COMBINATORIAL DEVELOPMENT OF 
${\text{Cu}}_{2}\text{SNS}_3$ AS AN EARTH ABUNDANT 
PHOTOVOLTAIC ABSORBER 

by

Lauryn L. Baranowski
A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Materials Science).

Golden, Colorado
Date ______________________

Signed: ______________________
Lauryn L. Baranowski

Signed: ______________________
Dr. Eric S. Toberer
Thesis Advisor

Golden, Colorado
Date ______________________

Signed: ______________________
Dr. Brian P. Gorman
Professor and Program Director
Department of Materials Science Program
ABSTRACT

The development of high efficiency, earth abundant photovoltaic absorbers is critical if photovoltaics are to be implemented on the TW scale. Although traditional thin films absorbers such as Cu(In,Ga)Se$_2$ and CdTe have achieved over 20% device efficiencies, the ultimately scalability of these devices may be limited by elemental scarcity and toxicity issues. To date, the most successful earth abundant thin film absorber is Cu$_2$ZnSn(S,Se)$_4$, which has achieved 12.6% efficiency as of 2014. However, chemical complexity and disorder issues with this material have made the path to higher efficiency CZTSSe devices unclear. As a result, many researchers are now exploring alternative earth abundant absorber materials.

In this thesis, we apply our “rapid development” methodology to the exploration of alternative photovoltaic absorbers. The rapid development (RD) methodology, consisting of exploration, research, and development stages, uses complementary theory and experiment to assess candidate materials and down-select in each stage. The overall result is that, in the time span of ~2-3 years, we are able to rapidly go from tens of possible absorber materials to 1-2 working PV device prototypes. Here, we demonstrate the RD approach as applied to the Cu-Sn-S system.

We begin our investigation of the Cu-Sn-S system by evaluating the thermodynamic stability, electrical transport, electronic structure, and optical and defect properties of candidate materials using complementary theory and experiment. We find that Cu$_2$SnS$_3$ is the most promising absorber candidate because of its strong optical absorption, tunable doping, and wide stability range. Our other candidate compounds suffer from serious flaws that preclude them from being successful photovoltaic absorbers, including too high experimental conductivity (Cu$_4$SnS$_4$), or poor hole transport and low absorption coefficient (Cu$_4$Sn$_7$S$_{16}$).

Next, we investigate the doping and defect physics of Cu$_2$SnS$_3$. We identify the origins of the changes in doping in sputtered cubic Cu$_2$SnS$_3$ thin films using combinatorial
experiments and first-principles theory. High S chemical potential during deposition decreases the enthalpy of formation of Cu vacancies, which are the dominant acceptor defect in Cu$_2$SnS$_3$. Unexpectedly, under Cu-rich conditions, alloying with an isostructural (cubic) metallic Cu$_3$SnS$_4$ phase occurs, causing high levels of p-type doping. Both of these effects lead to undesirably high electrical conductivity, thus Cu$_2$SnS$_3$ films must be grown both S- and Cu-poor in order to achieve moderate hole concentrations.

To understand the effects of structural disorder on the transport properties in Cu$_2$SnS$_3$ we develop synthetic techniques to control this disorder, and observe improvements in the majority carrier (hole) transport. However, when the minority carrier (electron) transport was investigated, minimal differences were observed between the ordered and disordered Cu$_2$SnS$_3$. By combining these results with first-principles and Monte Carlo theoretical calculations, we are able to conclude that even ostensibly “ordered” Cu$_2$SnS$_3$ displays minority carrier transport properties corresponding to the disordered structure. The presence of extended planar defects in all samples, observed in TEM imaging, suggests that disorder is present even when it is not detectable using traditional structural characterization methods.

Lastly, we attempt to integrate our Cu$_2$SnS$_3$ films into photovoltaic devices, which requires translating our growth techniques to conductive substrates. We survey a wide range of possible conductive substrates, but are not able to find a suitable back contact for Cu$_2$SnS$_3$ device integration, due to issues such as secondary phase formation and delamination. From a survey of successful Cu$_2$SnS$_3$ device literature, we are able to conclude that the issue may lie with our binary sputtering method in which the ternary compound formation and the film growth occur simultaneously.

At the conclusion of this study, we eliminated Cu$_2$SnS$_3$ as an absorber candidate for future development. However, the two main issues we encountered (eliminating structural disorder and difficulty growing on conductive back contacts) may both be related to our binary sputtering technique. We expect that interest in Cu$_2$SnS$_3$-based photovoltaics will continue to grow, and that further scientific understanding may shed light on our particular difficulties.
In the future, the RD methodology has the potential to greatly accelerate the discovery and development of non-traditional thin film absorbers, and may enable high impact material breakthroughs.
# TABLE OF CONTENTS

ABSTRACT ................................................................. iii

LIST OF FIGURES .......................................................... xi

LIST OF TABLES .......................................................... xviii

LIST OF SYMBOLS .......................................................... xix

LIST OF ABBREVIATIONS .................................................. xxi

ACKNOWLEDGMENTS ....................................................... xxiv

CHAPTER 1 INTRODUCTION & MOTIVATION .............................. 1

1.1 Issues facing traditional photovoltaics ............................... 1

1.2 Earth abundant thin film photovoltaics ............................... 2

1.3 The “rapid development” approach .................................... 3

1.4 The Cu-Sn-S system ................................................... 6

1.5 Thesis outline ........................................................ 6

1.6 Thesis contributions .................................................. 7

CHAPTER 2 BACKGROUND .................................................. 9

2.1 Historical perspective on Cu-chalcogenide photovoltaic absorbers ............................... 9

2.1.1 Cu$_2$S .......................................................... 10

2.1.2 Cu(In,Ga)Se$_2$ ................................................ 10

2.1.3 Cu$_2$ZnSn(S,Se)$_4$ ........................................... 11

2.2 Overview of the Cu-Sn-S family ..................................... 11

2.3 Thin film synthesis of Cu$_2$SnS$_3$ ................................... 12
2.3.1 Vacuum synthesis techniques ............................................. 13
2.3.2 Solution processing techniques ......................................... 14
2.4 Structure and morphology of Cu$_2$SnS$_3$ thin films .................. 14
2.5 Optoelectronic properties of Cu$_2$SnS$_3$ thin films ...................... 18
2.6 Opportunities for future material study of Cu$_2$SnS$_3$ .................. 20
2.7 Cu$_2$SnS$_3$ photovoltaic device integration and performance .......... 21
  2.7.1 Cu$_2$SnS$_3$ device performance metrics ............................... 21
  2.7.2 Characteristics of successful Cu$_2$SnS$_3$-based devices .............. 22
  2.7.3 Current deficiencies in Cu$_2$SnS$_3$ device understanding ............ 23
2.8 Opportunities for future improvement of Cu$_2$SnS$_3$-based photovoltaics ............................ 26

CHAPTER 3 EXPERIMENTAL METHODS ............................................. 28
3.1 Combinatorial materials synthesis ...................................... 28
3.2 Thin film deposition ....................................................... 29
3.3 Annealing of Cu$_2$SnS$_3$ films .......................................... 30
3.4 Combinatorial materials characterization ............................... 31
3.5 Advanced materials characterization .................................. 32
3.6 Photovoltaic device fabrication ........................................ 33
3.7 Photovoltaic device characterization .................................. 33

CHAPTER 4 EVALUATION OF PHOTOVOLTAIC MATERIALS WITHIN THE
CU-SN-S FAMILY & DOWN-SELECTION TO Cu$_2$SnS$_3$ ................... 35
4.1 Abstract ............................................................................. 35
4.2 Introduction ....................................................................... 35
4.3 Methods ............................................................................ 36
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.3.2</td>
<td>Film characterization</td>
<td>73</td>
</tr>
<tr>
<td>6.3.3</td>
<td>Computational methods</td>
<td>74</td>
</tr>
<tr>
<td>6.4</td>
<td>Results and discussion</td>
<td>75</td>
</tr>
<tr>
<td>6.4.1</td>
<td>Structural changes &amp; majority carrier transport</td>
<td>76</td>
</tr>
<tr>
<td>6.4.2</td>
<td>Terahertz spectroscopy investigation of minority carrier transport</td>
<td>78</td>
</tr>
<tr>
<td>6.4.3</td>
<td>Theoretical explanation of terahertz spectroscopy results</td>
<td>81</td>
</tr>
<tr>
<td>6.4.4</td>
<td>Microscopy investigations</td>
<td>82</td>
</tr>
<tr>
<td>6.4.5</td>
<td>Implications of this work for CZTS and other disordered semiconductors</td>
<td>86</td>
</tr>
<tr>
<td>6.5</td>
<td>Conclusions</td>
<td>87</td>
</tr>
<tr>
<td>7</td>
<td>PHOTOVOLTAIC DEVICE INTEGRATION OF Cu₂SnS₃ FILMS</td>
<td>88</td>
</tr>
<tr>
<td>7.1</td>
<td>Introduction</td>
<td>88</td>
</tr>
<tr>
<td>7.2</td>
<td>Methods</td>
<td>88</td>
</tr>
<tr>
<td>7.3</td>
<td>Results and Discussion</td>
<td>90</td>
</tr>
<tr>
<td>7.3.1</td>
<td>Growth of Cu₂SnS₃ films on Mo</td>
<td>90</td>
</tr>
<tr>
<td>7.3.2</td>
<td>Growth of Cu₂SnS₃ films on other conductive substrates</td>
<td>91</td>
</tr>
<tr>
<td>7.3.3</td>
<td>Annealing of Cu₂SnS₃ on conductive substrates</td>
<td>95</td>
</tr>
<tr>
<td>7.3.4</td>
<td>Photovoltaic device testing</td>
<td>97</td>
</tr>
<tr>
<td>7.4</td>
<td>Discussion</td>
<td>98</td>
</tr>
<tr>
<td>7.5</td>
<td>Conclusions</td>
<td>100</td>
</tr>
<tr>
<td>8</td>
<td>SUMMARY, CONCLUSIONS, AND FUTURE DIRECTIONS</td>
<td>102</td>
</tr>
<tr>
<td>8.1</td>
<td>Summary and conclusions</td>
<td>102</td>
</tr>
<tr>
<td>8.2</td>
<td>Future of Cu₂SnS₃ photovoltaics</td>
<td>103</td>
</tr>
</tbody>
</table>
8.3 Future applications of the “rapid development” approach .......................... 104

REFERENCES CITED ................................................................................. 107

APPENDIX A - SUPPORTING INFORMATION: CHAPTER 4 .......................... 120

APPENDIX B - SUPPORTING INFORMATION: CHAPTER 5 .......................... 121

APPENDIX C - SUPPORTING INFORMATION: CHAPTER 6 .......................... 125

APPENDIX D - PERMISSIONS ................................................................... 129

APPENDIX E - PUBLICATION LIST ............................................................. 142
## LIST OF FIGURES

| Figure 1.1  | Annual possible electricity production calculated from known economic reserves and annual production for a variety of thin film PV materials | 4 |
| Figure 1.2  | The rapid development approach consists of exploration, research, and development stages. Figure by A. Zakutayev | 5 |
| Figure 2.1  | Historical efficiencies of Cu-chalcogenide photovoltaic devices. The successes and failures of Cu$_2$S, Cu(In,Ga)Se$_2$, and Cu$_2$ZnSn(S,Se)$_4$ can guide the development of new Cu-chalcogenide photovoltaic absorbers, such as Cu$_2$(Sn,Ge)S$_3$ | 9 |
| Figure 2.2  | (a) In recent years, the number of publications on Cu$_2$SnS$_3$ for photovoltaic applications has increased exponentially. (b) Efficiency records for Cu$_2$SnS$_3$-based devices have also been rising rapidly, reaching 4.63% in 2015 for pure Cu$_2$SnS$_3$ and 6.0% when Ge is alloyed into the absorber layer | 13 |
| Figure 2.3  | Cu$_2$SnS$_3$ can exist in cubic, tetragonal, and monoclinic crystal structures, depending on the degree of cation disorder. Figure made using VESTA | 15 |
| Figure 2.4  | By XRD alone, it is difficult to distinguish between the different crystal structures of Cu$_2$SnS$_3$, or the Cu$_3$SnS$_4$ impurity phase | 16 |
| Figure 2.5  | In recent years, most researchers have used Raman spectroscopy in addition to XRD as a structural characterization technique. This figure shows the use of Raman spectroscopy to differentiate between cubic Cu$_2$SnS$_3$ (peaks at 303 cm$^{-1}$ and 355 cm$^{-1}$) and tetragonal Cu$_2$SnS$_3$ (peak at 337 cm$^{-1}$), as well as detect impurity phases such as Cu$_3$SnS$_4$ (295 cm$^{-1}$ and 330 cm$^{-1}$) and Cu$_2$S (475 cm$^{-1}$) | 17 |
| Figure 2.6  | (a) SEM images of electrodeposited films, showing small grain sizes and pinholes. (b) Another example of a solution processed film, exhibiting surface roughness and voids. (c) A dense film with large grain sizes, produced by annealing of Cu/Sn layers in a S environment | 17 |
| Figure 2.7  | The calculated electronic density of states, from Zhai, et al. | 19 |
Several groups have provided evidence of two optical absorption edges at ∼0.92 and ∼1.0 eV. This observation may be due to disorder effects which can give rise to fluctuations in the band gap of Cu$_2$SnS$_3$.

Figure 2.9  

a: Example of a Cu$_2$SnS$_3$ device architecture, from . The device layers are chosen because they have been shown to be successful for Cu$_2$ZnSnS$_4$ devices, but the band alignment with Cu$_2$SnS$_3$ may not be optimal.  

b: Device efficiency as a function of Cu/Sn ratio, after . The sharp drop in device efficiency for Cu/(Cu+Sn)>0.667 is currently ascribed to the presence of Cu$_4$SnS$_4$ impurity phases, but is still not fully understood.

Figure 2.10  

Example of morphology improvement after annealing in an S atmosphere. Device efficiencies improved from 0% (un-annealed) to 3.66% after annealing.

Figure 2.11  

Device performance trends as functions of NaF/Cu ratio from . Little scientific explanation is provided for these trends.

Figure 2.12  

Differences in the incident photon to current conversion efficiency (IPCE) between devices with Cu$_2$SnS$_3$ and Cu$_2$Sn$_{0.83}$Ge$_{0.17}$S$_3$ suggest discrepancies in the device stacks.

Figure 3.1  

Combinatorial materials development involves the growth of intentionally graded samples, which are then automatically mapped to determine their physical properties. High throughput data analysis techniques are required to process the large amounts of mapping data.

Figure 3.2  

Specially designed substrate mount to generate a temperature gradient across the substrate, from.

Figure 3.3  

Schematic of the annealing set up. The thermocouple is suspended approximately 2 cm above the sample. The argon is maintained at a constant flow rate, leading to an approximately atmospheric pressure inside the quartz tube.

Figure 3.4  

Schematic showing the layers used to fabricate photovoltaic devices with our Cu$_2$SnS$_3$ absorbers (figure shows a CuSbS$_2$ absorber).

Figure 4.1  

There are many reported ternary phases in the Cu-Sn-S system. We perform an initial down-selection by considering the oxidation state of Cu in these compounds: +2 (in red), mixed +1/+2 (in blue), and +1 (in green).
Figure 4.2  The ternary Cu-Sn-S compounds of interest can all be found on the Cu$_2$-SnS$_2$ tie line. Two of the compounds (Cu$_2$SnS$_3$ and Cu$_4$SnS$_4$) are line compounds, whereas Cu$_4$Sn$_7$S$_{16}$ is reported to be stable over a range of compositions. Adapted from Ref. 39.

Figure 4.3  Experimentally determined composition dependence of (a) structural (XRD), (b) electrical, and (c) optical properties of the Cu-Sn-S system. Vertical dashed lines indicate Cu$_2$SnS$_3$ and Cu$_4$SnS$_4$ nominal compositions. 40

Figure 4.4  Calculated chemical potential phase space of Cu-Sn-S system. $\Delta\mu$ measures the atomic chemical potentials relative to the respective elemental phase. The wider bars indicate the location of the Cu$_4$SnS$_4$ and Cu$_4$Sn$_7$S$_{16}$ phases, which are marginally stable and marginally unstable, respectively. The dashed line indicates the upper bound $\Delta\mu_S=0.46$ eV for the sulfur chemical potential in the present deposition method, i.e., only compounds to the right and above of the dashed line were observed in experiment. 42

Figure 4.5  Left panels: Volume-normalized calculated density of states and its projections onto atomic orbitals. Black dashed lines indicate valence and conduction band edges; shaded areas denote the range between the maximum (Cu-rich) and the minimum (Cu-poor) energies where Fermi level will be pinned due to spontaneous formation of Cu vacancies. Right panels: Local coordination of Cu atoms within 3 Å. 43

Figure 4.6  Calculated optical absorption spectra for Cu$_4$SnS$_4$, Cu$_2$SnS$_3$, and Cu$_4$Sn$_7$S$_{16}$. Vertical dashed lines denote quasi-particle band gaps. 44

Figure 5.1  a: The Cu-Sn-S compositional phase space. The inset shows the region of interest, as determined by the phases observed in our sputtered films. The numbered lines represent the observed phase progressions for three different samples that we synthesized, referred to as libraries. From analysis of the impurity phase peaks in the XRD patterns, we have approximated the phase width of the Cu$_2$SnS$_3$ phase, shown in blue (see Figure 5.3a for further discussion of the phase width determination). b: The Cu-Sn-S chemical potential phase space, as calculated previously. The white lines indicate the same experimental libraries as those shown in (a). Each white line represents a constant S chemical potential, moving from high $\mu_S$ (library 1) to low $\mu_S$ (library 3). 49
Figure 5.2  X-ray diffraction patterns for three sample series synthesized at high, intermediate, and low S chemical potentials. The S chemical potential affects the phase progression as the Cu/(Cu+Sn) ratio increases (y-axis). These phase progressions can be mapped onto the compositional and chemical potential phase spaces, as shown in Figure 5.1. The horizontal white lines show the phase pure Cu$_2$SnS$_3$ region, as determined by XRD impurity phase analysis (see Figure 5.3a). For representative individual XRD patterns, see Fig.s S1, S2, and S3 in the Supporting Information.

Figure 5.3  a: Normalized integrated impurity peak intensities as a function of Cu/(Cu+Sn) for three sample libraries. The linear fits are extrapolated to the background level of impurity intensity, shown by the dotted black line. The intersections of the background impurity intensity with the linear fits is used to determine the range of Cu/(Cu+Sn) values over which the Cu$_2$SnS$_3$ phase exists free of any other crystalline impurity phases. Note that the phase boundaries of the Cu$_2$SnS$_3$ phase differ between libraries. b: Electrical conductivity as a function of film composition for three sample libraries. Within the Cu$_2$SnS$_3$ phase, the electrical conductivity varies by several orders of magnitude. Within each sample series, the conductivity increases with an increase in Cu content. Furthermore, at very low Cu contents, there is a slight increase in the conductivity. Comparing the three series illuminates a third trend, which is an increase in conductivity with increasing S chemical potential.

Figure 5.4  a: The enthalpy of formation for copper vacancies (V$_{Cu}$) as a function of S chemical potential, calculated using DFT (data in Table 5.1 and Table 5.2). The enthalpy of formation for V$_{Cu}$ is lower at higher (less negative) S chemical potentials. The upper and lower lines represent Cu-rich and Sn-rich conditions, respectively; the change in formation enthalpy resulting from varying the Cu/Sn ratio is small compared to the effects from changing the S chemical potential. b: The calculated enthalpies of mixing for cubic Cu$_2$SnS$_3$ - Cu$_3$SnS$_4$ alloys as a function of composition. The mixing enthalpies at various compositions are negligible when considering the thermal energy at the growth temperature (~50 meV). The insets show the two S-based tetrahedral motifs (S-Cu$_2$Sn$_2$ and S-Cu$_3$Sn), which can be used to build both the cubic Cu$_2$SnS$_3$ and cubic Cu$_3$SnS$_4$ structures. Insets prepared using VESTA.
Figure 5.5  **a:** Raman spectra for six samples with varying Cu/(Cu+Sn) ratio, normalized to the magnitude of the peak at 354 cm$^{-1}$. All spectra show major peaks at 303 cm$^{-1}$ and 354 cm$^{-1}$, characteristic of cubic Cu$_2$SnS$_3$. The intensities of these two peaks change relative to one another as the Cu content in the Cu$_2$SnS$_3$ phase increases, indicating a change in short-range ordering. The shoulder peaks (starred) could indicate small amounts of tetragonal Cu$_2$SnS$_3$ or tetragonal/orthorhombic Cu$_3$SnS$_4$.

**b:** Fluorescence yield from near edge X-ray absorption fine structure spectroscopy for five samples with varying Cu/(Cu+Sn) ratio. The spectra show four signature peaks (numbered 1-4), which are consistent with peaks found in other Cu-S materials. The changes in the relative areas of Peaks 1 and 3 could indicate the incorporation of the Cu$_3$SnS$_4$ phase.

**c:** Peak intensity (Raman) or peak area ratios (NEXAFS) as functions of Cu/(Cu+Sn) ratio. Changes in Raman and NEXAFS peak ratios provide evidence for the formation of a cubic Cu$_2$SnS$_3$ - Cu$_3$SnS$_4$ alloy. The correlation of these peak ratios with the conductivity (shown as a function of Cu/(Cu+Sn) in Figure 5.3b) suggests that this alloying is responsible for the observed increase in electrical conductivity (and thus carrier concentration).

Figure 6.1 As expected from the Cu-Sn-S chemical potential phase space, carrier concentration reductions are largest when the Cu$_2$SnS$_3$ films are annealed in equilibrium with SnS (square markers). Increasing anneal temperature shows some effect on the hole concentration; increasing anneal time causes more dramatic reductions. The pre-anneal values of carrier concentration were $\sim 2 \times 10^{19}$ cm$^{-3}$.

Figure 6.2  (a) After annealing, the Cu$_2$SnS$_3$ films display XRD patterns corresponding to the monolithic structure. Prior to annealing, structural determination is difficult using only one peak. (b) Raman spectroscopy allows for elucidation of the pre-anneal structure as a mixture of cubic and tetragonal Cu$_2$SnS$_3$. The post-annealed spectrum shows peaks corresponding the monoclinic structure, as expected from the XRD pattern.

Figure 6.3  (a) The as-deposited sample shows two decay processes in the measured reflectivity: a 0.3 ps decay and a 7 ps decay; the annealed sample shows only the 7 ps decay process. (b) When the excitation power is lowered, the 0.3 ps decay can be detected in the annealed sample, suggesting that this state can be saturated for high carrier injection.
Figure 6.4 (a) Calculation of the inverse participation ratio (IPR) for the disordered and ordered structures shows a high degree of charge localization (denoted by a high IPR value) for the disordered structure, suggesting that both of our samples exhibit disorder. Note that the ordered sample does not have states within the gap, resulting in an infinite IPR value at these energies. (b) The disordered structure results in significant band tailing and a mid-gap state, both of which would significantly impact the performance of a Cu$_2$SnS$_3$-based photovoltaic device.

Figure 6.5 (a) As-deposited films show columnar grains with an extremely high density of planar defects. (b) In the annealed films, the planar defect density is reduced in some grains, but remains high in others. (c) and (d) Transmission electron diffraction patterns confirm the zinc blende structure of the unannealed sample, and the complex TED pattern of the annealed sample suggests a monoclinic structure.

Figure 7.1 The standard “substrate” device design used in CIGS and CZTS. In this configuration, the absorber layers is grown on the conductive back contact, and then the buffer, transparent conducting oxide, and front contact layers are deposited on top.

Figure 7.2 An optimized Cu$_2$SnS$_3$ sample grown on Eagle-XG glass (EXG), with a wide Cu$_2$SnS$_3$ phase width.

Figure 7.3 (a) When the deposition in Figure 7.2 was repeated on Mo, it resulted in only a narrow phase width of Cu$_2$SnS$_3$. (b), (c), and (d) Further efforts to vary the deposition parameters did not produce the desired Cu$_2$SnS$_3$ phase width.

Figure 7.4 (a) The Pd substrate did not react during the sputter deposition, but unidentifiable phases were produced. (b) and (c) The Ni and Pt substrates reacted during deposition, as evidenced by lack of substrate peaks in the XRD patterns. (d) The Cu substrate reacted during deposition to produce a primarily Cu$_4$SnS$_4$ film.

Figure 7.5 Growth on fluorine doped tin oxide (FTO) resulted in a mixture of Cu$_2$SnS$_3$ and Cu$_3$SnS$_4$, likely due to a preferential nucleation issue.

Figure 7.6 (a) Although the Cu$_2$SnS$_3$ phase width on the W-Ti substrate was relatively narrow, this substrate did not result in unknown phases in the final film. (b) Growth of Cu$_2$SnS$_3$ on Au came closest to replicating the results seen on glass.

Figure 7.7 Annealing the film grown on Mo had minimal effects on the Cu$_2$SnS$_3$ phase width.
Annealing of $\text{Cu}_2\text{SnS}_3$ grown on Au did not result in any impurity phases. .................................................. 97

Delamination at back contact in a $\text{Cu}_2\text{SnS}_3$ film grown on Au-coated glass. .................................................. 98

Current-voltage behavior of as-deposited and annealed $\text{Cu}_2\text{SnS}_3$ devices with an Au back contact. .................................................. 98

Cross sectional SEM of CZTSSe grown on Au, W, and Pt layers. .......... 99

Representative single point XRD patterns for the “High S” library (library 1), showing the $\text{Cu}_3\text{SnS}_4$/Cu$_2$SnS$_3$ (a) - Cu$_2$SnS$_3$ (b) - Cu$_4$Sn$_7$S$_{16}$/Cu$_2$SnS$_3$ (c) phase progression. .................. 122

Representative single point XRD patterns for the “Intermediate S” library (library 2), showing the $\text{Cu}_3\text{SnS}_4$/Cu$_2$SnS$_3$ (a) - Cu$_2$SnS$_3$ (b) - SnS/Cu$_2$SnS$_3$ (c) phase progression. .................. 123

Representative single point XRD patterns for the “Low S” library (library 1), showing the Cu$_4$SnS$_4$/Cu$_2$SnS$_3$ (a) - Cu$_2$SnS$_3$ (b) phase progression. .................. 124

Three observed crystal structures of $\text{Cu}_2\text{SnS}_3$, resulting from different levels of Cu/Sn cation site disorder. Unit cells are not shown to scale. Figure prepared using VESTA. ............... 126

The increase in Hall mobility at low temperatures suggests that the hole transport is not grain boundary limited in the pre-annealed samples. .... 127

Carrier localization is suggested by the negative imaginary component of the frequency-dependent terahertz conductivity. ............... 128

The electronic effects of disorder are even more pronounced in the kesterite structure of CZTS than in Cu$_2$SnS$_3$. ............... 128
**LIST OF TABLES**

Table 5.1  Calculated enthalpies of formation ($\Delta H_F$) for charge neutral defects at the intersection of the Cu$_2$SnS$_3$ chemical potential phase region with the two phases listed in parentheses (see Figure 5.1b). There are two non-equivalent sulfur sites in the Cu$_2$SnS$_3$ crystal structure: S1 coordinated by two Cu and two Sn and S2 coordinated by three Cu and one Sn atoms. ................................. 59

Table 5.2  Thermodynamic transition levels of defects, calculated relative to the conduction band minimum (CBM). ................................. 60

Table 6.1  Summary of changes in crystal structure, film morphology, and majority and minority carrier transport for a Cu$_2$SnS$_3$ films annealed under SnS/argon atmosphere at 500$^\circ$C for 2 hrs. Significant changes were evident in the structure and morphology, and a concurrent improvement was observed in the majority carrier transport. However, the minority carrier transport was mostly unaffected by the annealing. .................. 80

Table 7.1  Summary of deposition results for Cu$_2$SnS$_3$ growth on a variety of conductive back substrates. All substrates investigated had issues that precluded their use in Cu$_2$SnS$_3$ photovoltaic devices, including secondary phases, a narrow Cu$_2$SnS$_3$ phase width, or delamination at the metal/Cu$_2$SnS$_3$ interface. .................. 93

C1  XRF data shows that we observed minimal film thickness or compositional changes were observed after annealing. .................. 127
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>Absorption coefficient</td>
</tr>
<tr>
<td>$E_g$</td>
<td>Band gap</td>
</tr>
<tr>
<td>$\Delta R$</td>
<td>Change in reflectivity</td>
</tr>
<tr>
<td>$\Delta \mu_{Cu}$</td>
<td>Chemical potential of Cu relative to elemental Cu</td>
</tr>
<tr>
<td>$\Delta \mu_{Sn}$</td>
<td>Chemical potential of Sn relative to elemental Sn</td>
</tr>
<tr>
<td>$c_1$</td>
<td>Constant from Drude-Smith model representing persistence of velocity after first scattering event</td>
</tr>
<tr>
<td>$V_{Cu}$</td>
<td>Copper vacancy</td>
</tr>
<tr>
<td>Cu (I)</td>
<td>Cu in +1 oxidation state</td>
</tr>
<tr>
<td>Cu (II)</td>
<td>Cu in +2 oxidation state</td>
</tr>
<tr>
<td>$Cu_{Sn}$</td>
<td>Cu on Sn antisite defect</td>
</tr>
<tr>
<td>$m^*$</td>
<td>Effective mass</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Efficiency</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Electrical conductivity</td>
</tr>
<tr>
<td>$\Delta H_F$</td>
<td>Enthalpy of formation</td>
</tr>
<tr>
<td>$E_F^{pin}$</td>
<td>Fermi level pinning energy</td>
</tr>
<tr>
<td>$d$</td>
<td>Film thickness</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Frequency</td>
</tr>
<tr>
<td>$m_e$</td>
<td>Mass of an electron</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Mobility</td>
</tr>
<tr>
<td>$V_{oc}$</td>
<td>Open circuit voltage</td>
</tr>
</tbody>
</table>
Reflectance ................................................................. \( R \)

