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Thickness Dependent Optical Properties of Thermally Evaporated SnS Thin Films

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Abstract

Thin films of tin sulphide (SnS) were prepared on glass substrates using the thermal evaporation method and the optical dispersion parameters investigated. The results obtained on the dispersion parameters and other optical constants indicated a strong thickness dependency. The results indicated that the refractive index data obeyed the single oscillator model. The dispersion energy (E_d), optical spectra moments (M^{-1}) and (M^{-3}) and the dielectric constant (\varepsilon) were all found to decrease with increase of film thicknesses. However, the oscillator energy (E_o) and angular frequency (\omega_p) are independent of film thickness. These results are useful tool for further understanding the electronic structure for this novel material.

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1. Introduction

Currently, the market share of thin film solar cell based on the use of advanced inorganic materials are still largely dominated by Copper indium gallium diselenide (CIGS) and Cadmium telluride (CdTe) solar cells. However, some of the constituent elements for these materials are either rarely abundant in nature or highly toxic to handle so that large scale production of the modules in the near future is difficult. This has rekindled interest in alternate materials for absorber layer applications in thin film solar cells. SnS is one such novel material that can be used for solar cell development. This is because Sn and S are highly abundant in nature and also non-toxic. It has a direct energy bandgap of 1.35 eV, near optimum for photovoltaic solar energy conversion. Also, it has a high optical absorption coefficient for photons with...
energies greater than the energy bandgap such that only a few microns of SnS are needed to absorb most of the incident light [1]. Layers of SnS are usually p-conductivity type with the electrical conductivity controlled using extrinsic dopants such as Al, Ag, Cl and Cu [2]. Since SnS can also be doped n-type it is also likely that counter-doping or oxidizing SnS at the grain boundaries will lead to effective grain boundary passivation. To date SnS layers have been made using a range of methods including thermal evaporation, spray pyrolysis, chemical bath deposition and electrodeposition [1-3,7-10]. Solar cells have also been made using SnS layers with CdS as the n-type layer and efficiencies up to 2% have been recorded in the best devices [3]. In this work, we investigated the effect of film thickness on the optical properties of thermally evaporated SnS films.

2. Experimental details

SnS films were deposited by thermal evaporation in a vacuum > 10^{-5} Torr on glass substrates. High purity SnS, obtained from Testbourne Company was used for evaporation. A quartz bottle-shaped crucible served as the evaporation source that was heated by a cylindrical tantalum heating element obtained from R.D. Mathias Company. The SnS granules were ground into a fine powder and then filled into the crucible. Spattering (the ejection of molten lumps of evaporant) of the material was avoided by placing quartz wool at the mouth of the crucible. Soda lime glass slides were used as the substrates. Prior to depositions, the glass slides were cleaned in an ultrasonic bath containing a mixture of Decon 90 and de-ionised water solution for 45 minutes. After a thorough rinse with de-ionised water, the substrates were washed in propan-2-ol (IPA) to remove any remaining contamination and were then dried. The temperatures were measured by thermocouples in direct contact with the crucible and the substrate respectively. The deposition time was controlled by a shutter placed between the evaporation source and the substrate. The films were deposited at a temperature of 300 °C. The thickness of the films, measured using ... surface profilometer was in the range, 2.4 – 4.3 \mu m. The optical reflectance and transmittance measurements were carried out using Shimadzu SolidSpec 3700 spectrophotometer in the wavelength rage (400 – 2600 nm).

3. Results and Discussions

The visual appearance of the as-deposited SnS layers indicated that the layers are dark bluish in colour, pinhole free and homogeneous.

The optical transmittance versus wavelength spectra of the films showed a very low transmittance due to higher thickness of the films and hence the reflectance versus wavelength spectra were used in this study. The appearance of the interference fringes in the reflectance versus wavelength spectra is an indication of good surface homogeneity and uniformity of the grown films. Figure 1 shows such spectra for SnS films of three different thicknesses grown in this study. A sharp fall in reflectance is seen from the figure near the fundamental absorption edge, which indicates a direct optical transition in this material. Also, all the spectra showed the fall in reflectance at the same wavelength, which indicates that the energy band gap is nearly independent of film thickness.

The absorption coefficient (\( \alpha \)), calculated from the reflectance versus wavelength spectra showed that all the films had an absorption coefficient > 10^4 cm^{-1}. Figure 2 shows the variation of absorption coefficient with wavelength for SnS films of two different thicknesses. It can be observed that the absorption coefficient decreased sharply near the fundamental absorption and then slowly at longer wavelengths for all the films as reported in literature [5]. The optical energy bandgap of direct band gap materials is evaluated using the relation [4],

\[
\alpha h \nu = B(h \nu - E_g)^2
\]  

(1)
where B is an energy independent constant, $E_g$ is the energy bandgap and $n = 1/2$ for direct allowed transition. The energy bandgap was calculated using the $(a \cdot h \nu)^2$ vs $h \nu$ plot by extrapolating it onto the $h \nu$ axis. In this study, the $E_g$ value is nearly constant with values in the range, 1.30-1.32eV. Figure 3 shows such a plot for SnS film of 3.37 $\mu$m thickness.

