

**GROWTH AND CHARACTERIZATION
OF MoS_2 , MoSe_2 , AND $\text{Mo}(\text{S}_x\text{Se}_{1-x})_2$
FORMED BETWEEN MO AND
 $\text{CuIn}(\text{S}_x\text{Se}_{1-x})_2$ DURING GROWTH**

by

Sarah Rickman

A thesis submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Master of Science in Materials Science and Engineering

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**GROWTH AND CHARACTERIZATION
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ABSTRACT

$\text{CuIn}(\text{S}_x, \text{Se}_{1-x})_2$ is a member of the semiconductor family $\text{Cu}(\text{In}_x, \text{Ga}_{1-x})(\text{S}_y, \text{Se}_{1-y})_2$ used in thin film photovoltaics. During the formation of a $\text{CuIn}(\text{S}_x, \text{Se}_{1-x})_2$ film, an interfacial layer is created between the semiconductor bulk film and the molybdenum back contact. Structural and chemical properties of the Mo- $\text{CuIn}(\text{S}_x, \text{Se}_{1-x})_2$ were evaluated for CuInSe_2 , CuInS_2 , and $\text{CuIn}(\text{S}_x, \text{Se}_{1-x})_2$ films grown by multi-source elemental evaporation. Mo films were reacted in H_2S , H_2Se , and a mixed $\text{H}_2\text{S}/\text{H}_2\text{Se}$ gas to provide a baseline comparison for the reaction during the growth of the $\text{CuIn}(\text{S}_x, \text{Se}_{1-x})_2$ films.

Chemical and structural analysis was performed using Electron Dispersive Spectroscopy (EDS), X-Ray Diffraction (XRD), and Glancing Angle X-Ray Diffraction (GIXRD). The interface between Mo and the semiconductor films was exposed by separating the glass and molybdenum from the semiconductor film. Independent measures were made on the bulk films and on the newly exposed Mo and semiconductor surfaces.

At 550°C Mo reacts with H_2Se to form MoSe_2 . MoSe_2 was seen at the interface between Mo and $\text{CuIn}(\text{S}_x, \text{Se}_{1-x})_2$ and between Mo and CuInSe_2 . The reaction of Mo with H_2S was much slower and a very thin layer of material was detected, presumably MoS_2 . A similar thin layer of material was seen at the interface between Mo and CuInS_2 but it is not known definitively at this time whether this layer is MoS_2 or MoSe_2 . Only MoSe_2 was seen when the gas mixed was used.

CHAPTER 1

MOTIVATION

1.1 Introduction

Today's society is heavily reliant upon petroleum to power the many structures and machines that make the everyday lifestyle people are used to possible. However, the supply of oil is not infinite and continues to dwindle as the demand for it increases each year. Research in alternative energy resources now is vital to prepare society for the switch to other power sources once the petroleum reserves run out. Possible forms of renewable energy include sunlight, water, wind and hydrogen to name a few. They all have the advantage that they exist in abundance and do not pollute the Earth; however the main caveat is producing devices cheaply that use these resources efficiently and safely.

Solar energy has shown promise as being a viable alternative to petroleum through the use of solar cells which convert sunlight to electricity. The first silicon solar cell was produced in about 1954 by RCA.[1] The rate of production has been increasing ever since at a rate of about 25% per year since 1997, creating as much as 744 MW/year as of 2004.[2] With an overall solar cell efficiency of around 10% the amount of area needed to provide enough power to the United States alone is approximately $10,000 \text{ m}^2$ ($25,000 \text{ km}^2$).[3]

However, if one looks at the problem from a smaller scale a family of four would only require 50 m^2 of solar panels to provide them with enough power each day assuming that each person uses 5 kWh/person/day. This is about the area typically

used by rooftops on houses making solar power a possibility for many families in terms of the area needed for enough power generation.[1]

Further research is being done to increase the efficiency of solar cells further so more power may be drawn from a smaller area but the real problem is reducing the cost of solar cells so that they are affordable to the average family and to industry. Right now electricity generation through photovoltaics is about five to ten times more expensive than electricity generated through other means. Also, an initial investment of at least \$10,000 is necessary to buy and install the solar modules.[4] Unless both the consumers and the government invest money to set up grid connected installations solar technology will continue to be confined to specific applications such as space exploration.[1]

Solar cells do offer advantages over conventional technology in that they may be recycled, there are no harmful byproducts generated from producing electricity, no danger of source exhaustion exists, and there is the possibility that they may be cost-effective. There has been extensive research into thin film solar cells as they reduce manufacturing costs because only a very thin layer of material is needed to create a functioning solar cell. The next section describes the underlying physics of how a solar cell works.[1]

1.2 Device Physics

A semiconductor is a material that has electrical properties halfway between a metal and an insulator. This is due to the difference in energy between the valence and conduction bands of the material which is referred to as the band gap. Figure 1.1 shows an ideal example of a band gap.[1]

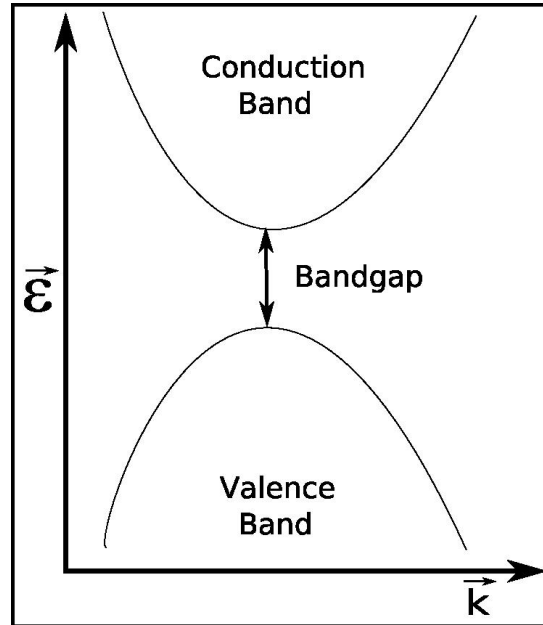


Figure 1.1: Example of a Band Gap From a Semiconductor^[1]

In metals the conduction and valence bands are continuous as a function of energy allowing electrons and holes to conduct very easily. In insulators the band gap between the filled valence bands and empty conduction bands is very large making it difficult if not impossible for electrons and holes to transit through the bands. A semiconductor has a band gap larger than that of a metal but smaller than that of an insulator.

If the energy of incident light on the semiconductor is greater than the band gap, then an electron will transition from the valence band to the conduction band leaving a hole behind in the valence band. This is assuming that the material has a direct band gap or that the minimum of the conduction band and the maximum of the valence band align at the same crystal momentum as seen in Figure 1.1. An indirect band gap is where the conduction band minimum and the valence band maximum do not line up at the same crystal momentum. In order for the momentum to be conserved a phonon or a vibration in the lattice is needed to give the extra energy required for the

electron to transition from the valence to the conduction band. CuInSe_2 and silicon are two types of semiconductors, the former having a direct band gap while the latter has an indirect band gap.[1]

Semiconductors can be doped with electrically active impurities. These dopants are classified into two categories the first being electron rich and the second electron poor. Semiconductors that are electron rich are called a n-type semiconductors and those that are electron poor are known as a p-type semiconductors. A very pure semiconductor is neither electron rich nor poor but has levels of electrons and holes intrinsic or native to the semiconductor. The material can be made into a p- or n-type semiconductor by doping or adding elements to the crystal lattice that give an excess or deficiency of electrons. Boron is commonly used to create p-type silicon and phosphorous to create n-type silicon.[1]

When an n-type semiconductor is placed next to a p-type semiconductor they form a p-n junction. Since the p-type semiconductor is electron poor, electrons in the n-type semiconductor will migrate over to the p-type semiconductor to minimize the electronic potential. By the same reasoning, holes will migrate over to the n-type material. This process forms regions in both materials where only electrons or holes are present and is known as the space charge region or depletion region. The area outside of the depletion region that has both carriers present is known as the quasi-neutral region. Eventually, the concentrations of both carriers (electrons and holes) will equilibrate and current injection or sunlight incident on the p-n junction is needed to cause the flow of carriers. Metal grids on the surfaces of the semiconductor are then connected to electrical contacts. This allows the collection of carriers from each type of semiconductor which generates electrical current.[1]

The generation of current by shining light on a semiconductor is known as the photoelectric effect. In 1839 Becquerel discovered this by shining light on two identical electrodes placed in an electrolyte. The first solar cell that relied on this principal was made by Fritts in 1883 by placing a thin sheet of selenium on a metal substrate and pressing a gold-leaf film to the selenium to create the top contact.[1] The photovoltaic effect is defined as “the creation of an electromotive force by the absorption of light (or any ionizing radiation) in an inhomogeneous solid”. [5] How well the solar cell uses this principal to produce electricity is dependent upon a number of factors which are described below.

One limitation in how much power a solar cell can generate is how much recombination takes place while current is being generated. Recombination occurs when an electron in the conduction band and hole in the valence band recombine. The concentrations of carriers will return to their thermal equilibrium states after having been removed from their equilibrium state (i.e. carrier injection). Figure 1.2 displays three common processes through which recombination takes place.[1]

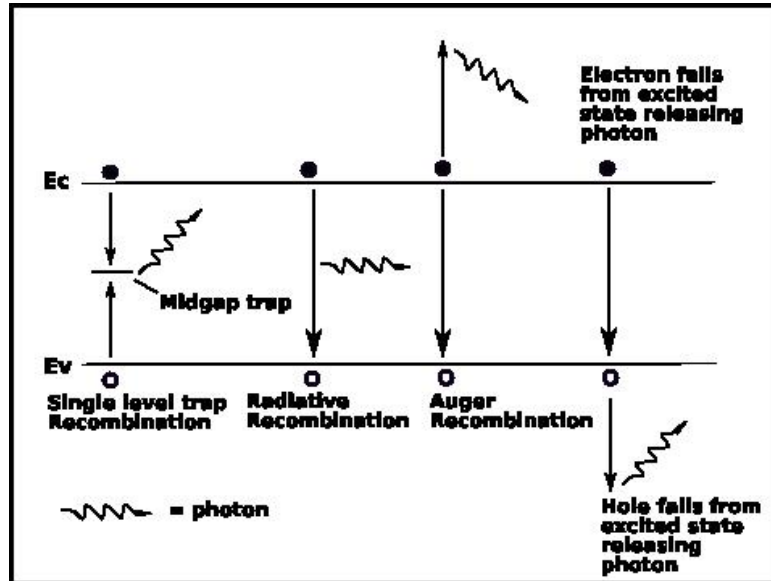


Figure 1.2: Diagram of Several Recombination Processes Present in Semiconductors^[1]

One of these processes is due to traps present within the band gap due to defects present within the crystal lattice. An electron may be trapped in a low energy site, often a defect in the crystal structure. A hole moving through the valence band will see the electron and combine with it emitting the excess energy as a phonon.[1]

Another recombination process is known as radiative recombination and occurs when an electron in the conduction band combines with a hole in the valence band emitting the excess energy as a photon. This process is easier in a direct band gap material as some of the energy given up by the electron is emitted as a phonon.[1]

The last recombination process is called Auger recombination and is similar to radiative recombination. This occurs when an electron falls from the conduction band and combines with a hole in the valence band but this time the energy from the fall of the electron is donated to another electron. This excites the

electron which relaxes thermally back to its initial state emitting the excess energy and momentum in the form of phonons. This same process may occur for holes as well.[1]

1.3 Electrical Properties of a Solar Cell

A solar cell is a device comprised of a p-n junction. When light is incident on the solar cell it develops a photovoltage across it. Current will flow once a load is connected to complete the circuit. The basic Shockley diode equation (Equation (1.1)) for a p-n junction can be modified further to describe the operation of a photovoltaic device (Equation (1.2)). [1]

$$I = I_0 \exp\left(\frac{qV}{k_B T}\right) - 1 \quad (1.1)$$

where q is the charge of an electron, V is the applied voltage, k_B is Boltzmann's constant, T is the temperature, and I_0 is the recombination current. Equation (1.2) shows the modified diode equation for a photovoltaic device. [1]

$$I = I_0 \exp\left(\frac{qV}{k_B T}\right) - 1 - I_L \quad (1.2)$$

where I_L is the light generated photocurrent. Figure 1.3 displays the I-V curve for a typical solar cell. [1]

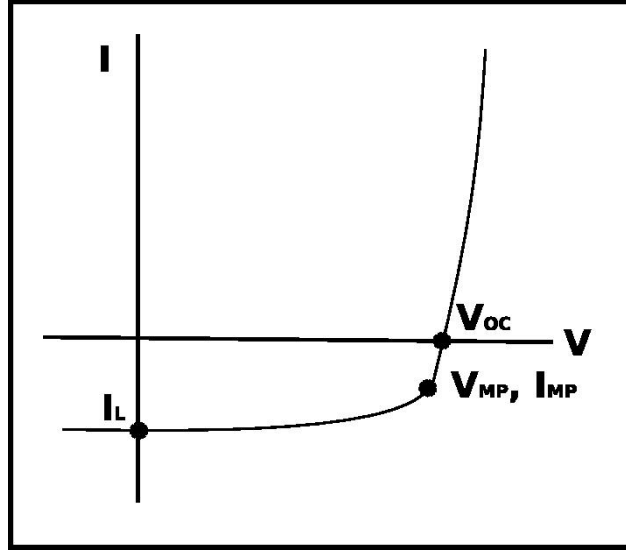


Figure 1.3: I-V Curve for a Solar Cell^[1]

When determining the electrical characteristics of a solar cell one is interested in the maximum power that it may produce. The voltage and current corresponding to the maximum power point is found at the knee of the I-V curve and determine the maximum power point P_{MP} . The open circuit voltage (V_{OC}) is given by the intersection of the I-V curve with the x-axis. It can also be computed using Equation (1.3). [1]

$$V_{OC} \approx \frac{k_B T}{q} \ln \frac{I_L}{I_o} \quad (1.3)$$

where k_B is Boltzmann's constant, T is the temperature, q is the charge of an electron, I_L is the light generated photocurrent, and I_o is the recombination current. When a small bias is applied I_L is much less than I_o and can be neglected. Since solar cells usually operate at low applied voltages I_o may be neglected from Equation (1.3).[1]

The light generated photocurrent (I_L) is given by the intersection of the I-V curve with the y-axis. The fill factor (FF) is a measure of how well the I-V curve forms a square and is a ratio of the maximum power point to the product of V_{OC} and I_L . [1]

$$FF = \frac{V_{MP} * I_{MP}}{V_{OC} * I_L} \quad (1.4)$$

The power conversion efficiency, η , of a solar cell describes how much of the power from the incident sunlight is converted to the maximum electrical power or [1]:

$$\eta = \frac{FF * V_{OC} * I_L}{P_{in}} \quad (1.5)$$

where P_{MP} is the maximum power generated by the solar cell, FF is the fill factor, V_{OC} is the open circuit voltage, I_L is the short circuit current, and P_{in} is the incident power from sunlight. [1]

The lumped equivalence circuit for silicon based solar cells is comprised of two diodes in parallel with a current source. The first diode accounts for the current from recombination in the quasi-neutral region and the second diode represents recombination current occurring in the depletion region. No load is attached to the circuit so it remains as an open circuit. Figure 1.4 shows the electrical model of a silicon solar cell. [1]

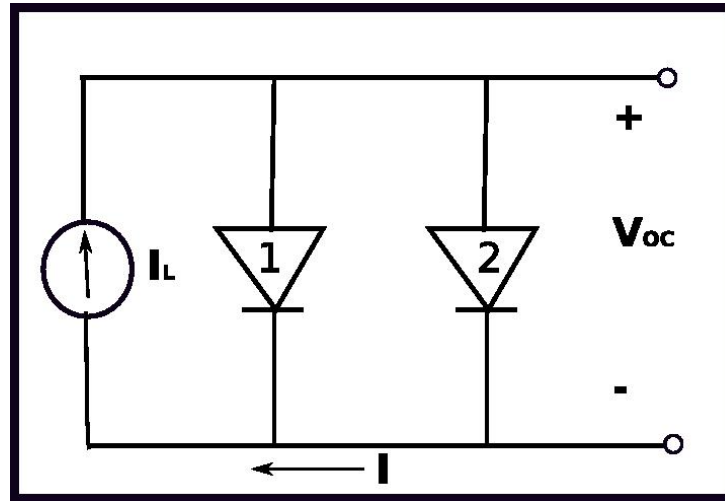


Figure 1.4: Model of a Solar Cell Showing Two Diodes in Parallel With a Current Source^[1]

As can be seen from the above equations there are many factors that go into how well a solar cell operates. The next section describes two main types of semiconductors that are used to make thin film solar cells.

