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Solution-Processed CuSbS₂ Thin Films and Superstrate Solar Cells with CdS/In₂S₃ Buffer Layers

Joel van Embden^{a*}, Joao O. Mendes^a, Jacek J. Jasieniak^b, Anthony S. R. Chesman^c, Enrico Della Gaspera^a

^a. School of Science, RMIT University, Victoria 3001, Australia.

^b. Department of Materials Science and Engineering, Monash University, Victoria 3800, Australia.

^c. CSIRO Manufacturing, Bayview Ave Clayton, Victoria 3168, Australia

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ABSTRACT: Herein we describe a method to deposit thin films of the semiconductor CuSbS₂ with micrometer-sized grains under inert atmospheres at mild processing temperatures. This is achieved through the decomposition of Cu and Sb dithiocarbamate precursors. Through careful optimization of the processing conditions, phase-pure p-type CuSbS₂ thin films with high photoconductivity have been achieved. Tunability of the Cu:Sb ratios is also demonstrated while maintaining phase purity. Photo-electrochemistry is conducted as a function of both processing temperature and Cu:Sb ratio with 10% copper deficient films annealed between 350 °C and 400 °C producing the highest relative photocurrent. Finally, to assess the performance of these thin films, planar thin film solar cells are fabricated. Superstrate solar cells (Glass/FTO/CdS/(In₂S₃)/CuSbS₂/SPIRO/Au) with either a CdS n-type window layer or a CdS/In₂S₃ dual n-type window/buffer layer are investigated. The use of a thin buffer layer further boosts the overall device performance and a champion power conversion efficiency of 1.72% is demonstrated. To date, this efficiency is among the best reported for CuSbS₂ solar cells and the highest for solution-processed devices using a planar thin film architecture.

INTRODUCTION

The ability to fabricate high quality semiconductor thin films using solution-based (vacuum free) processing conditions has opened the door to low-cost thin film devices, including photodetectors¹⁻³, batteries⁴, photocatalysts^{5,6}, and solar cells.⁷⁻¹⁰ A range of solution processes exist to produce crystalline semiconductor thin films. The most common methods include chemical bath deposition (CBD)¹¹⁻¹⁵, electrochemical deposition¹⁶⁻¹⁸, successive ion layer adsorption and reaction (SILAR)¹⁹⁻²¹, nanocrystal (NC) assembly²²⁻²⁷, and molecular precursors (MP)²⁸⁻³². Of these techniques, the use of molecular precursors provides perhaps the most versatile, reproducible, and facile approach to achieving semiconductor thin films across a wide range of materials.

At present, a multitude of investigations into the fabrication of metal chalcogenide thin films from MPs have been reported^{9, 33-40}. These reports focused largely on the generation of thin films for use in photodetectors and photovoltaic (PV) devices. In efforts to extend these methods the exploration of metal chalcogenide (nano)materials developed to include copper antimony sulfide (CAS) semiconductors. Since the first synthesis of a CAS nanomaterial by the current authors⁴¹, investigations into this class of materials have continued to expand. Numerous investigations have been conducted into the

dominant phases of CAS, namely, tetrahedrite (Cu₁₂Sb₄S₁₃)⁴²⁻⁴³, famatinite (Cu₃SbS₄)^{41, 46}, and chalcostibite (CuSbS₂)⁴⁷⁻⁵⁰, as well as few reports on the synthesis and characterization of skinnerite (Cu₃SbS₃)^{51, 52}. All these phases are p-type semiconductors with high absorption coefficients (~10⁴–10⁵ cm⁻¹), direct bulk band gaps that vary between ~1–1.8 eV, modest hole mobilities between 10–70 cm²/V.s^{42, 51, 53, 54}, and good defect tolerances^{53, 55}. Collectively, these properties make them suitable candidates for vis–NIR photodetectors or solar absorber layers in PV devices.

In addition to having the appropriate optical and electrical properties, CAS (and antimony containing chalcogenides in general) have very low melting points, for example; Sb₂S₃ (550 °C), Sb₂Se₃ (611 °C), CuSbS₂ (551 °C), and Cu₁₂Sb₄S₁₃ (580 °C). This property has previously been exploited to enhance the grain growth of CIGS thin films through the generation of antimony chalcogenide “flux agents”⁵⁶. Such low melting temperatures enable CAS to form microcrystalline thin films desirable for PV application under mild conditions, without the need for vacuum-based infrastructure or post-processing sulfurization/selenization steps. This provides a unique processing advantage over more established metal chalcogenide semiconductors.

In view of their well-suited optical properties, chemical stability, and processing advantages, recent research has focused on the implementation of CAS in solar cell devices. An

in-depth outline of current CAS device performances can be found in excellent recent reviews^{57, 58}. $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ ⁴⁴, Cu_3SbS_4 ⁵⁹, and Cu_3SbS_3 ⁶⁰ solar cells have all been fabricated, however, these solar cells have all suffered from very poor ($<<0.5\%$) efficiencies. The outlier within the CAS system is CuSbS_2 (isostructural with CuInS_2), with far more promising efficiencies emerging.

