Chalcostibite Copper Antimony Sulfide for Solution-Processed Thin Film Solar Cells

by
Jonathon Lopez

A THESIS

submitted to
Oregon State University
Honors College

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the requirements for the
degree of

Honors Baccalaureate of Science in Chemical Engineering
(Honors Scholar)

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Abstract approved:_____________________________________________________

Greg Herman

Copper antimony sulfide (CAS) is a ternary material that is of research interest for thin film photovoltaic applications due to its high absorption coefficient and tunable bandgap. The material is also ideal for sustainable manufacturing due the constituent elements being earth-abundant and less toxic than solar cell absorbers like gallium arsenide or copper indium gallium selenide. The chalcostibite and famatinite crystal phases of CAS can be feasibly utilized for solar cells. The chalcostibite (CuSbS$_2$) phase was studied in this work using X-ray diffraction, Raman spectroscopy, Secondary Electron Microscopy/Energy Dispersive X-ray Spectroscopy, and X-ray Absorption Near Edge Structure. It was found that depositing a precursor solution and annealing the resulting film in air could synthesize CuSbS$_2$. Subsequently, the crystallinity and the grain size of the synthesized material were increase while maintaining the desired crystal phase using a high temperature sulfur anneal. However, small amounts of impurities were formed during the processing making the method presented not ideal for solar cell applications.

Key Words: Copper, Antimony, Sulfide, Photovoltaic, Sustainable

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Introduction

One of the defining problems of the modern age is the human impact of technological development on the environment and the ramifications of those impacts such as climate change and pollution. Therefore, research aimed at reducing the influence of human derived impact on the environment has become an important area of focus for many institutions around the globe. The generation of energy in particular has been an area of intense research interest due to the large impact fossil fuel has on the environment. A possible solution to this problem that has, to some extent, been implemented is photovoltaic devices used to capture solar energy and generate electricity. This technology presents potential because the Earth is bombarded with $1.7 \times 10^5$ teraWatts of solar energy in the upper atmosphere, which translates to approximately 1 kiloWatt per square meter of incident solar energy on the Earth’s surface that could be converted to electricity\(^1\). However, the incident solar energy is not as concentrated as the radiation at the upper atmosphere; thus, high efficiency photovoltaic devices must be utilized in order to generate as much energy as possible from the incident energy\(^1\).

Photovoltaic devices, or solar cells, are a carbon-free and sustainable source of electricity. This technology incorporates layered semiconducting material referred to as a p-n junction. The semiconductors either have dopant elements inserted into the material to create n-type and p-type semiconductors or are intrinsically n or p-type, where n-type material is rich in electrons and the p-type

material is rich in holes\textsuperscript{2}. When these two layers are integrated into a device a depletion layer is formed at the junction of the p-type and n-type materials. An electrostatic barrier is consequently formed by electrons migrating to the p-type material and holes migrating to the n-type to neutralize the charge of the dopant atoms\textsuperscript{2}. This process equilibrates and forms an electrostatic potential with a positive charge lying on the n-type side and a negative charge lying on the p-type side, which functions to separate electron hole-pairs that will be generated by photons incident to the photovoltaic device\textsuperscript{2}. This physically occurs after a photon with enough energy to excite an electron from the valence band into the conduction band, the difference in energy is referred to as the bandgap, where the electron randomly moves through the crystal structure. Eventually entering the vicinity of the electrostatic barrier, it is then accelerated across or away from the junction to the n-type semiconductor\textsuperscript{2}. This device can then be connected to an external load via metal contacts on the n-type and p-type layers to create a single p-n junction solar cell\textsuperscript{2}.

Yet, single junction devices present problems inherent to the device architecture. The prevailing problems with the single junction are an inefficient use of the solar spectrum for energy generation and a low theoretical maximum efficiency of the device. Single junction devices poorly utilize the solar spectrum because the material is only capable of generating electron-hole pairs via photons with energies equivalent to or higher than the bandgap of the semiconductor used

in the photovoltaic. However, the most efficiently used photons are those with exactly the same energy as the bandgap of the semiconductor used$^2$. Otherwise, incident photons with more energy than the bandgap can generate heat in the solar cell via the transfer of energy during the photon’s interaction with an absorbing atom that is not used to free an electron from a bond but instead causes the bond to vibrate, which induces vibrations in the crystal lattice$^2$. Eventually the temperature of the photovoltaic device increases after a sufficient number of these interactions, at which point the vibrations of the lattice begin to interfere with the transmission of the electrons and holes, physically degrading the efficiency of the device$^2$. Low energy photons can also be transmitted through the material if it did not collide with an atom; nevertheless, low energy photons are wasted energy because it is a portion of the solar spectrum that physically cannot be used to generate electricity even if it is absorbed$^2$.

