Graphical Abstract (for review)

Equilibrium Vapor Pressure (Torr)

Self-regulated growth and tunable properties of CuSbS₂ solar absorbers

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Abstract

Polycrystalline thin film copper chalcogenide solar cells show remarkable efficiencies, and analogous but less-explored semiconducting materials may hold similar promise. With consideration of elemental abundance and process scalability, we explore the potential of the Cu-Sb-S material system for photovoltaic applications. Using a high-throughput combinatorial approach, Cu-Sb-S libraries were synthesized by magnetron co-sputtering of Cu₂S and Sb₂S₃ targets and evaluated by a suite of spatially resolved characterization techniques. The resulting compounds include Cu_{1.8}S (digenite), Cu₁₂Sb₄S₁₃ (tetrahedrite), CuSbS₂ (chalcostibite), and Sb₂S₃ (stibnite). Of the two ternary phases synthesized, CuSbS₂ was found to have the most potential, however, when deposited at low temperatures its electrical conductivity varied by several orders of magnitude due to the presence of impurities. To address this issue, we developed a self-regulated approach to synthesize stoichiometric CuSbS₂ films using excess Sb₂S₃ vapor at elevated substrate temperatures. Theoretical calculations explain that phase-pure CuSbS₂ is expected to be formed over a relatively wide range of temperatures and pressures, bound by the sublimation of Sb₂S₃ and decomposition of CuSbS₂. The carrier concentration of CuSbS₂ films produced within this regime was tunable from 10¹⁶ – 10¹⁸ cm⁻³ through appropriate control of Sb₂S₃ flux rate and substrate temperature. CuSbS₂ displayed a sharp optical absorption onset indicative of a direct transition at 1.5 eV and an absorption coefficient of 10⁵ cm⁻¹ within 0.3 eV of the onset. The results of this study suggest that CuSbS₂ holds promise for solar energy conversion due to its tolerant processing window, tunable carrier concentration, solar-matched band gap, and high absorption coefficient.

Keywords: Chalcogenide, Earth Abundant, CuSbS₂, Chalcostibite, Sputter Deposition, Antimony, Layered Structure, Combinatorial

1. Introduction

Given the exponential rise in energy consumption, any renewable energy source capable of replacing fossil fuels must be eminently scalable[1]. Advanced photovoltaic research is therefore benefitted by a focus on semiconductors synthesized with scalable processes, and composed of earth abundant, easily purified elements[2]. Many materials based on earth abundant anions have recently attracted attention, including sulfides (FeS₂[3, 4, 5], SnS[6, 7]), nitrides (ZnSnN₂[8, 9], CuTa₂N₂[10]), phosphides (Zn₃P₂[11, 12], ZnSnP₂[13, 14]) and oxides (Cu₂O[15, 16]). Choosing earth abundant cations for photovoltaic semiconductors can be daunting due to numerous criteria that solar cell absorbers have to satisfy, including strong optical absorption, moderate doping, long minority carrier lifetime, long-term stability etc. Polycrystalline photovoltaic absorbers also require that the defects created due to the crystal imperfections do not affect all of these required properties. Cu-based materials, such as binary Cu₂S, Cu₂O[17], Cu₃N[18] and related ternary[19, 20] and quaternary[21, 22] compounds offer a promising paradigm from which such defect tolerant semiconducting compounds can be found.