1.4 Silicon Thin Film Solar Cells

Silicon is the most commonly used semiconductor material to create photovoltaic modules and makes up more than 85% of the market at this time. After the first solar cell was made in 1954, silicon got its true start through the computer industry in the 1960's. This boom stemmed from the quest for smaller and faster processing chips.[1] Silicon has a band gap of 1.1 eV which is within the ideal range of 1.0 to 1.8 eV for good solar efficiency and is one of the most abundant minerals found in the Earth's crust.[4] These factors among others made it a strong candidate for use in solar cells.[1]

Silicon can be made in a number of forms including monocrystalline, polycrystalline, and amorphous (no regular crystal structure). The most commonly used way to make a single crystal or ingot of silicon is through the Czochralski method. Before this process may take place silicon must be created that is very pure referred to as Semiconductor Grade Silicon.[1]

The reason for this is that any impurities and defects present in the silicon will be crystalline defects and act as electrical dopants or traps. The traps cause the electrons to return to the conduction band before being collected by the metal grids. Since the ingot of silicon is usually cut into either 150 μm or 300 μm slices, (silicon is very brittle) the electrons must have a long path free of any obstacles so that they may be captured by the grids.[1]

First, quartz or amorphous SiO_2 is reduced with coke using an arc furnace generating Metallurgical Grade Silicon. The silicon is then highly purified through a process developed by Siemens Company which uses the fractional distillation of chlorosilanes. These are created by reacting hydrochloric acid with silicon.[1]

Now that the polysilicon is extremely pure (impurities below parts per billion level) the polycrystalline silicon must be converted to a single crystal to improve its electrical properties. The silicon is melted at temperatures above 1400°C and rotated around a seed that determines the orientation of the silicon. The seed is slowly pulled from the melt allowing the silicon to cool into an ingot about 100 cm in length and 25 cm in diameter. The ingot is cut into wafers and then doped to create p-n junctions on the surface of the wafer and metallic grids are then placed down to create the solar cell.[1]

Much of the ingot is lost during the cutting process to sawdust and the purification and conversion to monocrystalline silicon is expensive. The bulk of the cost of making a silicon-based solar cell lies in the wafer fabrication process. Thus, research into cheaper alternatives such as polycrystalline silicon and also ribbon silicon is underway. However, the electrical properties of polycrystalline and ribbon silicon are not as good as their monocrystalline counterparts and the process for creating ribbon silicon is much slower. Due to these challenges, exploration into other materials began seeking efficient, cheaper alternatives. The following section describes the properties of CuInSe_2 one promising candidate for solar cell technology.[1]

1.5 CuInSe_2 Thin Film Solar Cells

CuInSe_2 is another type of thin film semiconductor used in photovoltaic applications. It can be created by a number of methods including coevaporation, electrodeposition, and multistage processes. The coevaporation technique will be discussed in a later chapter.[1]

The study of this semiconductor material began in the 1970's at Bell Laboratories where crystals of CuInSe_2 were grown and their electronic, optical and structural properties were characterized. The first solar cells made using this material were comprised of a p-type single crystal of CuInSe_2 onto which n-type CdS was evaporated. Since such single crystals are very difficult to grow efforts in improving this technology are focused in thin films of this material. During the 1980's ARCO Solar and Boeing started to address manufacturing issues including scale-up, yield, and throughput making great strides forward in CuInSe_2 photovoltaics.[1]

Cu(In,Ga)Se_2 , similar in structure and properties to CuInSe_2 , has shown much promise in the solar cell industry reaching efficiencies of 19.3% which is not too far off from efficiencies in silicon solar cells which are currently at about 25%. [6, 7] The advantages that CuInGaSe_2 has over silicon include low cost and high rate depositions and high radiation resistance. This material may also be deposited on flexible substrates making it a potential candidate for space applications and it has also shown long term outdoor stability. [1]

CuInSe_2 is stable between 100°C and 800°C at approximately 24% copper content in the film as seen from Figure 1.5. CuInSe_2 is denoted as the α phase, σ is the high temperature sphalerite phase, γ is an Ordered Defect Compound (ODC) phase, δ_{HT} is a Cu_2Se high temperature phase and δ_{RT} is a Cu_2Se room temperature phase. Device quality films are usually made in the α phase region as they usually give the best electrical performance. However, functional devices can be made in the 15% to 23% copper content range which includes the $\alpha + \gamma$ and the $\alpha + \sigma$ phases. [1]

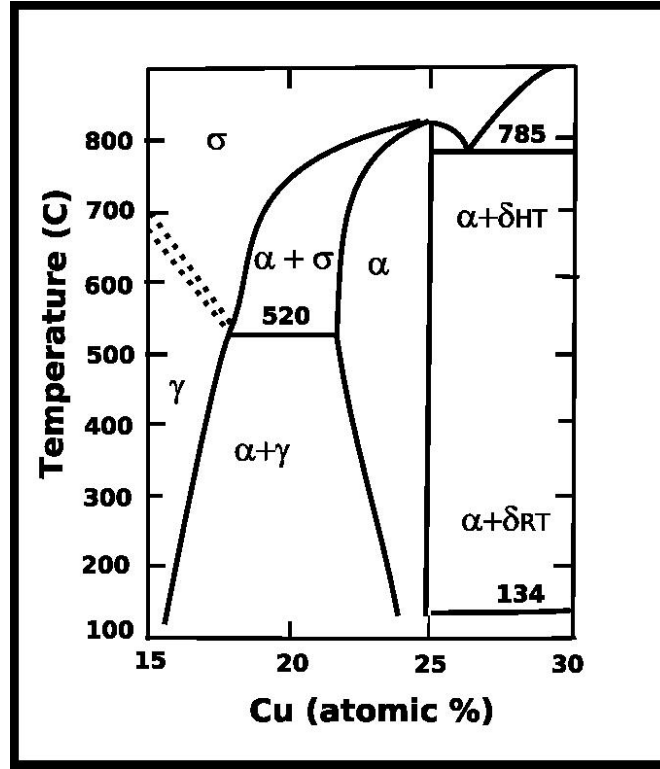


Figure 1.5: Phase Diagram of CuInSe₂^[1, 8]

CuInSe₂ or the α phase has a chalcopyrite crystal structure with lattice constants $a = 5.782$ angstroms and $c = 11.620$ angstroms.[9] (ODC) such as Cu₂In₄Se₇, CuIn₃Se₅, CuIn₅Se₈ and Cu₈In₁₈Se₃₂, etc, may also form in addition to the α or CuInSe₂ phase depending upon the overall composition of the film. What is unique about the CuInSe₂ ODC is that they all are comprised of the same chalcopyrite crystal structure.[8]

The material is so forgiving structurally and electronically due to defects present within the crystal lattice. Polycrystalline CuInSe₂ makes devices that are as good as the monocrystalline ones due to the passivation of the In_{Cu}^{2+} deep level by V_{Cu}^{-} (In_{Cu}^{2+} stands for a Cu²⁺ cation in a site normally occupied by In³⁺ and V_{Cu}^{-}

stands for a Cu vacancy). The ODC are made up of a combination of these two defects $2V_{Cu}^{-} + In_{Cu}^{2+}$ that occurs as a regular repeating unit forming $Cu_2In_4Se_7$, $CuIn_3Se_5$, $CuIn_5Se_8$, etc. $2V_{Cu}^{-} + In_{Cu}^{2+}$ is electrically neutral which explains why the ODC perform as well electrically as their chalcopyrite cousin and its formation energy is very low which favors its presence within the crystal lattice. $CuInSe_2$ can be made either n-type or p-type by changing the amount of copper present in the film. This property stems from the fact that copper vacancies have a very low formation energy and form shallow defect levels within the band gap that do not affect solar cell performance.[10] All of these properties give $CuInSe_2$ an advantage over silicon in terms of its flexibility.

Sodium present in the soda lime glass substrate has significant effects on these defects within the semiconductor crystal structure. This in turn influences both the electrical and structural properties of the semiconductor thin film. S. B. Z. Su-Huai Wei *et al.* found that sodium will reduce the number of intrinsic donor defects in $CuInSe_2$ by placing itself within a In_{Cu} defect. When the amount of sodium is small this substitution increases the number of holes available for conduction within the film. This lowers the Fermi energy of the film and decreases the number of carrier traps increasing the open circuit voltage. Too much sodium, however, will reduce the performance of the semiconductor through the removal of copper vacancies.[11]

Wei et al. also found that sodium and oxygen will make the $CuInSe_2$ film more stoichiometric by forming secondary phases on the surface of the film and in the grain boundaries. $CuInSe_2$ films with sodium tend to have a preferred (112) orientation due to the formation of $NaInSe_2$ with a preferred (112) orientation.

Cu (In,Ga)Se₂ can be made by replacing some of the indium in CuInSe₂ with gallium. Gallium is added to the semiconductor to increase the band gap of CuInSe₂ from 1.02 eV to between 1.1 and 1.2 eV.[1] Increasing the band gap is desirable as it increases V_{OC}. Larger values of V_{OC} are needed for high efficiency solar cells and tandem solar cell applications.

However once the atomic percentage of $\frac{Ga}{In + Ga}$ is greater than 0.3

Cu(In,Ga)Se₂ solar cells efficiencies start dropping. Wei et al. suggest that part of the reason for this is that the addition of Ga lowers the stability of the $2V_{Cu}^{-} + In_{Cu}^{2+}$ defect pair which would have an effect on device performance.[12] In other work a trap was discovered to exist at 0.8 eV that would shift towards the mid gap with increasing gallium content within the film. This change in position of the trap would make it a much more effective recombination center as the ratio of $\frac{Ga}{In + Ga}$ of increased.[13]

CuIn(S_x,S_{1-x})₂ may be produced by adding sulfur to CuInSe₂. This widens the band gap from 1.02 eV to about 1.43 eV to 1.53 eV.[14] Unfortunately, no studies have been conducted to deduce what effect sulfur has on the structure and band gap of this material.

In general, all of these materials may be grouped into sections based on their composition. Those with a deficiency of copper or $\frac{Cu}{In} < 1$ are termed as being copper poor. Samples with $\frac{Cu}{In} > 1$ are referred to as being copper rich. The films that are copper rich tend to have large grains and produce a CuS or Cu₂S layer on the top of the film to create a semiconductor layer with large stoichiometric grains with improved crystallinity.[15] The formation of the CuS or Cu₂S layer may be explained

by the high mobility of the Cu^+ ion.[16] Those films that were copper poor tended to have smaller grains and included ODC creating a multiphase film.[17]

A similar trend applies to the relative amounts of sulfur and selenium in the material in the case of $\text{CuIn}(\text{S}_x\text{S}_{1-x})_2$. This ratio, $\frac{S}{S + \text{Se}}$ has been found to have an effect on the morphology of the film. Yamaguchi found that as the atomic ratio $\frac{S}{S + \text{Se}}$ increased the grain sizes of the film decreased. The $\frac{S}{S + \text{Se}}$ ratio of about 0.2 produced 1 μm columnar grains that were optimal in maintaining high solar cell efficiency. This ratio also corresponded to a band gap of about 1.43 eV which fits into the desired band gap range for a high efficiency single junction solar cell.[14]

The next section describes how these materials fit into the overall solar cell structure displayed in Figure 1.6.[1]

1.6 Solar Cell Structure

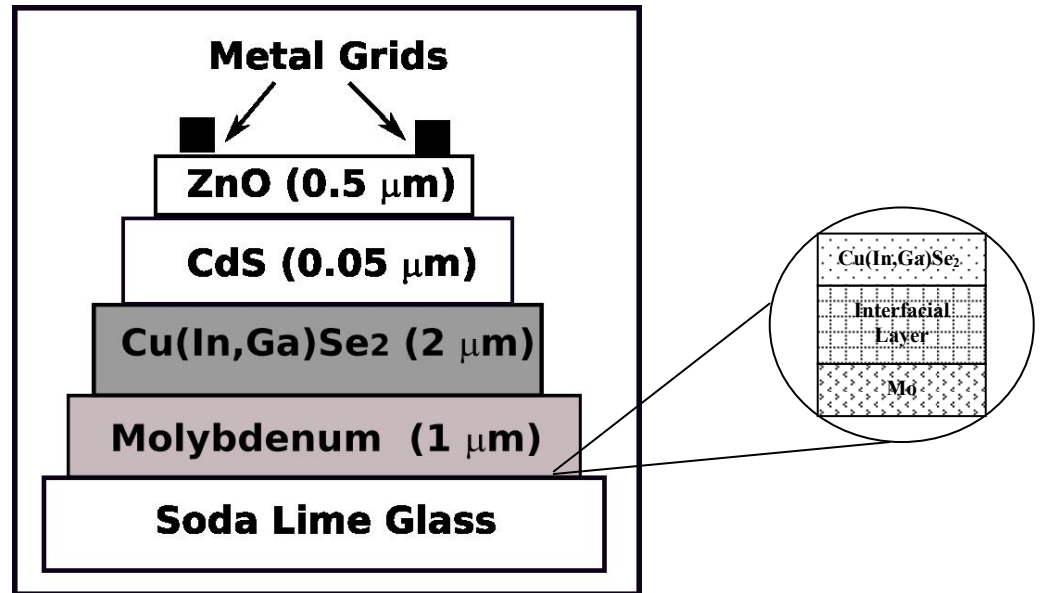


Figure 1.6: Diagram of a Cu(In,Ga)Se₂ Solar Cell^[1]

As can be seen from Figure 1.6 a typical solar cell is comprised of many layers including the semiconductor material. The substrate used is soda lime glass onto which 0.5 μm of molybdenum is deposited. About 2 μm of the semiconductor is then evaporated onto the molybdenum coated substrate. An interface is formed between the layer of molybdenum and the semiconductor.[1]

Next 0.05 μm of CdS which is n-type and forms the other end of the junction and 0.5 μm of ZnO are deposited. Two types of ZnO are deposited the first being a high resistance layer of ZnO and the second being a doped high conductivity layer. Both of these are deposited using sputtering or chemical vapor deposition. The CdS layer is deposited using a chemical bath. Lastly, metal grids or a monolithic series connection is placed onto the ZnO to complete the solar cell.[1]

Chapter 2

BACKGROUND

2.1 Properties of MoS₂

The interfacial layer mentioned in the previous chapter in Figure 1.6 can be one of three materials MoS₂, MoSe₂ or Mo(S_x,Se_{1-x})₂. This is based on the knowledge that copper and indium are insoluble with molybdenum.[18, 19] Gallium is soluble with molybdenum but only films with copper and indium are being considered in this study.[18]

MoS₂ is a type of semiconductor that has a hexagonal crystal structure with $a = 3.161$ angstroms and $c = 12.299$ angstroms. It may also form with a rhombohedral crystal structure with lattice parameters of $a = 3.165$ angstroms and $c = 18.371$ angstroms.[20] In the case of the hexagonal crystal structure each molybdenum atom is surrounded by six sulphur atoms. This creates trigonal prisms that are stacked on one another to form the crystal lattice. Films of this material are comprised of sheets of the hexagonal structures. Strong covalent bonds exist along the c-axis while weak Van der Waals forces exist between the layers of MoS₂. [21]

Historically, this material has been used as a lubricant due to its stability at very high temperatures and for its hexagonal crystal structure. It has also been used as a catalyst, for electrodes, and also as a material for solar cells primarily due to its favorable band gap. It has been fabricated in thin film form by a number of methods

including chemical deposition, Metal-Organic Chemical Vapor Deposition (MOCVD), sulphurization, and sputtering.[21]

Single crystals of this material have also been created using halogen vapor transport and vapor grown methods. The vapor grown method is preferred as the halogen may be incorporated into the crystal itself thus degrading the quality. This method is begun by placing molybdenum and sulfur in pure powder form into a silica ampoule and then vibrating the ampoule for 30 minutes to thoroughly mix the elements. The ampoule was then pumped down to a pressure less than 10^{-6} torr and then heated in a furnace to between 600 and 700°C in 50°C steps over 5 hours. The final temperature was maintained for about 24 hours and then allowed to cool. Since the reaction had not gone to completion the elements were mixed again for 30 minutes. The ampoule was placed back into the furnace and heated to between 1000 and 1050°C, remaining at that temperature for a week. This method may be varied slightly to produce single crystals of other dichalcogenide elements. In this case both hexagonal and rhombohedral crystals were created.[20]

MoS₂ is typically stable at temperatures between 0 and 1500°C with approximately between 39 to 44% sulfur. A phase diagram for this material may be found on pg. 2661 of Reference [19]. The heat of formation of this material at 298.15K is -223.0 ± 16.7 kJ/mol.[22] Since the heat of formation is negative the reaction is exothermic and thermodynamically favored. However, it has been demonstrated previously that temperatures of at least 800°C are needed to form crystalline MoS₂. [4] This indicates that there could be a large activation energy that must be overcome for MoS₂ to form.

