DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING

Investigation of Ohmic Contacts to Tin (II) Sulfide by Thermodynamic Assessment and Electrical Characterization

RAMYA GURUNATHAN
SPRING 2016

A thesis
submitted in partial fulfillment
of the requirements
for baccalaureate degree
in Material Science and Engineering
with honors in Materials Science and Engineering

Reviewed and approved* by the following:

Suzanne Mohney
Professor of Materials Science and Engineering and Electrical Engineering
Thesis Supervisor

R. Allen Kimel
Assistant Professor of Materials Science and Engineering
Honors Adviser

*Signatures are on file in the Schreyer Honors College.
Abstract

Tin (II) sulfide (SnS) is an attractive p-type absorber layer for thin film photovoltaics given its direct band gap corresponding to the sun’s peak emission wavelength, high absorption coefficient, and composition based on earth-abundant, non-toxic elements. However, a major obstacle to fabricating efficient devices is the high contact resistance and recombination loss at the back contact. In this thesis, a selection of high work function metals (Pd and Au) were surveyed as potential Ohmic contacts to p-type SnS. The metals were deposited via physical vapor deposition on patterned p-type SnS films deposited via sputter deposition, and the contact resistance was measured using circular transfer length method test structures. Additionally, for each metal assessed, an annealing study was performed from 250-400°C. To better understand the impact of annealing, the condensed phase equilibria for each metal-Sn-S ternary system was considered. When information for the ternary systems was not available in the literature, ternary phase diagrams were calculated using a MATLAB-based program. Whereas Au is predicted to be in thermodynamic equilibrium with SnS at moderate temperatures, Pd is expected to be reactive. The contact resistance values for Pd reduced with post-deposition annealing up to 400°C, and the system appeared reactive. Conversely, the Au contact resistance only changed slightly with annealing and did not appear reactive. Moreover, it was observed that annealing in a vacuum furnace provided very different results, and degraded the performance of the contact.
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Acknowledgements

First, I would like to thank my research advisor, Dr. Suzanne Mohney, for providing the opportunity to be a part of this engaging research work, and for offering mentorship and support over the past three years. Through working in this lab, I have honed skills in computational and experimental research, and have been motivated to pursue a research career focused on electronic materials. Thank you to Dr. Mark Horn for enabling a fruitful collaboration and continuously advising my work over the course of this project. I would also like to thank Dr. Rona Banai, Joseph Nasr, Jacob Cordell, and Anna Domask who were all directly involved in the progress of this project. Thank you also to the other members of the Mohney group for their continuous support and guidance. I would, additionally, like to acknowledge the support of the entire Department of Materials Science and Engineering at Penn State, the Schreyer Honors College, and the Presidential Leadership Academy for aiding me in my endeavors. And finally, thank you to my friends and family for their continuous love and support.
Chapter 1

Background

In this section, the materials and device considerations for photovoltaic cells are summarized, which highlights the importance of investigating new absorber layer materials and Ohmic electrical contacts. Additionally, background information on metal-semiconductor interfaces is provided along with a discussion of how the phase equilibria at an interface is interpreted and utilized for contact studies. An introduction to the theory and experimental methods associated with measuring contact resistance is then provided. Finally, the structure and properties of tin sulfide are delineated to explain why it is chosen here as an absorber layer material. The chapter concludes with a review of past research developments on electrical contacts to tin sulfide.
1.1 Photovoltaics

1.1.1 Motivation

The National Academy of Engineering lists “making solar energy economical” as one of the 14 grand engineering challenges for the coming century[1]. Fossil fuels are not expected to meet our energy needs in the very near future. By 2040, it is expected that energy production levels from oil and gas will drop to 20% of our current energy needs[2]. Solar energy stands as an alternative energy source that is both clean and renewable. However, current commercial silicon solar cells have efficiencies between 10-20%, and the cost of solar energy is still 3-6 times that of hydrocarbon sources. And as a result, solar barely penetrates the energy market, covering about 1% of total energy consumption in contrast to the roughly 85% coming from oil, natural gas, and coal[1].

Silicon photovoltaics currently dominate the solar market. Crystalline silicon solar cells show high efficiencies of about 12 to 16% in commercial single-junction modules, and 25% in the laboratory[3]. However, the highly pure silicon crystals required for these devices are costly and difficult to produce. Thin film solar cells are attractive because of the lower materials and production costs[4]. However, highly-researched materials for thin film solar cells including copper indium gallium sulfide/selenide (Cu(In, Ga)(S, Se)$_2$) and cadmium telluride (CdTe) are based on expensive, rare, and potentially toxic materials[5]. This motivates the search for alternative thin film solar cell materials which can achieve high efficiencies and are based on non-toxic, earth-abundant elements.

1.1.2 Solar Cell Structure and Operation

Solar Cell Structure

In a conventional, inorganic solar cell, sunlight first passes through a thin, transparent and heavily-doped n-type region known as the “window layer” which is generally thinly coated with a
dielectric material such as magnesium fluoride to prevent reflection. Then, there is a thicker, lightly doped p-type region known as the “absorber layer.” The electrical contacts to the n-type window layer are known as “finger electrodes” because of their long, branched structure which allows light to pass through while maximizing the contact surface area to minimize resistance and efficiently transport photo-generated electrons. The p-type absorber layer is connected to a large back contact to efficiently transport photogenerated-holes[6]. Figure 1.1 shows a schematic of a solar cell.

![Figure 1.1: Example schematic of inorganic solar cell.](image)

**Photo-generation and Charge Carrier Dynamics**

Solar cells operate by absorbing photons and generating electron-hole pairs. The photogenerated excess carriers are segregated through the use of a p-n junction in order to generate power. The photon energy range which can be harvested by the cell is mainly determined by the bandgap energy ($E_g$) of the absorber layer semiconductor. Only photons with an energy $h\nu \geq E_g$ will be absorbed and contribute to photogeneration of charge carriers, and any excess energy ($E_g - h\nu$) is lost to thermalization. An optimum bandgap for the absorber layer material to effectively capture the peak energy of the solar spectrum is about 1.1 eV[3].

To understand the charge carrier dynamics within a solar cell, it can be divided into three basic regions: the neutral n-region, depletion zone, and neutral p-region. In the neutral regions, excess minority carrier motion is dominated by diffusion, or random motion, while minority carrier motion in the depletion zone is dominated by drift, or directed motion of charge carriers by an electric field. Only excess charge carriers which reach the depletion zone will contribute to photogenerated current. This includes electron-hole pairs generated in the depletion zone or minority carriers
generated within a diffusion length of the depletion zone. Thus, the active region of a photovoltaic cell is really limited to \( L_h + W + L_e \), where \( L_h \) and \( L_e \) are the minority carrier diffusion lengths in the neutral n-type region and p-type region, respectively, and \( W \) is the width of the depletion zone. The minority carrier diffusion length is dependent on the diffusion coefficient \( (D) \) and the minority carrier lifetime \( (\tau) \) as shown in the equation below [7].

\[
L = \sqrt{D \cdot \tau}
\]  

(1.1)

According to Einstein’s relations, the diffusion coefficient is directly related to carrier mobility. Therefore, the active region can be maximized by using semiconductors with high electron and hole mobilities. The carrier lifetime is limited by sources of recombination in the solar cell materials. Structural defects and impurities in a material can introduce mid-gap states, which trap carriers and facilitate recombination.

Another important factor is the absorption depth of photons in the solar cell. High energy photons with shorter wavelengths will be absorbed in the n-region and depletion zone, whereas lower energy photons penetrate through to the p-region. The absorber layer should be thick enough to absorb long wavelength photons which are still energetic enough to excite an electron-hole pair. However, the longer the absorption depth, the longer the photogenerated carrier will have to travel to reach the depletion zone. Therefore, thick absorber layers make devices less robust against sources of recombination which reduce the minority carrier diffusion length. Therefore, absorber layer materials should have a high absorption coefficient to reduce the thickness required to capture incident photons. Figure 1.2 depicts the photogeneration of charge carriers and the carrier dynamics in the neutral regions and depletion zone.
1.1.3 Solar Cell Performance

The performance and ideality of a solar cell can be described in terms of the open circuit voltage ($V_{oc}$), the short circuit current ($I_{sc}$), the fill factor ($FF$), and, finally, the efficiency ($\eta$).

The open-circuit voltage is the maximum voltage that could be produced, which occurs when the cell electrodes are disconnected and there is zero current flow through the device. When excess electrons in the p-region reach the depletion zone and drift to the neutral n-region, they give the n-region a slight negative bias. Conversely, excess holes which drift from the n-region to the p-region will give the p-region a slight positive bias. This establishes an open-circuit voltage across the electrodes which opposes the built-in voltage within the junction[7].

Conversely, the short-circuit current is the largest current that can be drawn from a solar cell, which would occur when the voltage across the device is zero. For an ideal cell with no resistive loss, the short circuit current is equal in magnitude to the photocurrent, or current produced by the flow of excess electrons in the n-region through an external circuit to neutralize excess holes in the p-region[7].

Figure 1.3 shows an example of a current-voltage (I-V) curve for a solar cell in operation. The
open-circuit voltage and short-circuit current are the x- and y-intercepts, respectively. The green line represents the “load line” for which the slope equals $-1/R$, where $R$ is the resistance of the applied load. The intersection point of the load line and the I-V curve is the operating point with coordinates $(I', V')$[7]. In the plot below, the operating point is also the point of maximum power output. The fill factor ($FF$) helps describe how close a device is to ideal power output, and is defined as the ratio of the maximum power output to the product of $V_{oc}$ and $I_{sc}$. In the equation below for calculating fill factor, $V_{mp}$ and $I_{mp}$ are defined as the voltage and current at maximum power.

$$FF = \frac{V_{mp} \cdot I_{mp}}{V_{oc} \cdot I_{sc}}$$

(1.2)

Figure 1.3: I-V curve for example solar cell (red) with example load line (green)[7].

The efficiency of a solar cell ($\eta$) is the most common parameter used to compare two devices. It describes the ratio of the maximum power output from the cell to power input from the sun. The equation for efficiency is provided below[8].

$$\eta = \frac{P_{max}}{P_{in}} = \frac{(V_{oc} \cdot I_{sc} \cdot FF)}{(P_{in})}$$

(1.3)

Parasitic resistances within the device are often the cause of low fill factor and efficiency. The two categories of internal resistances include shunt (or parallel) resistance and series resistance. A low shunt resistance is unfavorable to device performance. It is caused by surface states and grain
boundaries which provide low resistance pathways for excess electrons and divert current away from the external circuit where it would be used to drive the load[7].

In contrast, a high series resistance will degrade device performance by reducing the voltage which is applied to the load. Series resistance originates from the scattering of excess charge carriers in the neutral regions as well as the contact resistance of the two electrodes. Therefore, low-resistance, Ohmic contacts are requisite for high-performance solar cell devices.

1.2 Electrical Contacts Considerations

1.2.1 Metal/Semiconductor Interface Physics

There are two primary types of metal-semiconductor contacts: Ohmic contacts and Schottky barrier junctions. Schottky barrier junctions have non-linear I-V characteristics which may show rectifying behavior as shown in Figure 1.4. Only an applied forward bias will lead to substantial current flow through the junction. In the reverse bias configuration, only a small leakage current is permitted until avalanche breakdown occurs. In contrast, an Ohmic contact is one that has linear or near-linear current-voltage (I-V) characteristics. Moreover, to be suitable for device applications, an Ohmic contact should be able to transport adequate current densities for device operation and the voltage drop across the contact should be negligible in comparison to the voltage across the active part of the device[9]. Note that the type of majority charge carrier transported across the interface is the same as the majority charge carrier in the semiconductor, electrons for n-type and holes for p-type semiconductors.
According to the Schottky theory for semiconductor-metal interfaces, the Schottky barrier height is the energy barrier faced by charge carriers traveling across a metal-semiconductor interface. The Schottky barrier height is defined simply as the difference between the metal work function ($\phi_f$) and the semiconductor electron affinity ($E_A$). Based on the model, three types of semiconductor-metal configurations, as depicted in Figure 1.5, can be defined: accumulation ($\phi_f < E_A$), neutral ($\phi_f = E_A$), and depletion ($\phi_f > E_A$)[9]. The accumulation state is suitable for Ohmic contacts because of the small barrier to carrier flow between the metal and semiconductor. However, in real devices, the barrier height is not as easily manipulated by the work function of the chosen metal. Defects at the interface or metal-induced gap states can fix the Fermi level of the semiconductor in a phenomena known as Fermi level pinning, which makes the barrier height more independent of the metal work function.
Additionally, the width of the barrier is inversely dependent on the doping level of the semiconductor, so increasing doping level will decrease the barrier width. The mechanism of carrier transport may change depending on the barrier width, and hence the doping level. For light doping, thermionic emission will dominate, meaning carriers will be thermally excited over the barrier at adequate temperatures. For intermediate doping ($10^{17} < N_d < 10^{19}$), thermionic-field emission takes place at adequate temperatures, meaning carriers can be thermally excited to some energy at which tunneling can occur. And finally, for heavy doping, field emission, or direct tunneling, occurs[9].