Relaxation scattering time ........................................ \( \tau \)

S atom coordinated by 2 Cu atoms and 2 Sn atoms ........... \( S\text{-Cu}_2\text{Sn}_2 \)

S atom coordinated by 3 Cu atoms and 1 Sn atom ........... \( S\text{-Cu}_3\text{Sn} \)

Short circuit current .................................................... \( J_{\text{sc}} \)

Sn on Cn antisite defect .............................................. \( \text{Sn}_{\text{Cu}} \)

Sn on Zn antisite defect .............................................. \( \text{Sn}_{\text{Zn}} \)

Sulfur chemical potential ........................................... \( \mu_S \)

Sulfur vacancy ........................................................ \( V_S \)

Tin vacancy ............................................................ \( V_{\text{Sn}} \)

Transmittance ......................................................... \( T \)
# LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC RF</td>
<td>Alternating current radio frequency</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>BC</td>
<td>Back contact</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
</tr>
<tr>
<td>CBM</td>
<td>Conduction band minimum</td>
</tr>
<tr>
<td>CIGS</td>
<td>Cu(In,Ga)Se$_2$</td>
</tr>
<tr>
<td>CZTSSe</td>
<td>Cu$_2$ZnSn(S,Se)$_4$</td>
</tr>
<tr>
<td>CZTS</td>
<td>Cu$_2$ZnSnS$_4$</td>
</tr>
<tr>
<td>CGS</td>
<td>CuGaSe$_2$</td>
</tr>
<tr>
<td>CIS</td>
<td>CuInSe$_2$</td>
</tr>
<tr>
<td>JV</td>
<td>Current-voltage</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>DFT+U</td>
<td>Density functional theory with onsite Coulomb potential</td>
</tr>
<tr>
<td>DOS</td>
<td>Density of states</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>EXG</td>
<td>Eagle-XG glass</td>
</tr>
<tr>
<td>EQE</td>
<td>External quantum efficiency</td>
</tr>
<tr>
<td>FF</td>
<td>Fill factor</td>
</tr>
<tr>
<td>FERE</td>
<td>Fitted elemental reference energies</td>
</tr>
<tr>
<td>FTO</td>
<td>Fluorine doped tin oxide</td>
</tr>
<tr>
<td>Term</td>
<td>Abbreviation</td>
</tr>
<tr>
<td>-------------------------------------------</td>
<td>--------------</td>
</tr>
<tr>
<td>Focussed ion beam</td>
<td>FIB</td>
</tr>
<tr>
<td>Fourier transform infrared spectroscopy</td>
<td>FTIR</td>
</tr>
<tr>
<td>Grain boundary</td>
<td>GB</td>
</tr>
<tr>
<td>Heyd-Scuseria-Ernzerhof</td>
<td>HSE</td>
</tr>
<tr>
<td>Incident photon to current conversion efficiency</td>
<td>IPCE</td>
</tr>
<tr>
<td>Indium doped tin oxide</td>
<td>ITO</td>
</tr>
<tr>
<td>Inverse participation ratio</td>
<td>IRP</td>
</tr>
<tr>
<td>National Aeronautics and Space Administration</td>
<td>NASA</td>
</tr>
<tr>
<td>National Renewable Energy Laboratory</td>
<td>NREL</td>
</tr>
<tr>
<td>Near edge X-ray absorption fine structure</td>
<td>NEXAFS</td>
</tr>
<tr>
<td>Optical pump terahertz probe spectroscopy</td>
<td>OPTP</td>
</tr>
<tr>
<td>Perdew-Burke-Ernzerhof</td>
<td>PBE</td>
</tr>
<tr>
<td>Photoluminescence</td>
<td>PL</td>
</tr>
<tr>
<td>Photovoltaic</td>
<td>PV</td>
</tr>
<tr>
<td>Projector augmented wave</td>
<td>PAW</td>
</tr>
<tr>
<td>Radio frequency</td>
<td>RF</td>
</tr>
<tr>
<td>Rapid development</td>
<td>RD</td>
</tr>
<tr>
<td>Scanning electron microscopy</td>
<td>SEM</td>
</tr>
<tr>
<td>Time resolved terahertz spectroscopy</td>
<td>TRTS</td>
</tr>
<tr>
<td>Transmission electron diffraction</td>
<td>TED</td>
</tr>
<tr>
<td>Transmission electron microscopy</td>
<td>TEM</td>
</tr>
<tr>
<td>Ultraviolet-Visible-Near Infrared</td>
<td>UV-Vis-NIR</td>
</tr>
<tr>
<td>Valence band maximum</td>
<td>VBM</td>
</tr>
</tbody>
</table>
Vienna Ab initio Simulation Package .......................... VASP
Visualization for Electronic and Structural Analysis ............... VESTA
X-ray diffraction ................................................... XRD
X-ray fluorescence ............................................... XRF
X-ray photoelectron spectroscopy ............................... XPS
ACKNOWLEDGMENTS

This work presented in this thesis (alternate title: *The Miseducation of Lauryn Baranowsk*) would not have been possible without the contributions of many, many people. Special thanks go to my advisors at Colorado School of Mines and the National Renewable Energy Laboratory, Eric Toberer and Andriy Zakutayev. Eric, thank you for convincing me to transfer to Mines rather than dropping out of grad school, and for always holding me to the highest of standards. Andriy, thank you for sharing your vast scientific knowledge with me, as well as your eternal and sometimes obnoxious optimism.

I am also grateful to my committee members Brian Gorman, Reuben Collins, and Jeramy Zimmerman for their guidance and advice. Huge thanks also go out to Adele Tamboli for acting as a unofficial advisor and tie-breaker vote in many meetings with my advisors. Thanks to the many students, postdocs, and NREL staff and scientists who helped me along the way, including (but surely not limited to) Angela Fioretti, Aaron Martinez, Adam Welch, Brenden Ortiz, Chris Caskey, Pawel Zawadzki, Stephan Lany, Phil Parilla, John Perkins, and Dave Ginley. Extra thanks to Emily Warren and Aaron Martinez for proof-reading help.

Thanks to my parents for always encouraging my love of science and my inquisitive nature, and especially to my mother for leading by example in a time when being a woman in science was much harder than it is now. Lastly, I am hugely grateful to Bradley MacLeod for standing by my side for the last two years of my PhD, always ready to offer his doctorly advice, encouragement, support, and humor.
In 2013, the world used 15 terawatts (TW) of energy, and this is projected to double by 2050 [1]. If CO₂ emissions are to stay at current levels, the world will require an addition 13-15 TW of renewable energy by 2050 [1, 2]. By far the most abundant renewable energy source comes from the sun: the total amount of incident solar radiation on Earth’s surface is $1.4 \times 10^{17}$ W. Covering just 1% of the earth’s surface with photovoltaic (PV) modules operating with 10% efficiency would produce around 25 TW [2]. Thus, the development of low cost and efficient PV technologies is critical for providing energy to the growing world population and arresting man-made climate change.

1.1 Issues facing traditional photovoltaics

By far the most well studied and commercially successful PV absorber is silicon. The first Si photovoltaic module was fabricated in 1955 by Bell Laboratories, and this technology was subsequently pursued by NASA to power spacecrafts [3]. However, Si photovoltaics for terrestrial applications did not become a popular area of research until the 1970s [3]. Development proceeded rapidly, largely because researchers could draw on the extensive Si processing experience of the microelectronics industry [4]. Silicon has maintained its dominance to the present day: as of 2013, more than 80% of the photovoltaics industry was based on Si wafer technologies [5]. However, Si is far from an ideal material for a photovoltaic absorber. Because of the indirect band gap of Si, the optical absorption is weak, and thus a thick absorber layer ($\sim 100 \ \mu m$) is required to absorb all of the incident light [6]. This increased absorber thickness necessitates long minority carrier diffusion lengths and lifetimes for efficient carrier extraction [6]. As a result, the raw material must have extremely low impurity levels and be carefully processed to minimize defects that could
increase recombination. This processing is energy intensive, and accounts for 85% of the total energy input for the finished module [7].

Both the high material usage and the need for long minority carrier diffusion lengths in silicon can be solved by moving to direct band gap materials, which require only a few \( \mu \text{m} \) of material to absorb the incident sunlight [8]. The two dominant thin film absorber technologies are Cu(In,Ga)Se\(_2\) (CIGS) and CdTe, which currently demonstrate record research cell efficiencies of 21.7% and 21.5%, respectively [9, 10]. Both CIGS and CdTe have been commercialized, most successfully in the case of First Solar (CdTe), which is currently the world’s largest thin film photovoltaic module manufacturer [1]. However, the long term scalability of these materials is uncertain. A 1 \( \mu \text{m} \) thick CIGS device operating at 12% efficiency would require 10,000 metric tonnes of In to supply 1 TW of peak power; in contrast, the worldwide production of In is only 600 metric tonnes per year [1]. Te is even less plentiful, limiting the production capacity of CdTe cells to about 20 GW per year [1]. Additionally, Cd is toxic and many countries restrict its use in consumer products [1].

1.2 Earth abundant thin film photovoltaics

The field of earth abundant photovoltaics seeks to develop alternatives to CIGS and CdTe by considering absorbers that could be scaled to the TW level without incurring material shortages. Although silicon is the second most abundant element in the earth’s crust, we will exclude it from our discussion of earth abundant absorbers to focus only on thin film absorber materials. With this in mind, one of the first earth abundant absorbers to be researched extensively was Cu\(_2\)S, a p-type material that was used with an n-type CdS buffer layer [11–13]. Cu\(_2\)S was developed in the 1960s and 70s, and devices reached 10% efficiency by the early 1980s [14]. However, the devices proved extremely unstable due to Cu migration to the Cu\(_2\)S/CdS interface, which caused shorts in the device [15]. Around the same time, CIGS and CdTe emerged onto the photovoltaics scene, and the research focus shifted to these materials for some time.
In the past ten years, the field of earth abundant PV has seen a resurgence, largely due to interest in the development of \( \text{Cu}_2\text{ZnSn(S,Se)}_4 \) (CZTSSe) \([1]\). Because of the similarities between CZTSSe and CIGS, the optimization of CZTSSe has proceeded at a fast pace. As of 2015, the record research cell efficiency for CZTSSe was an 12.6% solution processed cell developed by IBM \([16]\). However, the path to higher efficiency CZTSSe devices is unclear. Because of the chemical complexity of the base quaternary compound, there exists only a narrow compositional window in which phase pure material is formed \([17]\). Secondary phases such as ZnS and \( \text{Cu}_2\text{SnS}_3 \) are common. Furthermore, cation antisite defects have proven difficult to control, and can detrimentally impact the performance of CZTSSe devices \([18]\).

Despite the dominance of CZTSSe in the field of earth abundant absorbers, researchers are now considering a host of other materials. Just some of these new materials under investigation include \( \text{Zn}_3\text{P}_2 \), \( \text{SnS} \), \( \text{Cu}_2\text{O} \), \( \text{Cu}_3\text{N} \), \( \text{Cu}_2\text{SnS}_3 \), \( \text{CuSbS}_2 \), \( \text{Sb}_2\text{Se}_3 \), \( \text{FeS}_2 \), \( \text{Fe}_2\text{SiS}_4 \), \( \text{CuFeS}_2 \), and \( \text{ZnSnP}_2 \) \([19–28]\). Even the previously discarded \( \text{Cu}_2\text{S} \) is being reconsidered, with strategies being developed to stabilize this material \([29, 30]\). As shown in Figure 1.1, many of these new materials have the potential for much higher annual electricity production (based upon the known economic reserves and annual production) than traditional PV materials such as CdTe \([7]\). However, there are few reported devices using these new earth abundant absorbers, and efficiencies are considerably lower than those reported for CZTSSe devices \([20, 24, 25, 31]\).

1.3 The “rapid development” approach

The “rapid development” (RD) approach was created to address two key questions in the field of earth abundant photovoltaic materials: (1) How do we find new materials with the potential to be truly disruptive technologies? and (2) How can we rapidly screen and develop our potential materials to the 7-10% device level, such that they generate significant interest from the larger photovoltaics community? When we consider the arc of successful alternative absorber materials such as CZTSSe, it is clear that there is an explosion in the amount of research performed on these materials (as measured by number of publications)
with the successful demonstration of devices in the 7-10% range. Our aim is to accelerate the time between initial discovery and successful device integration, and to do this with radically new absorbers that have the potential to be disruptive to current PV technologies.

The current RD methodology consists of three stages: exploration, research, and development, as illustrated in Figure 1.2. In each stage, both theory and experiment are used to assess the candidate materials and down-select before proceeding to the next stage. The overall result is that, in the time span of ∼2-3 years, we are able to rapidly go from tens of possible absorber materials to 1-2 working PV device prototypes.

The exploration stage starts with 10s of candidate materials or alloys. First principles theory is used to compute the crystal structures, phase widths, and competing phases, as well as photovoltaic relevant properties such as the band gap, optical absorption spectrum, and effective masses. Combinatorial experiments, employing gradients in composition and growth temperature, are used to survey the candidate materials, and the composition, structure, and optical absorption are mapped to these gradients. The experimental and theoretical results are used to rule out candidate materials that are clearly not suitable for absorber applications. These include issues such as phase metastability, metallic behavior, or very indirect band
gaps. At the end of the exploration stage, the most promising 3-5 phases/alloys are selected to continue to the research stage.

In the research stage, targeted experiments and theory are used to consider effects such as doping and minority carrier transport. Defect formation energies and transition levels are considered, and theory is also used to evaluate potentially harmful effects such as disorder and charge trapping. More sophisticated synthetic techniques are developed, including multi-stage growth, and in-situ or ex-situ annealing. Single point characterization is performed on uniform regions of the samples, to investigate properties such as carrier concentration and mobility (Hall effect), radiative yield (photoluminescence), and morphology (scanning electron microscopy or atomic force microscopy). These techniques help identify “fatal flaws” in some of the candidate materials; examples from our own work include degenerate doping, band tailing due to disorder, and difficulty controlling surface morphology. These results allow for further down-selection to the 1-2 most promising materials for device integration.

The development stage considers other issues required for successful device integration of the candidate materials. The absorber/buffer interface properties are studied by calculating surface energies and band offsets. Experimental challenges addressed in this stage include translating the growth techniques developed in the research stage onto conductive substrates, as well as the choice of materials and deposition techniques for the buffer and
transparent conducting oxide layers. The device integration is informed by advanced character-
ization, including photoelectron spectroscopy (to investigate band offsets at interfaces),
and standard device metrics such as current-voltage (JV) and external quantum efficiency
(EQE) measurements.

1.4 The Cu-Sn-S system

This thesis illustrates the rapid development approach as applied to the ternary Cu-Sn-S
system. Because of the similarities to the Cu-Zn-Sn-S/Se system, we hope to be able to
draw from the over ten years of expertise on CZTSSe processing. However, these similarities
also make it somewhat less likely that the Cu-Sn-S system will yield a truly disruptive PV
absorber material. Cu-Sn-S materials are relatively unexplored, and this system is thus a
good candidate for the demonstration and refinement of the rapid development methodology.

We chose to draw inspiration from the success of Cu$_2$S absorbers, and couple this with
the stabilization effect demonstrated in the Cu-Se system through the addition of a third
element to form Cu(In,Ga)Se$_2$. We used theory to consider the defect tolerance of various
ternary Cu-S materials and determined that materials in the Cu-Sn-S system should have
high defect tolerance because of the lack of dangling bond states in the gap that could
cause recombination. Within the Cu-Sn-S system, several ternary compounds have been
investigated as candidates for photovoltaic absorbers, including Cu$_2$SnS$_3$, Cu$_3$SnS$_4$, Cu$_4$SnS$_4$,
Cu$_2$Sn$_3$S$_7$, and Cu$_5$Sn$_2$S$_7$ [23, 32–47].

1.5 Thesis outline

Each chapter within this thesis focuses on one of the three RD stages. After a discussion of
the literature background in Chapter 2, Chapter 3 details the experimental methods used in
the RD approach. In the exploration stage (Chapter 4), we down-select to three promising
Cu-Sn-S materials: Cu$_2$SnS$_3$, Cu$_4$SnS$_4$, and Cu$_4$Sn$_7$S$_{16}$. After considering the calculated
band structure and optical absorption, as well as the experimental electrical conductivity and
absorption spectra, we determine that Cu$_2$SnS$_3$ is the most promising photovoltaic absorber
material in the Cu-Sn-S system. The next two chapters (Chapters 5 and 6) demonstrate aspects of the research stage. In the case of Cu$_2$SnS$_3$, we focused on investigations into control of doping in through two different mechanisms (Chapter 5), and the role of disorder on carrier transport properties (Chapter 6). Lastly, the development stage (Chapter 7) studies the growth of Cu$_2$SnS$_3$ on conductive back substrates, a necessary step for PV device integration. The conclusion (Chapter 8) provides insights into both the future of Cu$_2$SnS$_3$ as a photovoltaic absorber and the future applications of the rapid development approach.

1.6 Thesis contributions

Chapter 4 is adapted from a publication co-written by Pawel Zawadzki (theory) and Lauryn Baranowski (experiment). The abstract, theoretical methods, and conclusion have been reproduced from the original work and were written by Pawel Zawadzki. The experimental methods and results have also been reproduced from the original work, and were written by Lauryn Baranowski. The introduction and theoretical results sections have been rewritten by Lauryn Baranowski to place the focus more on the experimental work, and several sections have also been added, to the same end. Further theory contributions were provided by Haowei Peng and Stephan Lany. Experimental support and guidance were provided by Eric Toberer and Andriy Zakutayev. David Ginley and William Tumas participated in discussion and editing.

The publication that comprises Chapter 5 was written by Lauryn Baranowski, who led the experimental synthesis and characterization efforts. Theory contributions were provided by Pawel Zawadzki and Stephan Lany. NEXAFS data acquisition and analysis were done by Steven Christensen and Dennis Nordland. Raman spectroscopy was performed by Lynn Gedvilas. Andriy Zakutayev and Eric Toberer provided experimental guidance, and Adele Tamboli, David Ginley, and William Tumas participated in discussion and editing.

The publication in Chapter 6 was also written by Lauryn Baranowski. Annealing experiments were performed by Lauryn Baranowski and Kevin McLaughlin. Theory contributions came from Pawel Zawadzki and Stephan Lany. Optical pump terahertz probe spectroscopy
and associated data analysis was performed by Hannes Hempel, with guidance from Rainer Eichberger and Thomas Unold. Andrew Norman provided TEM imaging and analysis. Eric Toberer and Andriy Zakutayev provided experimental guidance, discussion, and editing.

All other chapters are the work of Lauryn Baranowski.
CHAPTER 2
BACKGROUND

This chapter aims to place the current research on Cu$_2$SnS$_3$ into the larger context of work done in the past 40 years on Cu-based photovoltaic absorbers. We then discuss the prior work performed on Cu$_2$SnS$_3$ material development, and describe device integration efforts. Special emphasis is placed on gaps in the current knowledge, and opportunities for further materials and device development.

2.1 Historical perspective on Cu-chalcogenide photovoltaic absorbers

The successes of Cu-chalcogenide absorbers indicate the promise of these materials as photovoltaic absorbers. In this section, we discuss the development of Cu$_2$S, Cu(In,Ga)Se$_2$, and Cu$_2$ZnSn(S,Se)$_4$, and highlight the particular successes and failures of each material. These systems offer a wealth of experience to draw from when considering deposition techniques, material optimization, and device integration of new Cu-chalcogenide absorbers such as Cu$_2$SnS$_3$.

Figure 2.1: Historical efficiencies of Cu-chalcogenide photovoltaic devices. The successes and failures of Cu$_2$S, Cu(In,Ga)Se$_2$, and Cu$_2$ZnSn(S,Se)$_4$ can guide the development of new Cu-chalcogenide photovoltaic absorbers, such as Cu$_2$(Sn,Ge)S$_3$ [48, 49].
2.1.1 Cu$_2$S

Cu$_2$S absorbers possess many desirable properties for a photovoltaic material, including nontoxicity, elemental abundance, and a 1.2 eV direct bandgap with a high absorption coefficient [29]. Devices were developed using a CdS buffer layer because the band alignment of these two materials allowed for good carrier extraction [11]. By 1981, after several decades of development, efficiencies had reached 10% for Cu$_2$S/Cd$_{1-x}$Zn$_x$S devices [14] (see Figure 2.1). However, the performance of these devices deteriorated rapidly under ambient exposure, leading to device failure in a matter of weeks [50]. When the failure mechanisms were studied, it was concluded that Cu diffusion into the Cd$_{1-x}$Zn$_x$S buffer layer and to surface oxides caused the formation of the highly doped ($>10^{20}$ cm$^{-3}$) Cu$_{1.96}$S phase [15]. This phase transformation resulted in decreases in short circuit current, open circuit voltage, and device efficiency. However, in recent years, stabilization of Cu$_2$S has been reconsidered using techniques such as atomic layer deposition to deposit extremely thin layers (15-30 nm) of ZrO$_2$, TiO$_2$ and Al$_2$O$_3$ on either side of the Cu$_2$S absorber layer [29, 30].

2.1.2 Cu(In,Ga)Se$_2$

After the instability of Cu$_2$S absorbers proved problematic, the focus shifted to ternary Cu chalcogenides, such as CuInSe$_2$ (CIS) and CuGaSe$_2$ (CGS). In the early 1970s, CuInSe$_2$ was considered as a possible material for near-infrared light emitting diodes [51]. It was soon determined that CIS had several properties advantageous for thin film photovoltaics, including a high absorption coefficient and electronically benign defects [51]. Because the band gap of CIS is lower than desired for a single junction absorber (1.04 eV), Ga was alloyed on the In site to increase the band gap [52]. Several breakthroughs have allowed CIGS cells to reach 20% efficiency, including the development of two- and three-stage growth processes for enhanced film morphology, and the understanding of the role of Na within the CIGS absorber layer [53].
2.1.3 \( \text{Cu}_2\text{ZnSn(S,Se)}_4 \)

The first demonstration of the photovoltaic effect in \( \text{Cu}_2\text{ZnSn(S,Se)}_4 \) (CZTSSe) was in 1988, using a CZTSSe/CdSnO heterodiode [17]. Further development of CZTSSe as a photovoltaic absorber did not occur until the late 1990s, when, in 1996, a 0.66% efficient device was reported [6]. From then on, development progressed rapidly, with efficiencies climbing to 6.8% in 2008 using films deposited with vacuum techniques [6]. The development of hydrazine-based deposition processes enabled further efficiency gains: 9.7% devices were reported in 2010 [6]. The current record device, with 12.6% efficiency, was reported in 2014 and also makes use of a hydrazine-based deposition [16]. These gains in efficiency make it seem possible that CZTSSe could one day be a replacement for CIGS.

However, CZTSSe absorbers also present significant material challenges that may ultimately limit their efficiency. As a quaternary compound, there exists only a narrow stability window, outside of which secondary phases are easily formed [17]. The much higher volatility of Sn than the other constitutent elements makes achieving the desired stoichiometry even more difficult, especially when extended heat treatments are required [17]. Additionally, it is difficult to eliminate detrimental antisite defects such as \( \text{Cu}_{\text{Sn}} \) and \( \text{Sn}_{\text{Zn}} \) [18].

A 2013 analysis pointed out several challenges from a device perspective, most notably the low open circuit voltage (\( V_{oc} \)) in CZTSSe devices [54]. Both the temperature dependence of the \( V_{oc} \) and the photoluminescence (PL) spectrum of CZTSSe devices indicate a recombination activation energy that is lower than the measured band gap, suggesting that recombination is dominated by interface or defect mediated transitions [54].

2.2 Overview of the Cu-Sn-S family

There are a large number of phases within the Cu-Sn-S system; a paper by Fietcher, et al., cites 18 known ternary phases [33]. It is possible to classify the ternary phases according to the oxidation state of the Cu within the compound, which gives three categories: Cu exclusively in the 1+ oxidation state, Cu in a mixed 1+/2+ oxidation state, and Cu
exclusively in the 2+ oxidation state. The first category includes semiconducting compounds such as \( \text{Cu}_4\text{SnS}_4 \), \( \text{Cu}_2\text{SnS}_3 \), and \( \text{Cu}_4\text{Sn}_7\text{S}_{16} \). Of the material with mixed Cu valence, the most well investigated compound is \( \text{Cu}_3\text{SnS}_4 \). \( \text{Cu}_4\text{SnS}_6 \) is the only known compound for which Cu is exclusively in the 2+ oxidation state; this compound is reported to be metallic and electronically similar to CuS [55].

The main applications that have been suggested for compounds within the Cu-Sn-S system are as photovoltaic absorbers and thermoelectric materials. Most of the ternaries in this system are expected to have p-type conductivity, high minority carrier mobility, and band gaps around 1 eV, making them good candidates for photovoltaic applications [55]. Indeed, \( \text{Cu}_2\text{SnS}_3 \), \( \text{Cu}_3\text{SnS}_4 \), \( \text{Cu}_4\text{SnS}_4 \), and \( \text{Cu}_2\text{Sn}_3\text{S}_7 \) [23, 32–43, 45–47] have been investigated as potential solar absorbers. Most of these materials were found to have direct band gaps between 0.8 - 1.5 eV with corresponding high absorption coefficients (\( >10^4 \text{ cm}^{-1} \)). The compounds with Cu exclusively in the 1+ oxidation state (\( \text{Cu}_4\text{SnS}_4 \), \( \text{Cu}_2\text{SnS}_3 \), and \( \text{Cu}_4\text{Sn}_7\text{S}_{16} \)) are expected to be better solar absorbers than those with Cu in a mixed 1+/2+ oxidation state, as the multivalency of Cu can lead to high carrier concentrations (\( \sim10^{22} \text{ cm}^{-3} \)) or hole self-trapping [55]. Several other materials in the Cu-Sn-S family have been proposed as possible thermoelectric materials, including \( \text{Cu}_3\text{SnS}_4 \) and \( \text{Cu}_5\text{Sn}_2\text{S}_7 \) [44]. However, when the thermoelectric performance of \( \text{Cu}_3\text{SnS}_4 \) was investigated, the Seebeck coefficient was less than 100 \( \mu \text{V/K} \), and the highest reported thermoelectric figure of merit was 0.022 at 573 K [44], indicating that much more work will be required to optimize these compounds for thermoelectric applications.

### 2.3 Thin film synthesis of \( \text{Cu}_2\text{SnS}_3 \)

Vacuum and solution processing techniques have been used to synthesize \( \text{Cu}_2\text{SnS}_3 \) thin films and devices. As shown in Figure 2.2a, the number of publications on the thin film synthesis of \( \text{Cu}_2\text{SnS}_3 \) for photovoltaic applications has grown rapidly in recent years.
Figure 2.2: (a) In recent years, the number of publications on Cu$_2$SnS$_3$ for photovoltaic applications has increased exponentially. (b) Efficiency records for Cu$_2$SnS$_3$-based devices have also been rising rapidly, reaching 4.63% in 2015 for pure Cu$_2$SnS$_3$ and 6.0% when Ge is alloyed into the absorber layer [23, 56].

2.3.1 Vacuum synthesis techniques

Vacuum techniques used include evaporation, sputtering, and pulsed laser deposition. Most often, Cu and Sn are deposited simultaneously or in a layered structure, and then annealed under an S, Sn/S or H$_2$S atmosphere. A review of the literature suggests that it is the anneal conditions (temperature and atmosphere) that are most influential on the final phase and material quality, rather than the technique used to deposit the starting metal layers.

Reported anneal temperatures range from 350°C-600°C, and most device-quality films are produced by annealing between 550-580°C. Both the phase and crystal structure of the resulting film can be influenced by annealing temperature. Many studies have reported that the cubic phase results from higher temperature anneals (as compared to the tetragonal or monoclinic phases) [36, 42]. Fernandes, et al. found that by varying the annealing temperature in the range of 350-400°C, films could be produced in either the tetragonal or cubic Cu$_2$SnS$_3$ crystal structures. In the same study, increasing the annealing temperature above 500°C resulted in an orthorhombic Cu$_3$SnS$_4$ phase [36]. Additionally, some work has been done on the influence of anneal atmosphere: Guan, et al. found that annealing in an N$_2$/S$_2$ atmosphere produced Cu$_2$SnS$_3$, while annealing in H$_2$S resulted in the Cu$_4$SnS$_4$ phase.
2.3.2 Solution processing techniques

Compared with vacuum synthesis, there is an even wider range of solution processing techniques that have been used to synthesize Cu$_2$SnS$_3$ thin films. A comprehensive list includes spray pyrolysis, chemical bath deposition, electrodeposition, successive ionic layer adsorption and reaction, screen printing, spincoating, and dipcoating [35, 39, 40, 44, 47, 57, 58]. Although solution processing is often chosen because of the potential for commercialization, as of yet these techniques do not yield high device efficiencies. The highest reported device efficiency for a solution processed film was reported in 2012 by Koike, et al. who published a 2.84% device with an electrodeposited Cu$_2$SnS$_3$ absorber [43]. This is in contrast to device efficiencies of nearly 5% when vacuum growth techniques are employed. The lack of high efficiency solution processed devices may be related to the poor morphology typical of these films, as will be discussed in the next section.

2.4 Structure and morphology of Cu$_2$SnS$_3$ thin films

The Cu$_2$SnS$_3$ phase has been claimed to be observed in cubic, tetragonal, monoclinic, triclinic, and hexagonal crystal structures [35, 36, 59, 60]. A theoretical work by Zhai, et al., suggested that these different structures are representative of varying degrees of disorder on the cation sublattice, as shown in Figure 2.3 [61]. Full Cu/Sn disorder results in a cubic unit cell with a zinc blende structure; the tetragonal and monoclinic structures are formed in a zinc blende supercell with partial disorder and full order, respectively. These structures have been observed many times in experimental works via the synthesis methods detailed above. A metallic Cu$_2$SnS$_3$ phase with a hexagonal crystal structure was reported in 2007 by Wu, et al.; however, this finding has not been replicated [60]. In the few reports of triclinic Cu$_2$SnS$_3$, the provided X-ray diffraction (XRD) patterns bear a striking resemblance to the monoclinic diffraction pattern, and no efforts have been made to differentiate between XRD patterns from these two structures [35, 39, 62]. Thus, it is reasonable to conclude that Cu$_2$SnS$_3$ exists
only in the cubic, tetragonal, and monoclinic structures as discussed in the Zhai, et al. work.