The Shockely-Quiesser limit is the theoretical maximum limit of a single junction photovoltaic device’s efficiency. William Shockley and Hans Quiesser first calculated the detailed balance limit in 1961, which states that single junction solar cells are thermodynamically limited to a maximum efficiency of approximately 34% for devices with a bandgap of 1.1 eV$^3$. Current photovoltaic devices are approaching this maximum with silicon solar cells (1.1 eV bandgap) reaching an efficiency of 26.3%$^4$ and Gallium Arsenide solar cells (1.4 eV bandgap) near 28.8%$^4$. This calls for


further development of photovoltaic technology to continue to increase the device efficiency. Increasing the efficiency of solar cells would not only improve the possible amount of energy that each cell can generate but also would improve the economic viability of the technology to become a major producer of electricity.

A possible solution to the inefficient use of the solar spectrum and theoretical limit of currently implemented photovoltaic technology is a multijunction device that utilizes several different semiconducting materials with differing bandgaps to surpass the Shockley-Quiesser limit and more effectively use the available solar energy. Multijunction devices employ materials with different bandgaps to absorb photons that are closer to each respective material’s bandgap in order to minimize the amount of heat generated by the absorption of high energy photons. Additionally, this multijunction architecture allows photovoltaic devices to take advantage of a greater range of the solar spectrum by incorporating materials with high and low bandgaps to absorb previously underutilized or entirely wasted photons.

The use of several semiconductors in a device results in the possibility of surpassing the Shockley-Quiesser limit imposed on single junction solar cell. The calculations of the tandem photovoltaic detailed balance limit have been performed to estimate multijunction device efficiency. The calculated maximum efficiency of multijunction devices increases non-linearly with an increasing number of junctions\(^5\). Under nonconcentrated sunlight, a photovoltaic device with two

junctions has a maximum efficiency of approximately 42% with the bandgaps of the semiconductors being 1.9 eV and 1 eV. While a solar cell with four junctions has a calculated maximum efficiency of 53% with cell bandgaps of 2.6 eV, 1.8 eV, 1.2 eV, and 0.8 eV. The theoretical maximum efficiency of a multijunction photovoltaic is 68% under unconcentrated sunlight with an infinite number of junctions with smoothly varying bandgaps of the cells. Multijunction devices, therefore, offer a promising new architecture for solar cells because of the potential to nearly double the efficiency of generating electricity.

However, the manufacturing costs of tandem photovoltaic cells are much higher than single junction devices due to the need to match crystalline lattices in monolithic device structures via expitaxial growth methods like Metalorganic Chemical Vapor Deposition (MOCVD). The MOCVD technique for heteroepitaxial growth requires evacuation of the deposition chamber of atmospheric gases and the use of pure metal-organic vapors as reagents for the semiconductor film growth. The National Renewable Energy Laboratory (NREL) performed a manufacturing cost analysis of a monolithic multijunction solar cell in 2013 using InGaP and GaAs (device efficiency of 31.6%) manufactured via MOCVD. They reported that the cost of this device would be $12.40 per Watt and in the long term the cost would reduce to approximately $2.30 per watt. In comparison, currently implemented

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photovoltaic technology has a benchmark cost of $1.42 per Watt for Utility scale arrays and $2.93 per Watt for Residential scale systems. Therefore, the initial manufacturing cost of the multijunction solar cell estimated by NREL makes it economically unattractive to begin fabricating because it would be much more expensive than the currently available technology for consumers or industry to invest in for energy generation. The increased cost in manufacturing is due to the need for a vacuum-based deposition technique and the use of rare materials.

Therefore, there is a need to explore other processing techniques that do not utilize MOCVD in order to find an inexpensive and sustainable method for fabricating higher efficiency photovoltaic technology. Chalcogenide based materials are a class of semiconducting material that can be deposited via solution processed methods, which are less expensive methods to use in manufacturing compared to vacuum-based deposition methods. Some of the commonly researched thin film chalcogenide semiconductors used for photovoltaics are Cadmium Telluride (CdTe), Copper Indium Gallium Selenide (CIGS), and Copper Zinc Tin Sulfide Selenide (CZTS). All of the previously mentioned materials have optimal bandgaps for theoretically high efficiency single junction devices, which are 1.5 eV, 1.13 eV, and 1.14 eV respectively. The resulting single junction devices created using these materials have reached an efficiency of 21%, 21%, and 12.6%, respectively.

