

## Investigations Of Ternary $\text{Cu}_3\text{SbS}_3$ Thin Films As Absorber In Photovoltaic Devices

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### Abstract

Magnetron sputtered Cu-Sb metallic precursors were sulphidised on glass and molybdenum/glass substrates at 6 different temperatures. Two techniques were adopted for the elemental sulphidisation process. Precursors sulphidised using evaporated elemental sulphur were successfully converted into  $\text{Cu}_3\text{SbS}_3$  solar absorber layers on molybdenum substrates. The as-sulphidised films exhibited p-type conductivity were produced in the limited response when analysed using a Eu+ electrolyte arrangement to measure the photocurrent. The films exhibited an energy bandgap value of 1.84eV.

### Introduction

The current market share of thin film photovoltaics (PV) is dominated by technologies based on cadmium telluride (CdTe),  $\text{CuInGaSe}_2$  (CIGS) and amorphous silicon (a-Si). In the last decade, considerable improvements have been achieved for solar cells based on these absorbers, both in the laboratories and manufacturing plants. Indeed CIGS solar cells have now achieved efficiencies of 20.1% [1]. However the rarity and high costs of In, Ga and Te used in these absorber layers, could restrict the ability of these photovoltaic technologies to meet the demands of a multi-TW PV market [2, 3] making them unsustainable. Consequently, there is a need for new light absorbing semiconductors made from abundant elements. The semiconductor  $\text{Cu}_3\text{SbS}_3$  made from sustainable, low cost, elements offers a possible alternative. In this paper, we report on the preparation by a scalable 2-stage process of  $\text{Cu}_3\text{SbS}_3$  thin film absorber and their properties.

### Experimental

Cu-Sb metallic precursor films were deposited onto molybdenum coated soda-

lime glass substrates by DC magnetron sputtering from a 3" diameter alloy target with Cu to Sb atomic ratio of 3:1 and 5N purity. Constant rotation of the substrate ensured uniform thickness in the deposited layers. The thickness of these metallic layers was approximately 300nm. The precursors were sulphidised, either by placing them "as-deposited" in a sealed graphite box containing elemental sulphur powder, uniformly distributed onto the precursor or by evaporating elemental sulphur directly onto the precursor prior to placing them in the graphite box.. In both cases the box was placed into a tube furnace for heating to the conversion temperature. The furnace was evacuated to a primary vacuum and then backfilled with 1 mbar of argon before sulphidisation took place at the selected temperature. Those converted using the sulphur powder were heated to temperatures of 250-550 °C (dwell of 30min). The samples were left to cool down naturally at the end of the heating process. The same process was performed only at 500°C for the sample that used the evaporated sulphur.

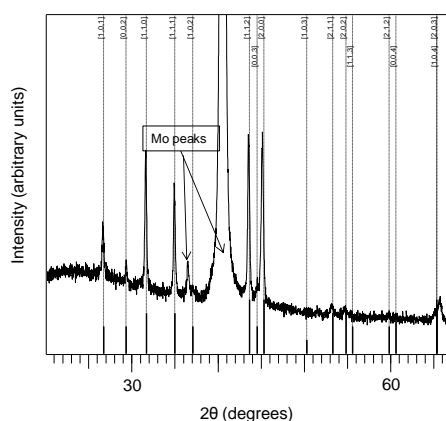
The morphology and composition of the converted layers were characterised using scanning electron microscopy (FEI (Philips) Environmental Scanning Electron Microscope (ESEM)) and dispersive X-ray microanalysis, respectively. Structural properties were determined by X-ray diffraction (Siemens X-Ray Diffractometer). The distribution of elements as a function of thickness was investigated using secondary ion mass spectroscopy (Hiden analytical MAXIM 500amu).

Examination of the opto-electronic properties of the converted layers without the need for cell fabrication is possible by using a liquid electrolyte to contact the front of the layer and the molybdenum coated substrate as the back contact of the layer. Photo electrochemical measurements of  $\text{Cu}_3\text{SbS}_3$  films were performed in aqueous 0.2 M  $\text{Eu}(\text{NO}_3)_3$ . Measurements were carried out in a three

electrode configuration using a glass cell with an Ag|AgCl reference electrode, and a platinum electrode as a counter electrode. Photocurrent spectra were recorded with a standard photoelectrochemical setup: Tungsten-halogen lamp, monochromator, and chopper; potentiostat, and lock-in amplifier. Spectra were recorded using chopped illumination with a frequency of 75 Hz and normalized against calibrated silicon and germanium photodiodes.