2.2 Properties of MoSe₂ and Mo(S_x,Se_{1-x})₂

Two other materials that are similar in properties and structure to MoS₂ are MoSe₂ and Mo(S_x,Se_{1-x})₂. They both have a hexagonal lattice structure like MoS₂ and can be made into single crystals as described in the above vapor grown process. The lattice dimensions for MoSe₂ are $a = 3.288 \pm 0.002$ angstroms and $c = 12.92 \pm 0.01$ angstroms. This material is stable at temperatures between 0 and 1200°C and at about 67% selenium. A phase diagram of this material may be found on pg. 2665 of Reference [19]. However, temperatures greater than 350°C are needed to generate a well organized film of MoSe₂. [23]

The heat of formation of MoSe₂ has been recorded as -234.2 ± 3.3 kJ/mol which is lower than the value for MoS₂. [24] This indicates that MoSe₂ is more stable than MoS₂ as the heat of formation of MoSe₂ is more negative than that of MoS₂.

The lattice dimensions for Mo(S_x,Se_{1-x})₂ will vary according to composition of sulfur and selenium present in the film in accordance to Vegard's Law. [25] The next two equations describe how the lattice parameters change with the atomic percentage of sulfur, x .

$$a(x) = (3.281 - 0.06315 x) \text{ angstroms} \quad (2.1)$$

$$c(x) = (12.918 - 0.310 x) \text{ angstroms} \quad (2.2)$$

In a work done by Drabek, the author could only get this compound to form as a single crystal at temperatures at 800°C and above. However, the author did get a complete range of solid solutions to form as published in Reference [25].

The presence of MoS₂, MoSe₂, and Mo(S_x,Se_{1-x})₂ have already been noted in a number of thin film semiconductor solar cells including Cu(In_x,Ga_{1-x})Se₂ (CIGS) and CIS₂. The next section gives the details of these findings.

2.3 The Role of MoSe₂, MoS₂, and Mo(S_xSe_{1-x})₂ in Semiconductor Thin Films

Studies have been conducted on how these interfacial layers affect solar cell performance. T. Wada et al suggest that the MoSe₂ layers act as an ohmic contact improving the efficiency of the solar cell. In this work, a copper poor CIGS film was created using a multistage coevaporation method. A high sensitivity Secondary Ion Mass Spectroscopy (SIMS) measurement was used to conclude that a compound with more than 50% selenium existed between the layers of CIGS and Mo. Using micro-Electron Dispersive Spectroscopy the lattice constants for this compound were determined to be $a = 0.33$ and $c = 1.3$ nm. These values are consistent with the hexagonal unit cell structure of MoSe₂ which was found to have planes oriented in the (100) and (110) directions.[26]

To evaluate what factors influenced the formation of MoSe₂ samples with an excess of selenium and indium and samples with an excess of copper were evaluated with X-Ray Diffraction (XRD) and Transmission Electron Microscopy (TEM). Only a few nanometers of MoSe₂ was formed in the copper rich case and about 100 nm of MoSe₂ was found in the indium and selenium rich case. This implies that an excess of copper present in the bulk film impedes the formation of this layer.[26]

To verify that the MoSe₂ layer acts as an ohmic contact two solar cells were made and tested for electrical performance. The quantum efficiencies (QE) of the samples were evaluated using monochromatic light with wavelengths between 300 and 1200 nm. AM 1.5 illumination was used to determine QE properties as well as I-V characteristics at low temperatures.[26]

One sample consisted of a glass substrate upon which a layer of SiO₂ was deposited followed by layers of molybdenum and CIGS. The purpose of the SiO₂

layer was to prevent any sodium from diffusing into the layer of molybdenum. The other sample was a standard CIGS solar cell as described in the previous chapter. The solar cell with the SiO_2 layer did not show any signs of having a MoSe_2 layer present based on XRD patterns. The standard CIGS sample, however, had a MoSe_2 layer 500 nm thick based on TEM measurements.

The sample without the MoSe_2 layer exhibited an efficiency of only 9% whereas the standard CIGS sample had an efficiency of 14%. The dark I-V curves for the SiO_2 sample demonstrated a slope that decreased with decreasing temperature in the forward-current region. This is typical behavior of a Schottky contact not an ohmic contact, or an interface between a metal and semiconductor which allows for the easy transport of carriers.[26]

From this study it appears that sodium aids in the formation of the MoSe_2 layer and that the presence of this layer increases the efficiency of the overall device. To test this assumption the authors used quantum efficiency curves to determine the band gap of MoSe_2 . The quantum efficiency curve of the sample with a MoSe_2 layer had an extra peak in it at about 870 nm which they attributed to the presence of MoSe_2 . The sample with the SiO_2 coating did not display such a peak. Thus, they were able to use the peak at 870 nm to calculate the band gap of the MoSe_2 layer which they determined to be 1.41 eV. This agrees with the accepted literature values of 1.35 – 1.40 eV for MoSe_2 . Also, this value is larger than that of the CIGS film above the MoSe_2 layer which would create an ohmic contact therefore increasing the efficiency of the overall solar cell.[26]

In another work by Nishiwaki et al. a number of CIGS films were deposited with varying compositions and temperatures using the coevaporation

method. First, a plain molybdenum coated soda lime glass sample was reacted with H_2Se gas at 550°C . This sample acted as a standard to which the other samples could be compared to since MoSe_2 would be generated from this experiment. Next a set of molybdenum coated soda lime glass substrates were exposed to fluxes from copper and selenium at 550°C . A set of copper rich $\text{Cu}(\text{In,Ga})\text{Se}_2$ samples were made at 550°C and also at 350°C . Lastly, two sets of In,Ga,Se samples were created at 350°C . From XRD it was determined that this sample had a (002) orientation meaning that the c-axis of the crystal structure was parallel to the substrate. A High Resolution Transmission Electron Microscope (HRTEM) photograph of this sample confirmed the XRD findings which can be seen in Figure 2 of Reference [23].

In the past there have been problems with the films peeling off from the substrate. Nishiwaki et. al believed that the orientation of this layer could explain this phenomenon. If the c-axis of the MoSe_2 layer is parallel to the substrate then covalent bonds exist between the MoSe_2 and the underlying molybdenum. However, if the c-axis is perpendicular to the molybdenum then only Van der Waals forces hold the MoSe_2 layer to the underlying layer making it easy to peel the semiconductor film off of the substrate.[23]

The next sample studied was a Cu_2Se on the molybdenum-glass substrate. Only a small (002) peak in the XRD pattern was visible which suggested that there is a higher tendency for molybdenum and selenium to react than for copper and selenium to react. The (002) peak was also quite weak in a copper rich CIGS sample indicating that not much MoSe_2 formed. Again, this also supports the previous findings that an excess of copper inhibits the formation of MoSe_2 .[23]

The most interesting result of this effort came from a $(\text{In,Ga})_2\text{Se}_3$ sample where XRD analysis detected the existence of (100) and (110) orientations within the MoSe_2 crystal structure. This means that the c-axis is orthogonal to the substrate which could cause adhesion problems later on. From this one can conclude that an environment that is rich in indium and gallium not only favors the formation of MoSe_2 but influences the orientation of the layer as well. This could be due to the formation of compounds such as GaMo and GaMo_3 before selenization occurs. In a work by M. Rusu et. al., TEM, X-Ray Fluorescence (XRF) , and Electron Dispersive Spectroscopy (EDS) measurements detected the presence of gallium metallic clusters at the CGS and molybdenum interface.[27] This supports the theory by Nishiwaki et al. A TEM micrograph that could contain a metallic cluster of Ga can be found in Figure 3 of Reference [23]. XRD measurements also confirmed this result.[23]

To determine when the MoSe_2 would start forming Nishiwaki *et al.* used a three stage process to deposit Cu(In,Ga)Se_2 films. During the first stage an $(\text{In,Ga})\text{Se}_2$ precursor layer is deposited onto the molybdenum coated soda lime glass substrate. During the second stage Cu and Se fluxes transform this layer into a copper rich Cu(In,Ga)Se_2 film. In the last stage small relative amounts of indium, gallium, and selenium are added to create a slightly indium and gallium rich film.[26] In this experiment, one set of samples was removed from the chamber before the second stage began. They found that this set of samples did not have an interfacial layer of MoSe_2 . [23]

The researchers also wanted to find out if the formation of the MoSe_2 layer is temperature dependent. One set of films was deposited at 550°C and another

was deposited at 350°C. The set of samples deposited at 350°C did not have an intermediate layer of MoSe₂. [23]

In a different study by the same group, a more refined temperature study was performed using CIGS films with a $\frac{Cu}{In + Ga}$ ratio of about 0.9. They deposited four films at 500°C, 525°C, 550°C, and 570°C. XRD analysis was performed on each of these films and they found that MoSe₂ was formed at temperatures above 500°C. For the films deposited at 525°C and above the (100) and (110) peaks were present in the XRD pattern that are typical of MoSe₂. This is displayed in Figures 2 and 4 of Reference [28].

The presence of MoSe₂ has also been noted in Cu_xGa_ySe₂ thin film solar cells. In a work by R. Würz et. al., Cu_xGa_ySe₂ (CGS) thin films were deposited by means of Chemical Vapor Deposition (CVD) apparatus used for III-V epitaxy. The films were deposited on plain soda lime glass, borosilicate glass (no sodium), and Mo covered substrates. High quality films with grains about 1 µm in diameter that were also slightly gallium-rich were obtained. The chemical composition of the films was determined using XRF. [29]

TEM measurements of the CGS films on molybdenum soda lime glass substrates realized a 170 nm interfacial layer present between the semiconductor and molybdenum. XRD measurements confirmed that this layer was MoSe₂ with a spacing of 6.7 angstroms which agrees with the literature value of 6.5 angstroms. [29]

Instead of seeing sheets of MoSe₂ that were either all perpendicular or all parallel to the interface, the authors saw a combination of the two. The sheets were perpendicular to the molybdenum grains until just before the interface where they

change to an almost parallel orientation. A TEM micrograph displaying this result may be found in Figure 1 of Reference [29].

To gain a better understanding of how the orientation of the layers changed as they went from being perpendicular to parallel to the surface, XRD measurements were performed on the films. The XRD results displayed (100) and (110) peaks which suggest layers of MoSe₂ with a perpendicular orientation. (002) and (004) peaks were also seen which suggests that there were layers present with a horizontal orientation. The patterns also displayed (103) and (105) peaks which indicated that there are layers bending from the perpendicular to horizontal orientations. Thus, these measurements confirmed what was seen in the TEM micrograph.[29]

The orientation of the layer is not only important for adhesion properties but also for electrical properties. The conductivity of MoSe₂ layers is anisotropic so the orientation of the layers can have a direct effect on the transport properties at the interface. Conductivity through the layers is about two times higher than conductivity perpendicular to the layers. This could explain the increased resistance seen in the samples with MoSe₂ layers oriented perpendicular to the molybdenum substrate. Those samples that had layers oriented parallel to the surface showed an increase in electrical performance.[29]

When the XRD patterns from the CGS on soda lime glass versus CGS on borosilicate glass were compared no major differences were seen between the two. However, when the films were peeled with glue stripe and the back of the CGS film was placed under the SEM, differences in the density of contact areas were seen. The CGS films that were on the molybdenum coated borosilicate glass had a much lower

density of contact area than the CGS films on molybdenum coated soda lime glass. The borosilicate glass films would peel right off for CGS film thicknesses greater than 400 nm. In contrast, the CGS films on the molybdenum coated soda lime glass displayed very good adhesion.[29]

Another result of this study was that for substrate temperatures above about 550°C the orientation of the MoSe₂ layer was found to be parallel to the substrate. Below 550°C it was found to be perpendicular to the substrate. The authors suggested that the reason why the orientation changes could be due to differences in the thermal expansions of Mo and MoSe₂. This could change the lattice mismatch between the two and cause a change in the orientation of the MoSe₂. The authors also determined the diffusion constant of selenium in MoSe₂ at 580°C and found it to be between $10^{-14} - 10^{-15}$ cm²/s. [30]

D. Abou Ras et al. conducted a study to better understand why the MoSe₂ layer would change orientation and how the selenization process occurs. Molybdenum coated silicon substrates were placed into a selenization chamber for different intervals of time at two different temperatures. Another set of samples were placed in the chamber for the same lengths of time but at different temperatures. Rutherford Backscattering Spectrometry (RBS) was used to determine the thickness of the resulting MoSe₂ layers. Those MoSe₂ films whose c-axis was perpendicular to the silicon substrate were thinner than those that had a parallel orientation to the silicon substrate. They reasoned that the perpendicular structure of the MoSe₂ allows for easier diffusion of the selenium gas through the MoSe₂ to the underlying molybdenum generating a higher growth rate of MoSe₂. [30]

In a separate study, Daniel Abou-Ras et al. found that the orientation of the MoSe₂ was independent of the orientation of the molybdenum substrate. Both polycrystalline molybdenum on silicon substrates and single crystal molybdenum on silicon substrates were selenized in this experiment.[31]

The authors also found that the MoSe₂ layers grown on single crystal molybdenum were thicker than the MoSe₂ grown on polycrystalline molybdenum. The polycrystallinity of the underlying molybdenum suppressed the growth of MoSe₂ possibly due to surface roughness which would reduce the diffusion of selenium.[31]

Lastly, they found that the presence of sodium suppressed the growth of MoSe₂ with a (101) and (100) orientations and encouraged the growth of the semiconductor in the (002) orientation. The higher the amount of sodium present, the thicker the MoSe₂ films were. [31]

At this time it is not completely understood why sodium increases the thickness of the MoSe₂ or why it changes the orientation of the layer. It has been suggested, however, that sodium atoms will diffuse through the underlying molybdenum into the MoSe₂ layer[31]. A change in the crystal structure of MoSe₂ was noted by Morales et. al, which they believed to be caused by the intercalation or insertion of sodium into the crystal structure of MoSe₂. [32]

Fewer studies have been conducted on MoS₂ and Mo(S_x,Se_{1-x})₂ possibly due to the fact that their crystal structure is so similar to MoSe₂. Also MoS₂ has only been seen in CIS₂ films as the addition of selenium facilitates the formation of MoSe₂ over MoS₂. In a work done by Alvarez-Garcia *et al.*, a MoS₂ layer was found in between the CIS₂ layer and the underlying molybdenum layer. The semiconductor was deposited onto the Mo covered substrate by the coevaporation method at 370°C

and 520°C. They found that MoS₂ formed at 520°C but not at 370°C through X-Ray Diffraction (XRD) and Raman Spectroscopy analysis. Also, the samples that were copper rich did not show signs of a MoS₂ layer whereas the copper poor samples did. This implies that MoS₂ tends to form at high temperatures possibly due to its heat of formation and when the semiconductor film is deficient in copper as seen previously.[15]

Mo(S_x,Se_{1-x})₂ has been noted by Palm et al. in pentenary chalcopyrite thin films, namely Cu(In_xGa_{1-x})(S_ySe_{1-y})₂(CIGSS). In this work a pilot line process was used to deposit the films. SIMS profiles of a standard CIGSS film showed a dramatic increase in the relative amounts of molybdenum, sulfur and selenium at the back of the film. XRD and EDS measurements corroborated the SIMS results, however, they were not included.[33]

As can be seen from the previous work presented in this chapter, a lot of research has been performed in trying to understand why and how MoSe₂ forms, and how it influences the electrical and adhesion properties of the solar cell. Also, much effort has been spent on the roles of indium and gallium in the formation of these interfacial layers.

