Characterization of Alkanethiolate Self-assembled Monolayers on Zinc Selenide Thin Films

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Characterization of Self-Assembled Monolayers

on Zinc Selenide Thin Films

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In Partial Fulfillment of the Requirements

For Departmental Honors in Chemistry

Under the Supervision of Alison Noble and Niklas Hellgren

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ABSTRACT

Alkanethiolate self-assembled monolayers (SAMs) have been formed on zinc selenide (ZnSe) through adsorption from solution. Zinc selenide as a SAM-supporting substrate is of particular interest due to its transparency in the infrared region of the electromagnetic spectrum, enabling interfacial interactions at the substrate surface to be studied through transmission IR spectroscopy. In the past, mechanically polished, optical quality ZnSe surfaces have been used to support SAM formation. This surface, however, typically has a rms roughness around 40 nm, meaning it cannot support highly-ordered SAMs. In order to promote more consistent formation of highly-ordered SAM, a smoother supporting substrate is required. A significantly smoother ZnSe surface has be produced through physical vapor deposition (PVD) onto silicon substrates. The PVD-generated zinc selenide thin film exhibits the same IR transparency as the mechanically polished substrate, but with a rms roughness in the range of 2.7 ± 0.9 nm, which is over an order of magnitude improvement in surface roughness. The thin film ZnSe-SAM system was characterized through Fourier Transform Infrared (FTIR) spectroscopy, contact angle goniometry and x-ray photoelectron spectroscopy (XPS). In the XPS spectra, the shifts and relative intensities of Zn 2p, Se 3d, S 2p, and C 1s peaks when SAMs adsorbed to the surface have been used to show whether the SAM is physiosorbed or chemisorbed. A significant shift in the S 2s peak for a ZnSe film with SAMs compared to free thiol literature values, which is indicative of a change in chemical environment, provides evidence for chemisorption of thiolate SAMs to the ZnSe thin film.

INTRODUCTION

There has been significant interest in and research on self-assembled monolayers (SAMs) over the last several decades due to their versatility and wide variety of applications. SAMs have
been recently used in studies involving biosensors and liquid crystal displays among other forms of technology. This study, however, is concerned more with the basic science of SAMs and a specific substrate, zinc selenide, in order to develop a fundamental understanding a framework for the more applied studies. Self-assembled monolayers share in common a basic structure comprised of a long carbon chain with a tail group, spacer, and head group (Fig. 1). Through a chemical or physical interaction, the head group adsorbs to a substrate. There are three classes of surfaces that are commonly used with self-assembly processes: metals, semiconductors, and oxides. Characteristic metals include gold (Au) (which is the most commonly used substrate\textsuperscript{1,2}), silver (Ag), platinum (Pt), palladium (Pd), copper (Cu), and mercury (Hg). Semiconductors include gallium arsenide (GaAs), indium phosphide (InP), cadmium selenide (CdSe), and zinc selenide (ZnSe); ZnSe is the semiconductor involved with this study. Common oxide surfaces include aluminum oxide (Al\textsubscript{2}O\textsubscript{3}), titanium dioxide (TiO\textsubscript{2}), and silicon dioxide (SiO\textsubscript{2}). Each of these surfaces has unique properties and will interact with head groups of monolayers in its own way.

In addition, the head groups can be varied so as to adsorb effectively to different substrates. One of the most successful combinations consists of thiol head groups adsorbing to metallic surfaces.\textsuperscript{1–3}

Figure 1: The basic structure of a SAM. The head groups are adsorbed to the substrate. Attached to the head group is an alkyl spacer that can vary in length. At the end of the spacer is the tail, or terminal group, which can be modified.
reaction that occurs at the SAM-substrate interface for thiolate SAMs on metal surfaces is a Lewis acid/base reaction between the metal (Lewis acid) and the sulfur (Lewis base). The sulfur component of the thiol group adsorbs well because of its capacity for multiple bonds and its attraction towards transition metal surfaces.\(^4\) This process of adsorbing the monolayers to a metallic surface is the most widely studied area of monolayers. The combination of these substrates, and the many different monolayers that can be developed and effectively adsorbed, create a wide range of possibilities for the applications of monolayers in the field of chemically designed surfaces. The rest of the chain, including the tail, or terminal, group can be modified to tune the molecule toward its intended purpose either before or after the metal-monolayer complex is formed.\(^6\)

