Investigating the Potential of SnS for Use in Photovoltaic Solar Cell Applications

Patrick A. Nwofe*, Ramakrishna K. T. Reddy*˙, John K. Tan*, Ian Forbes*,
Mark Leach□, D .Y. Jang□ and Robert W. Miles**

*Northumbria Photovoltaic Applications Centre, Northumbria University,
Newcastle upon Tyne, NE1 8ST, UK

˙Department of Physics, Sri-Venkateswara University, Tirupati-517 502, India,

□Seoul National University of Science & Technology, Seoul 139-743, Korea

**Corresponding author: robert.miles@northumbria.ac.uk

Abstract

Thin films of tin sulphide SnS were deposited by thermally evaporating the compound directly onto soda lime glass substrates, keeping the substrate and source temperatures constant at 350°C and 300°C respectively. The layers were then subjected to post deposition heat treatments in different environments, including air, H_2S in argon (5%) and elemental sulphur. The effects of film post-deposition annealing on the chemical and physical properties of the thin films were investigated for different thicknesses of the films.

Introduction

Tin sulphide SnS is a IV-VI compound with a threshold for optical absorption of 1.35eV, near the optimum for photovoltaic solar energy conversion. The 1.35eV direct energy bandgap results in a high optical absorption coefficient, $\alpha > 10^4 cm^{-1}$ for photons with energies greater than the energy bandgap indicating that only a few microns of material are needed to absorb the incident light. As this material consists of abundant, non-toxic elements and it can be doped both p and n conductivity types, it is becoming of interest for making low cost thin film solar cells.

SnS-based solar cells have been made using a range of methods including spray pyrolysis, chemical vapour deposition, thermal evaporation and by a range of chemical bath methods [1-4]. Despite the good potential of this material the highest efficiency device made using SnS to date is 1.3% [1].

This aim of this work is to investigate whether or not it is possible to improve the chemical and physical properties of thermally evaporated SnS by post-deposition annealing in a range of environments.

Experimental

The soda lime glass slides used as substrates were ultrasonically cleaned using decon-90, further cleaned with propan-2-ol, and were then dried using nitrogen gas. The SnS powder (99.999% pure) was thermally evaporated from a silica crucible onto the heated substrates, in a vacuum system operating in the 10^{-5}-10^{-6} Torr range of vacuum pressures; details of this method have been reported previously[5]. The post deposition annealing was performed in three different environments: air, 5% hydrogen sulphide in argon and in an elemental sulphur environment. The annealing was performed using a Carbolite annealing system, which was fitted with a Eurotherm 2132 temperature controller.

A FEI Quanta 200 ESEM (Environmental Scanning Electron Microscope) was used to observe the surface topology and topography of the layers and an Oxford Instrument energy dispersive X-ray analyser (EDAX) was used to determine the composition of the films. X-ray diffraction data was taken using a Siemens D5000 X-ray diffractometer (XRD) with a CuK_α radiation source ($\lambda=1.5406$Å). The transmittance (T) and reflectance (R) versus wavelength measurements were taken using a Shimadzu Solid Spec 3700UV-VIS-NIR spectrophotometer. The resistivity of each layer was measured using the 4-probe method and the van der Paw method.

Results and Discussions

The films deposited were dark blue in colour. SEM observations indicated that the layers were free from pinholes and

confirmed that the layers were conformal to the substrate.

A SEM micrograph of the surface topology is shown in figure 1(a) for a layer 0.2 μm thick grown using a deposition time of 60 seconds. The micrograph shows that the layers consisted of randomly orientated elongated grains, each of which was several microns long and less than 0.5 μm wide. Post-deposition of the layers in all the different environments caused a substantial increase in grain size to produce grains >3μm long and > 1μm in diameter as shown in figure 1 (b). The grain size could also be increased by increasing the film thickness and by increasing the substrate temperature; these effects have been reported previously [5-6].
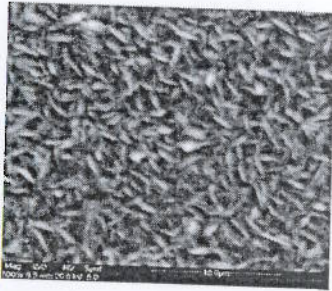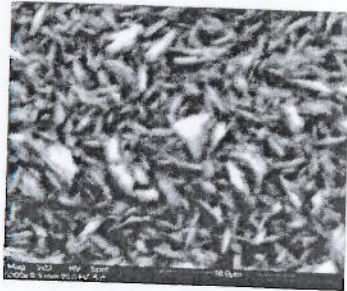

Figure1. SEM micrographs using same magnifications of 5000. (a) as deposited layer

