of the substrate is critical in determining the MoS<sub>2</sub> formed using CBD at room temperature, the following test was performed. Using room temperature CBD, MoS<sub>2</sub> was synthesized on a variety of substrates. The hydrophobic (low surface energy) substrates employed were PTFE (polytetrafluoroethylene) tape, which is commonly used to seal pipe threads, and hydrogen functionalized Si (H-Si). The hydrophilic (high surface energy) substrates used were soda-lime glass slides, and a native oxide covered silicon wafer (SiO<sub>2</sub>). On the low surface energy substrates Raman spectra show that 2H MoS<sub>2</sub> is deposited (Figure 3.5a), while the high surface energy substrates Raman spectra show that 1T MoS<sub>2</sub> is synthesized (Figure 3.5b). Thus, our hypothesis that the surface energy of the substrate is critical in determining the growth of the MoS<sub>2</sub> using room temperature CBD is confirmed. Further, the effect is a general one and does not require a surface with a well-ordered and known density of functional groups.

Using the surface energy of functionalized SAMs we can estimate the difference in surface energy required to stabilize the 1T MoS<sub>2</sub> films. While there are many reported measurements of the contact angles for functionalized SAMs, there are few studies that have quantified the surface energies of SAM surfaces. Takenga *et al*<sup>64</sup> observed that the surface energies of  $CH_3(CF_2)_n(CH_2)_{12-n}SH$  SAMs decreased substantially from 19 mJ/m<sup>2</sup> for tridecanethiol ( $CH_3(CH_2)_{12}SH$ ) to ~9mJ/m<sup>2</sup> for partially fluorinated SAMs. The surface energy was observed to remain approximately constant as the number of fluorinated carbons increased from n = 4 to

n = 10. Lamprou *et al*<sup>65</sup> measured the variation of the SAM surface energies as a function of the terminal group chemistry.



**Figure 3.5** Raman spectra of mechanically exfoliated  $MoS_2$  films which were deposited on a) PTFE tape, and Si-H; and b) soda lime glass, and silicon dioxide (SiO<sub>2</sub>). Note: The  $MoS_2$  film was not exfoliated from the PTFE tape, and so exhibits a Raman scattering peak at ~300 cm<sup>-1</sup> due to the presence of PTFE. Deposition time: 24 h.

They observed that the surface energy was consistent with the nature of the  $\omega$ -functional group:  $-OH > -COOH > -CH_3 >> -CF_3$ . For well-ordered -OH and -COOH terminated SAMs, the surface energy was ~30 to ~35 mJ/m<sup>2</sup> suggesting that this is the surface energy range required

to stabilize the 1T MoS<sub>2</sub> film. We note that the MHA SAM substrates employed in this study are likely to have a higher energy than the surface energy reported by Lamprou *et al.*<sup>65</sup> For MHA, the surface  $pK_{\frac{1}{2}}$  is ~8.0, which is the pH of the solution at which a surface is 50 % ionized.<sup>60</sup> Thus at the bath pH employed (pH ~11) the –COOH terminal groups is almost fully deprotonated, i.e. the terminal functional groups are carboxylates (COO<sup>-</sup>), leading to an increased surface energy.<sup>27, 60</sup>

It is interesting to note that the RMS roughness of the deposited  $MoS_2$  films on -OH terminated SAM substrates is approximately  $10\times$  higher than the underlying SAM and is significantly higher than the other deposited  $MoS_2$  films (Table 3.1). In the Raman spectra the majority of the samples exhibit 1T  $MoS_2$  features while 25% exhibit spectra characteristic of 2H  $MoS_2$ . These observations suggest that the high film roughness for  $MoS_2$  deposited on -OH terminated SAMs is due to the formation of a mixed  $MoS_2$  polytype surface; the layer is mostly 1T  $MoS_2$  but has some areas of 2H  $MoS_2$ . Since a mixed  $MoS_2$  layer is deposited on MHL substrates, the data also suggest that the surface energy of the -OH terminated SAM, ~30 mJ/m<sup>2</sup>,<sup>65</sup> is very close to the energy required to stabilize 1T  $MoS_2$ . Thus, for surfaces with energies less than 30 mJ/m<sup>2</sup>, thermodynamically stable 2H  $MoS_2$  is deposited.

## **3.4 Conclusions**

We have investigated the room temperature chemical bath deposition of  $MoS_2$  on a variety of substrates. Our results indicate that the substrate surface energy is critical in the deposition process and controls the polytype of the  $MoS_2$  deposited. On hydrophilic surfaces, which have a high surface energy, metastable 1T  $MoS_2$  is deposited. In contrast, on low energy surfaces (hydrophobic surfaces) the thermodynamically most stable polytype 2H  $MoS_2$  is deposited. Further, this process synergistically integrates the ease of solution-based synthesis with the scalability of

lithographically defined films, and thus enables the formation of new self-aligned structures with many technological applications in sensing, optoelectronics and nanoelectronics.

# 3.5 Methods

#### 3.5.1 Materials

All materials were used as received without any further purification. Ammonium molybdate (99.98%), hexadecanethiol (HDT) (99+%), 16-mercaptohexadecanoic acid (MHA) (90%), and 16-hydroxy-1-hexadecanethiol (MHL) (99+%), dichloromethane ( $\geq$  99.5%), sulfuric acid (95 – 98%) and acetone ( $\geq$  99.5%) were purchased from Sigma-Aldrich (St. Louis, MO). 14.8 M ACS-grade ammonium hydroxide was obtained from Ward's Science+ (Rochester, NY). Hydrazine monohydrate (98+%), thioacetamide (99% ACS grade), 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) (98+%), and pentafluorophenol (99%) were acquired from Alfa Aesar, Inc. (Ward Hill, MA). Ethanol (200 proof, undenatured) was purchased from Spectrum Chemical MFG Corp (New Brunswick, NJ). Hydrofluoric acid (49%), ammonium fluoride (40%), hydrogen peroxide (30%) were acquired from J.T. Baker (Avantor, Center Valley, PA). Acetone ( $\geq$  99.5%; histological grade) and isopropyl alcohol (99.5%) were obtained from Fisher Chemical (Thermo Fisher Scientific Inc., Waltham, MA) and BDH Chemicals (VWR International LLC, Radnor, PA) respectively.

PTFE thread seal tape (MIL SPEC. T -27730A;  $\frac{1}{2}$ ") was purchased from Home Depot. VistaVision<sup>TM</sup> soda lime glass microscope slides (75 × 25 × 1 mm<sup>3</sup>) and methanol (≥ 99.8%) were obtained from VWR International, LLC (Radnor, PA). Prior to use microscope slides were cut using a diamond scribe, rinsed in deionized water and then isopropyl alcohol, and dried using nitrogen gas. Additional methanol (99.8 %) was purchased from Macron Chemicals (Avantor, Center Valley, PA).

The gold substrates used in these studies were prepared in the Cleanroom Research Laboratory, University of Texas at Dallas. Briefly, silicon wafers ( $\langle 111 \rangle$  orientation) were acquired from Addison Engineering Inc. (San Jose, CA), and ~200 Å of chromium followed by ~1000 Å of gold were thermally deposited onto these substrates.

Native silicon oxide samples were prepared using silicon wafers ( $\langle 111 \rangle$  orientation; Addison Engineering Inc.). The wafer samples were sonicated for 10 min in acetone, and then thoroughly rinsed using methanol and followed by deionized water. The substrates were then dried using N<sub>2</sub> gas.

Hydrogen terminated silicon was prepared by using previously described methods.<sup>66</sup> Briefly, n-type silicon wafers (phosphorus-doped, resistivity 20-60  $\Omega$  cm; float zone; (111) orientation; Silicon Valley Microelectronics Inc. , Santa Clara, CA) were cut into ~(1.5 × 3.8) cm<sup>2</sup> pieces. The samples were then sonicated in dichloromethane, acetone and methanol for 10 min each, and then left in deionized water overnight. Afterwards, the silicon samples were cleaned at 80 °C in a Piranha etch bath (3:1 H<sub>2</sub>SO<sub>4</sub>: H<sub>2</sub>O<sub>2</sub>) for 30 minutes. Finally, Si was dipped in 49% hydrofluoric acid for 30 s and then ammonium fluoride for 2.5 min at room temperature. To ensure that the SiO<sub>2</sub> layer was fully reacted to Si-H, IR spectra of the silicon wafers was obtained before and after the HF/ammonium fluoride treatment.

# 3.5.2 Preparation of Self-Assembled Monolayers

The preparation of alkanethiolate self-assembled monolayers (SAMs) on Au has been previously described in detail.<sup>67, 68</sup> Briefly, a well-ordered SAM is prepared by immersing a gold substrate

into a 1 mM solution of desired alkanethiol (MHL, MHA or HDT) in ethanol for 24 hours at room temperature. The samples were then rinsed with ethanol and dried with nitrogen gas.

Preparation of perfluorinated MHA SAMs (MHA-PFP) on Au has previously been described in detail.<sup>69</sup> First, a MHA SAM on Au is prepared. The sample is then immersed in an isopropanol solution containing 0.1 M EDC and 0.2 M PFP. After 5 hours the substrate is removed from the reaction solution, thoroughly rinsed with deionized water and ethanol, and then dried with nitrogen gas.

After preparation, the SAM substrates were characterized using methods including single wavelength ellipsometry, time-of-flight secondary ion mass spectrometry and x-ray photoelectron spectroscopy.

## 3.5.3 Chemical Bath Deposition of Molybdenum Disulfide

The CBD of the MoS<sub>2</sub> films was adapted from the method reported by Pramanik and Bhattacharya.<sup>43</sup> First an aqueous solution containing 5% ammonium molybdate in 10 mL of water was prepared and stirred continuously while the other reagents were prepared. Next, 15 mL of 14.8 M ammonium hydroxide followed by 10 mL of 80% hydrazine hydrate were added to the solution. Finally, 15 mL of 1M thioacetamide was added. The deposition bath was then stirred for 2 minutes before immersing the substrate into solution. The sample was placed facing upwards in the deposition bath for the desired deposition time, usually ~24 hours. After deposition the samples were removed and washed with deionized water and dried with nitrogen gas prior to further characterization. All depositions were carried out at room temperature,  $21\pm2$  °C.

## **3.5.4 Optical Microscopy**

Optical microscopy was performed using a Keyence VHX-2000 digital microscope. Bright-field images were obtained from representative samples with 2500× magnification. The images shown are representative of the data obtained.

#### **3.5.5 Atomic Force Microscopy**

Atomic force microscope (AFM) measurements were collected using tapping mode of a Nanoscope Dimension 3100 microscope (Veeco Instruments, Inc., Plainview, NY). The images were processed using Gwyddion 2.50. The RMS roughness was obtained over  $(1 \times 1) \mu m^2$  from at least 3 different areas, and the data reported is the average of those measurements.

# **3.5.6 X-ray photoelectron Spectroscopy**

Ex-situ X-ray photoelectron spectroscopy (XPS) were measured using a PHI VersaProbe II Scanning XPS Microbrobe (Physical Electronics Inc., Chanhassen, MN) equipped with a monochromatic Al K $\alpha$  X-ray source (E<sub>p</sub> = 1486.7 eV). During measurement, the pressure was lower than 6.7 × 10<sup>-10</sup> mbar. High resolution spectra were collected with pass energy of 23.5 eV, energy step of 0.2 eV, and analysis angle of 45°. All spectra were collected using a charge compensation system with both electron and ion beams incident on the surface. The binding energies were calibrated using the C 1s binding energy (284.8 eV).<sup>70</sup> Spectra were analyzed using CasaXPS 2.3.17 (RBD Instruments, Inc., Bend, OR) and AA Analyzer 1.07.

## **3.5.6 Raman Spectroscopy**

Raman spectra were collected using a Thermo Scientific DXR Raman microscope equipped with a 532 nm diode laser and a  $50 \times$  objective lens. Measurements were collected with a laser power 0.3 mW through a 25 µm slit aperture, and the estimated laser spot size is 0.7 µm. The Raman
shifts were calibrated using the peak shift frequency of Si, 521 cm<sup>-1</sup>.<sup>71</sup> To reduce fluorescence,

"fluorescence correction" was employed.

# **3.6 References**

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#### **CHAPTER 4**

## FACILE ONE-POT SYNTHESIS OF MOLYBDENUM DISULFIDE: ROOM TEMPERATURE CHEMICAL BATH DEPOSITION

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## 4.1 Abstract

We have developed a facile, one-pot synthesis method for the chemical bath deposition of molybdenum disulfide at room temperature. We employ ammonium molybdate, thioacetamide and hydrazine under basic conditions. On highly oriented pyrolytic graphite (HOPG) substrates, the deposited molybdenum disulfide flakes are very large, ~100  $\mu$ m in width, and are 2H MoS<sub>2</sub>. We have investigated the reaction pathways involved using infrared spectroscopy, Raman spectroscopy, optical microscopy and time-of-flight secondary ion mass spectrometry. Our data indicates that hydrazine plays two critical roles in the MoS<sub>2</sub> deposition reaction. First, it reacts with thioacetamide to form hydrogen sulfide. The generated hydrogen sulfide reacts with the molybdate ions present in the solution leading to the formation of thiomolybdate. Second, hydrazine reduces the Mo(VI) species in the thiomolybdate ions to Mo(IV) in molybdenum sulfide.

#### **4.2 Introduction**

Molybdenum disulfide, MoS<sub>2</sub>, has applications in diverse fields from lubrication<sup>1, 2</sup> to catalysis<sup>3-6</sup> to electronics.<sup>5, 7</sup> This is due to the layered structure of 2H MoS<sub>2</sub>, which is the thermodynamically most stable form. Each layer is composed of S-Mo-S stacks, and within a layer the Mo atoms are surrounded by six sulfur atoms. The layers are connected by weak van der Waals interactions which enables the intercalation of hetero-atoms, such as Li, which enables its ability

to act as the cathode for solid state lithium ion batteries.<sup>3</sup> Molybdenum disulfide is also an efficient catalyst for both hydrogenation,<sup>6</sup> hydrogenolysis<sup>8</sup> and hydrodesulfurization.<sup>8-10</sup> The catalytic activity of MoS<sub>2</sub> has been demonstrated to be dependent on the particle size i.e. the number of Mo edge atoms where sulfur vacancies can form, and on the number of MoS<sub>2</sub> layers.<sup>6, 8-10</sup> For electronic devices 2H MoS<sub>2</sub> possesses many advantages. It is a semiconductor which is dependent on the number of layers in the materials. Single-layer MoS<sub>2</sub> has a direct bandgap of ~1.8 eV<sup>5, 11</sup> while the bulk bandgap is indirect and is ~1.2 eV.<sup>12</sup> This enables the further tuning of materials properties and enables the use of MoS<sub>2</sub> in electronics as well as optoelectronics.<sup>13</sup>

Chemical vapor deposition (CVD) methods are often employed to deposit MoS<sub>2</sub> on a wafer scale but these methods require vacuum equipment, are limited by the wafer size and often require high temperatures.<sup>5, 7, 14</sup> Alternatively, methods such as micromechanical and chemical exfoliation of MoS<sub>2</sub> are employed but it can be difficult to produce large area films with precise placement.<sup>15</sup> Solution-based deposition methods are attractive because they are low cost, and can be used to deposit films over large areas with precise placement.<sup>7, 16, 17</sup> Further, such methods are compatible with thermally sensitive substrates such as organic thin films used in flexible electronics.<sup>18</sup>

For catalytic and energy applications, free-standing nanoflakes are often synthesized using the thermal decomposition of ammonium tetrathiomolybdate at 300 - 400 °C:<sup>10, 15, 19</sup>

$$(NH_4)_2MoS_4 + H_2 \rightarrow MoS_3 + H_2S + 2NH_4$$

$$4.1$$

$$MoS_3 + H_2 \rightarrow MoS_2 + H_2S$$
 4.2

Similarly, in aqueous solutions amorphous  $MoS_3$  can be produced by reaction of ammonium thiomolybdate with  $H^+$ :<sup>8</sup>

$$MoS_4 + 2H^+ \rightarrow MoS_3 + H_2S \tag{4.3}$$

The resulting MoS<sub>3</sub> is then subsequently annealed at ~623 K – 673 K to produce MoS<sub>2</sub>. To lower the reaction temperature, Afanasiev and co-workers<sup>8</sup> demonstrated that ammonium thiomolybdate was reduced by hydrazine under reflux conditions for 6h to produce MoS<sub>2</sub>. In later experiments, Li *et al*<sup>6</sup> used a hydrothermal process by which to synthesize MoS<sub>2</sub> by forming ammonium molybdate *in situ* via the reaction of ammonium heptamolybdate with H<sub>2</sub>S.