Figure 2.3: $\text{Cu}_2\text{SnS}_3$ can exist in cubic, tetragonal, and monoclinic crystal structures, depending on the degree of cation disorder. Figure made using VESTA [63].

Traditional structural characterization of $\text{Cu}_2\text{SnS}_3$ has mainly utilized XRD to determine the phase purity of the product. However, phase identification by XRD alone has several limiting flaws. The major peaks for the different $\text{Cu}_2\text{SnS}_3$ structures (cubic, tetragonal, and monoclinic) are located at very close $2\theta$ values, making structural differentiation difficult (see Figure 2.4); this difficulty can be exacerbated by the preferential orientation effects often seen in thin films, and by the effects of lattice strain. Secondly, the $\text{Cu}_3\text{SnS}_4$ impurity phase can exist in the same cubic structure as $\text{Cu}_2\text{SnS}_3$, and the lattice parameters are sufficiently close as to make detection by XRD impossible, as shown in Figure 2.4. Furthermore, the detection limit of XRD is anywhere between 1-5%, and impurity phases in lower concentrations could still significantly influence the optoelectronic properties of the material.

Because of the uncertainty associated with XRD phase identification, most studies published in the last several years now supplement the structural characterization with Raman spectroscopy (as shown in Figure 2.5). The different $\text{Cu}_2\text{SnS}_3$ crystal structures are much more apparent in the Raman spectra because the peaks do not overlap, as in XRD. However, there has been no theoretical work to calculate the Raman active modes in $\text{Cu}_2\text{SnS}_3$ or other Cu-Sn-S phases. As a result, phase assignment is empirical and there is some disagreement in the field as to the exact peak position of various Cu-Sn-S phases. However, by combin-
Figure 2.4: By XRD alone, it is difficult to distinguish between the different crystal structures of Cu$_2$SnS$_3$, or the Cu$_3$SnS$_4$ impurity phase [36].

Using XRD and Raman, accurate phase identification can be achieved. More recently, other techniques such as X-ray photoelectron spectroscopy (XPS) have been used to characterize the oxidation states of the individual elements, and this data can additionally help to verify phase purity [64].

Due to the wide range of deposition methods for thin film Cu$_2$SnS$_3$, morphologies vary significantly. In general, the films produced by low temperature, solution depositions have poor morphologies, including voids, significant surface roughness, and/or small grain sizes, examples of which can be seen in the scanning electron microscopy (SEM) images in Figure 2.6a and b. Films that are annealed at relatively high temperatures (400-600°C) are typically dense and have larger grain sizes, as shown in Figure 2.6c. Reported grain sizes range from the 10s of nm to a maximum of 1-2 µm (typically limited by the film thickness). From the prior literature, these large grain sizes (>500 nm) seem to be necessary for high efficiency photovoltaic devices.
Figure 2.5: In recent years, most researchers have used Raman spectroscopy in addition to XRD as a structural characterization technique. This figure shows the use of Raman spectroscopy to differentiate between cubic Cu$_2$SnS$_3$ (peaks at 303 cm$^{-1}$ and 355 cm$^{-1}$) and tetragonal Cu$_2$SnS$_3$ (peak at 337 cm$^{-1}$), as well as detect impurity phases such as Cu$_3$SnS$_4$ (295 cm$^{-1}$ and 330 cm$^{-1}$) and Cu$_2$S (475 cm$^{-1}$) [44].

Figure 2.6: (a) SEM images of electrodeposited films, showing small grain sizes and pinholes [40]. (b) Another example of a solution processed film, exhibiting surface roughness and voids [41]. (c) A dense film with large grain sizes, produced by annealing of Cu/Sn layers in a S environment [23].
2.5 Optoelectronic properties of Cu$_2$SnS$_3$ thin films

The reported electronic properties for Cu$_2$SnS$_3$ vary significantly between studies. The electrical conductivity has been measured anywhere between 0.004 - 80 S/cm [37, 44, 65, 66]. This extremely wide range can be explained by many factors, including the presence of small amounts of conductive impurity phases such as Cu$_4$SnS$_4$ and Cu$_2$S, extrinsic impurities incorporated during the various processing steps, and variations in intrinsic defect concentrations resulting from different synthesis conditions. The material is always reported as p-type, with carrier concentrations ranging from $10^{17}$-10$^{20}$ cm$^{-3}$. In general, these values of carrier concentration are quite high for a photovoltaic absorber material. Characterization of majority carrier mobility (by Hall effect) has resulted in values form 0.4-11 cm$^2$/Vs [44, 45, 66, 67]. Avellaneda, et al., reported a mobility value of 80 cm$^2$/Vs, yet note in their work that a Cu$_8$S$_5$ phase can be observed by XRD, thus negating this measurement [35]. There does not seem to be a significant correlation between the majority carrier mobility and the grain size (as determined by SEM), likely because the carrier mean free path is limited by defects within the grains.

Several attempts have been made to understand the conduction mechanisms in Cu$_2$SnS$_3$. Bouaziz, et al. measured the electrical conductivity between room temperature and $\sim$85 K and observed two distinct conduction regimes. Above 238 K, the electrical conductivity - temperature relationship can be fit to Arrhenius’s law, and is thus attributed to thermal excitation of charge carriers. Below 238 K, Bouaziz, et al. find that the data can be fit to Mott’s law, indicating a variable range hopping mechanism [38]. Dias, et al. reached a similar conclusion, with a transition temperature of 275 K [68]. In contrast, Tiwari, et al. observe three different conduction regimes: from 5-50 K, transport is dominated by Mott variable range hopping, from 50-150 K by nearest neighbor hopping, and from 150-290 K by thermionic emission over grain boundaries [47]. However, in their second work on this subject, Tiwari, et al. explain the observed changes in transport behavior in terms of oxygen defects in their films that result from annealing in air [66]. Thus, it is unclear how
applicable the conclusions of the Tiwari, et al. works are with regards to films grown in vacuum environments.

The high reported absorption coefficient is consistent in all studies that report this value, in which it reaches $10^5$ cm$^{-1}$ at <1 eV above the band gap [32–34, 38, 39, 45, 57–59]. However, the reported values for the optical band gap vary widely. Values between 0.83-1.77 eV have been reported, and the nature of the gap has been characterized as direct, direct forbidden, or indirect [32, 35, 41]. However, the characterization of the band gap as direct forbidden or indirect is not consistent with the strong optical absorption reported in most experimental works. Additionally, multiple theoretical works have calculated the electronic density of states (DOS) for Cu$_2$SnS$_3$, as shown below in Figure 4.5, and all concluded that this material has a direct band gap at the Γ-point of 0.84-0.88 eV [31, 61]. In recent years, experimental reports of the band gap have converged to a range of 0.9-1.1 eV.

Several recent works have shown evidence of two optical absorption edges in Cu$_2$SnS$_3$ at 0.92-0.93 eV and 0.99-1.02 eV, as shown in Figure 2.8 [40, 56, 67]. In contrast to the experimental reports of two unique band gaps, all other possible transitions in the calculated DOS are at a significantly higher energy than the direct 0.88 eV Γ-point transition (see Figure 4.5. However, Zhai, et al., note that variations in the Cu/Sn order parameter could cause band gap fluctuations on the order of 0.1 eV; it is possible that these fluctuations are
giving rise to the observation of two band gaps within one Cu$_2$SnS$_3$ sample.

Figure 2.8: Several groups have provided evidence of two optical absorption edges at \( \sim 0.92 \) and \( \sim 1.0 \) eV [56]. This observation may be due to disorder effects which can give rise to fluctuations in the band gap of Cu$_2$SnS$_3$.

### 2.6 Opportunities for future material study of Cu$_2$SnS$_3$

From the prior work on Cu$_2$SnS$_3$ thin films, it is possible to identify several opportunities for future study. At this point, the basic structural and optoelectronic properties of Cu$_2$SnS$_3$ are well established, but much work remains in order to establish an in-depth understanding of device relevant properties. To date, there has been minimal investigation of the minority carrier transport properties in Cu$_2$SnS$_3$. Establishing minority carrier lifetimes and mobilities is critical to understanding the performance of Cu$_2$SnS$_3$ thin films as photovoltaic absorbers. As in all polycrystalline absorbers, focused studies of the grain boundaries (GBs) in Cu$_2$SnS$_3$ films are also necessary for device optimization. Areas of potential research include grain boundary stoichiometry, intrinsic and extrinsic defect behavior at GBs, and carrier transport across GBs.

Additional ideas for materials development can be drawn from the fields of CIGS and CZTSSe. For example, in CIGS, it is found that Na greatly enhances the device performance by changing the electrical potential at the grain boundaries [53].
vice performance by the incorporation of Na into the absorber layer has also been reported, but no studies have explored the changes in material properties resulting from the Na incorporation [56]. In CZTSSe, scientists are only now beginning to understand the detrimental effects of disorder on the material quality, including formation of non-stoichiometric clusters and band tailing. In Cu$_2$SnS$_3$, the effects of disorder on the optoelectronic properties and associated device performance are still poorly understood.

2.7 Cu$_2$SnS$_3$ photovoltaic device integration and performance

The first device using a Cu$_2$SnS$_3$ absorber was reported in 1987, by Kuku, et al. [32], and had an efficiency of 0.11%. Work on this material stagnated until 2012, when a 2.84% device was reported by Koike, et al. [43]. This device used a Cu$_2$SnS$_3$ absorber layer, a CdS buffer layer, and a ZnO:Al window layer. A standard device architecture is shown in Figure 2.9a [47]; typically either CdS or ZnO is used as the n-type heterojunction partner. The current efficiency record for a Cu$_2$SnS$_3$-based device is 4.63%, reported by Nakashima, et al., in 2015 [56]. In 2013, a work by Umehara, et al., reported a 6.0% device using an alloyed Cu$_2$Sn$_{0.83}$Ge$_{0.17}$S$_3$ absorber layer and similar device architecture [23]. As shown in Figure 2.2b, the reported efficiencies for Cu$_2$SnS$_3$-based devices have increased rapidly in recent years.

2.7.1 Cu$_2$SnS$_3$ device performance metrics

The record 4.63% efficient Cu$_2$SnS$_3$ device also exhibits the highest reported short circuit current ($J_{sc}$) and fill factor (FF) values, at 37.3 mA/cm$^2$ and 0.44, respectively. The reported $V_{oc}$ in the Nakashima study was 283 mV; a higher value of 320 mV was reported for a device using an In$_2$S$_3$ buffer layer [41]. Although Tiwari, et al. reported a device with 816 mV open circuit voltage, this value is far too high to be plausible when compared to the rest of the Cu$_2$SnS$_3$ literature. Tiwari, et al. attribute the high $V_{oc}$ to the formation of a Cu$_2$SnS$_3$-ZnS alloy at the Cu$_2$SnS$_3$/ZnO interface; however, this value of 816 mV is still significantly higher than the record for CZTS devices (513 mV) [16, 45]. In general, reported $V_{oc}$ values
range from 182-283 mV. The $J_{sc}$ and FF show significantly larger variations, from 5.8-37.3 mA/cm$^2$ and 0.24-0.44, respectively. When these device performance metrics are compared to the record 12.6% CZTS device ($V_{oc}=513$ mV, $J_{sc}=35.2$ mA/cm$^2$, FF=0.70), it is clear that the main opportunities for higher Cu$_2$SnS$_3$ device efficiencies lie in increasing the $V_{oc}$ and the FF.

### 2.7.2 Characteristics of successful Cu$_2$SnS$_3$-based devices

The majority of studies reporting successful devices use Cu$_2$SnS$_3$ absorbers that are synthesized under Cu-poor conditions [23, 40, 42, 47, 56, 69]. Koike, et al., performed a systematic study of device performance as a function of Cu/Sn ratio, and determined that devices with Cu/(Cu+Sn)$>0.67$ have conversion efficiencies near zero, as shown in Figure 2.9b [43]. The authors of that work attributed the poor performance of the Cu-rich devices to the presence of a Cu$_4$SnS$_4$ secondary phase. However, even slightly Cu-rich samples (e.g., Cu/(Cu+Sn)=0.68) show drastic performance degradation in the study by Koike, et al., without the associated Cu$_4$SnS$_4$ phase in the XRD pattern. In recent device reports, the stoichiometry is extremely Cu-poor, with Cu/(Cu+Sn) values ranging from 0.59-0.65. Although most recent studies use both XRD and Raman to confirm the phase purity of the absorber, it is not possible to reconcile true phase purity with these extremely off-stoichiometry values of Cu/(Cu+Sn) ratio. Since no secondary phases are observed in the XRD patterns or Raman spectra, it is possible that excess Sn is being incorporated as an amorphous phase. Similarly, many studies report a significant excess of S, with S/(Cu+Sn) values ranging from 1.1-1.9 (for stoichiometric Cu$_2$SnS$_3$, S/(Cu+Sn)=1), and it is unclear how this excess S is being accommodated.

Another characteristic of successful Cu$_2$SnS$_3$ devices is the incorporation of an annealing step during the absorber growth process. In most cases, sequential layers of Cu, Sn, and sometimes S are deposited by methods such as electron beam evaporation, electroplating, sputtering, or evaporation. Then, the films are annealed under a S, H$_2$S, or Sn/S atmosphere at temperatures in the range of 400-600°C. This typically results in the monoclinic crystal
structure (with a few reports of a cubic structure), and grain sizes on the order of 500 nm - 2 µm. The annealing step typically results in larger grain sizes than processes that do not involve anneals, and this improved morphology is likely an important contributor to the improved device efficiency. An example of this is shown below in Figure 2.10.

2.7.3 Current deficiencies in Cu$_2$SnS$_3$ device understanding

The record device efficiency papers are illustrative of a larger dearth of scientific understanding in the field. The 2015 Nakashima, et al. paper demonstrates the record 4.63% efficiency by incorporating NaF at a 7.5% NaF/Cu mole ratio. The control device in this study (no NaF) shows only slightly above 1% efficiency. There is no concurrent discussion of the effects of NaF on the electronic properties of the device, nor is any explanation offered for the variations in $V_{oc}$, $J_{sc}$ and efficiency at NaF/Cu values of 0-12%, as shown in Figure 2.11. The authors do state that Na incorporation in CIGS has been shown to increase carrier concentration and $V_{oc}$, and state that similar results were observed in their study. However, no data for this is provided, and the device performance metrics do not follow any clear trend with increasing NaF/Cu mole ratio. From the previous literature, it is evident that too low carrier concentration is not typically an issue found in Cu$_2$SnS$_3$. Furthermore,
Figure 2.10: Example of morphology improvement after annealing in an S atmosphere. Device efficiencies improved from 0% (un-annealed) to 3.66% after annealing [69].
the inclusion of NaF serves to actually decrease the grain size, making the increase in device efficiency even more surprising.

![Device performance trends as functions of NaF/Cu ratio from [56]. Little scientific explanation is provided for these trends.](image)

Figure 2.11: Device performance trends as functions of NaF/Cu ratio from [56]. Little scientific explanation is provided for these trends.

The 2013 Umehara, et al. work that reported 6% efficiency using a Cu$_2$Sn$_{0.83}$Ge$_{0.17}$S$_3$ absorber also provides little interpretation of the science behind this result. Although the authors of this study claim that the efficiency increase is due to an increase in band gap due to alloying, it is unlikely that this is actually the case. Moving from a Cu$_2$SnS$_3$ absorber (from the same work) to a Cu$_2$Sn$_{0.83}$Ge$_{0.17}$S$_3$ absorber afforded an increase in efficiency from 2.13% to 6.0%, with a band gap increase of only 0.1 eV (0.93 to 1.02 eV) [23]. Moreover, the morphologies of the Cu$_2$SnS$_3$ and the Cu$_2$Sn$_{0.83}$Ge$_{0.17}$S$_3$ films differ significantly, with the Ge-alloyed film showing significantly larger grain sizes. Because transport properties such as electrical conductivity or carrier mobility were not reported in this study, it is difficult
to definitively state that the efficiency increase was due to improved carrier transport, but this seems a more likely explanation than the 0.1 eV band gap increase. Further, when the plot of incident photon to current conversion efficiency (IPCE) is examined (Figure 2.12), it is clear that the two curves for Cu$_2$SnS$_3$ and Cu$_2$Sn$_{0.83}$Ge$_{0.17}$S$_3$ differ significantly in the 300-500 nm range. If an identical CdS (E$_g$=2.4 eV / 517 nm) buffer layer was used in both devices, the IPCE spectra should be identical below 500 nm; the clear differences indicate that the buffer layer varied between the Cu$_2$SnS$_3$ and Cu$_2$Sn$_{0.83}$Ge$_{0.17}$S$_3$ devices.

Figure 2.12: Differences in the incident photon to current conversion efficiency (IPCE) between devices with Cu$_2$SnS$_3$ and Cu$_2$Sn$_{0.83}$Ge$_{0.17}$S$_3$ suggest discrepancies in the device stacks [23].

2.8 Opportunities for future improvement of Cu$_2$SnS$_3$-based photovoltaics

Overall, the device data suggests a limited understanding of the fundamental physics of Cu$_2$SnS$_3$. Papers reporting device efficiencies rarely report electronic transport properties, such as carrier concentration or mobility. A few device studies report carrier concentrations in the range of $3\cdot10^{18}$ - $8\cdot10^{19}$ cm$^{-3}$, and mobility values of 0.4-0.5 cm$^2$/Vs. These carrier concentrations are significantly higher than the desired value for device-quality material. Additionally, the extreme off-stoichiometry of some of the highest efficiency devices indicates that there is some influence of secondary phases on the device performance. The
lack of analysis on how these properties correlate with device performance metrics such as efficiency, $V_{oc}$, and $J_{sc}$ makes it difficult to determine the best path forward towards higher efficiency devices. In order to develop strategies for further device development, significant materials characterization of successful devices will be necessary to understand what fundamental material properties are ultimately responsible for improving $\text{Cu}_2\text{SnS}_3$ device efficiency. More in-depth device characterization, such as device testing at different temperatures or illumination conditions, could also help shed light on the current performance limitations.

There has also been minimal optimization of buffer and window layers for $\text{Cu}_2\text{SnS}_3$ devices. The majority of reported devices use a CdS buffer layer, and a ZnO:Ga or ZnO:Al window layer; however, these materials are chosen only because they have proven successful in CZTSSe devices. Future device design would benefit from the determination of the energy levels in $\text{Cu}_2\text{SnS}_3$, which would allow for the buffer and window layers to be chosen for optimized band alignment. A recent work used photoelectron spectroscopy to analyze a $\text{Cu}_2\text{SnS}_3$/Al:ZnO heterojunction, and found that the conduction band minimum (CBM) of the Al:ZnO was 0.9 eV higher than the CBM of $\text{Cu}_2\text{SnS}_3$ [70]. When the position of the conduction band edges of Al:ZnO and CdS are considered, this indicates that the CBM of CdS may also be higher than the CBM of $\text{Cu}_2\text{SnS}_3$, which ultimately reduces device performance. This suggests that further interface studies of $\text{Cu}_2\text{SnS}_3$ are warranted and could likely contribute to higher efficiency devices.
CHAPTER 3
EXPERIMENTAL METHODS

This chapter will outline the general methodology used to perform the research in this thesis. For specific experimental details, see the Methods sections of Chapters 4, 5, 6 and 7.

3.1 Combinatorial materials synthesis

Combinatorial materials development is a unique method for rapid investigation of materials systems. In the most general sense, combinatorial synthesis is the simultaneous synthesis of multiple samples with different chemical compositions, deposition temperatures, or reactant activity [71–73]. For a continuous chemical composition gradient, the source positions relative to the substrate, as well as the source fluxes, are designed to give the desired compositional spread (Figure 3.1). Orthogonal to this, a specially designed heater mount can be used to induce a temperature gradient across the sample. This design is shown in Figure 3.2 [21]. The specific design used in our system allows for a nonlinear temperature gradient of about 100°C.

![Figure 3.1: Combinatorial materials development involves the growth of intentionally graded samples, which are then automatically mapped to determine their physical properties. High throughput data analysis techniques are required to process the large amounts of mapping data.](image)

28
3.2 Thin film deposition

We chose sputtering as the growth technique for our Cu$_2$SnS$_3$ thin films. In the most general sense, sputtering accelerates ionized atoms into a surface, resulting in the ejection of atoms from that surface. These ejected atoms condense onto a substrate to form a thin film. Sputtering is widely used for semiconductor research and development, and has many advantages over other film deposition methods such as evaporation or chemical vapor deposition (CVD). The flux produced by sputtering has a high surface mobility on the substrate, resulting in smooth and dense films [74]. Unlike evaporation or CVD, sputtering preserves the stoichiometry of the targets, which can allow for better phase control [74].

RF magnetron sputtering was chosen because it provides several technological advantages over other types of sputtering, such as DC sputtering. The use of an alternating current radio frequency (AC RF) source results in higher levels of gas ionization as compared to a direct current (DC) source [74]. The AC RF power couples to electron motion in the plasma, which results in longer electron residence times in the plasma and higher plasma densities. Additionally, RF plasmas can sputter insulating materials, which cannot be achieved with a DC plasma. The use of magnetron sources further increases the electron residence time in the plasma and the plasma density. This results in fast deposition rates [74].
The radio-frequency (RF) sputtering depositions were performed from 50 mm diameter Cu$_2$S and SnS$_2$ targets in $3 \times 10^{-3}$ torr of Ar in a chamber with a base pressure of less than $10^{-6}$ torr. Films were deposited onto 50×50 mm Eagle-XG glass substrates heated to 275-325°C, located 10 cm from the targets. Gun powers between 25-50 W and the gun angle of ~25 degrees with respect to the normal to the substrate were used to provide the desired chemical compositional spread across the substrates. Typical film deposition times were 2-3 hrs, which resulted in film thicknesses from 500-1000 nm. An RF solids cracker (RFK30, Oxford Applied Research) filled with S powder (99.98%, Aldrich) was used to provide additional S flux for some samples.

### 3.3 Annealing of Cu$_2$SnS$_3$ films

We investigated a variety of annealing conditions to determine their effects on the transport properties of Cu$_2$SnS$_3$. Our experimental set up allowed us to easily vary the annealing temperature, atmosphere, and duration. Each of these parameters was investigated independently to determine the effects on the carrier concentration. A diagram of the annealing set up is shown in Figure 3.3.

![Figure 3.3: Schematic of the annealing set up. The thermocouple is suspended approximately 2 cm above the sample. The argon is maintained at a constant flow rate, leading to an approximately atmospheric pressure inside the quartz tube.](image)

SnS powder was synthesized using Sn (Alfa Aesar, 99.9%) and S (Alfa Aesar, 99.5+%%) powders in a stoichiometric ratio. The reactants were sealed under static vacuum (<5 mTorr) in a quartz ampoule, heated to 400°C, and held for 10 hrs. Then, the reactants were heated to 900°C and held for 18 hrs, before cooling to room temperature. This resulted in a phase pure SnS powder. The SnS$_2$ powder was synthesized by ball-milling the SnS powder with
excess S for 2 hrs in a SPEX 8000D Mixer/Mill. The ball milled mixture was sealed in a quartz ampoule under static vacuum and held at 425°C for 18-24 hrs, resulting in a phase pure SnS₂ powder.

3.4 Combinatorial materials characterization

The combinatorial libraries are characterized using automated measurement techniques (Figure 3.1). For each technique, the samples are mapped in a 4x11 grid, for a total of 44 samples on each substrate. This configuration was chosen because of the spot size of the XRD measurement, which is rectangular and is the largest spot size of any mapping instrument. Current mapping capabilities at NREL include X-ray diffraction (XRD), X-ray fluorescence (XRF), Raman spectroscopy, atomic force microscopy (AFM), electrical conductivity (4 pont probe), optical transmittance and reflectance (UV/Vis/NIR), Fourier transform infrared spectroscopy (FTIR), and photoluminescence (PL). High throughput analysis techniques are required to match the pace of data generation from the combinatorial synthesis and characterization. Custom software packages in Igor PRO have been created to analyze the spatially resolved data sets (Figure 3.1).

X-ray fluorescence spectra were collected using a System-SMX instrument and analyzed using MTF-FP software to obtain both the Cu/Sn ratios and the thickness of the films. The XRD patterns were collected using Cu K-α radiation and a proportional 2D detector (Bruker D8 Discover with General Area Detector Diffraction System software). Raman spectra were collected using a Renishaw inVia confocal Raman microscope configured with 532 nm laser excitation at 5% power, an 1800 mm⁻¹ grating and CCD array detector. To compensate for the small spot size of the Raman measurement (~10 μm), six measurements were taken on each sample and averaged to provide a final spectrum. The sheet resistance was measured using a collinear four point probe with 1 mm distance between probes. Optical transmittance and reflectance were mapped from 300-1700 nm using a fiber-optics-based spectrometer with deuterium (DT1000 CE UV/Vis, Analytical Instrument Systems, Inc.) and tungsten/halogen (LS-1, Ocean Optics) light sources and Si and InGaAs detector arrays.
The absorption coefficient was calculated from the measured reflectance (R) and transmittance (T) spectra, and the measured film thickness (d) from the XRF, using the relationship $\alpha = -\ln\left[\frac{T}{1-R}\right]/d$.

### 3.5 Advanced materials characterization

Some advanced optoelectronic measurements were carried out in a non-combinatorial fashion. Room temperature Hall effect measurements (BioRad HL5500 PC) were used to determine carrier concentration and majority carrier mobility; the p-type electrical conduction was confirmed by measuring the Seebeck coefficient on a homebuilt system. The acceptor activation energy was determined by measuring temperature dependent Hall effect (BioRad HL5500 PC) between 200-350 K. The work function was determined using a Kelvin-probe (SKP SPV LE 450, KP Technology) with a 1 mm diameter gold-coated probe. The Kelvin-probe system was calibrated before and after performing measurements using Au and Al standards with reference work functions of 5.1 and 4.1 eV, respectively. Near-edge X-ray absorption fine structure spectroscopy (NEXAFS) was used to probe the oxidation state of Cu in the Cu$_2$SnS$_3$ samples, and was performed at the Stanford Synchrotron Radiation Lightsource by Dennis Nordland and Steven Christensen (see Methods section of Ch. 5 for full details). Optical pump terahertz probe spectroscopy (OPTP) was used to investigate the minority carrier transport, including carrier lifetime and mobility. This work was performed at Helmholtz Zentrum Berlin; experiments were conducted by Hannes Hempel, with guidance from Rainer Eichberger and Thomas Unold (see Methods section of Ch. 6 for full details).

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to evaluate the structure and morphology of our Cu$_2$SnS$_3$ films. SEM was performed at the Colorado School of Mines using a JEOL JSM7000F field emission SEM, and at NREL using a Nova NanoSEM with 3 kV accelerating voltage and 0.64 nA current. Transmission electron microscopy (TEM) cross-section samples were prepared using a conventional focussed ion beam (FIB) lift out technique and examined at 300 kV in an FEI Tecnai G2 30
3.6 Photovoltaic device fabrication

The baseline devices are fabricated in a “substrate” configuration, as shown in Figure 3.4 [75]. A molybdenum back contact is evaporated onto a soda lime glass substrate. The p-type absorber layer of the device is then grown directly on top of the Mo layer (in Figure 3.4, the absorber shown is CuSbS$_2$, but the rest of the device structure is the same). Approximately 50 nm of CdS is deposited as an n-type heterojunction partner using chemical bath deposition [76]. A thin (∼50nm) layer of intrinsic ZnO is sputtered onto the CdS, followed by an Al-doped ZnO transparent conducting oxide. Finally, the front contact is sputtered through a shadow mask to create a pattern of Al pads and fingers for contacting the device, and to enhance current collection, respectively. Devices are isolated by mechanical scribing.

![Figure 3.4: Schematic showing the layers used to fabricate photovoltaic devices with our Cu$_2$SnS$_3$ absorbers (figure shows a CuSbS$_2$ absorber) [75].](image)

3.7 Photovoltaic device characterization

The current-voltage behavior of prototype devices were tested under one sun illumination using an automated mapping solar simulator. The lamp intensity was calibrated using a Si reference cell. The bias voltage was swept from -0.5 to 1.0 V, and the current measured. The
area of the device (0.44 cm$^2$) was used to calculate the current density. Because of the difficulties of integrating Cu$_2$SnS$_3$ films into photovoltaic devices, extensive device characterization was not performed.
CHAPTER 4
EVALUATION OF PHOTOVOLTAIC MATERIALS WITHIN THE CU-SN-S FAMILY & DOWN-SELECTION TO CU$_2$SNS$_3$


Pawel Zawadzki$^1$, Lauryn L. Baranowski$^{1,2}$, Haowei Peng$^1$, Eric S. Toberer$^{1,2}$, David S. Ginley$^1$, William Tumas$^1$, Andriy Zakutayev$^1$ and Stephan Lany$^1$

$^1$National Renewable Energy Laboratory, Golden, CO 80401  $^2$Physics Department, Colorado School of Mines, Golden, CO 80401

4.1 Abstract

Next-generation thin film solar cell technologies require earth abundant photovoltaic absorber materials. Here we demonstrate an alternative approach to design of such materials, evaluating candidates grouped by constituent elements rather than underlying crystal structures. As an example, we evaluate the thermodynamic stability, electrical transport, electronic structure, and optical and defect properties of Cu-Sn-S candidates using complementary theory and experiment. We conclude that Cu$_2$SnS$_3$ avoids many issues associated with the properties of Cu$_4$SnS$_4$, Cu$_4$Sn$_7$S$_{16}$, and other Cu-Sn-S materials. This example demonstrates how this element-specific approach quickly identifies potential problems with less promising candidates and helps focusing on the more promising solar cell absorbers.