The thermodynamically-driven self-assembly phenomenon, as well as the wide variety of potential components, of these monolayers, creates interest in both fundamental and applied areas of scientific study. Fundamentally, SAMs can be used to increase understanding of the chemical surface interactions between different types of substrates and monolayers. Characterization of the SAM-substrate interface facilitates a deeper understanding of processes such as lubrication, corrosion, catalysis and optics to biomedicine, and artificial enzymes.\(^5\) More specifically, SAMs enable the characterization of the various surface properties such as wetting, electron transfer, and protein binding\(^3\) which apply to a wide range of important chemical processes on surfaces. Understanding these properties aids in acquiring knowledge about larger concepts and achieving relevant goals in the realm of surface chemistry. Due to the highly ordered nature and chemical manipulability of SAMs, they are among the most versatile systems employed in nanotechnology.\(^2,4\) Organic synthesis can be used to make monolayer molecules an extensive range of possible functional groups at the terminus, creating a wide range of applications and an avenue
for targeted chemical design of surfaces. The stability and reliability of these single-layer nanoscale films is another benefit to nanotechnological applications. Due to their compatibility with biological molecules, SAMs have potential in biological and chemical sensing\textsuperscript{4}, given the appropriate monolayer and substrate combination.

As mentioned previously, most SAM studies have utilized gold as a substrate for the formation of the monolayer films as it is a clean, inert substrate that can be made atomically flat by evaporating Au onto Si. The preparation of SAMs (specifically alkanethiols) on gold has been thoroughly researched and the process for formation of this type of SAM is well understood.\textsuperscript{1} There has, however, been recent study into the use of zinc selenide (ZnSe) as a substrate for SAMs.\textsuperscript{3} ZnSe is a robust semiconductor that is transparent in the entire infrared region, making it an excellent candidate for studying the substrate-monolayer interactions via vibrational spectroscopy.\textsuperscript{3} This property of ZnSe allows the further study of surface interactions that metals like gold cannot offer because the investigations can be carried out in transmission, rather than reflection IR geometries. The studies into ZnSe

\textbf{Figure 2.} AFM images of (a) clean ZnSe (not exposed to adsorbate solution) and (b) the same sample after a 24 h exposure to a 1 mM solution of 1-hexadecanethiol in ethanol.\textsuperscript{3}
as a monolayer substrate have demonstrated that it does have the ability to form monolayers on its surface in a manner that is similar to silver.\textsuperscript{3} There are, however, some challenges with using a polished ZnSe substrate due to higher-than-ideal surface roughness. Atomic force microscopy (AFM) techniques have been used to characterize the mechanically polished ZnSe surface. Many imperfections and variations in height can be seen in the topography of the substrate (Fig. 2).\textsuperscript{3} When the monolayers are formed, they mimic the topography of the surface and the substrate defects are translated into the monolayer film. These imperfections hinder the overall functionality of the monolayers by decreasing the homogeneous chemical modification of the substrate. The ZnSe surface is not smooth at a molecular level and therefore is likely to promote less ordered monolayers than what would be observed on the smooth metal surfaces typically used for self-assembled monolayers.

In order to develop an effective SAM system as shown in figure 3, the substrate has to be atomically flat.\textsuperscript{1} The flat surface promotes ordered SAMs leading to increased functionality due to the uniformity in position of the tail groups.\textsuperscript{7,8} While SAMs have been shown to form on ZnSe, using ZnSe as a substrate would be more attractive if these defects due to surface roughness could be significantly decreased. Employing advanced mechanical polishing techniques that have been applied does decrease the defects in the surface, but mechanical polishing of ZnSe cannot achieve surfaces that are smooth at the molecular

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{ZnSe-SAM.png}
\caption{Proposed ZnSe-SAM system.}
\end{figure}
or atomic level. To generate materials that are smoother and more suitable to SAM formation, the ideal option would be to generate the ZnSe thin film via a chemical or physical vapor deposition onto a smooth substrate, such as Si. Thin films of this sort are useful for all kinds of technology and surfaces and are used in optical, electrical, thermal, and mechanical applications.