On surfaces, chemical bath deposition (CBD) is often used to deposit inorganic chalcogenides, oxides and other materials.<sup>6</sup> It is generally described as an ion exchange reaction in which the deposition rate is controlled by the concentration of the "free" metal ion. There have been several methods developed to deposit MoS<sub>2</sub> thin films using CBD. Generally two approaches are taken. First, ammonium thiomolybdate is employed as a single source precursor, and hydrazine is employed to reduce the Mo(VI) species in (NH)<sub>4</sub>MoS<sub>4</sub> to Mo(IV) in MoS<sub>2</sub>.<sup>3,7</sup> Second, ammonium paramolybdate is as the molybdenum precursor, and reduced to form MoS<sub>2</sub> using either H<sub>2</sub>S, formed by the decomposition of Na<sub>2</sub>S,<sup>7</sup> or HS<sup>-</sup>, formed by reaction of thioacetamide with hydrazine.<sup>20</sup> However, these methods have a number of disadvantages. Ammonium thiomolybdate is unstable and must be stored in an inert atmosphere.<sup>21</sup> Second many of these CBD methods require relatively high temperatures.<sup>7, 20</sup>

In this work, we report a facile, one-pot CBD method by which to deposit large-area  $MoS_2$  at room temperature. The resulting  $MoS_2$  flakes deposited on highly oriented pyrolytic graphite (HOPG) surfaces are 2H MoS<sub>2</sub> and are very large (~100 µm in width). We employ ammonium molybdate as the molybdenum source and thioacetamide as the sulfur source. Under basic conditions, we demonstrate that thioacetamide can be reduced to form H<sub>2</sub>S which subsequently reacts with ammonium molybdate to form ammonium thiomolybdate *in situ*. Subsequently,

hydrazine reduces the ammonium molybdate to molybdenum disulfide. Our results suggest that other metal sulfides and chalcogenides can be deposited by CBD at room temperature, which have not previously been synthesized, using similar approaches.

#### 4.3 Experimental

### 4.3.1 Materials

All chemicals were used as received without further purification. Hydrazine monohydrate (98+%), thioacetamide (99% ACS grade), and highly oriented pyrolytic graphite (HOPG) (10x10x1 mm) were acquired from Alfa Aesar, Inc. (Ward Hill, MA). Ammonium hydroxide (14.8 M ACS) was purchased from Ward's Science+ (Rochester, NY). Ammonium molybdate 99.98% was acquired from Sigma Aldrich (St. Louis, MO).

## 4.3.2 Chemical Bath Deposition

The CBD of the MoS<sub>2</sub> films was based on the method reported by Pramanik and Bhattacharya.<sup>20</sup> First an aqueous solution containing 5% ammonium molybdate in 10 mL of water was prepared and stirred continuously while the other reagents were prepared. Next, 15 mL of 14.8 M ammonium hydroxide followed by 10 mL of 80% hydrazine hydrate were added to the solution. Finally, 15 mL of 1M thioacetamide was added. The deposition bath was then stirred for 2 minutes before immersing the substrate into solution. The sample was placed facing upwards in the deposition bath for the desired deposition time, usually ~24 hours. After deposition the samples were removed and washed with deionized water and dried with nitrogen gas prior to further characterization. All depositions were carried out at room temperature,  $21\pm2$  °C.

#### 4.3.3 Attenuated Total Reflectance Infrared Spectroscopy (ATR IR)

ATR IR spectra were collected using a Nicolet iS50 FTIR spectrometer (Thermo Scientific, Madison WI) equipped with a horizontal ATR sampling accessory. For each measurement, a 10µL droplet of the prepared solution was pipetted onto the ATR crystal. The resulting spectra were analyzed using OMNIC (Thermo Scientific, Madison WI). To remove the water and hydrazine absorbances, the spectra reported are referenced to the IR spectrum of an aqueous hydrazine hydrate solution.

The solutions for the ATR IR studies were prepared at the reactant concentrations used in the deposition. The "deposition solution" contains all reagents, was prepared as described in section 2.2, and measured approximately 24 hours after the solution was prepared. Solution 1 was prepared in a similar manner but the thioacetamide was omitted. Solutions 2 and 3 also were prepared using the method described in section 2.2 but in this case the ammonium molybdate was omitted. Solution 1 and the yellow solution 2 were analyzed ~24 hours after preparation. Solution 3, which was pink, was prepared 48 hours in advance of the spectrum acquisition.

### 4.3.4 Optical Microscopy, Atomic Force Microscopy and Scanning Electron Microscopy

Optical images of the deposition solution and solutions 1-3 were obtained using a cellular telephone camera (iPhone model SE).

Atomic force microscopy (AFM) measurements were collected using tapping mode of a Nanoscope Dimension 3100 microscope (Veeco Instruments, Inc., Plainview, NY). The images were processed and analyzed using WSxM 5.0.<sup>22</sup> The RMS roughness was obtained over (10 × 10)  $\mu$ m<sup>2</sup> from at least 3 different areas, and the data reported is the average of those measurements.

Scanning electron microscopy (SEM) images measurements were obtained using a Supra-40 SEM (Carl Zeiss SMT Inc., Peabody MA). To prevent sample charging, prior to analysis the sample was sputter coated with a thin layer of gold (~60Å) using a Hummer VI plasma sputter system (Anatech USA, Hayward CA) to prevent sample charging. The resulting images were analyzed using ImageJ 1.50i (National Institutes of Health, USA).<sup>23</sup>

### 4.3.5 Raman Spectroscopy

Raman spectra were collected using a Thermo Scientific DXR Raman microscope equipped with a 532 nm diode laser and a 50× objective lens. Measurements were collected with a laser power 1.0 mW through a 25  $\mu$ m slit aperture, and the estimated laser spot size is 0.7  $\mu$ m. The Raman shifts were calibrated using the peak shift frequency of Si, 521 cm<sup>-1</sup>.<sup>24</sup> To reduce fluorescence, "fluorescence correction" was employed.

### **4.3.6 X-ray Photoelectron Spectroscopy**

X-ray photoelectron spectra (XPS) was collected using a PHI VersaProbe II (Physical Electronics, Inc., Chanhassen, Minnesota) equipped with a monochromatic Al K $\alpha$  source (E = 1486.8 eV). During data collection, the chamber pressure was maintained below 6.7 x 10<sup>-10</sup> mbar. High resolution spectra were collected with a pass energy of 23.5 eV, an energy step of 0.2 eV, analysis area (100 × 100) $\mu$ m<sup>2</sup>, and an analysis angle of 45°. Several samples were sputtered using 1 keV Ar<sup>+</sup> in a (1 x 1) mm<sup>2</sup> area before analysis. All spectra were collected using a charge compensation system with both electron and ion beams incident on the surface. Peak fitting and analysis were done using CasaXPS Version 2.3.17PR1.1 (Casa Software Ltd, (RBD Instruments, Inc., Bend, Oregon)). The binding energies were calibrated using the C 1s binding energy (284.7 eV).<sup>25</sup>

### 4.3.7 Time-of-Flight Secondary Ion Mass Spectrometry

Time-of-flight secondary ion mass spectrometry (TOF SIMS) data were collected using an ION TOF IV instrument (ION TOF Inc., Chestnut Hill NY) equipped with a  $Bi_n^{m+}$  (n = 1-7, m = 1,2) liquid metal ion gun. There are three chambers: a load lock, preparation chamber and analysis chamber. During data collection, the pressure of the analysis chamber was  $\leq 5 \times 10^{-9}$  mbar. The Bi<sup>+</sup> primary ions has a kinetic energy of 25 keV, and were contained in a ~100 nm probe beam. The analysis area was (100 × 100)µm<sup>2</sup>. The data were acquired in the static SIMS regime, and three spectra were collected from three separate areas to ensure the spectra were representative of the sample.

### 4.4 Results and Discussion

After 27 h deposition at room temperature, x-ray photoelectron and Raman spectra indicate that  $MoS_2$  has deposited on HOPG. In the photoelectron spectra between 224 eV and 235 eV, we observe three peaks at 226.4 eV, 229.8eV and 232.9 eV which correspond to S 2s, Mo  $3d_{5/2}$  and Mo  $3d_{3/2}$  of 2H MoS<sub>2</sub> (Figure 4.1a).<sup>26</sup> Further the intensities of the Mo 3d and S 2s photoelectron peaks indicate that the film is composed of MoS<sub>2</sub> within experimental error. In the Raman spectra we observe two peaks at 382 cm<sup>-1</sup> and 406 cm<sup>-1</sup> which are assigned to the  $E_{2g}^1$  and  $A_{1g}$  modes of 2H MoS<sub>2</sub> (Figure 4.1b).<sup>26-30</sup>



Figure 4.1 a) Mo 3d and S 2s photoelectron spectra and b) Raman spectrum of  $MoS_2$  after deposition on HOPG for 27 h at room temperature.

Scanning electron microscopy (SEM) images show that the deposited MoS<sub>2</sub> film is composed of large flakes (Figure 4.2). The flakes are approximately 100  $\mu$ m in width and have an average area of 750  $\mu$ m<sup>2</sup> (N = 274). AFM analyses show that the rms roughness of the deposited film is ~4.2 nm (~6 MoS<sub>2</sub> layers<sup>5</sup>) (see Appendix Figure A4.1). We note that the flake size is likely constrained by strain induced by the lattice mismatch between HOPG and MoS<sub>2</sub> as well as the presence of grain boundaries.<sup>31, 32</sup>



Figure 4.2 SEM image of MoS<sub>2</sub> after deposition on HOPG for 27 h at room temperature.

# 4.4.1 Film Formation and Reaction Mechanism

Upon addition of thioacetamide to a bath containing ammonium molybdate and hydrazine, the solution changes from colorless to yellow in the first two minutes. After 1h the solution is orange, and after 2h the deposition bath is dark red/black and opaque. The formation of gas bubbles is also observed. The color changes in the bath suggest that during the deposition there is formation of the red thiomolybdate anion,  $MoS_4^{2,3}$  and the formation of insoluble products such as  $MoS_2$ .



Figure 4.3 Optical image of the deposition bath after reaction for 2h.

To further investigate the  $MoS_2$  deposition mechanism, the role of hydrazine was investigated in the reduction of Mo(VI) (in  $(NH_4)_2MoO_4$ ) to Mo(IV) (in  $MoS_2$ ). Pramanik and Bhattacharya<sup>20</sup> suggested that hydrazine reduces  $MoO_4^{2-}$  to  $Mo^{4+}$  via:

$$(NH_4)_2MoO_4 + N_2H_4 + 4H_2O \rightarrow 2Mo^{4+} + N_2 + 12 OH^{-}$$
 4.4

We prepared a solution containing ammonium molybdate and hydrazine at pH 11 (ie. the deposition bath without thioacetamide) (solution 1). No color changes nor gas bubbles were observed indicating that a reaction did not occur. Further, upon lowering or increasing the pH of the solution, no reaction was observed.

Next the reaction of hydrazine with thioacetamide was investigated at pH 11 (ie. the deposition bath without ammonium molybdate) (Figure 4.4). Initially, the solution was colorless but over 3h changed to yellow (solution 2). Gas bubbles were also observed to form. After 18h, the solution color changed from yellow to orange and after 25 h again changed from orange to red. The red solution (solution 3) was stable at room temperature for 2 weeks indicating that the reaction product is stable. These observations suggest that a critical step in the deposition mechanism is the reaction of thioacetamide with hydrazine, and that there is a by-product formed which has a red color.



**Figure 4.4** Optical images of the reaction of hydrazine with thioacetamide at room temperature and different reaction times: a) 3.5 min; b) 1 h; c) 3 h; d) 18h; e) 25 h; and f) 42 h.

To identify the species present in the deposition bath, we employed ATR-IR spectroscopy of the solutions 1-3 and the deposition bath, and Raman spectroscopy and mass spectrometry of the precipitates formed. Figure 4.5 displays the ATR-IR spectra of the deposition bath and solutions 1-3. In all spectra (Figure 4.5a) we observe a peak at ~1114 cm<sup>-1</sup> which is a characteristic vibration of NH<sub>4</sub><sup>+</sup> from ammonium hydroxide.<sup>33</sup> In the deposition bath and solution 1 there is a relatively broad peak at ~828 cm<sup>-1</sup> which we assign to the Mo-O stretch modes of ( $v_s$ (M-O) 833 cm<sup>-1</sup> and  $v_{as}$ (M-O) 798 cm<sup>-1</sup>) of MoO<sub>4</sub><sup>2-10</sup> We note that the intensity of the peak is much larger in solution 1 than in the deposition bath suggesting that the molybdate ion is reacting to form thiomolybdate ions and MoS<sub>2</sub>. The modes associated with the Mo-S vibrations are too low in frequency to be detected in the ATR IR instrument.<sup>9, 10</sup> In the deposition bath, and solutions 2 and 3 vibrational modes characteristic of thioacetamide are observed including at 996 cm<sup>-1</sup> and 659 cm<sup>-1</sup> which are assigned to v(C-C)+r(CH<sub>3</sub>)+v(C-S), and w(NH<sub>2</sub>) and t(NH<sub>2</sub>).<sup>34, 35</sup>

At higher frequencies, further information about the reactants and products are obtained (Figure 4.5b). For all solutions, there are broad peaks at ~1455 cm<sup>-1</sup> and 1610 cm<sup>-1</sup> which are assigned to a deformation mode of  $NH_4^+$  and an N-H bending mode, respectively.<sup>33</sup> These peaks are expected because there is both ammonium hydroxide and ammonium molybdate in the solutions. In most CBD reactions under basic conditions, thioacetamide decomposes to form acetate and bisulfide ions:<sup>16</sup>

$$C_2H_5NS + 2OH^- \rightarrow CH_3COO^- + NH_3 + HS^-$$

$$4.5$$

However, this reaction does not appear to be occurring because there is no strong absorbance observed at ~1578 cm<sup>-1</sup>, which is characteristic of the acetate ion,<sup>36</sup> or H-S str. (2600 - 2550 cm<sup>-1</sup>; weak) (data not shown) present in the spectra.<sup>37</sup> Rather we observe peaks at ~1394 cm<sup>-1</sup>,

1548 cm<sup>-1</sup> and 1630 cm<sup>-1</sup> in the deposition bath, and solutions 2 and 3. We assign these to a C-H deformation mode, a N=C-N ring mode, and  $\delta$ (NH<sub>2</sub>) combination mode respectively.<sup>38, 39</sup>



**Figure 4.5** ATR IR spectra of the deposition bath and solutions 1-3 from a)  $500 - 1800 \text{ cm}^{-1}$  and b)  $1250 - 1800 \text{ cm}^{-1}$ . The "deposition solution" contains all reagents and was measured approximately 24 hours after the solution was prepared. Solution 1 contains ammonium molybdate, hydrazine and ammonium hydroxide. Solutions 2 and 3 contain thioacetamide, hydrazine and ammonium hydroxide. The spectra of solutions 1 and 2, which is yellow, were obtained ~24 h reaction time. The spectrum of solution 3, which is pink, was obtained ~48h reaction time.