## Results and discussion

Precursors deposited on either glass or Mo/glass substrates from the binary target had an atomic composition of 68%Cu and 32%Sb. The corresponding XRD pattern of films (Figure 1) indicated the presence of a binary alloy, matching with the standard data for  $\text{Cu}_2\text{Sb}$  (pdf 3-1023). The same match with this standard was observed for precursor deposited on glass substrates.



**Figure 1.** X-ray powder diffraction pattern of metallic Cu-Sb precursor deposited on Mo/SLG substrate, showing good agreement with the standard XRD pattern for  $\text{Cu}_2\text{Sb}$  tetragonal lattice (pdf 3-1023).

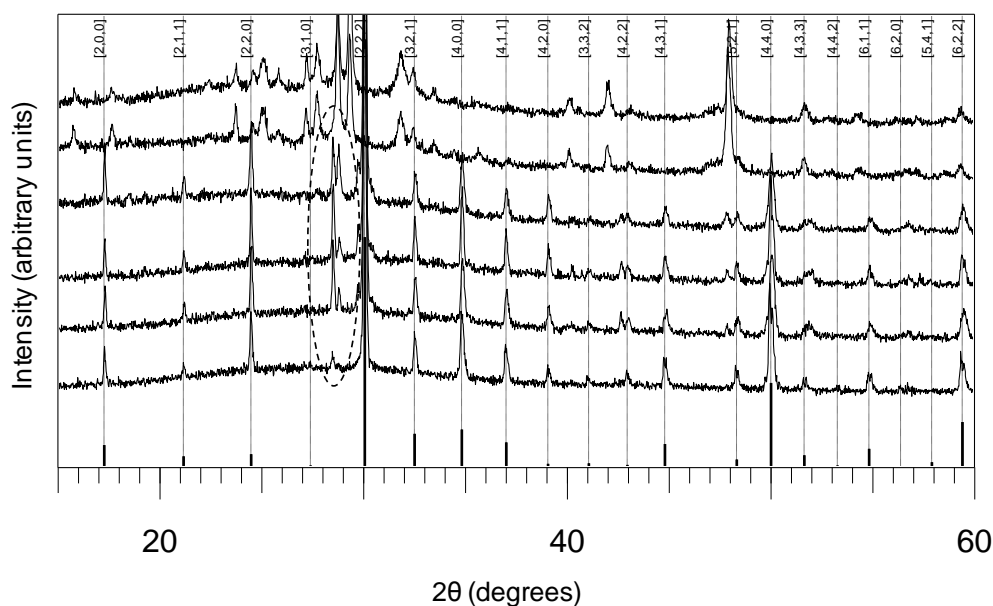
The metallic precursor films deposited either on Mo or Mo/SLG substrates, were sulphidised at 7 different temperatures between 250-550 °C in 50 °C steps, using elemental sulphur powder. Absorber layers treated at 250 °C and 300 °C and 500 °C exhibited good adhesion on both Mo/glass and glass substrates. Poor adhesion was observed for the samples treated at temperatures between 350-400 °C, with complete evaporation of the film sulphidised at 550 °C. A rough surface

was observed for all the samples except for the one sulphidised at 500 °C.

Figure 2 shows the XRD patterns collected for the films annealed at the above temperatures on glass substrates, and the standard powder pattern for  $\text{Cu}_3\text{SbS}_3$  (cubic structure powder diffraction file: 075-1574). Peaks matching the standard XRD patterns of CuS and  $\text{Sb}_2\text{S}_3$  (pdf files 079-2321 and 002-0374 respectively) are observed for the samples sulphidised at 250 °C and 300 °C, indicating a mixture of CuS and  $\text{Sb}_2\text{S}_3$  phases at these temperatures. The XRD spectrum for the sulphidised film at 350 °C exhibits a clear transition of phase, with formation of dominant  $\text{Cu}_3\text{SbS}_3$  phase. A possible secondary  $\text{CuSbS}_2$  phase was also identified at this temperature. However the disappearance of chalcocostibite ( $\text{CuSbS}_2$  pdf file: 044-1417) indicated in the XRD spectra in Figure 2 (peaks within the dotted line), indicates that a temperature of 500 °C is required for the formation of single phase  $\text{Cu}_3\text{SbS}_3$ .

