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## PROPERTIES OF THIN FILMS OF TIN SULPHIDE PRODUCED USING THE THERMAL EVAPORATION METHOD

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**ABSTRACT:** SnS is of interest for use as an absorber layer and the wider energy bandgap phases e.g. SnS<sub>2</sub>, Sn<sub>2</sub>S<sub>3</sub> and Sn/S/O alloys of interest as Cd-free buffer layers for use in thin film solar cells. In this work thin films of tin sulphide have been thermally evaporated onto glass substrates with the aim of optimising the properties of the material for use in photovoltaic solar cell device structures. In particular the effects of source temperature, substrate temperature, deposition rate and film thickness on the chemical and physical properties of the layers deposited were investigated. Energy dispersive x-ray analysis was used to determine the film composition, x-ray diffraction to determine the phases present and structure of each phase, transmittance and reflectance versus wavelength measurements to determine the energy bandgap and other optical constants and scanning electron microscopy to observe the surface topology and topography and the properties correlated to the deposition parameters. Using the optimised conditions it is possible to produce thin films of tin sulphide that are pinhole free, conformal to the substrate and that consist of densely packed columnar grains. The composition, phases present and the optical properties of the layers deposited were found to be sensitive to the deposition conditions used.

**Keywords:** Thin Film, Optical Properties, Characterisation.

### 1 INTRODUCTION

The most advanced materials for making thin film solar cells are those based on the use of cadmium telluride (CdTe) or copper indium gallium diselenide (Cu(In,Ga)Se<sub>2</sub> or CIGS) absorber layer materials [1]. Despite the excellent achievements made with these materials problems remain. There are concerns with respect to the environmental acceptability of using cadmium in the former devices and concerns with respect to the lack of abundance of gallium and indium for the latter devices [2]. It is possible that there are other inorganic compound semiconductors that can be used to make efficient cells that do not have these problems. One promising candidate is tin sulphide (SnS), as in common with CdTe and CIGS, this material has a near optimum energy bandgap and it is amphoteric with a wide energy bandgap oxide, promising the possibility of grain boundary passivation. Not only does SnS consist of relatively abundant elements but large scale production processes already exist for producing thin films of tin and for converting metals into the corresponding sulphide using a range of sulphidisation processes.

In the literature thin films of SnS have been deposited using a variety of techniques including spray pyrolysis [3], electrodeposition [4], chemical vapour deposition [5] and vacuum evaporation [6]. The attempts to use the SnS in device structures are limited but previous studies have shown that cells with efficiencies up to 1.3% can be produced [7]. The work presented here is part of our effort to determine whether or not stable and efficient cells can be produced using this novel material.

### 2 EXPERIMENTAL

The evaporations were made in an oil pumped vacuum system operated in the 10<sup>-5</sup> to 10<sup>-6</sup> Torr range of vacuum pressures. Both the substrate and the source material were heated using resistive elements with a shutter incorporated to control the deposition time. The

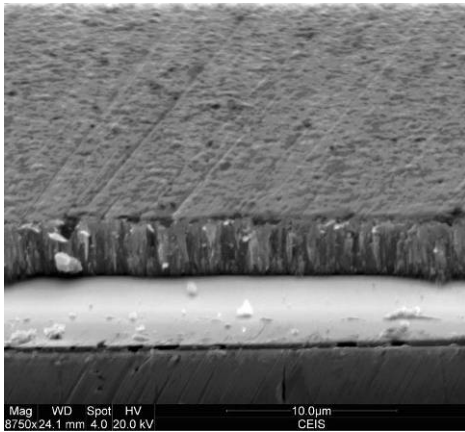
source material was obtained from Alfa-Aesar and was 99.99% pure. The substrates used for the depositions were either soda-lime glass microscope slides or fluorine-doped SnO<sub>2</sub>-coated glass slides. Each substrate was cleaned in an ultrasonic bath containing a mixture of Decon 90 and de-ionised water solution for one hour. After a rinse with de-ionised water, the substrate was washed in propan-2-ol (IPA) to remove any remaining contamination. The evaporation source was quartz, bottle-shaped crucible that was heated by a cylindrical tantalum heating element supplied by the R.D. Mathis Company. The SnS evaporant was placed in the crucible and quartz wool placed above it to minimise the effects of "spattering", *i.e.* the ejection of molten lumps of material from the source that can damage the growing film. Films were then deposited using source temperatures in the range 300°C to 600°C and for substrate temperatures in the range 100°C to 400°C. These temperatures were measured by thermocouples in direct contact with the crucible and substrate, respectively. The deposition time was typically less than 5 minutes.