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Copper Antimony Sulfide (CAS), a chalcogenide compound with semiconducting phases, has promising optical and electronic properties for applications in single and multijunction photovoltaic devices. Additionally, copper, antimony, and sulfur are much more earth abundant\textsuperscript{8} and less toxic\textsuperscript{8} than, the commonly utilized chalcogenide semiconductors, CdTe and CIGS. However, CZTS is earth abundant but, it is prone to defects due to its quaternary chemistry making its processing very challenging\textsuperscript{9}. Thus, CAS is a viable semiconducting material for sustainable solar cell manufacturing due to its abundance, low toxicity, and ternary chemistry.

\textbf{Figure 1:} Comparison of commonly used elements in semiconductors utilized in photovoltaic devices in terms of Earth Abundance and Price of the element. (Information originally found in the article “Advances in Nanostructured Thin Film Materials for Solar Cell Applications” written by N. Ali and colleagues)
The optical properties of CAS are promising for photovoltaic applications because the material is classified as optically superabsorbing in the near-infrared and visible regions of the electromagnetic spectrum with an absorption coefficient\(^{10,11}\) greater than \(10^4 \text{ cm}^{-1}\). CAS also has three semiconducting phases with bandgaps\(^{10,11}\) ranging from approximately 1 eV to 1.8 eV, which spans the near infrared range to near ultraviolet range of light. The high absorption coefficient and tunable bandgap of this material makes it a versatile semiconductor for thin film solar cell applications.

The focus of the presented research is on the chalcostibite phase of Copper Antimony Sulfide (CuSbS\(_2\) or 112), which has a very high absorption coefficient\(^{10,11}\) in the near infrared and visible range of light and has a bandgap\(^{10,11}\) of approximately 1.5 eV. The bandgap of this phase of CAS allows the chalcostibite phase to be incorporated into a multijunction solar cell as an intermediate bandgap. This phase could also be used to fabricate as a single junction thin film solar cell due to its optimal bandgap for high single junction device efficiency. Additionally, several studies have synthesized chalcostibite phase CAS via thermal treatment of a spin casted\(^{12,13,14}\) film of precursor material for the desired phase of the p-type thin

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film absorbing layer. Therefore, the chalcostibite phase of CAS has the potential to be a sustainably manufactured material for high efficiency solar cells due to the desirable optoelectronic properties, use of earth abundant materials, and ability to use non-vacuum solution deposition methods to fabricate devices.


Characterization Techniques

X-Ray Diffraction (XRD)

X-ray diffraction is commonly utilized to determine the crystal phase and the crystallinity of material, which can be a bulk powder or a thin film. Thin film samples and powder samples are characterized in a similar manner. Determining the crystal phase of thin film samples is important for the solar cell applications because it can reveal if the film contain bulk impurity phases that would decrease device performance. Additionally, characterizing the crystallinity of the absorber film is important for photovoltaic applications because the transport of carriers depends on how crystalline the semiconducting layer is.

This characterization technique utilizes monochromatic X-rays as a photon source to shine on a crystalline sample to be diffracted by the lattice of the sample. The electron cloud of each atom in the sample scatters X-rays\textsuperscript{15}. However, planes of atoms are associated with different crystallographic planes, which reflect x-rays with various path lengths. If the path length difference between two reflected photons is an integer number of wavelengths different, the photons will constructively interfere, which increases the amplitude of the resulting photon and subsequently the intensity of the detected signal. Conversely, when the photons have a path length difference that is a non-integer number of wavelengths they destructively interfere, which decreases or causes the absence of a detected signal. Crystalline materials have long-range symmetry with repeating parallel planes of

atoms, which act as diffraction gratings for the incident x-rays that creates a
characteristic pattern of photon intensity based on the lattice parameters of the
material\textsuperscript{15}. X-rays are diffracted at different angles depending on the wavelength of
light, and the spacing between crystallographic planes of atoms. The angle of
diffraction is predicted by Bragg's Law\textsuperscript{15}, which relates the wavelength of light used,
the interplanar spacing of atoms (commonly referred to as d-spacing), and the angle
of diffraction.

\begin{align*}
n \times \lambda &= 2 \times d \times \sin(\theta) \quad \text{Eq. 1}
\end{align*}

where \( n \) is the order of scattering, \( \lambda \) is the wavelength of incident X-rays, \( d \) is the interplanar spacing, and \( \theta \) is the incident angle of x-rays