Of particular relevance to this study are copper based sulfides. The binary Cu₂S has more than three decades of experimental photovoltaic research[23] quickly reaching 10% efficiency in 1980s, but early work showed that Cu₂S device quality degrades due to a light- and bias-enhanced room temperature mobility of Cu[24]. Researchers therefore began to focus on ternary compounds, most notably CuInSe₂, and subsequently Cu(In,Ga)Se₂ (CIGS), which had similar properties but did not suffer the Cu diffusion problem[25]. CIGS research progressed well, producing stable solar cells in excess of 20% efficiency[26]. However, there is concern that achieving terawatt levels of energy generation may be limited by the low supply of indium and gallium, especially considering the high demand for these elements in flat panel displays and other technologies[27]. Replacing indium and gallium with more earth abundant elements, such as Zn and Sn, has resulted in 11% efficient Cu₂ZnSn(S,Se)₄ (CZTS) photovoltaic devices[28]. However, further improvements in the chemically complex quaternary CZTS may be hampered by a high number of deep trap defect states[29], potential fluctuations, and band tailing[30]. This situation has created a resurgence of interest in less complex ternary copper sulfides such as Cu-Sn-S[20, 31, 32], recently leading to 6% efficient Cu₂(Sn,Ge)S₄ solar cells[33].

Antimony based copper sulfide ternaries are another good

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alternative, with potential economic and chemical advantages over CuInS_2 . Antimony is a relatively earth-abundant element, currently sixty times less expensive than indium, and significantly greater in estimated world reserves[34]. In addition, indium/gallium and antimony share a common oxidation state (+3) producing analogous chemistry. Both CuSbS_2 [35, 36, 37] and CuInS_2 [25] share a direct band gap of 1.5 eV that is well-suited for terrestrial solar energy conversion. The more subtle chemical differences between these cations, specifically the non-bonding lone pair of electrons in the group-V Sb atom, may lead to steeper absorption onsets in CuSbS_2 than in its indium counterpart[19]. Reports on the solar cell related properties of Cu-Sb-S compounds can be found in literature[38]; such as CuSbS_2 [39, 40, 41], Cu_3SbS_3 [42], Cu_3SbS_4 [43] and $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ [44]. Other potential applications have also been investigated, including thermoelectrics,[45, 46, 47] and batteries[48]. Very recently, 3% efficient CuSbS_2 photovoltaic device prototypes have been reported[49], pointing to the need for improved control of the device parameters, in particular absorber composition of this line compound.

Here we report on a promising approach to scalable sputter synthesis[50] of highly stoichiometric CuSbS_2 by self-regulated growth in excess Sb_2S_3 vapor, and discuss the electrical transport and optical absorption properties of the resulting high-quality thin films. First, we present a brief introduction of the known ternary phases of Cu-Sb-S, focusing on the two phases which were successfully synthesized in this study; CuSbS_2 and $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$. Then we analyze the electrical properties of combinatorial thin film libraries of these two phases, which narrows our interest to CuSbS_2 . Most importantly, we identify a relatively broad region of growth conditions where the stoichiometric phase-pure CuSbS_2 line compound can be synthesized by a self-regulated deposition in excess Sb_2S_3 vapor. We use density functional theory (DFT) calculations to evaluate the formation enthalpy of these ternary compounds and their competing phases, along with an analysis of thermochemical stability to explain the experimentally observed phenomenon of self-regulated CuSbS_2 growth. Additionally, a control of carrier concentration via Sb_2S_3 flux (RF power ratio) and growth temperature is described. Finally, we investigate the optical properties of CuSbS_2 with specific focus on sub-gap absorption. The results of this study build a solid foundation for further development of CuSbS_2 based thin film solar cells with improved energy conversion efficiencies.

2. Methods

A systematic analysis of photovoltaic absorber properties within a broad parameter space benefits greatly by the application of high-throughput combinatorial methodology[51, 52]. Our current thin film implementation of the combinatorial approach[53] consists of physical vapor deposition with orthogonal composition and temperature gradients, matched to spatially resolved characterization of chemical, structural and optoelectronic properties. The large amount of data is processed and analyzed by semi-automated custom software routines. This technique has been shown useful in optimizing chemically

complex ternary and quaternary p-type transparent conductive oxides (TCOs) such as Zn-Ni-Co-O [54], $\text{Co}_2(\text{Ni,Zn})\text{O}_4$ [55], Ag_3VO_4 [56] and Cr_2MnO_4 [57], as well as simple binary materials, ZnO:Ga [58], Cu_2O [59] and Cu_3N [60], and previously unreported compounds[61]. Similar to this Cu-Sb-S study, the high-throughput combinatorial approach has been recently used to investigate ternary Cu-Sn-S absorber family[20], with particular emphasis on Cu_2SnS_3 [62].