However, not as much work has been done in trying to understand the properties of MoS₂ and Mo(S,Se)₂, and the effect that sulfur and selenium have on the growth and properties of these dichalcogenide layers. In this work the relative reactivities of sulfur, selenium, and molybdenum will be investigated by reacting molybdenum with H₂S, H₂Se, and a combination of the two. The role of sodium in these reactions will be studied by examining samples with and without sodium present in the glass substrate.

Also, the role of sulfur and selenium in the formation of the intermediate layer in the chalcopyrite thin films will also be determined. This will be done by examining the interfacial layers in CuInSe_2 , CuInS_2 , and $\text{CuIn}(\text{S}_x\text{Se}_{1-x})_2$ through techniques such as symmetric XRD and asymmetric XRD. These two techniques will also be used to determine the relative thicknesses and reaction rates in the molybdenum substrates that had been reacted with the various gases.

Chapter 3

EXPERIMENTAL

3.1 Evaporation Technique

The $\text{CuIn}(\text{S}_x, \text{Se}_{1-x})_2$ samples examined in this work were created using a coevaporation chamber. The chamber consists of five elemental sources three of which are metals and the remaining two contain chalcogenides. Using these sources copper, indium, gallium, sulfur and selenium may all be evaporated at once to form a ternary film up to a pentenary film comprised of these elements. Figure 3.1 displays an overall schematic of the system apparatus.

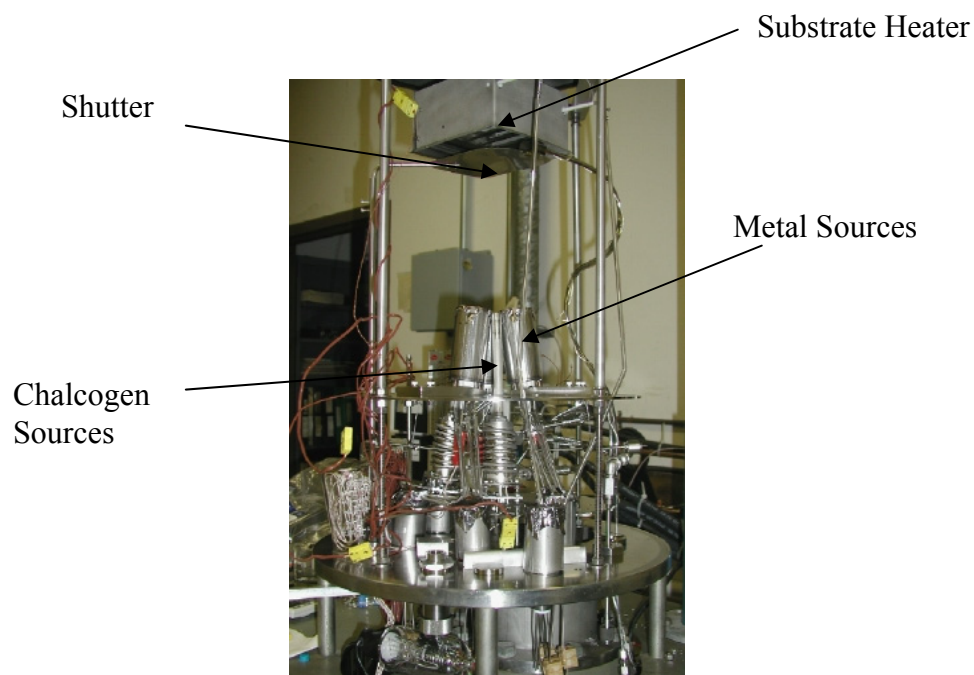


Figure 3.1: Photograph of Coevaporation Chamber^[34]

As can be seen in Figure 3.1 the chamber consists predominately of a substrate heater, quartz crystal monitor and five elemental sources. The substrate heater holds eight 1 inch by 1 inch samples and a thermocouple used to measure the substrate temperature. Films are usually deposited at about 550°C to help ensure that device quality films are formed.

The quartz crystal monitor is used to estimate the thickness of the film during deposition. The quartz crystal vibrates at a certain frequency before the film is deposited. As material begins to form on the substrate, a film of material also deposits on the monitor decreasing the frequency of vibration proportional to the weight of the deposit. How much it decreases may then be translated to the thickness of the film.

The temperatures of the five elemental sources are measured through thermocouples attached to 818 Eurotherm controllers. The temperature of the sources controls the elemental vapor pressure. How quickly the elemental vapor escapes from the top of the source is the flux. The fluxes then translate to the composition of the semiconductor film. The controllers prevent the temperature of the sources from deviating from the temperature setpoint.

A shutter is present underneath the sample substrates and is opened only after the sources have reached their temperature setpoint. How long the shutter is open determines the thickness of the film. Semiconductor samples usually have a thickness of about 1-2 μm which corresponds to about an hour deposition time.

The chamber is connected to a pumping system through a series of valves. The gate valve and diffusion pump reside underneath the chamber. A cold trap is positioned between them to prevent the rise of pump oil into the main chamber. A roughing pump attached to the system through the roughing valve is used to pump

down the system from atmospheric pressure to about 5×10^{-5} to 1×10^{-4} torr where the diffusion pump may then pump the system down to about 10^{-6} torr. For a complete system description and run procedures please see Reference [34].

3.2: Selenization and Sulfurization of Molybdenum Substrates

A selenization chamber was used to determine how sulfur and selenium would react with molybdenum-coated substrates. Three molybdenum coated soda lime glass substrates were placed into the front of the quartz chamber. The system was pumped down to about 5×10^{-6} torr.

An insulating jacket with thermocouples used to measure the chamber temperature was wrapped around the center of the tube. The chamber was heated to 550°C under argon flow during a twenty minute time frame. This step purged the chamber of any remaining gas and removed oxygen from the system.

The samples were introduced to the chamber and 0.35% H_2Se was added to the flow of argon for a total flow rate of 1318.56 sccm. The samples remained under H_2Se flow at 550°C for one hour to allow the formation of MoSe_2 . After 80 minutes the samples were removed from the selenization chamber. This procedure was repeated using H_2S and a 50/50 mix of H_2S and H_2Se . In all cases the total flow rate of gas was 1318.56 sccm.

The temperature was chosen to be 550°C based on previous experimental work. Well organized films of MoSe_2 were formed at temperatures above approximately 400°C . Also, soda lime glass will begin to melt at temperatures above approximately 575°C . A temperature was needed that was below the melting point of the glass but high enough for MoSe_2 to form. This temperature is also the deposition

temperature of the semiconductor film and would make a good reference out of the selenized films.

The effect of sodium on the formation of MoSe_2 , MoS_2 and $\text{Mo}(\text{S}_x, \text{Se}_{1-x})_2$ was also explored in this experiment. Eight samples of borosilicate glass that did not have any sodium present within them were reacted with the gasses as described above. Two samples instead of three were reacted in each experiment.

3.3: Peeling of $\text{CuIn}(\text{S}_x, \text{Se}_{1-x})_2$ Films

In order to study the crystal structure and composition of the intermediate layer present between the molybdenum back contact and the semiconductor film XRD measurements were performed. Since the intermediate layer present in these semiconductor films is usually only about 80 to 200 angstroms thick traditional symmetric XRD measurements would not provide the information needed about the crystal structure. The signal exhibited by the semiconductor film would drown out any signal generated from this very thin layer. Thus removing the semiconductor film on top was necessary to allow the signal from the dichalcogenide layer to come through.

This was done by using superglue to bind the film to a plate of stainless steel a little larger than the sample. The adhesive was allowed to dry overnight and then the edge of stainless steel that extruded from the glass was placed into a vice. The arm of the vice was tightened and the glass substrate was pushed off the stainless steel. This generated a glass substrate with the molybdenum and interfacial layer on top and the semiconductor film face down on the steel. By analyzing these two pieces information could be gathered about the nature of the interfacial layer.

3.4: Symmetric and Glancing Angle X-Ray Diffraction Analysis

Two different XRD analysis techniques were used in this work to gain a better understanding of the overall CISS film and the interfacial layer. The first is known as symmetric XRD due to the fact that the incident and detected x-rays have the same angle. The experimental apparatus consists of an x-ray source, divergence slits, sample holder, receiving slits, curved-crystal monochromator, counter tube and goniometer. The x-ray source is comprised of an x-ray tube which contains a tungsten filament that is surrounded by glass. The filament will generate a stream of electrons once a potential is applied across it.[35] These electrons are focused by a focusing cup before hitting a metal target which may be copper, molybdenum, chromium, or other metals. X-rays are generated from the bombarding electrons which then pass through a glass window to begin their path towards the sample. A beryllium window on the other side of the target prevents the escape of electrons from that side of the tube. The x-ray source is continuously cooled with water to prevent overheating. [35]

Once the x-rays have left the source they pass through a set of divergence slits which help to further focus the x-rays. They then diffract from the sample and then pass through the receiving slit to the curved-crystal monochromator which separates the x-rays by 2θ . Those x-rays are then counted by a tube at the end of the apparatus.[35]

When the x-rays hit the sample they pass through the planes of the crystal lattice and diffract by a mechanism known as Bragg diffraction. Bragg's Law is listed below where n is the order of reflection, λ is the wavelength, d is the lattice spacing and θ is the incidence and diffracted angle of the x-rays.[35]

$$n\lambda = 2d\sin\theta \quad (3.1)$$

This equation shows is that when these x-rays interact with the planes of the crystal lattice they have a certain angle and phase. After they scatter from the planes, they will leave the crystal lattice at many different angles and phases with respect to one another.

At specific angles given by Equation (3.1), those x-rays that are in phase will undergo constructive interference and combine to form a larger wave of x-ray radiation. The remaining x-rays that are out of phase will cancel each other or undergo destructive radiation. Thus, only those x-rays that meet Bragg's law and are at the angle selected by the researcher will be counted by the detector. Through equation (3.1) one may find the lattice spacings and crystal structure of the specimen.

The θ term in Equation (3.1) is measured with the goniometer present in the x-ray apparatus. The x-ray source is attached to what can be envisioned as a large wheel divided into degrees like what is done with the unit circle except that the goniometer only goes to about 160° since the scale is in units of 2θ .

During the x-ray measurement the x-ray source will be moved along this circle in time periods and step sizes designated by the researcher. This allows the researcher to query the crystal planes present in the sample. Only when the Bragg Law is satisfied will the plane be seen by the detector. A wide range of angles will allow many of the crystal planes to be analyzed.

The symmetric XRD apparatus used in this work was a Phillips/Norelco 1948 X-Ray Diffractometer. A voltage of 35 kV and a current of 20 mA were used to collect data from a $\text{CuK}\alpha$ source with $\lambda = 1.54$ angstroms.

The second XRD technique used in this work is referred to as Glancing Incidence X-Ray Diffraction (GIXRD) and is the same as the previous technique

except that the incoming and outgoing x-rays are not at the same angle. This allows the incoming angle to be controlled by the researcher and it may go down to angles less than a degree. Thus, crystalline layers as thin as 5 nm may be analyzed by this technique which is ideal for the thin interfacial layer being analyzed in this work.

However, GIXRD may not be used in intensity studies such as grain or particle size and orientation studies. Only those grains with x, y and z coordinates that meet Bragg's Law will be seen by the detector so not all the grains may be seen by the detector. Grains within the film may not always grow in columns but may be tilted and thus not seen by the detector. The intensity of the XRD pattern is related to the amount of grains with a particular orientation present within the film. Since not all of them may be detected only symmetric XRD measurements may be used in intensity studies.

Symmetric XRD does have the advantage that orientations of the film may be determined along with other intensity studies. This includes using the intensities to find the particle size of the film, texture orientation coefficients, and composition. One must keep in mind, however, that symmetric measurements take crystallographic data over the entire film generating an average of all planes. Thus it will not be able to see very thin layers like the GIXRD as the signal generated from the bulk film will drown out the small signal from a thin layer.

In this work a Rigaku D/Max 2200 was used for GIXRD analysis. It also used a Cu K α source and a voltage of 40 kV and current of 40 mA was used to take all data. The next section will discuss the results found from these two techniques.

Chapter 4

RESULTS

4.1: Selenization and Sulfurization of Molybdenum Substrates

The first part of this research effort was to determine how molybdenum would react in the presence of sulfur and selenium and their relative reaction rates. Three sets of molybdenum coated soda lime glass substrates were reacted with H_2S , H_2Se or a combination of the two under 65% argon flow in a selenization chamber. The primary assumption is that the reaction mechanism using H_2Se and H_2S in this chamber is the same as in the multi-source evaporation chamber used to deposit $\text{CuIn}(\text{S}_x\text{Se}_{1-x})$. The following table outlines the specifics of this experiment.

Table 4.1: Experimental Parameters for Selenization Experiment

Number of Samples	Gas Used in Reaction	Total Concentration of Gas	Reaction Temperature	Length of Reaction
3	H_2Se	0.35%	550°C	1 hour
3	H_2S	0.35%	550°C	1 hour
3	50/50 mix of H_2S and H_2Se	0.35%	550°C	1 hour

Once the samples had been reacted the structure of film was evaluated using symmetric XRD with a $\text{CuK}\alpha$ source ($\lambda = 1.54$ angstroms). Figure 4.1 shows the resulting XRD patterns for each of the three different types of samples and Table 4.2 indexes the peaks.