A Siemens D5000 X-Ray diffractometer (XRD), with a CuK $\alpha$  radiation source ( $\lambda = 1.5406\text{\AA}$ ), was used to identify the phases present and structure of each phase. The optical transmittance and reflectance versus wavelength measurements were made using a Shimadzu SolidSpec 3700 UV-VIS-NIR spectrophotometer. Observations of the surface topology and topography were carried out using an FEI Quanta 200 ESEM, while energy dispersive x-ray analysis (EDS) analysis was done using an Oxford Instruments EDS system.

### 3 RESULTS AND DISCUSSION

The tin sulphide films were deposited using source temperatures in the range 300°C to 600°C and for substrate temperatures in the range 100°C to 400°C. All the thin films deposited were adherent to the substrate, uniformly thick and pinhole free. The films deposited

with thicknesses  $< 3 \mu\text{m}$  had smooth surface topologies and were yellow-brown in colour whereas films with thicknesses  $> 10 \mu\text{m}$  thick were a darker black colour and had rougher surface textures. The former films were deposited using relatively short times and for the higher substrate temperatures whereas the thicker films resulted for the lower substrate temperatures and for longer deposition times. Fig. 1 shows a cross-sectional view, taken with the SEM, of a layer of SnS deposited at a substrate temperature of  $300^\circ\text{C}$  for a source temperature of  $350^\circ\text{C}$  and for a deposition time of 2 minutes. The layer is approximately  $3 \mu\text{m}$  thick and it consists of densely packed columnar grains that extend throughout the film thickness.



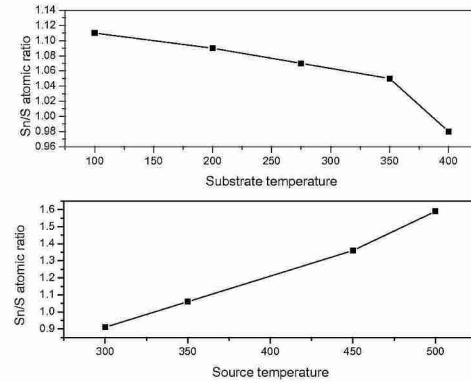
**Figure 1:** SEM micrograph of a SnS layer deposited using a  $300^\circ\text{C}$  substrate temperature, a  $350^\circ\text{C}$  source temperature and a deposition time of 2 minutes.

These observations were made for all the layers deposited with thicknesses  $> 0.6 \mu\text{m}$ . They indicate good potential for using such layers in solar cell devices, because with columnar grains, minority carriers generated by incident light can diffuse to the junction without crossing a grain boundary. Work is currently in progress to increase the grain size, densify the grains and passivate the grain boundaries further by post-deposition annealing in a range of environments.

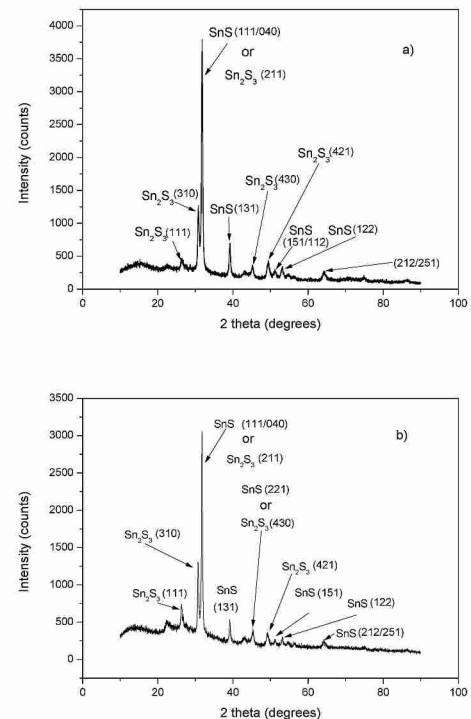
Energy dispersive X-ray analysis was used to determine the ratio of the constituent elements in the deposited films and to identify impurities present within the films. Fig. 2 shows how the ratio of tin to sulphur varied with (a) substrate temperature (keeping the source temperature constant) and (b) with source temperature keeping the substrate temperature constant. It is evident from Figs. 2 (a) and (b) that the films become more Sn-rich with decreasing substrate temperature, and with increasing source temperature. The change in stoichiometry with the deposition conditions is expected to alter the electrical properties of the films. All the films deposited and tested were found to be p-type, the resistivity tending to be lower for the more Sn-rich films. It should be noted that oxygen was observed to be present in all the thin films deposited.