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Figure2}
\caption{Graphical derivation of Bragg's Law, which relates the path length difference between diffracted x-rays and photon interference. If the path length difference \((2 \times d \times \sin(\theta))\) is equivalent to an integer number of wavelengths, then the photons will constructively interfere.}
\end{figure}

In X-ray diffraction, each crystalline plane is present in the sample, and this
distribution creates a cone of diffracted X-rays from the sample at the
corresponding angles predicted by Bragg's Law\textsuperscript{16}. The radii of the respective cones
correspond to crystallographic planes and the specific pattern formed is

characteristic of materials present in the sample. The diffraction pattern of the sample is obtained by sweeping a range of angles between the incident beam of X-rays and the X-ray detector by physically moving the detector to intersect the Debye cones of diffracted x-rays from the sample; where a Debye cone is the manner in which x-rays are diffracted by different crystallographic planes in a ring that is centered on the incident beam of X-rays. The cones are diffracted from the varying crystalline planes are detected as rings of varying photon intensity as areas of constructive interference are detected, which results in peaks on a diffractogram. The intensity and the full-width at half maximum (FWHM) of the diffraction peaks are related to the crystallographic plane that is diffracting the X-rays and the size of the crystalline grains in the sample. The latter is described by the Scherrer equation\textsuperscript{16,17} which relates the size of the crystal grains in the powder X-ray diffraction sample to the full-width at half maximum of the diffraction peaks.

\[
B = \frac{K \lambda}{D \cos(\theta_{\text{Bragg}})} \quad \text{Eq. 2}
\]

where \(B\) is the full-width at half maximum, \(K\) is a numerical constant, \(\lambda\) is the wavelength of the incident x-rays, \(D\) is the diameter of the spherical particle (or grain), and \(\theta_{\text{Bragg}}\) is the Bragg angle (or the angle at which constructive interference occurs).

The size of the sample grains is inversely related to the FWHM. This implies that the narrower the detected diffraction peaks the larger the crystalline grains are that are present in the sample.

**Raman Spectroscopy**

Raman spectroscopy is a characterization technique that utilizes visible light to non-destructively identify phase and composition of a sample based on the scattering of the incident light on the sample. The spectroscopy technique utilizes the phenomena of Raman scattering, which describes the change in incident light frequency due to inelastic interactions of the light with electrons. The interaction between an electron and a photon has three possible outcomes: the electron can absorb no energy (elastic interaction), absorb energy (inelastic interaction), or lose energy (inelastic interaction).

![Diagram of Raman Scattering](image)

**Figure 3:** Incident light excites electrons to a higher energy state. The subsequent relaxation to the ground state emits a photon. There is a chance that the incident photon can impart energy to the electron that would emit a photon of less energy or, the electron can decrease in energy emitting a photon of larger energy relative to the incident photon.

The electronic relaxation related to the three possible light-matter interactions result in the emission of a photon of either the same energy (Rayleigh Scattering), lower energy (Stokes-Raman Scattering), or higher energy (Anti-Stokes...
Raman Scattering). Stokes-Raman scattering occurs when the excited electron absorbs a portion of the energy of the incident photon and increases in vibrational energy level, which decreases the energy of the scattered photon. The Stokes scattering of a sample is characteristic of the constituent material, which allows for compound and phase identification of the sample material. Thus, Raman spectroscopy compliments X-ray diffraction because it can both corroborate the results from X-ray diffraction and identify possible impurities within the material that may be obscured in the X-ray diffractogram. The bulk impurity phases can be obscured either by overlapping of the impurity peak with a more intense peak from the desired material or the impurity diffraction peak has a weak intensity that can blend into the noise of the XRD instrument. Similarly, information pertaining to the crystallinity can be obtained from the narrowness of the peaks in the Raman spectra. All of which make Raman spectroscopy a powerful characterization tool for thin film semiconductors.