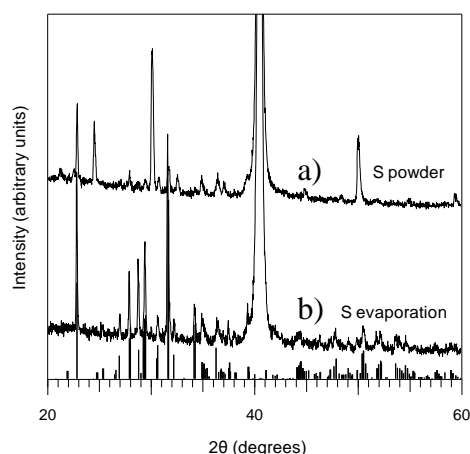
Similar results were observed for the sulphidisation of the precursors deposited on molybdenum substrates at these temperatures. However two different structures of  $\text{Cu}_3\text{SbS}_3$  (cubic and orthorhombic, pdf files 075-1574 and 083-0563 respectively) with the same intensity were observed in the XRD pattern at 500 °C, indicating a possible influence of the molybdenum substrate in the growth of the film.

In order to obtain greater control over the sulphidisation process, elemental sulphur was evaporated directly onto the precursor with a measured thickness of the sulphur layer. A comparison between sulphidised samples at 500 °C on molybdenum substrates with two different techniques is shown in Figure 3. The upper plot shows the XRD pattern of the precursor processed with sulphur powder evenly distributed onto its surface. The lower plot shows the same precursor processed using an approximately 1.5 μm thick sulphur layer. The film obtained through evaporation of sulphur exhibits a good adhesion to the substrate and shows a good agreement with the standard XRD pattern of  $\text{Cu}_3\text{SbS}_3$  (orthorhombic system pdf file: 083-0563). On the other hand the precursor processed with sulphur powder shows a mixture of  $\text{Cu}_3\text{SbS}_3$  phases as described



**Figure 2.** X-ray powder diffraction patterns of the sulphidised Cu-Sb precursor films, deposited on glass substrates at different temperatures. The sample sulphidised at 500°C shows a good match with the standard XRD powder pattern for the cubic structure of  $\text{Cu}_3\text{SbS}_3$  (pdf 075-1574). The area in the dotted line indicates the evolution of the main peaks associated with chalcocostibite  $\text{CuSbS}_2$  phase (pdf 075-1574)

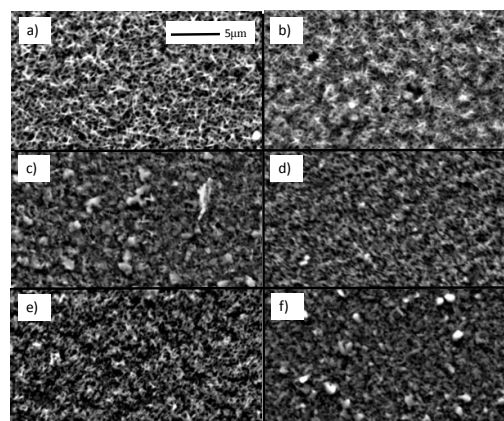
earlier. In conclusion the introduction of a controlled evaporation of sulphur onto the precursor resulted in improved adhesion of the film and formation of single phase  $\text{Cu}_3\text{SbS}_3$ .



**Figure 3.** XRD patterns of films processed with a) sulphur powder and b) evaporated sulphur, annealed at 500 °C on Mo/SLG.

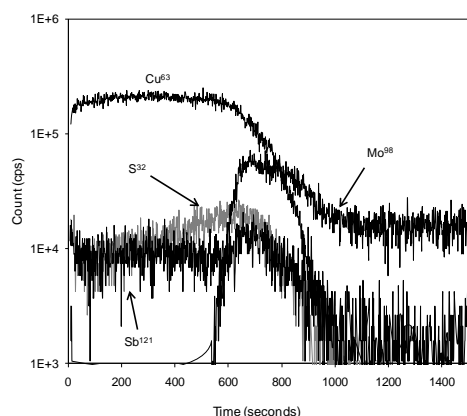
SEM micrographs of the precursor layers sulphidised at different temperatures are shown in **Error! Reference source not found.** panels (a-f). Similar morphology for the samples sulphidised at 250 and 300

°C Figure 4 panels (a) and (b) respectively) can be seen and these exhibit star shaped crystallites. The morphology for conversion temperatures higher than 300 °C appears to change abruptly, then remaining similar for all the subsequent films Figure 4 panels (c), (d), (e) and (f) ), in accord with the variation observed in the XRD analysis above reported.