Figure 1: The 44 sample points superimposed onto a photograph of an 2"x2" combinatorial library display the XRD identified majority phase. Each point has an associated data set for substrate temperature, composition, structure, conductivity, and photon absorption. The top (red) graph shows a measured temperature profile along one of the four rows, at a set point of 350°C. The right (blue) graph illustrates recorded compositional data for one of the eleven columns.

Figure 1 displays a photograph of a Cu-Sb-S combinatorial thin film sample library created by setting the composition and the temperature gradient across the substrate orthogonal to each other, so that each point experiences a unique combination of synthesis conditions. The compositional gradient (side panel in Fig. 1) was achieved by radio frequency (RF) magnetron co-sputtering of Cu_2S and Sb_2S_3 targets (99.999% pure) at an angle with respect to the stationary substrate located 15 cm from the substrate. Adjusting the power ratio of the targets produces a wide range of compositional flux on the substrate. The temperature gradient (top panel in Fig. 1) was created by a previously described[58, 59, 60] intentional non-uniform thermal contact to the substrate. A calibration of substrate temperature was done by a thermocouple in direct contact with a clean substrate. Prior to the depositions, the 50x50 mm glass sub-

strates were cleaned with detergent, sonicated in acetone and isopropanol, and finally exposed to a 5 min. oxygen plasma prior to deposition. All the depositions were done under 3mTorr flow of argon (99.99%). The chamber base pressure was 10^{-7} Torr.

After deposition, each library was characterized at 44 spatially resolved points by XRD (Bruker D8 Discover), XRF (Solar Metrology System SMX), and four point probe (custom). The arranged 4x11 rectangular grid is shown schematically in Fig. 1 by superimposed symbols corresponding to dominant phase XRD pattern identifications. XRF was taken in air, and was therefore not able to resolve a sulfur signal, so full stoichiometry was extrapolated from XRF reported Cu/Sb ratios combined with XRD results. To complement the mapping data with more in-depth characterization of the regions of interest, individual small samples were obtained by physically cleaving out 0.5 cm² sections of a library. For these samples, optical absorption data was taken on a Cary 5000 UV/Vis/NIR spectrometer which incorporates diffuse transmission and diffuse reflectivity, and Hall Effect measurement were taken in a Hall Effect apparatus (Accent HL5500) with the van der Pauw geometry. Scanning electron microscope (SEM) images were taken in a JEOL JSM-7000F at 7 kV acceleration voltage and a 10 mm working distance. Finally, the large amount of data produced as a result of both mapping and single-point measurement was systematically analyzed by custom processing algorithms in IgorPro© v.6.22 software.

For the theoretical component of this work, density functional calculation (DFT) was used with on site Coulomb potential U of 5 eV applied to the Cu(d) states, and Perdew-Burke-Ernzerhof [63] exchange correlation functionals were performed using the VASP code[64]. Formation energies of Cu-Sb-S compounds were calculated with fitted reference atomic energies (FERE)[65]. The Gibbs free energy of vaporization of Sb(s) and Sb₂S₃ (s) was calculated from vapor pressures[66, 67].