4.2 Introduction

Thin film photovoltaics such as Cu(In,Ga)Se$_2$ and CdTe have achieved efficiencies over 20% and have penetrated commercial PV markets [9, 10]. However, the ultimate scalability of these technologies is limited by their use of rare and/or toxic elements, including In, Te, and Cd [1]. To enable commercial photovoltaic installations on the terawatt scale,
researchers must look to materials that are composed solely of earth abundant and nontoxic elements. Thus far, the main strategy for this has been to replace rare elements with more earth abundant alternatives without significantly altering the atomic or electronic structures. This strategy has led to the development of Cu$_2$ZnSn(S,Se)$_4$ (based on Cu(In,Ga)Se$_2$), which has now surpassed 12% efficiency [16]. However, further optimization of this material may be difficult, because of the complexity inherent in compounds incorporating four or more elements [17].

In this work, we propose an alternative approach to discovering new earth abundant solar absorbers, which we refer to as an “element-specific” approach (rather than the “structure-specific” approach described above). We choose to focus on ternary materials, which offer more tunability than a binary, but avoid the complexity issues seen in multinary compounds such as CZTSSe. In our element-specific approach, we select three elements and consider all reported ternary compounds made from these three elements. Theory and experiment are used to assess the promise of each compound as a photovoltaic absorber, by considering photovoltaic relevant properties such as chemical stability, defect formation energies, electronic transport, and optical absorption.

We select the Cu-Sn-S family of compounds as a model system to illustrate our approach. We find that Cu$_2$SnS$_3$ is the most promising absorber material in the Cu-Sn-S system. Other compounds, such as Cu$_4$SnS$_4$ and Cu$_4$Sn$_7$S$_{16}$ suffer from issues such as high carrier concentrations, poor electronic transport, and weak optical absorption. Our finding is consistent with current results from Cu$_2$SnS$_3$ and Cu$_2$(Sn,Ge)S$_3$-based devices, which have achieved efficiencies of 4% and 6%, respectively [23, 56].

4.3 Methods

Density functional theory with onsite Coulomb potential (DFT+U) calculations were performed with Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional within the projector augmented wave (PAW) formalism [77] as implemented in the VASP code [78]. An effective on-site potential $U=5$ eV was applied to Cu d states [79]. The fitted elemen-
tal reference energies (FERE) [80, 81] were used for the calculation of the thermodynamic stability, which improves the accuracy of the calculated compound formation enthalpies to about 50 meV/atom [81]. Band gaps were calculated within GW approximation [82] following the approach of Ref. [83], where the DFT+U wavefunctions are maintained, but the eigenenergies are iterated to self-consistency. In order to compensate for the overestimated d-orbital energies in GW an onsite d-state potential of $V_d=2.8$ eV was applied to the Cu-d states [83]. This setting reproduces well the band gaps of the related chalcopyrites, e.g., CuGaS$_2$ and CuInS$_2$. (Note that uncertainties in the order of 0.2 eV in the predicted band gap energies remain even for main group compounds and somewhat larger uncertainties should be expected for electronically more complex transition metal compounds [83].) The optical absorption spectra were calculated from the GW dielectric function in the independent particle approximation. Defect calculations for copper vacancies were performed using supercells of about 100 atoms. Since defect formation energies are critically dependent on proper positioning of band edges [84] we used the valence band maximum and conduction band minimum values from GW calculations for the defect calculations. Electrostatic image charge and band filling corrections were applied to account for finite size effects [85]. The charge self-trapping energy was calculated using the methodology described in Ref. [86].

Thin films were synthesized using a high-throughput combinatorial approach, in which (a) an intentional and controlled spatial gradient of chemical composition is created across the substrate, (b) resulting sample libraries are characterized with spatial resolution, and (c) the data is semiautomatically analyzed [87]. In this study, the Cu-Sn-S thin films were deposited using angled co-sputtering from 50 mm diameter Cu$_2$S and SnS$_2$ targets on 50×50 mm stationary non-rotated glass substrates [88]. The cation compositional gradients were controlled by both changing the relative Cu$_2$S/SnS$_2$ power ratio and the substrate temperature (50/50W and 475°C for Cu-poor, 50/25W and 500°C for Cu-rich) [88]. Each of the resulting combinatorial libraries was automatically mapped at 44 points (4x11 grid) to find the properties of the material as a function of chemical composition [72]. The samples were
characterized using X-ray fluorescence (XRF) to determine the film thickness and Cu/Sn ratio, X-ray diffraction (XRD) to determine the phases present and their crystal structures, optical transmittance and reflectance, and a four point probe technique to determine sheet resistance. The resulting experimental data were analyzed using custom user functions written in the Igor PRO software package. For this analysis, the measured thickness-dependent optical and electrical properties were combined with film thickness from XRF to obtain thickness independent absorption coefficient and conductivity values. These thickness independent properties were correlated with cation ratios and crystal structures. See supplementary material for more details on computations and experiments.

4.4 Results and discussion

![Figure 4.1: There are many reported ternary phases in the Cu-Sn-S system. We perform an initial down-selection by considering the oxidation state of Cu in these compounds: +2 (in red), mixed +1/+2 (in blue), and +1 (in green).](image)

There are a large number reported phases in the Cu-Sn-S ternary system, as shown in Figure 4.1. We began our down-selection by considering the formal oxidation state of Cu in these compounds: +2 (in red), mixed +1/+2 (in blue), and +1 (in green).

There are a large number reported phases in the Cu-Sn-S ternary system, as shown in Figure 4.1. We began our down-selection by considering the formal oxidation state of Cu (+1 and/or +2) in each compound. One compound, Cu$_4$SnS$_6$, has Cu exclusively in the +2 oxidation state, and has been reported to be metallic. Several compounds, including Cu$_{10}$Sn$_2$S$_{13}$, Cu$_3$SnS$_4$, and Cu$_5$Sn$_2$S$_7$, have Cu in a mixed valence state (+1 and +2), which is likely to lead to either an extremely high hole density ($\sim 10^{22}$ cm$^{-3}$), or hole trapping. Thus, our first down-selection restricts us to four compounds in which Cu is found only in the +1
oxidation state: Cu$_4$Sn$_4$, Cu$_2$SnS$_3$, Cu$_4$Sn$_7$S$_{16}$, and Cu$_4$Sn$_{15}$S$_{32}$. These compounds can all be placed on the tie line between Cu$_2$S and SnS$_2$, as shown in Figure 4.2. In this pseudobinary phase diagram, we note that Cu$_2$SnS$_3$ and Cu$_4$SnS$_4$ are shown as line compounds, while Cu$_4$Sn$_7$S$_{16}$ spans a finite compositional range, especially at elevated temperatures. In the following sections, we use experiment and theory to assess these candidate compounds with regards to photovoltaic relevant properties, including the phase stability, defect properties, electronic structure, and optical properties.

Figure 4.2: The ternary Cu-Sn-S compounds of interest can all be found on the Cu$_2$S-SnS$_2$ tie line. Two of the compounds (Cu$_2$SnS$_3$ and Cu$_4$SnS$_4$) are line compounds, whereas Cu$_4$Sn$_7$S$_{16}$ is reported to be stable over a range of compositions. Adapted from Ref. [33].

4.4.1 Experimental exploration of Cu-Sn-S phases

We synthesized two experimental libraries with Cu/(Cu+Sn) contents ranging from 0.5-1.0. Changes in the Cu/(Cu+Sn) ratio resulted from changing relative sputtering powers on the Cu$_2$S and SnS$_2$ targets, and by changing the deposition temperature. With increasing Cu content, the observed phase assemblage changes from two-phase SnS/Cu$_2$SnS$_3$ to cubic Cu$_2$SnS$_3$, then through Cu$_2$SnS$_3$/Cu$_4$SnS$_4$ to Cu$_4$SnS$_4$, and finally through Cu$_4$SnS$_4$/Cu$_2$S to Cu$_2$S. Note that the phase pure cubic Cu$_2$SnS$_3$ is formed at more Sn-rich composition [0.52<x(Cu)<0.62] than expected [x(Cu)=0.67], which may be caused by a systematic error of the XRF measurements (up to 5% for Sn-containing compounds). At the composition
expected to produce phase pure Cu$_4$Sn$_4$ [x(Cu)=0.80], no Cu$_2$Sn$_3$ or Cu$_2$S secondary phases were present according to XRD. We have not detected Cu$_4$Sn$_7$S$_{16}$ or Cu$_4$Sn$_{15}$S$_{32}$ in the deposited films, most likely because the sputter deposition was performed in S-poor environment (Ar gas only), whereas the theoretical phase diagram (Figure 4.4) shows that these materials should be stable in S-rich conditions. Nevertheless, we include Cu$_4$Sn$_7$S$_{16}$ in further analysis, as it has been reported stable below 500°C in Ref. [33].

![Graphs showing structural, electrical, and optical properties of Cu-Sn-S system](image)

**Figure 4.3:** Experimentally determined composition dependence of (a) structural (XRD), (b) electrical, and (c) optical properties of the Cu-Sn-S system. Vertical dashed lines indicate Cu$_2$Sn$_3$ and Cu$_4$Sn$_4$ nominal compositions.

The experimental results for Cu-Sn-S materials (Figure 4.3b) show large changes in electrical conductivity of nearly three orders of magnitude across the composition range of Cu/(Cu+Sn)=0.5-1.0. In the cubic Cu$_2$Sn$_3$ phase, the electrical conductivity ranges between 0.03 and 0.5 S/cm. Increasing Cu content causes an increase in electrical conductivity: the Cu$_4$Sn$_4$ phase shows intermediate values of conductivity (∼3 S/cm), and the Cu$_2$S phase
has the highest electrical conductivity (~20 S/cm). For the most part, we attribute large differences in conductivity of Cu-Sn-S materials to variations in hole density rather than hole mobility, because 2-3 orders of magnitude changes in mobility are unlikely for chemically related materials deposited under similar conditions. This trend and its explanation are consistent with the theoretically calculated differences in defect formation energies. We also note that the high conductivity of Cu$_4$SnS$_4$ suggests that this material as a photovoltaic absorber may face problems similar to those in Cu$_2$S [89].

Concurrent with our theory of high hole density in Cu$_4$SnS$_4$, the optical absorption spectrum shows significant sub-band edge absorption (theoretical $E_g$=0.84 eV), which could be due to free carrier absorption. Conversely, the apparent absorption edge for Cu$_2$SnS$_3$ at 0.9 eV matches well with the theoretical band gap of 0.68 eV.

### 4.4.2 Theoretical evaluation of Cu-Sn-S candidate materials

The first theoretical metric on which our four candidate compounds were assessed was phase stability. To compare the relative stability windows of these compounds, we calculated the Cu-Sn-S chemical potential phase space, as shown in Figure 4.4. In this type of phase space, a larger area indicates a more stable compound. We see that Cu$_2$SnS$_3$ and Cu$_3$SnS$_4$ are by far the most stable ternary compounds in the Cu-Sn-S phase space; Cu$_4$SnS$_4$ and Cu$_3$Sn$_7$S$_{16}$ have only narrow regions of stability. The other candidate compound, Cu$_4$Sn$_{15}$S$_{32}$ was found to be marginally unstable with respect to Cu$_2$SnS$_3$ and SnS$_2$, and is thus is not present on this diagram. We note that the metallic, mixed Cu valence, Cu$_3$SnS$_4$ has a cubic zinc blende structure similar to that of Cu$_2$SnS$_3$, which may make identification of this impurity phase difficult (spoiler alert!).

We next consider the electronic structure of Cu$_4$SnS$_4$, Cu$_2$SnS$_3$, and Cu$_4$Sn$_7$S$_{16}$, by calculating the electronic density of states (DOS). Besides giving information about the electronic band gap of the compound in question, the DOS can also inform us about the formation energies of defects within the material. In Cu-based chalcogenide materials such as CIGS, the Cu vacancy ($V_{Cu}$) is the most common acceptor defect which controls the level of p-type...
Figure 4.4: Calculated chemical potential phase space of Cu-Sn-S system. $\Delta \mu$ measures the atomic chemical potentials relative to the respective elemental phase. The wider bars indicate the location of the Cu$_4$SnS$_4$ and Cu$_4$Sn$_7$S$_{16}$ phases, which are marginally stable and marginally unstable, respectively. The dashed line indicates the upper bound $\Delta \mu_S = 0.46$ eV for the sulfur chemical potential in the present deposition method, i.e., only compounds to the right and above of the dashed line were observed in experiment.

doping. The presence of these defects is necessary to create a sufficiently doped material such that a p-n junction can be formed. However, if the formation energy of $V_{Cu}$ is too low, then the hole densities will be degenerate, or high numbers of compensating donor defects will form, resulting in potentially harmful gap states.

The formation energy of $V_{Cu}$ in each material can be evaluated by considering the Fermi level pinning energy, $E_{F}^{\text{pin}}$, which is defined as the Fermi level at which the defect formation energy becomes zero. In practice, $E_{F}^{\text{pin}}$ is an energy range, rather than a specific energy, because the defect formation energies depend on the chemical potentials of the constituent elements. In Figure 4.5, the Fermi level pinning region is shown in grey. In Cu$_4$Sn$_7$S$_{16}$, this region is located entirely within the band gap (edges of which are shown by the black dashed lines), indicating a high probability that the negative effects mentioned above will be observed in this compound. Although not as pronounced, this effect can also be seen in Cu$_4$SnS$_4$. In Cu$_2$SnS$_3$, $E_{F}^{\text{pin}}$ lies well into the conduction band, avoiding any pinning effects, even if alloying with Si or Ge is used to increase the band gap (alloying with these elements is expected to raise the conduction band edge). When the absolute $V_{Cu}$ formation energies are considered, we would expect Cu$_2$SnS$_3$ to have a hole concentration in the range of $10^{15}$

42
- $10^{18}$ cm$^{-3}$, a suitable range for a photovoltaic material.

One other notable feature of the DOS is the extremely high density of states at the valence band edge in Cu$_4$Sn$_7$S$_{16}$ as compared to the other two compounds. This narrow band, which results from the octahedral coordination of Cu in this compound, is likely to lead to a high effective mass and suggests that Cu$_4$Sn$_7$S$_{16}$ may be prone to hole self-trapping. This result suggests the likelihood of poor hole transport in this compound, including increased recombination rates and short carrier lifetimes.

![Figure 4.5](image)

Figure 4.5: Left panels: Volume-normalized calculated density of states and its projections onto atomic orbitals. Black dashed lines indicate valence and conduction band edges; shaded areas denote the range between the maximum (Cu-rich) and the minimum (Cu-poor) energies where Fermi level will be pinned due to spontaneous formation of Cu vacancies. Right panels: Local coordination of Cu atoms within 3 Å.

Lastly, we compute the optical absorption spectra for our three candidate compounds, as shown in Figure 4.6. The absorption spectra of Cu$_2$SnS$_3$ and Cu$_4$SnS$_4$ are similar, with both having direct band gaps (0.68 eV and 0.84 eV, respectively) and high absorption coefficients
that reach $10^5 \text{ cm}^{-1}$ at about 1.0 eV above the band gap. Cu$_4$Sn$_7$S$_{16}$ is calculated to have an indirect band gap at 1.23 eV, with the direct band gap only slightly higher in energy at 1.27 eV. However, the overall absorption coefficient remains low, even at high energies.

![Figure 4.6: Calculated optical absorption spectra for Cu$_4$SnS$_4$, Cu$_2$SnS$_3$, and Cu$_4$Sn$_7$S$_{16}$. Vertical dashed lines denote quasi-particle band gaps.](image)

4.5 Conclusions

In this work, we used theory and experiment to assess the potential of several Cu-Sn-S compounds as photovoltaic absorbers. Of the compounds evaluated, we conclude that Cu$_2$SnS$_3$ is the most promising solar absorber material. This compound is predicted to have a wide stability range, and this prediction is confirmed by experiment. Cu$_2$SnS$_3$ is also expected to avoid any Fermi level pinning and to have tunable doping in the range of $10^{15}$-$10^{18} \text{ cm}^{-3}$. The theoretical band gap is direct, if slightly lower than ideal at 0.68 eV, and we experimentally observe strong optical absorption above 0.9 eV. Our other candidate compounds suffer from serious flaws that preclude them from being successful photovoltaic absorbers, including too high experimental conductivity (Cu$_4$SnS$_4$), or poor hole transport and low absorption coefficient (Cu$_4$Sn$_7$S$_{16}$).

The example of Cu-Sn-S materials family presented in this work demonstrates an alternative element-specific (rather than structure-specific) way to search for earth abundant solar
cell absorbers. The results of our comparative study of ternary Cu-Sn-S materials family clearly suggests that Cu$_2$SnS$_3$ is the best candidate material for solar absorber applications and points out to potential problems with other members of this family such as too high electrical conductivity in Cu$_4$SnS$_4$ or poor hole mobility and Fermi level pinning in Cu$_4$Sn$_7$S$_{16}$. Thus, the present work has generated a clear understanding of the most critical issues in the individual Cu-Sn-S compounds, which forms the basis for further optimization of the PV materials in this composition space. Overall, the alternative element-specific approach exemplified in this work by Cu-Sn-S materials holds a promise to accelerate the development of photovoltaic technologies in the future.
Chapter 5

Control of Doping in Cu$_2$SnS$_3$ Through Defects and Alloying


Lauryn L. Baranowski$^{1,2}$, Pawel Zawadzki$^1$, Steven Christensen$^1$, Dennis Nordland$^3$, Stephan Lany$^1$, Adele C. Tamboli$^1$, Lynn Gedvilas$^1$, David S. Ginley$^1$, William Tumas$^1$, Eric S. Toberer$^{1,2}$ and Andriy Zakutayev$^1$

$^1$National Renewable Energy Laboratory, Golden, CO 80401  $^2$Physics Department, Colorado School of Mines, Golden, CO 80401  $^3$Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, CA 94023

5.1 Abstract

As the world’s demand for energy grows, the search for cost competitive and earth abundant thin film photovoltaic absorbers is becoming increasingly important. A promising approach to tackle this challenge is through thin film photovoltaics made of elements that are abundant in the Earth’s crust. In this work, we focus on Cu$_2$SnS$_3$, a promising earth abundant absorber material. Recent publications have presented 3% and 6% device efficiencies using Cu$_2$SnS$_3$ based absorber materials and alloys, respectively. However, little is understood about the fundamental defect and doping physics of this material, which is needed for further improvements in device performance. Here, we identify the origins of the changes in doping in sputtered cubic Cu$_2$SnS$_3$ thin films using combinatorial experiments and first-principles theory. As expected, high S chemical potential during deposition decreases the enthalpy of formation of Cu vacancies, which are the dominant acceptor defect in Cu$_2$SnS$_3$. Unexpectedly, under Cu-rich conditions, alloying with an isostructural metallic
Cu$_3$SnS$_4$ phase occurs, causing high levels of p-type doping. Both of these effects lead to undesirably high electrical conductivity, thus Cu$_2$SnS$_3$ films must be grown both S- and Cu-poor in order to achieve moderate hole concentrations. These new insights enable the design of growth processes that target the desired carrier concentrations for solar cell fabrication. Using the strategies described above, we have been able to tune the carrier concentration over 3 orders of magnitude, and achieve films with p-type doping of $\leq 10^{18}$ cm$^{-3}$.

5.2 Introduction

The development of earth-abundant photovoltaic materials is critical if photovoltaics are to supply a significant fraction of the world’s energy needs. Photovoltaic cells using Cu$_2$S absorber layers have been demonstrated to have efficiencies up to 10%, however, these devices have also proven to be extremely unstable due to Cu vacancy migration [50]. In the Cu-Se system, stabilization can be achieved by adding a third element (e.g., CuInSe$_2$ or CuGaSe$_2$), which has led to the development of $>20\%$ efficient CuIn$_{1-x}$Ga$_x$Se$_2$ absorbers [91]. It is expected that a similar stabilization effect should occur when a third element is added to the Cu-S system. For example, in the Cu-Sn-S system several ternary compounds have previously been investigated as candidates for photovoltaic absorbers, including Cu$_2$SnS$_3$, Cu$_3$SnS$_4$, Cu$_4$Sn$_3$S$_7$, Cu$_2$Sn$_3$S$_7$, and Cu$_5$Sn$_2$S$_7$ [23, 32–47]. However Cu$_2$SnS$_3$ is the only phase in this ternary system that has been demonstrated in a photovoltaic device [23, 40–43, 47]. Recent computations by GW methods confirmed by experiments suggests that Cu$_2$SnS$_3$ is the most promising compound in the Cu-Sn-S system because of its wide stability range and lack of Fermi level pinning [55]. Theory has also been used to assess several other ternary Cu-Sn-S compounds and found that they suffered problems such as too high electrical conductivity (Cu$_4$Sn$_3$S$_4$) or poor hole mobility and Fermi level pinning (Cu$_4$Sn$_7$S$_{16}$) [55]. Although Cu$_2$SnS$_3$ is the most studied phase in the ternary Cu-Sn-S system, there is still a lack of knowledge about what controls the doping in this material, which is critical to further progress in device development.
A variety of techniques have been reported for the synthesis of Cu$_2$SnS$_3$ thin films, although sulphurization of Cu/Sn metal layers and solution processing techniques dominate the literature [23, 34–40, 42, 43, 47]. The crystal structure (triclinic, tetragonal, cubic, and monoclinic) of the Cu$_2$SnS$_3$ films is strongly influenced by synthesis temperature. The experimental optical band gap is reported to be direct in the 0.93-1.35 eV range depending on the structure. For all the structures, the absorption coefficient slightly above the bandgap is measured to be 10$^4$-10$^5$ cm$^{-1}$ [36, 45, 59]. Reports of the electrical conductivity ($\sigma$=0.5-80 S/cm) and majority carrier mobility ($\mu$=1-80 cm$^2$/Vs) range over several orders of magnitude [35, 36, 38, 39, 47]. There have also been a few published works on devices made using Cu$_2$SnS$_3$ absorbers [23, 40–43, 92, 93]. In 2012, a 2.84% device using a Cu$_2$SnS$_3$ absorber layer, a CdS buffer layer, and a ZnO:Al window layer was published [43]. In 2013, Ge incorporation enabled a 6% efficient device with a Cu$_2$Sn$_{0.83}$Ge$_{0.17}$S$_3$ absorber layer ($E_g$=1.0 eV) and similar device architecture [23]. The majority of studies reporting successful devices use Cu$_2$SnS$_3$ absorbers that are synthesized under Cu-poor conditions [23, 40, 42, 47]. In one systematic study, it was determined that devices with Cu/Sn>2 have conversion efficiencies near zero [43], and the poor performance of these Cu-rich devices was attributed to the presence of a Cu$_4$SnS$_4$ secondary phase (i.e. Cu/Sn = 4), though even slightly Cu-rich samples (e.g., Cu/Sn=2.1) showed drastic performance degradation. Thus, it appears that further understanding of the fundamental physics of Cu$_2$SnS$_3$ is necessary for rational device development.

In this work, we concentrate on the Cu$_2$SnS$_3$ phase of the Cu-Sn-S ternary phase diagram (Figure 5.1a) and chemical potential phase space (Figure 5.1b) as a function of Cu and Sn composition and S chemical potential. Experimentally, we find that the cubic Cu$_2$SnS$_3$ phase spans a wide region of the chemical potential phase space and that there is a 1000x change in electrical conductivity across this ostensibly single-phase region. Next, we determine theoretically that the Cu and Sn composition and S chemical potential are responsible for controlling the carrier concentration of the resulting Cu$_2$SnS$_3$ through two separate ef-
a: The Cu-Sn-S compositional phase space. The inset shows the region of interest, as determined by the phases observed in our sputtered films. The numbered lines represent the observed phase progressions for three different samples that we synthesized, referred to as libraries. From analysis of the impurity phase peaks in the XRD patterns, we have approximated the phase width of the Cu$_2$SnS$_3$ phase, shown in blue (see Figure 5.3a for further discussion of the phase width determination).

b: The Cu-Sn-S chemical potential phase space, as calculated previously [55]. The white lines indicate the same experimental libraries as those shown in (a). Each white line represents a constant S chemical potential, moving from high $\mu_S$ (library 1) to low $\mu_S$ (library 3).

Figure 5.1: a: The Cu-Sn-S compositional phase space. The inset shows the region of interest, as determined by the phases observed in our sputtered films. The numbered lines represent the observed phase progressions for three different samples that we synthesized, referred to as libraries. From analysis of the impurity phase peaks in the XRD patterns, we have approximated the phase width of the Cu$_2$SnS$_3$ phase, shown in blue (see Figure 5.3a for further discussion of the phase width determination).  

b: The Cu-Sn-S chemical potential phase space, as calculated previously [55]. The white lines indicate the same experimental libraries as those shown in (a). Each white line represents a constant S chemical potential, moving from high $\mu_S$ (library 1) to low $\mu_S$ (library 3).

First, the Cu/Sn ratio controls alloying with a metallic Cu$_3$SnS$_4$ phase, which results in highly doped p-type (10$^{20}$ cm$^{-3}$ or higher) films when grown under Cu-rich conditions. Second, the S chemical potential is responsible for controlling the concentration of copper vacancies in the material, which also can cause similarly high doping levels when growth is performed under S-rich conditions. We support these theoretical mechanisms by experimental in-lab and synchrotron-based spectroscopy measurements. Overall, we find that in order to achieve non-degenerating doping, Cu$_2$SnS$_3$ films must be grown both Cu- and S-poor. The need to grow Cu-poor films is not unexpected, as this is true for other Cu-based ab-
sorbers such as Cu$_2$ZnSn(S,Se)$_4$ and CuInSe$_2$ [94, 95]. However, the necessity of maintaining S-poor conditions during deposition represents a new insight in the growth of Cu$_2$SnS$_3$. This understanding of the origins of varying doping density in Cu$_2$SnS$_3$ films enables the design of growth processes that target the desired carrier concentrations for device integration, achieving here non-degenerate doping levels of less than $10^{18}$ cm$^{-3}$.

5.3 Experimental methods

Combinatorial experiments were performed to survey the Cu$_2$SnS$_3$ compositional space. Further single point measurements were performed on specific samples. First principles and GW theory were used to calculate defect formation energies and alloying energies.

5.3.1 Combinatorial experiments

The experimental components of this work have been performed using a combinatorial approach [73]. The films described in this paper were deposited using combinatorial RF sputtering [88] from 50 mm diameter Cu$_2$S and SnS$_2$ targets. The targets were positioned relative to the substrate such that a Cu-Sn composition gradient was created across the sample. The depositions were performed in a chamber with a base pressure of less than $10^{-6}$ torr, which was filled with $3 \times 10^{-3}$ torr of Ar during the deposition. Films were deposited onto 50 mm $\times$ 50 mm Eagle-XG glass substrates heated to 275-325°C. The substrates were located 10 cm from the targets, and gun powers between 25-50 W were used to provide the desired chemical compositional spread across the substrates. An RF solids cracker (RFK30, Oxford Applied Research) filled with S powder (99.98%, Aldrich) was used to provide additional S flux for some samples. The resulting 50x50mm sample libraries were mapped at 44 points (4x11 grid) to determine the properties of the material as functions of the spatial coordinates [72]. Mapping capabilities were employed for measurements of X-ray fluorescence (XRF), X-ray diffraction (XRD), Raman spectroscopy, four point probe, and optical transmittance and reflectance. The large amounts of data from these spatially resolved measurements were processed using custom software packages created in Igor PRO. X-ray fluorescence spectra
were collected using a System-SMX instrument and analyzed using MTF-FP software to obtain both the Cu/Sn ratios and the thickness of the films. The XRD patterns were collected using Cu K-α radiation and a proportional 2D detector (Bruker D8 Discover with General Area Detector Diffraction System software). Raman spectra were measured using a Renishaw inVia confocal Raman microscope with a CCD array detector, with an excitation wavelength of 532 nm. The sheet resistance was measured using a collinear four point probe with 1 mm distance between probes. Optical transmittance and reflectance were mapped from 300-1700 nm using a fiber-optics-based spectrometer with deuterium (DT1000 CE UV/Vis, Analytical Instrument Systems, Inc.) and tungsten/halogen (LS-1, Ocean Optics) light sources and Si and InGaAs detector arrays (Ocean Optics). The absorption coefficient was calculated from the measured reflectance (R) and transmittance (T) spectra, and the measured film thickness (d) from the XRF, using the relationship $\alpha = -\ln[T/(1-R)]/d$.

5.3.2 Single point experiments

Further experimental single point measurements were carried out on specific samples. Room temperature Hall effect measurements (BioRad HL5500 PC) were used to determine carrier concentration and majority carrier mobility; the p-type electrical conduction was confirmed by measuring the Seebeck coefficient on a homebuilt system. Temperature dependent Hall effect measurements (BioRad HL5500 PC) were performed from 200-350 K. The work function was determined using a Kelvin-probe (SKP SPV LE 450, KP Technology) with a 1 mm diameter gold-coated probe. The Kelvin-probe system was calibrated before and after performing measurements using Au and Al standards with reference work functions of 5.1 and 4.1 eV, respectively. The near edge X-ray absorption fine structure (NEXAFS) data was collected at the Stanford Synchrotron Radiation Lightsource. Beamline 10-1 uses a wiggler insertion device and a spherical grating monochromator, yielding a linear polarization of $\sim 80\%$, an energy resolution ($\Delta E/E$) better than $2 \cdot 10^{-4}$, and a spot size of $<1\text{mm}^2$. The analysis chamber is operated at a vacuum of $\sim 10^{-9}$ torr and is equipped with a cylindrical mirror analyzer (CMA, PHI Inc.) and a diode for detecting fluorescence yield. The total
electron yield (from the drain current) and the fluorescence yield are collected simultaneously. The incoming flux was normalized by monitoring the beam flux with a gold mesh mounted upstream of the main chamber. The slits of the monochromator were opened to provide intermediate energy resolution (<0.2 eV) in the NEXAFS. The energy scale of the NEXAFS scans was calibrated by first correcting monochromator energy drifts by simultaneous collection of a reference spectra from a calibration sample intercepting a few percent of the beam upstream of the main chamber for all scans. This reference data was then fit to the data of a highly ordered pyrolytic graphite control according to the method presented in Ref. [96]. The absolute energy scale was then determined by comparison to the leading peak in CuO, found at 931.3 eV [97]. Fitting analysis was conducted to quantify systematic changes in the NEXAFS spectra. First, the NEXAFS step features were removed using the method presented in Ref. [98]. The processed data were fitted with Gaussian functions. Four peaks were fitted in the energy range of 925.8-937.3 eV. The peak near 936.2 eV was constrained in width and position due to its overlap with the step function.

