On the Structural and Optical Properties of SnS Films Grown by Thermal Evaporation Method

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Abstract. Tin sulphide (SnS) has a direct energy band gap of 1.35 eV and it consists of abundant, non-toxic elements. It is therefore of interest for use as an absorber layer material in thin film photovoltaic solar cells. In this work, SnS layers with thicknesses in the range 2-3.6 μm, were thermally evaporated onto glass substrates using substrate temperatures in the range 280°C to 360°C, and the way the structural and optical properties of the layers varied with the deposition conditions investigated. X-ray diffraction spectra showed a strong (040) reflection as the most prominent peak for films formed between 320°C to 360°C. The peak intensity ratio, crystallite size and grain size were observed to increase with increasing substrate temperature whilst the strain decreased. All the layers were highly light absorbing with the optical absorption coefficient, α >10⁴ cm⁻¹. The optical energy band gap was found to be in the range, 1.30-1.34eV, it not changing substantially with substrate temperature. Other optical parameters such as the refractive index and optical conductivity were also evaluated for the layers grown at different substrate temperatures.

1. Introduction

Recently, the need to harness the potentials of SnS for use in various applications especially in solar photovoltaic cells has witnessed a dramatic increase due to the favourable inherent properties of this material. Though thin film solar cells based on the use of polycrystalline inorganic thin film compounds dominates the market share at present, with efficiencies >20% for cells from copper indium gallium diselenide (CIGS), efficiencies > 16.7% using cadmium telluride (CdTe), and modules with efficiencies >10% using both technologies [1], the lack of abundance of the core elements (In and Ga) in the CIGS is expected to limit the large scale production of modules using this technology and to keep material costs high. Also there remain concerns with respect to the use of cadmium, a highly toxic element in some countries. In the countries where the technology is acceptable then it is expected there will be the need for the controlled disposal of CdTe modules after use. These concerns have led to the investigation of other inorganic materials that do not have these problems, one such material being tin sulphide (SnS).

Tin sulphide is a semiconductor with a direct energy bandgap of 1.35 eV and it consists of abundant non toxic elements. The near optimum energy bandgap makes it of interest for application as an absorber layer in thin film solar cells. SnS is also amphoteric and this means that the grain boundaries could be in principle, be passivated by counterdoping p-SnS using an n-type dopant.
Although there have been some studies of the properties of SnS, work on this material to date is limited [2-3].

In this work, structural and optical properties of SnS films grown by evaporation method with a range of substrate temperatures have been investigated with respect to the suitability of the grown films as suitable absorber layers for use in photovoltaic solar cell applications.

2. Experimental

SnS layers with thicknesses in the range (2-3.6μm) were deposited using the thermal evaporation method, performed in an oil pumped vacuum system, operating in the 10⁻⁵ to 10⁻⁶ Torr range of vacuum pressures. The substrate and source material were heated via resistive elements and the deposition time controlled using a shutter that was incorporated in the thermal evaporation plant. The source material used for absorber was 99.99% purity SnS obtained from Testbourne Ltd. A quartz bottle-shaped crucible served as the evaporation source and was heated by a cylindrical tantalum heating element supplied by the R.D Mathis Company. Spattering (i.e. the ejection of molten lumps of material) was eliminated by placing quartz wool in the crucible and by using a source-substrate distance of 40mm. The substrate temperature was varied between 280°C to 360°C while the deposition time was between 1-5 minutes. The temperatures were measured by thermocouples in direct contact with the crucible and the substrate respectively.

The as-deposited films were characterized using appropriate techniques. A Siemens D5000 X-ray diffractometer (XRD) with a CuKα radiation source (λ = 0.15406 nm) was used to determine the structural properties of the films. The surface topography of the layers was observed using an FEI Quanta 200 ESEM (Environmental Scanning Electron Microscope) while the surface morphology and elemental composition of the films were determined using an Oxford Instrument EDAX system. The optical transmittance (T) versus wavelength measurements was recorded using a Shimadzu SolidSpec 3700 spectrophotometer.

3. Results and Discussion

The visual observation indicated that the layers are pinhole free and appear bluish black in colour. Fig.1 shows the Sn/S ratio for SnS films grown at different substrate temperatures, determined using EDAX. It can be seen from the figure that Sn/S ratio for the films initially raised sharply up to the deposition temperatures of 300 °C, became relatively stable with stoichiometric composition in the temperature range, 300 -340 °C and then increased gradually afterwards. Similar behaviour has been observed by other authors [4]. The observed non-stoichiometry at growth temperatures < 300°C and > 340°C was due to the effect of differential vapour pressures of tin and sulphur; the higher vapour pressure of sulphur leads to its re-evaporation from the film surface at higher substrate temperatures.