3. The Cu-Sb-S Ternary System

The equilibrium Cu-Sb-S system contains four stable ternary compounds: CuSbS₂ (chalcostibite), Cu₁₂Sb₄S₁₃ (tetrahedrite), Cu₃SbS₃ (skinnerite), and Cu₃SbS₄ (famatinite). CuSbS₂ is a layered orthorhombic (Fig. 2(c)) line compound up to a congruent melting temperature of 552.6°C on the quasi binary join Cu₂S to Sb₂S₃[69]. The cubic Cu₁₂Sb₄S₁₃ (Fig. 2(b)) phase is reported to have variable concentrations of highly mobile interstitial copper atoms[70]. The term tetrahedrite applies to both bulk synthetic compounds and natural samples with other transition metals substituting on Cu sites. The synthetic tetrahedrite compounds have been shown[70] to include two similar but immiscible phases; Cu_{12.4}Sb₄S₁₃ (Cu poor) and Cu_{13.8}Sb₄S₁₃ (Cu rich). Cu₃SbS₃ has at times been confused with Cu₁₂Sb₄S₁₃ due to their similar chemical composition, but the two phases have very different structures that are easily distinguishable by XRD[68]. Finally, Cu₃SbS₄ (famatinite) is structurally the most simple among the three Cu-rich Cu-Sb-S materials with a simple cubic zincblende derived, tetrahedrally-bonded structure.

Figure 2: (a) A subsection of the isothermal (300°) ternary phase space of Cu-Sb-S which contains all stable ternary compounds[68]. The phase progression from Cu_{1.8}S (digenite) through to Sb₂S₃ (stibnite), highlighted in red, is the focus of this investigation. Also shown are (b) the cubic Cu₁₂Sb₄S₁₃ structure, and (c) the layered orthorhombic structure of CuSbS₂. All atoms are represented by the oxidized atomic diameter; sulfur (yellow), antimony (red), and copper (blue).

All of these phases appear in Figure 2(a), which represents a subset of the full compositional space reproduced from mineralogical studies[68]. The chosen subsection enhances an important subtlety of the Cu-Sb-S ternary diagram; namely that Cu₃SbS₃, Cu₁₂Sb₄S₁₃ and Cu₃SbS₄ are three separate and stable phases[68, 71, 72], varying by only a slight difference in sulfur content. This means Cu-rich compositions of CuSbS₂ should co-exist with either Cu₃SbS₃, Cu₁₂Sb₄S₁₃, or Cu₃SbS₄, depending on the level of sulfur incorporation. Cu₃SbS₃ is the most sulfur poor, Cu₃SbS₄ the most sulfur rich, and between them is the off-stoichiometric compound Cu₁₂Sb₄S₁₃. This difference is important to the current study because, despite the use of Cu₂S target, the observed materials (Fig. 1) lie along the off-stoichiometric phase progression highlighted in red in Fig. 2(a): Cu_{1.8}S - Cu₁₂Sb₄S₁₃ - CuSbS₂ - Sb₂S₃.

4. Results and Discussion

4.1. Compositionally graded Cu-Sb-S thin film combinatorial libraries

Preliminary thin film experiments with a temperature gradient revealed that, within the accessible flux range, Sb₂S₃ would

not deposit at substrate temperatures greater than 350°C. This was also true during co-sputtering, though at higher temperatures, and can be seen by the distinct color change between high and low temperature regions of the sample in Figure 1. The high temperature region on the left appears more gray and contains only $\text{Cu}_{1.8}\text{S}$, while lower temperature regions appear darker and contain Cu-Sb-S ternary phases. Thus, to fully cover the Cu/Sb composition range, thin film combinatorial libraries were produced under isothermal conditions with the substrate temperature set below 300°C.

Figure 3: XRD patterns, normalized by scan time and film thickness, are plotted for each XRF reported composition. $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ is the identified impurity phase on the Cu-rich side of CuSbS_2 , and Sb_2S_3 on the Sb-rich side. Detailed phase identification is reproduced in appendix A.