1.2.2 Contact Resistance: Definitions and Measurement Technique

The total resistance between two metal contacts to a semiconductor device is described in Equation 1.4, and is comprised of three components: (1) resistance of the metal ($R_m$), (2) contact resistance ($R_c$), and (3) resistance of the semiconductor ($R_{semi}$).

$$R_T = 2R_m + 2R_c + R_{semi}$$  (1.4)

The contact resistance (in units of $\Omega$) emerges from the interface between the metal and semi-
conductor, but also includes a small portion of the metal and a small portion of the semiconductor immediately surrounding the interface, as well as current crowding effects and spreading resistance. Another important parameter is the specific contact resistance ($\Omega \cdot \text{cm}^2$), also referred to as contact resistivity or specific contact resistivity, which is independent of contact area such that contacts of different sizes and geometries are comparable.

The majority of the current flow into and out of the contact occurs at the edge which can be the cause of significant current crowding. The voltage is highest at the edge and drops exponentially with distance into the contact. The distance at which the voltage drops to “$1/e$” is defined as the transfer length ($L_T$), which is essentially the distance from the contact edge over which the majority of the current is transferred between the metal and semiconductor. The transfer length is determined from the specific contact resistance ($\rho_c$) and the sheet resistance of the semiconductor ($R_{sh}$) by the relation shown in Equation 1.5. For a low resistance contact ($\rho_c \leq 10^{-6} \Omega \cdot \text{cm}^2$), the transfer length is typically less than a micron. For a contact with a length of $L > 1.5L_T$ and a width of $Z$, the area of the active region of the contact can be given by $L_T Z$.

$$L_T = \sqrt{\frac{\rho_c}{R_{sh}}}$$ (1.5)

In order to measure specific contact resistance without it being confounded by current crowding, the transfer length method (TLM) is used, which utilizes an array of contacts with a length of $L$ and a width of $W$ separated by gaps of various spacing. An example of a linear TLM structure is depicted in Figure 1.6. Typically, four probes are used to make the measurements: a pair of $I^+$ and $I^-$ probes to pass current and a pair of $V^+$ and $V^-$ probes to measure voltage. If the total resistance ($R_T = V/I$) is plotted against gap spacing, the linear fit will correspond to Equation 1.6 below.

$$R_T = \frac{R_{sh}d}{Z} + 2R_C \approx \frac{R_{sh}}{Z}(d + 2L_T)$$ (1.6)

The transfer length, contact resistance, and sheet resistance of the semiconductor can be at-
tained from the x-intercept, y-intercept, and slope of the line, respectively, as depicted in Figure 1.6. Then, the specific contact resistance can be calculated from the transfer length using Equation 1.5. It is important to note, however, that determination of the specific contact resistance by the transfer length method relies on the assumption that $\rho_c > 0.2R_{sh}t^2$, where $t$ is the thickness of the semiconductor film. This is particularly important to check when the sheet resistance of the semiconductor is large, such as several M$\Omega$/□. Additionally, calculation of the specific contact resistance relies on the assumption that the resistance of the semiconductor both under the contact and between contacts is the same. If the metal and semiconductor are reactive and the semiconductor is consumed beneath the contacts, then specific sheet resistance can not be determined by this method. Only contact resistance ($R_c$) can be reported in units of $\Omega$ or $\Omega$·mm if multiplied by the width of the contact.

In the linear TLM structure, if the width of the sample is larger than the width of the contact ($W > Z$), then there can be current flow around the contacts which is unaccounted for, leading to an inaccurately high $\rho_c$ measurement. To avoid the issues presented when $W > Z$, the circular transfer length method (CTLM) can be applied, which is the technique used in this thesis. CTLM test structures utilize a circular inner metallic contact with a radius $L$, a gap with a width of $d$, and a metallic outer region which serves as the second contact. In this modified layout, the current can

Figure 1.6: Example of a conventional transfer length method (TLM) test structure
only flow from the inner to outer contact. A typical test structure will include an array of circular contacts with gap spacings varying from a few microns to tens of microns as depicted in Figure 1.7[9]. Equation 1.7 for the total resistance between the inner and outer contacts is given below, where $I$ and $K$ are modified Bessel functions of the first kind.

$$R_T = \frac{R_{sh} L T}{2\pi} \left[ \frac{L}{L} I_0(L/L_T) + \frac{L}{L+d} K_0(L/L_T) + \ln(1 + \frac{d}{L}) \right]$$

(1.7)

1.2.3 Condensed Phase Equilibria and Ternary Phase Diagrams

Studying the condensed phase equilibria at a metal-compound semiconductor interface allows one to predict whether an interfacial reaction is likely to occur or whether the compound semiconductor is expected to exist in equilibrium with the elemental metal. The thermodynamics discussion in this thesis is reflective of bulk systems, but the conclusions can help inform studies on thin films.

The thermodynamics approach involved a literature search and calculations of metal-tin-sulfur ternary phase diagrams. In a ternary system, there are four independent variables: temperature, pressure, and the percentage composition of two of the components. However, to avoid having to construct a four dimensional plot to represent the system, pressure is typically held constant. This allows for the construction of a 3D ternary diagram as shown in Figure 1.8a which is generally plotted as a triangular prism with temperature varying along the vertical axis and composition of
each of the three components varying along each side of the triangular base. In this configuration, each side of the prism is a temperature-composition binary phase diagram\cite{11}. This study utilized isothermal 2D ternary phase diagrams which are generated by taking horizontal cross-sections of the 3D diagram as shown in Figure 1.8b\cite{11}. Unless otherwise indicated, the ternary phase diagrams discussed in this thesis are at room temperature and therefore only look at solid-state reactions.

![3D Ternary Phase Diagram](image1.png)  ![2D Isothermal Phase Diagram](image2.png)

Figure 1.8: Example of 3D ternary phase diagram (a) and corresponding 2D isothermal plot at room temperature (b).

Line compounds in the ternary system are designated as points on the 2D phase diagram, and two-phase equilibria regions are represented by one-dimensional tie lines connecting the two phases. No two tie lines can intersect, except at special invariant points, because the intersection point would represent a four-phase equilibrium that violates Gibbs phase rule when temperature and pressure are fixed. If there are phases which participate in three-phase equilibirum, this is indicated by a triangle formed by the tie lines connecting these three phases.
1.3 Tin Sulfide: Structures, Properties, Performance

Tin (II) sulfide is chosen here as an attractive material to replace silicon in thin film solar cells. Tin (II) sulfide, over other prominent absorber layer materials including cadmium telluride (CdTe), CZTS (copper zinc tin sulfide), and CIGS (copper indium gallium selenide), has the benefits of being based on earth-abundant materials and having a simple stoichiometry. The next sections will delineate the structures and attributes of the three stoichiometries of tin sulfide (SnS, SnS$_2$, and Sn$_2$S$_3$) with a specific emphasis on the tin(II) sulfide (SnS) phase.

1.3.1 Structure and Properties

In the Sn-S binary system, there are three discrete line compounds: SnS, SnS$_2$, and Sn$_2$S$_3$ as shown in Figure 1.9[12]. In these compounds, tin may take the oxidation state +2 or +4 while sulfur may take the state -2, -1, or 0. Figure 1.10 depicts the crystal structures for the three compounds. In this section, the structure, properties, and functions of each phase will be discussed with a particular emphasis on the SnS phase which is the material of focus in this study[13].

Figure 1.9: Tin-Sulfur binary phase diagram[12]
Figure 1.10: The ground state crystal structures for the three intermetallic compounds in the Sn-S system: (a) SnS (b) SnS$_2$ (c) Sn$_2$S$_3$[13]. Tin is depicted with gray and sulfur is depicted with yellow.

SnS$_2$ and Sn$_2$S$_3$

SnS$_2$ is an intrinsically n-type semiconductor which is being explored for several optoelectronic applications. It is being investigated as a window layer material for photovoltaics due to its wider band gap and n-type conductivity. Moreover, it is a non-toxic alternative to CdS, which is the primary material used in thin film photovoltaics[14]. SnS$_2$ is also a member of the layered metal dichalcogenide family of materials. Single-layer or few-layer SnS$_2$ films can be exfoliated from bulk crystals for the fabrication of ultrathin transistors[15].

Sn$_2$S$_3$ is a mixed valence compound with tin in both the +2 and +4 oxidation states, and can vary in terms of the relative amounts of each. Sn$_2$S$_3$ is a semiconductor whose optoelectronic properties depend on the precise crystal structure and stoichiometry. It is a candidate for homojunction solar cells with either p-n or p-i-n structures. It has also been incorporated into devices which generate and detect infrared radiation through near-lattice-matched heterojunctions between Sn$_2$S$_3$ and compounds such as CdTe, GaSb, and AlSb[14].

Sn$_3$S$_4$ is another studied stoichiometric compound with a reported melting point of 710 °C. However, it has been excluded from more contemporary phase diagrams. Recent works have regarded it as a metastable phase or simply a mixture of SnS and Sn$_2$S$_3$ [16].

Tin (II) Sulfide (SnS)

The primary material of interest to this study is the tin monosulfide phase (SnS) which is
intrinsically p-type. However, it should be noted that SnS has more than one structural phase, as listed in Table 1 below[17].

<table>
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<th>Crystal Structure</th>
<th>Polymorph</th>
<th>Space Group</th>
<th>Lattice Parameters (a,b,c) (in nm)</th>
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<td>Pbnm</td>
<td>(4.3291, 11.1923, 3.9838)</td>
</tr>
<tr>
<td>4-4-3831</td>
<td>Orthorhombic</td>
<td>β-SnS</td>
<td>Cmcm</td>
<td>(4.128, 11.48, 4.173)</td>
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<tr>
<td>4-4-3833</td>
<td>Herzenbergite</td>
<td>α-SnS</td>
<td>Pbnm</td>
<td>(4.242, 11.32, 4.05)</td>
</tr>
<tr>
<td>4-4-8426</td>
<td>Cubic</td>
<td>Rock Salt</td>
<td>Fm3m</td>
<td>(5.8, 5.8, 5.8)</td>
</tr>
<tr>
<td>4-4-8696</td>
<td>Herzenbergite</td>
<td>α-SnS</td>
<td>Pbnm</td>
<td>(4.32, 11.15, 3.97)</td>
</tr>
</tbody>
</table>

The dominant structural phase is the herzenbergite α-SnS phase with the space group Pbnm. Other possible secondary phases include the orthorhombic β-SnS (Cmcm) and cubic (Fm3m) phase[4]. SnS thin films with multiple phases present are expected to have higher carrier recombination rates because of the large number of defect sites. Large recombination rates impede device efficiency by contributing to the series resistance. Therefore, it is favorable to fabricate films with a uniform α-SnS structure. In Banai et al.[4], SnS films are fabricated via RF sputter deposition and the phases are identified using X-ray diffraction. It was found that the thin films all exhibited mixtures of the α-SnS phase and β-SnS phase as well as other possible secondary phases. Moreover, the results suggested that lower pressures and large throw distances provided a more dense and uniform film. Increasing the substrate temperature also provided increased mobility of adatoms resulting in a more ordered structure, while lowering the target power combated the formation of numerous orientations to promote uniform growth[4].

SnS has emerged as an attractive absorber material for thin film solar cells due to intrinsic p-type conductivity, suitable bandgap energy, and high absorption coefficient. Both amorphous and crystalline SnS films have shown a direct bandgap of about 1.0-1.65 eV and an indirect bandgap of about 1.0-1.45 eV[14]. By applying the Shockley-Quiesser criteria, which represents a rough approximation at ideal conditions, to a direct band gap material of about 1.3 eV, efficiencies of up
to 33% are predicted. The lower temperature, lower symmetry $\alpha$-SnS phase exhibits higher band gap energies of 1.6 eV (direct) and 1.8 eV (indirect) than the high temperature $\beta$-SnS phase[14].

### 1.3.2 SnS Solar Cell Fabrication and Performance

Table 1.2 summarizes the photovoltaic properties of several SnS solar cells fabricated and studied over the past 15 years (adapted from a review compiled by Arvizu et al.)[14]. In each cell structure, SnS is used as the p-type absorber in combination with window layer materials such as CdS, ZnO, or even n-type SnS. Despite the theoretical efficiency of 33%, the highest reported efficiency for an SnS-based cell is 4.36%, achieved by Sinsermsuksakul et al. in 2014[18]. This increase in efficiency is largely attributed to the annealing of SnS and modifications made to the Zn(O,S) buffer layer. Annealing of SnS increased crystallite size, which increased mobility and reduced the number of grain boundaries that act as sites for recombination. Additionally, buffer layers in thin film photovoltaics are typically used to improve the quality of the absorber layer’s interface through passivation, thereby reducing the amount of carrier recombination at the interface. In Sinsermsuksakul et al.[18], the ZnO:ZnS ratio in the buffer layer is tuned to provide a “spike”-type conduction band offset which suppresses recombination. Moreover, nitrogen dopants in the buffer layer trapped free electrons, which reduced carrier concentration and made the layer more resistive.

In addition to improving the quality of the SnS films and optimizing the buffer layer, Sinsermsuksakul suggests that increases in efficiency could be achieved by reducing the contact resistance and carrier recombination at the contact[18]. In these record-breaking solar cells, as well as many other fabricated and tested solar cells (as shown in Table 1.2), molybdenum (Mo) is utilized as a back contact metal. The SnS absorber layer is deposited directly onto Mo-coated glass, followed by a buffer layer and transparent conducting oxide, which acts as the window layer, as demonstrated in Figure 1.11[14]. This is a standard adapted from CdTe and CIGS thin film solar cells given that Mo is a metal with a moderately high work function and low electrical resistivity, and is therefore attractive as a contact metal to p-type semiconductors. But at the tin sulfide in-
interface, Mo could easily form MoS$_2$ which would block hole transport, a phenomena which has already been diagnosed as an issue in copper zinc tin sulfide (CZTS) solar cells[5].

