Effect of Thickness on Optical Properties of Thermally Evaporated SnS Films

M. S. Selim, M. E. Gouda, M. G. El-Shaarawy, A. M. Salem and W. A. Abd El-Ghany

Electron Microscope and Thin films Dept. Physic Division, National Research Center, Cairo, Egypt.

Physics Dept. Faculty of science, Benha University, Banha, Egypt.

ABSTRACT

The effect of film thickness on the structure and optical properties of thermally evaporated SnS film has been studied. SnS films with different thicknesses in the range 155-585 nm were deposited onto clean glass substrates at room temperature. X-ray diffraction study revealed that SnS films of thickness ≥ 283 nm are crystalline, whereas films of lower thickness exhibit poor crystalline with more amorphous background. The crystalline nature of the lower film thickness has been confirmed using transmission electron microscope and the corresponding electron diffraction pattern. The thicker films samples showed nearly stoichiometric chemical composition, however, lower sample showed deficient in S and rich in Sn. The optical property of the deposited films has been investigated in the wavelength range 450-2500 nm. The refractive index increases notably with increasing the film thickness. The refractive index for the investigated film thicknesses are adequately described by the effective-single-oscillator model. The static refractive index and the static dielectric constant have been calculated. Analysis of the optical absorption coefficient revealed the presence of direct optical transition and the corresponding band gap values was found to be decreases as the film thickness increases.

Key words: SnS film, thin film, optical properties

Introduction

Recent investigations on new photovoltaic materials have been considerable interest in SnS thin films (Biswajit et al., 2011; Ristov et al., 2001; Ghosh et al., 2008) and other optoelectronic devices like holographic recording system Rador (1977), solar control device Nair et al., (1991) and near-infrared detector Nikolic et al., (1987).

SnS belongs to the IV–VI compounds whose constituent elements are abundant in nature. It crystallizes in an orthorhombic structure as a deformed sodium chloride structure and is a layered material that presents interesting semiconducting properties Qing Li et al., (2002). It has different optical band gap values ranging from 1 to 2.33 eV (El-Nahass et al., 2002; Koteswara et al., 1998; Ghazali et al., 1998) depending on the resulting structure obtained by different techniques and the occurring type of electron transitions.

For photovoltaic applications p-type SnS being the absorber material requires an n-type wide band gap transparent semiconductor as the heterojunction partner Ghosh et al., (2008). Essentially among all known transparent semiconductor, non-stoichiometric or doped oxides and sulfides such as SnO2, ZnO, CdS and ZnS may be the best choice for n-type material as the heterojunction partner for p-type SnS. The performance of such of these heterojunction partners is strongly limited by the thickness and various characteristics properties of deposited SnS films. The change of material properties particularly with film thickness could be due to the variation of the crystal size. The influence of the crystal size on the physical properties has aroused much interest in semiconductor devices. The structure of the deposited films change with the change of the film thickness, which will in turn affect the optical transmittance and electronic properties (Lai et al., 2005; Bruggeman et al., 2003; Qiao et al., 2004).
A study of properties in relation to the film thickness has a greater importance in order to obtain films that are capable to assure stable and efficient device.

In the present work, we study the effect of film thickness on the structure and optical properties of thermally evaporated SnS films deposited onto glass substrates.

2. Experimental Technique:

SnS thin films of different thicknesses were deposited from the pre-synthesized ingot material via thermal evaporation technique onto clean glass substrates held at room temperature. The deposition process was carried out using a high vacuum coating unit (Type Edwards, E306A) in a vacuum pressure of $\sim 2 \times 10^{-4}$ Pa. The film thickness as well as the deposition rate was controlled during deposition process by means of quartz thickness monitor (Type Edwards, FTM4).

The structural characteristic of the deposited films was examined using an X-ray diffraction (Philips X’pert) with CuKα radiation. The microstructure of the films was investigated using transmission electron microscope (TEM) (Type JEOL JEM-1230) operating at 120 kV. The chemical composition of the deposited films was examined using energy dispersive X-ray spectrometry (EDX) which is attached to JEOL JEM-850 scanning electron microscope (SEM).

A double beam spectrophotometer, with automatic computer data acquisition (Type Jasco, V-570, Rerll-00, UV–VIS–NIR) was employed at normal light incidence to record the optical transmission and reflection spectra of the deposited films over the wavelength range 450-2500 nm. The measurements were made at room temperature on various parts of the deposited films, scanning the entire sample, and a very good reproducibility of the spectra was generally achieved.

