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Citation: Ogah, Ogah E., Zoppi, Guillaume, Miles, Robert and Forbes, Ian (2008) Investigation of how the chemical and physical properties of thermally evaporated SnS vary with source and substrate temperatures. In: 4th Photovoltaic Science Application and Technology Conference and Exhibition (PVSAT-4), 2-4 April 2008, Bath, United Kingdom.

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# Investigation of how the Chemical and Physical Properties of Thermally Evaporated SnS Vary With Source and Substrate Temperatures

Ogah E. Ogah, Guillaume Zoppi, Ian Forbes, Robert W. Miles\*

Northumbria Photovoltaics Applications Centre, Northumbria University, Ellison Building, Newcastle upon Tyne, NE1 8ST, UK

\*Corresponding Author: robert.miles@northumbria.ac.uk

## Abstract

Thin films of tin sulphide have been thermally evaporated onto glass and SnO<sub>2</sub>:F coated glass substrates with the aim of optimising the properties for use in photovoltaic solar cell device structures. In particular the effects of source temperature, substrate temperature, and film thickness on the chemical and physical properties of the layers deposited were investigated. Using a wide range of conditions it was 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 optical properties of the layers were found to depend on deposition conditions. It was however possible to produce SnS thin films with energy band gaps near the optimum for photovoltaic solar energy conversion i.e. 1.5 eV. The applicability of using these films in photovoltaic solar cell device structures is discussed.

## 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 99.999% purity SnS source material was obtained from Alfa-Aesar. 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 a 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.

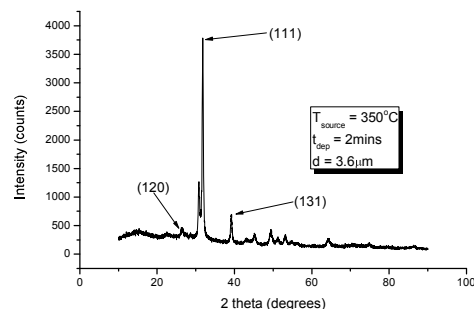
A Siemens D5000 X-Ray diffractometer (XRD), with a  $\text{CuK}\alpha$  radiation source ( $\lambda = 1.5406\text{\AA}$ ), was used to identify the phases present and structure of each phase. The optical transmittance and reflectance versus wavelength measurements were made using a Shimadzu SolidSpec 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  $300\text{ }^\circ\text{C}$  to  $600\text{ }^\circ\text{C}$  and for substrate temperatures in the range  $100\text{ }^\circ\text{C}$  to  $400\text{ }^\circ\text{C}$ . 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.

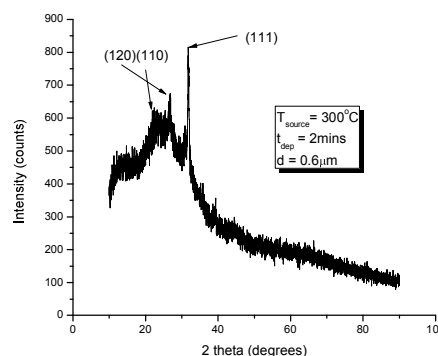
EDS data showed that when the source temperature was kept constant at  $300\text{ }^\circ\text{C}$  and the substrate temperature varied from  $100\text{ }^\circ\text{C}$  to  $300\text{ }^\circ\text{C}$  the samples were tin rich and showed a trend of decreasing tin concentration with increasing substrate temperature. When the substrate temperature was held constant at  $300\text{ }^\circ\text{C}$  and the source temperature varied from  $300\text{ }^\circ\text{C}$  to  $500\text{ }^\circ\text{C}$  the trend was one of increasing tin concentration with an increase source temperature. Oxygen was found to be present in all the films deposited.

The x-ray diffraction data for layers with thicknesses  $> 0.6\mu\text{m}$  were as given in fig. 1. The 3 predominant peaks corresponding to SnS are the (111), (120), 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 (061), (212), and (141) 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.



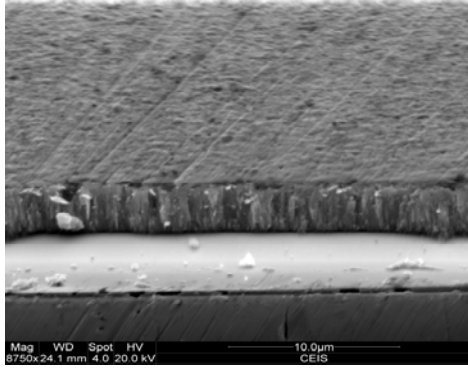
**Figure 1** XRD of a SnS layer deposited using a  $350\text{ }^\circ\text{C}$  source temperature, a  $300\text{ }^\circ\text{C}$  substrate temperature and a deposition time of 2 minutes ( $t = 3.6\mu\text{m}$ )

For layers with thicknesses  $< 0.6\mu\text{m}$  the x-ray diffraction pattern is as shown in fig.2. The diffuse diffraction behaviour is due to layers with thicknesses  $< 0.6\mu\text{m}$  consisting of very small grains / the films being amorphous.