5.3.3 Theoretical calculations

Theoretical DFT+U calculations were performed with PBE exchange-correlation functional [77] within the PAW formalism as implemented in the VASP code [78]. An effective on-site potential [79] $U = 5$ eV was applied to Cu d-states. The electronic band gap was calculated within the GW approximation [82] following the approach in Ref. [83]. In order to compensate for the overestimated d-orbital energies in GW, an on-site d-state potential of $V_d = -2.8$ eV was applied to the Cu d-states. For the calculation of the thermodynamic stability, we used the fitted elemental reference energies (FERE) [80, 81]. For the defect calculations, we used 96 atom supercells of monoclinic Cu$_2$SnS$_3$ and applied finite size corrections [86]. Since defect formation energies are critically dependent on proper positioning of band edges [84], the values of the valence band maximum (VBM) and the conduction band minimum (CBM) were taken from GW calculations. To construct alloy structures we have performed a canonical Metropolis Monte Carlo simulations using the model Hamiltonian described in
Ref. [55]. Random 384 atom Cu$_2$SnS$_3$-Cu$_3$SnS$_4$ alloy samples were first heated to 3000 K, then slowly cooled to 0 K; for each composition 8 samples were simulated for $\sim$100000 steps. For these calculations the Cu$_2$SnS$_3$ composition and 4 intermediate Cu$_2$SnS$_3$-Cu$_3$SnS$_4$ alloy compositions were considered, but the Cu$_3$SnS$_4$ was omitted since it required a sample larger than 384 atoms.

5.4 Results and discussion

This section presents the results of our study, and discusses the implications for future work on Cu$_2$SnS$_3$.

5.4.1 Experimental control of conductivity by composition

Figure 5.2 shows the X-ray diffraction patterns for three selected sample libraries as a function of Cu/(Cu+Sn) ratio in the $\sim$0.6 - 0.8 range. Each library contained a region of Cu$_2$SnS$_3$ at intermediate Cu/(Cu+Sn) values, the boundaries of which are shown by the white lines, but the three sample libraries showed different bounding phases at Cu-rich and Cu-poor conditions, including Cu$_3$SnS$_4$, Cu$_4$SnS$_4$, Cu$_4$Sn$_7$S$_{16}$, and SnS. The major peaks for each of these phases are circled in Figure 5.2. The phase progressions within each sample library allowed us to map the libraries onto the chemical potential phase space in Figure 5.1b. Although the S chemical potential is not shown explicitly in Figure 5.1b, it can be calculated from the values of the Cu and Sn chemical potentials and the calculated heats of formation of the compounds, assuming thermodynamic equilibrium conditions (i.e. the stoichiometry weighted sum of chemical potentials equals the heat of formation of the compound). Each library was represented with a line of constant S chemical potential. These lines were drawn such that they intersected the observed bounding phases on either side of the Cu$_2$SnS$_3$ phase. Although we were not able to determine the absolute S chemical potential for each library, the constraints imposed by the bounding phases gave us upper and lower limits of S chemical potential for each phase progression. For visualization purpose, the lines representing the libraries in Figure 5.1b are placed at approximately the middle of the range of S chemical
potentials for that library, rather than representing exact values of S chemical potential or its boundaries.

Figure 5.2: X-ray diffraction patterns for three sample series synthesized at high, intermediate, and low S chemical potentials. The S chemical potential affects the phase progression as the Cu/(Cu+Sn) ratio increases (y-axis). These phase progressions can be mapped onto the compositional and chemical potential phase spaces, as shown in Figure 5.1. The horizontal white lines show the phase pure Cu$_2$SnS$_3$ region, as determined by XRD impurity phase analysis (see Figure 5.3a). For representative individual XRD patterns, see Fig.s S1, S2, and S3 in the Supporting Information.

The intermediate S chemical potential library was synthesized by sputtering from Cu$_2$S and SnS$_2$ targets at 275°C with no additional S source. This gave a phase progression of SnS - Cu$_2$SnS$_3$ - Cu$_3$SnS$_4$ (Figure 5.2b). This phase progression was mapped to the S chemical potential on Figure 5.1b, corresponding to a range of S chemical potentials between -0.59 and -0.37 eV. To increase the S chemical potential, an atomic S source was used during deposition. This resulted in the phase progression for the S-rich library, shown in Figure 5.2a: Cu$_4$Sn$_7$S$_{16}$ - Cu$_2$SnS$_3$ - Cu$_3$SnS$_4$. When mapped onto the chemical potential phase space, we
see that this phase progression does indeed indicate a higher S chemical potential between -0.06 and -0.37 eV. Finally, to decrease the S chemical potential, the deposition temperature was increased by 50°C. Assuming that S can be approximated as an ideal gas (in contrast to Cu or Sn), an increase in temperature should cause a decrease in S chemical potential [22]. As shown in Figure 5.2c, this temperature increase resulted in a Cu$_2$SnS$_3$ - Cu$_4$SnS$_4$ phase progression. As per the chemical potential phase diagram (Figure 5.1b), this phase progression is representative of lower S chemical potential between -0.59 and -0.90 eV.

The data from the three sample series shown in Figure 5.2 also allowed us to investigate the compositional phase width of the Cu$_2$SnS$_3$ phase space. Although Cu$_2$SnS$_3$ has been reported to be a line compound [33], we find that our synthesis technique allows us to access a relatively broad composition space for this compound. For each library, the range of 2θ values for the impurity phases was identified. Then, the XRD signal intensity was integrated over this 2θ range for all samples. This integrated impurity peak intensity was plotted as a function of Cu/(Cu+Sn) content, as shown in Figure 5.3a. Linear fits (also shown in Figure 5.3a) were used to extrapolate the impurity intensity to the level of the background intensity. The intersection of these two allowed us to identify the stability window of Cu$_2$SnS$_3$. This is shown by the horizontal white lines in Figure 5.2; note that the boundaries of the Cu$_2$SnS$_3$ phase differ between the libraries. Finally, these phase boundaries were mapped onto the ternary phase diagram shown in Figure 5.1a. The blue region in this phase diagram gives an approximate representation of the compositional phase width of the Cu$_2$SnS$_3$ phase. The phase boundary points were connected by straight lines; however, this is an approximation and the true behavior of the phase boundaries likely deviates from these straight lines.

Trends in electrical conductivity

Figure 5.3b shows the electrical conductivity as a function of Cu/(Cu+Sn) ratio for the three experimental libraries (high, intermediate, and low S chemical potential). Because the
Figure 5.3: a: Normalized integrated impurity peak intensities as a function of Cu/(Cu+Sn) for three sample libraries. The linear fits are extrapolated to the background level of impurity intensity, shown by the dotted black line. The intersections of the background impurity intensity with the linear fits is used to determine the range of Cu/(Cu+Sn) values over which the Cu$_2$SnS$_3$ phase exists free of any other crystalline impurity phases. Note that the phase boundaries of the Cu$_2$SnS$_3$ phase differ between libraries. b: Electrical conductivity as a function of film composition for three sample libraries. Within the Cu$_2$SnS$_3$ phase, the electrical conductivity varies by several orders of magnitude. Within each sample series, the conductivity increases with an increase in Cu content. Furthermore, at very low Cu contents, there is a slight increase in the conductivity. Comparing the three series illuminates a third trend, which is an increase in conductivity with increasing S chemical potential.

Values of Hall mobility for these films are roughly constant (1-2 cm$^2$/Vs), these changes in conductivity are indicative of changes in the carrier concentration (the carrier concentration was not measured for all points on the sample, because this measurement was destructive to the sample). The hole concentrations (shown on the right axis of Figure 5.3b) ranged from $\sim 10^{18}$ - $10^{21}$ cm$^{-3}$. Focusing on the single phase Cu$_2$SnS$_3$ region, three trends in the electrical conductivity become clear. The first trend is an increase in the conductivity of the Cu$_2$SnS$_3$ phase with increasing Cu content. This is the strongest trend that is present in the conductivity data for each individual library. Also within each individual library,
we see a slight increase in the conductivity at very low Cu content, which is the second trend. The third trend is revealed by the differences in conductivity range between the three libraries. Because the three libraries are synthesized under differing S chemical potentials, the observed differences in conductivity between them would suggest that an increase in S chemical potential causes an increase in the electrical conductivity of the Cu$_2$SnS$_3$ phase.

In order to explain these three trends in conductivity (and thus carrier concentration), we turn to first-principles theory. We first consider a point defect model, which finds that copper vacancies are the dominant acceptor defect. The formation energy of $V_{Cu}$ varies with S chemical potential, and this can be used to explain the changes in conductivity between the different sample libraries and the slight increase of conductivity at low Cu content (trends 2 and 3 discussed above). However, the point defect model fails when we consider the increase in conductivity with an increase in Cu with the Cu$_2$SnS$_3$ phase (trend 1): if $V_{Cu}$ is the dominant acceptor defect, then an increase in Cu should result in a decrease in carrier concentration, which is the opposite of the experimentally observed trend. Understanding the origins of this effect requires the use of an alloy model, in which we consider alloying between a semiconducting Cu$_2$SnS$_3$ phase and an isostructural metallic Cu$_3$SnS$_4$ phase. In the following sections, we explain both of these effects in more detail.

5.4.2 Theoretical explanation for varying carrier concentration

$Cu_2SnS_3$ point defect model

We performed a theoretical investigation into the energetics of defects in the monoclinic Cu$_2$SnS$_3$ material. The neutral defect formation energies, and the transition levels relative to the valence band maximum are shown in Table 5.1 and Table 5.2, respectively. As reported before [55], similar to other copper chalcogenides, such as Cu(In,Ga)Se$_2$ [99, 100] and BaCuChF ($Ch=$S, Se, Te) [101], Cu vacancies ($V_{Cu}$) are the main acceptor defect. These are shallow defects with a thermodynamic transition level 0.04 eV above the VBM. The main donor defect is Sn atoms on Cu sites ($Sn_{Cu}$). These defects have deep states with
the transition from +1 to +3 located 0.2 eV below the CBM, corresponding to change in Sn oxidation state from +4 to +2. These ionized Sn\text{Cu} defects may serve as recombination centers. The sulfur vacancies (V\text{S}) have relatively low formation energy but no transition levels in the gap. Other defects, such as tin vacancies (V\text{Sn}) and copper on tin sites (Cu\text{Sn}) are less energetically favorable to form in the monoclinic Cu\text{2SnS}_3 structure.

The formation enthalpy of copper vacancies (V\text{Cu}) as a function of S chemical potential is shown in Figure 5.4a. As the S chemical potential increases (becomes less negative), the energy penalty to form a V\text{Cu} is lowered. This trend can be rationalized by considering that an anion (S) rich stoichiometry is analogous to a cation (Cu or Sn) poor stoichiometry, leading to cation vacancies. Since V\text{Cu} is a lower energy defect than V\text{Sn}, the cation poor conditions lead an increased concentration of V\text{Cu} rather than V\text{Sn}. Thus, at higher S chemical potentials more V\text{Cu} are formed, leading to films that are more p-type. This point defect model can be used to explain the effects of S chemical potential on carrier concentration (the carrier concentration is the largest in the “High S” library, Figure 5.3b). The data shown in Figure 5.4a can also be used to explain the slight increase in carrier concentration at low Cu contents (Figure 5.3b). For each value of S chemical potential, there is in fact a range of defect formation energies for V\text{Cu}. When the films are synthesized Cu-poor, the V\text{Cu} formation energy is lowered slightly (closer to the bottom line in Figure 5.4a), and thus a slight increase in electrical conductivity is observed. However, this effect is much smaller compared to the effects of S chemical potential on the V\text{Cu} formation enthalpy.

\text{Cu}_2\text{SnS}_3 - \text{Cu}_3\text{SnS}_4 alloy model

The calculated defect formation energies and transition levels (Table 5.1 and Table 5.2) do not explain the increase in p-type conductivity with the increase in Cu/(Cu+Sn) ratio, and in fact predict n-type behavior at Cu rich conditions. We attribute the observed p-type behavior of Cu\text{2SnS}_3 at Cu-rich growth conditions to alloying of this materials with an isostructural metallic Cu\text{3SnS}_4 phase. In Cu\text{3SnS}_4, one out of every three Cu is in the
formal +2 oxidation state, and therefore the Cu(d) states that constitute the valence band in Cu$_2$SnS$_3$ are partially empty in Cu$_2$SnS$_4$. As a result, Cu$_3$SnS$_4$ can be highly p-type conductive and should have hole density of $\sim 10^{22}$ cm$^{-3}$. Since both Cu$_2$SnS$_3$ and Cu$_3$SnS$_4$ can have the same underlying cubic zincblende-derived lattices[102] and because their lattice constants (effective atomic volumes) differ by only 1.5%, we would expect the mixing enthalpy between the two compounds to be low, and it is indeed the case, as described below. There are several possible alternative explanations for the conflict between theoretical model and experimental evidence for the Cu$_2$SnS$_3$ conductivity at Cu-rich conditions. First, inaccuracies of the theoretical band gap, although taken into account via band edge shift, could propagate throughout the calculation and result in the predicted n-type behavior, especially for the relatively narrow gap materials like Cu$_2$SnS$_3$. Second, the calculations were performed for the ordered monoclinic Cu$_2$SnS$_3$ phase, whereas the synthesized thin films are cubic and disordered. Calculating point defects in a disordered cubic Cu$_2$SnS$_3$ phase is a challenging task that warrants a separate publication.

Table 5.1: Calculated enthalpies of formation ($\Delta H_F$) for charge neutral defects at the intersection of the Cu$_2$SnS$_3$ chemical potential phase region with the two phases listed in parentheses (see Figure 5.1b). There are two non-equivalent sulfur sites in the Cu$_2$SnS$_3$ crystal structure: S1 coordinated by two Cu and two Sn and S2 coordinated by three Cu and one Sn atoms.

<table>
<thead>
<tr>
<th>Defect</th>
<th>$\Delta H_F$ (eV) (Cu$_4$SnS$_4$/SnS)</th>
<th>$\Delta H_F$ (eV) (Cu$_4$SnS$_4$/Cu$_3$SnS$_4$)</th>
<th>$\Delta H_F$ (eV) (SnS/SnS$_2$)</th>
<th>$\Delta H_F$ (eV) (Cu$_3$SnS$_4$/SnS$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_{Sn}$</td>
<td>3.17</td>
<td>2.71</td>
<td>3.17</td>
<td>2.71</td>
</tr>
<tr>
<td>Sn$_{Cu}$</td>
<td>1.46</td>
<td>1.92</td>
<td>1.46</td>
<td>1.92</td>
</tr>
<tr>
<td>V$_{Cu}$</td>
<td>1.72</td>
<td>1.57</td>
<td>1.19</td>
<td>1.04</td>
</tr>
<tr>
<td>V$_{Sn}$</td>
<td>5.74</td>
<td>5.12</td>
<td>5.21</td>
<td>4.59</td>
</tr>
<tr>
<td>V$_{S1}$</td>
<td>0.51</td>
<td>0.82</td>
<td>1.04</td>
<td>1.35</td>
</tr>
<tr>
<td>V$_{S2}$</td>
<td>0.23</td>
<td>0.54</td>
<td>0.75</td>
<td>1.06</td>
</tr>
</tbody>
</table>
Table 5.2: Thermodynamic transition levels of defects, calculated relative to the conduction band minimum (CBM).

<table>
<thead>
<tr>
<th>Defect</th>
<th>Transition</th>
<th>Energy (eV)</th>
<th>Transition</th>
<th>Energy (eV)</th>
<th>Transition</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSn</td>
<td>0 → -1</td>
<td>-0.64</td>
<td>-1 → -2</td>
<td>-0.49</td>
<td>-2 → -3</td>
<td>-0.14</td>
</tr>
<tr>
<td>SnCu</td>
<td>0 → +1</td>
<td>0.00</td>
<td>+1 → +2</td>
<td>-0.16</td>
<td>+2 → +3</td>
<td>-0.20</td>
</tr>
<tr>
<td>V_Cu</td>
<td>0 → -1</td>
<td>-0.66</td>
<td>-1 → -2</td>
<td>-0.55</td>
<td>-2 → -3</td>
<td>-0.23</td>
</tr>
<tr>
<td>V_Sn</td>
<td>0 → -1</td>
<td>-0.66</td>
<td>-1 → -2</td>
<td>-0.55</td>
<td>-2 → -3</td>
<td>-0.23</td>
</tr>
</tbody>
</table>

The potential for alloying between cubic Cu$_2$SnS$_3$ and cubic Cu$_3$SnS$_4$ was assessed by considering the enthalpy of mixing between these two phases. The enthalpy of mixing ($\Delta H_m$) was calculated for the entire range of alloy compositions using the annealed structures and PBE+U energies, and is plotted as a function of fractional Cu$_3$SnS$_4$ content in Figure 5.4b. In all cases, the enthalpy of mixing is less than 5 meV/atom. For comparison, the value of $kT$ at the growth temperature (~300°C) is about 50 meV, so the thermal energy during film growth should be sufficient to overcome any barriers to alloying. The low mixing enthalpy between Cu$_2$SnS$_3$ and Cu$_3$SnS$_4$ can be explained with two effects. First, there are no topological barriers to mixing between the two phases. This is largely because the alloy structures are built from the same two sulfur-based tetrahedral motifs as the Cu$_2$SnS$_3$ and Cu$_3$SnS$_4$ parent compounds: Cu$_2$SnS$_3$ is built from sulfur atoms surrounded by two copper and two tin atoms (S-Cu$_2$Sn$_2$) and sulfur atoms surrounded by three copper atoms and one tin atom (S-Cu$_3$Sn) motifs in a S-Cu$_2$Sn$_2$:S-Cu$_3$Sn = 2:1 ratio; Cu$_3$SnS$_4$ is built entirely from S-Cu$_3$Sn motifs (see Figure 5.4b). Hence, mixing of the two phases does not change the first coordination shell of either cation and anion. Second, the formation energy of (Cu,Sn)S zincblende derived structures is linear in motifs concentration [103], and thus mixing two structural motifs without formation of other motifs should be accomplished with negligible mixing enthalpy.
Figure 5.4: **a:** The enthalpy of formation for copper vacancies (V\textsubscript{Cu}) as a function of S chemical potential, calculated using DFT (data in Table 5.1 and Table 5.2). The enthalpy of formation for V\textsubscript{Cu} is lower at higher (less negative) S chemical potentials. The upper and lower lines represent Cu-rich and Sn-rich conditions, respectively; the change in formation enthalpy resulting from varying the Cu/Sn ratio is small compared to the effects from changing the S chemical potential. **b:** The calculated enthalpies of mixing for cubic Cu\textsubscript{2}SnS\textsubscript{3} - Cu\textsubscript{3}SnS\textsubscript{4} alloys as a function of composition. The mixing enthalpies at various compositions are negligible when considering the thermal energy at the growth temperature (~50 meV). The insets show the two S-based tetrahedral motifs (S-Cu\textsubscript{2}Sn\textsubscript{2} and S-Cu\textsubscript{3}Sn), which can be used to build both the cubic Cu\textsubscript{2}SnS\textsubscript{3} and cubic Cu\textsubscript{3}SnS\textsubscript{4} structures. Insets prepared using VESTA [63].

5.4.3 Experimental evidence of Cu\textsubscript{2}SnS\textsubscript{3} - Cu\textsubscript{3}SnS\textsubscript{4} alloying

It was not possible to differentiate the predicted cubic Cu\textsubscript{3}SnS\textsubscript{4} phase using XRD, because the structure is very similar to that of the cubic Cu\textsubscript{2}SnS\textsubscript{3} phase (see the XRD pattern presented for cubic Cu\textsubscript{3}SnS\textsubscript{4} in Ref. 102). We selected the “Intermediate S” sample library for further characterization, with the goal of distinguishing these two phases. We used Raman spectroscopy to in an attempt to probe the short range ordering of the material, which would be expected to change as the Cu\textsubscript{3}SnS\textsubscript{4} phase is formed with increasing Cu content. Additionally, the transition from Cu\textsubscript{2}SnS\textsubscript{3} to Cu\textsubscript{3}SnS\textsubscript{4} requires that some of the Cu (I) is
converted to Cu (II), or that some holes should appear in the valence band, making Cu₃SnS₄ metallic. In order to probe the oxidation states of the Cu in our material, we used near edge X-ray absorption fine structure spectroscopy (NEXAFS).

**Short range ordering**

Selected Raman spectra are shown in Figure 5.5a. The two main peaks in the spectra are located at 303 cm⁻¹ and 354 cm⁻¹ and can be assigned to cubic Cu₂SnS₃ [36, 44, 57]. Contrasting the Cu-poor vs. Cu-rich sample spectra, there is a small but consistent change in the relative intensities of these two characteristic peaks. With an increase in Cu content, the peak at 354 cm⁻¹ increases relative to the peak at 303 cm⁻¹. Slight shoulder peaks can also be observed in the Raman spectra at 319 cm⁻¹ and 338 cm⁻¹. These peaks could be due to tetragonal Cu₂SnS₃ (335 cm⁻¹) [36, 44, 57] and tetragonal or orthorhombic Cu₃SnS₄ (315-318 cm⁻¹) [36, 44, 57]. However, the intensities of these shoulder peaks are constant for all samples. Thus, it is unlikely that the low level impurity phases that may be responsible for the shoulder peaks is influencing the electrical conductivity.

Analysis of the changes in relative peak intensities is complicated by the fact that there has been no investigation of which vibrational modes correspond to specific peaks in the Raman spectrum of Cu₂SnS₃. However, we can use an analogy to a Raman study of the order-disorder transition in Cu₂ZnSnS₄ (CZTS) to provide a framework for analyzing our data. When comparing the Raman spectra of ordered vs. disordered kesterites, it has been noted that the relative intensities of the second and third A modes changed dramatically depending on the degree of disorder in the material [104]. In CZTS, the A modes correspond to the vibrations of the S anion sublattice, and are influenced by the local S coordination [104, 105]. Thus, it is possible that changes in the local S coordination are responsible for the changes in relative peak intensities in the Raman spectra.

As discussed above, the cubic Cu₂SnS₃ can be created out of two structural “motifs” or S coordination environments: S-Cu₃Sn and S-Cu₂Sn₂. These same two structural motifs, in
different relative amounts, can be used to create the cubic Cu$_3$SnS$_4$ structure. Thus, alloying with Cu$_3$SnS$_4$ changes the local S coordination environment. By analogy with the study by Scragg, et al., this change in local S coordination could result in changes in relative peak intensities in the Raman spectra, potentially explaining the small but consistent changes in the relative peak intensities of the two major peaks at 354 cm$^{-1}$ and 303 cm$^{-1}$, (Figure 5.5a). However, a full understanding of these changes in relative peak intensities will require the calculation of theoretical Raman spectra for the cubic Cu$_2$SnS$_3$ and Cu$_3$SnS$_4$ phases.

Cu oxidation state

The Cu 2p NEXAFS fluorescence yield data are shown in Figure 5.5b for five points within the Cu$_2$SnS$_3$ phase region. The data show several distinct spectral features positioned near 931.6 eV (Peak 1), 932.5 eV (Peak 2), 934 eV (Peak 3), and 936 eV (Peak 4). These four peaks were fitted to allow us to compare the differences in relative peak areas between samples with different Cu/(Cu+Sn) ratios. The fine structure region (926-937 eV) shows line shapes that are consistent with other copper-sulfur materials [106–110], but our observed peak positions are lower in energy. However, we note that energy shifts due to environmental changes (i.e., vacuum vs. air) have been previously observed in Cu$_5$FeS$_4$ samples [106].

The analysis of NEXAFS spectra of Cu-S compounds has generated some controversy as to the existence of a formal Cu (II) oxidation state. A thorough history of this debate, including experimental results indicating the presence of only the formal Cu (I) oxidation state in CuS can be found in Ref.s [110] and [111]. The lack of Cu (II) has also been experimentally demonstrated in Cu$_5$FeS$_4$ by other groups [107]. However, some authors have contradicted these claims by assigning some of the NEXAFS peaks to a formal Cu (II) oxidation state in materials such as Cu$_5$FeS$_4$ and CuFeS$_2$ [106, 112]. With regards to this position, we note that electron paramagnetic resonance spectroscopy has been used to demonstrate the existence of Cu (II) in Cu$_3$SnS$_4$[102]. We also note that classification of the local electronic structure of Cu in terms of strict d-count is only valid for ionic compounds.
such as oxides. As softer ligands such as S and Se are involved, hybridization effects become more important, and it is difficult to assign an integer value to the effective valence state. This is particularly true for Cu-containing compounds, for which mixed valence character is expected due to good energy match of a filled d-shell and the resulting stronger hybridization with more covalent ligands, such as S, Se, P and N [113].

Regardless of which of the above interpretations is correct, the previous work on Cu-S materials allows us to analyze our NEXAFS results in terms of the “Cu$_2$S-like” and “CuS-like” character (by formal charge counting, the Cu(I) and Cu(II) states, respectively) of our Cu$_2$SnS$_3$ - Cu$_3$SnS$_4$ alloy thin films. In the pure Cu$_2$SnS$_3$ end member of the alloy, all of the Cu should display the “Cu$_2$S-like” electronic character. As the amount of Cu$_3$SnS$_4$ content is increased, some of this Cu must take on the “CuS-like” character. Papers from both schools of thought report the Cu$_2$S peak at $\sim$935 eV, and the CuS peak at 932.4 eV [111, 112], the shapes of which correspond to our Peaks 1 and 3, respectively. In our data, we see an increase in the area of Peak 1 relative to the area of Peak 3 as the Cu content of the thin film is increased. This indicates an increase in the “CuS-like” character of the material, consistent with an increase in the Cu$_3$SnS$_4$ content of the alloy. Although even the most Sn-rich Cu$_2$SnS$_3$ sample that we measured has a large “CuS-like” peak, we note that this peak has been shown to be $\sim$25 times more intense than the signal from an equivalent “Cu$_2$S-like” peak [107], and thus the amount of Cu with “CuS-like” character is likely smaller than it appears from the raw data. Elucidating the possible origins of this peak in the Sn-rich Cu$_2$SnS$_3$ sample warrants further work, but surface oxidation and nano-scale phase segregation are among the most likely options.

**Compositional dependence**

Finally, we have correlated the changes in the Raman and NEXAFS spectra with measured changes in chemical composition. The changes in the local coordination spectra and the Cu electronic state were quantified using the ratios of peak intensity and areas from peak
fitting, respectively. For the Raman spectra, the ratio of the peak intensity at 303 cm\(^{-1}\) to the peak intensity at 354 cm\(^{-1}\) was used, similar to the quantification performed in literature [104]. For the NEXAFS data, we took the ratio of the area of the fitted Peak 1 to Peak 3. When these metrics are plotted as functions of Cu/Sn ratio (Figure 5.5c), it appears that the changes in the Raman spectra and the electronic character of the Cu are correlated with the changes in Cu/Sn ratio.

The changes in the local S coordination environment, and the relative increase of Cu with “CuS-like” character can both be explained by the fact that the high Cu content “Cu\(_2\)SnS\(_3\)” samples are in fact cubic Cu\(_2\)SnS\(_3\)-Cu\(_3\)SnS\(_4\) alloys. Adding further support to this hypothesis is the observed correlation between the changes in local S coordination, the changes in Cu electronic character, and the increase in conductivity (Figure 5.3b), which could also be explained by the increased incorporation of highly conductive Cu\(_3\)SnS\(_4\). Although further investigation of this question is still warranted, we have not obtained any evidence, experimental or theoretical, that contradicts our Cu\(_2\)SnS\(_3\)-Cu\(_3\)SnS\(_4\) alloy model. This insight into the alloy-forming character of the Cu\(_2\)SnS\(_3\) material requires a revision of the compositional and chemical potential phase spaces shown in Figure 5.1a and b, where the region of interest is labeled as a “Cu\(_2\)SnS\(_3\)-Cu\(_3\)SnS\(_4\)” alloy region. It is possible that this alloying effect could limit the utility of Cu\(_2\)SnS\(_3\) as a photovoltaic absorber. However, the moderate doping levels achieved in this work (≤10\(^{18}\) cm\(^{-3}\)) suggest that it is possible to design growth techniques which limit the formation of the Cu\(_2\)SnS\(_3\) - Cu\(_3\)SnS\(_4\) alloy.