Vacuum-based solar cell fabrication methods for CuSbS_2 include the high temperature sulfurization of electro-deposited metal stacks, metal salts, or nanoparticles, as well as the co-sputtering and co-evaporation of the corresponding binary sulfides⁶¹⁻⁶⁴. These solar cells are predominantly built on molybdenum substrates and have produced the best efficiencies to date. However, solution-based methods are still lagging behind. There remains significant impetus to further develop such methods as they have the ability to circumvent vacuum-based deposition and/or high temperature chalcogenization steps and make use of the aforementioned processing advantages afforded by the low melting point of CuSbS_2 . To date, the best performing CuSbS_2 solution processed cells are based on nanostructured architectures, with sensitized ZnO nanorods ($n=1.61\%$)⁶⁵ and mesoporous TiO_2 ($n=3.1\%$)⁶⁶ the current top performers.

Thin film (not sensitized) architectures are far more challenging. For planar thin film solar cells film quality is paramount, requiring careful optimization of the processing conditions, thin film morphology, and cell interfaces given that charge transport cannot be simply driven by the mesoporous or nanostructured scaffold material. Over the past few years numerous efforts have been put into developing high quality CuSbS_2 thin films by solution processes. Such approaches to CuSbS_2 thin films have included thiol-amine mixtures⁵⁴, metal xanthates⁶⁷, and thioglycolic acid-amine mixtures⁶⁸. However, despite reporting their film quality, in each of these cases no CuSbS_2 devices were fabricated from the resultant films. Notable exceptions include studies by Tang et al. who fabricated CuSbS_2 thin films from hydrazine with efficiencies at 0.5% ⁵³ and Dai et al. who used MPs to reach 0.68% ⁶⁹. Other approaches have also been employed, including CBD⁷⁰ and spray-coating⁷¹ methods, but again only poor cell efficiencies (up to 0.66%) were reported. To date, the record efficiency for solution processed thin film CuSbS_2 solar cells remains below the benchmark of 1% for emergent devices.

Here we provide a comprehensive investigation into CuSbS_2 thin films fabricated from dithiocarbamate (DTC) MPs. A method to fabricate high quality CuSbS_2 thin films with large grain sizes (without the need for sulfurization) is presented. The structural, optical, and photo-electrochemical properties of these films are investigated. In depth studies into the effects of temperature and Cu/Sb composition on the optical and optoelectronic properties of the thin films are presented with a view to generating optimal photoactive thin CuSbS_2 films. Finally, superstrate CuSbS_2 planar thin film solar cells are fabricated and analyzed. Record devices were fabricated using double n-type $\text{CdS}/\text{In}_2\text{S}_3$ “window” layers, which greatly improve the device characteristics over a single CdS buffer layer, breaking the 1% efficiency barrier in such devices for the first time.

RESULTS AND DISCUSSION

CuSbS_2 Thin Film Characterization

The films were prepared as outlined in the Experimental section. X-ray Diffraction (XRD) was used to establish the phase purity of the as-deposited thin films. The film thicknesses of the samples were adjusted to ~ 500 nm, with a deviation in the film thickness of less than 10% . Figure 1a shows multiple XRD patterns from films prepared with different stoichiometries ranging from copper poor (Cu:Sb; 0.8:1) to copper rich (Cu:Sb; 1.2:1). All films display clear sharp peaks indicative of a highly crystalline material. Each of these peaks and their corresponding intensities match perfectly to orthorhombic chalcocite CuSbS_2 (ICDD# 00-044-1417).

Figure 1: a) XRD patterns of CuSbS_2 thin films annealed at 350°C as a function of Cu:Sb mole ratios in the precursor solutions. It can be seen that copper deficient precursor solutions (Cu:Sb <0.9) lead to the formation of Sb_2S_3 in addition to CuSbS_2 , while copper-rich (Cu:Sb ≥ 1.1) solutions favor Cu_9S_5 formation. b) The effect of annealing temperature on CuSbS_2 thin films with Cu:Sb; 1:1.

It is well known that tuning the stoichiometry of ternary and quaternary semiconductors can have a dramatic effect on their optoelectronic properties⁷²⁻⁷⁵. With this in mind the copper/antimony mole ratio within the molecular precursor solutions was altered to evaluate phase purity of the resultant films as a function of composition. In the case of the most copper deficient films (Cu:Sb; 0.8:1; light green trace) the precipitation of a secondary phase is seen to occur as indicated by the appearance of multiple additional peaks in the XRD pattern (triangle markers). Upon analysis each of these peaks may be indexed to Sb_2S_3 (ICDD# 00-042-1393). Conversely, for copper-rich films (Cu:Sb; 1.1:1; dark blue trace, and Cu:Sb; 1.2:1; purple trace) a small additional peak at $\sim 27.8^\circ$ may be observed, which can be indexed to Cu_9S_5 (ICDD#00-047-1748). Slightly copper-poor films with Cu:Sb; 0.9:1 could be

made without the formation of any secondary phases. From these results it is clear that the CuSbS₂ lattice is slightly more tolerant to copper deficiencies compared to the accommodation of excess copper. One of the possible causes of this tolerance is the unusual stability of the defect pair ($2V_{\text{Cu}}^0 + \text{In}_{\text{Cu}}^0$).⁷⁶ These findings are consistent with other copper containing semiconductors, such as CuSnSe₃, CuZnSnS₄, CuInS₂ and CuIn_xGa_{1-x}Se₂.⁷⁷