*Secondary Electron Microscopy/Energy Dispersive X-ray Spectroscopy*

Electrons are used for microscopy due to the quantum mechanical nature of electrons, which is described by the deBroglie relationship that correlates the momentum of a particle and its effective wavelength. Since electrons have mass, the effective wavelength of electrons is much smaller than visible light used in optical microscopes which allows for improved resolution at smaller scales. Images from secondary electron microscopy (SEM) are formed by the detection of scattered

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electrons when a sample is bombarded with a beam of electrons that is rastered across its surface. Electrons are scattered in three primary ways in SEM: backscattered electrons (elastic collisions), secondary electrons (ejection of electrons from inelastic collisions), and Auger electrons\(^{19}\). Secondary electrons are a result of inelastic collisions of the electron beam with electrons in the sample. As a result, secondary electrons have lower energies and lower mean free paths relative to backscattered electrons\(^{19}\). Therefore, more topographically sensitive images are produced from secondary electrons due to the shallower escape depth relative to backscattered electrons\(^{19}\). Additionally, characteristic X-rays are emitted from components within the sample via inelastic collisions of the electron beam with atoms in the sample\(^{19}\). These inelastic collisions create photoelectrons, and the resulting relaxation of another electron into that vacancy emits X-rays with energies unique to specific elements (Energy Dispersive X-ray Spectroscopy or EDS). Thus, SEM and EDS is a useful characterization method for inspecting a film’s surface, cross-section, and composition.

**X-Ray Absorption Near Edge Structure (XANES)**

XANES is a characterization technique that utilizes the pre-edge, edge, and near-edge regions of an X-ray absorption spectra for a specific elemental species. Absorption of X-rays only occurs at distinct photon energies, which are associated with specific electron transitions from a ground state orbital to an unoccupied orbital of allowed transition, following quantum mechanical selection rules\(^\text{20}\). X-ray absorption spectroscopy probes the unoccupied electron states that are available to a specific element in a sample, which translates to understanding the chemical environment in which the atom exists.

<table>
<thead>
<tr>
<th>Table 1: Summary of X-ray absorption edges that are commonly investigated.</th>
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<tr>
<td>X-Ray Absorption Edge</td>
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<tr>
<td>K</td>
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<td>L1</td>
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<td>L2 and L3</td>
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<td>M1</td>
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<td>M2 and M3</td>
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<tr>
<td>M4 and M5</td>
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</table>

The chemical environment of the atom impacts the X-ray and matter interaction by shifting the X-ray absorption edge due to changes in electron binding energies, which results from chemical bonding. The electron transitions are detected by two primary methods, either X-ray fluorescence or total electron yield. Both methods of detection result from a relaxation of an electron to a core electron shell vacancy. Core electron vacancies are generated by the absorption of a high-energy photon (X-rays) that produces a photoelectron from the core shell leaving a very high-energy

core electron hole\textsuperscript{21}. Electrons from higher energy shells consequently relax down to the core vacancy; in the process, energy is released in the form of an X-ray or ejection of an electron (Secondary and Auger electron). Total electron yield measurements are more surface sensitive relative to X-fluorescence due to the mean free path of secondary and Auger electrons being much shorter than X-rays. X-ray fluorescence is the method of detection that will be presented in this work for the characterization of the synthesized thin films.

Experimental Methods

The chalcostibite copper antimony sulfide (CuSbS₂, CAS, or 112) thin film was created by spin coating a CAS precursor solution, which was then thermally treated to synthesize the material on the substrate.

Figure 4: Overview of the process used to form the chalcostibite thin films.

A precursor solution was formed by sequential addition of reagents. The precursor solution is statically dispensed on to molybdenum coated glass. Sulfurization anneal crystallizes the film and increases grain size.

A precursor solution was formed by dissolving copper (II) chloride and antimony (III) chloride in a mixture of isopropyl alcohol and methoxyethanol with thiourea as sulfur source for the reaction. The order of addition of the precursors to the solution determined whether the mixture was stable in the liquid phase or not. Stable solutions were made by first dissolving 0.62 grams (2.72 mmol) of SbCl₃ in 1.06 grams (17.64 mmol) of isopropyl alcohol with 30 minutes of mixing in an inert nitrogen atmosphere to prevent the oxidation of antimony. Next, 3.52 grams (46.26 mmol) of methoxyethanol was added followed by 0.38 grams (2.23 mmol) of CuCl₂ dihydrate. The solution was mixed until it became green and clear. Lastly, 0.86 grams (11.30 mmol) of thiourea was dissolved in the solution. At this point, the solution began to solidify but, with time and continued mixing the solution became clear yellow and stable again.
The final precursor solution was then deposited on a 200 nm Mo coated (Eagle® 2000, 800 µm of thickness) glass substrate using spin coating as the deposition method. In order to ensure that precipitates that were possibly formed were not present on the substrate, the precursor solution was casted through a syringe filter. The substrate was coated using static dispensed spin coating where the solution was dispensed on to the substrate and allowed to stay on the substrate for 1 minute prior to accelerating the substrate. The film was spun at 1000 rpm for 10 seconds (Acceleration 002) then the angular velocity was accelerated to 3000 rpm for 10 seconds (Acceleration 006). After the deposition, the film was then annealed in two steps in air. A soft bake at 145°C was performed for 5 minutes followed by a hard bake at 250°C for 1 minute, which removed the remaining solvent from the film and synthesized the CuSbS₂ on the substrate.