**Figure 4.** SEM plan view of the sulphidised samples at (a) 250°C (b) 300°C (c) 350°C (d) 400°C (e) 450°C (f) 500°C.

Depth profiles of the elements by SIMS analysis of the converted films indicated a uniform distribution of Cu, Sb and S. Figure 5 shows the time/depth profile for the sample sulphidised using evaporated sulphur. A slight increase in the sulphur content at the molybdenum/absorber interface may indicate the presence of  $\text{Mo}_2\text{S}_3$ , identified in the XRD analysis.



**Figure 5.** SIMS analysis, for a photo-active film sulphidised at 500 °C with sulphur evaporated on precursor.

Photoelectrochemical measurements were performed for the photo-active layers. The measured photo-current was maximised by adjusting the bias voltage. The film annealed at 500 °C using evaporated sulphur, resulted in a final film thickness of approximately 1.2  $\mu\text{m}$ . This was found the only film to be photoactive and of p-type conductivity. None of the films produced at lower temperatures utilising powder in the conversion, exhibited photo-activity. The External quantum efficiency spectrum of the photo-active sample is plotted in Figure 6. The potential with respect to the Ag|AgCl reference electrode was adjusted to maximise the output photo-current. The fabricated layer showed a weak response of around 4% in the photon range of 1.1 – 3.0 eV.

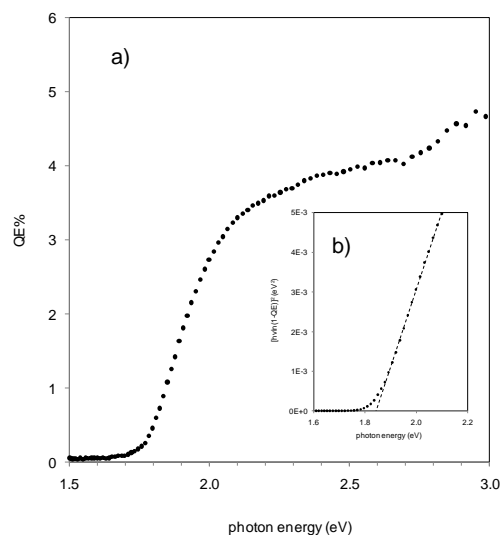
The external quantum efficiency spectrum can be used to derive the band gap  $E_g$  of the produced films [4]:

$$EQE = 1 - \exp(-\alpha W) \quad (1)$$

For a direct transition, the dependence of the absorption coefficient on photon energy is given by:

$$ahv \propto (hv - E_g)^{1/2} \quad (2)$$

where  $h\nu$  is the photon energy. Therefore a plot of  $[h\nu \ln(1-EQE)]^2$  as function of photon energy, yields a straight line which intersects the x-axis for  $h\nu = E_g$  (Figure 6b). The calculated band gap is 1.84 eV.



**Figure 6.** (a) External quantum efficiency for a photo-active film sulphidised at 500°C with sulphur evaporated on precursor, and (b) determination of the energy bandgap of the absorbers assuming a direct bandgap at 1.84 eV.

## Conclusions

In this study a process to produce  $\text{Cu}_3\text{SbS}_3$  films has been investigated. Sputtered Cu-Sb metallic precursors on molybdenum/glass and glass substrates were sulphidised using powder as source of sulphur in the reaction chamber. A range of conversion temperatures were investigated, and the important role of the substrate in the growth of the films was highlighted. Layers grown on glass substrates and processed at 500 °C exhibited a uniform and nearly single phase  $\text{Cu}_3\text{SbS}_3$  (cubic system). Whereas precursors annealed on molybdenum coated glass substrates at 500 °C did not form single phase  $\text{Cu}_3\text{SbS}_3$  but exhibiting a mixture of orthorhombic and cubic  $\text{Cu}_3\text{SbS}_3$  structures. In order to have better control of the sulphidisation, evaporated sulphur films of known thickness were directly deposited onto the precursors. Using this new technique  $\text{Cu}_3\text{SbS}_3$  films (orthorhombic system) annealed on

Mo/glass at 500 °C, showed photo-activity, good adhesion, p-type conductivity and nearly single phase structure. The film so produced exhibited a band-gap of 1.84 eV.

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