In the presence of large amounts of sulfur (from the excess dithiocarbamate ligands), the continued decrease in copper concentration facilitates the homogeneous nucleation of antimony sulfide. It should be noted that antimony sulfide was found to be the dominant impurity in Cu:Sb (1:1) mixtures if copper acetate was used instead of copper oxide in the synthesis of the dithiocarbamate precursor (see Supporting Information, Figure S1). This indicates that the speciation (counter anion) of the copper precursors also plays a significant role in the reactivity of the metal-DTC molecular precursor, its decomposition pathway and the subsequent phase purity of the film.⁷⁸ Additional evidence of this phenomenon was gleaned from early trials using metal thiourea precursors. It was observed that the reactivities of the metal complexes with thiourea and with each other were vastly different depending on the counter anion used. Clear solutions (without precipitate) could only be achieved when using both Cu and Sb chlorides. In cases where viable thiourea-based precursors solutions were formed the resulting films were nonetheless of poor quality (for details see Supporting Information, Table S1). Overall, the observation that metal oxide-derived DTC molecular precursors provides phase pure high-quality films while tuning metal ratios is evidence that (unlike thiourea precursors) the reactivity of both the copper and antimony DTC species are well matched.

Figure 1b shows the effect of annealing temperature on the XRD patterns of the CuSbS₂ thin films (Cu:Sb; 1:1). All of the films were initially fabricated in air by spin coating multiple layers with an intermediate decomposition step at 200 °C. The samples were then heated in an inert atmosphere (glove box) for 30 min at the designated temperature. Each film was approximately the same thickness (600 ± 34 nm). As such, the observed changes in the intensity of the peaks in the XRD patterns are a direct consequence of changes in the annealing temperature alone.

Remarkably, quite sharp peaks are observed at temperatures as low as 200 °C. The low-temperature crystallization of CuSbS₂ may be primarily attributed to the highly reactive nature of the dithiocarbamate precursors^{36, 79}. Notably, systems employing metal-thiourea complexes do not show comparative crystallinity until 300 °C and are not claimed to be phase pure until 500 °C. However, in this case only questionable evidence exists that thiourea precursors are able to generate phase pure CuSbS₂ without Sb₂S₃ impurities⁶⁶. With an increase in annealing temperature the samples became more crystalline, as indicated by an increase in the intensity of the diffraction peaks. No significant changes to the XRD patterns were observed for annealing temperatures above 300 °C. The ability to achieve phase pure CuSbS₂ at 200 °C is further testament to the balanced reactivity of both precursors at such low temperatures. A table including the crystallite size evaluated from the diffraction peaks is available in the Supporting Information as Table S2.

XPS was also performed on the stoichiometric (Cu:Sb, 1:1) films (see Supporting Information, Figure S2 for details).

Collectively, all the peaks matched with those of the elements in their expected oxidation states; Sb(III), Cu(I), and S(2-) and free from oxide peaks from contaminants and from Cu(II) inclusions, unlike observed in other CAS phases⁴².

It has been determined that the processing environment can have a dramatic effect on the crystal phase within the CAS system⁴². As such, we conducted investigations into the effect of processing environment on CuSbS₂ films, with the objective of elucidating what conditions induce chemical changes in CuSbS₂. Such an understanding is valuable given that even trace contaminant regions (undetectable using XRD) within CuSbS₂ may act as recombination centers that may ultimately inhibit device performance. As such, experiments were performed to observe the long-time behavior of annealing CuSbS₂ thin films in different chemical environments (see Supporting Information, Figure S3 and related text for details). Briefly, it was observed that heating CuSbS₂ in an inert atmosphere of nitrogen at 500 °C for one hour has no effect on the phase, while heating even at a lower temperature of 400 °C in a sulfur-rich atmosphere induced a phase change to famatinite CuSbS₄ and was accompanied by the loss of Sb₂S₃. It may be concluded that (unlike its famatinite and tetrahedrite analogues) the presence of sulfur in the annealing atmosphere and not temperature is the requisite driving force behind phase changes in the CuSbS₂ system, which provides confidence in the processing of these films in inert atmospheres.

Figure 2: Top view SEM images of CuSbS₂ thin films annealed at different temperatures in a glove box for 30 min. Scale bars 1 μm . The bar chart shows the distribution of grain sizes (>100 individual

grains) versus annealing temperature. It can be seen clearly that increasing the annealing temperature results in large-scale grain growth with average grain sizes of ~ 500 nm at 350°C . Further heating does not greatly increase the average grain size, although several $1\text{--}1.5\ \mu\text{m}$ are observed at or above 400°C .

Scanning Electron Microscopy (SEM) was used to analyze the morphology of the CuSbS_2 films at different annealing temperatures. Each film was heated for 30 minutes at the designated temperature. Figure 2 shows top view SEM images of the as-deposited films from $200\text{--}450^\circ\text{C}$. The as-deposited film at 200°C appears porous with no evidence of individual grains. Heating the films to 350°C results in a gradual change of the film's morphology from porous to microcrystalline. Clear individual grains with an average size of ~ 500 nm in diameter can be seen at 350°C . Further heating has little effect on the average grain size, however some micron sized grains are observed at $400\text{--}450^\circ\text{C}$ (see histogram of grain size distribution versus annealing temperature).