Following the air-annealing step, a high temperature anneal in a nitrogen and sulfur-rich atmosphere was performed to increase the crystallinity of the synthesized material. The high temperature anneals were performed in a quartz tube furnace that had been purged with nitrogen for 1 hour after the film was placed inside the quartz tube. The substrate was placed with film side down on an alumina crucible filled with sulfur. The reactive anneal is later referred to as sulfurization and it is performed to keep the chalcostibite phase from transitioning to another phase while crystallizing the film.

Between each of the air annealing and the sulfurization processes, the chalcostibite films were characterized using spectroscopic methods. Specifically, the techniques that were used to characterize the films were X-ray diffraction (XRD),
Raman spectroscopy, scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDS), and x-ray absorption near edge structure (XANES). The X-ray diffractometer that was used to determine the crystal structure of the film was a Rigaku Ultima IV diffractometer ($\lambda_{\text{Cu-K}\alpha} = 0.1542$ nm, 40 kV, 40 mA, Fixed incident angle $\omega = 1.5$ °) using grazing incidence X-ray diffraction geometry. The Raman scattering characteristic to the synthesized film was found using a Horiba-Jobin Yvon HR-800 Raman spectrometer ($\lambda = 532$ nm). The secondary electron microscope used to image the films and collect the EDXS spectra was a FEI Quanta 600 FEG SEM with 5-30 kV accelerating voltage. The L3 X-ray absorption edge for copper was measured using the Advanced Light Source at the Lawrence Berkeley National Laboratory on Beamline 8.0.1.3. The energy resolution of the beamline was 0.5 eV and the diffraction grating used for the experiment was 1200 lines/mm grating and the experimental chamber had a base pressure of $10^{-8}$ Torr.
Results and Discussion

The spin coating conditions that produced the most visually continuous and uniform films was a 10 second spread cycle at 1000 rpm followed by a 3000-rpm final speed for 10 seconds with an acceleration from the spread cycle to final speed of 006. In addition to spin coating conditions, the ratio of antimony to copper in the precursor solution was optimized to produce a stoichiometric ratio of Cu:Sb:S as close as possible to 1:1:2. Using EDS, it was determined that a 1:1 Sb:Cu ratio produced antimony poor films (CuSb$_{0.85}$S$_{2.1}$) while a 1.2:1 Sb:Cu ratio synthesized a film with the correct stoichiometry (CuSbS$_2$). Subsequently, the air annealing process was optimized. The air annealing method that produced the most uniform and dense films with few defects was two-step annealing method. A soft bake at 145°C for 5 minutes was used to evaporate the remaining solvent and densify the film where it was found that this temperature evaporated the solvent slow enough to reduce bubble formation while keeping processing time low. The temperature of the hard bake was found by testing different temperatures ranging from 250°C to 400°C. A change in the proper copper to antimony ratio was observed at temperatures higher than 300°C (confirmed by EDS). The material can lose antimony due to the high vapor pressure of antimony sulfide$^{22}$, which can result in the formation of other phases like copper sulfide or Cu$_3$Sb$_4$. Thus, the hard bake temperature was set to 250°C for 1 minute to avoid the formation of oxides and the loss of copper and antimony after further optimization. SEM cross sectional images

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were collected to determine the best conditions for deposition (Figure 4). At these optimized precursor deposition conditions, films were fairly continuous (Figure 4) and smooth enough to grow together during sulfurization.