5.4.4 In-depth investigation of S-poor Cu\(_2\)SnS\(_3\)

We have performed additional characterization of a sample grown as Cu-poor and S-poor as was achievable with our current experimental setup, i.e., as close as possible to the optimum growth conditions. It is likely that further optimization could be achieved though better control of the S chemical potential during deposition. The optical absorption edge for this sample is located at \(\sim 0.8\) eV, in agreement with previous literature. The absorption coefficient reaches \(10^5\) cm\(^{-1}\) around 1 eV above the absorption edge, which confirms the
potential of this material for use as a thin film absorber. The film showed moderate p-type doping, with a carrier concentration of $7 \times 10^{17}$ cm$^{-3}$. The acceptor activation energy was determined from temperature dependent measurements of the carrier concentration; the obtained value of 150 meV is in keeping with previous measurements of shallow acceptor activation energies for $V_{Cu}$ in CuInSe$_2$. The measured work function of 5.1 eV suggests that either CdS or ZnO could be used as possible n-type heterojunction partners with good band alignment.
Figure 5.5: 

a: Raman spectra for six samples with varying Cu/(Cu+Sn) ratio, normalized to the magnitude of the peak at 354 cm$^{-1}$. All spectra show major peaks at 303 cm$^{-1}$ and 354 cm$^{-1}$, characteristic of cubic Cu$_2$SnS$_3$. The intensities of these two peaks change relative to one another as the Cu content in the Cu$_2$SnS$_3$ phase increases, indicating a change in short-range ordering. The shoulder peaks (starred) could indicate small amounts of tetragonal Cu$_2$SnS$_3$ or tetragonal/orthorhombic Cu$_3$SnS$_4$.

b: Fluorescence yield from near edge X-ray absorption fine structure spectroscopy for five samples with varying Cu/(Cu+Sn) ratio. The spectra show four signature peaks (numbered 1-4), which are consistent with peaks found in other Cu-S materials. The changes in the relative areas of Peaks 1 and 3 could indicate the incorporation of the Cu$_3$SnS$_4$ phase.

c: Peak intensity (Raman) or peak area ratios (NEXAFS) as functions of Cu/(Cu+Sn) ratio. Changes in Raman and NEXAFS peak ratios provide evidence for the formation of a cubic Cu$_2$SnS$_3$ - Cu$_3$SnS$_4$ alloy. The correlation of these peak ratios with the conductivity (shown as a function of Cu/(Cu+Sn) in Figure 5.3b) suggests that this alloying is responsible for the observed increase in electrical conductivity (and thus carrier concentration).
5.5 Summary and Conclusions

In this work, we synthesized Cu$_2$SnS$_3$ films with varying Cu/Sn ratio and varying S chemical potential. Synthetic control of these parameters allowed us to investigate the origins of the large variations in carrier concentration found in Cu$_2$SnS$_3$. Our experimental and theoretical results suggest that doping of cubic Cu$_2$SnS$_3$ is determined by two effects: the varying concentration of V$_{Cu}$ in response to S chemical potential changes at Cu-poor conditions and the alloying with isostructural metallic Cu$_3$SnS$_4$ under Cu-rich conditions. The latter effect can give rise to high levels of doping in Cu$_2$SnS$_3$ and result in carrier concentrations up to $10^{21}$ cm$^{-3}$. Thus, achieving the desired carrier concentrations for device integration will require that growth is performed under both Cu- and S-poor conditions. Using this scientific understanding, we have demonstrated control of the hole concentration over 4 orders of magnitude and have achieved films with moderate p-type doping ($7 \times 10^{17}$ cm$^{-3}$). The carrier concentration in Cu$_2$SnS$_3$ could likely be reduced further with more precise control of the Cu and S chemical potentials. These insights will allow the growth of high quality Cu$_2$SnS$_3$ absorbers and accelerate the development of the earth abundant photovoltaics field.
CHAPTER 6
EFFECTS OF DISORDER ON CARRIER TRANSPORT IN Cu2SnS3

Submitted to Physical Review Applied, 2015 [114].
Lauryn L. Baranowski1,2, Kevin McLaughlin2, Pawel Zawadzki1, Stephan Lany1, Andrew
Norman1, Hannes Hempel3, Rainer Eichberger3, Thomas Unold3, Eric S. Toberer1,2 and
Andriy Zakutayev1
1National Renewable Energy Laboratory, Golden, CO 80401 2Physics Department, Colorado School of Mines, Golden, CO 80401 3Helmholtz Center Berlin for Materials and
Energy, Hahn-Meitner-Platz 1, D-14109 Berlin, Germany

6.1 Abstract

Cu2SnS3 is a promising new absorber material that has attracted significant interest in recent years. However, similar to CZTS, Cu2SnS3 displays cation disorder, which complicates the scientific understanding and technological applications of these materials. In this work, we use post-deposition annealing to convert disordered Cu2SnS3 thin films to the ordered structure. After annealing, we observe crystal structure changes and detect improvements in the majority carrier (hole) transport. However, when the minority carrier (electron) transport was investigated using optical pump terahertz probe spectroscopy, minimal differences were observed in the lifetimes of the photoexcited charge carriers in the ordered and disordered Cu2SnS3. By combining these results with first-principles and Monte Carlo theoretical calculations, we are able to conclude that even ostensibly “ordered” Cu2SnS3 displays minority carrier transport properties corresponding to the disordered structure. The presence of extended planar defects in all samples, observed in TEM imaging, suggests that disorder may be present even when it is not detectable using traditional structural characterization methods such as X-ray diffraction or Raman spectroscopy. The results of this study highlight some of the challenges in the development of Cu2SnS3-based photovoltaics, and have
implications for other disordered multinary semiconductors such as CZTS.

6.2 Introduction

The development of efficient and scalable photovoltaics is an important challenge in today’s energy landscape. Although highly efficient thin film photovoltaics have been commercially available for some time, these technologies may be limited in their scalability by the use of rare or toxic elements [115–117]. Cu$_2$SnS$_3$ (CTS) is a promising thin film photovoltaic absorber material which uses only abundant and nontoxic elements. Interest in this compound has rapidly increased in the past several years, and device efficiencies of 4% and 6% have been reported using Cu$_2$SnS$_3$-based absorber materials and alloys, respectively [118, 119].

Besides the reported device efficiencies, previous theoretical and experimental works have revealed promising attributes of Cu$_2$SnS$_3$ for photovoltaic absorber applications. First principles calculations showed a wide range of phase stability, high optical absorption coefficient, and lack of Fermi level pinning in this material [55]. Experimental reports of the band gap of Cu$_2$SnS$_3$ range from 0.9-1.35 eV, well suited for a single-junction PV device [36, 40]. Furthermore, band gap tuning can be achieved either by alloying with Si or Ge on the Sn site (increasing band gap), or with Se on the S site (decreasing band gap) [119–121]. Research has demonstrated that Cu$_2$SnS$_3$ can be synthesized by several potentially scalable techniques such as sputtering and solution processing [35, 43, 119].

A variety of crystal structures have been reported for Cu$_2$SnS$_3$ thin films, including cubic, tetragonal, monoclinic, and triclinic [35, 42, 119]. These varying crystal structures result from different degrees of Cu/Sn disorder on the cation sites of the zinc blende-based lattice. In Ref. [61], the authors calculate the structures resulting from varying degrees of random disorder, ranging from cubic (fully disordered), to tetragonal (partially disordered), to monoclinic (fully ordered). A recent theoretical work has suggested that this disorder takes the form of compositional inhomogeneities caused by entropy-driven clustering (rather than fully random cation disorder), and could lead to nano-scale potential fluctuations that
negatively affect the carrier transport in Cu$_2$SnS$_3$ \cite{103}. It has been demonstrated that annealing Cu$_2$SnS$_3$ thin films at higher temperatures promotes a transformation from the tetragonal to the monoclinic structure \cite{122}. A few other studies have considered annealing of Cu$_2$SnS$_3$, including an investigation of the behavior of extrinsic oxygen defects in this material \cite{66}. However, there has been no work on the behavior of intrinsic defects during the annealing process, or the effects of annealing on the electronic properties of Cu$_2$SnS$_3$.

The reported hole concentrations in Cu$_2$SnS$_3$ are often high, reaching $10^{20}$ cm$^{-3}$ in some reports \cite{44, 67}. This level of doping is generally considered too high for a photovoltaic absorber material, as it leads to a tunneling-enhanced increase in recombination within the absorber layer and at the heterojunction interface, and is unfavorable in polycrystalline films due to a short depletion width. In our prior work, we determined that two mechanisms control the doping in Cu$_2$SnS$_3$ \cite{90}. Firstly, films must be grown Cu-poor to avoid alloying with a metallic Cu$_3$SnS$_4$ phase. Secondly, the S chemical potential during film growth controls the concentration of Cu vacancies, which are the dominant acceptor defect. Using the chemical potential phase space for this system \cite{55}, we determine that the lowest Cu and S chemical potentials are found when Cu$_2$SnS$_3$ is in equilibrium with SnS (although still single phase, with no actual SnS impurities). Thus, film growth in this region of the phase space should lead to desired carrier concentrations on the order of $10^{17}$ cm$^{-3}$.

In this work, we equilibrated our as-deposited Cu$_2$SnS$_3$ with SnS by annealing the films under an SnS atmosphere. We found that this equilibration with SnS caused a transformation from the cubic/tetragonal structure to the monoclinic structure (corresponding to an increase in cation ordering), along with a decrease in the hole concentration and increase in hole mobility. We used optical pump terahertz probe spectroscopy to investigate the minority carrier transport in our Cu$_2$SnS$_3$ films. Despite significant cation order/disorder differences, both samples had short electron decay times of 0.1-10 ps, and similarly high degrees of charge localization. From the electronic structure calculations, these short decay times and high degree of charge localization are characteristic of a disordered structure. When the samples
were imaged with transmission electron microscopy, both the cubic and monoclinic films were found to have high densities of stacking faults and/or twins. We conclude that the existence of planar defects results in local disorder even in the monoclinic Cu$_2$SnS$_3$, and has a negative impact on the electronic transport in this material. The findings in this work have implications not only for Cu$_2$SnS$_3$, but also for Cu$_2$ZnSn(S,Se)$_4$ (CZTS) and other multinary disordered semiconductors.

6.3 Methods

Here we describe our film synthesis and characterization methods, and the parameters used for film annealing. We also describe the computational methods used to calculate ordered and disordered density of states and inverse participation ratios.

6.3.1 Initial film growth and annealing

The films described in this paper were deposited using combinatorial RF sputtering from 50 mm diameter Cu$_2$S and SnS$_2$ targets on heated 50x50 mm Eagle XG glass substrates, under conditions described in Ref. [90]. We note that, after sputter deposition, the films are already in the Cu$_2$SnS$_3$ phase, which is different from many other studies, in which metal precursors are deposited and annealed to form the final ternary phase. Eagle XG glass was chosen for its low Na content, so that Na diffusion during film growth or annealing would not affect the measured transport properties. Further information about combinatorial synthesis approaches as applied to other absorber materials can be found in Ref.s [22, 73, 75, 123].

Annealing was performed by placing the samples in a quartz tube along with \(~1\) g of SnS or SnS$_2$ powder in an alumina boat (details regarding synthesis of the SnS and SnS$_2$ powders can be found in Ch. 3). A thermocouple was inserted into the tube such that it was positioned directly over the sample. A constant flow of argon gas was supplied to the quartz tube, and exited via a bubbler filled with mineral oil (pressure within tube was assumed to be close to atmospheric). The samples were heated in a tube furnace with a 5 hour total ramp time to the desired temperature. After the desired hold time, the furnace was turned
off and allowed to cool naturally to room temperature. A diagram of the annealing set up can be found in the Supplementary Material (Fig. S1).

6.3.2 Film characterization

Characterization was performed on small (12.5 mm x 12.5 mm) sections of the original films, which were determined to be uniform with regards to composition and morphology (due to the shallow initial compositional gradient and size of film sections). X-ray fluorescence spectra were collected using a Fischer XDV-SDD instrument to obtain both the Cu/Sn ratios and the thickness of the films. A table of this data can be found in the Supplementary Material. The XRF was calibrated with ~20 elemental standards from Fischer that span the entire energy range of the XRF measurement. The X-ray diffraction patterns were collected using a θ – 2θ geometry with Cu K-α radiation and a proportional 2D detector (Bruker D8 Discover with General Area Detector Diffraction System software). Raman spectra were collected using a Renishaw inVia confocal Raman microscope configured with 532 nm laser excitation at 5% power, an 1800 mm⁻¹ grating and CCD array detector. To compensate for the small spot size of the Raman measurement (~10 µm), six measurements were taken on each sample and averaged to provide a final spectrum.

Room temperature Hall measurements (BioRad HL5500 PC) were used to determine carrier concentration and majority carrier mobility. Room temperature Hall measurements were attempted on all annealed samples; however, for some samples, the Hall voltages were within the noise of the instrument and thus the data was not valid. We found that all samples annealed in the SnS atmosphere (for which successful Hall measurements were performed) had carrier mobilities ranging from 2-5 cm²/Vs; the average value was 2.5 cm²/Vs. This value of mobility, combined with the electrical conductivity, was used to calculate the carrier concentration for samples that were not successfully measured using the Hall effect. The p-type electrical conduction was confirmed by measuring the Seebeck coefficient on a home-built system. Transmission electron microscopy (TEM) cross-section samples were prepared using a conventional focused ion beam (FIB) lift out technique and examined at 300 kV in
an FEI Tecnai G2 30 S-TWIN TEM.

We used optical pump terahertz probe spectroscopy (OPTP), also known as time resolved terahertz spectroscopy (TRTS), to measure the decay of pump induced conductivity in the ps range as well as the complex charge carrier mobility. The OPTP spectrometer has been described earlier \cite{124}. The setup has been modified recently to record the pump induced change in THz reflection configuration. The transients were measured at the point of maximum change in THz amplitude, which represents the averaged THz conductivity decay, while the mobilities were analyzed by fitting the recorded THz reflection spectra to an optical model using the transfer matrix method \cite{125}. We assumed that the decay in conductivity is caused by a decaying carrier concentration where the maximum of the transient corresponds to all initially induced carriers. While the measured mobility is an average over all excited charge carriers, the conductivity is dominated by the electron (minority carrier) properties if the electron mobility can be assumed to be larger than the hole mobility \cite{126}.

6.3.3 Computational methods

Density of states (DOS) and projected density of states were calculated using the VASP code \cite{78}. Because of the band gap problem of the semi-local density functional theory (DFT) and large cells necessary to describe disorder in Cu$_2$SnS$_3$ we performed non-self consistent HSE calculations \cite{127}. The wave functions for HSE were generated with DFT+U \cite{79} using Perde-Burke-Ernzerhof \cite{77,128} exchange correlation functional and on-site potential $U = 7$ eV applied to Cu($d$) states.

To compare degree of charge localization in the ordered (SG=$Cc$) and disordered Cu$_2$SnS$_3$ we also calculated inverse participation ratio (IPR). IPR measures the inverse of the fraction of atoms over which a given state is delocalized and takes the form

$$IPR = \frac{N \sum_i^N c_i^4}{(\sum_i^N c_i^2)^2}$$  \hspace{1cm} (6.1)

where the sums run over $N$ atoms in the unit cell and $c_i$ are atom-projected density of states. For instance, for a state that is delocalized over all atoms in the unit cell, $IPR = 1$; for a
state delocalized over half of the atoms in the unit cell, $IPR = 2$.

For the disordered Cu$_2$SnS$_3$, the DOS and IPR were averaged over four independent atomic structures generated using Metropolis Monte Carlo method with a local motif-based model Hamiltonian described in Ref. [103].

6.4 Results and discussion

Figure 6.1: As expected from the Cu-Sn-S chemical potential phase space, carrier concentration reductions are largest when the Cu$_2$SnS$_3$ films are annealed in equilibrium with SnS (square markers). Increasing anneal temperature shows some effect on the hole concentration; increasing anneal time causes more dramatic reductions. The pre-anneal values of carrier concentration were $\sim 2 \cdot 10^{19}$ cm$^{-3}$.

We investigated a variety of annealing conditions to determine their effects on the transport properties of Cu$_2$SnS$_3$. The annealing temperature, atmosphere, and duration were independently explored to determine the effects on the carrier concentration, and these results are presented in Figure 6.1. As expected from the chemical potential phase space, the lowest hole concentrations were achieved under an SnS/Ar atmosphere (square data points in Figure 6.1) [90]. Comparing the results for 30 min, 2 hrs, and 8 hrs (red, blue, and green data points, respectively), we found that the kinetics of the annealing process were relatively slow. Further discussion of these results can be found in the Supplementary Material. As
a representative sample, we selected the film that was annealed under an SnS/argon atmosphere at 500° for 2 hours. All further results presented in this work are taken from this sample.

6.4.1 Structural changes & majority carrier transport

We assessed changes in the crystal structure of the Cu$_2$SnS$_3$ films using X-ray diffraction (XRD) and Raman spectroscopy. Overall, we saw a change from a cubic/tetragonal as-deposited structure, to a monoclinic post-annealed structure. This indicated a change from a disordered cation sublattice (cubic/tetragonal) to an ordered sublattice (monoclinic). For more information and figures of these structures, please see Fig. S2 in the Supplementary Material.

Prior to annealing, the XRD pattern displayed only one peak at ∼28.5°, shown in Figure 6.2a. With only this peak, it is difficult to assign a definitive crystal structure to this XRD pattern: this peak could correspond to the cubic (PDF #04-002-6009), tetragonal (PDF #04-009-7947), or monoclinic (PDF #04-010-5719) structures of Cu$_2$SnS$_3$ (oriented in the \{111\}, \{112\}, or \{200\} directions, respectively). Thus, we used Raman spectroscopy to further probe the structure of the preferentially oriented films. The pre-anneal Raman spectrum, shown in Figure 6.2b, showed two major peaks at 299 and 351 cm$^{-1}$, corresponding to the cubic Cu$_2$SnS$_3$ structure. Secondary peaks at 317 and 338 cm$^{-1}$ could be ascribed to the tetragonal crystal structure [36]. We did not see any peaks in the 450-500 cm$^{-1}$ range, indicating the absence of Cu$_{2-x}$S secondary phases.

Post-anneal, the XRD pattern showed peaks corresponding to the monoclinic Cu$_2$SnS$_3$ structure. The Raman spectrum had two major peaks at 290 and 351 cm$^{-1}$, which can be assigned to the monoclinic structure [59]. Two secondary peaks can be seen at 315 and 371 cm$^{-1}$. In Ref. [59] these peaks are ascribed to a Cu$_2$Sn$_3$S$_7$ secondary phase, with the corresponding cation ratio (determined by energy dispersive X-ray spectroscopy) of Cu/(Cu+Sn)=0.47. However, the cation ratio of our film, as determined by X-ray fluorescence, was Cu/(Cu+Sn)=0.63, suggesting that the amounts of secondary phase present
are minimal. Again, no secondary phase peaks belonging to Cu$_{2-x}$S phases were observed.

We used X-ray fluorescence (XRF) to measure the stoichiometry of the films before and after annealing. We did not observe any statistically significant changes in the Cu/Sn ratio of the films, or changes in the film thickness. This data can be found in Table S1 in the Supplementary Material.

Figure 6.2: (a) After annealing, the Cu$_2$SnS$_3$ films display XRD patterns corresponding to the monolinic structure. Prior to annealing, structural determination is difficult using only one peak. (b) Raman spectroscopy allows for elucidation of the pre-anneal structure as a mixture of cubic and tetragonal Cu$_2$SnS$_3$. The post-annealed spectrum shows peaks corresponding the monoclinic structure, as expected from the XRD pattern.

Concurrent with the change in crystal structure upon annealing, we observed an improvement in the majority carrier transport. The carrier concentration decreased from 2·10$^{19}$ cm$^{-3}$.
for the as-deposited sample to $8.0 \cdot 10^{17}$ cm$^{-3}$ after annealing. Additionally, the Hall mobility increased from 0.56 cm$^2$/Vs to 8.2 cm$^2$/Vs. There are several possible explanations for the increase in hole mobility, including a reduction in grain boundary scattering due to grain growth during annealing, a reduction in ionized defect density, or a change in the effective mass between the ordered and disordered structure. Measuring the Hall mobility of the pre-annealed samples as a function of temperature shows the expected increase in mobility at low temperatures, suggesting that the hole transport is not grain boundary limited (see Fig. S3). When this data is considered in conjunction with the reduction in carrier concentration, it suggests that the increase in hole mobility is likely related to a reduction in ionized defect density, but a reduction in effective mass may also play a role in this observed mobility trend.

### 6.4.2 Terahertz spectroscopy investigation of minority carrier transport

In order to probe the minority carrier transport in the as-deposited and annealed Cu$_2$SnS$_3$, we performed optical pump terahertz probe spectroscopy (OPTP). In contrast to the improvement observed in the hole (majority carrier) transport, the changes in electron (minority carrier) transport after annealing were less pronounced. A summary of these results can be found in Table 6.1.

In the as-deposited sample, the measured reflectivity as a function of time showed two decay processes: one with a decay time of 0.3 ps, and a second with a decay time of 7 ps (see Figure 6.3a). When the reflectivity of the annealed Cu$_2$SnS$_3$ is compared to that of the as-deposited sample, it is clear that the 0.3 ps decay process is absent, but that the 7 ps decay process remains. However, when the excitation power is lowered from $2 \cdot 10^{18}$ cm$^{-3}$ to $2 \cdot 10^{17}$ cm$^{-3}$ (as measured in terms of excited carriers at the surface of the sample), the 0.3 ps decay process can be detected even in the annealed sample, as shown in Figure 6.3b. This suggests that the trap or defect states responsible for the 0.3 ps decay can be saturated for high carrier injection. At one sun conditions in a good absorber (100 ns carrier lifetime), there are $3 \cdot 10^{16}$ cm$^{-3}$ photoexcited carriers, which suggests that the 0.3 ps decay process would still dominate under normal solar cell operating conditions.
Figure 6.3: (a) The as-deposited sample shows two decay processes in the measured reflectivity: a 0.3 ps decay and a 7 ps decay; the annealed sample shows only the 7 ps decay process. (b) When the excitation power is lowered, the 0.3 ps decay can be detected in the annealed sample, suggesting that this state can be saturated for high carrier injection.
Table 6.1: Summary of changes in crystal structure, film morphology, and majority and minority carrier transport for a Cu$_2$SnS$_3$ films annealed under SnS/argon atmosphere at 500°C for 2 hrs. Significant changes were evident in the structure and morphology, and a concurrent improvement was observed in the majority carrier transport. However, the minority carrier transport was mostly unaffected by the annealing.

<table>
<thead>
<tr>
<th></th>
<th>Pre-Anneal</th>
<th>Post-Anneal</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Structure</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crystal structure (XRD)</td>
<td>Cubic, oriented</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Crystal structure (Raman)</td>
<td>Cubic/tetragonal</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Crystal structure (TED)</td>
<td>Cubic, oriented</td>
<td>Monoclinic</td>
</tr>
<tr>
<td><strong>Morphology</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grain shape</td>
<td>Columnar</td>
<td>Equiaxed</td>
</tr>
<tr>
<td>Grain size</td>
<td>∼50 nm</td>
<td>200-500 nm</td>
</tr>
<tr>
<td>Defects</td>
<td>High density of planar defects</td>
<td>Some planar &amp; other intragrain defects</td>
</tr>
<tr>
<td><strong>Majority carrier transport</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hole concentration</td>
<td>$1 \cdot 10^{19}$ cm$^{-3}$</td>
<td>$8 \cdot 10^{17}$ cm$^{-3}$</td>
</tr>
<tr>
<td>Hole mobility</td>
<td>0.56 cm$^2$/Vs</td>
<td>8.2 cm$^2$/Vs</td>
</tr>
<tr>
<td><strong>Minority carrier transport</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electron decay times</td>
<td>0.3 ps, 7 ps</td>
<td>0.3 ps, 7 ps</td>
</tr>
<tr>
<td>Momentum relaxation time</td>
<td>33 fs</td>
<td>69 fs</td>
</tr>
<tr>
<td>Electron mobility</td>
<td>26 cm$^2$/Vs</td>
<td>55 cm$^2$/Vs</td>
</tr>
<tr>
<td>Electron localization constant</td>
<td>-0.91</td>
<td>-0.91</td>
</tr>
</tbody>
</table>
For both the as-deposited and annealed samples, the imaginary component of the terahertz conductivity is negative (Fig. S4). This negative value indicates charge carrier localization, which can be modeled using the Drude-Smith fit for conductivity [129]. Fitting our complex conductivity data results in a determination of the relaxation scattering time $\tau$ and a constant $c_1$, which represents the persistence of velocity after the first scattering event. The constant $c_1$ can vary from -1 to 0, with $c_1=0$ representing Drude conductivity and $c_1=-1$ representing complete carrier localization. For the as-deposited and annealed Cu$_2$SnS$_3$, the calculated value of $c_1$ is -0.91 (calculated 5-10 ps after excitation), indicating strong localization in both samples. The relaxation scattering times were 33 fs and 69 fs, for the as-deposited and annealed samples, respectively.

The minority carrier DC mobility of the samples can also be calculated from the Drude-Smith model (with $\omega=0$ for DC mobility), if the effective mass ($m^*$) is known or approximated. Here, we approximate $m^*$ as $0.2m_e$, the value calculated for CZTS [130]. However, it is also likely that the effective mass differs somewhat between the as-deposited and annealed samples, and this may be responsible for some of the changes in DC mobility. We calculate the minority carrier mobility to be 26 cm$^2$/Vs for the as-deposited Cu$_2$SnS$_3$, and 55 cm$^2$/Vs for the annealed sample. This factor of two increase in the electron mobility is related to the increase in the relaxation scattering time $\tau$, derived from the model discussed above; alternatively, it can be explained by the decrease in effective mass due to changes in cation ordering. When we consider the extremely short carrier lifetime, we would not expect the transport in this material to be grain boundary limited, as most carriers will recombine before reaching a grain boundary. This suggests that the increase in electron mobility is related to a reduction in ionized defect density with annealing, or a decrease in effective mass.

### 6.4.3 Theoretical explanation of terahertz spectroscopy results

To interpret our finding that both the ordered and disordered samples displayed high degrees of electron localization, we turn to the calculated inverse participation ratios (IPR) for ordered and disordered Cu$_2$SnS$_3$. The IPR values represent the degree of charge localization:
an IPR value of 1 indicates that charge is totally delocalized; an IPR value of 2 indicates that charge is localized on $\frac{1}{2}$ of the atoms present in the structure. As shown in Figure 6.4a, the ordered Cu$_2$SnS$_3$ has IPR ratios varying between 1-2 at the band edges (similar to values for traditional semiconductors such as Si or GaAs). In contrast, the disordered structure has high IPR values, especially at the conduction band edge, indicating a high degree of charge localization for the electrons. Both of our experimental samples, with their high degree of charge localization ($c_1$), are consistent with the calculated properties of the disordered sample. From the structural data (Figure 6.2), the post-anneal monoclinic sample is ostensibly “ordered”, however, it appears that low levels of disorder or other structural imperfections still dominate the transport properties.

If we now consider the calculated electronic density of states (DOS) for ordered and disordered (i.e., clustered) Cu$_2$SnS$_3$ (Figure 6.4b), the reason for poor minority carrier transport (Figure 6.3) becomes clear. The DOS for disordered Cu$_2$SnS$_3$ (Figure 6.4b) shows significant band tailing and a mid-gap state, and both of these could contribute to the picosecond electron decay times observed in the OPTP (Figure 6.3). Additionally, the band tailing reduces the band gap of Cu$_2$SnS$_3$ (0.9-1.35 eV), ultimately reducing the final device performance.

6.4.4 Microscopy investigations

To understand how the monoclinic, ostensibly “ordered” sample could still exhibit properties consistent with the theoretical disordered structure (such as high $c_1$ values and ps carrier lifetimes), we used transmission electron microscopy (TEM) to examine the microstructure of the two samples. As shown in Figure 6.5a, the as-deposited sample shows columnar grains ($\sim$50 nm across) that span the thickness of the film, and are strongly preferentially oriented in the $<111>$ growth direction (grain boundaries are highlighted by red dashed lines). All grains have an extremely high density of planar defects (stacking faults and twins), evidenced by the dark lines within the grains, an example of which is circled in red. The presence of these planar defects is confirmed by the visible streaks in the transmission electron diffraction (TED) pattern (see Figure 6.5c). The TED patterns also confirm the zinc blende (cubic)
Figure 6.4: (a) Calculation of the inverse participation ratio (IPR) for the disordered and ordered structures shows a high degree of charge localization (denoted by a high IPR value) for the disordered structure, suggesting that both of our samples exhibit disorder. Note that the ordered sample does not have states within the gap, resulting in an infinite IPR value at these energies. (b) The disordered structure results in significant band tailing and a mid-gap state, both of which would significantly impact the performance of a Cu$_2$SnS$_3$-based photovoltaic device.
crystal structure, as was previously determined from the XRD pattern and Raman spectrum.

The annealed sample shows a markedly different grain structure (Figure 6.5b). The grains are larger (200-500 nm) and equiaxed, with no detectable preferential orientation. In this film, some of the grains still have a high density of planar defects (an example is circled in red), while other grains do not exhibit visible planar defects (although it is possible that these grains still contain planar defects that are not oriented such that they can be viewed in our TEM images). We note that this sample was annealed for 2 hrs, and the 8 hr anneal resulted in a lower carrier concentration. It is possible that the 8 hr annealed sample has a higher fraction of grains without visible defects, and that even longer annealing times would further reduce the density of planar defects. The TED pattern for the annealed sample is complex, and is consistent with the monoclinic structure as determined by XRD and Raman (Figure 6.5d).

To understand the effects of stacking faults in Cu$_2$SnS$_3$, we define two different types of imperfections. The first we refer to as “0-Dimensional” (0-D) disorder, i.e., point defect disorder. This type of imperfection manifests itself in the cubic crystal structure as a result of Cu$_{Sn}$ and Sn$_{Cu}$ defects. However, we can also consider stacking faults to be a type of “2-Dimensional” (2-D) imperfection. Thus, although we do not observe the presence of 0-D disorder in the monoclinic sample, the TEM shows that we still have 2-D planar defects. This results in the observed charge localization and short minority carrier lifetimes that we measure in the annealed sample.