Notably, achieving grain growth of metal sulfide semiconductors on this scale with only heat treatment is rare. This may be attributed to the extremely low melting temperature of CuSbS_2 (551°C) compared to other commonly employed solar absorber materials, such as CZTS (990°C) and CIGS (1070°C). Although grain growth via simple heat treatment has been observed for analogous systems with low melting points, such as Sb_2S_3 and Sb_2Se_3 ^{28, 39}, typically a high temperature chalcogenization step between $500\text{--}550^\circ\text{C}$ is required to achieve grain growth at this scale for CZTS and CIGS thin films^{8, 9, 33, 68, 80}.

Thin Film Optical and Band Properties

Having obtained uniform pinhole-free phase-pure CuSbS_2 thin films we investigated their optical properties. Figure 3a shows an absorbance spectrum of a typical thin film (Cu:Sb; 1:1, thickness 95 nm, annealed at 350°C for 10 min). The absorbance is seen to increase strongly for energies above the band gap (~ 800 nm). A plot of the corresponding absorption coefficient as a function of energy is shown in Panel b. The absorption coefficient is seen to rise to $\sim 5 \times 10^4\text{ cm}^{-1}$ at around 2 eV, reaching a maximum of $\sim 8 \times 10^4\text{ cm}^{-1}$ at approximately 2.4 eV. Next, we evaluated the band gap as a function of annealing (processing) temperature (Panel c). The as-deposited films annealed in air at 200°C , although known to be quite crystalline from XRD, have a strong indirect character and an intercept of ~ 1.15 eV (see Panel d inset). This is somewhat expected given that at such low temperatures the partially sintered films contain numerous defects, which degrade the optoelectronic properties. In sharp contrast, at 250°C the films become highly direct in character with an extrapolated direct band gap of ~ 1.6 eV, which is consistent with previous reports on the band gap of CuSbS_2 ^{57, 69, 81}. The band gap remains almost constant for films treated at temperatures up to 350°C . Even higher annealing temperatures cause the band gap to decrease slightly (~ 40 meV) to ~ 1.56 eV consistent with increased grain growth. Panel d shows a plot of the phase pure films (Cu:Sb 0.9:1 and 1:1) annealed at 350°C . It is apparent from the Tauc analysis that there is no discernible change in band gap within this compositional range with both films having an extrapolated band gap of 1.6 eV.

To evaluate the band structure of the films Photoelectron Spectroscopy in Air (PESA) was conducted. Figure 3 Panel e

displays the PESA spectra for films treated at various temperatures. The as-deposited pre-annealed sample (200°C) was found to have a VBM close to -4.8 eV (relative to the vacuum level), which then decreased to -4.96 eV for films heated at temperatures above 350°C . The VBM of CuSbS_2 has been reported over a range of energies between -4.9 and -5.35 eV^{66, 55, 82}. To help clarify these discrepancies we conducted experiments to synthesize “bulk” CuSbS_2 as a means to provide our own additional reference. To accomplish this Cu, Sb and S powders were (orbital) ball milled into pure phase CuSbS_2 by optimizing the rotation speed and reaction time. It is well established that lattice strain (alterations of the periodic potential), the extent of p-type doping (in this case through copper vacancies) and quantization effects all affect the VBM of semiconductors within ~ 100 meV. As such, the use of pure powders consisting of large crystal grains is likely to provide the most accurate indication of the VBM of a given material. The PESA measurements of the powder samples gave higher energy VBM values consistently between $5.1\text{--}5.15$ eV (see Supporting Information, Figure S4).

Figure 3: (a) Absorption spectrum of a ~ 95 nm CuSbS_2 thin film. (b) Absorption coefficient of the film in panel A. (c) Tauc plot of CuSbS_2 thin films heated at different temperatures (Cu:Sb; 1:1). (d) Tauc plot of copper-poor and stoichiometric CuSbS_2 thin films

annealed at 350°C . The inset shows the stoichiometric film at 200°C showing indirect character with a band gap of ~ 1.15 eV. (e) Photoelectron Spectroscopy in Air (PESA) measurements as a function of annealing temperature (Cu:Sb; 1:1). (f) Schematic of the band positions of stoichiometric CuSbS_2 thin films and images of CuSbS_2 thin films with varying thicknesses annealed at 350°C .

For inorganic semiconductors the valence band maximum (VBM) and optical band gaps ($E_{g, opt}$) can be used to provide a reasonable approximation of the conduction band (CB) ($CB \approx VB - E_{g, opt}$). Panel f shows the band structure of the $CuSbS_2$ thin films investigated in this work. Specifically, the VBM was evaluated as -4.95 eV and the conduction band minimum at -3.35 eV. To highlight the quality of the thin films deposited from the dithiocarbamate precursors, photos of these films with thicknesses of 35 nm, 95 nm, and 135 nm are also shown. Importantly, ultra-thin highly uniform pinhole free films of ~ 35 nm can be readily deposited using the techniques described herein, which is made possible through the use of DTC precursors³⁶.