Table 1.2: Photovoltaic Properties and Efficiencies for Select SnS Solar Cells

<table>
<thead>
<tr>
<th>Cell</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
<th>$R_s$ (k$\Omega$cm$^2$)</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnS/CdS</td>
<td>260</td>
<td>9.6</td>
<td>53</td>
<td>1.3</td>
<td>0.023</td>
<td>2006</td>
</tr>
<tr>
<td>ZnO/SnS</td>
<td>120</td>
<td>0.04</td>
<td>33</td>
<td>0.003</td>
<td>5.57</td>
<td>2009</td>
</tr>
<tr>
<td>SnS(OR)/SnS(ZB)/CdS</td>
<td>370</td>
<td>1.23</td>
<td>44</td>
<td>0.2</td>
<td>0.5</td>
<td>2009</td>
</tr>
<tr>
<td>SnS/TiO$_2$</td>
<td>471</td>
<td>0.3</td>
<td>71</td>
<td>0.1</td>
<td>0.27</td>
<td>2010</td>
</tr>
<tr>
<td>p-SnS/n-SnS</td>
<td>280</td>
<td>9.1</td>
<td>29.9</td>
<td>0.74</td>
<td>–</td>
<td>2012</td>
</tr>
<tr>
<td>Mo/SnS(CVD)/CdS/ZnO</td>
<td>132</td>
<td>3.63</td>
<td>29</td>
<td>0.5</td>
<td>0.04</td>
<td>2012</td>
</tr>
<tr>
<td>Zn$<em>{0.83}$Mg$</em>{0.17}$O/SnS</td>
<td>270</td>
<td>12.1</td>
<td>64</td>
<td>2.1</td>
<td>–</td>
<td>2013</td>
</tr>
<tr>
<td>CdS/SnS</td>
<td>208</td>
<td>17.9</td>
<td>38</td>
<td>1.6</td>
<td>0.005</td>
<td>2013</td>
</tr>
<tr>
<td>SnS/CdS:In</td>
<td>302</td>
<td>3.98</td>
<td>33.5</td>
<td>0.4</td>
<td>0.169</td>
<td>2013</td>
</tr>
<tr>
<td>SnS/Zn(O,S)</td>
<td>244</td>
<td>19.42</td>
<td>42.97</td>
<td>2.04</td>
<td>–</td>
<td>2013</td>
</tr>
<tr>
<td>TCO/CdS/SnS/C/Ag</td>
<td>270</td>
<td>6</td>
<td>44</td>
<td>0.7</td>
<td>–</td>
<td>2014</td>
</tr>
<tr>
<td>Mo/SnS/Zn(O,S)/ZnO/ITO</td>
<td>261</td>
<td>24.9</td>
<td>44.4</td>
<td>2.9</td>
<td>–</td>
<td>2014</td>
</tr>
<tr>
<td>Glass/FTO/SnS/CdS/ZnO/ITO</td>
<td>200</td>
<td>15</td>
<td>40</td>
<td>1.2</td>
<td>–</td>
<td>2014</td>
</tr>
</tbody>
</table>

Figure 1.11: Example schematic of standard Mo back-contacted solar cell with p-type SnS as the absorber layer. Adapted from Arvizu et al[14].

1.3.3 Review of Studies on Contacts to SnS

As discussed in the previous section, most SnS solar cells have utilized Mo as a back contact which is a standard adapted from other thin film photovoltaic systems such as CdTe and CIGS. As far as the author is aware, there are only four main existing studies which directly investigate Ohmic contact metals to SnS.
In the study by Ghosh et al., indium (In), silver (Ag), copper (Cu), and aluminum (Al) contacts were screened by measuring the current-voltage (I-V) characteristics of metal-SnS-metal structures both as-deposited and with post-deposition annealing at 150°C, 250°C, and 350 °C[19]. The SnS films utilized in this study were electrochemically deposited, and the impact of annealing was first studied on the SnS films alone. Photoluminescence studies showed a decrease in the intensity of the emission band with annealing, suggesting the formation of non-radiative trap states. Energy-dispersive X-ray spectroscopy (EDX) analysis showed desulfurization with annealing which may be linked to surface trap state generation. The authors suggest that this would correspond to non-Ohmic behavior at high temperatures[19].

The In-SnS-In structure exhibited Ohmic behavior under all annealing conditions, and so indium was adopted as a top metal contact for all of the test structures. The Ag-SnS-In structures showed Schottky-type behavior as-deposited and the results became inconclusive with annealing. This phenomena was corroborated in this thesis work. The Ag contact test structures deposited on the sputtered SnS films used in this thesis demonstrated Schottky-type behavior during electrical probing. In Ghosh et al.[20], the Cu-SnS-In structures also showed inconclusive results that could not be well-reproduced both as-deposited and for all annealing conditions. The authors of the study attribute the inconclusive measurements to some interfacial change. The phase equilibria investigations in this thesis substantiate that claim. As shown in the reported ternary phase diagrams, Figures 1.12 and 1.13, both Ag and Cu are reactive with SnS, forming several room temperature ternary phases including $\text{Ag}_8\text{SnS}_6$ for the Ag-Sn-S system, and $\text{Cu}_4\text{SnS}_4$ and $\text{Cu}_4\text{Sn}_7\text{S}_{16}$ for the Cu-Sn-S system[21]. The absence of a metal–SnS tie line in both cases suggests that interfacial reactions are likely to occur. In the case of the Al-SnS-In structure, the barrier height was determined to decrease with annealing which was attributed to the formation of an Al-S alloy which de-pinned the Fermi level through the formation of a tunneling barrier. No values for specific contact resistance were reported in the Ghosh et al. study[19].
Figure 1.12: Reported ternary phase diagram for the Ag-Sn-S system which shows Ag to be reactive with SnS[12].

Figure 1.13: Reported ternary phase diagram for the Cu-Sn-S system which shows Cu to be reactive with SnS[12].
In the next study by Devika et al. [22], the contact metals screened included Ag, Al, In, and Sn, which were deposited via thermal evaporation on SnS films that were also synthesized using thermal evaporation. The contact structure was suitable for transmission line method (TLM) analysis of contact resistance. Electrical characterization was completed both as deposited and after post-deposition annealing at 300°C, 400°C, and 500°C. As deposited, the Ag/SnS structures only exhibited Ohmic behavior in the applied voltage range of \( \pm 6 \) V. However, with annealing, the contact resistance for Ag decreased and the range of Ohmic behavior increased to \( \pm 8 \) V. This is contradictory to the Schottky-type behavior observed for Ag contacts in Ghosh et al. The study by Devika et al. [22] attributes the decrease in resistance to the diffusion of Ag atoms into the SnS lattice which neutralizes defect states. It is possible that at these higher annealing temperatures and for this particular device geometry, the rate of Ag atom diffusion into the SnS lattice is higher than the interfacial reaction rate which accounts for the differing trend in resistance. The other contact metals showed Ohmic behavior at all conditions. Whereas the contact resistance for the Al/SnS structure decreased with annealing, the contact resistance of the In/SnS and Sn/SnS structures increased, which was attributed to the low melting temperatures of In and Sn. It is suggested that annealing may have caused re-evaporation of these metal layers which destroyed the electrical properties of the devices. The study does not report values for specific contact resistance, but rather contact resistance which is dependent on the geometry of the metal contacts [22].

A subsequent study by Reddy et al. [23] investigated zinc (Zn) contacts, and as in the study by Devika et al. [22], the metal contacts were thermally evaporated onto SnS films which were also synthesized via thermal evaporation. However, the Zn contacts were separated by a gap of 1 cm, and this was the only gap spacing tested. Current-voltage characteristics of the Zn contacts were measured both as-deposited and after post-deposition annealing for temperatures up to 200°C. The Zn contacts showed Ohmic behavior for all conditions and the resistance decreased with annealing temperature, which the authors attribute to diffusion of Zn atoms into the SnS lattice and the formation of a highly conductive ZnS compound at the interface [23]. The experimental Zn-Sn-S ternary phase diagram in Figure 1.14 taken from the *ASM Alloy Phase Diagram Database* shows
stability between the SnS and ZnS phases which is suggests the formation of ZnS at the Zn-SnS interface [12]. Again, the study does not report specific contact resistance values for the Zn contacts. The lack of specific contact resistance data for electrical contacts to SnS is one motivating factor for this thesis work.

Figure 1.14: Reported experimental ternary phase diagram for the Zn-Sn-S system which shows stable two-phase equilibrium between SnS and ZnS[12].

In the final contact study by Patel et al.[24], graphite, copper (Cu), molybendum (Mo), and nickel (Ni) are evaluated as back contact metals for solar cells with SnS as the absorber layer and In$_2$S$_3$ as the window layer. Impedance spectroscopy was the primary characterization method for this study in addition to cross-sectional scanning electron microscopy (SEM) imaging of the interfaces to study the degree of inhomogeneity. As depicted in Figure 1.15, a line profile was fitted to each interface and a interface non-uniformity index was calculated by taking the ratio of the pixel-integrated length of the line profile to the length of a straight line spanning the horizontal width.
of the interface[24]. According to this study, Cu had the greatest homogeneity and lowest contact resistance. Contrarily, the Ni and Mo contacts were found to be highly unsuitable, which the authors attributed to inhomogeneities that led to tunneling-assisted recombination that increased the series resistance and decreased the shunt resistance, lowering overall device performance. The paper also notes that the poor performance of these metals may be due to the formation of NiS or MoS\(_2\) at the interface[24]. Overall, it is suggested that alternatives to the standard Mo back contact be explored.

![Cross-sectional SEM images for several metal-SnS interfaces including Cu, graphite, Ni, and Mo. The yellow line tracks the interface[24].](image)

Figure 1.15: Cross-sectional SEM images for several metal-SnS interfaces including Cu, graphite, Ni, and Mo. The yellow line tracks the interface[24].

1.4 Accreditation Board for Engineering and Technology (ABET) Considerations

The Accreditation Board for Engineering and Technology (ABET) advocates for engineering design that is cognizant of economic issues, environmental concerns, sustainability, manufacturability, ethics, health and safety, and sociopolitical issues[25]. This thesis tackles many of these concerns by forwarding renewable energy technology using cheap, non-toxic, earth-abundant materials and scalable processes. The health and safety measures adopted for the execution of this experimental study are discussed in Section 3.4 of the “Experimental Methods” chapter.

The exigency for clean, renewable energy technology cannot be overstated. During the 2015
United Nations Climate Change Conference (COP 21) held in Paris, members of the UN agreed to reduce carbon emissions as swiftly as possible to keep global warming under $2^\circ$C. Dr. Jessika Trancik, Assistant Professor of Energy Studies at MIT, believes that reaching this goal will be achievable if the cost of solar power is reduced by 50%, and utilization of solar power is increased by a factor of five[26].

Currently, polycrystalline silicon (polysilicon) solar cells continue to dominate the commercial solar cell market, which is linked to its established prominence in the electronics industry. However, the manufacturing process is costly, energy intensive, and results in the emission of large amounts of greenhouse gas. The polysilicon used in solar cells has 10N (ten nines) purity and is synthesized by growing ingots via the Czochralski method and dicing them into wafers[27]. The life-cycle emissions for polysilicon solar cells equals about 40 g CO$_2$-eq/kWh, meaning that 40 grams of a greenhouse gas equivalent to CO$_2$ is released for every kilowatt-hour of power generated by the cell. In contrast, thin film solar cells are cheaper and require less energy to manufacture. The life-cycle emissions evaluated for cadmium telluride (CdTe) thin film solar cells were found to be half that of polysilicon cells, and 89-98% less than that of current fossil fuel sources[28]. For this study, both the tin sulfide thin films as well as the electrical contacts were deposited via sputter deposition, which is known to produce high-quality films and is easily scalable[29].

Additionally, in contrast to other thin film solar cell materials such as cadmium telluride (CdTe), gallium arsenide (GaAs), or copper indium gallium selenide (CIGS), tin sulfide is composed of cheap, non-toxic, and earth-abundant elements. China currently controls about 95% of global rare earth mineral production, which economists worry gives Chinese producers the price-setting control of a monopoly[30]. Moreover, heavy metal pollution in China has become alarming after rice grown in the Hunan Provence near a smelting plant exceeded the maximum allowable levels of cadmium, lead, mercury, and arsenic[31]. The environmental concerns have prompted China to cut its export quota for rare-earth minerals by 35%, which troubled electronics markets around the world. Given the worldwide environmental and political concerns, solar technology based on non-toxic, earth-abundant materials is an urgent need[30].
Chapter 2

Computational Methods

This section describes the calculation method utilized and the computational tools developed in order to determine several metal-Sn-S ternary phase diagrams. The calculation of these phase diagrams helps in predicting whether or not any intermetallic phases are expected to form at the interface between the metals contact and the SnS film and if so, what these phases are expected to be. The calculation method and MATLAB program described here for ternary phase diagram determination were also applied to several other metal-compound semiconductor systems including published work on transition metal dichalcogenides[32].

2.1 Calculation Method

The calculation method used to predict metal-Sn-S ternary phase diagrams has been used by others for several metal-compound semiconductor systems and is described in the work by Klingbeil and Schmid-Fetzer[33][32].

