Effect of annealing temperature on optical and electrical properties of SnS thin films

Najiba A. AL-Hamadni, Alia A.A. Shehab, Duha M. A.Latif

Abstract

SnS thin films have been deposited at R.T. with thickness (300 nm ± 0.01) by using a thermal evaporation technique and annealed at 200°C for 2 hour. The optical band gap of the SnS film determined from optical transmittance spectrum, in the range (400-1100 nm) and the data was used to calculate absorption coefficient and optical band gap. The film as grown and annealed has shown a direct band gap ~ 2.24 eV and 2.17 eV respectively. The optical constant such as extinction coefficient (k), absorption coefficient (α) and refractive index (n) have been evaluated. At the annealing temperature the SnS film had the best electrical properties the mobility was up to 52.35 cm²/V·s and the resistivity was about 0.14×10⁶ (Ω·cm).

Keywords: Tinsulfied, thinfilms, Thermal evaporation, Optical & electrical properties.

1. Introduction

In recent years, thin films of SnS have attracted much for photovoltaic applications due to the high absorption (>10⁴ cm⁻¹) [1,2] and high conductivity. SnS belongs to groups IV-VI compounds formed with Sn as the action and S as the anion. The constituent elements are inexpensive, nontoxic and abundant in nature leading to the development of devices that are environmentally safe and have public acceptability. SnS is an important optoelectronic material that is found in zinc blend with lattice constant (a=0.5845 nm) [3], orthorhombic with lattice constants (a=0.385 nm, b=1.142 nm c=0.438 nm) [4,6] crystal structures. The optical properties of SnS vary depending on synthesizing or fabrication method, but most work agrees with direct (1.2-1.5 eV) and indirect (1.0-1.2 eV) band gap values. These properties enable SnS thin films to be used as an absorption layer in the fabrication of heterojunction solar cell [7].
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SnS thin films can be fabricated by many methods such as thermal evaporation, pulse electro deposition, SILR, electron beam evaporation, chemical bath deposition [8,9,10]. The film in this study is grown by thermal evaporation, this method has many advantages, it is widely used because it is a simple, economic and viable technique, which produces films of good quality for device applications. In this work, an attempt has been made to prepare SnS films by thermal evaporation in order to investigate their optical and electrical properties.

2. Experimental

Tin sulphide thin films of thickness (300nm± 0.01) were deposited with rate deposition 48 nm/s at R.T. and they were annealed at 200°C on chemically and ultrasonically cleaned glass substrates with the high Vacuum Coating unit at a vacuum about 10⁻⁵ torr. The distance between source and substrate was maintained at 6.5 cm for the cases. The prepared films were annealed in vacuum at elevated temperature for 2 hour. Optical transmittance measurements for the film were carried out using UV/VIS double beam spectrophotometer (Schimadzu 160Å Japan Company) in the wavelength range (400-1100 nm). Based on Van der Pauw method, the electrical properties were determined by a HMS 3000 Hall measurement system.

3. Results and discussion

3.1. Optical Properties

The optical transmission (T) spectrum deposited films at R.T. and annealed at 200°C was taken by using spectrophotometer in the wavelength range of (400-1100 nm) in order to determine the optical characterization of SnS thin films. This spectra is shown in Fig. (1) it is obviously seen that the SnS thin film as prepared has transmission about 90%, while this value increase with annealing temperature, the transmission curve indicates a nearly saturated at 1100 nm, this may be due to high crystalline nature of the prepared films [11,12].
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Fig. (1) Transmittance versus wavelength for the as deposited films and annealed.

The absorption coefficient ($\alpha$) can be calculated according to formula (1) [13]:

$$\alpha = \frac{2.303 A}{d}$$  \hspace{1cm} (1)

where $A$ is the absorptance, and $d$ is thickness of the films.

Fig. (2) shows the curves of absorption coefficient $\alpha$ vs $h\nu$ of the two samples. It can be seen that both gradient of curves and the magnitude of $\alpha$ increase with annealing.

Fig. (2) Absorption coefficient curve of the SnS films deposited at R.T. and annealed.

The extinction coefficient ($k$) was calculated using the relation [14]:

$$k = \frac{\alpha \lambda}{4 \pi}$$  \hspace{1cm} (2)
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Where $\alpha$ is the absorption coefficient and $\lambda$ is the wavelength of the incident photon. Fig. (3) shows that the extinction coefficient as a function of photon energy as seen in the figure, this fig. show that $(k)$ increases for annealing film that due to the band –to band transition and increases in absorption coefficient in this film.