Results and discussions

Structural Characterization of the Deposited Films:

X-ray Diffraction Analysis:

The XRD patterns of as-deposited SnS films (of different film thicknesses) deposited onto glass substrates at room temperature are shown in Fig.1. The XRD pattern revealed that the as-deposited SnS films of thicknesses 283 and 470 nm shows a prominent peak appear at $2\theta = 31.66^\circ$ corresponding to the (111) plane matched well with the orthorhombic structure as compared to the JCPDS card No. 39-0354. With increase of thickness to 585 nm, the film showed another reflection peak observed at $2\theta = 30.62^\circ$ corresponding to (101) plane. The intensity of the (111) diffraction peak becomes more intense and sharp with increase of the film thickness, which indicates an improvement in the crystallinity of the deposited films. In general, an increase of film thickness increases the probability of crystallization Troffimov et al., (2006). Further, as-deposited SnS films of thickness 155 and 225 nm did not indicates clearly whether the films are amorphous or crystalline due to absent of any observable peaks in such patterns. This was due to poor crystallinity of the films with more amorphous background so that the generated XRD signals can’t be observed for lower film thickness. Further analysis will be performed below using the transmission electron microscope and electron diffraction to identify clearly whether SnS films of lower film thicknesses are amorphous or crystalline.

Fig.2 shows the transmission electron microscope and the corresponding electron diffraction pattern of as-deposited SnS film of thickness 100 nm. The transmission electron micrograph revealed that the as-deposited SnS films showed needle-like crystallites which are tightly bonded together formed a continuous dense network. The corresponding electron diffraction pattern showed continues faint rings indicate the crystalline nature of the as-deposited SnS films. Therefore, the absent of any observable peaks in the X-ray diffraction pattern for SnS films of thickness lower than 283 nm was attributed to crystal size effect.

Chemical Analysis of the Deposited SnS Films:

Fig. 3a, b show the EDX spectra of two representative SnS films samples corresponding to higher (585 nm) and lower (100 nm) film thicknesses. The EDX spectra for SnS film of thickness 585 nm deposited onto glass substrate (Fig3.a) shows only sharp peaks related to Sn and S in addition to strong Si peak observed at 1.74 eV coming from the glass substrate. However, the EDX spectrum (Fig3.b)for the sample, was investigated using EDX unit interface with transmission electron microscope, showed peaks corresponding to the elemental
Sn and S, beside other peaks observed at 0.93, 1.1, 8.05, and 8.98 eV are coming from the copper grid. The variation of Sn to S atomic ratio of SnS films with respect to lower and higher film thickness are listed in Table 1. It is clearly seen from the data reported in Table 1 that the compositional ratio of the as-deposited SnS film of thickness 585 nm was nearly stoichiometric. However, SnS film of lower film thickness (100 nm) was found poor in S and rich in Sn, which indicates non-stoichiometric composition.

This finding may be attributed to the long Sn–S bond in the crystal structure, which responsible for the release of sulfur for as-deposited thinner SnS films Biswajit et al., (2011).

Optical Properties of SnS Films:

Fig. 4 show the transmittance, $T$ and reflectance, $R$ spectra obtained for SnS with different film thicknesses. It is seen that the transmittance spectra for SnS films of thickness 470 and 585 nm exhibited sharp fall (sharp absorption edge) around 580 nm, indicates a good homogeneity in the grain shape and size, and low defect concentration in the films. However, for SnS films of thickness 155, 225, 283 nm, respectively, the absorption edge shifts towards lower wavelengths side. Above the absorption edge (beyond ~ 950 nm) with the increase in film thickness the transmission decreases almost uniformly with wavelength. It was also seen that in the near-infrared spectral region while the transmission increases, the reflection decreases, indicating that almost no scattering or absorption occur i.e. $T + R = 1$.