First, all existing intermetallic phases belonging to the system were recorded along with their
enthalpy and entropy of formation in order to calculate the Gibbs free energy change of formation, \( \Delta G_f \). In every case, systems with ternary compounds had to be ignored due to lack of thermodynamic data available for these compounds. More detail about the accumulation of intermetallic phase thermochemical data is provided in the following section. In the case of tin sulfide, the binary phases collected fell into one of three categories: metal sulfide, metal stannide, or tin sulfide (of which three compounds belong: SnS, \( S_2S_3 \), and SnS\(_2\)). Afterwards, all possible tie lines connecting these intermetallic phases were plotted. In the example A-B-C ternary diagram shown in Figure 2.1, three intermetallic phases (AC, AB\(_2\), and B\(_2\)C\(_3\)) are plotted with all possible tie lines depicted as dashed lines.

![Figure 2.1: Example ternary phase diagram with all possible tie lines depicted](image)

The points at which two tie lines intersect are a violation of Gibbs phase rule (except at special points such as a ternary eutectoid) and represent a chemical reaction in which the end points of one tie line are the reactants and the end points of the other tie line are the products. For example, one intersection point of the A-B-C system is between the A–B\(_2\)C\(_3\) and AC–AB\(_2\) tie lines. The following balanced chemical equation represents the reaction at this point.

\[
5 \text{A} + \text{B}_2\text{C}_3 \longrightarrow 3 \text{AC} + 2 \text{AB}
\]
By calculating the Gibbs free energy change for the reaction, \( \Delta G_{\text{rxn}} \), the dominant tie line can be determined depending on whether the reaction favors the reactants or the products. The reactant tie line would dominate in the case of a positive \( \Delta G_{\text{rxn}} \), while the product tie line would dominate in the case of a negative \( \Delta G_{\text{rxn}} \). The final ternary diagram will consist exclusively of tie lines that were dominant in every single “tie line intersection reaction” they belonged to. Therefore, the final diagram will contain no intersections. It should be noted that the \( \Delta G_{\text{rxn}} \) calculated for each reaction is calculated as J/mol of atoms rather than J/mol of formula units. This convention helps assure that two tie lines can be adequately compared.

In analyzing an entire ternary diagram such as the one depicted in Figure 2.1, one must compare every tie line with every other line that it intersects. To do this, Klingbeil and Schmid Fetzer suggest creating a reaction matrix with reactant tie lines representing the rows and and product tie lines representing the columns\[33\]. Each element of the matrix, therefore, represents an intersection of two tie lines and can therefore be filled in with the \( \Delta G_{\text{rxn}} \) of the reaction it represents or simply two asterisks ("**") if the system of equations cannot be solved, indicating that the tie lines do not in fact intersect. Table 2.1 shows an example reaction matrix based off of the Schmid-Fetzer approach with the \( \Delta G_{\text{rxn}} \) values provided in J/(mol of atoms)\[33\].

<table>
<thead>
<tr>
<th></th>
<th>A-B(_2)C(_3)</th>
<th>B-AC</th>
<th>C-AB(_2)</th>
<th>AB(_2)-AC</th>
<th>AB(_2)-B(_2)C(_3)</th>
<th>AC-B(_2)C(_3)</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-B(_2)C(_3)</td>
<td>**</td>
<td>-12000</td>
<td>-800</td>
<td>-12500</td>
<td>**</td>
<td>**</td>
<td>Rejected</td>
</tr>
<tr>
<td>B-AC</td>
<td>12000</td>
<td>**</td>
<td>-1300</td>
<td>**</td>
<td>-9000</td>
<td>**</td>
<td>Rejected</td>
</tr>
<tr>
<td>C-AB(_2)</td>
<td>800</td>
<td>1300</td>
<td>**</td>
<td>**</td>
<td>22000</td>
<td>**</td>
<td>Stable</td>
</tr>
<tr>
<td>AB(_2)-AC</td>
<td>12500</td>
<td>**</td>
<td>**</td>
<td>**</td>
<td>**</td>
<td>**</td>
<td>Stable</td>
</tr>
<tr>
<td>AB(_2)-B(_2)C(_3)</td>
<td>**</td>
<td>9000</td>
<td>**</td>
<td>**</td>
<td>**</td>
<td>**</td>
<td>Stable</td>
</tr>
<tr>
<td>AC-B(_2)C(_3)</td>
<td>**</td>
<td>**</td>
<td>-22000</td>
<td>**</td>
<td>**</td>
<td>**</td>
<td>Rejected</td>
</tr>
</tbody>
</table>

In the matrix approach, the minimum \( \Delta G_{\text{rxn}} \) in each row, referred to as the “row minimum value” is fetched. If the value is greater than zero, this indicates that the reactants in that row were more stable than any of the products they were tested against meaning that they belong to a viable tie line. Otherwise, the tie line is rejected. In order to account for error bars in the thermochemical...
data collected, a margin of error was incorporated into this step for the calculations completed in this thesis. Therefore, if the largest positive $\Delta G_{rxn}$ was less than or equal to 8000 J/(mol of atoms), then it would be kept on the diagram as a narrowly unstable tie line indicated by a dashed line.

Figure 2.2 depicts the final calculated ternary phase diagram based on the matrix-based calculation for the example system.

![Figure 2.2: Example ternary phase diagram with final tie lines depicted](image)

### 2.2 Thermodynamic Data Collection

As mentioned in the previous section, the first step in the calculation method used towards this thesis was to check if ternary phases exist in which case this method can not be applied. Additionally, it was important to accumulate the thermochemical data for all binary phases belonging to the ternary system. Most ternary phase information was provided in *Pearson’s Handbook of Crystallographic Data for Intermetallic Phases* and existing binary intermetallic phases were identified primarily through the online *ASM Alloy Phase Diagram Database* [12] [21].

The enthalpy ($\Delta H_f$) and entropy ($\Delta S_f$) of formation values were taken primarily from *Cohesion in Metals: Transition Metal Alloys* by de Boer in the case of the transition metal-Sn compounds and from *Materials Thermochemistry* by Kubaschewski in the case of the metal selenide compounds [34][35]. There were several important checks which had to be made when using a piece of data found in literature: 1) the value should consistently be expressed per mole of atoms
rather than per mole of formula units 2) the value should represent standard pressure and temperature conditions 3) the entropy value should represent the entropy change of formation ($\Delta S_f$) rather than the standard molar entropy ($S^\circ$).

Additionally, some approximations and estimations were used in the calculations performed towards this thesis which match the approximations made in Klingbeil and Schmid-Fetzer’s TertQuat method [33]. Any solid solubility was ignored, allowing one to treat intermetallic compounds as line compounds with defined stoichiometry. The vapor pressure of $S_2$ gas over tin sulfide compounds was also ignored because it was calculated to be significant (greater than $1 \times 10^{-6}$ atm) only at temperatures greater than 480 K. If the ($\Delta S_f$) value was unavailable, then it was taken to be zero. This approximation is agreeable since all of the phase transitions considered in these calculations are in the solid-phase such that the entropy change is small[32]. Finally, when the experimental $\Delta H_f$ values for intermetallic compounds were unavailable, values reported in *Cohesion in Metals* determined using Miedema’s estimate were used[35].

### 2.3 MATLAB-based Ternary Phase Diagram Tool

A MATLAB-based program was developed to complete the calculation method for M-X-Y phase diagrams rather than having to complete them by hand. The MATLAB program was implemented to allow for more expedited and thorough results. In this section, the program’s calculation process is described and the main MATLAB functions involved are detailed. The full, raw code for the MATLAB program can be found in Appendix 1.

The main function of the program is “ternary.m” which performs the following main tasks:

1. **Reads intermetallic compound data from Excel file** including the chemical formula, stoichiometry, and $\Delta G_f$. Prompts appear after the ternary program compiles asking the user to enter the file name and the sheet name containing the thermodynamic data for the appropriate system. All Excel sheets should follow the same format to assure that the data can be read by the program.
Figure 2.3 shows a screenshot of the input file for the palladium-tin-sulfur (Pd-Sn-S) system. Generalizing this to any M-X-Y system, the M-X compounds must always start on row 1, the M-Y compounds on row 7, the X-Y compounds on row 13, and the transition metal on row 19. From top to bottom, the information included for each intermetallic compound is (1) the chemical formula, (2) the atomic ratio following the convention: at.% X for M-X compounds, at.% Y for M-Y compounds, and at.% Y for X-Y compounds (3) the Gibbs free energy of formation per mole of atoms in (J/mol/K) (4) the stoichiometry of the compound giving the subscript for X, Y, and then M.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
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<tbody>
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<td>PdSn2</td>
<td>PdSn</td>
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<td>Pd2Sn</td>
<td>Pd3Sn</td>
<td>Pd8Sn16</td>
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</tr>
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<td>0.25</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
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<td>-34000</td>
<td>-40000</td>
<td>-61000</td>
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<td>2</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>16</td>
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</tr>
<tr>
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<td>0</td>
<td>0</td>
<td>0</td>
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Figure 2.3: Example Excel input file from which the ternary MATLAB program can read thermodynamic data. The format for any input file must follow this same syntax. Pd-Sn-S is the example taken here of an M-X-Y system.

2. **Defines a structural array for each of the three types of binary phases:** $M_a X_b$, $M_c Y_d$, and $X_e Y_f$ whose elements include all the existing intermetallic compounds of the appropriate type. Each element of the structural array has the following fields: chemical formula, atomic percentages, $\Delta G_f$, and “coordinates” which allows the program to virtually “plot” this intermetallic compound on the ternary phase diagram.
3. **Defines a structural array for each of the six types of tie lines**: $X-M_a X_b$, $Y-M_c Y_d$, $M_X e X_f$, $M_a X_b-Y_e Y_f$, $M_c Y_d-X_e Y_f$, and $M_a X_b-M_c Y_d$ whose elements correspond to the specific tie lines within that type. The elements of this structural array will have the following fields: formulas of the compounds at the endpoints of the tie line, $\Delta G_f$ values for both endpoint compounds, and the coordinates of the tie line’s endpoints.

4. **Generates a reaction matrix** by defining two variables: a reactant tie line and a product tie line. Every possible tie line is passed as both a reactant and a product. First, the “intersection.m” method is called to check whether the reactant and product tie line intersect. If they do, the “deltaG.m” method is called to calculate the $\Delta G_{rxn}$. If the calculated $\Delta G_{rxn}$ is less than -8000 J/(mol of atoms), then the reactant tie line is eliminated from consideration. If the value is between -8000 and 0 J/(mol of atoms) then it is eliminated, but the $\Delta G_{rxn}$ is printed for the user to see. Finally, if the $\Delta G_{rxn}$ is greater than 0, the value is stored in an array and the reactant tie line continues to remain viable. Once the reactant tie line has been compared to all possible product tie lines, it is added to the final list of viable tie lines if the minimum $\Delta G_{rxn}$ value in its array is greater than 0.

5. **Prints final list of viable tie lines**

The intersection.m function determines whether or not two tie lines intersect by applying the following logic and outputs “true” if the lines intersect and “false” if they do not:

1. **Calculates the slopes of the two tie lines using their endpoints** and checks to see whether the slopes are equal, indicating that the tie lines are parallel and therefore do not intersect. Checks to see if the two tie lines share any end points, which would also indicate that they do not intersect. If tie lines pass both checks, solves for the intersection point of the tie lines, otherwise outputs “false”.

2. **Calculates the area of each of the three triangles** that can be produced by connecting the point of intersection to two of the corners of the ternary phase diagram and sums these areas together (see Figure 2.4).
3. **Checks if the sum of the triangle areas is greater than the total area** which would indicate that the intersection point lies outside of the ternary phase diagram. Outputs “false” if the triangle sum is greater than the total area, or “true” if both values are equal (see Figure 2.4).