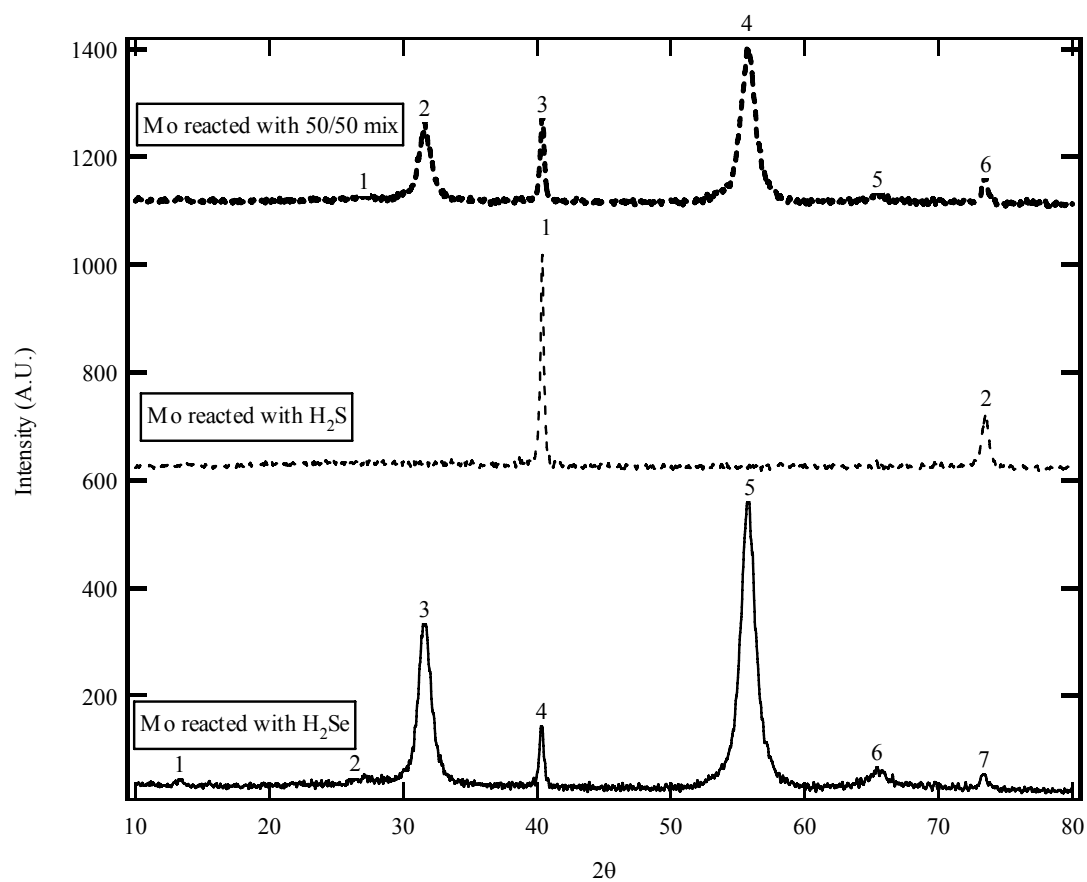


Figure 4.1: Symmetric XRD Results for Molybdenum Coated Soda Lime Glass Substrates^[36, 37]

Table 4.2: Symmetric XRD Peak Indexing for Molybdenum Coated Soda Lime Glass Substrates^[36, 37]

Peak Number	Corresponding Element or Compound	Peak Index	Measured Intensity (A.U.)	I/I(110)	JCPDS I/I ₀ (No: 42-1120, 29-0914)
Symmetric XRD Analysis of Mo Reacted with H₂Se					
1	MoSe ₂	(004)	30	10	15
2	MoSe ₂	(100)	168	54	55
3	Mo	(110)	173	100	100
4	MoSe ₂	(110)	314	100	40
5	MoSe ₂	(200)	34	11	3
-	MoSe₂	(103)	-	-	100
6	Mo	(211)	63	36	31
Symmetric XRD Analysis of Mo Reacted with H₂S					
1	Mo	(110)	410	100	100
2	Mo	(211)	118	29	31
Symmetric XRD Analysis of Mo Reacted with H₂S and H₂Se					
1	MoSe ₂	(002)	47	8	75
2	MoSe ₂	(004)	54	9	15
3	MoSe ₂	(100)	336	58	55
4	Mo	(110)	145	100	100
5	MoSe ₂	(110)	576	100	40
-	MoSe₂	(103)	-	-	100
6	MoSe ₂	(200)	70	12	3
7	Mo	(211)	56	39	31

Before the patterns were indexed a Rachinger correction and 5 point binomial smoothing was performed on the data using Igor Pro software to remove CuK α_2 radiation and reduce the noise level. As can be seen from Figure 4.1 and Table 4.2, each of the samples display two peaks from the unreacted molybdenum which are the Mo(110) and Mo(211) peaks indexed in Table 4.2.[36] These two peaks are typically used as a standard to ensure proper sample alignment and mounting.

Both the sample that was reacted in just H_2Se and the sample that was reacted in the mix of H_2Se and H_2S display strikingly similar XRD patterns. The d-spacings from these patterns match those given by JCPDS standard 29-0914 for MoSe_2 within experimental error or 0.02 angstroms. They each display peaks from the (100), (110), and (200) planes and both of these samples have a preferred orientation in the (100) and (110) planes. According to the JCPDS standard the XRD pattern of a randomly oriented MoSe_2 film should display a (103) peak having the largest intensity.[37] Neither of these samples displays this characteristic. From this information however, one may infer that the c-axis of these films is oriented perpendicular to the underlying molybdenum layer.

To gain a better understanding of the relative reaction rates in the H_2Se case versus the case of the 50/50 mix of the two gases, the intensities of the peaks generated from the MoSe_2 were normalized to the Mo(110) peak for that sample. This assumes that the thickness of the molybdenum layer was about the same for each of the samples. From previous analysis this assumption has been valid. Table 4.3 displays the results from this analysis.

Table 4.3: Comparison of Relative Reaction Rates of H_2Se versus H_2S and H_2Se

Gas used in Reaction	Peak Index	Normalized Peak Intensity
H_2Se	(100)	2
H_2Se	(110)	4
H_2Se	(200)	1
50/50 H_2Se and H_2S	(100)	1
50/50 H_2Se and H_2S	(110)	2
50/50 H_2Se and H_2S	(200)	< 1

Looking at Table 4.3 one can see that the normalized intensities of the peaks from the molybdenum sample reacted with just H_2Se are roughly twice that of the sample reacted with the mixture of H_2S and H_2Se . This makes sense since only half the amount of H_2Se was present to react with the molybdenum in the 50/50 mix of H_2Se and H_2S . Thus the reaction rate of molybdenum with H_2Se is about the same as that of molybdenum with H_2S and H_2Se . Also, in the presence of both sulfur and selenium the molybdenum only reacted with the selenium. This agrees with the reaction behavior predicted by the heats of formation of MoSe_2 and MoS_2 as stated in Chapter 2.

The sample that was exposed to H_2S gas only displays the two primary molybdenum peaks. This indicates that either the temperature was too low for any reaction to occur or the layer is too thin to be seen by symmetric XRD methods. Unreacted molybdenum has a shiny silver cast to it, and the surface of this sample had changed to a dark blue color after being reacted with H_2S in the selenization chamber. This indicated that a very thin layer of the molybdenum had reacted with the gas but it was too thin to be seen by symmetric XRD.

Thus the next step was to analyze this sample along with the other two using Glancing Angle XRD (GIXRD). Incidence angles of 0.7° and 1.0° were chosen to avoid total reflection and see roughly the first 200 nm of the film. This method is sensitive down to five nanometers which makes it relatively surface sensitive.[38] Figure 4.2 displays the GIXRD patterns for all three samples and Table 4.4 indexes these patterns. Figure 4.3 displays the (002) peak for each of these samples and will be discussed below.

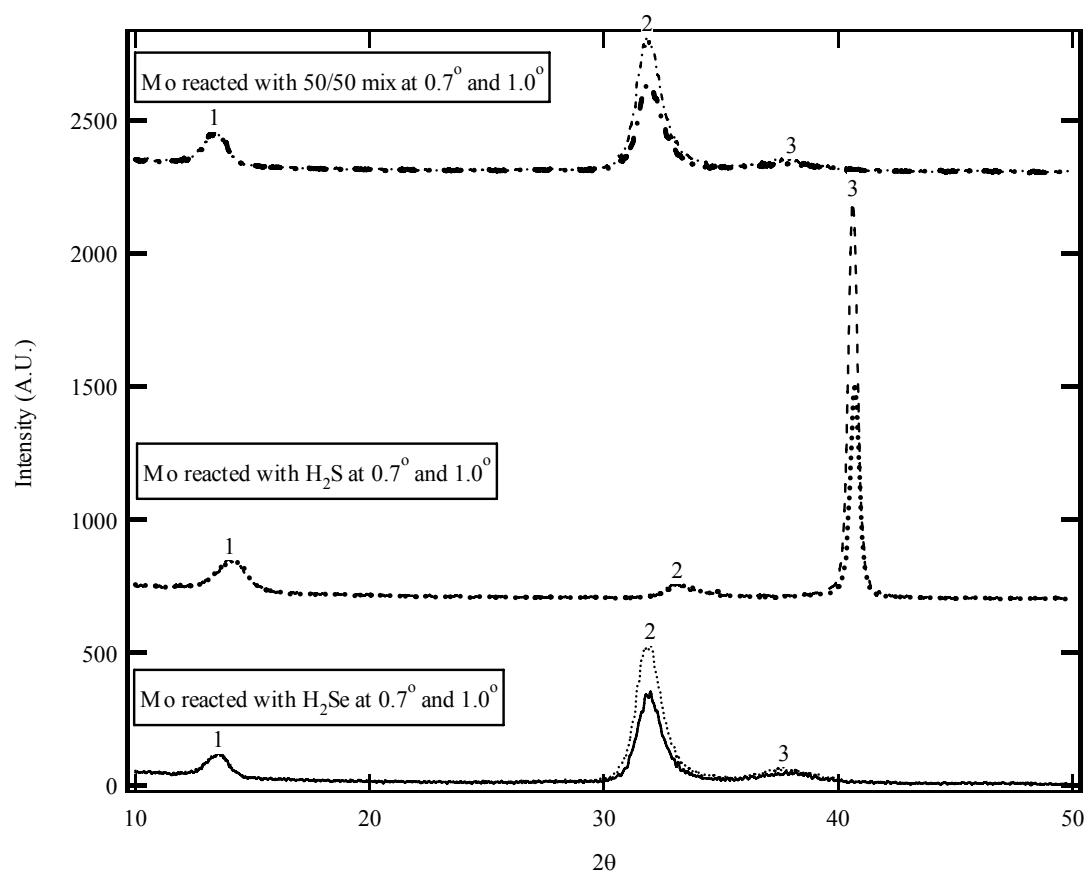


Figure 4.2: Asymmetric Analysis of Molybdenum Covered Soda Lime Glass Substrates Reacted With H_2S , H_2Se , or a 50/50 Mix of the Two^[36, 37, 39]

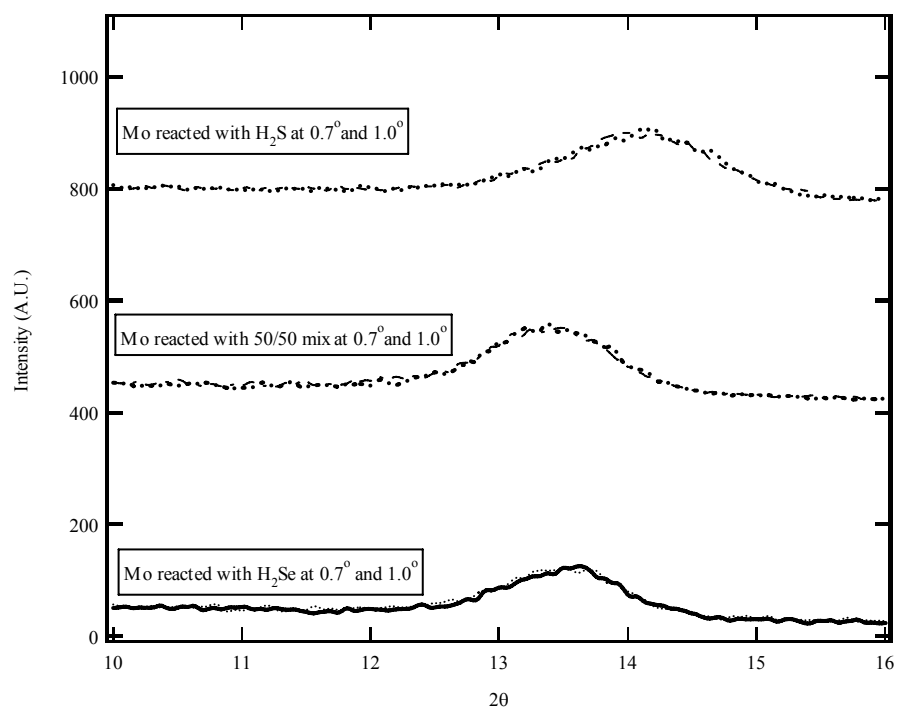


Figure 4.3: (002) Peaks of the molybdenum samples reacted with H_2Se , H_2S and a 50/50 mix of the two

Table 4.4: Asymmetric Peak Indexing of Molybdenum Coated Soda Lime Glass Substrates^[36, 37, 39]

Peak Number	Element or Compound	Peak Index
Asymmetric Analysis of Mo Reacted with H₂S and H₂Se		
1	MoSe ₂	(002)
2	MoSe ₂	(100)
3	MoSe ₂	(103)
Asymmetric Analysis of Mo Reacted with H₂S		
1	MoS ₂	(002)
2	MoS ₂	(101)
3	Mo	(110)
Asymmetric Analysis of Mo Reacted with H₂Se		
1	MoSe ₂	(002)
2	MoSe ₂	(100)
3	MoSe ₂	(103)

Looking at Figure 4.2 once again the patterns are identical in terms of position for both the sample that was reacted with H₂Se and the sample that was reacted with the mixture of gases. However, this time there is a peak present from the horizontal (002) plane and the (103) plane is present unlike in the symmetric XRD patterns.[37] Also, the (002) and (103) peaks are not changing intensity like the Mo (110) peak or MoSe₂ (100) peak with increasing incidence angle.

This feature of the previous GIXRD pattern could be explained in two different ways. The surface of the films reacted with H₂Se and the gas mix was studied using a Scanning Electron Microscope. In both of these micrographs, ball-like structures were seen scattered all over the surface of the films about 1 μm in diameter. Since the intensity of the peaks is not changing this means that the volume of material that the x-rays are seeing is not changing either as they probe deeper into the sample. A ball or cone-like structure would satisfy the physics behind this phenomenon.

Another explanation comes from the highly oriented nature of the samples. In a randomly oriented sample there are grains lying in many different orientations which all diffract the x-rays back to the detector assuming that they satisfy the Bragg condition. In a sense the surface of the sample can be thought of as a mirror. However, if a sample is highly oriented only certain areas of the surface will diffract x-rays back to the detector. As the incidence angle changes the x-rays will, in effect, be hitting a different part of the sample's surface. This is known as an orientation effect which means that the intensities of the pattern can not be relied upon to give accurate information about the sample.

To test these two ideas another asymmetric scan with an incidence angle of 5.0° was performed on the molybdenum covered soda lime glass sample that had been reacted with H_2Se . The 5.0° angle was chosen to allow the x-rays to penetrate through most of the film simulating the depth that a symmetric scan would cover. The idea was to see if the (002) and (103) peaks would still show up even when a large signal was being generated by the bulk of the film. Figure 4.4 displays the result and Table 4.5 shows the corresponding peak indexing.

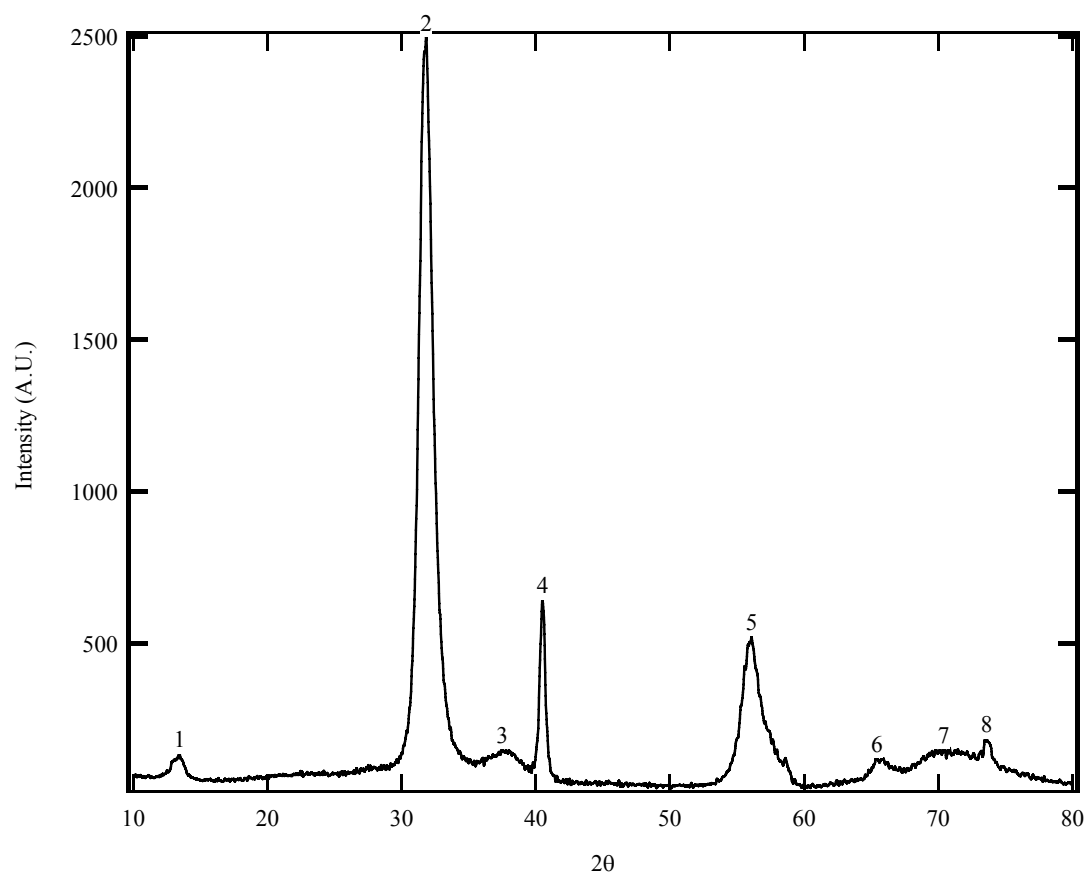


Figure 4.4: Asymmetric Scan of Mo Sample Reacted with H₂Se at Incidence Angle of 5.0°

Table 4.5: Peak Indexing of Mo Covered Soda Lime Glass Sample Reacted with H_2Se ^[36, 37, 39]

Peak Number	Element or Compound	Peak Index
1	MoSe_2	(002)
2	MoSe_2	(100)
3	MoSe_2	(103)
4	Mo	(110)
5	MoSe_2	(110)
6	MoSe_2	(200/108/203)
7	MoSe_2	(116)
8	Mo	(211)

Looking at Figure 4.4, it is very similar to the pattern seen in Figure 4.2 except for the presence of two peaks from the underlying molybdenum and a series of broad peaks starting at about 65° and ending at about 75° . Also, the (002) peak is still seen in this pattern and is very similar to the (002) peaks seen in Figure 4.2.