Several methods have been utilized to grow ZnSe thin films including chemical bath deposition\textsuperscript{11-13}, molecular beam deposition\textsuperscript{14}, high pressure magnetron sputtering\textsuperscript{15}, and radio frequency magnetron sputtering\textsuperscript{16}. In this study we will be using the last of these methods, radio frequency (RF) magnetron sputtering to grow ZnSe on smooth double-polished Si substrates. A diagram of the RF magnetron sputtering can be seen in figure 4. This process works by first evacuating the chamber to create a vacuum and then leaking in argon gas. The gas is then ionized to \( \text{Ar}^+ \) and is attracted to the target due a negative voltage applied to the magnetron. Secondary electrons are trapped by a magnetic field created by permanent magnets in the magnetron. This causes a sustained ionization and an argon plasma is formed above the target. Argon ions then bombard the target (in this case it is ZnSe) with enough energy to knock off Zn and Se atoms from the target. These atoms travel to the top of the vacuum and deposit on the substrate (in this study, Si is used), forming a thin film\textsuperscript{10,17}. Specifically, an RF system is used in this study to neutralize ZnSe as it is an insulator.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{RF_magnetron_sputtering.png}
\caption{Schematic of RF magnetron sputtering system}
\end{figure}
that would build up charge during this process.

Another important aspect to forming successful SAMs is to ensure that the monolayer molecules are chemisorbed to the surface. There are situations where the molecules can be attached to the substrate through a physical attraction instead of a chemical bond. A chemisorbed SAM is more advantageous than a physisorbed one due to the durability and reliability of the system. In accordance with any application of this system, the SAMs would need to stay attached to the substrate in a variety of solutions for a reasonable amount of time dependent on the application. The difference between these attractions can be seen in a shift in certain peaks in an x-ray photoelectron spectroscopy (XPS) spectrum. In this study, the sulfur 2s peak is examined to determine whether the monolayer molecules are chemisorbed or physisorbed.

As shown above, there has been much research into the areas of SAMs, ZnSe, thin films, and thin film formation methods. The problems that have occurred with SAM formation on ZnSe caused by the defects in the surface are hindering future research with these two components. The goal is to use the method of PVD with magnetron sputtering to create a ZnSe thin film, which is smoother than the bulk ZnSe surfaces that are currently available via mechanical polishing. The thin films are analyzed for their defects and overall smoothness and are characterized again, after the SAMs are applied, to determine the overall homogeneity of the ZnSe-supported monolayer. The smoother ZnSe surfaces, generated via thin film deposition, promote more highly ordered and homogeneous SAMs.
EXPERIMENTAL METHODS

Deposition of ZnSe on Silicon Substrate

The ZnSe thin films were deposited on silicon substrates by Alex Sredenschek under the supervision of Dr. Niklas Hellgren in the Department of Mathematics, Physics, and Statistics at Messiah College. A BOC Edwards Auto 500 magnetron sputtering system was used to make these films. Variations in the parameters such as temperature, pressure, bias, and power were introduced in order to vary the film characteristics. The smoothest films were produced using an argon gas pressure of 10 mTorr, an RF power of 150 W, and no heating of the substrate (T ≈ 25 °C).

Atomic Force Microscopy

A Digital Instruments Multimode AFM was used to characterize the ZnSe films and ZnSe mechanically polished substrates. Tapping mode was used to scan the surface topography so as to preserve surface integrity. Multiple scans were completed for each surface for 10 µm x 10 µm scan sizes. The main function of the AFM was to measure the roughness of the films compared to the polished ZnSe slides by means of a root mean square (rms) roughness measurement.9

Formation of SAMs on ZnSe Thin Films

Before the adsorption process can occur, all glassware and polytetrafluoroethylene (PTFE) containers were cleaned using the proper RCA/TL-1 cleaning procedure18. The films were also cleaned to remove organic contaminants form the surface. This was done by placing the films, in a UV ozone chamber (UVOC) for 20 minutes at a time, rinsing the films with ethanol afterward, and drying with a stream of nitrogen gas. This process was completed three times for each film; multiple films were cleaned at the same time.3,21 The cleanliness of the surface was determined using contact angle (CA) goniometry. A 5 µL drop of UltraPure Water was gently placed on the
film surface using a syringe and the contact angle was measured using a house made goniometer (Fig. 5). Contact angles were completed in triplicate for each film. A 5mM solution of 1-hexadecanethiol (HDT, Sigma Aldrich) and 200 proof ethanol (EtOH, Sigma Aldrich) of appropriate volume was prepared in a volumetric flask. The solution was poured into the PTFE container that was cleaned earlier and the film was placed in the solution with the film side facing up to ensure formation of SAMs on the ZnSe film side of the silicon wafer. The film was left in solution for 24-48 hours. After the film was done soaking, the sample was removed from solution, rinsed with ethanol, and dried with nitrogen gas.\textsuperscript{21}