![Figure 2.4: Visual representation of the triangles formed by the tie line point of intersection and ternary phase diagram endpoints. If the sum of these three triangles is not equal to the total area of the ternary diagram, then the intersection point must not lie within the diagram.](image)

Finally, the deltaG.m function balances the chemical reaction representing the intersection of the two tie lines and calculates the $\Delta G_{\text{rxn}}$ by performing the following steps:

1. **Performs matrix multiplication to balance chemical equation.** Using the example from Section 2.1, the matrix system for balancing equations is demonstrated below. Matrix “M” describes the stoichiometry of each component in the reaction while matrix “N” serves as the solution matrix. Finally, matrix “P” contains the coefficients of the balanced equation. Afterwards, the values stored in matrix P must be converted into whole numbers using the algorithm shown below.

   \[
   \begin{align*}
   dA + eB_2C_3 & \longrightarrow fAC + gAB
   \end{align*}
   \]
\[
M = \begin{bmatrix}
A & 1 & 0 & -1 & -1 \\
B & 0 & 2 & 0 & -1 \\
C & 0 & 3 & -1 & 0 \\
0 & 0 & 0 & 0 & 1
\end{bmatrix}
\]

\[
N = \begin{bmatrix}
0 \\
0 \\
0 \\
1
\end{bmatrix}
\]

\[
P = |M^{-1} \cdot N|
\]  

**Algorithm to Convert elements of Matrix P into Whole Numbers**

%Check if the maximum denominator of any element in matrix is greater than 1. Exit loop when every element has a denominator of 1.
while (maxDenominator>1)

%Convert elements in matrix to fractions
[Numerators,Denominators]=rat(P);

%Fetch maximum value for the denominators
maxDenominator= max(Denominators);

%Multiply every element in matrix by maximum denominator
P=P.*maxDenominator;
}

2. **Calculates Gibbs free energy of reactant and product states using Equations 2.2 and 2.3.** Notably, the \( \Delta G_f \) values for the components of the reaction are provided per mole of atoms. Therefore, the \( \Delta G_{rxn} \) value for each component is multiplied not only by the coefficient used for balancing, but also by the number of atoms in each formula unit.

\[
5 \text{ A} + \text{ B}_2\text{C}_3 \rightarrow 3 \text{ AC} + 2 \text{ AB}
\]

\[
G_{\text{reactants}} = 5G_f^A \cdot (1 \text{ atom/unit A}) + G_f^{B_2C_3} \cdot (5 \text{ atoms/unit B}_2\text{C}_3)
\]  

(2.2)
\[ G_{\text{products}} = 3G^A_C \cdot (1 \text{ atom/unit AC}) + 2G^A_B \cdot (5 \text{ atoms/unit AB}) \] (2.3)

3. **Calculates** \( \Delta G_{\text{rxn}} \) **using Equation 2.4.** Note that the final \( \Delta G_{\text{rxn}} \) value is divided by the total number of atoms participating in the reaction so that it is provided per mole of atoms.

\[ \Delta G_{\text{rxn}} = (G_{\text{products}} - G_{\text{reactants}})/(5 \cdot (1 \text{ atom/unit A}) + 5 \text{ atoms/unit B}_2\text{C}_3) \] (2.4)
Chapter 3

Experimental Methods

3.1 Sputter Deposition of Tin Sulfide Films

The tin sulfide films used in this thesis were provided by Joseph Nasr and Jacob Cordell, two students in Dr. Mark Horn’s group within the Department of Engineering Science and Mechanics. The films were fabricated by first depositing an amorphous tin sulfide film with high sulfur content on SiNₓ/Si substrates via RF sputter deposition using an SnS₂ target. Then, post-deposition annealing of the film was performed to convert it to the desired crystalline α-SnS phase[36]. The following deposition conditions were used to synthesize the films: target power of 115 W, deposition time of 10 minutes, and chamber pressure of 10 mtorr. RF sputtering using an SnS target, itself, was originally trialed, but this produced high-energy SnS thin films that were either strained or a mixture of the α-SnS and β-SnS phase.

During the post-deposition annealing used to drive the amorphous SnS₂ to crystalline α-SnS, the following four reactions may occur. When starting with an SnS₂ film, Reaction b has been found
to begin before Reaction a completes. The presence of sulfur gas during the anneal can inhibit the formation of SnS and cause the SnS₂ or Sn₂S₃ phases to form—for example, through the reverse of Reaction d [36].

**Reaction a** : SnS₂(s) → \( \frac{1}{2} \) Sn₂S₃(s) + \( \frac{1}{2} \) S₂(g)

**Reaction b** : Sn₂S₃(s) → 2 SnS(s) + \( \frac{1}{2} \) S₂(g)

**Reaction c** : SnS(s) → SnS(g)

**Reaction d** : Sn₂S₃(s) + SnS₂(s) → 3 SnS(s) + 5 S₂(g)

Experiments led by Dr. Rona Banai, a recent graduate of Dr. Mark Horn’s group, revealed that post-deposition annealing for one hour at 400°C with pressures maintained below 1 mbar (7.5 \( \times \) 10⁻⁴ Torr) would drive the formation of the \( \alpha \)-SnS phase [36]. The SnS films used in this thesis were annealed for 60 minutes at about 400°C in a vacuum furnace, and were then rapidly cooled using a constant flow of N₂ gas.

### 3.2 Contact Test Structure Fabrication

#### 3.2.1 Photolithographic Pattern Transfer

Photolithographic patterning of the thin films was completed in the Pennsylvania State University Nanofabrication Facility within the Class 100 Cleanroom area. The SnS films on SiNx/Si wafers were first degreased by cleaning with acetone, isopropanol, and water for one minute each and drying with a nitrogen gun. Then, the wafers were baked at 115°C for 5 minutes to drive off any moisture on the surface and subsequently cooled for 3 minutes.

The wafers were then spin-coated with a positive resist bi-layer suitable for a lift-off process. The first layer was the MicroChem SF9 resist which consists of polydimethylglutarimide (PMGI). PMGI resists are suitable as a first layer because they are nearly insoluble in other photoresist solvents, such that an i-Line, deep UV, or e-beam resist can be spin-coated on top without intermixing[37]. Moreover, PMGI resists are soluble in standard alkaline photoresist developers. The SF9 resist was spun at 4000 rpm for 40 seconds which yields a thickness of about 5000 Å
for this type of resist[37]. The sample was then baked at 190°C for 10 minutes and cooled for 3 minutes. The second resist layer was composed of the Megaposit SPR3012 resist which is sensitive to i-line (365 nm wavelength), g-line (436 nm), and broadband light. The SPR3012 resist was also spin-coated onto the wafer at 4000 rpm for 40 seconds which yields a thickness of about 1200 Å[38]. The wafer was then baked at 95°C for 1 minute and cooled for 3 minutes.

The resist layers were then exposed using a Karl Suss MABA6 Mask Aligner with a mercury (Hg) i-line wavelength of 365 nm at an intensity of 8 mW/cm² from an unfiltered Hg lamp[39]. A chrome mask with etched circular transfer length method (CTLM) patterns with 12 different gap spacing lengths in each set was used to pattern the resist. The resist was exposed for 6 seconds in the soft contact mode with a gap of 80 μm. Afterwards, the samples were developed in Microposit MF CD26 developer for 1 minute, rinsed with water, and dried with a nitrogen gun.

Samples were then exposed again using the OAI 30 LS Deep UV Flood Exposure tool for 10 minutes and then developed in MicroChem PGMI 101A developer for 10 seconds, rinsed in water, and dried with a nitrogen gun. The deep UV flood exposure aids in resist hardening and in establishing a bilayer undercut suitable for lift-off. The top layer of resist is cross-linked and hardened by exposure to the deep UV radiation such that when the sample is developed for the second time in 101A developer, the bottom resist layer is rapidly attacked by the developer while the top layer remains largely unaffected resulting in an overhanging structure as shown in Figure 3.1[40]. When the metal is deposited onto the resist structure, the undercut helps promote a clean lift-off process. The details of the metal thin film deposition and the lift-off procedure are discussed in the next section.
3.2.2 Metal Thin Film Deposition and Annealing

Prior to deposition of the thin film, the patterned samples were annealed in a UV-ozone furnace and rinsed with ammonium sulfide \((\text{NH}_4)_2\text{S}\) to clean and prepare the surface. The UV-ozone cleaning followed the standard protocol of a 10 minute anneal at 1 sccm of \text{N}_2/\text{O}_2\) gas flow. Subsequently, the samples were rinsed in 1:100 \((\text{NH}_4)_2\text{S}:\text{H}_2\text{O}\) solution for 1 minute, rinsed in water for 1 minute, and dried with a nitrogen gun. Several surface preparation techniques were trialed before adopting the \((\text{NH}_4)_2\text{S}\) cleaning. Comparing contact resistance measurements for samples with no surface preparation, UV-ozone and 5\% hydrochloric acid (HCl) aqueous solution surface cleaning, and, finally, UV-ozone and 1:100 \((\text{NH}_4)_2\text{S}:\text{H}_2\text{O}\) solution surface cleaning showed better results for the \((\text{NH}_4)_2\text{S}\) technique. Moreover, neither the HCl nor the \((\text{NH}_4)_2\text{S}\) seemed to etch the tin sulfide film significantly which was assessed via profilometry and optical microscopy.

Afterwards, 100 nm metal thin films were deposited via either electron beam evaporation. Both the gold (Au) and palladium (Pd) contacts were deposited by electron beam evaporation using an Edwards FL 400 system which is shown in Figure 3.2. The vacuum system reaches a pressure of \(7\times10^{-7}\) Torr using a roughing pump and turbomolecular pump alone, and the pressure is further dropped to \(2\times10^{-7}\) Torr using liquid nitrogen. The vacuum conditions were further improved by
evaporating 20 nm of titanium for gettering purposes with the shutter over the sample. Afterwards, 100 nm of the metal of choice was deposited on the sample at a rate of 1 Å/s. A quartz crystal monitor was used to measure the thickness over the course of the deposition.

Figure 3.2: Edwards FL 400 electron beam deposition system used for the deposition of the Pd and Au contacts. Labeled parts: (A) liquid nitrogen inlet, (B) deposition chamber, (C) beam alignment module, (D) high voltage source (E) crystal monitor module (F) pressure gauge and pump/vent control. Note: manual control of shutter on top of chamber.

After deposition, the sample was unloaded from the deposition chamber after cooling down for at least 30 minutes. To perform lift-off, the sample was submerged in Baker PRS-3000 Positive Resist Stripper solution. It was left in a covered dish for several hours on a hot plate heated to 85°C with a stir bar spinning at a rate of about 460 rpm. Afterwards, the sample was rinsed in isopropanol for 1 minute, water for 1 minute, and dried with a nitrogen gun. The quality of the lift-off was studied using optical microscopy to determine whether or not more lift-off time was required in the Baker solution.

After depositing the metal contacts, the samples were cleaved into 5-6 pieces, so that each piece could be annealed to a different temperature and electrically characterized separately. Samples were annealed for five minutes to 300°C, 400°C, and 500°C. Anneals were performed in a tube furnace with continuous ultra-high purity argon gas flow at 150 sccm. Post-deposition annealing to 400°C was also trialed in a vacuum furnace (approximately 10⁻⁶ torr) which operates using
resistive heating. However, annealing in vacuum greatly reduced the quality of the contacts. The results of two annealing conditions are compared in Section 4.4.2 of the “Results and Discussion” chapter.

3.3 Electrical Characterization of Metal Contacts to SnS Films

Electrical probing of the circular transfer length method (CTLM) test structures was performed on a Micromanipulator Company manual probe station with four probes—two probes injected current ($I^+$ and $I^-$) and two probes measured the voltage ($V^+$ and $V^-$). Generating current-voltage (I-V) curves involved sweeping the current and measuring the voltage. The range of the current sweep was determined based off of the resistance of the metal-semiconductor structure. Most I-V curves in this thesis used a current sweep of -10 μA to 10 μA. The measurements were taken in the dark with the microscope light and room lights off to avoid confounding the results with the addition of photogenerated excess charge carriers. Four sets of CTLM structures were measured for each sample, and the measurements were intentionally taken in different regions of the sample. The resistance measurements reported in Chapter 4 represent the average and standard deviation of the four sets.

After contact resistance measurements were completed, each gap spacing in a set of CTLM structures was measured using scanning electron microscopy. Three sets were measured for each sample and the average of the gap spacing measurements was used for contact resistance calculations.

The measured I-V curves were subsequently processed in Excel to extract values for the transfer length ($\mu$m), sheet resistance of the semiconductor ($\Omega/\square$), contact resistance ($\Omega\cdot$mm), and specific contact resistivity ($\Omega\cdot$cm$^2$). As introduced in Subsection 1.2.2 on contact resistance, the total resistance for CTLM measurements is represented by the equation reproduced below.

$$R_T = \frac{R_{sh}}{2\pi} \left[ \frac{L_T}{L} \frac{I_0(L/L_T)}{I_1(L/L_T)} + \frac{L_T}{L + d} \frac{K_0(L/L_T)}{K_1(L/L_T)} + \ln(1 + \frac{d}{L}) \right]$$  (3.1)
The BESSELI and BESSELK functions in Excel were used to evaluate the modified Bessel functions of the first kind. The Bessel function fit was optimized by calculating the sum of squared errors and minimizing this value by changing the values of the transfer length \((L_T)\) and the sheet resistance \((R_{sh})\) of the semiconductor. The following conditions were set for these values: \(0.09 < L_T(\mu m) < 100\) and \(0 < R_{sh}(\Omega/\square) < 1 \times 10^{18}\). Afterwards, the specific contact resistance was calculated from the transfer length and sheet resistance using Equation 1.5, and the contact resistance was calculated by dividing the specific contact resistance by the transfer length.

### 3.4 Safety Considerations

#### Engineering Controls

The photolithography steps were completed in the Class 100 cleanroom, where several engineering safety controls are in place to protect the user from the harsh chemicals. Spin coating and development steps were both performed in fume hoods with programmable exhaust control such as the one shown in Figure 3.4[39]. The fume hoods are equipped with a splash guard, fire alarm pull station, and waste chute. Solvent and non-solvent waste are segregated into different bins which are all kept in secondary containment. There are numerous fire alarms, toxic gas alarms, safety eye wash stations, and showers spread out throughout the Nanofabrication facility in case of an emergency[41]. The Karl Suss MABA6 mask aligner is semi-automated to avoid potential pinching hazards during the exposure step. All equipment in the cleanroom can only be activated by trained users who are provided equipment access by the cleanroom staff via the Research Instrumentation Management System (RIMS). Additionally, Materials Safety Data Sheets (MSDSs) are available on hand for all chemicals available in the cleanroom.
In the Mohney group laboratory, sample surface cleaning is performed in fume hoods with a maximum operating sash window height of 18 inches. Chemicals are stored in low, easy-to-reach cabinets underneath the fume hoods. Acids, bases, and solvents are segregated, and all waste containers are kept in secondary containment. The lab is also equipped with fire detection and alarms, toxic gas detection and alarms, telephones with contact lists posted nearby, eye wash stations, and safety showers. Any compressed gas tanks with potentially hazardous gases are kept in cabinets with leak detection and toxic gas alarms. All Materials Safety Data Sheets (MSDSs) for chemicals available in the lab and all standard operating procedures (SOPs) for typical activities performed in the lab are kept in a binder at the entrance.