Figure 3 plots XRD intensity patterns as a function of cation fraction ($X_{\text{Sb}} = \text{Sb}/(\text{Sb} + \text{Cu})$). The very Cu rich compositions ($X_{\text{Sb}} < 0.1$) contain peaks in good agreement with $\text{Cu}_{1.8}\text{S}$ (digennite), and do not match any Cu_2S (chalcocite) patterns. As the antimony content is increased, the phase content transitions from $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$, through to CuSbS_2 , and finally Sb_2S_3 . Individual XRD patterns from compositions associated with specific ternary phase stoichiometries are matched to reference patterns in Appendix A. The presence of $\text{Cu}_{1.8}\text{S}$ in the very copper rich compositions, and $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ on the Cu-poor side of CuSbS_2 , indicate the experimental conditions are accessing more sulfur-rich, off-stoichiometric compounds, (highlighted in red in Figure 2(a)). Given the use of Cu_2S and Sb_2S_3 targets, it might be expected that deposited compounds would fall along the strict pseudo-binary tie line between Cu_2S and Sb_2S_3 , but literature suggest this is unlikely. Cu_2S is well understood to de-

compose to Cu_{2-x}S compounds at moderate temperatures, and quenched melt studies[71] have shown Sb precipitation leads to the formation of Cu-rich $\text{Cu}_{12}\text{Sb}_4\text{S}_{13} + \text{Sb}$ rather than Cu_3SbS_3 at $X_{\text{Sb}} = 0.25$ (and 350°C). Considering these two effects, the identification of off-stoichiometric compounds in the Cu-rich compositions is reasonable.

CuSbS_2 peaks appear, without any other secondary phases, over a wider range of compositions ($0.40 < X_{\text{Sb}} < 0.60$) than might be expected for a line compound ($X_{\text{Sb}} = 0.50$). This is likely due to a combination of measurement error in the XRD and XRF data. There can be as much as 1-5% of crystalline impurity phase that is not resolved by XRD, which, combined with a 1-5% error in XRF reported composition, may lead to an apparent phase width of the CuSbS_2 single-phase region. There is also a small possibility for unresolved amorphous impurity phases on either side of stoichiometry ($X_{\text{Sb}} = 0.50$), but such a scenario unlikely in the present case as substrate temperatures near melting will allow for rapid diffusion and therefore complete crystallization.

Figure 4: Conductivity plotted as a function of composition reveals a six order of magnitude decline in the transition through the CuSbS_2 phase ($X_{\text{Sb}} = 0.50 \pm 0.2$). Hall effect results (inset), confirm this to be caused by a drop in carrier concentration. The shaded region depicts the placement of the hall effect data on the conductivity scale.

Figure 4 plots the conductivity of the Cu-Sb-S thin films for the same compositional range discussed in Fig. 3. The data included is from the same libraries, plus three more low temperature libraries providing more detail within the $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ - CuSbS_2 and CuSbS_2 - Sb_2S_3 transitions. Films of very copper rich compositions ($X_{\text{Sb}} < 0.35$) displayed similar conductivities on the order of 10^2 S/cm, and Hall effect measurements on $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ samples ($X_{\text{Sb}} = 0.35$) indicate hole concentrations in the high 10^{20} cm^{-3} , characteristic of a degenerate semiconductor. Conductivity near the CuSbS_2 compositions, ($0.35 < X_{\text{Sb}} < 0.75$), declines exponentially by six orders of

magnitude with increasing antimony content. Hall effect reveals this decrease is due to reduced carrier concentration, accompanied by a small increase in mobility, as shown in the inset of Figure 4. This large change in conductivity as a function of composition is likely due to the presence of impurity phases; $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ being highly conductive (10^2 S/cm), and Sb_2S_3 being very poorly conductive (10^{-8} S/cm)[73].

It is important to note that even for the nominally stoichiometric CuSbS_2 thin films ($X_{\text{Sb}} = 0.50$) the conductivity varies by 2-4 orders of magnitude from sample to sample (dashed line in Figure 4). This effect can be attributed to the fundamental difference between the relatively large compositional variations that can be detected by common measurement techniques (such as XRF) and the relatively small off-stoichiometry levels that can lead to large changes in doping levels. This disparity is not unique to CuSbS_2 , but is the case for most materials, since the majority of them are line compounds. Therefore, once the compositional regions of interest ($X_{\text{Sb}} = 0.5$ in this case) are identified using high-throughput combinatorial methods, it is necessary to perform follow-up studies of dedicated samples with uniform composition, as described for CuSbS_2 below.