![Figure 5: Scanning electron microscope cross section of films deposited at non-optimal (a) and optimal (b) spin coating/annealing conditions.](image_url)

The synthesized CuSbS$_2$ films were then annealed in a reactive atmosphere to maintain the phase of the material while increasing crystallinity and grain size. The sulfurization process needed to be optimized to achieve the aforementioned improvements to the film, which meant finding the appropriate temperature of the furnace and the duration of the anneal. The temperature of the sulfurization process was the first parameter that was optimized for the tube furnace and the 112 phase (Figure 6). The sample was annealed at 300°C and 350°C in sulfur for 10 minutes with X-ray diffraction data of the samples in Figure 6 plotted with diffraction angle versus intensity. The air-annealed sample has relatively low intensity but has the characteristic diffraction peaks of CuSbS$_2$ at 28.5° and 29.5° while the sample
annealed at 300°C in sulfur has intense and sharp peaks corresponding to the 
CuSbS$_2$. The sample annealed at 350°C has sharp and intense characteristic peaks 
for the Cu$_3$SbS$_4$ phase. Reference diffraction patterns for CuSbS$_2$ and Cu$_3$SbS$_4$ are 
located at the bottom of Figure 6 and were obtained from the RRUFF database along 
with the location of characteristic impurity peaks denoted by asterisks and 
triangles.

![Figure 6: X-ray diffractogram of samples that were sulfurized at two different temperatures and an air-annealed sample. [*=Sb$_2$S$_3$ from RRUFF (ID: R050066), ∆=Mo from RRUFF (ID: R100216)](image)](image)

It was found that at temperatures higher than 300°C, the chalcostibite (CuSbS$_2$) 
phase of CAS transitioned to famatinite (Cu$_3$SbS$_4$) due to the loss of antimony via 
antimony sulfide sublimation\textsuperscript{22}. Additionally, antimony sulfide (Sb$_2$S$_3$) formed at the 
350°C anneal alongside the famatinite phase of CAS. This phase transition is due to
the chemical potential\textsuperscript{23} of sulfur being too high for the CuSbS\textsubscript{2} phase to be stable at the conditions created in the furnace at temperatures above 300°C. According to Yang and colleagues, chalcostibite CAS and antimony sulfide coexist when the chemical potential of copper is low\textsuperscript{22}, which is true for the precursor solution used to create the samples because it is copper deficient (1.2:1 Sb:Cu). Low intensity diffraction peaks that are assignable to antimony sulfide were found in the diffraction pattern of the non-optimal sulfurized sample with trace amounts possibly present in the optimal sulfurized and air annealed samples. These findings seem to be consistent with the ternary phase diagram present in a paper by Braga et. al\textsuperscript{23} when the chemical potential of sulfur is increased, which is the case during sulfurization. An increase in crystallinity was found between the air anneal and sulfurization at 300°C in addition to the increase in grain size, which was observed in the increase in peak intensity and decrease in the full-width at half maximum of the peaks. Thus, the temperature was set at 300°C for the sulfurization process to avoid phase changes of the chalcostibite CAS while using a high temperature to induce crystallization and grain growth.

Subsequently, the duration of the sulfurization process was also optimized for the highest possible crystallinity and grain size while retaining the chalcostibite phase. The annealing time in the furnace was set at 10 minutes, 20 minutes and 60 minutes using 3.5 grams of sulfur at a temperature of 300°C (Figure 7). The Raman scattering of the samples in Figure 7 are plotted with the wavelength of light in

wavenumber versus Raman counts. The X-ray diffraction data of the samples in Figure 7 are plotted with diffraction angle versus intensity. The air-annealed sample is compared to the samples annealed for various times in the sulfurization process. The reference spectra and diffraction patterns for CuSbS₂ (RRUFF ID: R060262) and Cu₃SbS₄ (RRUFF ID: R110021) were obtained from the RRUFF database along with Sb₂S₃ (RRUFF ID: R050066) that is denoted with an asterisk. The characteristic Raman peak for CuSbS₂ at 335 cm⁻¹ decreased in intensity while the characteristic peak for Cu₃SbS₄ at 325 cm⁻¹ and Sb₂S₃ at 250 cm⁻¹. The characteristic peaks for CuSbS₂ were intense and sharp for each sulfurized sample in the X-ray diffraction patterns collected with increasing intensity of Sb₂S₃.

Figure 7: Raman spectra (a) and X-ray diffraction pattern (b) of films that were sulfurized for various times. (*=Sb₂S₃ from RRUFF (ID: R050066).
After comparing the Raman spectra and X-ray diffraction pattern of the films annealed for 20 and 60 minutes to the film annealed for 10 minutes, the optimal annealing time for the sulfurization process was found to be 10 minutes. It was observed that as the annealing time increased, the amount of famatinite and antimony sulfide impurities increased. The presence of impurities was predominately observed in the Raman scattering from the samples, which is due to the large degree of overlap between the diffraction patterns of the mentioned impurities. However, small distinct peaks belonging to the diffraction pattern of antimony sulfide were identifiable in the diffractogram collected for the samples. The 20-minute annealing time had a comparable diffraction pattern but a less intense Raman peak, which indicates a loss in the amount of the CuSbS$_2$ phase. Thus, a shorter 10-minute sulfurization process is more ideal for increasing the crystallinity and inducing grain growth of the deposited material while retaining the desired phase without drastically increasing the presence of the impurities in the film.