**Administrative Controls**

Before beginning work at any user research facility at Penn State, users must create an account in the Research Instrumentation Management System (RIMS), which requires completion of an initial in-person safety training and annual online refresher training. Additionally, to begin work in the Nanofabrication facility, users complete an in-person cleanroom-specific safety training and orientation. Afterwards, users working in the lithography section complete an in-person safety
course and lab tour for this section specifically. Finally, users undergo two hands-on training ses-
sions during which they perform their standard procedure under the guidance of a cleanroom staff
member. Only users who have completed the safety training have access to the cleanroom facility
and the ability to reserve and use equipment. Any user working after hours in the lithography area
must have a buddy in the research facility at all times.

Similarly, in the Mohney group laboratory, each piece of equipment has a designated “super
user” who oversees the equipment use. Any user must go through two safety training sessions with
the super user before operating the equipment independently. Each deposition tool has a log book
which users are required to fill out with their name and information about the process performed.

*Personal Protective Equipment (PPE)*

Photolithography was performed in the Class 100 cleanroom area, and to protect users while
avoiding contamination, required PPE includes the following: shoe covers, boots, full body suit,
hair net, hood, safety glasses, face mask, and gloves. When working in the fume hood, an ad-
ditional apron is required as well as durable gloves meant for solvent handling. Finally, when
pouring or transporting chemicals, splash goggles and a face shield is required.

In the Mohney group laboratory, safety glasses, lab coats, close-toed shoes, and full pants
are worn at all times. Nitrile gloves are worn whenever handling samples, using chemicals, or
operating vacuum systems.
Chapter 4

Results and Discussion

4.1 Surface Preparation Study

As mentioned in Section 3.2.2 of the “Experimental Methods” chapter, an initial study was completed to choose a surface preparation method for the patterned SnS films prior to metal deposition. Two solutions were assessed for surface cleaning of the films: 5% HCl in water and 1:100 (NH₄)₂S: H₂O. Neither solution appeared to etch the SnS film which was assessed through both optical microscopy and profilometry. Figure 4.1 shows the differences in contact resistance measured for equivalent samples (palladium contacts on p-type SnS films) with three different surface preparations prior to the thin film deposition: (1) no surface treatment, (2) UV-ozone cleaning and 1 minute cleaning in 5% HCl solution, (3) UV-ozone cleaning and 1 minute cleaning in 1:100 (NH₄)₂S: H₂O solution. The measured contact resistance is provided both as deposited and following a 300°C anneal of the contacts for 5 minutes. The reported contact resistance measurements are averaged over four measured CTLM structures with nine gap spacings each. The error bars repre-
sent the standard deviation for each measurement. As shown in Figure 4.1, the (NH₄)₂S cleaning procedure showed the lowest contact resistance which prompted the use of this surface treatment prior to all contact metal depositions.

![Surface Treatment Comparison](image)

Figure 4.1: Plot of measured contact resistance for various surface preparations prior to metal deposition. The data is shown for no surface preparation, UV-ozone and HCl cleaning, and finally UV-ozone and (NH₄)₂S cleaning. Blue dots depict as deposited measurements of palladium contacts on p-type SnS while orange dots depict measurements following a 300°C annealing of the contacts.

### 4.2 Electrical and Optical Characterization of SnS Films

The students in Dr. Mark Horn’s group completed initial electrical and optical characterization of the SnS films prior to the deposition of metal contacts. Hot point probe was used to determine whether or not the film is p-type or n-type. In this technique, a voltmeter is attached to the sample surface and one lead is connected to a heat source (soldering iron). Thermally generated majority carriers will diffuse away from the “hot” probe towards the “cold” probe. Therefore, a p-type sample will have a negative voltage reading while an n-type sample will have a positive voltage reading. The samples used for study were shown to be distinctively p-type with hot point probe measurements of about -40 mV. The resistivity of the SnS films, measured by four point probe, was about 1500 Ω·cm. Finally, UV-Visible spectroscopy was used to determine the absorption
coefficient and direct bandgap, which was about $1.2 \times 10^{-5}$ cm$^{-1}$ and about 1.9 eV, respectively.

4.2.1 Demonstration of Photoresponse

To demonstrate the photoresponse of the samples, electrical probing of the circular transfer length method (CTLM) structures was completed under “dark” conditions meaning that the microscope light at the probe station as well as the room lights were turned off. To demonstrate the photoresponse of the tin sulfide films, a set of measurements were taken with the microscope light and room lights kept on, and the sheet resistance of the semiconductor film was compared for both “dark” and “light” cases. The sample chosen for these measurements was a sputtered SnS film with evaporated gold contacts. As shown in Figure 4.2, the sheet resistance of the SnS film taken in the “light” condition is approximately half that of the “dark” condition. The difference can be attributed to a significant increase in the number of excess charge carriers when the SnS sample is exposed to light.

Figure 4.2: Plot of semiconductor sheet resistance in dark and light conditions to demonstrate photoresponse of SnS films
4.3 Palladium on Tin(II) Sulfide

4.3.1 Condensed Phase Equilibria Analysis

Thermochemical data on the binary Sn-S phases is listed in Table 4.1 and was collected from the reference books *Chemical Thermodynamics of Tin* and *Materials Thermochemistry*[16][34]. In each case, several experimental and computational studies were cited, and the values recommended by the author were used for this thesis. All of the values chosen were determined experimentally by either the transpiration method, calorimetry, dissociation pressure evaluation, or the Knudsen effusion method. The thermochemical data used for the binary Pd-Sn phases was all experimentally-derived at a temperature of 320 K and was collected from *Cohesion in Metals* by de Boer[35]. No entropy of formation is reported for these values, so the $\Delta G_f^\circ$ is taken to be equal to the $\Delta H_f^\circ$. Finally, information for the binary Pd-S phases, shown in Table 4.2, was collected from *Materials Thermochemistry*[34]. It should also be noted that room temperature ternary phases have been discovered for most metal-Sn-S systems. However, no ternary phases have been reported for the Pd-Sn-S or the Au-Sn-S systems[21]

Table 4.1: Thermochemical Data for Sn-S System

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<th>Phase</th>
<th>$\Delta H_f^\circ$ (kJ/mol atoms)</th>
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</tr>
</thead>
<tbody>
<tr>
<td>SnS</td>
<td>-54.0</td>
<td>77.0</td>
<td>-53.8</td>
<td>[16]</td>
</tr>
<tr>
<td>SnS$_2$</td>
<td>-50.50</td>
<td>87.400</td>
<td>-47.73</td>
<td>[16]</td>
</tr>
<tr>
<td>Sn$_2$S$_3$</td>
<td>-52.80</td>
<td>264.0</td>
<td>-50.72</td>
<td>[16]</td>
</tr>
</tbody>
</table>
Table 4.2: Thermochemical Data for Pd-Sn-S System

<table>
<thead>
<tr>
<th>Phase</th>
<th>$\Delta H_f^o$ (kJ/mol atoms)</th>
<th>$S^o$ (J/mol atoms)</th>
<th>$\Delta G_f^o$ (kJ/mol atoms)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>PdSn$_4$</td>
<td>-28</td>
<td>–</td>
<td>-28</td>
<td>[35]</td>
</tr>
<tr>
<td>PdSn$_3$</td>
<td>-34</td>
<td>–</td>
<td>-34</td>
<td>[35]</td>
</tr>
<tr>
<td>PdSn$_2$</td>
<td>-44</td>
<td>–</td>
<td>-44</td>
<td>[35]</td>
</tr>
<tr>
<td>PdSn</td>
<td>-61</td>
<td>–</td>
<td>-61</td>
<td>[35]</td>
</tr>
<tr>
<td>Pd$_3$Sn$_2$</td>
<td>62</td>
<td>–</td>
<td>-62</td>
<td>[35]</td>
</tr>
<tr>
<td>Pd$_2$Sn</td>
<td>-64</td>
<td>–</td>
<td>-64</td>
<td>[35]</td>
</tr>
<tr>
<td>Pd$_3$Sn</td>
<td>-59</td>
<td>–</td>
<td>-59</td>
<td>[35]</td>
</tr>
<tr>
<td>Pd$_4$S</td>
<td>-13.8</td>
<td>180.7</td>
<td>-13.6</td>
<td>[34]</td>
</tr>
<tr>
<td>PdS</td>
<td>-35.4</td>
<td>56.5</td>
<td>-33.4</td>
<td>[34]</td>
</tr>
<tr>
<td>PdS$_2$</td>
<td>-26.1</td>
<td>87.9</td>
<td>-24.7</td>
<td>[34]</td>
</tr>
</tbody>
</table>

From these values, the Pd-Sn-S diagram shown in Figure 4.3 was calculated. According to the diagram, there is no tie line between elemental Pd and SnS, so this system is expected to be reactive. The diagram also shows that SnS exists in equilibrium with several Pd-Sn intermetallic compounds. Because the mole fraction of Pd is less than that of Sn and S for the contact test structures, the composition of the sample at equilibrium would likely lie within the PdSn$_3$+SnS+PdSn$_4$ or the PdSn$_4$+SnS+Sn phase fields. The diagram suggests the eventual formation of a Pd-Sn compound at the Pd/SnS interface, which would also result in S-rich SnS or Sn$_2$S$_3$ as the Sn is consumed.
4.3.2 Electrical Characterization and Annealing Study

The measured specific contact resistance, contact resistance, and sheet resistance, all dropped with post-deposition annealing to moderate temperatures, and these values, which are listed in Table 4.3, were minimized after annealing to 400°C. Additionally, the standard deviations of the resistance measurements were minimized after annealing to 400°C, suggesting that the overall quality of the contacts was improved with this treatment. A surface color change was observed with annealing to 400°C and higher which suggests an interaction between the elemental Pd and
the SnS film. However, after annealing to 500°C, the contacts became extremely resistive and could no longer be measured. The sample which was annealed to 400°C in the vacuum furnace also became too resistive to measure. Additionally, the Pd contacts on this sample did not undergo the same color change that occurred when samples were annealed beyond 400°C in the tube furnace. The difference observed when annealing in the vacuum furnace, as opposed to the inert gas environment of the tube furnace, may be attributed to sulfur loss. It is also important to note that the determination of specific contact resistance ($\rho_c$) relies on the assumption that the semiconductor underneath the metal contact is unchanged relative to the rest of the film. This assumption does not hold true if the Pd-Sn-S system is reactive and consumes a portion of the semiconductor film, so the reported values for $\rho_c$ are provided tentatively. Future experiments will investigate the presence and depth of any interfacial reactions through depth profiling via X-ray photoelectron spectroscopy (XPS) and cross-section analysis via scanning electron microscopy (SEM). The resistance measurements taken on the Pd contacts both as-deposited (AD) and after annealing are plotted in Figure 4.4 with the error bars depicting the standard deviation.

Table 4.3: Resistance Measurements for Annealing Study on Palladium Contacts

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$R_{sh}$ (MΩ/□)</th>
<th>$\rho_c$ (mΩ·cm$^2$)</th>
<th>$R_c$ (Ω·mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AD</td>
<td>7.50</td>
<td>40.9</td>
<td>5510</td>
</tr>
<tr>
<td>300</td>
<td>6.28</td>
<td>11.9</td>
<td>2700</td>
</tr>
<tr>
<td>400</td>
<td>6.01</td>
<td>0.49</td>
<td>541</td>
</tr>
</tbody>
</table>
Figure 4.4: Resistance measurements on annealing study for palladium contacts to SnS (a) sheet resistance ($\Omega/\square$) (b) specific contact resistance ($\Omega\cdot\text{cm}^2$) (c) contact resistance ($\Omega\cdot\text{mm}$). Note: $\rho_c$ values will not be accurate if too much SnS was consumed in reaction with contact metal.
4.4  Gold on Tin(II) Sulfide

4.4.1  Condensed Phase Equilibria Analysis

The thermochemical data for the Au-Sn phases, listed in Table 4.4, was taken from previous calorimetry studies compiled in a work by Ghosh et al.[42]. When multiple values were reported, the value endorsed by the author was used. Otherwise, the newest study with the smallest error bar which was in good agreement with other work was selected. There are no stable Au-S intermetallic compounds[43]. However, the gold-sulfur interaction is described as semi-covalent with a binding energy of 45 kcal/mol[44]. The gold-sulfur system has been primarily studied in reference to thiolate-protected gold surfaces for self-assembled monolayers of organic molecules on gold. In these systems, thiol or disulfide groups can form stable bonds via chemisorption with the gold surface. Additionally, studies have shown that the gold (I) sulfide (Au$_2$S) phase can be synthesized in the form of nanoparticles[45]. Therefore, although the Au-S binary phase diagram reports nearly total immiscibility, gold and sulfur are not unreactive under certain conditions.