The optical properties of the deposited SnS films may be represented by the refractive index, $n$, and extinction coefficient, $k$, which are the real and imaginary parts of the complex refractive index $N = n - ik$, respectively. In the case of normal light incident the values of $n$ and $k$ were computed using a film thickness, $t$, and both recorded values of transmission and reflection spectra in the investigated wavelength optical range using a simple computer program based on the relations Pankove, (1975):

$$T = \frac{[(1-R^2)\exp(-\alpha t)]}{[1-R^2\exp(-2 \alpha t)]} \quad (1)$$

and

$$R = \frac{(n^2-1)^2 + k^2}{(n^2+1) + k^2} \quad (2)$$

where, $\alpha$ is absorption coefficient, $k = \frac{\omega}{\alpha 4\pi}$. Fig.5 shows the spectral variation of the refractive index as a function of wavelength for SnS films for different thicknesses. The figure depicts that the refractive index $n$ attains a peak in the absorption region (below 950 nm), which shifts towards higher wavelengths as the film thickness increases. Beyond the observed peaks the refractive index for different film thicknesses decreases with increasing wavelength and becomes fairly flat above 1300 nm, showing normal dispersion behavior. In addition, the magnitude of refractive index increases notably with increasing the film thickness. The lower value of refractive index for thinner films might be due to the poor packing density of the deposited layer Revathi et al. (2009).

The data of the dispersion refractive index, $n (i)$, may be analyzed using the single-effective-oscillator Wemple and DiDomenico model (1971). The model suggests that the data could be described by

$$n^2(\omega) = 1 + \frac{E_o E_d}{E_o^2 - (\hbar \omega)^2} \quad (3)$$

where $\hbar = h/2\pi$ ($h$ is Planck’s constant), $(\hbar \omega)$ is the photon energy, $E_o$ is the oscillator energy and $E_d$ is the dispersion energy or the oscillator strength.

The oscillator energy, $E_o$, is an “average” energy gap and can be related to the optical band gap $E_g$ in close approximation by $E_o \approx 1.5 E_g$. On the other hand, the dispersion energy, $E_d$, is a measure of the strength of interband optical transitions and can be considered as a parameter having very close relation with the charge distribution within the unit cell and therefore with the chemical bonding. This parameter follows a simple empirical relationship of the form:
\[ E_d = \beta N_c N_v Z_a \]

(4)

where \( \beta \) is a constant whose value depends on the chemical bonding character of a material, \( N_c \) is the coordination number of the cation nearest-neighbor to the anion, \( Z_a \) is the formal chemical valency of the anion, and \( N_v \) is the total number of valence electrons per anion).

Therefore, plotting \((n^2-1)^{-1}\) against photon energy, \((\omega\omega)^2\) and fitting a linear function to smaller energy data (see inset of Fig.5) allows the determination of the oscillator parameters, \( E_o, E_d \). The calculated values of \( E_o, E_d \) static refractive index, \( n_\ell(0) = (1 + E_d / E_o)^{1/2} \) as well as the static dielectric constant, \( \varepsilon_s = n_s^2(0) \) for different SnS film thickness are listed in Table 2. It is clearly seen from the data reported in Table 2 that, the oscillator energy \( E_o \) varies in a reverse manner to the calculated values of \( E_d \) and \( n_\ell(0) \). The observed decrease in the values \( E_o \) with increasing SnS film thickness can be attributed to the observed red shift of the optical transmission spectra in the short wavelengths spectral region (see Fig.4). In the other hand, the observed increases in the values of \( E_d \) with increasing film thickness can be attributed to the variation of the coordination number of the cation nearest-neighbor to the anion which mainly depends on the chemical composition of the deposited films and/or to the increased crystalline nature of the thicker film samples. The calculated values of \( E_d \) and \( E_o \) in the present work are in good agreement with the corresponding values obtained by El-Nahass et al., (2002) for thermally evaporated SnS films. It worth mentioned here that the \( E_o \) value gives quantitative information on the overall band structure of the material. This is in fact quite different from the information coming from the value of the optical gap, \( E_g \) that calculated from the fundamental absorption edge (as will be mentioned below).

![Fig. 1: X-ray diffraction patterns of as-deposited SnS films of different thicknesses.](image1)

![Fig. 2: TEM and the corresponding electron diffraction patterns of as-deposited SnS film of thickness 100 nm.](image2)
Fig. 3a: EDX spectra of as-deposited SnS films of thickness 585 nm.

Fig. 3b: EDX spectra of as-deposited SnS films of thickness 100 nm.

Fig. 4: Transmission and reflection spectra of as-deposited SnS films of different thicknesses.