(b) the layer annealed at 300°C for 30mins

The composition of the films from EDAX studies showed the presence of carbon and oxygen in the thinner layers deposited (film thicknesses < 0.5μm). It is possible that the oxygen was incorporated during film growth, while the carbon might be from the diffusion pump oil used in the deposition system. However, for film thicknesses >1μm the oxygen and carbon were not observed to be present. Figure 2(a) is the EDAX spectrum for as-deposited layer (2μm thick), figure 2(b) is

the spectrum for the layer annealed in air and figure 2(c) for the layer annealed in either 5% H_2S/argon or elemental sulphur. The air annealing results in Sn-rich samples whereas for the sulphur annealing, stoichiometry is preserved.
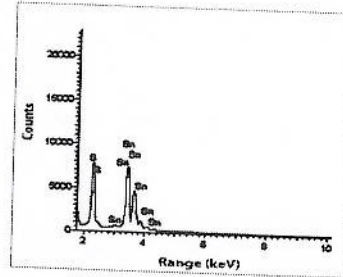

Figure 2.(a) EDAX spectrum of a SnS as-deposited layer.
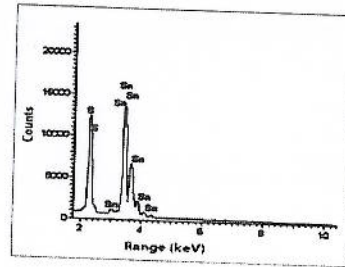

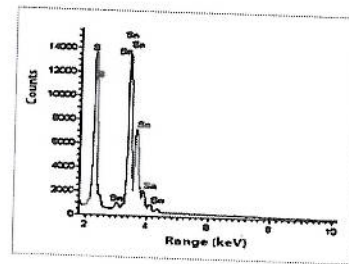Figure 2.(b) EDAX spectrum of a SnS layer annealed in air at 400°C for 30minutes.

Figure 2.(c) EDAX spectrum of a SnS layer after S annealed at 400°C for 30 minutes.

The XRD diffraction data consisted of highly orientated Bragg peaks indicating that the grown films were of high crystallinity. The most prominent peaks corresponded to those expected for single phase SnS. The XRD profiles are all consistent with the pdf file No: 00-039-0354 with the most prominent peaks due to diffraction from the {111} planes.
However in the thinner layers (grown using short deposition times), peaks

corresponding to other phases, were observed in the XRD profiles. It was observed that annealing the samples in air or in an environment containing excess sulphur brought about a reduction in the intensity of these reflections. A typical XRD plot for a layer, 0.2μm thick, is given in figure 3(a). XRD data for such layers annealed in different environments are shown in figures 3(b) and 3(c).
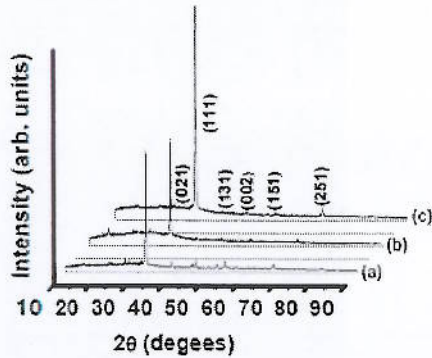

Figure 3.(a) Air annealing at 400°C for 30mins (b) S annealing (c) as deposited

Data taken from the XRD profiles for the SnS films at different film thicknesses were used to deduce the degree of preferred orientation in the as deposited films for the consistent reflections. The resulting behaviour is shown on figure 4. The degree of preferred orientation has been calculated using the relation

$$\sigma = \left[\frac{1}{N} \left(T_{C_{hkl}} - 1 \right)^2 \right]^{\frac{1}{2}} \qquad 1$$

where σ is degree of preferred orientation, $T_{C_{(hkl)}}$ is the texture coefficient and N is the number of reflections used in the analysis. The degree of preferred orientation increased with film thickness as expected.
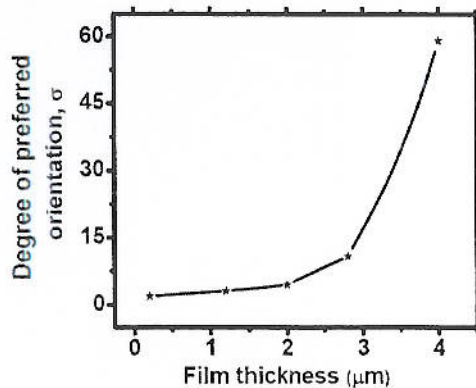

Figure 4. Variation of σ versus film thickness.

The optical transmittance and reflectance were studied in the range (400-1800nm). A typical reflectance versus wavelength spectra for a SnS film (2.8μm thick) is given in figure 5(a) and the effect of post deposition annealing in the different environments given in figures 5(b) and 5(c). It is observed that annealing lowered the reflectance of the sample. However there is no shift in the cut-off wavelength and hence in the corresponding energy bandgap of the sample. For this sample the energy bandgap is 1.35eV, a value close to that reported in the literature [7].
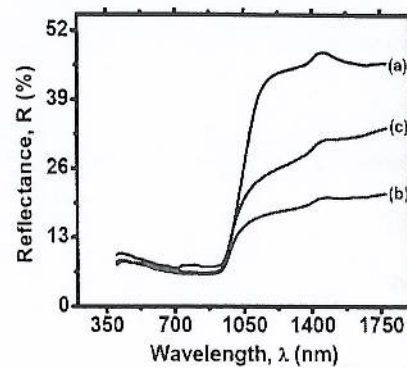

Figure 5. Reflectance versus wavelength

(a) as-deposited layer (b) air annealed at 400°C for 30 minutes (c) S annealed at 400°C for 30 minutes.