Table 4.4: Thermochemical Data for Pd-Sn-S System

<table>
<thead>
<tr>
<th>Phase</th>
<th>$\Delta H_f^\circ$ (kJ/mol atoms)</th>
<th>$S^\circ$ (J/mol atoms)</th>
<th>$\Delta G_f^\circ$ (kJ/mol atoms)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au$_5$Sn</td>
<td>-4.738</td>
<td>–</td>
<td>-4.738</td>
<td>[42]</td>
</tr>
<tr>
<td>AuSn</td>
<td>-15.10</td>
<td>–</td>
<td>-15.10</td>
<td>[42]</td>
</tr>
<tr>
<td>AuSn$_2$</td>
<td>-14.15</td>
<td>–</td>
<td>-14.15</td>
<td>[42]</td>
</tr>
<tr>
<td>AuSn$_4$</td>
<td>-7.744</td>
<td>–</td>
<td>-7.744</td>
<td>[42]</td>
</tr>
</tbody>
</table>

The Au-Sn-S ternary phase diagram shown in Figure 4.5 was calculated from these values. The presence of the Au-SnS tie line suggests that the system will remain unreactive at moderate temperatures.
4.4.2 Electrical Characterization and Annealing Study

The sheet resistance of the semiconductor improved with annealing up to an annealing temperature of 400°C. However, the contact resistance did not change dramatically with annealing. The lack of response to annealing further suggests that the gold contacts are not reactive with the SnS film. Additionally, there was no visible surface color change of the gold contacts with annealing. The highest quality contacts were achieved after annealing to 400°C in the tube furnace. Additionally, the sample tested annealed under vacuum showed extremely different results, perhaps due to
sulfur loss. The vacuum-annealed sample showed a comparatively large sheet resistance, specific contact resistance, and contact resistance. The electrical measurements taken on the gold contacts both as-deposited (AD) and after annealing are listed in Table 4.5 and plotted in Figure 4.6.

Table 4.5: Resistance Measurements for Annealing Study on Gold Contacts

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$R_{sh}$ (MΩ/□)</th>
<th>$\rho_c$ (mΩ·cm$^2$)</th>
<th>$R_c$ (Ω·mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AD</td>
<td>8.08</td>
<td>13.8</td>
<td>3300</td>
</tr>
<tr>
<td>300</td>
<td>4.62</td>
<td>30.3</td>
<td>3720</td>
</tr>
<tr>
<td>400 (in vacuum)</td>
<td>2.63</td>
<td>9.6</td>
<td>1590</td>
</tr>
<tr>
<td>400</td>
<td>6.58</td>
<td>189</td>
<td>11000</td>
</tr>
<tr>
<td>500</td>
<td>3.55</td>
<td>14.4</td>
<td>2250</td>
</tr>
</tbody>
</table>
Figure 4.6: Resistance measurements on annealing study for gold contacts to SnS (a) sheet resistance ($\Omega/\square$) (b) specific contact resistance ($\Omega\cdot\text{cm}^2$) (c) contact resistance ($\Omega\cdot\text{mm}$). The blue data point represents post-deposition annealing to 400°C under vacuum.
Chapter 5

Conclusion

The National Academy of Engineering describes “making solar energy more affordable” as one of the grand engineering challenges of the 21st century[1]. Tin (II) sulfide (SnS) is an attractive candidate for thin film solar cells because of its suitable bandgap, high absorption coefficient, and composition based on earth-abundant materials. Most SnS solar cells fabricated until today have utilized molybdenum (Mo) as a back contact; however, it has been shown that Mo is unsuitable because of the non-uniform interface and likelihood of forming MoS$_2$ at the interface[24]. Only a small set of metals have been investigated as contacts to SnS thus far, and none of the previous works reports values for specific contact resistance, making it difficult to adequately compare different metals. In this thesis, two metals, palladium (Pd) and gold (Au), were chosen based on thermodynamic predictions and investigated as contacts to SnS by measuring contact resistance as a function of post-deposition annealing temperature.

When performing the thermodynamic assessment, it was found that almost all transition metals have reported metal-Sn-S ternary phases at room temperature for which there is no thermodynamic data available. However, there are no reported ternary phases for either Pd or Au. The Pd-Sn-S and
Au-Sn-S ternary phase diagrams were calculated using thermochemical data from the literature as inputs into a MATLAB-based program. Pd was predicted to be reactive with SnS, whereas Au was predicted to maintain thermodynamic equilibrium with SnS.

The experimental study performed involved depositing both Pd and Au contact test structures on sputtered SnS films and measuring the electrical properties of the contacts. The Pd contacts reduced resistance with annealing to moderate temperatures. The best performing contact, with a contact resistance of 541 Ω·mm, was the Pd contact which received post-deposition annealing to 400°C in a tube furnace with sustained argon gas flow. In the case of the Au contacts, the resistance did not change dramatically with annealing. It was also found that annealing the contacts in vacuum rather than in an inert gas environment dramatically impacted the results, and degraded the quality of the contact. This may be due to loss of sulfur that occurs.

5.1 Future Work

This study presents thermodynamic predictions for the condensed phase equilibria at the interface between the contact metal and tin sulfide as well as trends in contact resistance with post-deposition annealing. Further characterization of the interface via spectroscopic techniques such as Auger electron spectroscopy (AES) or X-ray photoelectron spectroscopy (XPS) could provide further insight into the composition of phases at the interface. These results could be used to gauge the accuracy of the thermodynamic predictions, determine whether an interfacial reaction has occurred, and explain trends observed in the contact resistance of Pd and Au. Cross-sectional scanning electron microscopy (SEM) could be used to visualize the uniformity of the metal-semiconductor interface, assess whether the morphology of the phases at the interface changes with annealing temperature, and determine the depth of any metal-SnS reactions that may occur. Assessing the depth of a reaction would indicate how much of the SnS film is being consumed below the contact, which would impact the interpretation of the measured specific contact resistance values. Additionally, all of the electrical probing was completed at room temperature. To understand the mode
of carrier transport through the metal-semiconductor interface, electrical characteristics could be measured while the sample is being heated. This would elucidate thermionic or thermionic-field emission mechanisms at the interface.

A potential future study could look into the impact of acceptor doping in conjunction with the Ohmic contacts. Indium doping of SnS thin films has been shown to decrease the resistivity, increase carrier concentration, and retain the high absorption coefficient of the film. Future experiments may therefore involve depositing indium alloy contacts on SnS films and using post-deposition annealing to drive the indium into the tin sulfide film. Composition analysis via XPS or AES would help determine whether the indium was effectively doping the tin sulfide film, and electrical probing could be performed to quantify the impact on semiconductor sheet resistance and contact resistance.
Bibliography


Appendices
Appendix 1: Ternary Phase Diagram

Calculator MATLAB Code
NAME: ternary.m
DESCRIPTION: Function to generate viable tie lines for any M-X-Y system
INPUTS: file name and sheet name with thermodynamic data for system (assure that format of excel sheet follows syntax), symbol of the anion and cation in the compound semiconductor
OUTPUTS: List of viable tie lines in the M-X-Y system
%

% Define x and y coordinates for the corners of ternary phase diagram and positions of M (metal), X (cation in compound semiconductor), and Y (anion in compound semiconductor)
M.x= 0.5;
M.y= sqrt(3)/2;
X.x= 0;
X.y= 0;
Y.x= 1;
Y.y =0;

% Define axes of ternary phase diagram (other than the base)
%X-M axis (Axis 1)
syms x
y = sqrt(3)*x;
axis_1_y= matlabFunction(y);

%M-Y axis (Axis 2)
syms x
y = -sqrt(3)*x + sqrt(3);
axis_2_y= matlabFunction(y);

% Initialize structural arrays containing info about intermetallic compounds
m_X= struct;
m_Y= struct;
X_Y= struct;

% User entry of excel input file name and sheet name
file_name= input('Enter file name: ', 's');
sheet= input('Enter Sheet: ', 's');

% User entry of X (cation) and Y (anion) symbols
cation= input('Enter cation in compound semiconductor: ', 's');
anion= input('Enter anion in compound semiconductor: ', 's');

% Initialize value for delta G of formation and symbol for transition metal
[metal, metal_deltaG]= xlsread(file_name, sheet,'A19:A20');

% Initialize values for all M-X Compounds
[mX_int, mX_text]=xlsread(file_name, sheet, 'A1:M6');
m_X.form= char(mX_text); %chemical formula
m_X_num= size(m_X.form,1); %number of M-X compounds
m_X.comp= []; %atomic percentage of X
m_X.g= []; %delta G of formation
m_X.X= []; %stoichiometry subscript of X
m_X.M= []; %subscript of M
if m_X_num>0 %check if there are intermetallics of this type
  m_X.comp= mX_int(1,:); %fetch values from the excel spreadsheet
  m_X.g= mX_int(2,:);
  m_X.X= mX_int(3,:);
  m_X.M = mX_int(5,:);
end
m_X.x= 0.5*(1-m_X.comp); % x-coordinate of intermetallic on ternary diagram
m_X.y= axis_1_y(m_X.x); % y-coordinate of intermetallic on ternary diagram

% Initialize values for all M-Y Compounds
[mY_int, mY_text]=xlsread(file_name,sheet, 'A7:M12');
m_Y.form= char(mY_text);
m_Y_num= size(m_Y.form,1);
m_Y.comp= []; %atomic percentage of Y in compound
m_Y.g= []; %stoichiometry subscript of Y
m_Y.M= []; %stoichiometry subscript of M
if m_Y_num>0
  m_Y.comp= mY_int(1,:);
  m_Y.g= mY_int(2,:);
  m_Y.X= mY_int(4,:);
  m_Y.M = mY_int(5,:);
end
m_Y.x= 0.5*(m_Y.comp)+0.5; % x-coordinate of intermetallic on ternary diagram
m_Y.y= axis_2_y(m_Y.x); % y-coordinate of intermetallic on ternary diagram

% Initialize values for all X-Y Compounds
[X_int, XY_text]=xlsread(file_name,sheet, 'A13:M18');
X_Y.form= char(XY_text);
X_Y_num= size(X_Y.form,1);
X_Y.comp= []; %atomic percentage of Y in compound
X_Y.g= []; %stoichiometry subscript of X in compound
X_Y.X= []; %stoichiometry subscript of Y in compound
if X_Y_num>0
  X_Y.comp= XY_int(1,:);
  X_Y.g= XY_int(2,:);
  X_Y.X= XY_int(3,:);
  X_Y.Y= XY_int(4,:);
end
X_Y.x= X_Y.comp; % x-coordinate of intermetallic on ternary diagram
X_Y.y= 0*X_Y.comp; % y-coordinate of intermetallic on ternary diagram
%Generate Tie Lines and initialize values for each of the six different
tie line types listed below

%Tie Lines between X and M-Y intermetallic compounds (Type 1 Tie Lines)

```matlab
type1= struct; %initialize type1 structural array
if m_Y_num==0 %check if there are tie lines of this type
    empty1=1;
else
    empty1=0;
end
for k=1:m_Y_num
    type1(k).form= strcat(cation, ' and ', m_Y.form(k,:)); %chemical formulas
    of compounds
    type1(k).g= [0.0001, m_Y.g(k)]; %delta g of formation for compounds
    type1(k).end= [0, m_Y.x(k), 0, m_Y.y(k)]; %coordinates of these compounds
    in the ternary diagram
    type1(k).coeff= [1,0,0; 0,m_Y.Y(k), m_Y.M(k)]; %stoichiometry of compounds
end
```

%Tie Lines between M and X-Y intermetallic compounds (Type 2 Tie Lines)

```matlab
type2= struct; %initialize type2 structural array
if X_Y_num==0 %check if there are tie lines of this type
    empty2=1;
else
    empty2=0;
end
for k=1:X_Y_num
    type2(k).form= strcat('M and ', X_Y.form(k,:));
    type2(k).g= [metal_deltaG, X_Y.g(k)];
    type2(k).end= [0.5, X_Y.x(k), sqrt(3)/2, X_Y.y(k)];
    type2(k).coeff= [0,0,1; X_Y.X(k),X_Y.Y(k),0];
end
```

%Tie Lines between Y and M-X intermetallic compounds (Type 3 Tie Lines)

```matlab
type3= struct; %initialize type3 structural array
if m_X_num>0
    empty3=0;
else
    empty3=1;
end
for k=1:m_X_num
    type3(k).form= strcat(anion,' and ', m_X.form(k,:));
    type3(k).g= [0.0001, m_X.g(k)]; %was -9560
    type3(k).end= [1, m_X.x(k), 0, m_X.y(k)];
    type3(k).coeff= [0,1,0; m_X.X(k),0, m_X.M(k)];
end
```

%Tie Lines Between X-Y and M-X Compounds (Type 4 Tie Lines)

```matlab
type4= struct; %initialize type4 structural array
if X_Y_num==0 || m_X_num==0
```

68
empty4=1;
else
    empty4=0;
end
for k=1:X_Y_num
    for n= 1: m_X_num
        type4(t).form= strcat(X_Y.form(k,:), ' and ', m_X.form(n,:));
        type4(t).g= [X.Y.g(k), m_X.g(n)];
        type4(t).end= [X.Y.x(k), m_X.x(n), X.Y.y(k), m_X.y(n)];
        type4(t).coeff= [X.Y.X(k),X.Y.Y(k),0; m_X.X(n),0, m_X.M(n)];
        t=t+1;
    end
end

% Tie Lines Between X-Y and M-Y Compounds (Type 5 Tie Lines)
type5= struct; %initialize type5 structural array
if X_Y_num==0 || m_Y_num==0
    empty5=1;
else
    empty5=0;
end
t=1;
for k=1:X_Y_num
    for n= 1: m_Y_num
        type5(t).form= strcat(X_Y.form(k,:), ' and ', m_Y.form(n,:));
        type5(t).g= [X.Y.g(k), m_Y.g(n)];
        type5(t).end= [X.Y.x(k), m_Y.x(n), X.Y.y(k), m_Y.y(n)];
        type5(t).coeff= [X.Y.X(k),X.Y.Y(k),0; m_Y.X(n),0, m_Y.M(n)];
        t=t+1;
    end
end