4.2. Self-regulated growth of stoichiometric CuSbS_2 thin films in excess Sb_2S_3 vapor

Figure 5: Composition data plotted against effective Sb_2S_3 flux shows a flattening of compositional gradients at higher substrate temperatures due to sublimation of Sb_2S_3 impurities. A scanning electron micrograph (inset) shows the dense microstructure of a CuSbS_2 film grown under Sb_2S_3 sublimation conditions.

Libraries grown with higher substrate temperatures ($> 350^\circ\text{C}$) and an excess of Sb_2S_3 vapor (Fig. 5) displayed much smaller deviations from the ideal compositions ($X_{\text{Sb}} = 0.5$) and hence a much higher degree of CuSbS_2 phase purity than the compositionally graded libraries synthesized at lower temperature. The measured composition profile of three sample libraries grown at three different substrate temperatures, but identical Sb_2S_3 flux (controlled by Sb_2S_3 gun power), are shown

in Figure 5. The thin film samples deposited at 300°C are all antimony rich with respect to the $X_{\text{Sb}} = 0.5$ composition, with a linear dependence of composition on the effective flux of Sb_2S_3 (distance between Sb_2S_3 target to substrate). The additional Sb_2S_3 composition is accommodated by the presence of Sb_2S_3 impurities in the CuSbS_2 majority phase. In contrast, at the substrate temperature of 350°C , stoichiometric phase-pure CuSbS_2 is formed with no dependence on effective Sb_2S_3 flux. This dramatic difference illustrates the success of the self-regulated growth of phase-pure CuSbS_2 films; achieving stoichiometric ($X_{\text{Sb}} = 0.5$) films in an excess of Sb_2S_3 vapor and elevated substrate temperature. The inset of Figure 5 shows a scanning electron micrograph of the resulting film, revealing a dense morphology and grain size on the order of film thickness (400nm). Finally, a library grown at 400°C shows a similar flat composition profile, but a much lower X_{Sb} value near 0.25. XRD data confirm this library contains the $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ majority phase, due to the decomposition of phase pure CuSbS_2 into $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ and volatile Sb_2S_3 and Sb_4 species (which are likely to have sublimed).

The lower-end critical temperature ($T_c = 350^\circ\text{C}$ in Fig. 5), defines the onset of the phase pure growth. This temperature is a balance between the temperature-dependent equilibrium vapor pressure of Sb_2S_3 above the Sb_2S_3 impurity phase, and the chamber pressure (3×10^{-3} Torr). Above the critical substrate temperature, T_c , the Sb_2S_3 equilibrium vapor pressure is higher than that of the chamber. The excess Sb_2S_3 will therefore not deposit on the substrate, instead remaining in the vapor phase. In contrast, below T_c , Sb_2S_3 will be incorporated in the growing film, and will therefore require impractically precise control of the $\text{Cu}_2\text{S}/\text{Sb}_2\text{S}_3$ flux ratio for growth of the CuSbS_2 line compound. Thus, our data indicates growth at elevated substrate temperature, with an excess of Sb_2S_3 vapor, is a promising synthesis technique. It produces semiconductor-grade CuSbS_2 material with sufficient uniformity for solar cell absorber applications, within a wide range of precursor fluxes and substrate temperature variations. Similar over-flux strategies were developed more than half a century ago for the stoichiometric growth of III-V materials (e.g. desorption of As vapor from growing GaAs[74]), and were later exploited in the sputter deposition of CuInSe_2 with indium desorption[50].