From the TEM image shown in Figure 6.5b, it would appear that only some grains display 2-D imperfections in the form of stacking faults. Thus, one explanation for the poor minority charge carrier transport is that the remaining low level of 2-D imperfections still dominates transport. However, it is also possible that the “defect-free” grains do in fact still exhibit 2-D imperfections, but these stacking faults are now oriented such that they cannot be seen in the TEM. In that case, it would suggest that annealing does little to decrease the level of 2-D imperfections in Cu$_2$SnS$_3$. When the weak temperature dependence of disorder
Figure 6.5: (a) As-deposited films show columnar grains with an extremely high density of planar defects. (b) In the annealed films, the planar defect density is reduced in some grains, but remains high in others. (c) and (d) Transmission electron diffraction patterns confirm the zinc blende structure of the unannealed sample, and the complex TED pattern of the annealed sample suggests a monoclinic structure.
from Ref. [103] is taken into account, we would indeed not expect an appreciable change in disorder as a result of annealing. Moving forward, a better understanding of both 0-D and 2-D imperfections will be an important research challenge that must be addressed for future improvement of Cu$_2$SnS$_3$ photovoltaic devices.

6.4.5 Implications of this work for CZTS and other disordered semiconductors

Calculations of the inverse participation ratio for Cu$_2$ZnSnS$_4$ indicate similarly high degrees of charge localization in the kesterite structure (see Fig. S5). The detrimental impacts of disorder in CZTS have been discussed in multiple theoretical works, and include band tailing, potential fluctuations on the order of 200 meV, and the formation of nanoscale compositional inhomogeneities [103, 131, 132]. However, we note that randomly disordered CZTS (“disordered LT”, for low temperature) has an IPR distribution similar to that of the ordered kesterite; negative charge localization effects (high IPR values) are only seen in the clustered disordered structure (“disordered HT”, for high temperature). These challenges have proven difficult to address experimentally, and may slow further increases in the efficiency of CZTS-based photovoltaics. Although Cu$_2$SnS$_3$ is not nearly as well studied as CZTS, the similarities between these two materials suggest that Cu$_2$SnS$_3$-based devices may face similar development challenges in the future.

Newer photovoltaic materials with potentially advantageous disorder effects are also being investigated, such as disorder-related band gap tuning in ZnSnN$_2$ [133, 134]. These design ideas may offer advantages for the optical properties of the materials; however, the investigations will also need to take into account the effects of disorder on the carrier transport properties. Successful future investigations of disordered semiconductors will require the use of new modeling techniques to accurately assess the electronic effects of disorder, such as those developed in Ref. [103]. Experimental quantification of the effects of disorder is equally important, using not only structural analysis, but also techniques such as the terahertz spectroscopy and high-resolution TEM used in this study.
6.5 Conclusions

In this study, we investigated the impacts of cation disorder on the electronic and structural properties of \( \text{Cu}_2\text{SnS}_3 \). We demonstrated the transformation from a cubic to a monoclinic crystal structure upon equilibration of the \( \text{Cu}_2\text{SnS}_3 \) with \( \text{SnS} \), and a concurrent reduction in hole concentration by almost 2 orders of magnitude. We analyzed the as-deposited (cubic/disordered) and annealed (monoclinic/ordered) samples using optical pump terahertz probe spectroscopy, which detected 0.3 and 7 ps decay processes in both samples. By analyzing the complex electrical conductivity from the OPTP measurement, we determined that both samples displayed a high degree of charge localization. When theory was used to calculate the charge localization in ordered and disordered \( \text{Cu}_2\text{SnS}_3 \), it suggested that charge localization is only found in the disordered structure. TEM investigations revealed high densities of stacking faults and/or twins in both samples, which could be responsible for so-called 2-D disorder and the associated poor minority carrier transport.

Overall, the results presented in this work identify several challenges to the use of \( \text{Cu}_2\text{SnS}_3 \) as a photovoltaic absorber. It is possible that different synthesis techniques may result in material without the high density of planar defects exhibited in our sputtered films. However, it is also possible that the formation energy of stacking faults in \( \text{Cu}_2\text{SnS}_3 \) is particularly low, making the presence of these defects thermodynamically unavoidable. In this case, further efforts to improve upon the leading 4% efficient \( \text{Cu}_2\text{SnS}_3 \) may be hampered by both the existence of 2-D disorder, and the difficulty of detecting this disorder. As research into \( \text{Cu}_2\text{SnS}_3 \) moves forward, it will be critical to assess the charge localization and disorder effects, and to correlate these properties with photovoltaic device performance.
CHAPTER 7
PHOTOVOLTAIC DEVICE INTEGRATION OF Cu$_2$SnS$_3$ FILMS

Lauryn L. Baranowski$^{1,2}$, Adam W. Welch$^{1,3}$, Eric S. Toberer$^{1,2}$ and Andriy Zakutayev$^1$

$^1$National Renewable Energy Laboratory, Golden, CO 80401  
$^2$Physics Department, Colorado School of Mines, Golden, CO 80401  
$^3$Department of Chemical and Biological Engineering, Golden, CO 80401

7.1 Introduction

This chapter presents unpublished work on the integration of Cu$_2$SnS$_3$ films into photovoltaic devices. The main challenge of this work was to determine an appropriate conductive back contact that was compatible with our current Cu$_2$SnS$_3$ deposition techniques. Although we performed a survey of eight different back contacts (Mo, Au, Pt, Cu, Pd, Ni, and W-Ti coated glass, and commercial fluorine doped tin oxide (FTO)), we were not able to find a suitable material for this application. We found that many of the back contact metals reacted with the binaries (Cu$_2$S and SnS$_2$) during sputter deposition to form metal alloys. Several others presented persistent secondary phases, likely due to preferential nucleation issues. Only the Au and W-Ti coated glass substrates allowed for growth of phase pure Cu$_2$SnS$_3$. However, when these samples were annealed to improve absorber quality before device integration, we saw significant delamination at the absorber/metal interface. This delamination resulted in shunts within the photovoltaic devices. These results present a significant barrier to the device integration of Cu$_2$SnS$_3$ as grown by our binary sputtering technique.

7.2 Methods

The thin film synthesis and characterization was performed following the techniques outline in Chapter 5. The scanning electron microscopy imaging was performed by Bobby To
at the National Renewable Energy Laboratory using a Nova NanoSEM with 3 kV accelerating voltage and 0.64 nA current.

The photovoltaic devices were fabricated in a standard “substrate” device design, as shown in Figure 7.1. This device design is typically used for CIGS and CZTS research devices. We chose to use this design because of the substantial existing knowledge base at NREL regarding the manufacture of these substrate devices.

![Figure 7.1: The standard “substrate” device design used in CIGS and CZTS. In this configuration, the absorber layers is grown on the conductive back contact, and then the buffer, transparent conducting oxide, and front contact layers are deposited on top [135].](image)

Our device design employed a metal coated glass substrate as a conductive back contact, onto which the absorber layer was sputtered. The desired absorber layer thickness was between 1-2 µm. The absorber must be sufficiently thick so as to absorb all the incident light, and to prevent any shunting between the front and back contacts. However, if the absorber is too thick, photogenerated carriers produced towards the back of the device will recombine before reaching the junction, thus reducing the overall carrier collection efficiency. On top of the absorber layer, an n-type CdS buffer layer was deposited using a standard chemical bath deposition process [76]. A thin (~50nm) layer of intrinsic ZnO was sputtered onto the CdS, followed by an Al-doped ZnO transparent conducting oxide. Finally, the front contact was sputtered through a shadow mask to create a pattern of Al pads and fingers for
contacting the device, and to enhance current collection, respectively.

The devices were tested under one sun illumination using an automated mapping solar simulator. The lamp intensity was calibrated using a Si reference cell. The bias voltage was swept from -0.5 to 1.0 V, and the current measured. The area of the device (0.44 cm$^2$) was used to calculate the current density.

7.3 Results and Discussion

The optimized Cu$_2$SnS$_3$ growth on glass resulted in a Cu$_2$SnS$_3$ film without any detectible impurity phases (as determined by XRD) across nearly the entire 50 mm substrate. This is ideal for device integration, as it allows us to fabricate many Cu$_2$SnS$_3$ devices on one substrate. We refer to this herein as a “wide Cu$_2$SnS$_3$ phase width”. This can be seen in the XRD plot below (Figure 7.2). In this plot, the standard 2$\theta$ is shown on the x-axis. The y-axis shows the location at which the XRD pattern was taken on the 50 mm wide sample. The XRD peaks are shown by the color scale (log scale). From this plot, we see that only the peaks from cubic Cu$_2$SnS$_3$ are visible across most of the sample. There is a small amount of Cu$_4$SnS$_4$ that we can detect at the x=7.4 mm location (bottom-most diffraction pattern).

![Figure 7.2: An optimized Cu$_2$SnS$_3$ sample grown on Eagle-XG glass (EXG), with a wide Cu$_2$SnS$_3$ phase width.](image)

7.3.1 Growth of Cu$_2$SnS$_3$ films on Mo

The initial growth of Cu$_2$SnS$_3$ for device integration was done on Mo-coated soda lime glass substrates. This is the typical conductive back contact used for CIGS and CZTS
devices. In contrast to the wide phase width that we observed on glass (see Figure 7.2), we observed only a narrow region of impurity free Cu$_2$SnS$_3$ when this growth was repeated on Mo, as shown in Figure 7.3a.

We also needed to scale the deposition time such that the resultant Cu$_2$SnS$_3$ films were $\sim 2 \, \mu$m thick, the necessary thickness to ensure the absence of pinholes in a PV device. The film shown in Figure 7.3a was grown for 120 min, because we wanted to exactly replicate the conditions used to grow the film shown in Figure 7.2. When the same deposition parameters were used, but the growth time extended to 420 min (resulting in a 1.5-2 $\mu$m thick film), the resulting film did not show any impurity free Cu$_2$SnS$_3$ (Figure 7.3b).

To resolve these issues, we then applied an “overflux” growth technique, in which both the deposition temperature and the SnS$_2$ flux are raised. The increase in deposition temperature should cause excess SnS$_2$ in the film to enter the vapor phase, while the excess SnS$_2$ flux keeps the film from becoming Cu-rich. This technique typically results in a wide Cu$_2$SnS$_3$ phase width across the entire 50 mm sample. However, as shown in Figure 7.3c and d, this was not the case when growing on Mo. The standard overflux recipe (Figure 7.3c) resulted in mixed phase Cu$_2$SnS$_3$ and Cu$_3$SnS$_4$. When the Cu/Sn flux ratio was further decreased, we observed primarily Cu$_4$SnS$_4$.

### 7.3.2 Growth of Cu$_2$SnS$_3$ films on other conductive substrates

Because of the difficulties of growing Cu$_2$SnS$_3$ on Mo, we performed a survey of Cu$_2$SnS$_3$ growth on a variety of other conductive back contacts, as summarized in Table 7.1. These included Au, Pt, Cu, Pd, Ni, and W-Ti coated soda lime glass (SLG, metal depositions done at NREL), and fluorine doped tin oxide (FTO) coated glass (commercial product). The choice of these back contacts was inspired by a similar study performed for CZTSSe absorbers [136].

We found that many of these substrates (Pd, Ni, Pt, and Cu) reacted during sputtering to form metal alloys or other unidentified phases, as shown in Figure 7.4a-d. Figure 7.4a shows the resulting XRD pattern for the film grown on Pd-coated glass, as well as the
Figure 7.3: (a) When the deposition in Figure 7.2 was repeated on Mo, it resulted in only a narrow phase width of Cu$_2$SnS$_3$. (b), (c), and (d) Further efforts to vary the deposition parameters did not produce the desired Cu$_2$SnS$_3$ phase width.
reference patterns for the Pd substrate, and cubic and monoclinic Cu_{2}SnS_{3}. It appears that the Pd substrate did not react during sputtering, but the XRD peaks do not match those for Cu_{2}SnS_{3} in either structure, nor do they match any commonly observed impurity phases (SnS, Cu_{3}SnS_{4}, Cu_{4}SnS_{4}). When the XRD patterns for the films grown on Ni and Pt (Figure 7.4b and c) are compared with reference patterns for these substrates, it is clear that these metals have reacted during the sputter deposition to form unknown phases, making them unsuitable for use. The film grown on Cu (Figure 7.4d) was observed to be majority Cu_{3}SnS_{4} phase, with some traces of Cu_{2}SnS_{3} at the highest Sn content locations. This result suggests an interesting alternative method to growing Cu_{2}SnS_{3} by sputtering SnS_{2} onto a Cu-coated substrate.

When the Cu_{2}SnS_{3} deposition was performed on the FTO-coated glass, the resultant film was always a mix of Cu_{2}SnS_{3} and Cu_{3}SnS_{4}, as shown in Figure 7.5. We believe this to be due to preferential nucleation of the Cu_{3}SnS_{4} phase, influenced by the surface structure of the FTO.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>As-deposited</th>
<th>Post anneal</th>
</tr>
</thead>
<tbody>
<tr>
<td>EXG</td>
<td>Wide Cu_{2}SnS_{3} phase width</td>
<td>Improvement in material properties</td>
</tr>
<tr>
<td>Mo</td>
<td>Narrow Cu_{2}SnS_{3} phase width</td>
<td>Narrow Cu_{2}SnS_{3} phase width</td>
</tr>
<tr>
<td>Au</td>
<td>Wide Cu_{2}SnS_{3} phase width</td>
<td>Microscopic delamination at metal/Cu_{2}SnS_{3} interface</td>
</tr>
<tr>
<td>W-Ti</td>
<td>Narrow Cu_{2}SnS_{3} phase width</td>
<td>Macroscopic delamination at metal/Cu_{2}SnS_{3} interface</td>
</tr>
<tr>
<td>Pt</td>
<td>Reaction during growth</td>
<td>—</td>
</tr>
<tr>
<td>Cu</td>
<td>Reaction during growth</td>
<td>—</td>
</tr>
<tr>
<td>Ni</td>
<td>Reaction during growth</td>
<td>—</td>
</tr>
<tr>
<td>Pd</td>
<td>Unidentified phase formation</td>
<td>—</td>
</tr>
<tr>
<td>FTO</td>
<td>Cu_{3}SnS_{4} formation</td>
<td>—</td>
</tr>
</tbody>
</table>

We were able to achieve Cu_{2}SnS_{3} growth on both W-Ti and Au coated glass, as shown in Figure 7.6. On the W-Ti substrate, the Cu_{2}SnS_{3} phase width was relatively narrow (although
Figure 7.4: (a) The Pd substrate did not react during the sputter deposition, but unidentifiable phases were produced. (b) and (c) The Ni and Pt substrates reacted during deposition, as evidenced by lack of substrate peaks in the XRD patterns. (d) The Cu substrate reacted during deposition to produce a primarily Cu$_4$SnS$_4$ film.
Figure 7.5: Growth on fluorine doped tin oxide (FTO) resulted in a mixture of Cu$_2$SnS$_3$ and Cu$_3$SnS$_4$, likely due to a preferential nucleation issue.

not as narrow as on Mo), and the majority of locations on the sample showed predominately the Cu$_4$SnS$_4$ phase. On Au, we were able to achieve a wide phase width of Cu$_2$SnS$_3$, by far the most promising result on any of the conductive substrates surveyed.

7.3.3 Annealing of Cu$_2$SnS$_3$ on conductive substrates

To further improve the quality of the absorber before device integration, and in an attempt to widen the Cu$_2$SnS$_3$ phase width, we performed post-deposition annealing on films grown on Mo, W-Ti, and Au. After annealing the W-Ti sample for 2 hrs at 500°C under an SnS atmosphere, we saw macroscopic delamination of the Cu$_2$SnS$_3$ from the substrate, preventing further study of this sample. As shown in Figure 7.7, we observed minimal changes after annealing the film grown on Mo, and the narrow phase width of Cu$_2$SnS$_3$ persisted.

The XRD results after annealing the film on Au looked very promising (see Figure 7.8). The wide Cu$_2$SnS$_3$ phase width was maintained after the annealing, and the small amounts
Figure 7.6: (a) Although the Cu$_2$SnS$_3$ phase width on the W-Ti substrate was relatively narrow, this substrate did not result in unknown phases in the final film. (b) Growth of Cu$_2$SnS$_3$ on Au came closest to replicating the results seen on glass.

Figure 7.7: Annealing the film grown on Mo had minimal effects on the Cu$_2$SnS$_3$ phase width.
of Cu$_4$SnS$_4$ present in the as-deposited sample were not visible in the post-anneal XRD patterns. However, when the annealed sample on Au was examined by cross-sectional SEM (Figure 7.9), we saw significant delamination and void formation at the Cu$_2$SnS$_3$/Au interface. Additional studies determined that the delamination was significantly reduced when the anneal was performed at 300°C rather than 500°C. However, from our annealing studies (see Chapter 6), we know that this reduction in annealing temperature mostly negates the improvements in material quality seen after annealing. Thus, we did not pursue this line of investigation further.

Figure 7.8: Annealing of Cu$_2$SnS$_3$ grown on Au did not result in any impurity phases.

7.3.4 Photovoltaic device testing

The as-deposited and annealed Cu$_2$SnS$_3$ films grown on Au-coated glass were integrated into photovoltaic devices as described above. The current-voltage (J-V) behavior under one sun illumination is shown in Figure 7.10. For each sample, 11 nominally identical devices were fabricated across one row of the substrate. The as-deposited device showed extremely variable J-V response. Most of the devices were dominated by shunts, such that the J-V behavior appeared primarily resistive. Several of the devices showed diode-like behavior
in forward bias, but did not exhibit a photoresponse. The annealed devices showed much better reproducibility in the J-V behavior. All devices exhibited diode-like characteristics. However, there was significant current leakage in reverse bias, suggesting shunts within the device. These shunts are likely due to the delamination at the Cu$_2$SnS$_3$/Au interface, as shown in Figure 7.9. Furthermore, none of the devices exhibited a photoresponse.

7.4 Discussion

A similar study by Altamura, et al. grew CZTSSe absorbers onto Pd, Ni, Au, W, and Pt back contacts (BCs) deposited on Mo-coated SLG [136]. In that work, the ZnS, Cu and Sn layers were deposited onto the BCs and then annealed in an Ar/Se atmosphere to form the CZTSSe absorber. The Altamura, et al. study found that Pd and Ni diffused throughout the entire absorber layer during the growth process. CZTSSe was successfully grown on Au, W,
and Pt back contacts, but XRD and Raman measurements determined that both the W and Pt layers reacted to form $W(S,Se)_2$ and $PtSe_2$, respectively. These chalcogenide layers can be seen in panels (b) and (c) of Figure 7.11. Of all the alternative back contacts surveyed, only the Au did not show any chemical reactions during the absorber growth. However, when the CZTSSe film grown on Au was examined by cross-sectional SEM (panel (a) of Figure 7.11), the Au layer could not be seen. Altamura, et al. theorize that the Au layer dewets from the Mo during the annealing step to form Au particles on the bottom of the absorber (uniform Au layer was observed by SEM after the precursor deposition). Additionally, the CZTSSe film grown on Au was found to have a slightly lower band gap than the sample on Mo (0.92 eV vs. 1.03 eV), which could be due to Au substitution on the Cu sites in the absorber layer.

![Figure 7.11: Cross sectional SEM of CZTSSe grown on Au, W, and Pt layers [136].](image1)

We observed many similar results as those presented in the Altamura, et al. study. Reaction during sputtering was observed for both Pd and Ni BCs. We found that $Cu_2SnS_3$ could be grown on W-Ti and Au BCs without side reactions occurring, and did not observe the W chalcogenides seen in the CZTSSe work. Most strikingly, the delamination we observed at the Au/$Cu_2SnS_3$ interface after annealing could be due to the same dewetting mechanism that caused Au particle growth in the Altamura, et al. work. Similar void formation can be observed at the metal/absorber interface in both our samples (Figure 7.9) and the Altamuta, et al. sample (Figure 7.11(a)).

To understand the difficulties of growing $Cu_2SnS_3$ on Mo using our particular binary sputtering technique, we look to literature reports of successful growths of $Cu_2SnS_3$ on Mo.
Surveying the reports of Cu$_2$SnS$_3$-based devices highlights two techniques: (1) either sequential or co-deposition of Cu and Sn layers, followed by annealing under H$_2$ or S atmosphere [23, 42, 43, 56, 67, 69], or (2) preparation of Cu$_2$SnS$_3$ in powder form and subsequent deposition and annealing on Mo [64, 93]. In our syntheses, we attempted to form the ternary compound during the film growth, rather than before (method 2) or after (method 1) the film growth stage. This may contribute to our difficulties in achieving a wide Cu$_2$SnS$_3$ phase width. However, full understanding of the differences between these processes would require an in-depth study of the nucleation and growth kinetics for Cu$_2$SnS$_3$.

### 7.5 Conclusions

When attempting photovoltaic device integration of our Cu$_2$SnS$_3$ absorbers, we found that the main challenge was translating the thin film growth techniques developed on glass to conductive back contacts. Although we surveyed a wide range of back contact materials, we were not able to find a suitable BC for our Cu$_2$SnS$_3$ devices. We were not successful in replicating the results seen on glass when depositing on the standard Mo-coated soda lime glass. Au and W-Ti back contacts appeared initially promising, as we were able to grow Cu$_2$SnS$_3$ films without any side reactions during sputter deposition. However, after post-deposition annealing was performed to improve the absorber material properties, we observed delamination of the Cu$_2$SnS$_3$ film from the back contact for both the Au and W-Ti substrates. From these results, we conclude that our binary sputtering technique is not suitable for the growth of Cu$_2$SnS$_3$ absorbers for device integration. Judging from literature reports of Cu$_2$SnS$_3$ devices, deposition of elemental precursor layers, followed by annealing, seems to be the most promising synthesis route for producing device quality films.

Although it is difficult to provide an exact reason why our device integration failed, we can draw from other literature for some probable causes. The delamination at the Cu$_2$SnS$_3$/Au/glass interface could possibly be due to Au dewetting at the interface, as was observed for CZTSSe [136]. Furthermore, the difficult of growing Cu$_2$SnS$_3$ on Mo using our binary sputtering technique could be traced to our attempts to deposit the film and form the
ternary compound simultaneously. It is notable that in all other Cu$_2$SnS$_3$ device literature, the ternary phase is formed either before or after the film growth step. Fully understanding the shortcomings of our binary sputtering technique would require an in-depth study of the nucleation and growth mechanisms of Cu$_2$SnS$_3$. 
CHAPTER 8
SUMMARY, CONCLUSIONS, AND FUTURE DIRECTIONS

This chapter will summarize the research performed in this thesis, and present the main conclusions. Then, we will provide insights on the future of Cu$_2$SnS$_3$ as a photovoltaic absorber and discuss the future of the rapid development methodology.

8.1 Summary and conclusions

This thesis illustrated the “rapid development” methodology as applied to the development of Cu-Sn-S compounds for photovoltaic absorber applications. In the exploration stage of the RD methodology, we used experiment and theory to evaluate three candidate absorber materials: Cu$_2$SnS$_3$, Cu$_4$SnS$_4$, and Cu$_4$Sn$_7$S$_{16}$. We found that Cu$_4$SnS$_4$ suffered from too high experimental conductivity, and Cu$_4$Sn$_7$S$_{16}$ was expected to have poor hole transport and weak optical absorption. From this work, we concluded that Cu$_2$SnS$_3$ was the most promising candidate in the Cu-Sn-S family for photovoltaic absorber applications.

In the research stage of the RD approach, we performed two joint experimental and theoretical studies regarding the electronic transport properties of Cu$_2$SnS$_3$. The first study developed experimental techniques to control the level of p-type doping in Cu$_2$SnS$_3$ thin films. A theory evaluation of defect behavior in Cu$_2$SnS$_3$ highlighted two possible mechanisms to explain the variations in carrier concentration: changes in the concentration of Cu vacancies resulting from differences in the S chemical potential, and alloying with an isostructural metallic Cu$_3$SnS$_4$ phase. Raman and NEXAFS spectroscopy techniques were used to experimentally confirm the presence of the Cu$_3$SnS$_4$ alloy in the Cu-rich Cu$_2$SnS$_3$ films.

The second work on Cu$_2$SnS$_3$ investigated the effects of structural disorder on the electronic transport properties. We used annealing to experimentally control the degree of Cu/Sn disorder in the Cu$_2$SnS$_3$ thin films. Then, the majority and minority carrier transport were
measured in the disordered (as deposited) and ordered (annealed) samples. We found improvements in the majority carrier properties, including a reduction in carrier concentration and an increase in hole mobility. We used optical pump terahertz probe spectroscopy to assess the minority carrier transport, and found short carrier lifetimes and high degrees of charge localization for both the ordered and disordered samples. When theory was used to calculate the charge localization in ordered and disordered Cu$_2$SnS$_3$, it suggested that charge localization is only found in the disordered structure. TEM investigations revealed high densities of stacking faults and/or twins in both samples, which could be responsible for 2-D disorder and the associated poor minority carrier transport.

Lastly, in the development step of the RD approach, we explored the growth of Cu$_2$SnS$_3$ on conductive substrates for device integration. Translating the growth techniques developed for glass substrates to metal substrates proved to be challenging. Although we surveyed a wide range of back contact materials, we were not able to find a suitable back contact for our Cu$_2$SnS$_3$ devices. The standard Mo back contact resulted in a narrow Cu$_2$SnS$_3$ phase width. Au and W-Ti were explored as alternative back contacts, but delamination was observed after annealing these films. A literature survey highlighted a major difference between our process and other successful Cu$_2$SnS$_3$ growths on Mo: whereas we attempted to form the ternary compound at the same time as depositing the film, other works formed the ternary compound either before or after depositing the film on the Mo substrate. This difference may have contributed to our observations of significant secondary phase formation when we grew Cu$_2$SnS$_3$ on Mo. Fully understanding the differences between our process and others used in literature would require an in-depth study of the nucleation and growth kinetics of the Cu$_2$SnS$_3$ phase.

8.2 Future of Cu$_2$SnS$_3$ photovoltaics

As discussed in Chapter 2, Cu$_2$SnS$_3$-based photovoltaics have seen large increases in efficiency in recent years, reaching 4.6% in 2015 [31]. However, the findings presented in this work make it difficult to envision a path towards >10% efficiency Cu$_2$SnS$_3$-based devices.
The conclusions presented in Chapter 6 regarding disorder in the Cu$_2$SnS$_3$ structure, and the detrimental effects on minority carrier transport properties, are especially worrisome. A thought it is possible that our particular synthesis technique results in higher levels of disorder than other methods, it is also possible that disorder in Cu$_2$SnS$_3$ is unavoidable due to fundamental thermodynamic reasons. In this case, further efforts to improve Cu$_2$SnS$_3$ devices may be hampered by both the existence of so-called 2-D disorder.

In general, researchers in the field of thin film photovoltaics are now moving away from disordered materials as absorber candidates. In the case of CZTSSe, increases in efficiency much over 10% have proven difficult, and researchers are now realizing that this may be due to the deleterious effects of structural disorder. For many years, when screening potential thin film absorbers, tetrahedrally bonded materials have been considered good candidates because this bond structure should enable good carrier transport properties. However, many new candidate materials are non-tetrahedrally bonded materials with layered structures, such as Sb$_2$Se$_3$ (5.6%), SnS (4.4%), and CuSbSe$_2$ (3%) [20, 25, 137], and this line of investigation is expected to continue to grow.

8.3 Future applications of the “rapid development” approach

Although the application of the RD method to the Cu-Sn-S family of absorbers ultimately eliminated these materials as absorber candidates, the short time elapsed between initial exploration and elimination due to a “fatal flaw” (~2 years) can be considered a success in and of itself. Again contrasting our work on Cu$_2$SnS$_3$ with the development arc of CZTSSe, we see that the disorder issues in CZTSSe took over 10 years to be identified, in contrast to 2 years for Cu$_2$SnS$_3$. Overall, it is the opinion of this researcher that the RD approach holds great potential for the screening and development of new thin film absorbers. In order to yield high impact material breakthroughs, extremely non-traditional materials systems must be considered. The RD method represents an excellent approach to screening these candidates, and mitigates the risk associated with non-traditional materials by considering a large number of candidate materials and by greatly reducing the time
investment in any individual material.

The current synthetic and characterization capabilities at NREL are well suited for the “exploration” stage of the RD approach. These capabilities allowed us to synthesize a variety of Cu-Sn-S phases and characterize their basic properties (structure, composition, electrical conductivity, and optical absorption) in the space of a few months. However, once the project progressed to the “research” stage and the focus was narrowed to the $\text{Cu}_2\text{SnS}_3$ phase, the RD approach became more difficult to execute with the current capabilities. On the synthesis side, more work is needed to achieve smaller gradients in composition across the substrate, as optoelectronic properties may vary greatly with even small gradients. Temperature control is another important issue. The current substrate mount used to generate a temperature gradient results in a drop of 100$^\circ\text{C}$ across $\sim$25mm of the substrate. Although this variation in temperature is useful for the initial experiments in the exploration stage, the 100$^\circ\text{C}$ gradient was far too large for use in the research stage. It was also difficult to achieve a truly uniform temperature across the substrate when the temperature gradient mount was not used, because the temperature uniformity depended heavily on the techniques and materials used to mount the substrate. For better utilization of this capability in the research stage, new substrate mounts should be developed to give smaller temperature gradients, and to ensure better temperature uniformity.

The development of more advanced combinatorial characterization techniques will also help to extend the utility of the RD approach into the research stage. The range of characterization tools required in the research stage includes techniques such as Seebeck and Hall measurements, AFM, and PL. Although work has been done to develop combinatorial capabilities for some of these techniques, they remain underutilized in the research stage. For measurements such as Hall effect, samples must be synthesized nearly uniform, and then cleaved into $\sim$10mm pieces before characterization; these requirements largely negate the combinatorial aspects of the experiment. The development of a contactless Hall system could contribute significantly to combinatorial electrical characterization. Another issue in
the research stage was the difficulty of determining accurate stoichiometries and thicknesses of the films, due to the large amounts of uncertainty in the XRF measurements. Although other techniques exist to verify/calibrate the values from XRF (Rutherford Backscattering spectroscopy and profilometry), the need for more accurate determination of film stoichiometry in a combinatorial fashion remains.