*Confirmation of Alkanethiol SAMs on ZnSe Films*

As described above, the films with SAMs were characterized using XPS and AFM techniques. The SAMs were characterized further using Fourier Transform Infrared (FTIR) spectroscopy and CA goniometry. The Infrared (IR) spectra was collected in transmission mode on a Thermo Scientific Nicolet Avatar 380 FTIR Spectrometer. The OMNIC Series software was set to complete each spectrum with 128 scans and a resolution of 2 cm\(^{-1}\). The house made goniometer was used the same way as before to measure the contact angles for the films with SAMs.

*X-ray Photoelectron Spectroscopy*

A Kratos AXIS 165 X-ray photoelectric spectrometer at the University of Maryland was used to characterize the chemical composition of the surface of the films before and after exposure
to the 1-hexadecanethiol SAMs. Spectra were collected using Mg Kα X-rays with an energy of 1253.6 eV and a low-energy electron flood gun was applied for charge neutralization, since the ZnSe films are insulating. The measurements in this study were collected with a 90° electron take-off angle. Survey spectra were collected with a pass energy of 160 eV and the core level spectra were collected with a pass energy of 20 eV. X-ray photoelectron spectroscopy was used to analyze ZnSe surface with and without 1-hexadecanethiol SAMs adsorbed, in order to characterize chemical shift in any binding energy due to chemical bonds forming between the SAMs and the substrate. For reference, SAMs on Au substrates were also analyzed, since this is a well-characterized system. Specifically, the shift in sulfur indicated that the SAMs are chemisorbed to the surface.

RESULTS AND DISCUSSION

ZnSe Film Synthesis

AFM image roughness analysis was the method used to determine surface roughness of different samples. Figure 6 shows typical AFM images of mechanically polished ZnSe and synthesized ZnSe thin films. The ZnSe thin films synthesized for this study had a rms roughness of 3.63 ± 0.21 nm as compared to a rms roughness of 38 ± 8 nm for the mechanically polished ZnSe substrate. The improvement in surface roughness is a step toward producing highly-ordered SAMs.

Figure 6. AFM topographic images of the (a) optically polished ZnSe and (b) ZnSe thin film
Confirmation of SAMs on ZnSe thin films

FTIR spectroscopy and contact angle goniometry were the main methods used to confirm the presence of SAMs on the ZnSe substrates. Table 1 lists the contact angles for the ZnSe films developed in this study before treatment (after cleaning) and after immersion treatment in 0.1 mM 1-hexadecanethiol. Increasing contact angles means the surface is becoming more hydrophobic. This increase in contact angle between the untreated samples and SAM treated surfaces is as expected. The HDT molecules make the surface much more hydrophobic due to the majority hydrocarbon-nature of the molecules. Compared to the change in contact angles for the original optically polished ZnSe surface, the ZnSe films show a more hydrophilic untreated surface and a greater difference between the untreated and treated surface contact angles (Table 1). The greater difference between treated and untreated surface contact angles for the ZnSe films with and without SAMs allows for more definitive results about SAM formation using this method. In addition, the higher contact angles on the treated ZnSe films could indicate the presence of a more ordered and densely packed monolayer. When the molecules are more densely packed, the surface as a whole becomes more hydrophobic as there would be less ZnSe and more HDT contacting the water drop directly.