These observations suggest that a cyclic nitrogen-containing product is formed, and that the reaction between thioacetamide and hydrazine is critical in the  $MoS_2$  deposition process. Further, the data suggest that a triazole is produced.<sup>38, 39</sup>

After MoS<sub>2</sub> deposition, the excess precipitate (black/dark red color) was filtered from the deposition bath and dried in air. Subsequently the chemistry of the precipitate was investigated using Raman spectroscopy and TOF SIMS. The Raman spectra show characteristic features of molybdenum oxides and triazoles (Figure 4.6). We assign the mode at ~663 cm<sup>-1</sup> to the out-of-plane ring torsion mode of triazoles,<sup>38, 40-42</sup> while the peaks at 987 cm<sup>-1</sup> and 996 cm<sup>-1</sup> are characteristic of the in-plane ring deformation modes of triazoles.<sup>38, 43, 44</sup> The broad modes centered at ~815 cm<sup>-1</sup> (802 – 836 cm<sup>-1</sup>) and at ~375 cm<sup>-1</sup> are consistent with the presence of molybdenum oxides are likely to form part of the ark red/black precipitate for two reasons. First, there may be some unreacted ammonium molybdate in the deposition bath. Second, it is likely that any MoS<sub>2</sub> present in the precipitate oxidized to molybdenum oxide during the air drying process.



**Figure 4.6.** Raman spectrum of the dark red/black precipitate obtained from the deposition bath after reaction for 48 h at room temperature.

The TOF SIMS spectra confirm the presence of molybdenum oxides in the precipitate. In the negative ion spectra, we observe ions of the form  $Mo_xO_y^-$  and  $Mo_xS_y^-$  indicating that molybdenum oxides and sulfides are present (Figure 4.7a). Additionally, in the positive ion spectra we observe ions which are characteristic of triazole species (Figure 4.7b).



**Figure 4.7** a) Negative ion spectra centered at m/z 313 and b) positive ion spectra from m/z 2 – 120 of the dark red/black precipitate obtained from the deposition bath after reaction for 48 h at room temperature. In (a), the predicted isotope distributions of  $(MoS_2)_2^-$ ,  $Mo_2O_7^-$  and  $(MoO_4)_2^-$  are also shown for reference. In (b) M is 4-amino-4*H*-1,2,4-triazole, C<sub>2</sub>H<sub>4</sub>N<sub>4</sub> m/z 84.04.

We note that after reaction of hydrazine with thioacetamide at 50 °C for several days, King and Anson<sup>46</sup> observed the formation of a red precipitate which they identified as 4-amino-3,5-

dimethyl-1,2,4-triazole (N'-aminotriazole). The formation of N'-aminotriazole is consistent with both the Raman and SIMS spectra of the dark red/black precipitate formed in this reaction.

Taken together the data suggest that the following reaction mechanism is occurring. Under basic conditions, thioacetamide reacts with hydrazine to form N'-aminoethanimidamide and hydrogen sulfide. The N'-aminoethanimidamide undergoes a cyclization reaction followed by dehydration to yield the red by-product, N'-aminotriazole (scheme 4.1). We note that the formation of N'-aminotriazole is also consistent with the XPS analyses of the deposited film which show that there is a N-containing species deposited on the HOPG surface as well as  $MoS_2$ . This product can easily be removed by  $Ar^+$  sputtering (see Appendix Figure A4.2).



Scheme 4.1. Cyclization and dehydration reaction of N'aminoethanimidamide to form N'-aminotriazole.

The generated H<sub>2</sub>S reacts with ammonium molybdate to form ammonium thiomolybdate:

$$(NH_4)_2MoO_4 + 4H_2S \rightarrow (NH_4)_2MoS_4 + 4H_2O$$

$$4.6$$

The reaction of molybdate ( $MoO_4^{2-}$ ) or paramolybdate ( $Mo_7O_{24}^{6-}$ ) ions with gaseous H<sub>2</sub>S to form thiomolybdate ions ( $MoS_4^{2-}$ ) is well known.<sup>2, 3, 6, 47</sup> Thiomolybdate ions are also red, and this may explain the observation that the deposition bath turns red faster than a solution containing thioacetamide and hydrazine alone. Once ammonium molybdate has formed, it is reduced by hydrazine to form  $MoS_2$ :<sup>7, 8</sup>

$$(NH_4)_2MoS_4 + \frac{1}{2}N_2H_4 \rightarrow MoS_2 + \frac{1}{2}N_2 + (NH_4)_2S + H_2S$$
4.7

The gaseous  $H_2S$  can further react with ammonium molybdate to form ammonium thiomolybdate and  $MoS_2$ . Consistent with the experimental observations and chemical characterization, overall the reaction yields a  $MoS_2$  deposit, a red by-product N'-aminotriazole as well as the gaseous products  $H_2S$  and  $N_2$ , and aqueous ( $NH_4$ )<sub>2</sub>S.

#### 4.5 Conclusions

We have demonstrated a simple one-pot, room temperature method by which to grow large-area 2H MoS<sub>2</sub> flakes on HOPG. The data indicate that ammonium molybdate is reduced to MoS<sub>2</sub> by first reacting with  $H_2S$  to form ammonium thiomolybdate. The  $H_2S$  is generated *in situ* by the reaction of thioacetamide and hydrazine under basic conditions. The intermediate species, ammonium thiomolybdate, is then reduced to MoS<sub>2</sub> by hydrazine. These results suggest that other metal sulfides and chalcogenides can by synthesized at room temperature using similar approaches.

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#### CHAPTER 5

# CHEMICAL BATH DEPOSITION OF MOLYBDENUM DISULFIDE ON MICROPATTERNED SELF-ASSEMBLED MONOLAYERS: AREA SELECTIVE DEPOSITION

## **5.1 Introduction**

Facile area-selective deposition to produce precisely deposited thin films and nanostructures are attractive fabrication routes to create self-aligned gate structures,<sup>1-2</sup> memory devices,<sup>3</sup> and flexible electronics.<sup>4</sup> Solution based methods such as chemical bath deposition (CBD) and electroless deposition have previously been reported to selectively deposit materials to create useful semiconductor and metal contacts onto organic substrates.<sup>5-9</sup> These solution-based techniques are attractive because they are low-cost methods because they are performed under ambient conditions without the need for vacuum equipment.

In chapter 3 we demonstrated that polytype selective deposition is achieved by choosing low surface energy or high surface energy substrates to yield 2H or 1T MoS<sub>2</sub>. In this chapter we show that by using CBD the 2H and 1T MoS<sub>2</sub> can be spatially selectively deposited on micropatterned alkanethiolate self-assembled monolayers (SAMs). Patterned SAMs can be prepared by a variety of methods, and serve as useful substrates to investigate area-selective deposition.<sup>10</sup>

In this chapter, MoS<sub>2</sub> CBD is investigated on patterned –COOH/–CH<sub>3</sub> or –OH/–CH<sub>3</sub> SAM surfaces using Raman spectroscopy and x-ray photoelectron spectroscopy (XPS). Both the Raman and XPS spectra indicate that there are strong interactions between the Au substrate and the deposited MoS<sub>2</sub> film. These are known for Au nanoparticle and film deposition on MoS<sub>2</sub> films.<sup>11-</sup>

behavior and that the interaction of 1T MoS<sub>2</sub> with Au may be stronger than for 2H MoS<sub>2</sub>. Such interactions are likely to have important effects on the development of devices using MoS<sub>2</sub>. For example, modifying the in-plane lattice parameter of MoS<sub>2</sub> by as few as 1% alters the band gap by 0.1 eV.<sup>16</sup> Similarly, applying tensile strain of up to ~5% reduces the band gap by nearly 1 eV.<sup>16</sup>

Further, we also demonstrate for the first time that CBD can be employed to areaselectively deposit 1T MoS<sub>2</sub> and 2H MoS<sub>2</sub> on patterned substrates. Using Raman mapping in the –COOH and –OH terminated SAM areas we observe the deposition of 1T MoS<sub>2</sub> while on –CH<sub>3</sub> terminated SAMs we observe the deposition of 2H MoS<sub>2</sub>. The results suggest that CBD can be employed to create self-aligned transition metal dichalcogenide structures.

### **5.2 Experimental**

### **5.2.1 Sample Preparation**

Ammonium molybdate (99.98%), hexadecanethiol (HDT) (99+%), 16-mercaptohexadecanoic acid (MHA) (90+%), and 16-hydroxy-1-hexadecanethiol (MHL) (99+%) were purchased from Sigma-Aldrich (St. Louis, MO). 14.8 M ammonium hydroxide was acquired from Ward's Science+ (Rochester, NY). Thioacetamide (99% ACS grade), hydrazine hydrate (98+%), were acquired from Alfa Aesar, Inc. (Ward Hill, MA). Undenatured USP 200 proof dehydrated alcohol (ethanol) was acquired from Spectrum Chemical MFG CORP.

The gold substrates used in these studies were prepared in the Cleanroom Research Laboratory, University of Texas at Dallas. Briefly, silicon wafers ( $\langle 111 \rangle$  orientation) were acquired from Addison Engineering Inc. (San Jose, CA), and ~200 Å of chromium followed by ~1000 Å of gold were thermally deposited onto these substrates.

#### 5.2.2 Preparation of Self-Assembled Monolayers and UV-Photopatterning

The preparation of alkanethiolate self-assembled monolayers (SAMs) on Au has been previously described in detail.<sup>17-18</sup> Briefly, a well-ordered SAM is prepared by immersing a gold substrate into a 1 mM solution of desired alkanethiol (MHL, MHA or HDT) in ethanol for 24 hours at room temperature. The samples were then rinsed with ethanol and dried with nitrogen gas.

The MHL and MHA SAMs were then photopatterned using the procedures described by Zhou and Walker.<sup>17</sup> A mask (copper TEM grid of the appropriate pattern; Electron Microscopy Inc., Hatfield, PA) was placed on top of the MHL or MHA SAM. The sample was then placed approximately 50 mm from a 500 W Hg arc lamp equipped with a narrow band-pass UV filter (280 to 400 nm) and a dichroic mirror (Thermal Oriel, Spectra Physics Inc., Stratford, CT). To ensure that photooxidation was complete the MHL or MHA SAM was then exposed to the UV light for 2 hours. After photopatterning the SAM was rinsed with ethanol and then placed in a 1 mM ethanolic solution of HDT for 24 hours at room temperature. In the areas exposed to UV light the photooxidized MHL or MHA was displaced by a HDT creating a patterned –OH/–CH<sub>3</sub> or – OH/–CH<sub>3</sub> SAM surface. The samples were then washed with ethanol, dried with N<sub>2</sub> gas, and used immediately for deposition.

### 5.2.3 Chemical Bath Deposition of MoS<sub>2</sub>

Chemical bath deposition (CBD) of  $MoS_2$  was carried out using the method described in chapters 2 and 3. An aqueous solution containing 5% ammonium molybdate in 10 mL of water was prepared and stirred continuously while the other reagents were prepared. Next, 15 mL of 14.8 M ammonium hydroxide followed by 10 mL of 80% hydrazine hydrate were added to the solution. Finally, 15 mL of 1M thioacetamide was added. The deposition bath was then stirred for 2 minutes

before immersing the substrate into solution. The sample was placed facing upwards in the deposition bath for the desired deposition time, usually ~24 hours. After deposition the samples were removed and washed with deionized water and dried with nitrogen gas prior to further characterization. All depositions were carried out at room temperature,  $21\pm2$  °C

#### **5.2.4 Raman Spectroscopy and Mapping**

Raman maps and spectra were collected using a Thermo Scientific DXR Raman microscope (Thermo Scientific, Madison WI) equipped with a 532 nm laser source and a 50× objective lens. Raman spectra and maps were collected with laser powers of 1.0 mW and 0.3 mW, respectively, through a 25 $\mu$ m slit aperture. The maps were generated by collecting spectra at 10  $\mu$ m interval distances over the edge of a patterned sample area. In order to reduce fluorescence and photobleaching effects from the sample, fluorescence correct was turned on during collection and photobleaching was employed for 0.5 minutes prior to spectral collection. Additionally, optical images of the patterned samples a were also obtained using the microscope. a

### **5.2.5 X-ray Photoelectron Spectroscopy**

*Ex-situ* X-ray photoelectron spectroscopy (XPS) were measured using a PHI VersaProbe II Scanning XPS Microbrobe (Physical Electronics Inc., Chanhassen, MN) equipped with a monochromatic Al K $\alpha$  X-ray source (E<sub>p</sub> = 1486.7 eV). During measurement, the pressure was lower than 6.7 × 10<sup>-10</sup> mbar. High resolution spectra were collected with pass energy of 23.5 eV, energy step of 0.2 eV, and analysis angle of 45°. All spectra were collected using a charge compensation system with both electron and ion beams incident on the surface. The binding energies were calibrated to the Au 4f<sub>7/2</sub> binding energy (84.0 eV). Spectra were analyzed using CasaXPS 2.3.17 (RBD Instruments, Inc., Bend, OR) and AA Analyzer 1.07.

#### 5.3 Results and Discussion

# 5.3.1 Raman Spectroscopy and X-ray photoelectron spectroscopy of MoS<sub>2</sub>



**Figure 5.1** Raman spectra of MoS<sub>2</sub> films which were deposited on MHA, MHL and HDT SAMs. Highlighted areas represent expected peak position of  $E^{1}_{2g}$  and  $A_{1g}$  MoS<sub>2</sub> Raman modes. Deposition time: 24 h.