% Tie Lines Between M-X and M-Y Compounds (Type 6 Tie Lines)
type6= struct; %initialize type6 structural array
if m_X_num==0 || m_Y_num==0
    empty6=1;
else
    empty6=0;
end
t=1;
for k=1:m_X_num
    for n= 1: m_Y_num
        type6(t).form= strcat(m_X.form(k,:), ' and ', m_Y.form(n,:));
        type6(t).g= [m_X.g(k), m_Y.g(n)];
        type6(t).end= [m_X.x(k), m_Y.x(n), m_X.y(k), m_Y.y(n)];
        type6(t).coeff= [m_X.X(k),0, m_X.M(k); 0,m_Y.Y(n), m_Y.M(n)];
        t=t+1;
    end
end

%Generate Reaction Matrix
x=0:1;
m=1; 
deltaG_array=1; 
final_ties=' '; 

% typeA is the tie line type of the first tie line being considered 

for i= 1: 6 % first switch typeA 
    switch i 
        case 1 
            if empty1 ==0 %check to see if there are any tie lines of the 
                type you are considering 
                typeA= type1; 
                else 
                    continue 
                end 
        case 2 
            if empty2 ==0 
                typeA= type2; 
                else 
                    continue 
                end 
        case 3 
            if empty3 ==0 
                typeA= type3; 
                else 
                    continue 
                end 
        case 4 
            if empty4 ==0 
                typeA= type4; 
                else 
                    continue 
                end 
        case 5 
            if empty5 ==0 
                typeA= type5; 
                else 
                    continue 
                end 
        case 6 
            if empty6 ==0 
                typeA= type6; 
                else 
                    continue 
                end 
    end 

% switch through every tie line under the category typeA 

for j= 1:length(typeA) 
    n=1; 
    deltaG_array= 1; 
    deltaG1= typeA(j).g; 
    coeff1=typeA(j).coeff; 
    % now initialize typeB which is the type of tie line you are 
    % comparing to typeA
for k=1:6
    if i==k
        continue
    end
switch k
    case 1
        if empty1 == 0
            typeB= type1;
        else
            continue
        end
    case 2
        if empty2 == 0
            typeB= type2;
        else
            continue
        end
    case 3
        if empty3 == 0
            typeB= type3;
        else
            continue
        end
    case 4
        if empty4 == 0
            typeB= type4;
        else
            continue
        end
    case 5
        if empty5 == 0
            typeB= type5;
        else
            continue
        end
    case 6
        if empty6 == 0
            typeB= type6;
        else
            continue
        end
end
% iterate through every tie line in the category typeB
for l=1: length(typeB)
    % check to see if tie line A and tie line B even intersect
    if intersection_updated(typeA(j).end, typeB(l).end) == 0
        continue
    end
deltaG2 = typeB(l).g;
coeff2 = typeB(l).coeff;

% if tielines intersect, then find the delta G of reaction
deltaG_array(n) = deltaG_updated2(deltag1, coeff1, deltaG2, coeff2);
% if delta G of reaction is less than 8000 J/mol/K, print this reaction
if abs(deltaG_array(n)) < 8000
    fprintf('
Less than 8000');
    fprintf('
Reactants is %s
', typeA(j).form);
    fprintf('Products is %s
', typeB(l).form);
    fprintf('Delta G per atom: %10.4f
', deltaG_array(n));
end

% once there is a delta G of reaction that is less than 0,
% tie line A is no longer viable
% therefore, skip to the next tie line

if deltaG_array(n)<0
    break
end
n=n+1;

end

% double check that deltag_array contains no values less than 0
if min(deltaG_array)<0
    break
end
% if all of the delta G of reactions are greater than zero, we know
% that the tie line is viable
% store this tie line in the array labeled "final-ties"
minimum = min(deltaG_array);
if minimum>0
    final_ties = char(final_ties, typeA(j).form);
end
end

%display the final viable tie lines
disp(final_ties);
function f = intersection( endpt1, endpt2)
%
NAME: intersection.m
DESCRIPTION: Determines if tie lines intersect, returns 1 if they do and 0 if
they don't
INPUTS: endpoints of two different tie lines
OUTPUTS: 0 if tie lines intersect and 1 if they don't intersect
%

% Get endpoints
% Tieline 1
xa= endpt1(1);
xb= endpt1(2);
xa= endpt1(3);
xb= endpt1(4);
%
% Tieline 2
ya2= endpt2(1);
xb2= endpt2(2);
ya2= endpt2(3);
xb2= endpt2(4);

% Calculate the slope of the two tie lines
slope1= (yb-ya)/(xb-xa);
slope2= (yb2- ya2)/(xb2- xa2);

% check if slopes are parallel b/c then the tie lines definitely don't
% intersect
if slope1== slope2
    f=0;
    return
end

% if tie lines do intersect, check to see if intersection is outside of the
% ternary phase diagram

% get slope intercept form of tie lines
int1= ya- slope1*xa;
int2= ya2- slope2*xa2;
if (isinf(slope1))
    xi= 0.5;
    yi= slope2*xi+ int2;
elseif (isinf(slope2))
    xi=0.5;
    yi= slope1*xi+int1;
else
    xi= (int2- int1)/(slope1- slope2);
    yi= slope1*xi +int1;
end

% Find area of ternary diagram
area= tri_area_updated(0,0.5,1,0,sqrt(3)/2,0);
% Add up area of all three triangles (xi, yi) makes with the corners of the ternary diagram
area1 = tri_area_updated(0, 0.5, xi, 0, sqrt(3)/2, yi);
area2 = tri_area_updated(0, 1, xi, 0, 0, yi);
area3 = tri_area_updated(0.5, 1, xi, sqrt(3)/2, 0, yi);

% if any triangle areas are zero, then intersection point is on one of the axes of the ternary diagram, so return 0
if area1 <= 0.0001 || area2 <= 0.0001 || area3 <= 0.0001
    f = 0;
    return
end

% If sum_area is equal to the area of the ternary diagram then you know % that the intersection point lies within the diagram
sum_area = area1 + area2 + area3;

% return 1 if they do intersect and 0 if they don't
if abs(sum_area - area) >= 0.01 * area
    f = 0;
else
    f = 1;
end
end
function deltaGatom = deltaG(deltaG1, coeff1, deltaG2, coeff2)

%{
NAME: deltaG.m
DESCRIPTION: Determines the delta G of reaction for the system described by
the intersection of two tie lines
INPUTS: delta G of formation for reactants and products; number of M, X, and Y
atoms in each reactant and product
OUTPUTS: delta G of reaction given in J/mol of atoms
%}

%
coeff1(1,1); coeff1(1,2); coeff1(1,3): number of M, X, and Y atoms in the
first reactant
coeff1(2,1); coeff1(2,2); coeff1(2,3): number of M, X, and Y atoms in the
second reactant
Then, coeff2 corresponds to the products
%
%Matrix trick to balance equation
A= [coeff1(1,1), coeff1(2,1), -1*coeff2(1,1), -1*coeff2(2,1);
    coeff1(1,2), coeff1(2,2), -1*coeff2(1,2), -1*coeff2(2,2);
    coeff1(1,3), coeff1(2,3), -1*coeff2(1,3), -1*coeff2(2,3);
    0, 0, 0, 1];
B=[0;0;0;1];
C=A^-1*B;
C=abs(C); % C matrix stores the balanced coefficients for the reaction

% Store the total number of atoms for each compound in the reaction
AtomsCpd1 = coeff1(1,1)+coeff1(1,2)+coeff1(1,3);
AtomsCpd2 = coeff1(2,1)+coeff1(2,2)+coeff1(2,3);
AtomsCpd3 = coeff2(1,1)+coeff2(1,2)+coeff2(1,3);
AtomsCpd4 = coeff2(2,1)+coeff2(2,2)+coeff2(2,3);

% Convert values in C into whole numbers
LCM=1;
maxD=10;
while maxD>1
    [N,D]=rat(C); % Convert C to rational numbers with N as numerators and D
                  as denominators
    maxD= max(D); % Fetch maximum value for D
    C=C.*maxD;
    LCM= LCM*maxD; % Store new multiple as part of least common multiple
    factor
end

reactants= C(1,1)*deltaG1(1)*AtomsCpd1 +C(2,1)*deltaG1(2)*AtomsCpd2; % delta G
of formation for reactants
products= C(3,1)*deltaG2(1)*AtomsCpd3+C(4,1)*deltaG2(2)*AtomsCpd4; % delta G
of formation for products

deltaG= products- reactants; % delta G of reaction

% check to assure that equation is balanced
if int8(AtomsCpd1 * C(1,1)+AtomsCpd2* C(2,1)) ~= int8(AtomsCpd3 * C(3,1) + AtomsCpd4* C(4,1)) %check to see if equation is balanced properly
    fprintf('EQUATION NOT PROPERLY BALANCED\r\n'); %display error message if equation is not balanced
    fprintf('C= %10.4f \n',C );
    fprintf('AtomsCompd1= %10.4f \r\n',AtomsCpd1 );
    fprintf('AtomsCompd2= %10.4f \r\n',AtomsCpd2 );
    fprintf('AtomsCompd3= %10.4f \r\n',AtomsCpd3 );
    fprintf('AtomsCompd4= %10.4f \r\n',AtomsCpd4 );
end

deltaGatom=deltaG/((AtomsCpd1*C(1,1) + AtomsCpd2*C(2,1))); %delta G of reaction divided by total number of atoms participating in reaction
end
Appendix 2: Compilation of M-Sn-S Ternary Diagrams from Literature

Fe-Sn-S

Figure 1: Iron-Tin-Sulfur Isothermal Ternary Phase Diagram at 450°C[12]
Figure 2: Iron-Tin-Sulfur Isothermal Ternary Phase Diagram at 600°C[12]

*Cu-Sn-S*

Figure 3: Copper-Tin-Sulfur Isothermal Ternary Phase Diagram at 500°C[12]
Figure 4: Copper-Tin-Sulfur Isothermal Ternary Phase Diagram at 600°C[12]

Zn-Sn-S

Figure 5: Zinc-Tin-Sulfur Isothermal Ternary Phase Diagram at 600°C[12]
Mo-Sn-S

Figure 6: Molybdenum-Tin-Sulfur Isothermal Ternary Phase Diagram at 800°C[12]

Figure 7: Molybdenum-Tin-Sulfur Isothermal Ternary Phase Diagram at 1000°C[12]
Ag-Sn-S

Figure 8: Silver-Tin-Sulfur Isothermal Ternary Phase Diagram at 500°C[12]

W-Sn-S

Figure 9: Tungsten-Tin-Sulfur Isothermal Ternary Phase Diagram at 500°C[12]
Figure 10: Tungsten-Tin-Sulfur Isothermal Ternary Phase Diagram at 800°C[12]
Academic Vita of

Ramya Gurunathan

EDUCATION

Pennsylvania State University, Class of 2016 Aug 2012- May 2016
B.S. in Materials Science & Engineering: Semiconductor Option Minor in Nanotechnology
Member of Schreyer Honors College and Presidential Leadership Academy
Student Marshal of the College of Earth and Mineral Sciences
Recipient of Churchill Scholarship 2016

TECHNICAL EXPERIENCE

Undergraduate Research Assistant Pennsylvania State University
· Investigated, through computational and experimental methods, suitable sputter-deposited electrical contact materials to tin sulfide for solar cell applications
· Created computer model to assess the stability of various transition metal contacts on 2D chalcogenide materials

Aarts Magnetic and Superconducting Materials Group Aug - Dec 2015
EuroScholars Research Abroad Program Leiden University, Netherlands
· Fabricated spin-based switching devices using electron beam lithography
· Studied spin-injection from a ferromagnet to normal metal with applications to spintronics/magnetic memory

Chan Combinatorial Nanocrystal Synthesis Group June - Aug 2015
US Department of Energy Research Internship Lawrence Berkeley National Laboratory
· Developed a liquid-handling robot into a tool for high-throughput, automated nanoparticle synthesis
· Optimized robotic process for silver nanoparticle synthesis with high particle size selectivity

Suemitsu Solid State Electronics Group May - Aug 2014
NanoJapan: International Research Experience for Undergraduates Tohoku University, Japan
· Participated in 12-week NSF-funded research/cultural excursion program in Japan
· Developed a Monte Carlo model to study crystal defects in cubic silicon carbide and utilized model to study relationship between defect density and crystal size/orientation

Denbeaux Extreme Ultraviolet Lithography Group June - Aug 2013
Summer Research Intern SUNY Polytechnic Institute
· Constructed a DC sputter deposition system including full setup of pneumatic and electrical controls

LEADERSHIP EXPERIENCE

Teaching Assistant for Materials Selection and Design Course
Presidential Leadership Academy: Drafted policy proposal to reform university’s General Education program
Global Engagement Scholar Assistant: Organized student programs on global issues and multiculturalism
Director of Engineers Without Borders Local Outreach Team
Co-captain of PSU Natya: Lead representative of Penn State’s Classical Indian dance team

TECHNICAL STRENGTHS

Programming Skills C#, JAVA, MATLAB, Visual Basic, \LaTeX
Laboratory Techniques Photolithography, E-beam lithography, Sputter Deposition, SEM, Cryogenics XRD, Electrical Probing, Nanoparticle Synthesis, Vacuum System Setup

PUBLICATIONS