

Structural and Optical Properties of SnS Thin Films

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Abstract: Thin films of tin sulfide (SnS) were prepared by thermal evaporation technique on glass substrates, with thickness in the range of 100, 200 and 300nm and their physical properties were studied with appropriate techniques. The phase of the synthesized thin films was confirmed by X-ray diffraction analysis. Further, the crystallite size was calculated by Scherer formula and found to increase from 58 to 79 nm with increase of thickness. The obtained results were discussed in view of testing the suitability of SnS film as an absorber for the fabrication of low-cost and non toxic solar cell. For thickness, $t=300\text{nm}$, the films showed orthorhombic OR phase with a strong (111) preferred orientation. The films deposited with thickness $< 200\text{nm}$ deviated from stoichiometry and additional phases such as Sn₂S₃ was found to be present. Optical transmission spectra were recorded in the wavelength range 200-1100 nm, and the data was used to calculate absorption coefficient and optical band gap. SnS film grown with 300nm has shown a direct optical band gap of $\sim 1.7\text{ eV}$, with an absorption coefficient of 105cm^{-1} above the fundamental absorption edge. These polycrystalline and highly absorbing SnS thin films are suitable for the fabrication of hetero junction solar cells.

Keywords: Tin sulfide, Thin films, Photovoltaic materials, Thermal evaporation, Optical properties.

1. INTRODUCTION

Providing affordable renewable source of energy is paramount in this century in high energy demand country, with abundant sunlight. Affordable solar energy generation will be a key to sustain our economical growth. Solar photovoltaic (PV) is frequently cited as a promising but an economically unrealistic large scale energy supply options. One of the major hurdles for PV cell to become more popular is the fact that price of the electricity (cost/watt) produced by it is not yet competitive. This cost can be reduced by either improving the efficiency and/or reducing the production cost. Solar cell based on the use of CuIn (Ga)Se₂, CdTe, GaAs and crystalline silicon (c-Si) as an absorber material have produced with high efficiency ($>23\%$). Problems however remains with these technologies are the lack of abundance of indium and gallium, toxicity of cadmium and high energy processing of silicon. Analysis of PV materials, demonstrated an ample opportunity for fruitful new research and development based on low cost and commonly available materials. It is the fact that, the devices performing below 10% power conversion efficiencies deliver the same lifetime energy output as those above 20% when a 3/4 material reduction is achieved [1]. In this view it is necessary to focus our research on new photo voltaic materials which makes solar cell cheaper, more efficient and produces significantly more energy over its life time. One such material is tin monosulfide (SnS), which has some desirable properties for photovoltaic application. This is a IV-VI compound semiconductor material having direct optical band gap near to 1.3eV, which is close to optimal band gap (1.5 eV) of solar cells and high absorption coefficient ($\alpha > 10^4\text{ cm}^{-1}$) [2]. Its constituent elements Sn and S are abundant and are less toxic in nature. SnS has p-type electrical conductivity and it has theoretical light conversion efficiency, greater than 24% according to Loferski diagram [3]. Better understanding of material, and optimized device design may lead to SnS based solar cell with efficiency greater than 10% [4]. In this paper, we report on the preparation and characterization of thermally evaporated SnS thin films in order to study their suitability for the device application.

2. EXPERIMENTAL DESCRIPTION

Source material, SnS was prepared by melting high purity elements (99.99%) Sn and S in an evacuated quartz tube at a temperature of 1173 K. Tin sulfide films were deposited on corning 7059 microscopic glass substrate by thermal evaporation technique under high vacuum (10⁻⁵ Torr) with different thicknesses varied from 100 to 300nm. The distance between source and substrates, the rate of deposition have been maintained as constant at 15 cm, and 8 Å/s, respectively. The as-deposited thin films of SnS were characterized for morphology, structural, and optical properties. The composition of the films was estimated using atomic absorption spectroscopy AAS. The structural studies of the films were carried out using x-ray. The Preparation and Characterization of SnS Thin Films for Solar Cell. The optical transmittance measurements were made in the wavelength range 200-1100 nm, using uv-visible spectrometer. The optical energy gap E_{opt} of the SnS prepared with different thicknesses t are measured throughout plotting $(\alpha h\nu)^{1/r}$ and $(h\nu)$ the intercept on $(h\nu)$ axis when $(\alpha h\nu)^{1/r} = 0$ is the optical energy gap. The optical constants represented by the refractive index (n), extinction coefficient (k), and dielectric constants (the real ϵ_r and imaginary ϵ_i) are calculated for the as deposited thin films using Eqs. [(4),(5), (6) and (7)] respectively [5.6]

$$n = \left(\frac{4R}{(R-1)^2} - k^2 \right)^{\frac{1}{2}} - \frac{(R+1)}{(R-1)} \quad (4)$$

Where n is the real refractive index.

$$k = \frac{\alpha \lambda}{4\pi} \quad (5)$$

where α is the absorption coefficient and λ is the wavelength.