The Raman spectra (Figure 5.1) clearly show that the gold substrate affects the spectra of the deposited MoS<sub>2</sub> in a similar manner to that observed for thin film gold film or nanoparticles deposited on MoS<sub>2</sub>.<sup>11, 14</sup> For MoS<sub>2</sub> there are two prominent first-order Raman active modes which correspond to the  $E_{2g}^1$  (~383 cm<sup>-1</sup>) and  $A_{1g}$  (~408 cm<sup>-1</sup>) modes.<sup>19-20</sup> In figure 5.1 it can be seen that there is a blue shift of the  $A_{1g}$  mode and a red shift of the  $E_{2g}^1$  mode, and that the modes are broadened. The in-plane  $E_{2g}^1$  mode is due to the vibration of the Mo and S atoms in opposite directions. The red shift of this mode can be interpreted in the following way:<sup>14</sup> Au has a large dielectric constant<sup>21</sup> which increases the screening of electron-electron interactions in the material. Thus, the planar interionic interactions are weakened leading to the red shift of the in-plane phonon mode. The out-of-plane  $A_{1g}$  mode results from the symmetric vibration of S atoms along the caxis. The mode is stiffened due to the interaction between the Au and MoS<sub>2</sub> leading to the blue shift of this phonon mode.<sup>14</sup> It is noted that there is a weaker mode also centered at ~155 cm<sup>-1</sup> for 2H MoS<sub>2</sub> deposited on the –CH<sub>3</sub> terminated SAM which is likely due to strain induced in the deposited MoS<sub>2</sub> leading to the broadening of the  $(A_{1g} - LA(M))$  mode.<sup>14, 19</sup>

In chapter 3, it was demonstrated that 2H MoS<sub>2</sub> deposits atop  $-CH_3$  terminated SAMs (HDT) while 1T MoS<sub>2</sub> is deposited on -OH (MHL) and -COOH terminated SAMs. For exfoliated 1T MoS<sub>2</sub> films deposited on MHL and MHA, three additional modes are observed at ~160 cm<sup>-1</sup>, ~225 cm<sup>-1</sup> and ~338 cm<sup>-1</sup> which correspond to the J<sub>1</sub>, J<sub>2</sub> and J<sub>3</sub> modes.<sup>20, 22</sup> In Figure 2.1 these modes are considerably broadened and are observed as one broad peak at ~150 cm<sup>-1</sup>. We also note that the  $E_{2q}^1$  mode may also be convolved with the J<sub>3</sub> mode.

In addition to Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) can be used to determine MoS<sub>2</sub> polytype.<sup>23</sup> For 2H MoS<sub>2</sub> the Mo  $3d_{5/2}$ , Mo  $3d_{3/2}$  and S 2s binding energies are at 229.8 eV, 232.7 eV and 226.6 eV, respectively while for 1T MoS<sub>2</sub> these binding energies are lower by ~0.9 eV (see chapter 3, Figure 3.3). In Figure 5.2 high-resolution photoelectron spectra of the Mo 3d and S 2s region are shown for MoS<sub>2</sub> deposited on the SAM substrates.



**Figure 5.2** Mo 3d and S 2s photoelectron spectra of MoS<sub>2</sub> films which were deposited on MHA, MHL and HDT SAMs. Deposition time: 24 h.

For  $-CH_3$  terminated SAMs, the peak binding energies are at 229.4 eV, 232.6 eV and 226.5 eV which correspond to the Mo  $3d_{5/2}$ , Mo  $3d_{3/2}$  and S 2s peaks, respectively, of 2H MoS<sub>2</sub>.<sup>23</sup> A small decrease in binding energies is also observed by Lin *et al*<sup>15</sup> for Au deposition on chemical vapor deposited (CVD) grown MoS<sub>2</sub> films. For -OH and -COOH terminated SAMs, the peak binding energies are at 229.6 eV, 232.7 eV and 226.6 eV which correspond to the Mo  $3d_{5/2}$ , Mo  $3d_{3/2}$  and S 2s peaks, respectively. On these SAMs 1T MoS<sub>2</sub> is deposited (see chapter 3) indicating that the interaction of the MoS<sub>2</sub> with the Au substrate leads to an increase in binding energy of ~1.1 eV.

The Raman spectra and XPS data together clearly indicate that the gold substrate interacts strongly with the deposited  $MoS_2$  film. The broadening of the Raman modes suggests that there may be strain in the  $MoS_2$  film.<sup>14</sup> Further, the XPS data suggest that the interaction of the metallic 1T  $MoS_2$  layers with the underlying Au substrate is larger than for the semiconducting 2H  $MoS_2$
layers; there is a large binding energy shift observed for the Mo 3d and S 2s photoelectron peaks for 1T MoS<sub>2</sub> while only a small differences in binding energies are observed for 2H MoS<sub>2</sub>.

5.3.2 Raman Mapping of MoS<sub>2</sub> deposited on Micropatterned SAMs



**Figure 5.3** Schematic representing a) a micropatterned SAM surface with  $-CH_3$  SAMs in the square areas (red) and -OH SAMs in the bar areas (blue). After UV-photopatterning the bar areas are either -OH or -COOH terminated. b) shows a Raman microscope image of MoS<sub>2</sub> deposited on an  $-OH/-CH_3$  patterned SAM after 24 hours deposition time.

Figure 5.3a shows a schematic representation of a prepared micropatterned –OH/–CH<sub>3</sub> SAM. In this chapter, micropatterned SAMs are either prepared as patterned –OH/–CH<sub>3</sub> patterned or –COOH/–CH<sub>3</sub> patterned. In both patterned surfaces the substrate maintains –CH<sub>3</sub> in the square areas of the pattern. In this example (Figure 5.3), the hydrophilic –OH terminated SAMs is in the bar areas and the –CH<sub>3</sub> terminated SAMs is in the square areas. Figure 5.3b shows a Raman microscope image of MoS2 deposited on a –OH/–CH<sub>3</sub> micropatterned SAM after 24 hours.

Figure 5.4 shows an optical image and Raman maps centered at 435 cm<sup>-1</sup>, 326 cm<sup>-1</sup> and 184 cm<sup>-1</sup> after MoS<sub>2</sub> CBD for 24 h at room temperature. It can be seen in Figure 5.4a that the MoS<sub>2</sub> deposit appears to be thicker in the –CH<sub>3</sub> terminated SAM area compared to the –COOH terminated SAM area. This is confirmed by examination of the individual Raman spectra in the –COOH and –CH<sub>3</sub> terminated SAM areas; the intensity of the  $A_{1g}$  and  $E^{1}_{2g}$  modes are stronger for the –CH<sub>3</sub> terminated SAM (Figure 5.5).



**Figure 5.4** Images after MoS<sub>2</sub> deposition for 24 h on –COOH/–CH3 micropatterned SAMs. The –COOH terminated SAM is in the inverted "L" area while the –CH3 terminated SAM is in the bottom left square area. a) Optical image of the mapped area (shown by the red box); and Raman maps centered at b) 425 cm-1; c) 326 cm-1; and d) 184 cm-1. Raman maps shown using a heat scale.

However, the 1T modes centered at ~155 cm<sup>-1</sup> are more intense on the –COOH terminated SAM. It is noted that there is a weaker mode also centered at ~155 cm<sup>-1</sup> on the –CH<sub>3</sub> terminated SAM which is likely due to strain induced in the deposited MoS<sub>2</sub> leading to the broadening of the  $(A_{1q} - LA(M))$  mode. <sup>14, 19</sup>



**Figure 5.5** Representative Raman spectra collected in the –COOH and –CH<sub>3</sub> terminated SAM areas after deposition of MoS<sub>2</sub> for 24 h on micropatterned –COOH/–CH<sub>3</sub> terminated SAMs.

In the Raman maps (Figures 5.4 b-d), as expected the  $E_{2g}^1$  (326 cm<sup>-1</sup>) and  $A_{1g}$  (425 cm<sup>-1</sup>) modes have similar intensity across the whole area. For the map centered at (184 cm<sup>-1</sup>), there is higher intensity in the –COOH terminated SAM area which is consistent with the presence of the 1T MoS<sub>2</sub> J modes. Taken together the Raman maps clearly indicate that 1T MoS<sub>2</sub> has been deposited in the –COOH terminated SAM areas while on the –CH<sub>3</sub> terminated SAM areas 2H MoS<sub>2</sub> has been deposited.



**Figure 5.6** Images after  $MoS_2$  deposition for 24 h on  $-OH/-CH_3$  micropatterned SAMs. The -OH terminated SAM is in the inverted "L" area (top right) while the  $-CH_3$  terminated SAM is in the bottom left square area. a) Optical image of the mapped area (shown by the red box); and Raman maps centered at b) 425 cm<sup>-1</sup>; c) 326 cm<sup>-1</sup>; and d) 184 cm<sup>-1</sup>. Raman maps shown using a heat scale.

The data is more complicated for  $MoS_2$  deposition on patterned  $-OH/-CH_3$  terminated SAMs (Figure 5.6). Similar to the  $-COOH/-CH_3$  patterned SAM, it can be seen in Figure 5.6a that the  $MoS_2$  deposit appears to thicker in the  $-CH_3$  terminated SAM area compared to the -OH terminated SAM area. This is confirmed by examination of the individual Raman spectra in the -OH and  $-CH_3$  terminated SAM areas (Figure 5.7); the intensity of the  $A_{1g}$  and  $E^{1}_{2g}$  modes are stronger for the  $-CH_3$  terminated SAM. However, the 1T modes centered at ~155 cm<sup>-1</sup> are more intense on the -OH terminated SAM. Further, the mode centered at ~155 cm<sup>-1</sup> on the  $-CH_3$ 

terminated SAM, which is likely due to strain-induced broadening of the  $(A_{1g} - LA(M))$  mode, <sup>14, 19</sup> is more intense.



**Figure 5.7** Representative Raman spectra collected in the –OH and –CH<sub>3</sub> terminated SAM areas after deposition of MoS<sub>2</sub> for 24 h on micropatterned –OH/–CH<sub>3</sub> terminated SAMs.

Figure 5.6 shows the Raman map analysis collected on MoS<sub>2</sub> deposited on micropatterned –OH/–CH<sub>3</sub> terminated SAMs and is similar to the data obtained on the micropatterned –COOH/ –CH<sub>3</sub> terminated SAMs. As expected, the  $E_{2g}^1$  (326 cm<sup>-1</sup>) and  $A_{1g}$  (425 cm<sup>-1</sup>) modes have high intensities across the whole area. It is noted that due to the different thickness of the MoS<sub>2</sub> deposit these modes appear more intense in the –CH<sub>3</sub> terminated SAM areas. For the map centered at (184 cm<sup>-1</sup>), there is little spatial variation in the Raman map suggesting that the J and  $(A_{1g} - LA(M))$ modes are more intense in this region.

To eliminate the large Raman mode intensity differences of the deposited  $MoS_2$  in the –OH and –CH<sub>3</sub> terminated SAM areas, the spectra were normalized so that the highest spectral intensity observed was 1. Regenerating the Raman maps using the normalized spectra revealed greater differences in the region between 100 - 200 cm<sup>-1</sup>, where the 1T modes are observed.<sup>20, 22</sup>

The greatest spectral difference between the -OH and  $-CH_3$  terminated SAM areas was observed at 145cm<sup>-1</sup> which is close to the J<sub>1</sub> mode of 1T MoS<sub>2</sub> (Figure 5.8). <sup>20, 22 24</sup> Figure 5.8 shows the Raman map generated at this Raman shift.



**Figure 5.8** Images after  $MoS_2$  deposition for 24 h on  $-OH/-CH_3$  micropatterned SAMs. The – OH terminated SAM is in the inverted "L" area (top right) while the  $-CH_3$  terminated SAM is in the bottom left square area. a) Optical image of the mapped area (shown by the red box); b) Raman maps centered at b) 145 cm<sup>-1</sup>.

### **5.4 Conclusions**

The XPS and Raman data indicate that the deposited MoS<sub>2</sub> strongly interacts with the Au substrate. In Raman spectra, we observe the blue shift of the  $A_{1g}$  mode and a red shift of the  $E_{2g}^1$  mode. Additionally, for the first time, we report that the J modes of 1T MoS<sub>2</sub> are significantly broadened. In the XPS spectra we observe that the Mo 3d and S 2s binding energies increase by ~1.1 eV for 1T MoS<sub>2</sub> while on for 2H MoS<sub>2</sub> the binding energy shift is negligible indicating that the interaction of the metallic 1T MoS<sub>2</sub> is likely stronger with the Au substrate.

Second, we demonstrate the area-selective  $MoS_2$  deposition patterned  $-COOH/-CH_3$  or  $-OH/-CH_3$  SAM surfaces. Using Raman mapping in the -COOH and -OH terminated SAM areas we observe the deposition of 1T  $MoS_2$  while on  $-CH_3$  terminated SAMs we observe the deposition

of 2H MoS<sub>2</sub>. The results suggest that CBD can be employed to create self-aligned transition metal

dichalcogenide structures.

# 5.5 References

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#### **CHAPTER 6**

# COMPOSITIONAL CHANGES IN COPPER SULFIDE THIN FILMS GROWN BY CHEMICAL BATH DEPOSITION ON FUNCTIONALIZED SELF-ASSEMBLED MONOLAYERS

## 6.1 Introduction

Copper sulfide is an attractive material due to its earth abundance<sup>1</sup> and non-toxic qualities<sup>2-3</sup> making it a practical and low-cost option for many technological applications including in biochemistry,<sup>4-6</sup> photocatalysis,<sup>7</sup> solar cells,<sup>2-3, 8-9</sup> and nanoelectronics.<sup>10-11</sup> One of the reasons that copper sulfide has many applications is that its stoichiometry can be varied from  $1 \le Cu/S \le 2$  leading to a wide variety of electrical and other materials properties. In general copper sulfides are semiconductors but can act as metallic conductors.<sup>12-14</sup> The stoichiometric forms of copper sulfide are covellite (CuS) and chalcocite (Cu<sub>2</sub>S), but there are other less common, naturally occurring forms including spionkopite (Cu<sub>1.39</sub>S), geerite (Cu<sub>1.6</sub>S), anilite (Cu<sub>7</sub>S<sub>4</sub>) and digenite(Cu<sub>9</sub>S<sub>5</sub>) phases.<sup>15</sup>

Therefore one of the challenges in synthesizing copper sulfide thin films is the precise control of the film composition. Copper sulfide has been synthesized by various techniques including atomic layer deposition,<sup>16</sup> chemical vapor deposition.<sup>17-19</sup>, hydrothermal,<sup>9, 20-23</sup> solvothermal,<sup>23</sup> microwave assisted,<sup>24</sup> thermolysis,<sup>22</sup> spray pyrolysis,<sup>25</sup> and sonoelectrochemical methods.<sup>22</sup> However, these methods either require high temperatures, vacuum equipment, and/or expensive precursors. Further, it can be difficult to control the composition of the deposit.<sup>17-18, 25</sup>

Chemical bath deposition (CBD) is a solution-based ion-exchange method that has been used to deposit a wide range of semiconducting materials including metal oxides,<sup>26</sup> selenides,<sup>27-28</sup> and sulfides.<sup>29</sup> CBD is an attractive technique because it is low cost, and can be performed under ambient conditions at low temperatures.<sup>30</sup> There have been a number of studies of the CBD of copper sulfide films.<sup>13, 31-44</sup> Depending on the reaction conditions, such as the bath pH and temperature, both CuS and Cu<sub>2</sub>S have been observed to deposit as well as non-stoichiometric copper sulfides. Further, the composition of the deposit can be altered by the addition of Cu<sup>2+</sup> ions in the deposition solution<sup>37</sup> or by annealing the film.<sup>37, 42</sup> It has also been demonstrated that the substrate chemistry can affect the properties the deposited copper sulfide film.<sup>36, 43</sup> However, the mechanisms underlying these effects are not well understood.