For thin samples (<0.5μm thick) the behaviour observed is shown in figure 6. The most striking feature to be observed is that the energy bandgap is much wider than for the thicker layers grown. This shift in the energy band gap for thin layers has been observed by other workers and is attributed to the presence of other wider energy bandgap phases being present in the thinner layers e.g. SnS_2, Sn_2S_3 and SnO_2 [8].

The appearance of interference fringes for the 2.8μm thick layer shows that there is a good surface homogeneity in the films and that the grown films are of uniform thickness. The steep fall in the transmittance spectra for this layer indicates that the transition is direct and allowed.
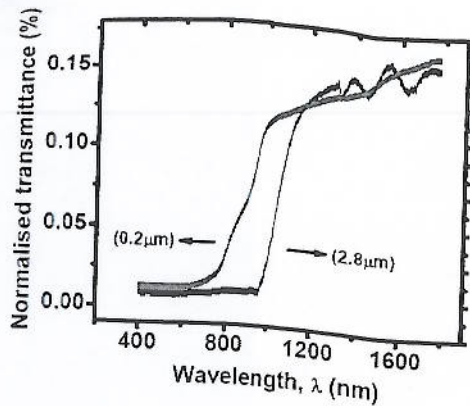
Figure 6. Normalised transmittance versus wavelength.

The electrical properties of the films were studied using the Van der Paw method, hot probe and four point probe technique and it was observed that the film retained it p-conductivity type after the heat treatments. However, the p-type conductivity was stronger in the air annealed case. Similar behaviour has been reported in the literature for SnS samples grown using other methods [9]. The sheet resistance decreased slightly for the thicker films with sulphur annealing as shown on figure 7.
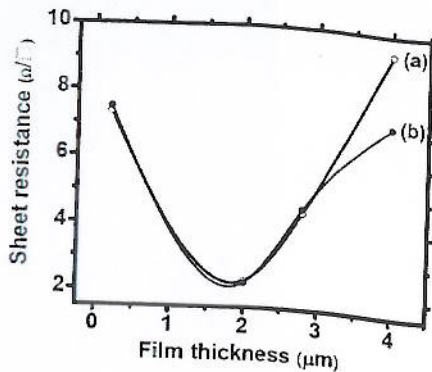

Figure 7.(a) Sheet resistivity versus thickness of an as deposited layer (b) sheet resistivity versus thickness after S annealing.

Conclusion

The layers of SnS grown with thicknesses > 1 μm were stoichiometric, free from secondary phases, had an energy bandgap of 1.35 eV (as expected), and they were p-conductivity type with resistivities of 1-40Ωcm. The thinner layers grown with thicknesses <0.5μm exhibited

exhibited different behaviour. They were found to contain high concentrations of carbon and oxygen, contain secondary phases of binary compounds e.g. SnS_2 and to have a higher energy bandgap than single phase SnS.

In both cases annealing the layers in air increased the grain size although there was some loss of stoichiometry (sulphur loss) due to the annealing. Annealing in a sulphur containing environment produced both grain growth while maintaining stoichiometry for the thicker layers.

The results indicate that device quality layers can be produced using the thermal evaporation method especially when sulphur annealing is used to enhance grain growth.

Acknowledgements

References

[1] K.T.R. Reddy, N.K. Reddy and R.W. Miles, Solar Energy Materials & Solar Cells 90 (2006) 3041-3046.

[2] A. Sánchez-Juárez, A. Tiburcio-Silver and A. Ortiz, Thin Solid Films 480-481 (2005) 452-456.

[3] R.W. Miles, O.E. Ogah, G. Zoppi and I. Forbes, Thin Solid Films 517(2009) 470

[4] D. Avellanda, G. Delgado, M.T.S. Nair and P.K. Nair, Thin Solid Films 515 (2007) 5771-5776.

[5] P.A. Nwofe, K.T. Ramakrishna Reddy, G. Sreedevi, J.K. Tan, I. Forbes and R.W. Miles, Proceedings of the International Conference on Materials for Advanced Technologies (ICMAT) Singapore (2011) p.38.

[6] N.K. Reddy and K.T.R. Reddy, Solid St. Elect. 49 (2005) 902-906.

[7] M. Devika, K.T.R. Reddy, N.K.Reddy. K.Ramesh, R.Ganesan, E.S.R. Gopal and K.R. Gunasekhar, Journal of Applied Physics 100 (2006) 023518.

[8] S. Lopez, S. Granados, A. Ortiz, Semicond. Sci. Technol.,11(1996) 433.

[9] C. Sekhar. M. Ray, K. Karanjai and D. DasGupta, Thin Solid Films 350 (1999) 76.