The broad peaks seen in the figure above have been seen before by Liang et al. who studied poorly crystalline MoS_2 . This group took XRD patterns of MoS_2 that had been created by thermally decomposing ammonium thiomolybdate to create amorphous MoS_3 in dry N_2 flow at 250°C for four hours. The MoS_3 was then heated to 400°C , 500°C and 800°C in 15% H_2S and 85% H_2 for four hours to create three samples of MoS_2 that had different relative amounts of crystallinity. The patterns of MoS_2 at the two lower temperatures showed a series of long broad peaks similar to that seen in the previous figure. Liang et al. also did a modeling study of the crystal structure of the MoS_2 to try and match the experimental XRD patterns with those calculated based on the theoretical crystal structure of MoS_2 .^[40]

It is already known that a decrease in grain size will cause symmetric line broadening and linear or planar defects can cause symmetric or asymmetric peaks

and/or broadening. They found that if they decreased the number of layers in the crystal structure or shifted the position of one layer with respect to another, this would cause the (002) peak to shift away from its accepted position given by JCPDS card No 37-1492. They also found that rotating the layers along the c-axis or bending the layers gave good agreement with the experimental patterns that were collected on MoS₂. The previous figures display small (002) peaks with either symmetric or asymmetric broadening whose locations are different from the accepted value. Thus, it is possible that the layers of MoSe₂ or MoS₂ that are generating these broad peaks are microcrystalline in size and comprised of only a few layers which are bent.[40]

In Figure 4.2, it is worth noting that the molybdenum peaks are not observed in the H₂Se and gas mixture cases since the x-rays are not penetrating deeply enough to see the underlying molybdenum. This means that the MoSe₂ layer formed is at least as thick as the penetration depth of the x-rays which is approximately 200 nm.

The GIXRD pattern for the molybdenum sample that was reacted with H₂S is very similar to the other two patterns except that both peaks are very weak and broad and in different positions from each other on the 2 θ scale. Though it is hard to index these peaks based on d-spacings, the positions roughly correspond to those generated by MoS₂. [39] The (101) peak is not nearly as strong as the (103) peak in the H₂Se and gas mixture cases suggesting that the structure of this film is even less organized than the other two. It appears that temperatures higher than 550°C are needed to create a thick well formed film of MoS₂. This conclusion is based on the fact that GIXRD was needed to see a very disorganized crystal structure represented by two very weak peaks shown in Figure 4.2

In the case where molybdenum was reacted with H_2Se , it is apparent from the symmetric analysis that MoSe_2 was created from this reaction. However, in the case where molybdenum was reacted with H_2S , the material formed was not thick enough to be seen by symmetric analysis methods. GIXRD had to be used to determine if a material with some amount of crystal structure was present at all. The d-spacings from those GIXRD spectra cannot be readily used to determine what material is generating them due to the breadth of the peaks. Thus, it is very hard to say for certain that these patterns are being generated by MoS_2 . However, since only sulfur was present to react with the molybdenum it is a reasonable guess to assume that MoS_2 is generating the GIXRD spectrum. Since the peak locations are different for the H_2S case versus the H_2Se and gas mix case, this does support the idea that two different materials are generating these patterns.

The role of sodium in this reaction was also investigated by switching to a different type of substrate. Instead of reacting molybdenum coated soda lime glass substrates with the gases, molybdenum coated borosilicate (7059 glass) samples were reacted under the same three conditions outlined in Table 4.1. The results of the symmetric XRD analysis are shown in the Figure 4.5 which is indexed in Table 4.6.

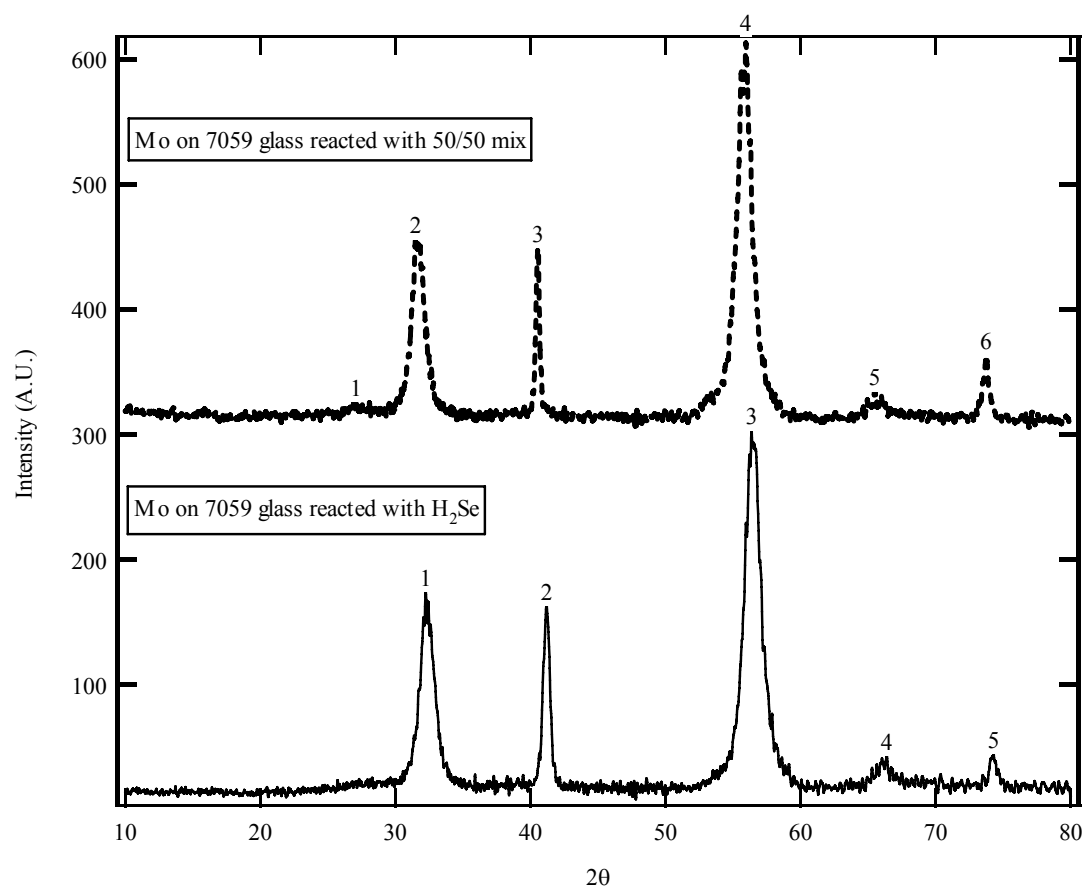


Figure 4.5: Symmetric XRD Analysis of Molybdenum Coated 7059 Glass Substrates^[36, 37]

Table 4.6: Peak Indexing of 7059 Glass Substrates Reacted with H₂S, H₂Se and 50/50 Mix^[36, 37]

Peak Number	Corresponding Element or Compound	Peak Index	Measured Intensity (A.U.)	I/I(110)	JCPDS I/I ₀ (No: 42-1120, 29-0914)
Mo Reacted with H₂S and H₂Se					
1	MoSe ₂	(004)	26	8	15
2	MoSe ₂	(100)	154	49	55
3	Mo	(110)	149	100	100
4	MoSe ₂	(110)	313	100	40
-	MoSe₂	(103)	-	-	100
5	MoSe ₂	(200)	35	11	6
6	Mo	(211)	63	42	31
Mo Reacted with H₂Se					
1	MoSe ₂	(100)	175	58	55
2	Mo	(110)	164	100	100
3	MoSe ₂	(110)	304	100	40
4	MoSe ₂	(200)	43	14	6
-	MoSe₂	(103)	-	-	100
5	Mo	(211)	45	27	31

As can be seen from Figure 4.5 and Table 4.6, the results for the substrates reacted with only H₂Se are the same as for the substrates reacted with both H₂S and H₂Se. They also match the d-spacings given by JCPDS card 29-0194 for MoSe₂ within experimental error or 0.02 angstroms. The symmetric XRD pattern for the substrates that were reacted in just H₂S is not shown as it gave a pattern for just molybdenum as before.

From this information the sodium could have had an effect on the reaction between the molybdenum and sulfur and/or selenium in one or more of the following ways. The sodium could have changed the orientation of the resulting layer or MoSe₂ or MoS₂. This would have been observed through a change in the peaks seen in XRD

patterns generated from the soda lime glass and borosilicate glass substrates.

However, in this case, the peaks seen in both cases are identical. Therefore it can be concluded that sodium did not have an effect on the orientation of the MoSe₂ layer.

The sodium could also have changed the relative reaction rates between molybdenum and sulfur and/or selenium. To determine if this was the case, the intensities of the XRD spectra were normalized relative to the Mo peak as shown previously. Table 4.7 outlines the result of that analysis.

Table 4.7: Comparison of Relative Reaction Rates Between H₂Se and 50/50 Mix for 7059 Glass Substrates

Gas used in Reaction	Peak Index	Normalized Peak Intensity
H ₂ Se	(004)	< 1
H ₂ Se	(100)	1
H ₂ Se	(110)	2
H ₂ Se	(200)	< 1
50/50 H ₂ Se and H ₂ S	(004)	<1
50/50 H ₂ Se and H ₂ S	(100)	1
50/50 H ₂ Se and H ₂ S	(110)	2
50/50 H ₂ Se and H ₂ S	(200)	< 1

Looking at the previous table one may infer that the reaction rates were roughly equivalent for the reaction with just H₂Se and for the reaction with the gas mix. In the previous case where molybdenum was reacted with H₂Se in the presence of sodium the normalized intensities were roughly twice that of those in the gas mix case. This implies that the sodium present in the soda lime glass substrates enhanced the reaction with the gases by a factor of two, reviewing the results in Table 4.3.

Lastly, the sodium could also have either enhanced or suppressed the reaction of molybdenum with sulfur. However, since only GIXRD data is available from this study a conclusion on this possibility cannot be made. Intensity studies using GIXRD data are never valid, particularly since an orientation effect could be present. The intensities in the XRD patterns for MoS_2 are not changing with increasing incidence angle as seen in the GIXRD patterns for MoSe_2 . Thus, symmetric studies on a much thicker film of MoS_2 are needed to draw a conclusion on this point.

GI-XRD analysis was not performed on the samples reacted with just H_2Se and the samples reacted with the mixture of H_2Se and H_2S since the symmetric XRD patterns between the two different substrates were identical. The sample reacted with H_2S , however, was placed into the asymmetric XRD to verify that a similar layer of MoS_2 had in fact been created. Figure 4.6 displays the result and Table 4.8 indexes the corresponding peaks.

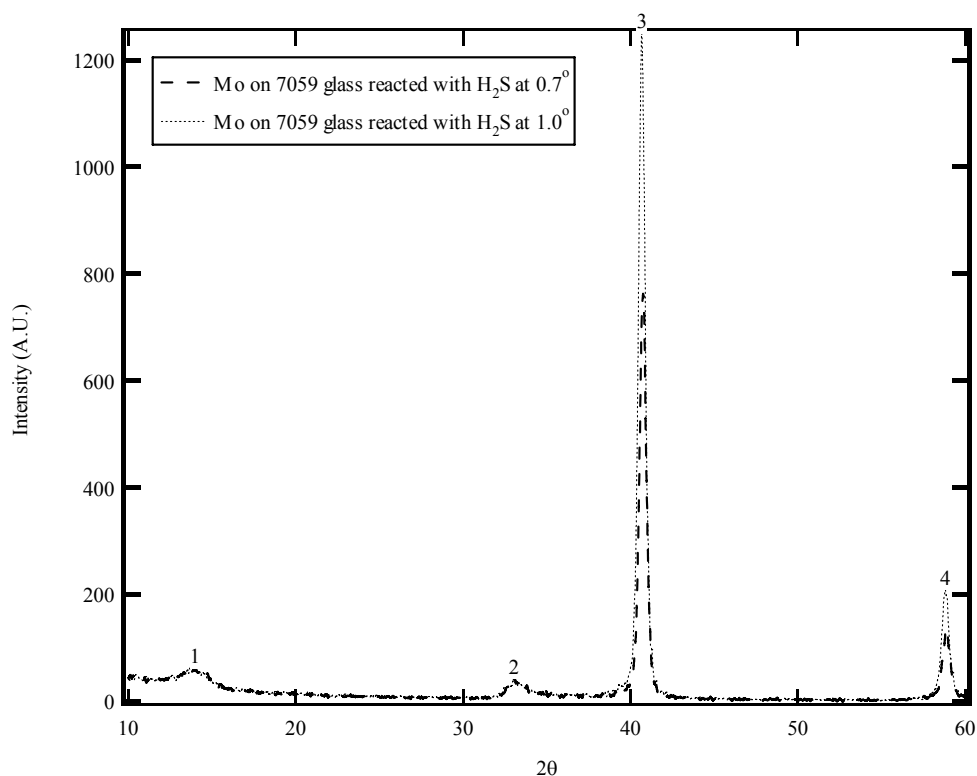


Figure 4.6: Asymmetric XRD Analysis of 7059 Glass Substrates Reacted with H_2S ^[36, 39]

Table 4.8: Peak Indexing for Asymmetric Analysis of 7059 Glass Substrates Reacted with H_2S ^[36, 39]

Peak Number	Element or Compound	Peak Index
1	MoS_2	(002)
2	MoS_2	(101)

As can be seen from Figure 4.6 and Table 4.8 this XRD pattern is identical in terms of peak position to the one generated from the molybdenum coated soda lime glass substrates (see Figure 4.2). From this study it appears that sodium

does not have an effect on the crystal structure of the film formed from the reaction of molybdenum with sulfur and selenium but on the relative reaction rates. In each case, the same crystal structure for MoSe_2 and MoS_2 was generated. The next section of this chapter describes the results from the XRD analysis of the chalcopyrite thin films. These films were studied to gain a better understanding of how MoSe_2 and MoS_2 form in these films in terms of composition and crystal structure.