Fig. 5: Spectral variation of the refractive index $n$ vs. wavelength for SnS films with different thicknesses. Inset show the variation of $(n^2-1)^{-1}$ vs. photon energy squared.
The low wavelength absorption data for the as-deposited SnS films are related to the fundamental absorption which refers to the band-to-band transition, i.e. to the excitation of an electron from the valence band to the conduction band. The absorption coefficient, $\alpha$ calculated using the above mentioned relations for different film thicknesses are shown in Fig. 6. It is seen that the absorption coefficient of the investigated film thickness range varies between $4 \times 10^4$-2 $\times 10^5 \text{cm}^{-1}$.

Fig. 6: Spectral variation of the absorption coefficients vs. photon energy for SnS of different thicknesses.

Fig. 7: Plots of $(\alpha \hbar \omega)^2$ vs. $(\hbar \omega)$ for SnS films of different thicknesses.
The optical band gaps, $E_g$, values are calculated by assuming a direct transition between the edges of the valence and the conduction bands, for which the variation of the absorption coefficient, $\alpha$, with photon energy is given by Pankove (1975):

$$(\alpha \omega) = A(\hbar \omega - E_{g, \text{opt}})^{1/2}$$  \hspace{1cm} (5)

By plotting $(\alpha \omega)^2$ versus $(\hbar \omega)$ and extrapolating the linear region of the resulting curve as shown in Fig. 7, $E_g$ can be obtained. It is seen that the optical band gap of SnS films decreased from 1.57 to 1.32 eV with increase of the film thickness from 155 to 585 nm. The decrease in optical band gap energy with increase film thickness is likely attributed to an improvement in the crystallinity of the deposited films as indicated from the XRD analysis. The estimated band gap value for different film thicknesses is also listed in Table 2.

### Table 1: EDX results and Sn/S ratios of SnS films at different conditions.

<table>
<thead>
<tr>
<th>Element</th>
<th>Film thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$t = 585 \text{ nm}$</td>
</tr>
<tr>
<td>Sn</td>
<td>50.53</td>
</tr>
<tr>
<td>S</td>
<td>49.47</td>
</tr>
<tr>
<td>Sn/S</td>
<td>1.02</td>
</tr>
</tbody>
</table>

### Table 2: Optical parameters of SnS films of different thicknesses.

<table>
<thead>
<tr>
<th>Film thicknesses [nm]</th>
<th>$E_g$ [eV]</th>
<th>$E_o$ [eV]</th>
<th>$n_s(0)$</th>
<th>$\varepsilon_s$</th>
<th>$E_{g, \text{opt}}$ [eV]</th>
<th>$E_{g, \text{dir}}$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>155</td>
<td>16.814</td>
<td>2.211</td>
<td>2.933</td>
<td>8.605</td>
<td>1.47</td>
<td>1.57</td>
</tr>
<tr>
<td>225</td>
<td>20.792</td>
<td>2.119</td>
<td>3.288</td>
<td>10.814</td>
<td>1.41</td>
<td>1.53</td>
</tr>
<tr>
<td>283</td>
<td>22.824</td>
<td>2.047</td>
<td>3.486</td>
<td>12.148</td>
<td>1.37</td>
<td>1.48</td>
</tr>
<tr>
<td>470</td>
<td>24.380</td>
<td>1.963</td>
<td>3.664</td>
<td>13.422</td>
<td>1.31</td>
<td>1.46</td>
</tr>
<tr>
<td>585</td>
<td>24.789</td>
<td>1.894</td>
<td>3.754</td>
<td>14.089</td>
<td>1.26</td>
<td>1.32</td>
</tr>
</tbody>
</table>

### Conclusions:

SnS films with different thicknesses have been prepared onto clean glass substrates by thermal evaporation technique. The X-ray study revealed that SnS films of thickness $\geq 283$ nm are crystalline, whereas films of lower thickness exhibit poor crystalline with more amorphous background. The crystalline nature of the lower film thickness has been confirmed using transmission electron microscope and the corresponding electron diffraction pattern. The chemical composition of thicker films samples showed nearly stoichiometric, however, lower sample showed deficient in S and rich in Sn. The refractive index increases notably with increasing the film thickness. Analysis of the refractive index dispersion on the basis of the Wemple and DiDomenico model showed that a reduction in the values of the oscillator energy $E_o$ has been observed as the film thickness increases in a reverse manner to the values of $E_g$ and also with the static refractive index $n_s(0)$. Analysis of the optical absorption coefficient revealed the presence of direct optical transition. The calculated optical band gap values of the deposited SnS films decreased from 1.57 to 1.32 eV with increase of film thickness from 155 to 585 nm.

### References