$CuSbS_2$ Thin Film Photo-electrochemistry

To test the photo-response of the thin films, the molecular precursor solutions were spin coated onto FTO-coated glass

substrates (see the Experimental Section for details). The films (3 layers from 0.1 M solutions to avoid pinholes) were carefully adjusted to similar thicknesses (150–160 nm by surface profilometry) to ensure comparable results. These films were mounted to a custom built three-electrode photoelectrochemical cell with a coiled Pt mesh-basket working electrode and a $Ag/AgCl$ reference electrode containing an aqueous Eu^{3+} electrolyte as an electron acceptor similar to previous work⁴². Europium (III) was chosen as it does not absorb light at the

probe wavelength and it has a reduction potential energetically below the conduction band edge of $CuSbS_2$, which enables photoreduction.

Photo-electrochemistry is an excellent means to probe the optoelectronic properties of a thin film absorber layer without the complications associated with additional contacts. Photo-electrochemical data, in conjunction with SEM data, provides valuable insights into the conditions required to achieve high-performance photoactive thin films. Figure 4 displays the photo-electrochemistry of stoichiometric $CuSbS_2$ thin films on FTO-coated glass as a function of temperature and composition. Figure 4a shows the photo-response of $CuSbS_2$ films under chopped light annealed at temperatures between 200–450 °C in an inert atmosphere. Firstly, it can be seen that the films exhibit a strong p-type photo-response, as indicated by the increased photocurrent under negative bias. Furthermore, the response is rapid with rise/fall times $\ll 10$ ms, which is indicative of low capacitance and rapid charge transport within the film.

Analysis of the data reveals that the photocurrent remains relatively constant for annealing temperatures up to 300 °C. However, increasing the annealing temperature to 350 °C results in a massive jump in photocurrent ($\sim 45\%$). Importantly, this increase is coincident with the onset of grain formation between 300 °C and 350 °C as indicated by SEM data. The transition to distinct grains (from the more porous morphology observed at 300 °C) typically culminates in a reduction in the number of defect “trap” states within the film and thus improves photo-response. Further heating to 400 °C reduces the prevalence of grain boundaries and results in a slight further improvement to the photocurrent. The photo-response is seen to be negligible after heating at 450 °C, which places an upper limit on the processing temperature. The inset shows a column graph summarizing the maximum photocurrent achieved (at 536 meV negative bias vs $Ag/AgCl$) at the different annealing temperatures.

Figure 4: (a) Photo-response of $CuSbS_2$ thin films annealed at various temperatures under chopped light. The films show a strong p-type photocurrent that steadily increases up to annealing temperatures of 400 °C. The inset shows the maximum photocurrent at each temperature. (b) Steady state photocurrent at -0.5 V (vs. $Ag/AgCl$) as a function of composition from copper poor to copper rich. The inset shows the maximum photocurrent as a function of compositional ratio.

To examine the effect of composition on the photocurrent, multiple thin films were prepared with different Cu:Sb ratios, ranging from Cu-poor (Cu:Sb; 0.9:1) to Cu-rich (Cu:Sb; 1.1:1) Figure 4b shows ~ 8 sec sections of the stabilized photo-response (at 0.5 V negative bias vs $Ag/AgCl$) from $CuSbS_2$ thin films with varying compositions annealed at 350 °C for 30 min. The compositions were based in the range of 10% copper poor to 10% copper rich as these samples gave phase-pure $CuSbS_2$ (with the exception of Cu:Sb; 1.1:1, which is known to precipitate trace Cu_3S_2 impurities, although we expect this impurity to have negligible effect on photocurrent). Analysis of the data reveals a clear trend wherein increasingly copper deficient films were found to exhibit increased photocurrents. Specifically, the stoichiometric sample exhibited a photocurrent of ~ 0.57 mA/cm², which rose to nearly 1 mA/cm² for the 10% Cu-poor film. We may attribute this increase in photo-current to both the increased carrier concentration and p-type nature of the films that contain higher concentrations of copper

Figure 5: A) Band diagram of the solar cells fabricated in this work. B) Device statistics for solar cells without the In₂S₃ (CdS only) and with various thicknesses of In₂S₃ interlayers. C) Cross-section SEM image of a top performing solar cell. Each of the five device layers is clearly visible. Scale bar is 500 nm. D) HRTEM of a focused ion beam cut section of a top-performing solar cell. The regions of interest within each of the key device layers is color coded to the corresponding lattice images and FFTs on the right (CdS-red; In₂S₃-green; CuSbS₂-blue). The lattice planes and FFTs confirm the crystallinity of each layer without any notable lattice expansions or contractions due to strain or dopant inclusions. E) Average device power conversion efficiencies for solar cells with and without the In₂S₃ interlayer. F) Current-voltage curve under 1 sun illumination for the champion device.

vacancies(V_{Cu}) in the lattice^{53, 73}. The inset displays the photocurrent achieved at 0.5 V negative bias vs Ag/AgCl as a function of the Cu:Sb atomic ratio. It can be seen clearly that the photo-response increases linearly as the films become more copper deficient. From these data it is evident that 10% Cu-poor films are the best films for achieving the greatest photo-response while maintaining phase purity.