4.2 XRD Analysis of the Chalcopyrite Thin Films

The next step in this work was to perform symmetric and asymmetric XRD analysis of four chalcopyrite thin films. These films were grown using a multi-source coevaporation chamber on soda lime glass substrates. An understanding of how molybdenum reacts in the presence of selenium and/or sulfur has been gained from the first part of this work. The goal now is to better understand how molybdenum reacts with sulfur and selenium present within the chalcopyrite thin films, and what dichalcogenide layer is formed during deposition of the semiconductor thin film. How do sulfur and selenium affect the composition and crystal structure of the dichalcogenide layer that is formed? As presented in the second chapter, MoSe_2 and MoS_2 only formed in a copper poor environment. Thus, in this work, only copper poor samples were used in this work.

To constrain experimental parameters the Cu/III ratio was held at approximately 0.9 and the S/VI ratio was varied from zero to one. Films with a thickness of approximately 2 μm thick were chosen to ensure that the experimental conditions were the same. A CuInSe_2 and CuInS_2 sample were analyzed to understand the growth conditions for the intermediate layer in the presence of only sulfur or selenium.

Two $\text{CuIn}(\text{S}_x\text{Se}_{1-x})_2$ films were analyzed as well with two different S/VI ratios to generate a S/VI concentration dependence. To determine the overall crystal structure of these films, symmetric XRD was performed on the front of each of these samples listed in the table below. The amounts of copper, indium, sulfur, and selenium were measured using EDS and are given in atomic percent in Table 4.9.

Table 4.9: Description of the Four Semiconductor Thin Films

Material	% Cu	%In	%S	%Se	Cu/III	S/VI	Thickness (μm)
CuInSe_2	24.2	25.7	0.0	50.1	0.94	0.00	~ 2.0
$\text{CuIn}(\text{S}_x\text{Se}_{1-x})_2$	21.8	26.6	12.0	39.6	0.82	0.24	~ 1.4
$\text{CuIn}(\text{S}_x\text{Se}_{1-x})_2$	23.5	26.7	26.9	22.9	0.88	0.54	~ 2.7
CuInS_2	25.2	26.1	48.4	0.3	0.96	1.00	~ 2.4

The first step was to perform symmetric XRD to gain an overall idea of the structure of the film and to determine if any peaks from the interfacial layer would appear. Figure 4.7 displays the result for the CuInSe_2 film and Table 4.10 indexes the peak displayed in the figure.

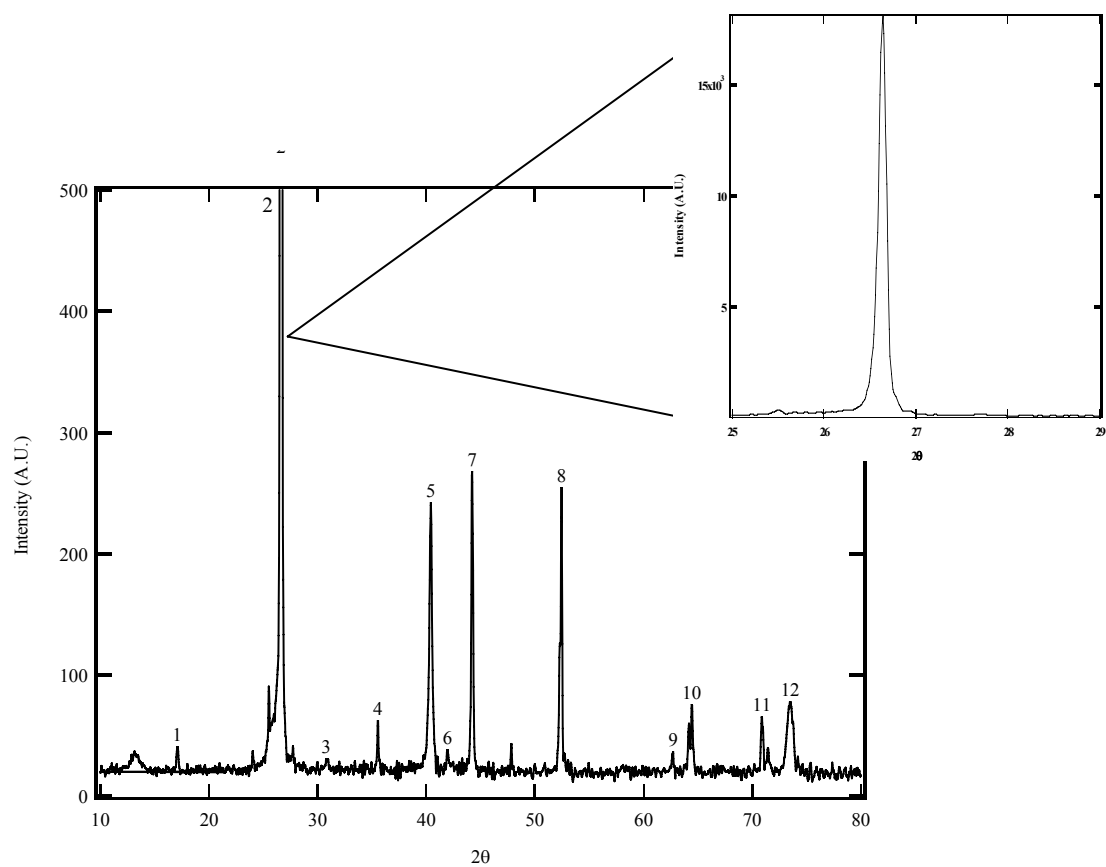


Figure 4.7: Symmetric XRD Analysis of CuInSe_2 Sample^[36, 41]

Table 4.10: Peak Indexing of Symmetric Analysis of CuInSe₂ Sample^[36, 41]

Peak Number	Element or Compound	Peak Index	Measured Intensity (A.U.)	I/I(112)	JCPDS I/I ₀ (No: 40-1487, 42-1120)
1	CuInSe ₂	(101)	41	<1	6
2	CuInSe ₂	(112)	18,089	100	100
3	CuInSe ₂	(200)	31	<1	1
4	CuInSe ₂	(211)	63	<1	7
5	Mo	(110)	243	100	100
6	CuInSe ₂	(105/213)	39	<1	2
7	CuInSe ₂	(220)	268	1	51
8	CuInSe ₂	(312)	255	1	25
9	CuInSe ₂	(305/323)	37	<1	3
10	CuInSe ₂	(332)	66	<1	4
11	CuInSe ₂	(325/413)	40	<1	2
12	Mo	(211)	79	33	31

Looking at Table 4.10 and Figure 4.7 one sees all of the typical peaks expected from CuInSe₂ according to JCPDS card 40-1487.[41] The experimental error of the d-spacings used to index the peaks and identify the material in all cases of symmetric analysis is 0.02 angstroms. The inset of Figure 4.7 displays a refined scan of the (112) peak for this film. What is unusual about this spectra is that it is highly (112) oriented with an intensity over 18,000 counts. There is a possibility that the peak at about fourteen degrees is from the interfacial layer but the scan is not resolved enough to determine if that is the case. A slow, refined scan is needed to confirm that the peak is in fact from MoSe₂. GIXRD on the peeled molybdenum substrate of this sample will give a better measure of the d-spacing associated with that peak. Figure

4.8 displays the symmetric XRD results for the other three samples and Table 4.11 displays the indexing for the patterns.

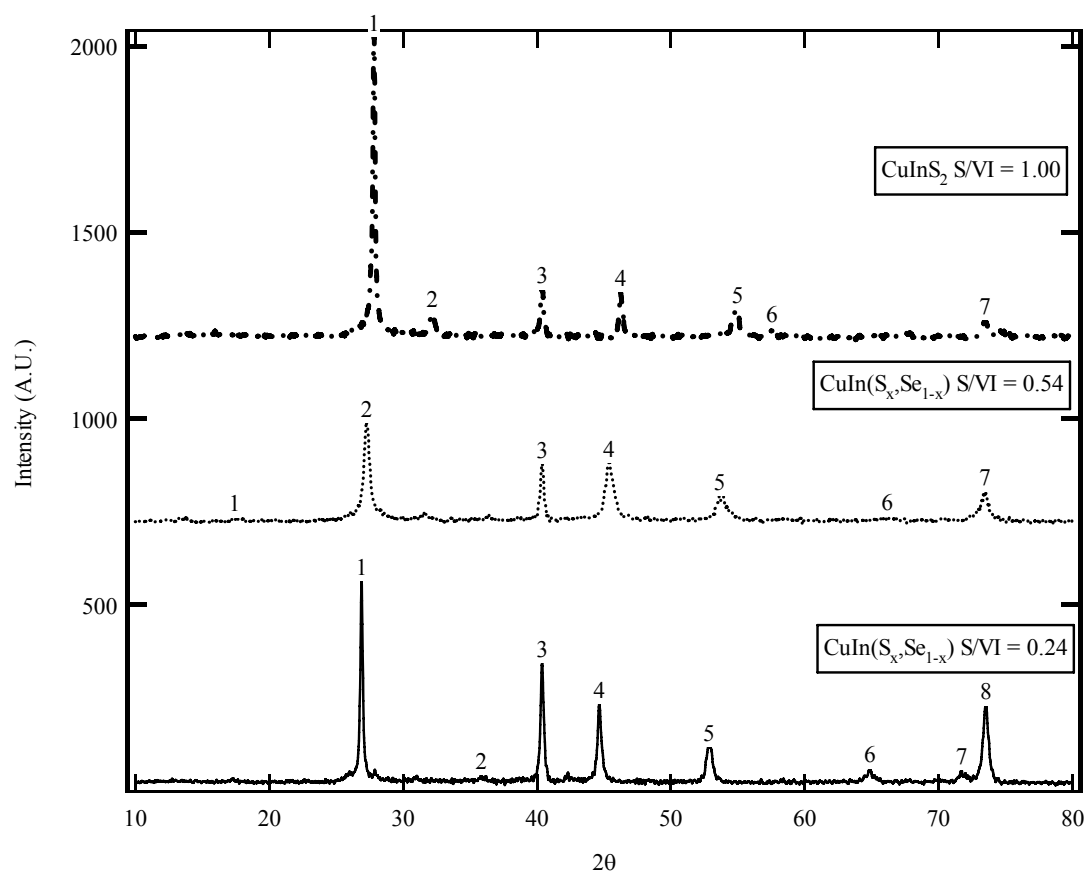


Figure 4.8: Symmetric XRD Analysis of the $\text{CuIn}(\text{S}_x\text{Se}_{1-x})_2$ and CuInS_2 Samples^[36, 41, 42]

Table 4.11: Peak Indexing for Symmetric Analysis of CuInS₂ and CuIn(S_x,Se_{1-x})₂ Samples^[36, 41, 42]

Peak Number	Element or Compound	Peak Index	Measured Intensity (A.U.)	I/I(112)	JCPDS I/I ₀ (No: 40-1487, 42-1120, 27-0159)
Symmetric Analysis of CuInS₂					
1	CuInS ₂	(112)	2660	100	100
2	CuInS ₂	(004)	84	3	6
3	Mo	(110)	148	100	100
4	CuInS ₂	(204/220)	142	3	25/10
5	CuInS ₂	(116/312)	94	4	6/12
6	CuInS ₂	(224)	44	2	4
7	Mo	(211)	65	44	31
Symmetric Analysis of CuIn(S_x,Se_{1-x})₂ (S/VI = 0.54)					
1	CuIn(S _x ,Se _{1-x}) ₂	(101)	35	12	8
2	CuIn(S _x ,Se _{1-x}) ₂	(112)	290	100	100
3	Mo	(110)	180	100	100
4	CuIn(S _x ,Se _{1-x}) ₂	(204/220)	183	63	32
5	CuIn(S _x ,Se _{1-x}) ₂	(312/116)	93	32	18
6	CuIn(S _x ,Se _{1-x}) ₂	(008/400)	37	13	4
7	Mo	(211)	105	58	31
Symmetric Analysis of CuIn(S_x,Se_{1-x})₂ (S/VI = 0.24)					
1	CuIn(S _x ,Se _{1-x}) ₂	(112)	566	100	100
2	CuIn(S _x ,Se _{1-x}) ₂	(211)	44	8	5
3	Mo	(110)	344	100	100
4	CuIn(S _x ,Se _{1-x}) ₂	(204/220)	235	42	32
5	CuIn(S _x ,Se _{1-x}) ₂	(312/116)	119	21	18
6	CuIn(S _x ,Se _{1-x}) ₂	(008/400)	61	11	4
7	CuIn(S _x ,Se _{1-x}) ₂	(332)	57	10	3
8	Mo	(211)	230	67	31

Once again the typical spectra for CuInS₂ and CuIn(S_x,Se_{1-x})₂ are seen in the previous figure and table with no trace of the interfacial layer. Vegard's Law was used to interpolate between the d-spacings for CuInSe₂ and CuInS₂ generating the d-spacings for CuIn(S_x,Se_{1-x})₂. It is readily understood that GIXRD on the peeled

surfaces is needed to pick up any signs of an interfacial layer since the signal generated from it is quite weak. Figure 4.9 displays the results for GIXRD analysis of the back of the peeled thin films and Table 4.12 identifies the peaks .

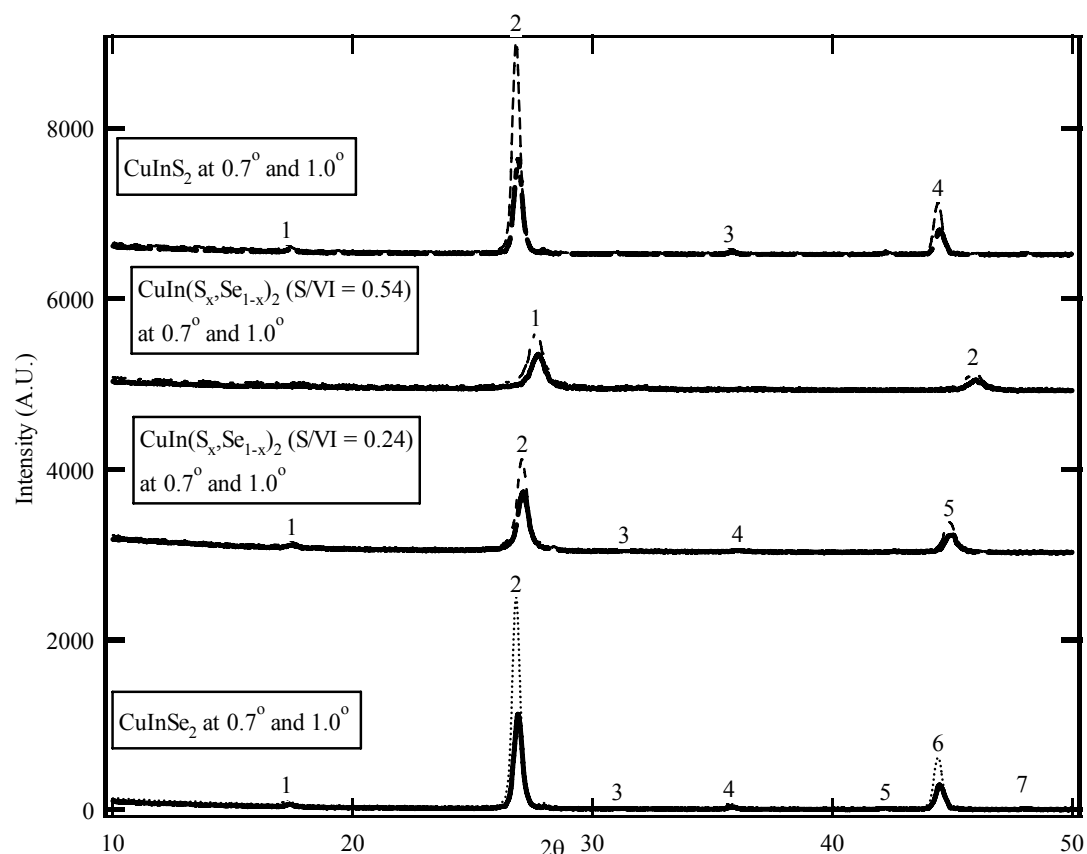


Figure 4.9: GIXRD Analysis of the Back of the Peeled Chalcopyrite Thin Films^[36, 41, 42]

Table 4.12: Peak Indexing for GIXRD Analysis of the Back of Peeled Films^[36, 41, 42]

Peak Number	Element or Compound	Peak Index
Asymmetric Analysis of CuInSe₂		
1	CuInSe ₂	(101)
2	CuInSe ₂	(112)
3	CuInSe ₂	(200)
4	CuInSe ₂	(211)
5	CuInSe ₂	(220/204)
6	CuInSe ₂	(213/105)
7	CuInSe ₂	(301)
Asymmetric Analysis of CuIn(S_x,Se_{1-x})₂ (S/VI = 0.24)		
1	CuIn(S _x ,Se _{1-x}) ₂	(101)
2	CuIn(S _x ,Se _{1-x}) ₂	(112)
3	CuIn(S _x ,Se _{1-x}) ₂	(200)
4	CuIn(S _x ,Se _{1-x}) ₂	(211)
5	CuIn(S _x ,Se _{1-x}) ₂	(213/105)
Asymmetric Analysis of CuIn(S_x,Se_{1-x})₂ (S/VI = 0.54)		
1	CuIn(S _x ,Se _{1-x}) ₂	(112)
2	CuIn(S _x ,Se _{1-x}) ₂	(220/204)
Asymmetric Analysis of CuInS₂		
1	CuInS ₂	(101)
2	CuInS ₂	(112)
3	CuInS ₂	(211)
4	CuInS ₂	(220/204)

As can be seen from the previous table and figure all the peaks correspond to either CuInS₂, CuInSe₂, or CuIn(S_x,Se_{1-x})₂ according to JCPDS cards 27-0159 and 40-1487. Vegard's Law was used to interpolate between the d-spacings for CuInSe₂ and CuInS₂ generating the d-spacings for CuIn(S_x,Se_{1-x})₂. These were within 0.02 angstroms of the experimental data. No peaks are seen from molybdenum or any metal dichalcogenide which agrees with the literature. This suggests that this was a clean peel.