The upper-bound of the self-regulated growth window is defined by the decomposition of CuSbS_2 (400°C in Fig. 5). The calculated lowest enthalpy decomposition pathway leads to the formation of $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$:

and requires 21 meV/atom. Decompositions to Cu_3SbS_3 and Cu_3SbS_4 are not considered because they are slightly higher in energy, and furthermore, were not detected under the relevant deposition conditions used in this study. To evaluate CuSbS_2 stability against decomposition into $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ (in terms of pressures and temperatures), we calculate partial pressures of $\text{Sb}_4(\text{g})$ and $\text{Sb}_2\text{S}_3(\text{g})$ in thermodynamic equilibrium with CuSbS_2 as a function of temperature. Since the entropy of any solid phase is much smaller than any gaseous phase, and

Figure 6: Calculated vapor pressures show the point of Sb_2S_3 sublimation, and CuSbS_2 decomposition, outlining a temperature processing window for phase pure deposition (orange shaded).

since such entropy change between solid phases should largely cancel out, we neglect the entropy change in reaction (1).

Figure 6 shows the partial pressures of $\text{Sb}_4(\text{g})$ and $\text{Sb}_2\text{S}_3(\text{g})$ as a function of temperature, indicating that the incoming Sb_2S_3 rather than Sb flux is the limiting factor for CuSbS_2 growth. According to these calculations, for any given incoming Sb_2S_3 flux ratio, there should be about 70°C temperature window above T_c where phase-pure stoichiometric CuSbS_2 can be synthesized by the self-regulated approach. Our experimental data (Fig. 5) confirms the decomposition of CuSbS_2 occurs about 50°C above T_c , and that $T_c = 350^\circ\text{C}$ at a chamber pressure of 3 mTorr. Fig. 6 also suggests that for a given substrate temperature, phase pure CuSbS_2 can be grown in a 10^2 dynamic range of Sb_2S_3 vapor (or flux), suggesting that no precise control of the precursor sources are required for synthesis of semiconductor-grade CuSbS_2 for solar cell absorber applications.

4.3. Optoelectronic Properties of phase-pure CuSbS_2 thin films

Figure 7 compares histograms of the electrical conductivity distribution obtained from samples synthesized above and below the critical temperature at which Sb_2S_3 sublimation occurs. Both libraries have CuSbS_2 stoichiometry and strong CuSbS_2 XRD patterns. The sample library represented in blue was grown at a substrate temperature of 300°C , RF power ratio ($\text{Sb}_2\text{S}_3/\text{Cu}_2\text{S}$) of 1.3, and shows a very wide distribution of conductivity values, (over six orders of magnitude), consistent with the data in Figure 4. In contrast, the sample library shown in orange, which has been grown at substrate temperatures greater than 350°C (RF power ratio = 2.0), shows a much tighter distribution of conductivity, suggestive of the formation of phase pure material. Carrier concentration and mobility values for the high temperature films were on the order of 10^{16} cm^{-3} , and $0.2 \text{ cm}^2/\text{V}\cdot\text{s}$ respectively. These values are comparable to current

Figure 7: A histogram analysis of conductivity for two combinatorial libraries grown at different substrate temperatures, 300°C , (blue) and 375°C (orange). Both datasets contain the same average elemental composition, ($X_{\text{Sb}}=0.5$), but the lower temperature library contains high conductivity impurity phases. The inset shows the same 375°C dataset, plus additional libraries grown at the same flux ratio, to illustrate the trend of increasing conductivity with substrate temperature and/or flux ratio. The data point is the library's mean average conductivity value, and the error bars the standard deviation. Carrier concentration values on the top axis are calculated assuming constant mobility of $0.2 \text{ cm}^2/\text{V}\cdot\text{s}$.

CIGS layers[75] and therefore promising for potential device integration.