In this chapter we investigate the chemical bath deposition (CBD) of copper  $-CH_3$ , -OH and -COOH terminated self-assembled monolayers (SAMs). SAMs are ideal model substrates to investigate deposition reactions because they have a known well-ordered structure and are synthetically flexible.<sup>45-47</sup> We demonstrate that copper sulfide deposition is strongly dependent on the bath pH which can be attributed to the decomposition of the sulfur source, thiourea. We also demonstrate for the first time that the chemical identity of the deposit can be altered by exploiting the interaction of the deposition precursors with the substrate. We show that on -OH and -COOH terminated SAMs the covellite is always deposited, which can be attributed to the interaction of S<sup>2-</sup> ions with the negatively charged SAM surfaces. In contrast, on  $-CH_3$  terminated SAMs, the deposit changes from covellite to chalcocite as the bath pH increases.

## 6.2 Experimental

## 6.2.1 Materials

All reagents were used as received without further purification. Thiourea (99%) was obtained from Alfa Aesar, Inc. (Ward Hill, MA). Sodium hydroxide (≥98%, pellets) were purchased from Fisher Chemicals (Thermo Fisher Scientific Inc., Waltham, MA). 16-mercaptohexadecanoic acid (90%)

(MHA), 1-hexadecanethiol (99%) (HDT), ethylenediaminetetraacetic acid (98%) (EDTA), and copper (II) sulfate pentahydrate (98%) were acquired from Sigma-Aldrich Inc. (St. Louis, MO). 16-Hydroxy-1-hexadecanethiol (99%) (MHL) was obtained from Frontier Scientific Inc. (Logan, UT). Ethanol (200 proof, undenatured) was purchased from Spectrum Chemical MFG Corp (New Brunswick, NJ).

The gold substrates were prepared in the Cleanroom Research Laboratory, University of Texas at Dallas. Briefly, silicon wafers ((111) orientation) were acquired from Addison Engineering Inc. (San Jose, CA), and ~200 Å of chromium followed by ~1000 Å of gold were thermally deposited onto these substrates.

## 6.2.2 Self-Assembled Monolayer Preparation

The preparation of alkanethiolate self-assembled monolayers has been described in detail previously.<sup>48-51</sup> In brief, a well-ordered SAM was prepared by immersing a gold substrate into a 1 mM solution of the desired alkanethiol (MHL, MHA or HDT) in ethanol for 24 hours at room temperature. After removal from the alkanethiol solution, the samples were then rinsed with ethanol and dried with nitrogen gas.

## 6.2.3 Chemical Bath Deposition of Copper Sulfide

The deposition bath was composed of 0.006 M copper sulfate pentahydrate, 0.016 M EDTA, and 0.012 M sodium hydroxide. To investigate the effect of the pH on the deposition, the bath pH was varied from pH 9 to pH 12. The pH of the deposition bath was adjusted using sodium hydroxide and sulfuric acid prior to the addition of the sulfur source, 0.012 M thiourea. The SAM substrate was immediately immersed into the bath for deposition times from 30 min to 24 hours. All samples

were sonicated in water for 2 minutes, rinsed with deionized water, and dried using nitrogen gas prior to further characterization.

### 6.2.4 X-ray Photoelectron Spectroscopy

*Ex-situ* x-ray photoelectron spectroscopy (XPS) measurements were collected using a PHI VersaProbe II (Physical Electronics Inc., Chanhassen, MN) equipped with an Al K $\alpha$  source (E<sub>b</sub> = 1486.7 eV). During data acquisition, the pressure in the main chamber was maintained < 5×10<sup>-10</sup> mbar. High-resolution photoelectron spectra were collected with a pass energy of 23.5 eV, energy step of 0.2 eV, and analysis angle of 45°. All spectra were obtained using a charge compensation with an electron beam incident on the surface. The binding energies were calibrated to the Au 4f<sub>7/2</sub> binding energy (84.0 eV). The data were analyzed using CasaXPS 2.3.17 (RBD Instruments, Inc., Bend OR).

## 6.2.5 Time-of-Flight Secondary Ion Mass Spectrometry

Time-of-flight secondary ion mass spectrometry (TOF SIMS) data were collected with an ION TOF IV (ION TOF Inc., Chestnut Hill, NY) equipped with a Bi liquid metal ion gun. The instrument is comprised of three chambers: a loadlock, a preparation chamber and an analysis chamber. During data collection, the pressure of the analysis chamber was kept  $< 5 \times 10^{-9}$  mbar during data collection. The Bi<sup>+</sup> primary ions had a kinetic energy of 25 keV, and were contained in a ~100 nm probe beam. The analysis area was (100 × 100) µm<sup>2</sup>. All spectra were acquired using an analysis area of (100 × 100) µm<sup>2</sup>, and within the static regime using a total ion dose less than  $10^{10}$  ions cm<sup>-2</sup>. For each experimental condition, at least three samples were prepared, and three areas on each sample were examined.

#### **6.3 Results and Discussion**

### 6.3.1 Deposition of Cu<sub>x</sub>S Films

After 24 h deposition, the photoelectron and TOF SIMS spectra clearly show that copper sulfide has deposited on the –CH<sub>3</sub>, –OH and –COOH terminated SAMs. In the SIMS spectra, ions of the form  $Cu_xS_y^-$  are observed indicating that copper sulfide deposition has occurred. Further, the data indicate that the molecular cluster ion intensities,  $Au_2M^-$  and  $AuM_2^-$  (where  $M = -S(CH_2)_{15}CH_3$ , - $S(CH_2)_{15}CH_2OH$  or  $-S(CH_2)_{15}COOH$ ) have significantly decreased indicating that the SAMs are covered by a deposited layer (Figure 6.1).

The Cu 2p (Figure 6.2) photoelectron spectra also show that copper sulfide has deposited. At pH 9 the Cu  $2p_{3/2}$  binding energy is 932.2 eV on –OH and –CH<sub>3</sub> terminated SAMs which indicates that CuS has deposited.<sup>52-54</sup> On –COOH terminated SAMs, the Cu 2p photoelectron peak intensities are significantly smaller indicating that there is less Cu<sub>x</sub>S deposited. The binding energy of the Cu  $2p_{3/2}$  peak is 932.2 eV which is consistent with the deposition of CuS.<sup>52-54</sup> As the deposition bath pH increases from 9 to 12, the binding energy of the Cu  $2p_{3/2}$  peak remains constant for Cu<sub>x</sub>S deposited on –OH and –COOH terminated SAMs indicating that the deposit remains CuS. In contrast, for –CH<sub>3</sub> terminated SAMs the Cu  $2p_{3/2}$  binding energy increases from 932.2 eV at pH 9 to 932.3 eV at pH 11 to 932.4 eV at pH 12 suggesting that the deposit is changing from CuS to Cu<sub>2</sub>S.<sup>52-54</sup> The binding energies of the Cu  $2p_{1/2}$  peaks are consistent with the Cu  $2p_{3/2}$ photoelectron energies. For –OH and –COOH terminated SAMs the bath pH is changed from pH 9 to pH 12, the binding energy remains constant, 952.0 eV, indicating that CuS has deposited.<sup>52</sup> For –CH<sub>3</sub> terminated SAMs the Cu  $2p_{1/2}$  binding energy increases by +0.2 eV suggesting that the oxidation state of the copper is changing and that Cu<sub>2</sub>S has deposited.<sup>52-54</sup>



**Figure 6.1** High resolution negative ion spectra of  $Au_2M^-$  ((where  $M = -S(CH_2)_{15}CH_3 -S(CH_2)_{15}CH_2OH$  or  $-S(CH_2)_{15}COOH$ ) after deposition of copper sulfide for 24 h at room temperature on a)  $-CH_3$ ; b) -OH and c) -COOH terminated SAMs. The deposition bath pH was varied from pH 9 to pH 12.



**Figure 6.2** Cu 2p photoelectron spectra after deposition of copper sulfide for 24 h at room temperature on a)  $-CH_3$ ; b) -OH and c) -COOH terminated SAMs. The deposition bath pH was varied from pH 9 to pH 12.

Perry and Taylor<sup>53</sup> observed distinct differences in the S 2p photoelectron spectra of CuS and  $Cu_2S$  both in the lineshape and a difference in binding energy of 0.8 eV. Figure 6.3 shows the S 2p photoelectron spectra of  $-CH_3$ , -OH and -COOH terminated SAMs after  $Cu_xS$  CBD for 24h. We note that the intensities of the S 2p peaks are much lower than the Cu 2p peaks because the photoelectron cross-section of S is much lower than for Cu.<sup>55</sup> For the bare alkanethiolate SAMs, there is a small S 2p peak observed at ~162.0 eV. After copper sulfide deposition for 24h, the intensity of the S 2p peak has significantly increased. Taken together with the Cu 2p photoelectron spectra, this observation is consistent with the deposition of a Cu<sub>x</sub>S layer. For pH 9, the binding energy of the S 2p photoelectron is ~162.5 eV for all SAMs studied indicating that CuS has deposited in agreement with the Cu 2p photoelectron spectra. Further, the line shape is indicative of covellite, CuS. The lineshape is broad suggesting that there are two doublets present corresponding to the S<sup>2-</sup> and S<sub>2</sub><sup>2-</sup> ligands in covellite.<sup>53, 56</sup> As the bath pH increases, for -COOHand -OH terminated SAMs the intensity of the S 2p peak increases but the binding energy remains the same ~162.5 eV indicating that more CuS is deposited. In contrast for -CH<sub>3</sub> terminated SAMs the S 2p photoelectron decreases in binding energy to ~161.8 eV and the lineshape slightly narrows which is consistent with the deposition of Cu<sub>2</sub>S.<sup>52-53</sup>

Additional information about the Cu<sub>x</sub>S deposit can be obtained from the x-ray initiated Auger electron spectroscopy (XAES) Cu LMM peak (Figure 6.4). This is because the Auger kinetic energy shifts are generally more sensitive to changes in chemical environment than the core photoelectron lines. In agreement with the Cu 2p and S 2p photoelectron data, for –COOH and –OH terminated SAMs, as the pH of the deposition bath is increased the kinetic energy of the Cu LMM peak remains ~918.2 eV indicating that the deposit is CuS.<sup>52-54, 57</sup>



**Figure 6.3** S 2p photoelectron spectra after deposition of copper sulfide for 24 h at room temperature on a)  $-CH_3$  b) -OH and c) -COOH terminated SAMs. The deposition bath pH was varied from pH 9 to pH 12.

Further, the Cu LMM peak shape is consistent with the deposition of covellite, CuS.<sup>57</sup> For -CH<sub>3</sub> terminated SAMs, the Cu LMM kinetic energy decreases from 918.2 eV at pH 9 and pH 11 to 917.6 eV at pH 12 indicating that the deposit changes from covellite, CuS, to chalcocite, Cu<sub>2</sub>S. <sup>52-54, 57</sup> The Cu LL peak also changes line shape and has a smaller shoulder on the high kinetic energy which also suggests that Cu<sub>2</sub>S has deposited.<sup>54, 57</sup> The differences in the photoelectron binding energies and the XAES kinetic energies are very small, and, taking into account the experimental errors in determining the line positions it is difficult to unambiguously determine the deposit composition. The modified Auger parameter,  $\alpha$ ', can be employed to unambiguously determine film compositions without the interference of effects such as sample charging. For copper, the modified Auger parameter is the sum of the Cu 2p<sub>3/2</sub> binding energy and the Cu LMM kinetic energy. For CuS and Cu<sub>2</sub>S, the modified Auger parameters are 1850.3±0.2 eV and 1849.8±0.2 eV.<sup>52-54</sup> Table 6.1 displays the values of the Cu 2p<sub>3/2</sub> binding energies, the kinetic energies of the Cu LMM XAES peak, and the modified Auger parameters after Cu<sub>x</sub>S CBD for 24 h on -CH<sub>3</sub>, -OH and -COOH terminated SAMs. The data show that for all SAMs studied at CuS is deposited at pH 9 and pH 11. For pH 12, in agreement with the S 2p photoelectron spectra, the data show that on -COOH and -OH terminated SAMs the deposit remains covellite, CuS, but on -CH<sub>3</sub> terminated SAMs the deposit is chalcocite, Cu<sub>2</sub>S.



**Figure 6.4** Cu LMM peak measured for deposition on all three SAMs at pH 9, 11 and 12. Deposition time = hours.

**Table 6.1** The values of the binding energies of the  $Cu2p_{3/2}$  peak, kinetic energies of the Cu LMM XAES peak and calculated Auger parameter,  $\alpha$ ', after  $Cu_xS$  CBD for 24 h on  $-CH_3$ , -OH and -COOH terminated SAMs.

SAM Terminal	Deposition Bath	Binding Energy	Kinetic Energy	α' (eV)
Group	рН	Cu2p3/2 (eV)	Cu LMM (eV)	
CH3	9	932.2	918.2	1850.4
	11	932.2	918.1	1850.3
	12	932.4	917.6	1850.0
-OH	9	932.2	918.2	1850.4
	11	932.2	918.2	1850.4
	12	932.2	918.2	1850.4
-СООН	9	932.4	918.0	1850.4
	11	932.2	918.2	1850.4
	12	932.4	918.0	1850.4

# 6.3.2 Reaction Pathways of Cu<sub>x</sub>S CBD on Functionalized SAMs

Chemical bath deposition of metal sulfides have been extensively studied.<sup>30</sup> Typically in a CBD reaction the concentration of both the chalcogenide ion and the cation are controlled. Under basic reaction conditions (i.e. in the presence of  $OH^{-}$ ),  $Cu_xS$  was deposited using the following (unbalanced) reaction equation:<sup>30</sup>

$$Cu^{2+} + EDTA^{4-} \rightarrow [Cu(EDTA)]^{2-}$$
6.1

 $SC(NH_2)_2 + OH^- \rightarrow CN_2H_2 + H_2O + HS^-$  6.2

$$\mathrm{HS}^{-} + \mathrm{OH}^{-} \rightarrow \mathrm{S}^{2-} + \mathrm{H}_{2}\mathrm{O}$$
 6.3

$$Cu^{2+} + S^{2-} \to CuS \tag{6.4}$$

$$2\mathrm{Cu}^{+} + \mathrm{S}^{2-} \to \mathrm{Cu}_2\mathrm{S} \tag{6.5}$$

In reaction 6.1, the concentration of "free" copper ions is controlled by a complexing agent, ethylenediaminetetraacetic acid (EDTA). Thiourea reacts with hydroxide ions present in solution to form bisulfide ions,  $HS^-$  (reaction 6.2). Subsequently the bisulfide ions decompose to  $S^{2-}$  ions (reaction 6.3) which then react with  $Cu^{2+}$  ions to form covellite (CuS) (reaction 6.4) or chalcocite (reaction 6.6).