At the optimized sulfurization conditions of 300°C for 10 minutes, the synthesized chalcostibite phase of CAS increased in crystallinity and has larger grains relative to the as-deposited air annealed films (Figure 8). This is observed in and corroborated by the comparison of the X-ray diffraction pattern and Raman scattering of film processed in optimal sulfurization conditions to the as-deposited film in Figure 8. The Raman scattering of the samples in Figure 8 are plotted with the wavelength of light in wavenumber versus Raman counts. The X-ray diffraction data of the samples in Figure 8 are plotted with diffraction angle versus intensity.
The plotted references for CuSbS$_2$ (RRUFF ID: R060262) and Cu$_3$SbS$_4$ (RRUFF ID: R110021) were obtained from the RRUFF database along with Sb$_2$S$_3$ (RRUFF ID: R050066) that is denoted with an asterisk.

Figure 8: Raman scattering (a) and X-ray diffraction patterns (b) of an air-annealed and sulfurized sample. Reference Raman spectra and XRD Diffraction Patterns for Chalcostibite and Famatinite from RRUFF database. (Reference ID: R060262 and R110021, respectively) (*=Sb$_2$S$_3$ from RRUFF (ID: R050066)).

The increase in XRD peak intensity from the air-annealed sample to the sulfurized sample indicates a large increase in the crystallinity of the film while the narrowness of the peaks indicate that the grains of CAS have increased in size, according to the Scherrer equation (Eq. 2). Additionally, there was little change in the Raman spectra indicating that only minute impurity formation occurred and the negligible change in intensity indicates that the amount of the chalcostibite phase in the film is similar to the as-deposited film. The improvement in film quality was also visually confirmed in the cross-sectional SEM images taken of representative air-annealed and optimally sulfurized films (Figure 9).
The high temperature anneal through the sulfurization process allows the grains of synthesized material to grow together, which creates a more smooth and uniform film. This is in contrast to the films created after deposition and air anneal which tend to have varying grain size with varying gaps between the grains, making a rough surface. A rough surface is undesirable for deposition of other material layers and ensuring high-quality devices.

Further material characterization was conducted to obtain more information about the bonding of the synthesized material and any possible impurity formation using XANES. The X-ray fluorescence of the sample was measured to investigate the bulk properties of film at different stages of processing (Figure 10). The sample spectra were compared to CuS and CuS₂ reference spectra from literature²⁴ and a Cu reference was collected from a sample stored in the instrument. The XANES spectra

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of the samples are compared to the references to determine what the bulk chemical environment of copper at the different stages of processing. Each absorption spectra has the characteristic X-ray absorption edge for copper at 932.5 eV except the edge is shift to a varying degree higher than 932.5 eV depending on the oxidation state of copper in the other spectra.

Figure 10: X-ray Fluorescence measurement of air-annealed and sulfurized chalcostibite CAS films on Beamline 8.0.1.3 of the Advanced Light Source at Lawrence Berkeley National Laboratory.

According to the obtained XANES spectra, the bulk material of the air annealed and sulfurized samples maintained an oxidation state of 1+ due to the lack of an L3 pre-edge feature that is characteristic of the 2+ oxidation state of copper.
Conclusions
Through this research, it was found that a new, less toxic, solution-based method of depositing chalcostibite phase of copper antimony sulfide adequately synthesizes the desired CAS phase in air. The synthesized layer can be subsequently treated using reactive thermal annealing to improve the crystallinity and grain size of the material. This post-deposition processing was found to improve film continuity and smoothness for integration into a photovoltaic device. The characterization results of the films processed at the optimal sulfurization conditions indicate that the film is predominately crystalline chalcostibite copper antimony sulfide with only minor contamination of antimony (III) sulfide and copper (I) sulfide. However, the presence of impurities in the synthesized films will possibly cause devices to function at low efficiencies because the impurities will likely impede carrier motion, induce carrier recombination, or prevent carrier generation. Thus, applying chalcostibite copper antimony sulfide via the process developed in this research for photovoltaic devices will require further study due to the difficulty in obtaining phase pure films of this ternary material. The films produced in this research would likely produce poorly performing thin film solar cells even for the optimized processing condition.
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