CuSbS₂ Thin Film Solar Cells

The optimized CuSbS₂ semiconductor thin films prepared were integrated into solar cells. Details on solar cell fabrication can be found in the Experimental Section as well as the effect of additional processing parameters in Supporting Information, Figure S5 and Figure S6. The composition of the CuSbS₂ and the processing conditions for the CuSbS₂ absorber layer required to achieve optimal cell performance were based on the XRD, SEM, and photo-response data from the photo-electrochemistry experiments collectively.

To begin we fabricated devices with a standard superstrate structure common to CIGS and CdTe solar cells, with an FTO/CdS/CuSbS₂/HTL/Au architecture. The driving force behind device development was centered on improving the fill factor and open circuit voltage through reductions to the shunt conductance and improving the p-n junction, which are known to be problematic in this specific device structure^{53, 69}. Due to its n-type behavior and favorable band positions, In₂S₃ has been

used as a buffer layer both on its own and in tandem with CdS to improve junction quality and decrease the voltage deficit across a wide range of solar cell types, including CIS, CIGS, and CZTSSe.⁸³⁻⁸⁶ Although popular for other cell types, the use of In₂S₃ buffer layers has yet to be applied to CAS. Figure 5a shows a band diagram of the superstrate solar architecture developed in this work. The use of an optional interlayer of In₂S₃ is highlighted inside the dashed box. The values for the band positions were taken from well-established literature values^{53, 69, 85, 87} and the measurements of CuSbS₂ conducted in this work. It can be seen that CuSbS₂/CdS forms an effective Type II heterojunction and that the introduction of In₂S₃ forms a graded Type II heterojunction both of which are applicable for charge separation and high efficiency devices.

To investigate the effect of introducing an In₂S₃ buffer layer we conducted initial studies to evaluate the effect of buffer layer thickness on device performance. Figure 5b shows a bar chart of the averaged cell statistics collected for a series of 20 solar cell devices with a single CdS window layer and a double CdS/In₂S₃ window/buffer layer with various In₂S₃ thicknesses. It can be seen that even upon the introduction of an ultrathin 25–30 nm In₂S₃ interfacial layer there is a pronounced increase in all the key device parameters, in particular the short circuit current, which is indicative of an increased collection probability through reduced interfacial defects and an improved p-n junction. This is not surprising as CdS is known to generate a partially defective junction upon heat treatment with copper-

based materials^{88, 89}. Upon the deposition of thicker In_2S_3 layers the J_{sc} stabilizes and no further enhancements are observed. This also highlights that the In_2S_3 buffer layer does not contribute significantly to the J_{sc} of the devices. The overall trend in photogenerated current is consistent with the observed increases to the open circuit voltage through a reduced surface recombination at the In_2S_3 interface⁶⁶. Suns–Voc measurements revealed a decay of ~ 100 meV Voc per decade and a slope of ~ 1.7 kT/q, indicating further improvements to junction quality are still possible (see Supporting Information, Figure S7).

The fill factor is seen to steadily increase with In_2S_3 layer thickness reaching a plateau at layer thicknesses around 60 nm. Fill factors consistently at or above 50% for these devices were observed and are among the highest values reported for CuSbS_2 solar cells. The largest single contributor to the improved device efficiencies is the vast improvements to fill factor, which are driven mainly through the increased shunt resistance of devices with thicker In_2S_3 layers ($185 \text{ } \Omega/\text{cm}^2$ – CdS only; $401 \text{ } \Omega/\text{cm}^2$ – 30 nm In_2S_3 ; $504 \text{ } \Omega/\text{cm}^2$ – 60 nm In_2S_3). Modest increases to the average open circuit voltages are also observed (~ 65 meV at peak). Solar cells with CdS-only window layers had on average slightly lower reverse saturation current densities than the double window/buffer layer devices. Although slightly higher leakage currents through the junction reduce open circuit voltage, this was offset by the reduced current and highly shunted behavior of the CdS-only devices. From these data it was determined that for the best overall device performance the optimal In_2S_3 thickness is around 50–60 nm.

Figure 5c shows a cross-section SEM image of a typical top-performing dual window layer solar cell. The solar cell is highly uniform and planar with the morphology of each layer clearly identifiable. For clarity the FTO has been color coded blue, while the other layers are CdS (yellow), In_2S_3 (orange), CuSbS_2 (brown), SPIRO-MeOTAD (purple) and the Au top electrode (green). Top view SEM images of the CdS window layer and a typical ~ 60 nm In_2S_3 thin film on CdS can be found in the Supporting Information, Figure S8. To investigate the structure and morphology of the CuSbS_2 solar cells in more detail a section of the cell shown in Panel C was cut into a lamella using a Focused Ion Beam SEM (FIBSEM) and subsequently thinned to c.a. 100 nm using a gallium beam for imaging inside a TEM. Figure 5d shows a HRTEM image of the cell in cross section. The top and bottom electrodes have been highlighted for clarity. From the bottom up these layers are FTO (450 nm); CdS (87 nm); In_2S_3 (59 nm) CuSbS_2 (172 nm); SPIRO-MeOTAD (~ 125 nm); Au (~ 70 nm). Close inspection of the cross section reveals that the CdS and CuSbS_2 layers are highly dense while the In_2S_3 layer has a more nanostructured morphology (this can also be observed in the cross-section SEM). Within the lamella a segment of each layer was analyzed to determine its crystallinity, phase purity, and the presence of any lattice strain after the processing of the solar cell devices.