The data show that the  $Cu_xS$  deposition is strongly dependent on the bath pH. As the bath pH increases, the Cu 2p and S 2p photoelectron intensities indicate that more  $Cu_xS$  is deposited at pH 12 than at pH 9. This effect is particularly strong for –COOH terminated SAMs. Second, on –CH<sub>3</sub> terminated SAMs, the deposit changes from CuS to  $Cu_2S$  whereas on –COOH and –OH terminated SAMs the deposit remains CuS.



**Figure 6.5** The average Cu  $2p_{3/2}$  photoelectron peak height after deposition of copper sulfide for 24 h at room temperature on  $-CH_3$ , -OH and -COOH terminated SAMs. The deposition bath pH was varied from pH 9 to pH 12.

The increase in the amount of Cu<sub>x</sub>S deposited can be explained in the following way. As the pH increases, more HS<sup>-</sup> is produced (reaction 6.2) leading to an increase in the concentration of S<sup>2-</sup> ions in solution and consequently more Cu<sub>x</sub>S is deposited. We estimate that for at bath pH of 9, the concentration of S<sup>2-</sup> ions is  $5 \times 10^{-9}$  M and at a bath pH of 12, the concentration has increased to  $5 \times 10^{-6}$  M. However, we only observe an increase of  $\sim 3 \times$  in the Cu  $2p_{3/2}$  peak heights (or intensities) (Figure 6.5) indicating that there are other factors that affect the Cu<sub>x</sub>S deposition. It is interesting to note that at pH 9, on –COOH terminated SAMs there is the least amount of CuS deposited but at pH 12 the largest amount of CuS is deposited. In contrast for –CH<sub>3</sub> terminated SAMs, while there is an increase in the amount of copper sulfide deposited from pH 9 to pH 12 it is not as large for –COOH terminated SAMs. Further on –CH<sub>3</sub> terminated SAMs, the copper sulfide deposit changes from covellite (CuS) to chalcocite (Cu<sub>2</sub>S).

The above discussion indicates that the chemistry nature of the substrate is critical factor in the deposition of copper sulfide films by CBD. The larger increase in the amount of CuS deposited on –COOH terminated SAMs can be explained in the following way. For –COOH terminated SAMs, the surface  $pK_{\frac{1}{2}}$  is ~8.0, which is the pH of the solution at which a surface is 50 % ionized.<sup>58</sup> Thus as the bath pH increases the –COOH terminal group deprotonates to form carboxylate ions, COO<sup>-</sup>, and at pH 11 the surface is almost fully deprotonated. The increase in the copper sulfide deposition can be attributed to the formation of copper-carboxylate ions which serve as the nucleation sites for subsequent deposition.<sup>59-64</sup> In the SIMS spectra after Cu<sub>x</sub>S CBD we observe ions of the form Cu(COO)CH<sub>x</sub><sup>+</sup> (Figure 6.6). The intensity of these ion increase with bath pH and deposition time.



**Figure 6.6** High resolution positive ion spectra centered at m/z 163 after deposition of Cu<sub>x</sub>S at pH 11 on –COOH terminated SAMs (MHA) at various time points including bare MHA (time = 0), 30 minutes, 5 hours and 24 hours.

It is also observed that the Cu<sub>x</sub>S deposit changes, and is dependent on both the substrate and bath pH. For –COOH and –OH terminated SAMs, covellite is deposited at all bath pH studied. In contrast for –CH<sub>3</sub> terminated SAMs, covellite is deposited at pH 9 and pH 11 but chalcocite is deposited at pH 12. These observations can be explained in the following way. Above pH 9, the –COOH terminated SAM is almost completely deprotonated leading to the formation of a charged surface composed of COO<sup>-</sup> ions at the solution-substrate interface. The C-OH terminal bond of –OH terminated SAMs is polar with the –OH group having a small negative charge ( $\delta^{-}$ ). Consequently, as the bath pH increases these negatively charged surfaces repel the S<sup>2-</sup> ions present in solution. Thus, the deposit CuS which is composed of S<sub>2</sub><sup>2-</sup> and S<sup>2-</sup> ions ligands.<sup>53</sup> In contrast for –CH<sub>3</sub> terminated SAMs, the C-H bonds of the methyl terminal group are not polar. In this case, the S<sup>2-</sup> ions are not repelled by the –CH<sub>3</sub> terminated SAMs, and consequently S<sup>2-</sup> deposition is preferred on these surfaces and chalcocite forms at a bath pH of 12. We note that on –CH<sub>3</sub> terminated SAMs the modified Auger parameter of the deposit decreases with bath pH. This suggests that the deposited copper sulfide layer changes from CuS at pH 9 to a mixed CuS/Cu<sub>2</sub>S film at pH 11 to Cu<sub>2</sub>S at pH 12.

# 6.4 Conclusions

Copper sulfide deposition using the CBD method reported here is strongly dependent on the pH of the deposition bath. First, as the bath pH increases the amount of copper sulfide deposited increases which can be attributed to the decomposition of the thiourea sulfur source. Second, as the bath pH increases, the deposit changes from CuS to  $Cu_2S$  on  $-CH_3$  terminated SAMs. However,

on -OH and -COOH terminated SAMs the deposit is CuS at all deposition bath pHs investigated.

This effect can be attributed to the interaction of the  $S^{2-}$  ions with the SAM terminal groups.

# 6.5 References

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#### **CHAPTER 7**

# COPPER SULFIDE THIN FILMS GROWN BY CHEMICAL BATH DEPOSITION ON FUNCTIONALIZED SELF-ASSEMBLED MONOLAYERS: SELECTIVE DEPOSITION

## 7.1 Introduction

Copper sulfide has many technological applications including in biochemistry,<sup>1-3</sup> photocatalysis,<sup>4</sup> solar cells,<sup>5-8</sup> and nanoelectronics.<sup>9-10</sup> It can be synthesized by various techniques including atomic layer deposition,<sup>11</sup> and chemical vapor deposition.<sup>12-14</sup>, hydrothermal,<sup>8, 15-18</sup> solvothermal,<sup>18</sup> microwave assisted,<sup>19</sup> thermolysis,<sup>17</sup> spray pyrolysis,<sup>20</sup> sonoelectrochemical methods,<sup>17</sup> and chemical bath deposition (CBD).<sup>21-35</sup> CBD is an attractive method for organic thin film substrates because it can be performed a low temperatures, is carried out under ambient conditions and does not require a conductive substrate.

Little is known about the role of the substrate chemistry in the deposition efficiency and selectivity of CuS deposition. It has also been reported that the substrate chemistry can affect the properties of the deposited copper sulfide film,<sup>26, 34</sup> but the mechanisms underlying these effects are not well understood. In CBD, the formation of surface complexes<sup>36-39</sup> and the hydrophobic/hydrophilic properties of self-assembled monolayers<sup>40</sup> have been employed to perform selective growth of ZnO<sup>37</sup>, ZnS,<sup>38</sup> CdSe<sup>36</sup> and PbS.<sup>37, 39</sup> In general the interaction of the surface with the metal cation has been critical in determining the selective growth of these films. For example, the formation of M<sup>2+</sup>-carboxylate surface complexes, where M = Zn, Cd and Pb, have been demonstrated to act as the nucleation sites for site-selective deposition of ZnO<sup>37</sup>, ZnS,<sup>38</sup> CdSe<sup>36</sup> and PbS.<sup>39</sup>

In this chapter we investigate the CBD of CuS on  $-CH_3$ , -OH and -COOH terminated SAMs at room temperature using thioacetamide as a sulfur source. We demonstrate that the deposition selectivity is strongly dependent on the interaction of the SAM terminal group with the deposit precursors. At pH 9, more copper sulfide is deposited on  $-CH_3$  terminated SAMs than -OH and -COOH terminated SAMs. In contrast, at pH 12 more copper sulfide is deposited on -COOH terminated SAMs than on  $-CH_3$  and -OH terminated SAMs. These changes in deposition selectivity can be attributed to three competing effects. As the bath pH increases the thioacetamide decomposition rate greatly increases leading to a higher concentration of S<sup>2-</sup> available for the deposition reaction. Second, the interaction of the S<sup>2-</sup> ions with the -OH and -COOH SAMs for bath pH > 9, copper-carboxylate surface complexes can form which act as the nucleation sites for subsequent CuS film formation. For  $-CH_3$  terminated SAMs, there is no specific interaction with the deposition bath reagents.

#### 7.2 Methods

## 7.2.1 Materials

All reagents were used without further purification. Thioacetamide (99%) was obtained from Alfa Aesar, Inc. Sodium hydroxide (≥98%, pellets) were acquired from Fisher Chemicals (Thermo Fisher Scientific Inc., Waltham, MA). 16-Hydroxy-1-hexadecanethiol (99%) (MHL) was purchased from Frontier Scientific Inc. (Logan, UT). 16-mercaptohexadecanoic acid (90%) (MHA), 1-hexadecanethiol (99%) (HDT), ethylenediaminetetraacetic acid (98%) (EDTA), and copper (II) sulfate pentahydrate (98%) were purchased from Sigma Aldrich Inc. (St. Louis, MO).

Ethanol (200 proof, undenatured) was obtained from Spectrum Chemical MFG Corp (New Brunswick, NJ).

The gold substrates used in this study were prepared in the Cleanroom Research Laboratory, University of Texas at Dallas. Briefly, silicon wafers ((111) orientation) were acquired from Addison Engineering Inc. (San Jose, CA), and ~200 Å of chromium followed by ~1000 Å of gold were thermally deposited using a CHA-50 e-beam evaporator (CHA Industries, Freemont CA) onto these substrates.

## 7.2.2 Preparation of self-assembled monolayers on gold substrates

The preparation of alkanethiolate self-assembled monolayers has been described in detail previously.<sup>41-44</sup> Briefly, a well-ordered SAM was prepared by immersing a gold substrate into a 1 mM solution of the appropriate alkanethiol (MHL, MHA or HDT) in ethanol for 24 hours at room temperature. After removal from the alkanethiol solution, the samples were then rinsed with ethanol and dried with nitrogen gas.

## 7.2.3 Chemical bath deposition of copper sulfide

The deposition bath was composed of 0.006 M copper sulfate pentahydrate, 0.016 M EDTA, and 0.012 M sodium hydroxide, and 0.012 M thiourea. To investigate the effect of the pH on the deposition, the bath pH was varied from pH 6 to pH 12. The pH of the deposition bath was adjusted using sodium hydroxide and sulfuric acid prior to the addition of the sulfur source, 0.012 M thioacetamide. The SAM substrate was immediately immersed into the bath for 24 hours at room temperature. After deposition all samples were sonicated in water for 2 minutes, rinsed with deionized water, and dried using nitrogen gas prior to further characterization.

We note that at pH 12 the bath color changes from blue to green during deposition. The solution also becomes cloudy. At pH 6 and pH 9, the deposition solution remains blue throughout deposition.

### 7.2.4 X-ray photoelectron spectroscopy

*Ex-situ* x-ray photoelectron spectroscopy (XPS) measurements were acquired using a PHI VersaProbe II (Physical Electronics Inc., Chanhassen, MN) equipped with an Al K $\alpha$  source (E<sub>b</sub> = 1486.7 eV). During data collection, the chamber pressure was maintained < 5 × 10<sup>-10</sup> mbar. High-resolution photoelectron spectra were collected with a pass energy of 23.5 eV, energy step of 0.2 eV, and analysis angle of 45°. All spectra were obtained using a charge compensation with both electron and ion beams incident on the surface. The binding energies were calibrated to the Au 4f<sub>7/2</sub> binding energy (84.0 eV).

The data were analyzed using CasaXPS 2.3.17 (RBD Instruments, Inc., Bend OR). The Cu  $2p_{3/2}$  peak height was obtained in the following way. The Cu 2p spectra were fit with a Shirley background. The peak height was obtained from the difference between the number of counts at the Cu  $2p_{3/2}$  photoelectron peak maximum and the Shirley background.

### **7.2.5 TOF SIMS**

Time-of-flight secondary ion mass spectrometry (TOF SIMS) data were collected with an ION TOF IV (ION TOF Inc., Chestnut Hill, NY) equipped with a Bi liquid metal ion gun. The instrument is comprised of three chambers: a loadlock, a preparation chamber and an analysis chamber. During data collection, the pressure of the analysis chamber was kept  $< 5 \times 10^{-9}$  mbar during data collection. The Bi<sup>+</sup> primary ions had a kinetic energy of 25 keV, and were contained in a ~100 nm probe beam. All spectra were acquired using an analysis area of (100 × 100)  $\mu$ m<sup>2</sup>,

and within the static regime using a total ion dose less than  $<<10^{10}$  ions cm<sup>-2</sup>. For each experimental condition, at least three samples were prepared, and three areas on each sample were examined. The spectra shown are representative of these data.

### 7.3 Results and Discussion

For every bath pH investigated after deposition, the TOF SIMS data clearly show that copper sulfide has deposited:  $Cu_xS_yH_z^{\pm}$  ions are observed in the positive and negative ion mass spectra. Further, the data show that the molecular cluster ion intensities,  $AuM_2^-$  and  $Au_2M^-$  (where  $M = -S(CH_2)_{15}CH_3$ ,  $-S(CH_2)_{15}CH_2OH$  or  $-S(CH_2)_{15}COOH$ ) also decrease (Figure 7.1). After deposition at pH 6 and pH 9, the intensity of these ions is reduced suggesting that the SAMs are not fully covered by the deposited layer. At pH 12 no molecular ions are observed indicating that the SAMs are fully covered by the deposited copper sulfide layer.

Further information about the deposited layer can be obtained from the Cu 2p and S 2p photoelectron spectra, and the x-ray initiated Auger electron spectroscopy (XAES) Cu LMM peak. For every deposition bath pH we observe that the Cu  $2p_{3/2}$  binding energy is 932.2 eV on all the SAM substrates indicating that CuS has deposited (Figure 7.2).<sup>45-47</sup> The Cu  $2p_{1/2}$  are consistent with the Cu  $2p_{3/2}$  photoelectron energies. Since the intensities of photoelectron spectra are directly related to the amount of material present in the sample, in Figure 7.2 it can be clearly seen that the amount of copper sulfide deposited significantly increases as the bath pH changes from pH 6 to pH 12. Further, at pH 9 there is more CuS deposited on the –CH<sub>3</sub> terminated SAM than on the –OH and –COOH terminated SAM surface suggesting that copper sulfide preferentially deposits on the –CH<sub>3</sub> SAM surface.



**Figure 7.1** High resolution negative ion spectra of  $Au_2M^-$  (where  $M = -S(CH_2)_{15}CH_3$ ,  $-S(CH_2)_{15}CH_2OH$  or  $-S(CH_2)_{15}COOH$ ) after deposition of copper sulfide for 24 h at room temperature on a)  $-CH_3$ ; b) -OH and c) -COOH terminated SAMs. The deposition bath pH was varied from pH 6 to pH 12. Also shown for reference are the mass spectra of the bare SAMs.


**Figure 7.2** Cu 2p photoelectron spectra after deposition of copper sulfide for 24 h at room temperature on a) –CH<sub>3</sub>; b) –OH and c) –COOH terminated SAMs. The deposition bath pH was varied from pH 6 to pH 12.