The X-ray diffraction data for layers grown using different substrate temperatures are given in Fig. 3. The 3 predominant peaks corresponding to SnS are the (111), (040), and (131) reflections clearly indicating that the predominant phase present is SnS. It should however, be

noted that for most of films other less intense reflections were also observed. Some of the peaks can be attributed to reflections from the (151), (122), and (251) planes of SnS although it is possible that these and some of the other less intense reflections could be due to the presence of other phases in the films



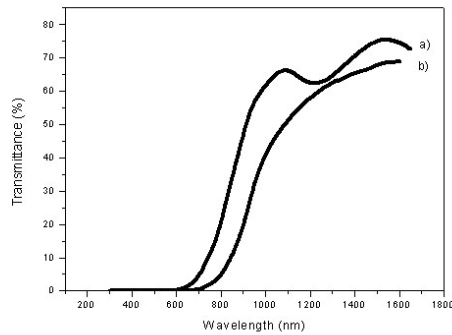
**Figure 2:** (a) Variation of Sn/S atomic ratio with substrate temperature. (The source temperature was kept constant at  $300^\circ\text{C}$  and deposition time constant at 2 minutes). (b) Variation of Sn/S atomic ratio with source temperature. (The substrate temperature was kept constant at  $300^\circ\text{C}$  and deposition time constant at 2 minutes)



**Figure 3:** (a) XRD spectra of SnS layers deposited using (a) a  $300^\circ\text{C}$  source temperature,  $350^\circ\text{C}$  substrate temperature ( $d = 3.6 \mu\text{m}$ ) and (b) a  $300^\circ\text{C}$  source temperature, a  $300^\circ\text{C}$  substrate temperature ( $d = 3.4 \mu\text{m}$ ).

The transmittance versus wavelength behaviour of the films was surprising in that the optical absorption edge shifted when the deposition conditions were varied.

Data for two samples deposited using a source temperature of 300°C and substrate temperatures of 300°C and 350°C and 3  $\mu\text{m}$  thick are shown in Fig. 4.



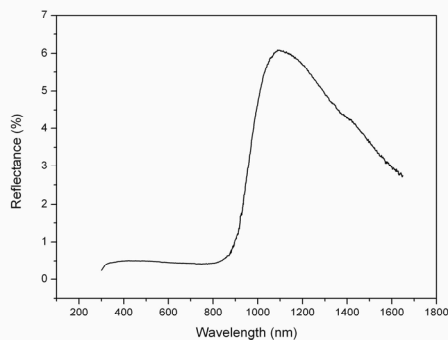
**Figure 4:** Transmittance vs. wavelength plot of SnS layers grown at (a) 300°C and (b) 350°C substrate temperatures with the source temperature fixed at 300°C

Figure 5 shows a typical reflectance vs. wavelength plot for a deposited layer.

