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Self-regulated growth and tunable properties of $CuSbS_2$ 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 Cu_2S and Sb_2S_3 targets and evaluated by a suite of spatially resolved characterization techniques. The resulting compounds include $Cu_{1.8}S$ (digenite), $Cu_{12}Sb_4S_{13}$ (tetrahedrite), $CuSbS_2$ (chalcostibite), and Sb_2S_3 (stibnite). Of the two ternary phases synthesized, $CuSbS_2$ 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 $CuSbS_2$ films using excess Sb_2S_3 vapor at elevated substrate temperatures. Theoretical calculations explain that phase-pure $CuSbS_2$ is expected to be formed over a relatively wide range of temperatures and pressures, bound by the sublimation of Sb_2S_3 and decomposition of $CuSbS_2$. The carrier concentration of $CuSbS_2$ films produced within this regime was tunable from 10^{16}–10^{18} cm^{-3} through appropriate control of Sb_2S_3 flux rate and substrate temperature. $CuSbS_2$ displayed a sharp optical absorption onset indicative of a direct transition at 1.5 eV and an absorption coefficient of 10^5 cm^{-1} within 0.3 eV of the onset. The results of this study suggest that $CuSbS_2$ holds promise for solar energy conversion due to its tolerant processing window, tunable carrier concentration, solar-matched band gap, and high absorption coefficient.

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 (FeS_2 [3–5], SnS [6,7],) nitrides ($ZnSnN_2$ [8,9], $CuTaN_2$ [10]), phosphides (Zn_3P_2 [11,12], $ZnSnP_2$ [13,14]) and oxides (Cu_2O [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 Cu_2S, Cu_2O [17], Cu_3N [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 Cu_2S has more than three decades of experimental photovoltaic research [23] quickly reaching 10% efficiency in 1980s, but early work showed that Cu_2S 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 $CuInSe_2$, and subsequently $Cu(In,Ga)Se_2$ (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

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displays and other technologies [27]. Replacing indium and gallium with more earth abundant elements, such as Zn and Sn, has resulted in 11% efficient $Cu_2ZnSn(S,Se)_4$ (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 $Cu_2(Sn,Ge)S_4$ solar cells [33].

Antimony based copper sulfide ternaries are another good 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 $CuSbS_2$ [35–37] 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 the literature [38], such as $CuSbS_2$ [39–41], Cu_3SbS_3 [42], Cu_3SbS_4 [43] and $Cu_{12}Sb_4S_{13}$ [44]. Other potential applications have also been investigated, including thermoelectrics [45–47] 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 $Cu_{12}Sb_4S_{13}$. 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], $Co_2(Ni,Zn)O_4$ [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].

Fig. 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 [58–60] 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 50×50 mm glass substrates 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 3 mTorr 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 4×11 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 cm^2 sections of a library. For these samples, optical absorption data was taken on a Cary 5000 UV/Vis/NIR spectrometer

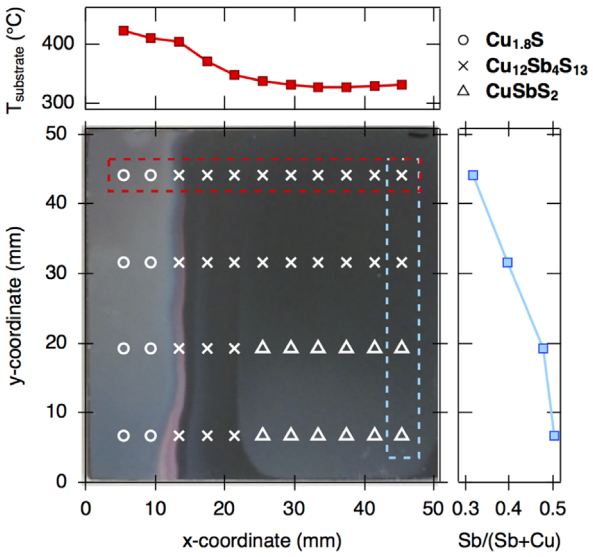

Fig. 1. The 44 sample points superimposed onto a photograph of an 2 in $\times$ 2 in combinatorial library display the XRD identified majority phase. Each point has an associated data set for substrate temperature, composition, structure, conductivity, and photon absorption. The top (red) graph shows 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. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this article.)