The S 2p photoelectron spectra confirm that covellite (CuS) has deposited on the SAM surfaces (Figure 7.3). The S 2p peak shape and binding energy indicate that CuS has deposited. Although the S 2p cannot be resolved into the  $2p_{3/2}$  and  $2p_{1/2}$  doublet the peak binding energy, ~162.5 eV, are consistent with the deposition of CuS.<sup>46, 48</sup> Further, the lineshape is broad suggesting that there are two doublets present which correspond to the S<sup>2-</sup> and S<sub>2</sub><sup>2-</sup> ligands present in CuS.<sup>46, 48</sup> In addition, as the bath pH increases from 6 to 12, there is a significant increase in the intensities of the S 2p photoelectron peaks indicating that more copper sulfide is deposited. We also note that at pH 9 the intensity of S 2p photoelectron peak is larger after deposition on –CH<sub>3</sub> terminated SAMs than on –OH and –COOH terminated SAMs indicating that there is preferential deposition of copper sulfide on the methyl-terminated surface.

To confirm that covellite has deposited, the Cu LMM XAES kinetic energy was obtained and the modified Auger parameter,  $\alpha$ ', calculated (Table 7.1). The modified Auger parameter can be employed to unequivocally determine the copper sulfide composition without the interference of final state effects such as sample charging. For copper, the modified Auger parameter is the sum of the Cu 2p<sub>3/2</sub> binding energy and the Cu LMM kinetic energy. For covellite, CuS, the modified Auger parameter is 1850.3±0.2 eV.<sup>45-47</sup> The data clearly show that the modified Auger parameter for the deposited films is consistent with the deposition of covellite, CuS (Table 7.1).



**Figure 7.3** S 2p photoelectron spectra after deposition of copper sulfide for 24 h at room temperature on a)  $-CH_3$ ; b) -OH and c) -COOH terminated SAMs. The deposition bath pH was varied from pH 9 to pH 12.

**Table 7.1** The values of the binding energies of the  $Cu2p_{3/2}$  peak, kinetic energies of the Cu LMM XAES peak and calculated Auger parameter,  $\alpha$ ', after  $Cu_xS$  CBD for 24 h on  $-CH_3$ , -OH and -COOH terminated SAMs.

SAM Terminal	Deposition Bath	<b>Binding Energy</b>	Kinetic Energy	α' (eV) <sup>1</sup>
Group	pH	Cu2p <sub>3/2</sub> (eV)	Cu LMM (eV) <sup>1</sup>	
-CH3	6	932.2	-	-
	9	932.2	918.0	1850.2
	12	932.2	918.4	1850.6
–OH	6	932.2	-	-
	9	932.4	-	-
	12	932.2	918.2	1850.4
-СООН	6	932.2	-	-
	9	932.2	-	-
	12	932.4	918.2	1850.4

<sup>1</sup>The Cu LMM kinetic energy could not be accurately determined for some deposition conditions because the peak intensity was very weak. Consequently, not modified Auger parameter could be calculated.



**Figure 7.4** Variation of the average Cu  $2p_{3/2}$  peak height bath pH after CuS CBD for 24 h on –COOH, -OH and –CH<sub>3</sub> terminated SAMs.

To further investigate the apparent differences in the amount of copper sulfide deposited on –CH<sub>3</sub>, –OH and –COOH terminated SAMs, the variation of the Cu 2p<sub>3/2</sub> photoelectron peak height with bath pH was obtained (Figure 7.4). The peak height is related to the peak intensity (area), and can be employed here as a measure of the amount of copper sulfide deposited because there are no overlapping peaks or interferences in the photoelectron spectra which would lead to inaccuracies in the quantitative estimation. In Figure 7.4, it can clearly be seen that as the bath pH increases the amount of copper sulfide deposited also increases. However, there are differences observed for the different functionalized SAMs. On –CH<sub>3</sub> terminated SAMs, the amount of copper sulfide steadily increases with pH. Further, at pH 9 the amount of copper sulfide is largest on – CH<sub>3</sub> terminated SAMs. For –OH terminated SAMs there is also an increase in the amount of copper deposited but it is slower. In general, on hydroxyl terminated SAM surfaces we observe the least amount of copper sulfide deposition. In contrast, the largest amount of copper sulfide is deposited on –COOH terminated SAMs at pH 12 but little copper sulfide is deposited at pH 6 and pH 9.

#### 7.3.1 Reaction Pathways

The reaction pathways involved in the CBD of CuS on functionalized SAMs using thioacetamide must account for the following observations:

- a) At pH 6 very little copper sulfide is deposited;
- b) At pH 9 the largest amount of CuS is deposited on –CH<sub>3</sub> terminated SAMs but at pH 12 the largest amount of CuS is observed on –COOH terminated SAMs;
- c) The steady increase in the amount of CuS deposited on –CH<sub>3</sub> terminated SAMs as the bath pH increase; and

d) The large increase in the amount of CuS deposited on –COOH terminated SAMs as the bath pH increases from pH to pH 12.

In CBD reactions, the concentration of the metal ion and the chalcogenide ion are controlled.<sup>49</sup> Under basic reaction conditions (i.e. pH 9, and pH 12) CuS can be deposited using the following (unbalanced) reaction pathway:<sup>49-50</sup>

$$Cu^{2+} + EDTA^{4-} \rightarrow [Cu(EDTA)]^{2-}$$
7.1

$$CH_3CSNH_2 + 2OH^- \rightarrow CH_3COO^- + NH_3 + HS^-$$
7.2

$$\mathrm{HS}^{-} + \mathrm{OH}^{-} \rightarrow \mathrm{S}^{2-} + \mathrm{H}_{2}\mathrm{O}$$
 7.3

$$Cu^{2+} + S^{2-} \to CuS$$
 7.4

The concentration of "free" copper ions is controlled by a complexing agent, ethylenediaminetetraacetic acid (EDTA) (reaction 7.1). Thioacetamide reacts with hydroxide ions present in solution to form bisulfide ions, HS<sup>-</sup> (reaction 7.2). Subsequently the bisulfide ions decompose to  $S^{2-}$  ions (reaction 7.3) which then react with  $Cu^{2+}$  ions to form covellite (CuS) (reaction 7.4). However in weakly acidic solutions (ie. pH 6), the deposition reaction may proceed through the decomposition of a  $Cu^{2+}$ -thioacetamide complex rather than formation of intermediate bisulfide and sulfide ion.<sup>49</sup> This reaction is much slower than the hydrolysis of thioacetamide under basic conditions (reactions 7.2 and 7.3), and so less copper sulfide is deposited at pH 6 than pH 9 or pH 12. Reactions 7.2 and 7.3 also clearly show that as the bath pH increases, i.e. the concentration of OH<sup>-</sup> ions in the bath increases, the deposition rate is likely to increase. This is because by Le Chatelier's principle the increased [OH<sup>-</sup>] concentration will drive reactions to 7.2 and 7.3 to the product side leading to an increase in the S<sup>2-</sup> concentration and more CuS deposited (reaction 7.4).

Our experiments indicate that the reaction pathways involved in CuS CBD are more complicated than the above discussion suggests. The data also clearly show that the chemical nature of the SAM terminal group is also important in the deposition process. Methyl-terminated SAMs are hydrophobic while hydroxyl- and carboxylic-acid terminated SAMs are hydrophilic. deposition However, this cannot account for the differences observed. If hydrophobicity/hydrophilicity of the substrates controlled the CBD process, we would expect that the least amount of CuS would be deposited on the -CH<sub>3</sub> terminated SAMs at every bath pH studied. However, at pH 9 there is more copper sulfide deposited on the hydrophobic  $-CH_3$ terminated SAM than on the -COOH and -OH terminated SAMs! This indicates that it is the interaction of the precursor ions with the SAM terminal groups that lead to the differences in the observed deposition.

We propose that the deposition can be explained via a kinetically controlled reaction. On  $-CH_3$  terminated SAMs, the terminal C-H bonds are non-polar. Consequently, there is no specific interaction between either the Cu<sup>2+</sup> or S<sup>2-</sup> ions in solution and the  $-CH_3$  terminal group. Nucleation of the copper sulfide layer likely occurs due to trapping (most likely at defects) of either Cu<sup>2+</sup> or S<sup>2-</sup> ions or by the precipitation of small clusters (cluster-by-cluster growth).<sup>36-39, 50-51</sup> As the pH of the deposition bath increases, there is a steady increase in the amount of copper sulfide deposited because the concentration of S<sup>2-</sup> in solution increases. Hydroxyl-terminated SAMs have a polar terminal C-OH bond with -OH group having a small negative charge ( $\delta^{-}$ ). As the deposition bath pH increases, the negatively charged -OH group repels some of the S<sup>2-</sup> ions in solution leading to less CuS deposited than on  $-CH_3$  terminated SAMs.



**Figure 7.5** High resolution positive ion spectra centered at m/z 163 after deposition of CuS for 24 h at pH 6, pH and pH 12 on –COOH terminated SAMs.

The large increase in the amount of CuS deposited on –COOH terminated SAMs can be explained in the following way. For –COOH terminated SAMs, the surface  $pK_{\frac{1}{2}}$  is ~8.0, which is the pH of the solution at which a surface is 50 % ionized.<sup>52</sup> Thus as the bath pH increases the – COOH terminal group deprotonates to form carboxylate ions, COO<sup>-</sup>, and at pH 12 the surface is almost fully deprotonated. This leads to two competing effects. The large increase in the copper sulfide deposition can be attributed to the formation of copper-carboxylate complexes which serve as the nucleation sites for subsequent deposition.<sup>36-39, 51, 53</sup> After CuS CBD, we observe ions of the form Cu(COO)CH<sub>x</sub><sup>+</sup> (Figure 7.5), which are characteristic of the formation of copper-carboxylate surface complexes.<sup>51</sup> In Figure 7.5, it can be seen that at pH 6 there are no Cu(COO)CH<sub>4</sub><sup>+</sup> ions present in the mass spectrum which is consistent with the measure surface  $pK_{\frac{1}{2}}^{52}$ ; at this bath pH, the –COOH terminal group is fully protonated. Above pH 9, the ion intensity of Cu(COO)CH<sub>4</sub><sup>+</sup> increases suggesting that more copper-carboxylate complexes form at higher bath pH (i.e. pH 12). Thus at pH 12 there is more copper sulfide deposited on –COOH terminated SAMs than on –CH<sub>3</sub> and –OH terminated SAMs. However, the equilibrium constant, *K*, for the complexation of Cu<sup>2+</sup> and carboxylic acids (<100)<sup>54</sup> is very low. In the deposition bath there is a large concentration of EDTA and Cu<sup>2+</sup> has a very high binding constant to EDTA, ( $5 \times 10^{18}$ ),<sup>55</sup> and so it is likely that few copper-complexes will form. This suggests that the surface is negatively charged and similarly to –OH terminated SAMs there is repulsion between some of the S<sup>2-</sup> ions in solution. Therefore at pH 9, there is less CuS deposited on –COOH terminated SAMs than on –CH<sub>3</sub> terminated SAMs.

### 7.4 Conclusions

Copper sulfide CBD using thioacetamide is strongly dependent on the pH of the deposition bath. Our data suggests that this is due to the interaction of the deposit precursors with the functionalized SAMs. For  $-CH_3$  terminated SAMs, there is no specific interaction with the deposition bath reagents. As the bath pH increases there is a steady increase in the amount of CuS deposited due to an increase in the S<sup>2-</sup> concentration in the bath. For -OH terminated SAMs, there is also a steady increase in the CuS deposited with bath pH which can also be attributed to the increase in the S<sup>2-</sup> concentration. However, the amount of CuS deposited is less than on  $-CH_3$  terminated SAMs because the S<sup>2-</sup> in solution are repelled by the slightly negatively charged, polar -OH terminal group.

Copper sulfide deposition on –COOH terminated SAMs is very strongly dependent on the deposition bath pH due to two competing effects: the formation of copper-carboxylate surface complexes which can serve as the nucleation sites for film growth, and the repulsion of  $S^{2-}$  ions by the negatively charged –COO<sup>-</sup> terminated surface at pH 9 and pH 12. Thus, at pH 9, more copper sulfide is deposited on –CH<sub>3</sub> terminated SAMs but at pH 12 more copper sulfide is deposited on the carboxylic acid terminated SAM.

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#### **CHAPTER 8**

#### **CONCLUSIONS AND FUTURE WORK**

#### **8.1 Conclusions**

One of the major challenges for the fabrication and integration of nanomaterials into everyday technologies is the development of simple, low-cost, low temperature, and chemically and area selective deposition techniques for semiconducting materials. In this dissertation, room temperature chemical bath deposition (CBD) methods were developed to deposit semiconductor materials including molybdenum disulfide (MoS<sub>2</sub>) and copper sulfide (Cu<sub>x</sub>S) thin films onto organic substrates, in particular self-assembled monolayers (SAMs).

We have developed a room temperature chemical bath deposition method by which to deposit MoS<sub>2</sub> using ammonium molybdate as the Mo source and thioacetamide as the S source. Using Raman spectroscopy and XPS, we demonstrate that at room temperature the deposited MoS<sub>2</sub> polytype can be controlled by the surface energy of the substrate. On low energy, hydrophobic surfaces, such as  $-CH_3$  and  $-CO_2C_6F_5$  terminated SAMs, 2H MoS<sub>2</sub> is deposited. In contrast on high energy, hydrophilic surfaces, such as -OH and -COOH terminated SAMs, 1T MoS<sub>2</sub> is deposited. Further, this effect does not require well-ordered surfaces. On hydrophobic surfaces including PTFE tape, which is used to seal pipe threads, and hydrogen functionalized silicon (H-Si), 2H MoS<sub>2</sub> is deposited. On hydrophilic substrates, such as a soda-lime glass slide, 1T MoS<sub>2</sub> is deposited. Using the known surface energies of the SAMs, we estimate that the surfaces with energies larger than ~30 mJ/m<sup>2</sup> will stabilize the 1T MoS<sub>2</sub> film.

Using XPS, Raman spectroscopy, ATR IR spectroscopy, optical microscopy, AFM, SEM and TOF SIMS the reaction pathways involved in the CBD of MoS<sub>2</sub> have been investigated using ammonium molybdate as the Mo source and thioacetamide as the S source. The data shows that the reagent hydrazine is critical to the process. Hydrazine reacts with thioacetamide in the deposition bath to form hydrogen sulfide. In turn, the hydrogen sulfide reacts with the molybdate ions,  $MoO_4^{2-}$ , to form thiomolybdate ions,  $MoS_4^{2-}$ . After the formation of the thiomolybdate ions, the Mo(VI) species are reduced to Mo(IV) to form  $MoS_2$  by hydrazine. The interaction of the deposited  $MoS_2$  with the gold substrates has also been studied. Similar to gold nanoparticles and thin films deposited on  $MoS_2$  films, it is observed that the deposited  $MoS_2$  strongly interacts with the Au substrate. In Raman spectra, the blue shift of the  $A_{1g}$  mode exhibits a blue shift while the  $E_{2g}^1$  mode is red shifted. Additionally, for the first time, it is observed that the J modes of 1T  $MoS_2$ are significantly broadened. Further, in the XPS spectra the Mo 3d and S 2s binding energies increase by ~1.1 eV for 1T  $MoS_2$ , while for 2H  $MoS_2$  the binding energy shift is negligible. This suggests that the interaction of the metallic 1T  $MoS_2$  is likely stronger with the Au substrate.