For direct energy bandgap semiconductors, the optical absorption coefficient  $\alpha$  is given by:

$$\alpha = A(h\nu - E_g)^{1/2} / h\nu \quad (1)$$

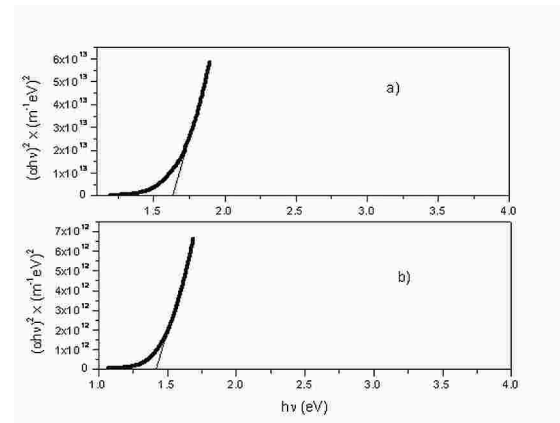
where A is a constant. This means that a plot of  $(\alpha h\nu)^2$  versus  $h\nu$  should be a straight line with an intercept on the  $h\nu$  axis equal to  $E_g$ . Such plots are shown in Fig. 6 for the samples shown in Fig. 4. Plots of how the energy bandgap changed with substrate temperature (keeping the source temperature and film thickness constant) are given in Fig. 7(a), and how it varied with film thickness keeping the substrate and source temperatures constant in Fig. 7(b).



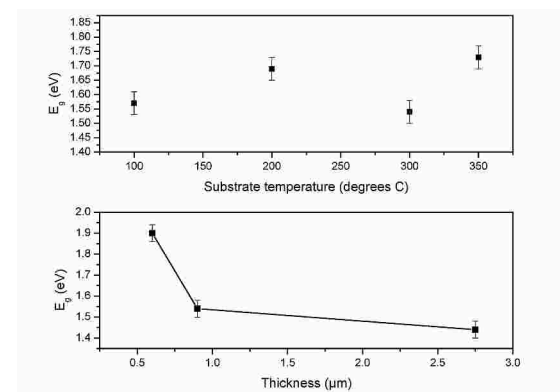
**Figure 5:** Reflectance vs. wavelength plot of SnS layer grown using a 350°C substrate temperature with the source temperature fixed at 300°C.

Fig. 7 (a) shows that if the film thickness is 0.8  $\mu\text{m}$  the energy bandgap is in the range 1.55–1.70 eV for substrate temperatures up to 300°C. Fig. 6 (b) shows that increasing the film thickness to > 1  $\mu\text{m}$  resulted in a reduction of the energy bandgap to < 1.55 eV. The shift in optical absorption edge and hence energy band gap with deposition conditions has been observed by other

workers, the most detailed study having been made with layers produced using chemical spray pyrolysis [7]. These workers attribute the change in the optical absorption edge to the presence of other phases of tin sulphide i.e. SnS<sub>2</sub> ( $E_g = 2.44$  eV), Sn<sub>2</sub>S<sub>3</sub> ( $E_g = 2.0$  eV) and SnO<sub>2</sub> ( $E_g = 2.5$ -3.5 eV) [8]. The Sn<sub>2</sub>S<sub>3</sub> phase was also observed to be present in this work and it is hence most likely that the energy bandgap changes observed here were for the same reason.



**Figure 6:**  $(\alpha h\nu)^2$  vs  $h\nu$  plot of SnS layers at (a) 350°C substrate temperature and (b) 300°C substrate temperatures with the source temperature fixed at 300°C



**Figure 7:** (a) Plot of how the energy bandgap  $E_g$  shifted with substrate temperature. The source temperature was kept constant at 300°C and the film thickness at 0.8±0.2  $\mu\text{m}$  (b) Plot of how the energy bandgap shifted with thickness. The source and substrate temperature were kept constant at 300°C

#### 4 CONCLUSIONS

Using the thermal evaporation method it is possible to produce stoichiometric thin films of SnS, that are conformal and highly adherent to the substrate and that consist of densely packed columnar grains. Despite the energy gap of the layers varying with the deposition conditions, it is possible to produce thin films of SnS, a few  $\mu\text{m}$  thick, with energy bandgaps in the range, 1.3 – 1.7 eV, i.e near to the optimum for photovoltaic energy conversion (1.5 eV). The layers are also p-type giving flexibility to the device design to be used. Work is in

progress to investigate in detail the electrical properties of the films, to investigate the influence of post-deposition annealing on the structural, electrical and optical properties of the layers and to fabricate and characterise solar cells made using optimised layers.

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