The key regions of analysis correspond to CdS (red box), In_2S_3 (green box), and CuSbS_2 (blue box). Analysis of the CdS layer reveals a perfect match to wurtzite hexagonal CdS with measured lattice spacings of 3.59 Å and 3.38 Å. These match well to the (100) and (002) orthogonal lattice planes of hexagonal CdS with d-spacings of 3.586 Å and 3.359 Å respectively. The corresponding FFT also shows consistent (101) and (102) spacings. These results corroborate the bulk XRD analysis of the as-prepared CdS thin films (see Supporting Information, Figure S9). Analysis of the In_2S_3 layer shows a

lattice spacing of 3.24 Å, which matches to the expected 3.249 Å d-spacing of the dominant (109) lattice plane of tetragonal β - In_2S_3 . Likewise, the corresponding FFT gives the correct positions for the lower intensity (116) and (206) lattice planes. As expected from XRD, the high-resolution imaging of the CuSbS_2 layer reveals that the layer is highly crystalline with clearly visible lattice planes. The recurrent lattice spacing observed throughout the layer was 2.98 Å, corresponding to the (301) of orthorhombic CuSbS_2 (100% intensity according to PDF 44-1417), expected d-spacing 2.985 Å). Larger areas are shown in Supporting Information, Figure S10. The lattice spacing of all crystalline regions were calculated from an average of 20 or more consecutive lattice planes. From the clearly defined layered structure observed in the HRTEM cross-section and the close match of the d-spacings in the high-resolution lattice images to their expected values we observe that the materials are not significantly strained by anomalous doping and that the interfaces are well maintained after device assembly.

Figure 5e shows the comparative efficiency statistics of devices with and without the optimal 60 nm In_2S_3 interlayer. These statistics were developed from 24 solar cells of each type. It is immediately evident that the solar cells have improved efficiencies upon the introduction of the In_2S_3 interlayer as discussed previously. The median cell efficiencies with CdS and CdS/ In_2S_3 were 0.73% and 1.54%, with the champion cells of each type reaching 1.04% and 1.72% respectively. The full cell statistics can be found in the Supporting Information, Figure S11. Figure 5f shows the current–voltage curve for the champion device with CdS/ In_2S_3 window/buffer layer structure ($V_{\text{oc}} = 0.483$ V; $J_{\text{sc}} = 6.45 \text{ mA}/\text{cm}^2$; FF= 55.2%; PCE=1.72%). These results are the highest efficiency solution-processed planar CuSbS_2 solar cells to date, with over three times the efficiency of the current best hydrazine-based methods, and over double the previous record for thin film solar cells of any other MP-based method. A table outlining comparative performances of record efficiency solution processed CuSbS_2 solar cells to date can be viewed in the Supporting Information, Table S3. The efficiencies achieved in this work are validation of both the high quality of the carefully optimized thin films and interlayer strategy outlined herein.

Conclusions

We have presented a method to achieve high-quality semiconductor thin films of CuSbS_2 at mild processing temperatures. Unlike existing thiourea-based precursors, the low decomposition temperature and balanced reactivity of metal–DTC precursors yielded high quality films and phase-pure materials at low temperatures. Micrometer-sized grains could be achieved without the need for multistep procedures or high temperature sulfurization, which represents a significant advantage in the rapid processing of devices using CuSbS_2 photoactive layers. Through careful optimization of the cation ratio and annealing steps phase-pure p-type CuSbS_2 thin films with high photoconductivity have been demonstrated. These optimized films were incorporated into superstrate structured solar cell devices that reached 1.7%. Improvements to device efficiency were realized through the use of an In_2S_3 buffer electron transport layer. The devices fabricated here are the highest efficiency solution-processed planar CuSbS_2 solar cells to date. Further improvements could be realized by using thinner and denser In_2S_3 layers. We are confident that the facile sulfurization-free methods to produce high-quality CuSbS_2 thin

films outlined here will prove invaluable to furthering the advancement of thin films devices and solar cells.

EXPERIMENTAL

Materials:

Copper(I) oxide (99.999%), antimony(III) oxide (99.999%), butylamine (99.5%), ethanol (dry absolute), europium(III) chloride hexahydrate (99.9%), copper metal (99.999%), and antimony metal (99.999%) were procured from Sigma Aldrich. Carbon disulfide (99.9%) was purchased from Merck. 2,2',7,7'-Tetrakis-(N,N-di-4-methoxyphenyl amino)-9,9'-spirobifluorene (SPIRO-MeOTAD) was purchased from Lumtec. FTO-coated glass was purchased from Latech Scientific Supply ($15 \Omega/\square$). All reagents and solvents were used as received without further purification.