Using the understanding of the reaction pathways gained, area-selective deposition of 2H and 1T MoS<sub>2</sub> is demonstrated on micropatterned –COOH/–CH<sub>3</sub> or –OH/–CH<sub>3</sub> SAM surfaces. Using Raman mapping it is demonstrated that 1T MoS<sub>2</sub> is deposited on the –COOH and –OH terminated SAM areas while 2H MoS<sub>2</sub> is deposited on the –CH<sub>3</sub> terminated SAM areas.

The CBD of copper sulfide is strongly dependent on the bath pH and the terminal group of the SAM. As the bath pH increases the amount of copper sulfide deposited increases, which is attributed to the increase in the decomposition rate of the sulfur precursors, thiourea or thioacetamide to form sulfide ions. Using thiourea as a sulfur source, it is shown for the first time that the copper sulfide deposit can be changed from covellite, CuS, to chalcocite, Cu<sub>2</sub>S on  $-CH_3$ 

terminated SAMs. However on –COOH and –OH terminated SAMs the deposit is CuS due to the interaction of the sulfide ions with the terminal SAM groups.

Using thioacetamide as a sulfur source it is observed that the covellite, CuS, is deposited on –OH, –COOH and –CH<sub>3</sub> terminated SAMs. The deposition selectivity is strongly dependent on the interaction of the SAM terminal group with the CBD precursors. At pH 9, more copper sulfide is on –CH<sub>3</sub> terminated SAMs than –OH and –COOH terminated SAMs. In contrast, at pH 12 more copper sulfide is deposited on –COOH terminated SAMs than on –CH<sub>3</sub> and –OH terminated SAMs. The changes in deposition selectivity can be attributed to three different effects: the thioacetamide decomposition rate to form sulfide ions; the interaction of the formed S<sup>2-</sup> ions with the –OH and –COOH SAM terminal groups; and at pH > 9 on –COOH terminated SAMs the formation of copper-carboxylate surface complexes which act as the nucleation sites for subsequent CuS film deposition.

#### 8.2 Future Work

In chapter 5 MoS<sub>2</sub> deposited by CBD onto micropatterned SAMs showed polytype selectivity. On  $-OH/-CH_3$  and  $-COOH/-CH_3$  patterned SAMs, the optical images and Raman spectra intensities suggest that there is a thicker MoS<sub>2</sub> layer on the  $-CH_3$  terminated SAM. These reactions should be carried out at shorter deposition times to observe early stages of the growth to understand the processes by which this preferential growth occurs. Similarly, in chapters 6 and 7, the data shows that  $Cu_xS$  deposits faster on  $-CH_3$  terminated SAMs than on -OH and -COOH terminated SAMs, which are hydrophilic.

Taken together these results suggest that chemical bath deposition of  $Cu_xS$  and  $MoS_2$  are strongly dependent on the interaction of the precursors with the surface. It appears that in a similar manner to electroless nanowire deposition on micropatterned substrates (ENDOM) that these metallic sulfides preferentially deposit on the uncharged –CH<sub>3</sub> terminated SAM surface, and that at short deposition times nanowire formation will be observed at the junction of patterned –CH<sub>3</sub> and –OH or –COOH terminated SAMs.

Finally, the CBD methods shown in this work can be used to develop new deposition methods to produce other semiconductor and TMD materials. Understanding the reaction pathways involved in the CBD of  $MoS_2$  has led to new insights for the deposition of TMDs which have been previously inaccessible using room temperature methods, e.g.  $WS_2$ .

#### **APPENDIX**

## **Chapter 3 Appendix**



**Figure A3.1** S 2p photoelectron spectra of mechanically exfoliated  $MoS_2$  films deposited on MHA, MHL, HDT, and MHA-PFP SAMs. Deposition time: 24 h.



**Figure A3.2** Valence band spectra of mechanically exfoliated MoS<sub>2</sub> films deposited on MHA, MHL, HDT, and MHA-PFP SAMs. Deposition time: 24 h.



Figure A3.3 Raman spectra of thicker MoS<sub>2</sub> films deposited on MHA and MHL.

## **Chapter 4 Appendix**



Figure A4.1 AFM of MoS<sub>2</sub> deposited on HOPG. Deposition time ~ 27 h.



**Figure A4.2** Mo 3p and N 1s photoelectron spectra of the deposited film on HOPG after sputtering with 1 keV  $Ar^+$  for times from 0 min (no sputtering) to 8min.

In the Mo 3p region, the photoelectron spectra show that there is also a nitrogen-containing species present on the surface. The Mo  $3p_{1/2}$  and  $3p_{3/2}$  binding energies are 413.0 eV and 395.0 eV which indicates that MoS<sub>2</sub> has been deposited in agreement with the Mo 3d and S 2s binding energies. Upon sputtering with 1keV Ar<sup>+</sup>, the binding energies of Mo do not change indicating that the MoS<sub>2</sub> layer is present. In contrast the N1s photoelectron peaks decrease in intensity indicating that the nitrogen-containing species is being removed from the sample, and that it is only present at the deposit surface. Initially a single N 1s photoelectron is observed with binding energy 400 eV. Upon Ar<sup>+</sup> sputtering the photoelectron peak decreases sharply in intensity, and a second peak at ~397 eV is observed indicating that the nitrogen-species is being reduced. These binding energies are consistent with triazoles present on the surface<sup>2</sup> as well as molybdenum-containing complexes.<sup>1</sup>

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### **BIOGRAPHICAL SKETCH**

Jenny Orbeck was born in Oak Park, Illinois in 1990. After obtaining her Bachelor of Science in Chemistry from The University of Iowa in 2012, she received an internship at Argonne National Laboratory in the Energy Systems division supported by the U.S. Department of Energy. She remained at Argonne until June 2014 when she moved to Dallas, Texas to pursue her doctoral education at The University of Texas at Dallas.

### **CURRICULUM VITAE**

## JENNY K. ORBECK (NEÉ: HEDLUND)

#### **EDUCATION:**

University of Texas at Dallas Richardson, TX Ph.D. in Chemistry Defense: December 2018 GPA: 3.50/4.00 Advisor: Dr. Amy V. Walker

#### University of Iowa

Iowa City, IA B.S. Chemistry, Minor Spanish Graduation Date: December 2012 GPA: 3.21/4.00

## **RESEARCH AND TEACHING EXPERIENCE:**

## **Research Assistant: University of Texas at Dallas (June 2014 – Present)** Develop solution phase deposition techniques for MoS<sub>2</sub> and Cu<sub>x</sub>S nanomaterials Sample analysis using ToF SIMS, XPS, Raman spectroscopy, SEM, AFM, ATR-IR, and optical microscopy

**Graduate Teaching Assistant: University of Texas at Dallas (Aug. 2014 – May 2015)** Teaching assistant for general chemistry I and II lab courses

# Chemistry Assistant, Special Term Appointee: Argonne National Laboratory, Energy Systems (Aug. 2013 – May 2014)

ALD materials research in Dr. Jeffrey Elam's lab In-situ FTIR study of ALD  $GaS_x$  films, high-temperature high-pressure ALD catalyst testing, and sample analysis using GC-MS

# Undergraduate Laboratory Intern: Argonne National Laboratory, Energy Systems (Jan. 2013 – Aug. 2013)

Studied ALD synthesis and material characterization under the supervision of Dr. Jeffrey Elam and Dr. Joseph Libera

# Undergraduate Laboratory Intern: Argonne National Laboratory, Center for Nanoscale Materials (May 2012 – Aug. 2012)

Nanoparticle synthesis for biomedical applications in Dr. Tijana Rajh's lab

# Undergraduate Research Assistant: University of Iowa (May 2010 – May 2012)

Noble metal nanoparticle synthesis and characterization in Dr. Amanda Haes' lab

# ANALYTICAL TOOLS

X-Ray photoelectron spectroscopy, time-of-flight secondary ion mass spectrometry (ToF SIMS), Raman spectroscopy, attenuated total internal reflection infrared spectroscopy, scanning electron microscopy, atomic force microscopy, optical microscopy, UV-visible spectroscopy, Fouriertransform infrared spectroscopy, single-wavelength ellipsometry, and gas chromatography-mass spectrometry.

# **COLLABORATIVE PROJECTS**

Amon Carter Museum of American Art, January 2017 – Present Project: Studying removal of damaging adhesives from José Posada prints using solvent fuming and subsequent sample analysis with optical microscopy and ToF SIMS.

**Louisiana State University, J.R. Ragains**, August 2015 **Project:** Employed ToF SIMS and XPS to study the formation of fluorinated thin films on gold.

University of Texas at Dallas, J.Y. Chan, August 2014 Project: Identified oxidation states in  $Pr_2Fe_{4-x}Co_xSb_5$  (1 < x < 2.5) crystals using XPS.

**Performed ad hoc analyses for the following:** Essilor of America Inc., Cavendish Kinetics Inc., Texas Instruments Inc., and Daikin America Inc.

# **PROFESSIONAL SOCIETIES**

American Vacuum Society American Chemical Society

# **PROFESSIONAL ACTIVITIES**

American Vacuum Society, DFW Metroplex Student Chapter – Treasurer 2017 Chemistry Graduate Student Association, University of Texas at Dallas – President 2016/17 Chemistry Graduate Student Association, University of Texas at Dallas – Vice President 2015/16 Chemistry Graduate Student Association, University of Texas at Dallas – Co-founder 2014 Women in Science and Technology, Argonne National Laboratory – Member 2013/14 Alpha Chi Sigma, University of Iowa – House Treasurer 2012 Alpha Chi Sigma, University of Iowa – Events Chair 2011 American Chemical Society, University of Iowa Student Chapter – President 2012 University of Iowa Health Care Community Education Program – Education Leader 2011 University of Iowa Hospitals and Clinics – Student Leader Board Member 2010 & 2011 Alpha Delta Pi Sorority, University of Iowa – Vice President 2010

## AWARDS

2D Focus Topic Student Travel Award, AVS 64<sup>th</sup> International Symposium, 2017
AVS Student Travel Award, AVS DFW Metroplex Student Chapter, 2017
Science Undergraduate Laboratory Internship: Argonne National Laboratory, U.S. Department of Energy, 2013
Russel K. Simms Scholarship, Department of Chemistry, University of Iowa, 2011
Alpha Chi Sigma Professional Chemistry Scholarship, University of Iowa, 2011
Distinguished Poster Award, Spring Undergraduate Research Festival, University of Iowa, 2011
Iowa Center for Research for Undergraduates Research Fellow, University of Iowa, 2010
Student Leader Board Scholarship, University of Iowa Hospitals and Clinics, 2010-2011
UI Iowa Heritage Award, University of Iowa, 2008-2012

## **CONFERENCE PRESENTATIONS**

Presenting author is underlined.

- J.K. Hedlund, A.V. Walker, "Chemical Bath Deposition of Substrate Selective Molybdenum Disulfide," AVS Texas Chapter Conference 2018, Fort Worth, TX, Aug. 1<sup>st</sup> – Aug. 3<sup>rd</sup>, 2018.
- J.K. Hedlund, A.V. Walker, "Chemical Bath Deposition of Substrate Selective Molybdenum Disulfide," SIMS USA / Applied Surface Analysis / AVS Pacific Northwester Chapter Symposium, Richland, WA, June 19<sup>th</sup> – June 22<sup>nd</sup>, 2018.
- J.K. Hedlund, A.V. Walker, "Chemical Bath Deposition of Phase Selective MoS<sub>2</sub> on Templated Surfaces," AVS 64<sup>th</sup> International Symposium & Exhibition, Tampa, FL, October 29<sup>th</sup> – November 3<sup>rd</sup>, 2017.
- 4. <u>J.K. Orbeck</u>, A.V. Walker, "Chemical Bath Deposition of Molybdenum Disulfide Ultra-Thin Films," European Conference on Surface Science 32<sup>nd</sup> Annual, Grenoble, France, August 28<sup>th</sup> – September 2<sup>nd</sup>, 2016.
- J.K. Hedlund, R.P. Joshi, A.V. Walker, "Studying Copper Sulfide Chemical Bath Deposition Reactions on Organic Surfaces," AVS Texas Chapter Conference 2016, Richardson, TX, August 3<sup>rd</sup> – August 4<sup>th</sup>, 2016.
- J.K. Hedlund, A.V. Walker, "Chemical Bath Deposition of MoS<sub>2</sub> Ultra-Thin Films and Nanowires", AVS Texas Chapter Conference 2015, Richardson, TX, August 5<sup>th</sup> – August 6<sup>th</sup>, 2015.

- J.K. Hedlund, A.V. Walker, "Reducing Agent Effect of Cu Deposition on Organic Substrates", AVS Texas Chapter Conference 2014, Richardson, TX, August 6<sup>th</sup> – 7<sup>th</sup>, 2014. (Poster)
- 8. <u>J.K. Hedlund</u>, D.C. Cronauer, J.A. Libera, A.J. Kropf, V.R.R. Pendyala, J.W. Elam, "Ruthenium Hydrotreating Catalysts Prepared by Atomic Layer Deposition," Institute for Atom Efficient Chemical Transformations (IACT) Meeting, Argonne, IL, 2014. (Poster)
- J.K. Hedlund, M. Pierre, B. Shrestha, A.J. Haes, "Sensing drug mimics using size tunable solution phase SERS substrates", Midwest/Great Lakes Joint Regional ACS Meeting, St. Louis, MO, October 19<sup>th</sup> – October 22<sup>nd</sup>, 2011.
- 10. <u>J.K. Hedlund</u>, B. Shrestha, M. Pierre, A.J. Haes, "Synthesizing Nanoparticles with Lightning Rod Effects," Summer Undergraduate Research Festival 2011, Iowa City, IA. (Poster)
- 11. <u>J.K. Hedlund</u>, B. Shrestha, A.A. Volkert, A.J. Haes, "Interactions of Biomarkers with Functionalized Gold Nanoparticles," Spring Undergraduate Research Festival 2011, Iowa City, IA. (Poster)
- 12. J.K. Hedlund, A.A. Volkert, A.J. Haes, "Self-Assembly of Monolayers onto Noble Metal Nanoparticles," Fall Undergraduate Research Festival 2010, Iowa City, IA. (Poster)
- J.K. Hedlund, S. Nath, A.A. Volkert, A.J. Haes, "Encapsulating Noble Metal Nanoparticles with Silica," Summer Undergraduate Research Festival 2010, Iowa City, IA. (Poster)

## **PUBLICATIONS**

- 1. <u>Hedlund, J.K.</u>; Walker, A.V., Facile One-Pot Synthesis of Molybdenum Disulfide Thin Films. **2018**, *Manuscript in preparation*.
- 2. <u>Hedlund, J. K.</u>; Walker, A.V., Polytype Control of MoS<sub>2</sub> Using Chemical Bath Deposition. **2018**, *To be submitted to the Journal of Chemical Physics*, American Institute of Physics.
- 3. <u>Hedlund, J. K.</u>; Ellsworth, A. A.; Walker, A. V., (Invited)Using Surface Chemistry to Direct the Deposition of Nano-objects for Electronics. *ECS Transactions* **2018**, *86* (3), 89-101.
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