**Figure 2** XRD of a SnS layer deposited using a  $300\text{ }^\circ\text{C}$  source temperature, a  $300\text{ }^\circ\text{C}$  substrate temperature and a deposition time of 2 minutes ( $t = 0.6\text{ microns}$ )

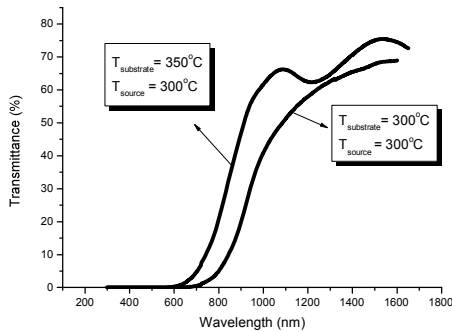
Fig.3 shows a cross-sectional view, taken with the SEM, of a layer of SnS deposited at a substrate temperature of  $300\text{ }^\circ\text{C}$ , for a source temperature of  $350\text{ }^\circ\text{C}$  and for a deposition time of 2 minutes. The layer is approximately  $3\mu\text{m}$  thick and it consists of densely packed columnar grains that extend throughout the film thickness.



**Figure 3** SEM micrograph of a SnS layer deposited using a 300°C substrate temperature, a 350°C source temperature and a deposition time of 2 minutes.

This observation was made for films deposited with thicknesses as small as 0.8 µm and for films > 10 µm thick.

The transmittance versus wavelength behaviour of the films was surprising in that the optical absorption edge shifted with a change in the conditions used for depositing the SnS films. Data for two samples deposited using a source temperature of 300°C and substrate temperatures of 300°C and 350°C and 3µm thick are shown in fig.4.



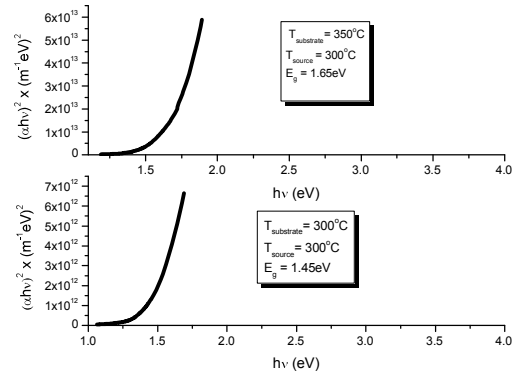
**Figure 4** Transmittance versus wavelength plot of SnS layers grown at 300°C and 350°C substrate temperatures with the source temperature fixed at 300°C.

If the samples have a direct energy bandgap then the following formula should fit the behaviour:

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

where A is an energy independent constant. This means that a plot of  $(\alpha h\nu)^2$  versus  $h\nu$  should be a straight line and the intercept on the  $h\nu$  axis give a value for the energy

bandgap  $E_g$ . Such plots are shown in fig.5 for the samples used in fig.4.



**Figure 5**  $(\alpha h\nu)^2$  versus  $h\nu$  plots of SnS layers deposited using 300°C and 350°C substrate temperatures with the source temperature fixed at 300°C

The straight lines imply that the SnS samples have direct energy bandgaps of 1.45eV and 1.65eV respectively. If the source and substrate temperature were kept constant, then the energy bandgap depended on film thickness, it being > 1.9eV for film thicknesses less than 0.6µm. As the film thickness increased, the energy bandgap reduced in value to < 1.5eV for film thicknesses > 3µm. For films that were approximately 3µm thick and a source temperature of 300°C the energy bandgap was typically in the range 1.4 to 1.6 eV for substrate temperatures in the range 280 to 350°C i.e near the optimum needed for photovoltaic solar energy conversion (1.5eV). The shift in optical absorption edge and hence energy bandgap has been observed by other workers producing thin films of SnS using other methods [8]. The most detailed study has been made with layers produced using chemical spray pyrolysis [9]. 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>, Sn<sub>2</sub>S<sub>3</sub>, and SnO<sub>2</sub> [8]. It is however possible that there are other reasons for the change in energy bandgap; these include alloying of the SnS with oxygen or a change in the orientation of the grains associated with the orthorhombic structure of SnS. The x-ray diffraction data did show significant changes in film structure with film thickness and this was correlated to the change in energy bandgap. However there was still a change in energy bandgap if the film thickness was kept constant and the source or substrate temperature varied. The x-ray diffractograms for these films did not vary significantly and it is possible that the energy

bandgap shift was at least partially due to one of the other mechanisms.

#### 4. Conclusions

Using the thermal evaporation method it is possible to produce 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 near to the optimum for photovoltaic energy conversion. Work is in progress to more fully understand why the chemical and physical properties of the layers vary with the deposition conditions. Work is also in progress to incorporate the 1.5 eV bandgap layers into a range of different photovoltaic device structures and to characterise these devices.

The potential for SnS as a tin based PV technology is excellent in terms of the availability of tin and techniques that can be used for large scale deposition of thin films. To exploit this potential, it is essential to investigate and establish control over the processing and materials properties in order to produce devices that improve on the current best performances of about 1%. This work has shown that SnS based absorbers can be produced with properties that make them suitable as absorber layers in thin film PV devices. It has also shown that there is considerable scope to further improve and optimise materials properties to this end.

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