Precursor Solutions:

Full details on the preparation of the copper and antimony dithiocarbamate molecular precursor solutions can be found in the Supporting Information.

Window and Buffer Layer Fabrication:

The method used to fabricate of CdS thin films via chemical bath deposition (CBD) was reported previously⁸. The as-prepared films were treated sequentially with H_2O_2 and $CdCl_2$ in methanol sequentially and then heated in air at 400 °C for 5 mins. See Supporting Information for details. The In_2S_3 thin films were spun onto FTO/CdS substrates from a 0.1 M ethanolic indium butyldithiocarbamate (In-DTC molecular precursor;) solution made from $In(OH)_3$, butylamine, and CS_2 to afford a final In:DTC ratio of 1:6. After 2 days of stirring, the solution of indium butyldithiocarbamate was filtered to remove residual $In(OH)_3$ and the concentration adjusted to provide the required layer thicknesses as measured by profilometry.

CuSbS₂ Thin Film Fabrication:

To produce an ~100 nm film a 0.1 M Cu/Sb precursor solution was pipetted onto FTO-coated glass substrates and spun at 2000 rpm for 30 sec, followed by a drying/decomposition step at 200 °C. Heating at 200 °C resulted in an immediate color change from clear/yellow to dark brown, indicating the decomposition of the metal dithiocarbamate precursors to form $CuSbS_2$ (see Figure 1a). Unless otherwise stated all films were heated at 200 °C for 10 min in air followed by transfer to a nitrogen glovebox for final annealing at the specified temperatures for the specified times. We note here that the use of a pure Sb-DTC precursor resulted in the fabrication of well-formed pure-phase Sb_2S_3 thin films (See Supporting Information, Figure S12).

Instrumentation:

UV-vis-NIR absorption spectra of the thin films were collected at room temperature using a PerkinElmer Lambda 1050 spectrophotometer with an integrating sphere attachment. X-ray diffraction (XRD) was performed on a Bruker D8 diffractometer equipped with a $Cu K\alpha$ radiation source and operated at 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) was performed on a Kratos Axis HSi using an $Al K\alpha$ X-ray source. Photoelectron spectroscopy in air (PESA) measurements were performed on a Riken Keiki AC-2 spectrophotometer. Scanning electron micrographs were collected on a FEI Nova NanoSEM 200 FEGSEM. Lamella cutting was performed using a gallium ion beam in a FEI Scios

Dualbeam FIBSEM. Images were conducted in a JEOL 2100F FEGTEM/STEM equipped with a Gatan OneView 4k CCD Camera. Evaporations were conducted using a Daedong HighTechnologies Solar-Bridge thermal evaporator system.

Photo-Electrochemistry:

The films were fixed to a custom-built electrochemical cell, which consisted of a mesh-basket platinum working electrode and an Ag/AgCl reference electrode. The voltage of the cell was manipulated using a Powerlab 4/20 controlled using EChem software (ver. 1.5.2, AD Instruments). The light source consisted of a 455 nm blue LED (LUXEON "Royal Blue") equipped with a diffuser. The sample was illuminated through the FTO onto the back contact. The light intensity at the sample was measured using a Hamamatsu silicon photodiode (0.43 mA on 6.6 mm²). The calculated light intensity from calibration curves yielded ~1.85 mW incident upon the photo-diode corresponding to a total flux of ~28 mWcm⁻².

Solar Cell Fabrication and Measurement:

Solar cells were fabricated in the following architecture: FTO (450 nm); CdS (~90 nm); In_2S_3 (~60 nm) $CuSbS_2$ (~180 nm); SPIRO-MeOTAD (~125 nm); Au (~70 nm). Firstly, CdS was deposited on FTO by chemical bath deposition (CBD) and treated as described previously. Next, the buffer layer was deposited and annealed at 400 °C in the glove box for 5 mins. Then the absorber layer was deposited layer-by-layer by spin coating three layers (4000 rpm, 30 sec) of 0.075 M Cu/Sb precursor solution (Cu:Sb; 0.9:1) with a decomposition step at 200 °C between each layer. The final three-layer structure was annealed at 350 °C for 2 min, achieving a final thickness of ~180 nm. Next, the hole extraction layer (SPIRO MeOTAD) was deposited by spin coating (3000 rpm, 30 sec) a solution consisting of 80 mg/mL SPIRO-MeOTAD in chlorobenzene, 11 μ L of 520 mg/mL bis(trifluoromethane) sulfonimide lithium salt (Li-TIFSI) and 11 μ L 4-tert-butylpyridine (TBP). Finally, the gold electrodes were deposited by thermal evaporation through a shadow mask. Measurements were conducted via illumination (Oriel Sol3A Class AAA Solar Simulator) through a laser cut mask (0.100 cm²) using a custom-built set up and a Keithley 2401 Source Meter following the guidelines for best measurement technique⁹⁰.

ASSOCIATED CONTENT

Supporting Information

Synthetic procedure for MP inks as well as additional experiments and analysis, including XRD, SEM, HRTEM, XPS, PESA. The Supporting Information is available free of charge on the ACS Publications website.

AUTHOR INFORMATION

Corresponding Author

* joel.vanembden@rmit.edu.au

Notes

The authors declare no competing financial interests.

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