![Figure 1. Reflectance versus wavelength spectra.](image1)

![Figure 2. Absorption coefficient, $a$ versus wavelength spectra](image2)

![Figure 3. Plot of $(a \cdot h \nu)^2$ versus $h \nu$.](image3)

The refractive index ($n$) was calculated using the Swanepoel’s method [6] and the results showed a decrease of $n$ with the increase of wavelength ($\lambda$) as reported in literature [6,7]. Figure 4 shows the change of $n$ with $\lambda$ in SnS films grown in this study. Also it can be seen from the figure that the refractive index was higher for lower film thickness. Such a behaviour has been observed in other chalcogenides also [8]. The results equally showed that the refractive index increased with increasing photon energies, appearing more rapid toward the fundamental edge. This may be attributed to the effect of direct interband transitions towards the higher energies (shorter wavelengths) close to the fundamental
absorption [7,9]. Also the refractive index maximum (n_{max}) at different film thicknesses that indicated a decreasing trend with film thickness. Similar trend has been observed for other optical properties by other workers [10-11]. This is shown in figure 5. Thickness dependent relation on some optical constants has been reported by [10]. It was also observed that the extinction coefficient decreased at the onset probably due to the effect of free carrier absorption, and gradually increased towards higher wavelength. Similar findings have been reported by several authors [11]. The extinction coefficients were also higher for lower film thicknesses. This is shown on figure 6. From the values obtained for the refractive index and extinction coefficient, the real \( \epsilon_1 \) and imaginary part \( \epsilon_2 \) of the dielectric constants were calculated using the relation [8-10],

\[
\epsilon_1 = n^2 - k^2 \tag{2}
\]

\[
\epsilon_2 = 2nk \tag{3}
\]

It was observed that \( \epsilon_1 \) and \( \epsilon_2 \) both increased with photon energy as shown in fig.7. This has been observed in other chalcogenides thin films [12-14]. The dielectric constant \( \epsilon \) of the films was calculated using the relation [7] where \( \epsilon_1 \) and \( \epsilon_2 \) retains their usual meanings.

\[
\epsilon = \epsilon_1 + \epsilon_2 = \left( \epsilon_1^2 + \epsilon_2^2 \right)^{1/2} \tag{4}
\]

The present study indicated that \( \epsilon \) decreased with film thickness. It also decreased with wavelength, tending to converge at higher wavelength and the values of \( \epsilon \) are higher at lower film thickness. This is shown on figures 8(a) and 8(b).

Figure 4. Refractive index vs. wavelength spectra.  
Figure 5. \( n_{max} \) versus film thickness.
The dissipation factor (tan $\delta$) was also evaluated using the relation [13,14] and was found to decrease with increasing photon energies. The behaviour is shown in figure 9.

$$\tan \delta = \frac{\varepsilon_2}{\varepsilon_1}$$  \hspace{1cm} (5)

The dissipation factor gives a measure of the loss-rate of power of a mechanical mode such as an oscillation in a dissipative system. The dissipation factor equally decreased with increasing film thickness. This has been observed in some chalcogenides by other workers [14].
The spectral dependence of the dispersive refractive index data for the region $hv < E_g$ where $E_g$ is the bandgap can be evaluated using the Wemple and DiDomenico single-effective oscillator model [12] hence the refractive index $n$ is related to the photon energy $hv$ as

$$n^2 = 1 + \frac{E_o E_d}{E_0^2 - (hv)^2}$$

(6)

where $E_o$ is the average excitation energy otherwise known as the oscillator energy, $c$ is the dispersion energy which is a measure of the average strength of inter-band optical transition or the oscillator strength. From the above relation, the oscillator parameters $E_o$ and $E_d$ as well as the moments of optical dispersion spectra $M_1$ and $M_3$ were evaluated at different thickness where

$$E_0^2 = \frac{M_{-1}}{M_{-3}}$$

(7)

$$E_d^2 = \frac{M_3}{M_{-3}}$$

(8)

The result obtained showed that the dispersion energy and the moments of optical dispersion spectra all decreased with film thickness while the oscillator energy exhibited thickness independent behaviour. These are shown as figure 10 (a – c).
4. Conclusions

Thin films of SnS have been grown by the thermal evaporation method and the optical properties investigated with respect to the film thickness. The refractive index evaluated using Swanepoel method at the transparent region indicated a decrease with wavelength and an increase for lower film thickness. The dispersive refractive index data was found to fit the Wemple and DiDomenico single-effective oscillator model. The evaluated optical dispersion parameters and moment of optical dispersion spectra were found to decrease with thickness except for the oscillator energy. The high absorption coefficient obtained, is an indication that SnS thin films could make good absorber layers in photovoltaic solar cell applications.

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