Similarly, the potential of the “development” stage of the RD approach remains under-utilized. This is largely due to reproducibility issues in device performance. Although the capabilities exist for fabrication and testing of 44 individual devices on one substrate, often 5-6 identical devices are required to achieve reliable performance statistics. When this issue is combined with edge effects on the substrate, the number of unique devices able to be tested is greatly reduced. In the case of CuSbS$_2$, the device reproducibility has been greatly improved with post-deposition annealing and the use of photolithography for device isolation (instead of mechanical scribing). Further work in the development stage should focus on other techniques to improve the reproducibility, so that the combinatorial capabilities for device fabrication and testing can be fully utilized.
REFERENCES CITED


[135] NREL Photovoltaic Research: Polycrystalline Thin-Film Materials and Devices R&D, 6 2015.

Density functional theory with onsite Coulomb potential (DFT+U) calculations were performed in a plane wave basis set with the expansion cutoff of 320 eV. The Brillouin zone was sampled with density of at least 430 k-points/(number of atoms in the unit cell) that was found sufficient to converge total energies to 1 meV/atom. All structures were relaxed until a convergence criterion of 0.02 eV/Å for the maximal force component in each direction on each atom is achieved.

We have modeled disordered structures of Cu$_4$Sn$_7$S$_{16}$ and Cu$_3$SnS$_4$ using the following ordered structures: The crystallographic 81 atom cell of Cu$_4$Sn$_7$S$_{16}$ (R3-m) exhibit disorder on tetrahedral Cu sites: the Cu1 site is six-fold degenerated and has fractional occupation of 0.5; the Cu2 and Cu3 site are three-fold degenerated and have fractional occupations of 0.6 and 0.4, respectively. Cu sites are arranged in three layers. We find that the ordered structure with the lowest formation energy has one Cu1 site vacant per layer. Occupation of either the Cu2 site or the Cu3 site leads to the same formation energy because these sites are closely degenerated. Such ordered structure of Cu$_4$Sn$_7$S$_{16}$ was used for the calculation of phase diagram (Figure 4.1). Since the 81 atom crystallographic cell of Cu$_4$Sn$_7$S$_{16}$ is too large for computationally expensive GW calculations we constructed also a smaller model for the Cu$_4$Sn$_7$S$_{16}$ structure based on the rhombohedral 28 atom cell of spinel structure. In this cell we arrange Cu and Sn atoms such that the distance between the empty tetrahedral site and the Cu on the octahedral site is the same as in the crystallographic cell and equals to 6.7 Å. The thus constructed 27 atom cell has formation energy that is only 2 meV/atom higher that that of the 81 atom ordered structure of Cu$_4$Sn$_7$S$_{16}$. Cu$_3$SnS$_4$ structure exhibits disorder on cationic sites of underlying zinc blend structure. For the calculation of phase diagram (Figure 4.1) we constructed an order structure built from tetrahedral S-Cu$_3$Sn motifs. Presence of other motives, such as S-Cu$_2$Sn$_2$ and S-Cu$_4$, leads to higher formation energies.
Figures B1 (High S library), B2 (Intermediate S library) and B3 (Low S library) show individual XRD patterns corresponding to the data shown in Fig. 2. The XRD peaks were matched with the reference patterns for cubic Cu$_2$SnS$_3$ (ICSD #43532), orthorhombic Cu$_3$SnS$_4$ (ICDD #00-036-0217), trigonal Cu$_4$Sn$_7$S$_{16}$ (ICSD #50964), orthorhombic Cu$_4$SnS$_4$ (ICSD #833), and orthorhombic SnS (ICSD #24376).
B1: Representative single point XRD patterns for the “High S” library (library 1), showing the Cu$_3$SnS$_4$/Cu$_2$SnS$_3$ (a) - Cu$_2$SnS$_3$ (b) - Cu$_4$Sn$_7$S$_{16}$/Cu$_2$SnS$_3$ (c) phase progression.
B2: Representative single point XRD patterns for the “Intermediate S” library (library 2), showing the $\text{Cu}_3\text{SnS}_4/\text{Cu}_2\text{SnS}_3$ (a) - $\text{Cu}_2\text{SnS}_3$ (b) - SnS/\text{Cu}_2\text{SnS}_3 (c) phase progression.
B3: Representative single point XRD patterns for the “Low S” library (library 1), showing the Cu₄Sn₄/Cu₂Sn₃ (a) - Cu₂Sn₃ (b) phase progression.
Investigation of annealing conditions

From our previous work, we know that the lowest doping levels in Cu$_2$SnS$_3$ are achieved in Cu-poor and S-poor environments [90]. Consulting the Cu-Sn-S chemical potential phase space in Ref. [55] we see that these conditions are achieved when Cu$_2$SnS$_3$ is in equilibrium with SnS. To verify this theoretical result, we annealed the Cu$_2$SnS$_3$ films under three different atmospheres: Ar only, SnS$_2$+Ar and SnS+Ar (note that SnS sublimes congruently, while the SnS$_2$ powder would be expected to produce a S-rich atmosphere). As expected, the SnS atmosphere resulted in the largest reduction in carrier concentration (see Figure 6.1 in the main text). The SnS$_2$ atmosphere resulted in moderate carrier concentration reductions, which is likely because the atmosphere was more S-rich than the SnS anneal. Finally, the Ar only atmosphere produced very small reductions in carrier concentration. This can be attributed to the fact that this atmosphere is Sn-poor (analogous to Cu-rich) compared to the other two atmospheres investigated. Concurrent with the decreases in carrier concentration, we observed a slight increase in mobility for the sample annealed in the SnS atmosphere. This increase in mobility is likely connected to a decrease in defect-related scattering caused by the carrier concentration reductions.

To investigate the kinetics of annealing in the SnS atmosphere, we annealed the Cu$_2$SnS$_3$ films at temperatures of 300, 400, and 500°C, while keeping the anneal duration constant at 30 minutes. Above 500°C, significant material loss and film delamination was observed. As shown in Figure 6.1, the 400°C and 500°C annealing temperatures showed significant reductions in carrier concentration as compared to the 300°C sample. It is possible that temperatures higher than 500°C could result in further carrier concentration decreases, but as mentioned above, this was not possible due to material losses at higher temperatures. Thus, we also investigated longer anneal durations at 500°C. We observed that increasing
the anneal duration from 30 minutes to 2 hrs resulted in a lower carrier concentration, and an 8 hr anneal time resulted in further carrier concentration decreases. This indicates that the kinetics of the defect reduction is fairly slow. Although it is possible that further decreases would be observed at anneal times longer than 8 hrs, longer anneals were not investigated in this study.

The structural change from cubic to monoclinic was only observed for the longer time anneals (2 hrs and 8 hrs). For all the 30 minute anneals (at 300°C, 400°C, and 500°C), the XRD pattern suggested a cubic structure after annealing. After annealing, the films lost their preferential orientation: all expected diffraction peaks were observed, as opposed to only the \{111\} peak observed prior to annealing.

Shown below in Table S1 are the film thicknesses and Cu/(Cu+Sn) ratios for all samples discussed in this work. For each sample, 1 row was used as a control. Note that the measured Cu/(Cu+Sn) value for stoichiometric Cu$_2$SnS$_3$ is \(\sim 0.62\). This is a result of a systematic XRF error that is caused by spurious Sn signals from the glass substrate. As shown by the data in Table C1, we see minimal changes in film thickness or composition after annealing, except for the lowest temperature (300°C) and shortest time (0.5 hr) anneals.

Figures C1, C2, C3, and C4 are referenced in Chapter 6.

C1: Three observed crystal structures of Cu$_2$SnS$_3$, resulting from different levels of Cu/Sn cation site disorder. Unit cells are not shown to scale. Figure prepared using VESTA.
C1: XRF data shows that we observed minimal film thickness or compositional changes were observed after annealing.

<table>
<thead>
<tr>
<th>Anneal time (hr)</th>
<th>Anneal temp (°C)</th>
<th>Anneal atm</th>
<th>Thickness (µm)</th>
<th>Cu/(Cu+Sn)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample #444</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td></td>
<td></td>
<td>0.567</td>
<td>0.62</td>
</tr>
<tr>
<td>0.5</td>
<td>300</td>
<td>SnS</td>
<td>0.605</td>
<td>0.57</td>
</tr>
<tr>
<td>0.5</td>
<td>400</td>
<td>SnS</td>
<td>0.571</td>
<td>0.62</td>
</tr>
<tr>
<td>0.5</td>
<td>500</td>
<td>SnS</td>
<td>0.572</td>
<td>0.62</td>
</tr>
<tr>
<td>Sample #489</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td></td>
<td></td>
<td>1.12</td>
<td>0.62</td>
</tr>
<tr>
<td>0.5</td>
<td>500</td>
<td>SnS</td>
<td>1.13</td>
<td>0.62</td>
</tr>
<tr>
<td>2</td>
<td>500</td>
<td>SnS</td>
<td>1.15</td>
<td>0.62</td>
</tr>
<tr>
<td>8</td>
<td>500</td>
<td>SnS</td>
<td>1.10</td>
<td>0.62</td>
</tr>
<tr>
<td>Sample #491</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td></td>
<td></td>
<td>0.917</td>
<td>0.63</td>
</tr>
<tr>
<td>0.5</td>
<td>400</td>
<td>Ar</td>
<td>1.06</td>
<td>0.63</td>
</tr>
<tr>
<td>0.5</td>
<td>400</td>
<td>SnS₂</td>
<td>0.957</td>
<td>0.61</td>
</tr>
<tr>
<td>0.5</td>
<td>400</td>
<td>SnS</td>
<td>1.06</td>
<td>0.56</td>
</tr>
<tr>
<td>Sample #501</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td></td>
<td></td>
<td>1.08</td>
<td>0.59</td>
</tr>
<tr>
<td>2</td>
<td>500</td>
<td>SnS</td>
<td>1.00</td>
<td>0.60</td>
</tr>
</tbody>
</table>

C2: The increase in Hall mobility at low temperatures suggests that the hole transport is not grain boundary limited in the pre-annealed samples.
C3: Carrier localization is suggested by the negative imaginary component of the frequency-dependent terahertz conductivity.

C4: The electronic effects of disorder are even more pronounced in the kesterite structure of CZTS than in Cu$_2$SnS$_3$. 
APPENDIX D - PERMISSIONS

Permissions to include papers in Chapters 4, 5, and 6 from the publishers and non-committee co-authors are included below.
# AIP PUBLISHING LLC LICENSE TERMS AND CONDITIONS

**Jun 09, 2015**

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

<table>
<thead>
<tr>
<th><strong>License Number</strong></th>
<th>3644910787506</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Order Date</strong></td>
<td>Jun 09, 2015</td>
</tr>
<tr>
<td><strong>Publisher</strong></td>
<td>AIP Publishing LLC</td>
</tr>
<tr>
<td><strong>Publication</strong></td>
<td>Applied Physics Letters</td>
</tr>
<tr>
<td><strong>Article Title</strong></td>
<td>Evaluation of photovoltaic materials within the Cu-Sn-S family</td>
</tr>
<tr>
<td><strong>Author</strong></td>
<td>Pawel Zawadzki, Lauryn L. Baranowski, Haowei Peng, et al.</td>
</tr>
<tr>
<td><strong>Online Publication Date</strong></td>
<td>Dec 18, 2013</td>
</tr>
<tr>
<td><strong>Volume number</strong></td>
<td>103</td>
</tr>
<tr>
<td><strong>Issue number</strong></td>
<td>25</td>
</tr>
<tr>
<td><strong>Type of Use</strong></td>
<td>Thesis/Dissertation</td>
</tr>
<tr>
<td><strong>Requestor type</strong></td>
<td>Author (original article)</td>
</tr>
<tr>
<td><strong>Format</strong></td>
<td>Electronic</td>
</tr>
<tr>
<td><strong>Portion</strong></td>
<td>Excerpt (&gt; 800 words)</td>
</tr>
<tr>
<td><strong>Will you be translating?</strong></td>
<td>No</td>
</tr>
<tr>
<td><strong>Title of your thesis / dissertation</strong></td>
<td>Combinatorial Development of Cu2SnS3 as an Earth Abundant Photovoltaic Absorber</td>
</tr>
<tr>
<td><strong>Expected completion date</strong></td>
<td>Aug 2015</td>
</tr>
<tr>
<td><strong>Estimated size (number of pages)</strong></td>
<td>150</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>0.00 USD</td>
</tr>
</tbody>
</table>

## Terms and Conditions

AIP Publishing LLC ("AIPP") hereby grants to you the non-exclusive right and license to use and/or distribute the Material according to the use specified in your order, on a one-time basis, for the specified term, with a maximum distribution equal to the number that you have ordered. Any links or other content accompanying the Material are not the subject of this license.

1. You agree to include the following copyright and permission notice with the reproduction of the Material: "Reprinted with permission from [FULL CITATION]. Copyright [PUBLICATION YEAR], AIP Publishing LLC." For an article, the copyright and permission notice must be printed on the first page of the article or book chapter. For photographs, covers, or tables, the copyright and permission notice may appear with the Material, in a footnote, or in the reference list.

2. If you have licensed reuse of a figure, photograph, cover, or table, it is your responsibility to ensure that the material is original to AIPP and does not contain the copyright of another entity, and that the copyright notice of the figure, photograph, cover, or table does not indicate that it was reprinted by AIPP, with permission, from another source. Under no circumstances does AIPP, purport or intend to grant permission to reuse material to which
it does not hold copyright.
3. You may not alter or modify the Material in any manner. You may translate the Material into another language only if you have licensed translation rights. You may not use the Material for promotional purposes. AIPP reserves all rights not specifically granted herein.
4. The foregoing license shall not take effect unless and until AIPP or its agent, Copyright Clearance Center, receives the Payment in accordance with Copyright Clearance Center Billing and Payment Terms and Conditions, which are incorporated herein by reference.
5. AIPP or the Copyright Clearance Center may, within two business days of granting this license, revoke the license for any reason whatsoever, with a full refund payable to you. Should you violate the terms of this license at any time, AIPP, AIP Publishing LLC, or Copyright Clearance Center may revoke the license with no refund to you. Notice of such revocation will be made using the contact information provided by you. Failure to receive such notice will not nullify the revocation.
6. AIPP makes no representations or warranties with respect to the Material. You agree to indemnify and hold harmless AIPP, AIP Publishing LLC, and their officers, directors, employees or agents from and against any and all claims arising out of your use of the Material other than as specifically authorized herein.
7. The permission granted herein is personal to you and is not transferable or assignable without the prior written permission of AIPP. This license may not be amended except in a writing signed by the party to be charged.
8. If purchase orders, acknowledgments or check endorsements are issued on any forms containing terms and conditions which are inconsistent with these provisions, such inconsistent terms and conditions shall be of no force and effect. This document, including the CCC Billing and Payment Terms and Conditions, shall be the entire agreement between the parties relating to the subject matter hereof.

This Agreement shall be governed by and construed in accordance with the laws of the State of New York. Both parties hereby submit to the jurisdiction of the courts of New York County for purposes of resolving any disputes that may arise hereunder.

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.
Multi author permission for thesis - 2013 APL

5 messages

Lauryn Baranowski <l.baranow@mines.edu>  
To: pwlzawadzki@gmail.com, David Ginley <David.Ginley@nrel.gov>, "Tumas, Bill" <bill.tumas@nrel.gov>, "Lany, Stephan" <Stephan.Lany@nrel.gov>, haowei.peng@temple.edu

Hi all,

As part of my upcoming PhD thesis, I will be reprinting some of the figures from Pawel's "Evaluation of photovoltaic materials within the Cu-Sn-S family", published in APL in 2013. Mines dictates that, in addition to permission from AIP, I also need obtain permission from any other authors on this publication to include the figures in my thesis.

Please give your permission by replying to this email.

Thanks,
Lauryn

Paweł Zawadzki <pwlzawadzki@gmail.com>  
To: Lauryn Baranowski <l.baranow@mines.edu>

You have my permissions.

Best regards,

Pawel Zawadzki

Lauryn Baranowski <l.baranow@mines.edu>  
To: Paweł Zawadzki <pwlzawadzki@gmail.com>

Thanks Pawel! Sorry for having to spam you three times :)

Haowei Peng <tuf86680@temple.edu>  
To: Lauryn Baranowski <l.baranow@mines.edu>

I am okay with that.

Best,
Haowei

Paweł Zawadzki <pwlzawadzki@gmail.com>  
To: Lauryn Baranowski <l.baranow@mines.edu>

No problem. Have a nice day!
PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.

9 messages

Laurn Baranowski <lbaranow@mines.edu>  
Tue, Jun 9, 2015 at 1:00 PM  
To: pwlzawadzki <pwlzawadzki@gmail.com>, "Christensen, Steven" <Steven.Christensen@nrel.gov>, Dennis Nordlund <nordlund@slac.stanford.edu>, "Lany, Stephan" <Stephan.Lany@nrel.gov>, "Tamboli, Adele" <adele.tamboli@nrel.gov>, lynn.gedvilas@nrel.gov, "Tumas, Bill" <bill.tumas@nrel.gov>, David Ginley <David.Ginley@nrel.gov>

Hi all,

As part of my upcoming PhD thesis, I will be reprinting my Chemistry of Materials paper "Control of doping in Cu2SnS3 through defects and alloying" from 2014. Mines dictates that, in addition to permission from ACS, I also need obtain permission from any other authors on this publication to include it in my thesis.

Please give your permission by replying to this email.

Thanks,
Laurn

Ginley, David <David.Ginley@nrel.gov>  
Tue, Jun 9, 2015 at 1:03 PM  
To: Lauryn Baranowski <lbaranow@mines.edu>  
Cc: pwlzawadzki <pwlzawadzki@gmail.com>, "Christensen, Steven" <Steven.Christensen@nrel.gov>, Dennis Nordlund <nordlund@slac.stanford.edu>, "Lany, Stephan" <Stephan.Lany@nrel.gov>, "Tamboli, Adele" <Adele.Tamboli@nrel.gov>, "Gedvilas, Lynn" <Lynn.Gedvilas@nrel.gov>, "Tumas, Bill" <Bill.Tumas@nrel.gov>

You certainly have my permission
Dave

Sent from my iPad
[Quoted text hidden]

Tumas, Bill <Bill.Tumas@nrel.gov>  
Tue, Jun 9, 2015 at 1:04 PM  
To: Lauryn Baranowski <lbaranow@mines.edu>, pwlzawadzki <pwlzawadzki@gmail.com>, "Christensen, Steven" <Steven.Christensen@nrel.gov>, Dennis Nordlund <nordlund@slac.stanford.edu>, "Lany, Stephan" <Stephan.Lany@nrel.gov>, "Tamboli, Adele" <Adele.Tamboli@nrel.gov>, "Gedvilas, Lynn" <Lynn.Gedvilas@nrel.gov>, "Ginley, David" <David.Ginley@nrel.gov>

Fine with me

William Tumas  
Associate Lab Director, Materials and Chemical Science and Technology-MCST Directorate  
National Renewable Energy Laboratory  
15013 Denver West Parkway  
Golden, CO  80401  
Cell: 720-362-0270  
Office: 303-384-7955  
bill.tumas@nrel.gov
From: Lauryn Baranowski <lbaranow@mines.edu>  
Date: Tuesday, June 9, 2015 1:00 PM  
To: pwlzawadzki <pwlzawadzki@gmail.com>, "Christensen, Steven" <Steven.Christensen@nrel.gov>, Dennis Nordlund <nordlund@slac.stanford.edu>, "Lany, Stephan" <Stephan.Lany@nrel.gov>, "Tamboli, Adele" <Adele.Tamboli@nrel.gov>, Bill Tumas <bill.tumas@nrel.gov>, "Ginley, David" <David.Ginley@nrel.gov>  

Hi all,

[Quoted text hidden]

From: l.l.baranowski@gmail.com [mailto:l.l.baranowski@gmail.com]  
On Behalf Of Lauryn Baranowski  
Sent: Tuesday, June 09, 2015 1:01 PM  
To: pwlzawadzki; Christensen, Steven; Dennis Nordlund; Lany, Stephan; Tamboli, Adele; Gedvilas, Lynn; Tumas, Bill; Ginley, David  

Hi all,

[Quoted text hidden]

Pawel Zawadzki <pwlzawadzki@gmail.com>  
To: Lauryn Baranowski <lbaranow@mines.edu>  

You have my permissions.

Best regards,  
Pawel Zawadzki  
[Quoted text hidden]

Christensen, Steven <Steven.Christensen@nrel.gov>  
To: Lauryn Baranowski <lbaranow@mines.edu>  

You have my permission.

-Steve
On Jun 9, 2015, at 1:00 PM, Lauryn Baranowski <lbaranow@mines.edu><mailto:lbaranow@mines.edu>>

[Quoted text hidden]

**Tamboli, Adele**<Adele.Tamboli@nrel.gov>
To: Lauryn Baranowski <lbaranow@mines.edu>

Fine with me

From: Lauryn Baranowski <lbaranow@mines.edu><mailto:lbaranow@mines.edu>>
Date: Tuesday, June 9, 2015 1:00 PM
To: pwlzawadzki <pwlzawadzki@gmail.com><mailto:pwlzawadzki@gmail.com>>, "Christensen, Steven"<Steven.Christensen@nrel.gov><mailto:Steven.Christensen@nrel.gov>>, Dennis Nordlund <nordlund@slac.stanford.edu><mailto:nordlund@slac.stanford.edu>>, "Lany, Stephan"<Stephan.Lany@nrel.gov><mailto:Stephan.Lany@nrel.gov>>, Adele Tamboli <adele.tamboli@nrel.gov><mailto:adele.tamboli@nrel.gov>>, "Gedvilas, Lynn"<Lynn.Gedvilas@nrel.gov><mailto:Lynn.Gedvilas@nrel.gov>>, "Tumas, Bill"<Bill.Tumas@nrel.gov><mailto:Bill.Tumas@nrel.gov>>, "Ginley, David"<David.Ginley@nrel.gov><mailto:David.Ginley@nrel.gov>>

[Quoted text hidden]

**Lany, Stephan**<Stephan.Lany@nrel.gov>
To: Lauryn Baranowski <lbaranow@mines.edu>

yes, sure

Stephan Lany, PhD
Sr. Scientist, National Renewable Energy Laboratory
15013 Denver West Pkwy
Golden, CO 80401
e. Stephan.Lany@NREL.gov<mailto:Stephan.Lany@NREL.gov>
p. 303-384-6652
f. 303-384-6432

From: Lauryn Baranowski <lbaranow@mines.edu><mailto:lbaranow@mines.edu>>
Date: Tuesday, June 9, 2015 1:00 PM
To: pwlzawadzki <pwlzawadzki@gmail.com><mailto:pwlzawadzki@gmail.com>>, "Christensen, Steven"<Steven.Christensen@nrel.gov><mailto:Steven.Christensen@nrel.gov>>, Dennis Nordlund <nordlund@slac.stanford.edu><mailto:nordlund@slac.stanford.edu>>, Stephan Lany <stephan.lany@nrel.gov><mailto:stephan.lany@nrel.gov>>, "Tamboli, Adele"<Adele.Tamboli@nrel.gov><mailto:Adele.Tamboli@nrel.gov>>, "Gedvilas, Lynn"<Lynn.Gedvilas@nrel.gov><mailto:Lynn.Gedvilas@nrel.gov>>, "Tumas, Bill"<Bill.Tumas@nrel.gov><mailto:Bill.Tumas@nrel.gov>>, "Ginley, David"<David.Ginley@nrel.gov><mailto:David.Ginley@nrel.gov>>

[Quoted text hidden]

8 messages

Lauryn Baranowski <l.l.baranowski@gmail.com>

Tue, Jun 9, 2015 at 1:05 PM
To: pwlzawadzki <pwlzawadzki@gmail.com>, "Lany, Stephan" <Stephan.Lany@nrel.gov>, andrew.norman@nrel.gov, hannes.hempel@helmholtz-berlin.de, unold@helmholtz-berlin.de, eichberger@helmholtz-berlin.de

Hi all,

As part of my upcoming PhD thesis, I will be reprinting my Physical Review Applied paper "Effects of disorder on carrier transport in Cu2SnS3" that is currently under review. Mines dictates that, in addition to permission from APS, I also need obtain permission from any other authors on this publication to include it in my thesis.

Please give your permission by replying to this email.

Thanks,
Lauryn

---

Lauryn Baranowski <l.l.baranowski@gmail.com>

Tue, Jun 9, 2015 at 1:07 PM
To: "kevin.r.mclaughlin@vanderbilt.edu" <kevin.r.mclaughlin@vanderbilt.edu>

Hi Kevin,

Hope your year is going well! I am finally getting around to publishing the annealing work you helped with on Cu2SnS3 last summer. The paper I submitted is attached, and is currently being peer reviewed at Physical Review Applied. Once it gets accepted somewhere, I'll send you the final version.

I will also be including this work in my thesis. Because it is a multi-author work, I need you to approve the use of the work. You can just email me back saying that you give your permission.

Thanks!
Lauryn

---

Effects of disorder on carrier transport in Cu2SnS3.pdf
418K

Paweł Zawadzki <pwlzawadzki@gmail.com>

Tue, Jun 9, 2015 at 1:14 PM
To: Lauryn Baranowski <l.l.baranowski@gmail.com>

You have my permissions.

Best regards,
Paweł Zawadzki

Kevin Ross McLaughlin <kevin.r.mclaughlin@vanderbilt.edu>

Tue, Jun 9, 2015 at 1:32 PM
To: Lauryn Baranowski <l.l.baranowski@gmail.com>

https://mail.google.com/mail/u/0/?ui=2&ik=64b3d5d19f&view=pt&se...l=14dd9b66736334ab&siml=14ddc8d428e768d7&siml=14ddd087f8518ae3
Hi Lauryn,

Congratulations! I give you full permission. Thanks so much for including me. Please let me know when the paper gets approved and published, I'm excited about it. Hope you're doing well, and good luck with your thesis!

Kevin

Unold, Thomas <unold@helmholtz-berlin.de>
To: Lauryn Baranowski <l.l.baranowski@gmail.com>
Cc: pwlzawadzki <pwlzawadzki@gmail.com>, "Lany, Stephan" <Stephan.Lany@nrel.gov>, "andrew.norman@nrel.gov" <andrew.norman@nrel.gov>, "Hempel, Hannes" <hannes.hempel@helmholtz-berlin.de>, "Eichberger, Rainer" <eichberger@helmholtz-berlin.de>

Fine with me
Thomas

Norman, Andrew <Andrew.Norman@nrel.gov>
To: Lauryn Baranowski <l.l.baranowski@gmail.com>, pwlzawadzki <pwlzawadzki@gmail.com>, "Lany, Stephan" <Stephan.Lany@nrel.gov>, "hannes.hempel@helmholtz-berlin.de" <hannes.hempel@helmholtz-berlin.de>, "unold@helmholtz-berlin.de" <unold@helmholtz-berlin.de>, "eichberger@helmholtz-berlin.de" <eichberger@helmholtz-berlin.de>

Hi Lauryn,

I approve you, good luck with your thesis.

Andrew

[Quoted text hidden]

Hempel, Hannes <hannes.hempel@helmholtz-berlin.de>  
To: Lauryn Baranowski <l.l.baranowski@gmail.com>  

Hey,

It's fine.

Hannes

Von: Lauryn Baranowski [l.l.baranowski@gmail.com]  
An: plwzawadzki; Lany, Stephan; andrew.norman@nrel.gov; Hempel, Hannes; Unold, Thomas; Eichberger, Rainer  

[Quoted text hidden]

Helmholtz-Zentrum Berlin für Materialien und Energie GmbH
Mitglied der Hermann von Helmholtz-Gemeinschaft Deutscher Forschungszentren e.V.

Aufsichtsrat: Vorsitzender Prof. Dr. Dr. h.c. mult. Joachim Treusch, stv. Vorsitzende Dr. Beatrix Vierkorn-Rudolph
Geschäftsführung: Prof. Dr. Anke Rita Kaysser-Pyzalla, Thomas Frederking

Sitz Berlin, AG Charlottenburg, 89 HRB 5583

Postadresse:
Hahn-Meitner-Platz 1
D-14109 Berlin

http://www.helmholtz-berlin.de

Eichberger, Rainer <eichberger@helmholtz-berlin.de>  
To: Lauryn Baranowski <l.l.baranowski@gmail.com>, plwzawadzki <plwzawadzki@gmail.com>, "Lany, Stephan" <Stephan.Lany@nrel.gov>, "andrew.norman@nrel.gov" <andrew.norman@nrel.gov>, "Hempel, Hannes" <hannes.hempel@helmholtz-berlin.de>, "Unold, Thomas" <unold@helmholtz-berlin.de>  

No problem,
Rainer

Von meinem Windows Phone gesendet

Von: Lauryn Baranowski  
Gesendet: 09.06.2015 21:06  
An: plwzawadzki; Lany, Stephan; andrew.norman@nrel.gov; Hempel, Hannes; Unold, Thomas; Eichberger, Rainer

[Quoted text hidden]

Helmholtz-Zentrum Berlin für Materialien und Energie GmbH

Mitglied der Hermann von Helmholtz-Gemeinschaft Deutscher Forschungszentren e.V.

Aufsichtsrat: Vorsitzender Prof. Dr. Dr. h.c. mult. Joachim Treusch, stv. Vorsitzende Dr. Beatrix Vierkorn-Rudolph
Geschäftsführung: Prof. Dr. Anke Rita Kaysser-Pyzalla, Thomas Frederking

Sitz Berlin, AG Charlottenburg, 89 HRB 5583

Postadresse:
Hahn-Meitner-Platz 1
D-14109 Berlin

http://www.helmholtz-berlin.de
APPENDIX E - PUBLICATION LIST

\( \text{Cu}_2\text{SnS}_3 \)


\textbf{Review papers}


\textbf{Other PV materials}


Si-Ge clathrates for optoelectronic applications


Solar thermoelectric generators

