Improvement Photoactivity Properties of SnS Thin Film by Chemical Spray Pyrolysis Method

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Abstract. Tin sulphide (SnS) thin films were produced using low-cost chemical spray pyrolysis method (CSP). The optical and structural properties of SnS Nano films were examined by varying thickness. The films exhibit an orthorhombic structure with preferential orientation in the (111) direction, according to X-ray diffraction studies. The films show a reduction in crystallite as films thickness increases. The results showed that the films had about < 70% transparency in the visible portion. Optical band gap exhibited same behavior. The thickness dependency is mentioned in the results produced by dispersion parameters and other optical constants.

Key word: (CSP), SnS thin film, XRD, UV-VIS, AFM.

1. Introduction

Such a novel material for photovoltaic solar energy conversion, SnS is highly abundant in nature, non-toxic and have a direct energy band gap of 1.35 eV. Also, It has a high absorption coefficient, requiring Only a few microns of SnS are required for absorption. the maximum amount of incident light [1]. CIGS and CdTe are widely used in solar cells. However, some of these materials high cost and toxic so there was many trials to replace these materials by suitable one for using in solar cells. The electrical conductivity controlled using also the SnS layers / p-conductivity type with dopant materials like Al, Ag, Cl and Cu [2]. Therefore, SnS :CdS with n-type layer have also been made using to enhancement of Solar cells devices to reach up to 2% have been recorded [3]. Moreover, SnS then film has been prepared using varies techniques including spray pyrolysis, thermal evaporation, electrode position, and chemical bath deposition. [1-10]. This work will reflect effects of SnS film thickness on optical and structural properties.

2. Experimental Details

Thin films of Tin sulfide were deposited with different thicknesses (150, 300, 450) nm utilizing spray pyrolysis method. A matrix materials consist of 0.1 M SnCl₂, 5H₂O and 0.1 M SC (NH₂) ₂ (Supplied from Merck Chemicals UK) dissolved in deionized water was used to prepare Tin sulfide. This solution was precipitated onto heated glass substrate at 400 °C. After many trials the optimal parameters were reached at the followings. Substrate to nozzle distance was 28 cm, spraying rate was 4 mL/min, The carrier gas was Nitrogen, and the spraying time was 10 minutes followed by a 1.5 minute interval to avoid excessive cooling. The results in range of 300± 30 nm and they were determined using the gravimetric method. A double beam spectrophotometer (Shimadzu-Japan) was used to measure an optical characteristics such as transmittance and absorbance in the wavelength from 200 to 900 nm. The XRD (Type-6000) used to figure out the structure of the films, also using the SEM (type- JSM 6335F) and AFM (type -AA3000 SPM) to determine the morphology of the surfaces.
3. Results and discussion

3.1. Optical properties

The transmission spectra of SnS Nano thin films are shown in Figure 1a. For the SnS thin films and different thickness, the transmission seems more than 70% in the visible and near IR portion. SnS Nano film with 300 nm thickness exhibits good transmission. The values of optical band gap was calculated by Eq. (1) [11,12].

\[
ahv = A(hv - E_g)^n
\]

\[
a = \ln(1/Td)
\]

where \(\alpha\) represent absorption coefficient, Figure 1b shows \(\alpha\) against wavelength, and for direct transitions \(n\) is equal to 0.5, \(A\) is constant, \(h\nu\) is photon energy. \(a\) can be calculated by using Eq. 2, where \(d\) is the thickness. Therefore, direct band gap value of SnS, can be determined from plotting \((\alpha h\nu)^2\) against \(h\nu\) as shown in Figure 2, that present the reliance of band gap of SnS nano thin films. At 150 nm thickness, the optical band gap of the SnS film is 1.55 eV, and band gap decreasing occurs at 300nm SnS Nano-thin films thickness to 1.3 eV. The Identical behavior was observed by Vani et al. [13].

![Figure 1](image)

**Figure 1.** (a) Transmittance versus wavelength of deposited films (b) \(\alpha\) against wavelength.
3.2. Structure

The SnS with different thicknesses 150, 300 and 450 nm are studded by (XRD) for crystalline structure. Figure 3 shows the pattern of SnS films deposited. The standard card (JCPDS card no.05.0640) implying that each sample are polycrystalline with orthorhombic layered structure of SnS. The orientation of the SnS thin films reached in high values with increasing the thicknesses in nano sized. The intensity of preferred peak at 31.53° corresponding to (111) plane and was increased in sample of thickness 450 nm. The XRD spectra of films grown at a lower thickness (t ≤150nm) showed the existence of Sn₂S₃ phase, along with predominant SnS phase. The films deposited with t=300 nm and 450 nm showed peaks mainly of SnS phase with minor peaks conformable to zinc blend phase (ZB) of SnS. Peak intensity of zinc blend phase was decreased as thickness increases to 450 nm. Degree of crystallinity was increase as thickness increase. Surface morphology seems homogeneous with spherical shapes nanoparticles and the grain size was increased from 26 nm to 28nm with an increasing the thickness from 150 to 450nm, as shown in Table (1).
By using Scherrer’s formula we calculate crystallite size (D) in the Table 1 [14]:

\[ D = \frac{0.9\lambda}{\beta \cos \theta} \]  

---(3)

Where D is crystallite size, \( \beta \) is full width at half maximum (FWHM) and \( \lambda \) is X-ray wavelength (1.54056 Å). Instrumental broadening with single crystal silicon line broadening was used to rectify the crystallite size.

Dislocation density \( \delta \) and the strain \( \varepsilon \) for reflection (111) are calculated by using formula (5) and (6)[15].

\[ \delta = \frac{1}{D^2} \]  

---(4)

\[ \varepsilon = \frac{\beta \cos \theta}{4} \]  

---(5)

### 3.3 AFM Characterization

Figure 4 (a,b and c) represent AFM images. Surface morphology of SnS Nano-thin films illustrates that granules of spherical shape are evenly dole out with the average grain size. In the Table 2, shown the average diameter of the SnS film with different thickness was arranged 136.46-93.93 nm, with the root-mean-square (rms) from 0.923 to 0.718 nm and the average roughness of the surface between 0.755 to 0.585 nm. The thickness increase, the grains are small in dimensions, also the roughness exhibits the same variations in behavior for thin films.

### Table 2. AFM morphology of SnS with different thickness by (CSP).

| Thickness (nm) | Avg. Diameter (nm) | Average roughness (nm) | R. M. S. (nm) |
|---------------|--------------------|------------------------|--------------|
| 150           | 136.46             | 0.755                  | 0.923        |
| 300           | 108.45             | 0.751                  | 0.886        |
| 450           | 93.93              | 0.585                  | 0.718        |
4. Conclusions
SnS thin films with different thicknesses on glass substrates were successfully grown by a (CSP). The optical properties of the films are found to be 70% in visible and near IR region. The grain size was increased with increase in thickness. Films deposited at t=450nm were extremely crystalline. The dislocation density of prepared films was minimized with increase in thickness. All SnS films have shown $\alpha > 10^5 \text{ cm}^{-1}$. This shift in band gap could be refer to the grain size effect. These films might be used as an absorber in photovoltaic devices.

5. References
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