![Graph showing variation of Sn/S ratio with substrate temperature](image-url)
Fig. 2 shows the XRD profiles of the SnS films grown at different temperatures. The X-ray diffraction studies showed that all the films were polycrystalline, containing only SnS phase. All the peaks observed from the XRD spectra corresponds to the orthorhombic structure of the SnS and the evaluated lattice parameters were $a = 0.433\text{nm}$, $b = 1.119\text{nm}$, $c = 0.398\text{nm}$. The layers formed at lower temperatures (280 - 300°C) had the (111)/(040) orientation appearing almost simultaneously along with the (110), (120), (021), (101) and (131) peaks. However the intensity of the latter peaks reduced drastically with the increase of substrate temperature. Between the temperatures 320°C and 360°C, the intensity of these smaller reflections along the (111) peak was largely suppressed so that the (040) plane became the most prominent peak.

\[ D = \frac{k\lambda}{\beta \cos \theta} \]  

(1)

where $k$ is a constant (0.94), $\beta$ is the (full width half maximum) FWHM value, $\lambda$ is the wavelength of CuK\(_\alpha\) radiation source ($\lambda = 0.15406\text{nm}$) and $\theta$ is the Bragg angle. The strain ($\varepsilon$) developed in the film was estimated using the following relation [9] in order to evaluate the quality of the grown films and is shown in Fig. 3.

\[ \varepsilon = \frac{\Delta \theta}{2(\tan \theta)} \]  

(2)

where $\theta$ is the diffraction angle and $\Delta \theta$ is the fringe width at half maximum (FWHM). The results showed a decrease of strain in the films with substrate temperature. This is due to the increase of crystallite size with temperature that led to a reduction in the inter-crystalline barriers or grain boundary area in the layers. This is also shown in Fig. 3.
Fig. 3. Dependence of stress and crystallite size on substrate temperature.

The XRD data was also used to calculate the peak intensity ratio of the SnS films along the SnS (111) and SnS (040) plane with respect to the SnS (131) plane on the same scale to estimate the crystallinity. Fig. 4 shows the variation of the peak intensity ratio and grain sizes (evaluated from SEM) with substrate temperature. As expected, the peak intensity ratio increased with increase of substrate temperature, which is an indication of an improvement in the crystallinity of the films. This is because at higher growth temperatures, the surface mobility increases, allowing the films to decrease its total energy by growing larger grains thereby decreasing its grain boundary area [5]. The grain appeared to increase slowly up to a growth temperature of 340 °C and then steeply afterwards. A similar behaviour has been observed in literature in SnS films deposited by spray pyrolysis [7].

Fig. 4. Peak intensity ratio and grain size vs substrate temperature.

The SEM studies indicated that the layers contain very large grains that were densely packed. Fig. 5 shows the surface topography of SnS layers deposited at two different substrate temperatures. An evaluated grain size of 10µm was obtained for the highest substrate temperature investigated in the study. Some authors [8] attributed the increase of grain size with substrate temperature to the formation of clusters in the crystallites in SnS layers. However, the observed variation of grain size in this study has been attributed to the change in the peak intensity ratio from (111)/(040) to (040) plane as observed in the XRD spectra.
Fig. 5. SEM micrographs of SnS films formed at (a) 300°C and (b) 360°C.

The optical transmittance with wavelength of SnS films was measured in wavelength range of 400-1800 nm. Fig. 6 shows such a plot for SnS films. Although a low optical transmittance was observed due to the film thicknesses, however, a clear interference fringes can be observed from the spectra, indicating uniformity of film thickness and optical homogeneity in the grown films. This implies that either scattering or absorption did not occur at the long wavelength region. The spectra also indicated a steep fall in the transmittance spectra near the fundamental absorption edge indicating the absence of other phases in these films as evidenced in the literature [10].

Fig. 6. Optical transmittance versus wavelength spectra of SnS films.

From the transmittance versus wavelength data, the optical absorption coefficient ($\alpha$) was evaluated for all the films and found to be $>10^4$ cm$^{-1}$ above the fundamental absorption edge. The optical bandgap was determined using the $(\alpha h \nu)^2$ versus ($h \nu$) plots by extrapolating the plots on the $h \nu$ axis and found to vary in the range, 1.30-1.34 eV for layers grown at different substrate temperatures. The refractive index was calculated in the region where the effect of free carrier absorption is most pronounced in the $(\alpha h \nu)$ versus ($h \nu$) plots, using Manifacier’s theory for weak absorption region [11]. Fig. 7 shows the change of refractive index with substrate temperature. It can be seen from the figure that the refractive index increases with temperature up to 340°C and then decreased. The optical conductivity was calculated using the relation [12]

$$\sigma = \frac{\alpha n c}{4 \pi}$$

(3)
where $\alpha$ and $n$ retain their meanings and $c$ is the speed of light. The optical conductivity depends directly on the absorption coefficient and the refractive index of the material. However, it was observed to decrease marginally with substrate temperature up to 340°C and then increased. This might be due to the difference in orientation in the layers grown at lower substrate temperatures.

![Graph showing variation of n and $\sigma$ with substrate temperature](image)

Fig.7. Variation of $n$ and $\sigma$ with substrate temperature

4. Conclusion

The structural and optical properties of SnS thin films have been investigated with respect to the suitability of the grown films as good absorber layers for solar cell applications. The elemental composition of the films exhibited a non-stoichiometric behaviour. However, high quality films of good crystallinity and very large grains of up to 10μm were recorded. Large values of absorption coefficient $>10^4$ cm$^{-1}$ were obtained in all the films. The appearance of interference fringes in the optical transmittance spectra indicates thickness uniformity, optical homogeneity and good surface states of the grown films, implying that the films could potentially be useful in various optoelectronic and photovoltaic solar cell applications.

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