For films grown above the critical temperature of 350°C , (Fig. 7 inset) the electrical conductivity can be tuned by changing the flux of Sb_2S_3 , or the substrate temperature. Increasing the RF power ratio to 2.3, or 2.5, raised the conductivity by nearly an order of magnitude, while the distribution of conductivity values remained tight, indicating a similar phase pure thin film. It was also noted that, for a given RF power ratio, further increasing the substrate temperature above 350°C also resulted in tight distributions of higher conductivity values, consistent with a point defect model of carrier concentration. These changes correspond to the $10^{15} - 10^{18} \text{ cm}^{-3}$ tunability range in hole concentration, as revealed by Hall measurements, allowing for the doping control needed for photovoltaic device applications. A library at an RF power ratio greater than 2.0 and substrate temperature of 400°C was not possible due to the limitations of the chamber. These conditions resulted in the decomposition of CuSbS_2 (Fig.5, orange line). The lowest car-

rier concentration of $5 \times 10^{15} \text{ cm}^{-3}$ is found at $\text{Sb}_2\text{S}_3/\text{Cu}_2\text{S}$ RF power ratios of 2.0, and a substrate temperature equal to T_c for 3 mTorr, (350°C).

Figure 8: Absorption spectra for $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ ($X_{\text{Sb}} = 0.25$), CuSbS_2 grown at higher temperature and excess Sb_2S_3 vapor ($X_{\text{Sb}} = 0.50$), and off-stoichiometries of CuSbS_2 ($X_{\text{Sb}} = 0.40, 0.60$) grown at lower temperatures.

Figure 8 displays the absorption spectra obtained from four Cu-Sb-S films with varying antimony content, revealing the CuSbS_2 band gap and absorption coefficient, two critical properties for photovoltaic applications. For the stoichiometric ($X_{\text{Sb}} = 0.50$) phase-pure CuSbS_2 thin films, the absorption onset occurs sharply at 1.5 eV, indicative of a direct transition and in agreement with literature[19, 37, 35]. The absorption coefficient reaches 10^5 cm^{-1} by 1.8 eV. The sub-bandgap absorption in the Cu-rich off-stoichiometric CuSbS_2 samples ($X_{\text{Sb}} = 0.40$) is likely indicative of $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ impurities. This is because thin films at $X_{\text{Sb}} = 0.25$ (stoichiometry of $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$) display significant sub-bandgap absorption, consistent with the degenerate semiconducting character of the $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ material caused by nominally Cu^{2+} valence states. In contrast, Sb-rich off-stoichiometric CuSbS_2 samples ($X_{\text{Sb}} = 0.60$), show similar absorption to the phase pure stoichiometric CuSbS_2 samples. This is consistent with the higher $\sim 1.9 \text{ eV}$ band gap of Sb_2S_3 [76]. However, we note that even for phase pure CuSbS_2 samples, there is some remaining degree of sub-band absorption, the origin of which is currently under investigation.

5. Conclusions

A combinatorial investigation of the Cu-Sb-S system was conducted to identify the conditions required to form ternary phases with potential for solar energy conversion. It was found that RF magnetron sputtering from Cu_2S and Sb_2S_3 targets results in the formation of films that fell on a phase progression from $\text{Cu}_{1.8}\text{S}$ to $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$, to CuSbS_2 , and finally

Sb_2S_3 . $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ was found to be overly conductive, whereas CuSbS_2 displayed moderate conductivity suitable for photovoltaic applications. CuSbS_2 thin films deposited at elevated temperature, with excess Sb_2S_3 vapor, exhibited a high degree of phase purity. This self-regulated growth process, where Sb_2S_3 impurities remain in the vapor phase (in the temperature range above Sb_2S_3 sublimation, and below CuSbS_2 decomposition), has been theoretical explained using first principles calculations combined with thermochemistry simulations. Furthermore, the carrier concentration in stoichiometric phase-pure CuSbS_2 thin films produced by the self-regulated deposition method can be tuned by controlling Sb_2S_3 flux and substrate temperature. The absorption spectra of these semiconductor-grade CuSbS_2 samples show sharp absorption onset at 1.5 eV and high absorption coefficient of 10^5 cm^{-1} within 0.3 eV higher energy. Overall, the results of this study leads to a conclusion that the optoelectronic properties of CuSbS_2 thin films prepared by self-regulated growth are suitable for photovoltaic absorber applications and further solar cell integration.

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Appendix A. XRD Profile Identification

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Figure A.9: XRD patterns for specific compositions matched to reference patterns.

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