Next the molybdenum substrates for these samples were analyzed using asymmetric XRD. Figure 4.10 and Table 4.13 display the results.

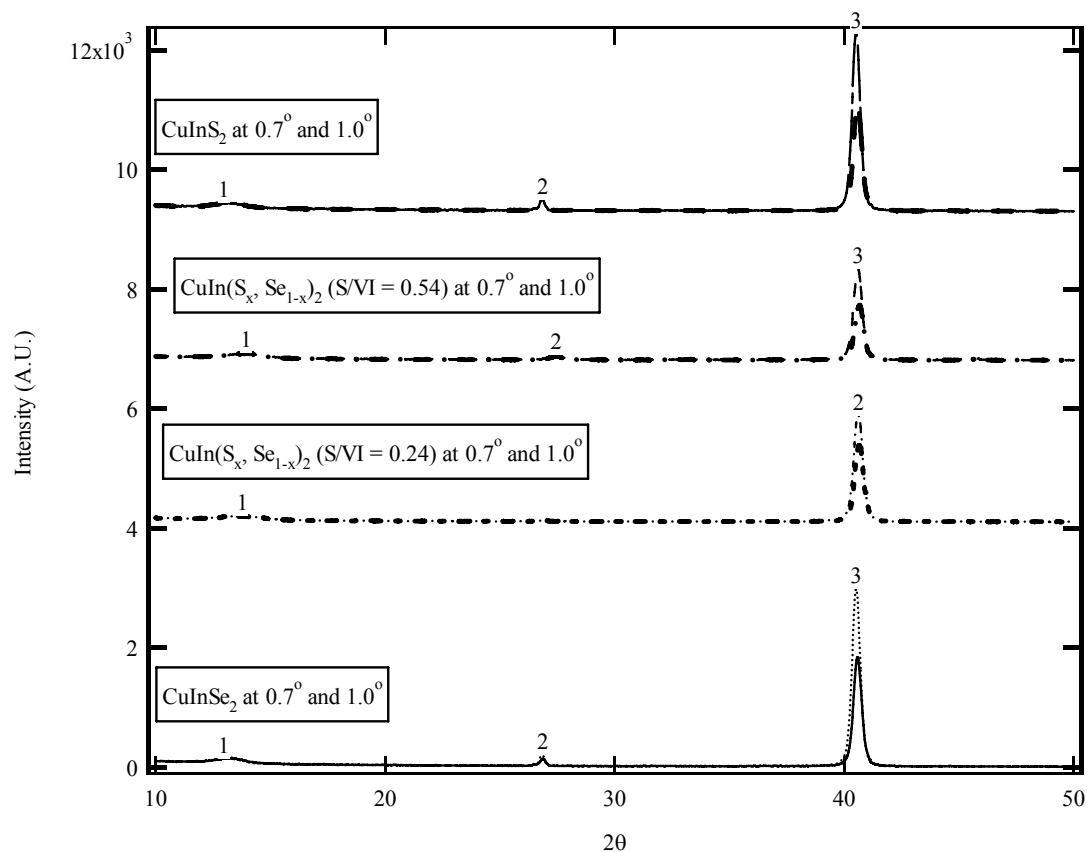


Figure 4.10: Asymmetric XRD Analysis of the Molybdenum Substrates of the Peeled Chalcopyrite Films^[36, 41, 42]

Table 4.13: Peak Indexing of Asymmetric Analysis of Peeled Molybdenum Substrates of Chalcopyrite Thin Films^[36, 41, 42]

Peak Number	Element or Compound	Peak Index
Asymmetric Analysis of Mo Substrate of CuInSe₂		
1	MoSe ₂ ?	(002)
2	CuInSe ₂	(112)
3	Mo	(110)
Asymmetric Analysis of Mo Substrate of CuIn(S_x,Se_{1-x})₂ (S/VI = 0.24)		
1	MoSe ₂ ?	(002)
2	Mo	(110)
Asymmetric Analysis of Mo Substrate of CuIn(S_x,Se_{1-x})₂ (S/VI = 0.54)		
1	MoSe ₂ ?	(002)
2	CuIn(S _x ,Se _{1-x}) ₂	(112)
3	Mo	(110)
Asymmetric Analysis of Mo Substrate of CuInS₂		
1	MoSe ₂ ?	(002)
2	CuInS ₂	(112)
3	Mo	(110)

As can be seen from the Figure 4.10 only a couple of small, broad, asymmetric peaks can be seen that could be from a very thin dichalcogenide layer. Figure 4.11 displays only the (002) peaks seen in the previous figure as they are the only ones generated from the layer of interest.

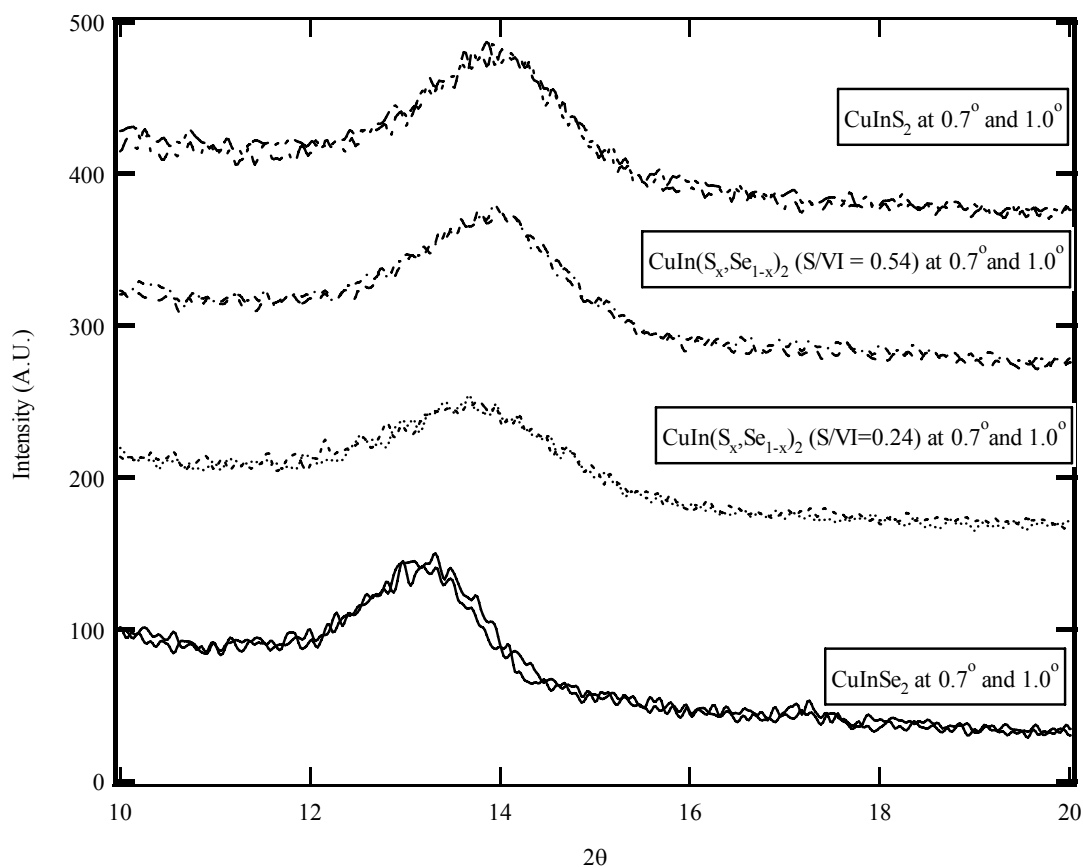


Figure 4.11: (002) Peaks of GIXRD Analysis of Peeled Molybdenum Substrates

What can be said is that this layer is not very well formed compared to the molybdenum substrates that were reacted with H_2Se in the selenization chamber. The overall pattern demonstrated in Figure 4.10 most closely resembles the one seen for the molybdenum substrate reacted with H_2S . The pattern is also lacking any kind of vertical component such as the (100) and (110) peaks seen earlier.

From the shape and broadness of the (002) peaks it looks like it could have a structure similar to that proposed by Liang et al. The fact that particulates were seen on the surface of the MoSe_2 sample also supports the idea that these layers are

not forming in solid sheets but are bending to produce a ball-like structure. These (002) peaks are very similar to the ones seen earlier that did not change intensity with increasing incidence angle. There is also the possibility that the interfacial layer is under stress which would also generate a broad peak. They could even be termed as amorphous due to the lack of organization in the layer evidenced in the shape of the peak. A couple of peaks are seen from the semiconductor layer which suggests that it did not cleanly peel off the substrate.

It is unclear at this point what role sulfur and selenium have in the formation of this layer within the chalcogenide semiconductor. Broad peaks were generated from the GIXRD analysis from the peeled molybdenum substrates that do not match the JCPDS standards for MoSe_2 and MoS_2 . This makes it hard to say for sure what role sulfur and selenium play in the formation of this layer as the composition (MoSe_2 vs MoS_2) is unknown.

What is known is that MoSe_2 is easier to form than MoS_2 based on the thickness of the layers and that sodium plays a minor role in the relative reaction rates during their formation. Unfortunately, the chemical composition cannot be determined from these GIXRD patterns partly due to the nature of the measurement and partly due to the broadness of the peaks. The next section outlines the results and future work that could help to answer these questions.

CHAPTER 5

CONCLUSIONS AND FUTURE WORK

5.1: Conclusions

5.1.1: Molybdenum Substrates Reacted With H_2Se , H_2S , and 50/50 Mix

In the first part of this work, the relative reactivities of molybdenum with sulfur and selenium were investigated. Two different types of substrates were placed in a selenization chamber at 550°C and were allowed to react with H_2S , H_2Se , and a 50/50 mix of the two for an hour. Soda lime glass substrates and borosilicate glass substrates were used to determine whether sodium had any effect on these reactions.

The symmetric XRD patterns of the soda lime glass substrates that were reacted with H_2Se and the 50/50 mix of H_2S and H_2Se were identical in terms of diffraction pattern. They also matched the symmetric XRD results of the borosilicate substrates that were reacted under the same two conditions. From the d-spacings determined from the patterns the film generated during the reactions was MoSe_2 within 0.02 angstroms. The MoSe_2 films had a strong (110) and (100) orientation based on the JCPDS card for a random powder of MoSe_2 . This does not agree with the work done by Daniel Abou-Ras et al who found that sodium suppressed the growth of MoSe_2 in the (100) and (110) planes and encouraged growth in the (002) plane.[31]

Symmetric XRD analysis of both types of molybdenum substrates that were reacted with just H_2S displayed peaks corresponding to a plain layer of

molybdenum. Since the visual appearance of the sample had changed it was assumed that the layer of material formed in the reaction was too thin to be seen by this method of XRD analysis.

Asymmetric XRD analysis of the surface of the MoSe₂ films demonstrated peaks corresponding to different crystal orientations than what was seen in the symmetric XRD patterns. The (103) peak that was missing in the symmetric XRD pattern was now present in the asymmetric patterns. Two possible explanations for this observation include the presence of particulates on the surface of the film or an orientation effect. Two small broad peaks were seen in the GIXRD pattern at low incidence angles for the samples of molybdenum that had been reacted with H₂S. It is likely that they originated from a very thin layer of MoS₂ on the surface of the samples that was not very well formed.

To gain a better understanding of the relative reaction rates of molybdenum reacting with H₂Se versus a 50/50 mix of H₂S and H₂Se the MoSe₂ peaks from the symmetric scans were normalized relative to the molybdenum (110) peak. From this analysis it was determined that the reaction rates of molybdenum with H₂Se and gas mix case were roughly equivalent when the soda lime glass substrates were used. However, in the case of the borosilicate substrates the relative reaction rates decreased by half. Thus it was concluded that sodium plays a role in the reaction rates of molybdenum with H₂Se but not in the crystal structure of the resulting MoSe₂.

5.1.2: CuIn(S_xSe_{1-x}) Thin Films

Four chalcopyrite thin films were analyzed using both symmetric XRD analysis and asymmetric XRD analysis varying the S/VI ratio from zero to one while

keeping the Cu/III as close to 0.90 as possible. Symmetric XRD analysis of the four films revealed patterns typical of a chalcopyrite thin film. The CuInSe₂ film that was analyzed had a very strong (112) orientation as the signal of the (112) peak was over 18,000 counts.

The films were then peeled to analyze the interfacial layer between the semiconductor thin film and the molybdenum back contact. A series of asymmetric scans was performed on both the backside of the film and the molybdenum substrate. The scans on the back of the films revealed typical XRD patterns of the chalcopyrite thin films. No peaks from molybdenum, MoSe₂, or MoS₂ were seen in any of the scans.

The GIXRD patterns from the molybdenum substrates revealed a single broad peak for each of the substrates which could be the (002) peak of MoSe₂, MoS₂, or Mo(S_x,Se_{1-x})₂. Small (112) peaks from the semiconductor were also present which suggest that the peel was not completely clean at the Mo/semiconductor interface.

The (002) peaks from the substrates resemble the broad (002) peaks seen in the reacted films. This suggests that the interfacial layer is not a flat film but could be comprised of only a few layers that are bent as seen by Würz et al.[29]

It appears that the interfacial layer is beneficial to the performance of the solar cell. However, it is not clear at this time what role these layers play in the adherence of the semiconductor film to the substrate. More information is needed about the nature of these dichalcogenide layers before any conclusions can be drawn about them. The next section proposes several methods of analysis that could be used to better understand the characteristics of the interface between the semiconductor thin film and the molybdenum back contact.

5.2: Future Work

In order to better assess the chemical composition of each of these interfacial layers a surface sensitive technique such as X-Ray Photoelectron Spectroscopy (XPS) is needed to determine which dichalcogenide is forming at the interface. XPS is sensitive down to about 0.2 nanometers which would allow the composition and chemical bonding states of these layers to be understood.

TEM micrographs of a cross section of one of these films would give a much better understanding of the structure of the interface in each of the samples. HR-TEM could also give a chemical analysis of the interface and an electron diffraction pattern would give more information about the structure of these layers.

Lastly, it would also be informative to remove the particulates from the surface of the MoSe₂ samples. This would determine if the particulates are actually causing the broad peaks seen in the asymmetric scans. From the information gathered using these techniques a much better understanding of the chemical and structure nature of the dichalcogenide layers may be obtained.

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