Table 1. Comparison of contact angles across different samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average Contact Angle Pre-SAM deposition</th>
<th>Average Contact Angle Post-SAM deposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSe Optically-Polished Slide</td>
<td>49.6 ± 1.1°</td>
<td>95.5 ± 2.7°</td>
</tr>
<tr>
<td>ZnSe Film 2.2</td>
<td>22.8 ± 2.8°</td>
<td>121.3 ± 3.2°</td>
</tr>
<tr>
<td>ZnSe Film 2.4</td>
<td>13.3 ± 1.5°</td>
<td>114.2 ± 8.2°</td>
</tr>
</tbody>
</table>
FTIR analysis of the treated ZnSe films was performed to confirm the HDT molecules were interacting with the ZnSe films in the same way as on the original, optically polished ZnSe. This analysis gave rise to the characteristic C-H stretching peaks at approximately 2920 cm\(^{-1}\) and 2850 cm\(^{-1}\) as seen in Figure 7. The presence of these stretches, which are the same for HDT on optically polished ZnSe, indicates the same orientation of HDT molecules on the ZnSe film surface as seen on the optically polished ZnSe.\(^3\) The amplitude of the peaks is also significant. A single layer of HDT molecules should give rise to peaks with an amplitude of \(~0.002\) absorbance units,\(^3\) which can be seen in the data presented in Figure 7.

\textit{XPS analysis}

Due to the overlap of the Se 3p and S 2p regions (Fig. 8), the less traditionally studied S 2s is the focus of this part of the study. Previous studies show that a free thiol on a long carbon chain would have an S 2s binding energy at 217 eV.\(^{19}\) To properly compare the spectra, the C 1s peaks were aligned at 284.0 eV (Fig. 9). Three samples were compared using this technique: ZnSe with SAMs, ZnSe without SAMs, and gold with the same SAMs as the ZnSe and their survey spectra can be seen in figure 10. As seen
in Figure 11, there is a small shift in the Se 3d region between the ZnSe samples with and without SAMs. This shift could be indicative of a change in binding energy of selenium when SAMs are deposited, but it is difficult to draw conclusions from this. The shift to higher binding energy in the sample with SAMs could indicate a change in chemical environment of the selenium, indicating a potential interaction between the SAMs and the selenium. Even though this small shift is present, it does not change the assumption that any large change in the S 2s peak from the literature value is significant. As seen in Figure 12, there is a difference of about 10 eV between the S 2s peak of the ZnSe with SAMs and the literature free thiol value. The gold sample with SAMs has an S 2s peak at 225.0 eV which is much closer to the peak in the treated ZnSe sample at 227.1 eV. This means the binding energy for the gold-sulfur bond is similar to the

**Figure 9.** C 1s region of three samples (a) Au with SAMs (b) ZnSe without SAMs and (c) ZnSe with SAMs to show charge correction.

**Figure 10.** Survey spectra of three samples (a) Au with SAMs (b) ZnSe without SAMs and (c) ZnSe with SAMs with relevant regions labeled.

**Figure 11.** Se 3d region of two samples; ZnSe with and without monolayers.
binding energy of the ZnSe-sulfur bond. Gold is known to support chemisorbed thiolate monolayers, which has been confirmed by this study through the difference in binding energy between a free thiol and the S 2s peak of the gold-SAM sample (Figure 12), therefore, it can be assumed due to the similar binding energies, that the SAMs are also chemisorbed to the ZnSe film. The difference in binding energy between the S 2s binding energies of the ZnSe with SAMs and Au with SAMs is to be expected. The sulfur atom is in a different chemical environment which will change the binding energy slightly. The main comparison to be made is between the free thiol binding energy and the S 2s peak in both spectra separately, as described above.

CONCLUSIONS AND FUTURE DIRECTIONS

The wide variety of applications associated with SAMs, along with their favorable formation process, make the fundamental understanding of these systems essential. The smoother substrate developed in this study was able to support alkanethiolate monolayers in a way that resembles the support provided by the optically polished substrate. Studies in our lab have already begun to develop smoother ZnSe film with various methods to allow for further characterization of the SAM-ZnSe interface with Angle Resolved-XPS. If smoother ZnSe films can be synthesized, properties like tilt angle of the monolayer can be determined. With the chemisorption of SAMs now confirmed, studies on micro-contact printed SAMs on ZnSe films can continue. Amide or carboxylic acid terminated thiol molecules will be functionalized with fluorescein to ensure SAM
adsorption has occurred using fluorescence microscopy. Future projects will be developed to functionalize the monolayer for potential applications in biotechnology.
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I would also like to acknowledge and thank anyone who was a source of encouragement and support during the completion of this project; I could not have done it without this support.
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