Fig(3). Extinction coefficient Vs. photon energy for deposited and annealed film

For the allowed direct transition, the variation of $\alpha$ with photon energy ($h\nu$) obeys Tauc's plot expressed as [14]:

$$(\alpha h\nu)^2 = A(h\nu - E_g)$$

(3)

Where A is a constant, $E_g$ the optical band gap, $h$ the plank constant and $\alpha$ the absorption coefficient. In Eq. (4) $E_g$ denoted the energy gap between the valence band and conduction band. According to Tauc's plot shown in Fig.(4), the optical band gap were determined by extrapolating the linear region of the resulting curve. They were varied from 2.24eV to 2.17eV for as deposited film and for annealed film respectively. It is mainly attributed to the room temperature deposited.
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Fig. (4) . \((\alpha h\nu)^2\) Vs \(h\nu\) curve of the SnS film deposited at R.T and annealed

Fig. (5) shows the refractive index of the SnS films for prepared and annealed as a function of photon energy, the refractive index increases for the annealing sample from \((1.1-2.5)\) and it varies with photon energy and seems to have its maximum value at the peak maxima which was nearly constant for two samples.

The refractive index \((n)\) of the films was calculated using the relation \([15]\) :

\[
n=\left[\frac{1+R}{1-R}\right]^2 - (k^2+1)\sqrt{2} + \frac{1+R}{1-R}
\]

Where \((R)\) is the reflectance and \((k)\) is the extinction coefficient

Fig. (5) Refractive index versus photon energy for the as deposited and annealed films
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2. Electrical Properties

At room temperature, semiconducting properties of the films were measured by a HMS-3000 Hall measurement system. The results are listed in Table 1. Compared with the unannealed sample, the semiconducting properties of the annealed sample has been improved.

The carrier concentration \( n_H \) of the films was calculated using the relation [16]:

\[ n_H = \frac{1}{R_H} \cdot e \]  
(4)

where \( R_H \) is the Hall Coefficient and \( e \) is the charge of electron.

The mobility \( \mu_H \) of the films was calculated using the relation [17]:

\[ \mu_H = \frac{R_H \cdot \sigma}{e} \]  
(5)

where \( \sigma \) is the conductivity.

It can be seen from Table 1 the carrier concentration of the films decreases from \( 15.37 \times 10^{11} \) cm\(^{-3} \) (un annealing) to \( 8.02 \times 10^{11} \) cm\(^{-3} \) with annealing temperature, and their resistivity decreases from \( 1.239 \times 10^6 \Omega \).cm (un annealing) to \( 0.147 \times 10^6 \Omega \).cm with annealing temperature. In addition, the carrier concentration for two samples is positive, which indicates that the SnS films are of p-type conduction. Therefore, the annealing can decreases the carrier concentration, reduce the resistivity, the phenomenon can be explained by the fact that at the annealing temperature, better crystallization and greater grain size in the films lead to decrease defects density and crystal-boundary, therefore the resistivity decreases. These results are similar to result of Hong-Jie Jia et al. [18].

Table 1. Hall measurement results for SnS thin films at R.T. and annealed

<table>
<thead>
<tr>
<th>Sample</th>
<th>( (n_H) ) carrier concentration ( (cm^{-3}) \times 10^{11} )</th>
<th>( (\mu_H) ) Mobility ( (cm^2.V^{-1}.s^{-1}) )</th>
<th>Resistivity ( (\Omega.cm) \times 10^6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>As deposited</td>
<td>15.37</td>
<td>3.278</td>
<td>1.239</td>
</tr>
<tr>
<td>Annealing at 200°C</td>
<td>8.02</td>
<td>52.35</td>
<td>0.147</td>
</tr>
</tbody>
</table>

4- Conclusion

The SnS thin films were deposited on glass substrate using thermal evaporation technique and the effect of annealing on optical & electrical properties were investigated. It was revealed that the effect of annealing lead to decreased the band gap from \( 2.24-2.217 \) eV and decreased in absorption, extinction coefficient. In addition to, the carrier concentration for two samples is positive, which indicate that the SnS films are of p-type conduction.
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The effect of annealing temperature on the optical and electrical properties of SnS thin films was studied. The films were deposited on glass substrates at different temperatures ranging from 200 to 400°C. The optical properties were investigated using UV-Vis spectroscopy, while the electrical properties were measured using a four-probe method.

The optical band gap of SnS films was found to decrease with increasing annealing temperature. The electrical conductivity showed an increase with temperature, indicating a semiconductor behavior. The films exhibited a high optical transparency and low electrical resistance, making them suitable for various applications.

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Keywords: SnS, annealing temperature, optical properties, electrical properties.