The real part of dielectric constant which represents the polarization term .

$$\epsilon_r = n^2 - k^2 \quad (6)$$

$$\epsilon_i = 2nk \quad (7)$$

3. 3. RESULTS AND DISCUSSION

3. 1. Structural studies

Figure.1 depicts XRD spectra of SnS thin films deposited with different thicknesses in the range 100-300nm. The less intense reflection of the peaks could be due to the presence of other phases in the film i.e. the spectra reveal the presence of traces of other phases along with predominant SnS phase for the orthorhombic structure. The intensity of the main peak corresponding to the reflection plane (111) is found to be increased in sample with thickness 300nm prepared at room temperature indicating to the better crystallinity. The broadening intensity arises due to small crystalline (grain) size and strain (lattice distortion). The XRD spectra of films grown at lower thickness ($t \leq 100\text{nm}$) showed presence of Sn₂S₃ phase, along with dominant SnS phase along with dominant SnS phase. The films deposited with $t=200\text{nm}$ and 300nm showed peaks mainly of SnS phase along with minor peaks corresponding to zinc blend phase(ZB) of SnS. The intensity of the peak corresponding to zinc blend phase get to decrease as the thickness increases to 300nm, no peaks are observed corresponding to SnS₂ for both thicknesses 200 and 300nm. Degree of crystallinity was also found to increase with the increase of thickness. Structural parameters such as crystallite size, dislocation density were calculated from XRD pattern. The crystallite size of the film was calculated from the Debye Scherer's formula, $D = 0.94\lambda / (\beta \cos\theta)$, where β is the FWHM intensity in radians. The dislocation density values were estimated using following standard relation. Dislocation density $\delta = 1/D^2$. The grain size was increased from 58 nm 79nm with increase of thickness from 200 to 300nm, see table(1). It was observed that

dislocation density decreased with increase of grain size. This is an essential property for the fabrication of good quality thin film to use in optical devices.

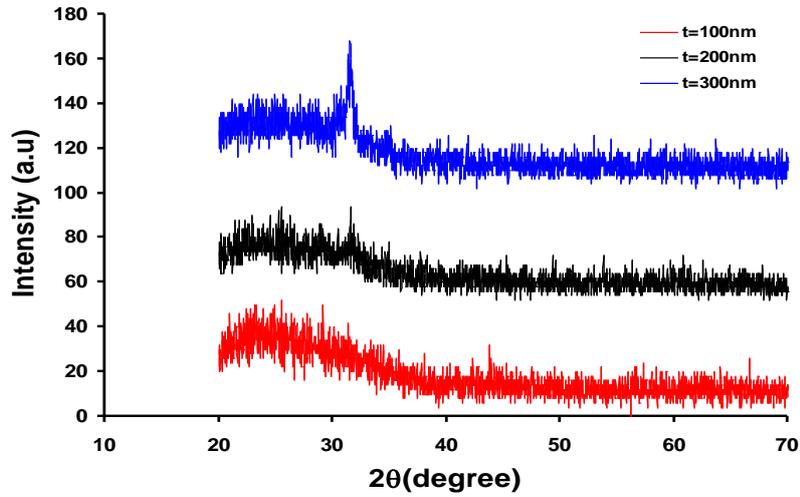


Figure.1. XRD of as deposited SnS Thin Films with different thicknesses.

Table.1 X-ray diffraction analysis of SnS Thin Films with different thicknesses

Thickness nm	hkl	d(Å) Exp	2 θ	FWHM (β)	Grain Size(D) Å	Dislocation density $\times 10^{-4} \text{ nm}^{-2}$
100	(040)(OR)	2.68	33.39	0.0767	56.52	3.13
	(131)(OR)	2.77	32.17	0.0625	69.13	2.09
	(420)Sn ₂ S ₃	2.56	34.49	0.0867	50.1	3.98
200	(111)(OR)	2.82	31.60	0.0733	58.84	2.89
	(120)(ZB)	3.38	26.29	0.0673	63.36	2.49
	(021)(OR)	3.36	25.68	0.0533	79.9	1.57
300	(111)(OR)	2.83	31.55	0.0540	79.84	1.57
	(200)(ZB)	2.90	30.78	-----	-----	-----
	(101)(OR)	2.92	30.56	0.0480	89.65	1.24

3. 2. Optical properties

Optical transmittance spectra recorded showed a sharp fall in transmittance at different wavelengths, which corresponds to fundamental absorption edge. Fig.2 Transmittance spectra of SnS thin films deposited at different thickness. In general, we can observe from Fig. 2 that transmittance decreases with increasing of thickness which means an increase in the reflection and absorption. The shifts of transmittance toward lower energies accompanied the thickness increment explained according to the fact that increasing of thickness approaches structure of the samples from bulk material which reflects the shifting of the absorption edge toward lower energies values as will be seen in the next section.

The optical properties of the as deposited SnS films with different thicknesses (100,200 and 300nm) have been determined by using transmittance and absorbance spectrum in the region (100-1100nm). The reflectance spectrum has been measured. Also the energy gap and optical constants have been determined The absorption coefficient (α) was calculated using the relations $\alpha = (1/t) \ln (1/T)$, where t is the thickness of the film. All the SnS films had high absorption coefficient, ($> 105 \text{ cm}^{-1}$) above the fundamental absorption edge. The direct optical band gap (E_{gopt}), estimated from the $(\alpha h\nu)^2$ versus photon energy ($h\nu$) plot is shown in Fig.3. Films grown $t=100\text{nm}$ have shown high optical band gap value of 2.1 eV. This large band gap value may be due to presence SnO₂ ($E_g = 2.44 \text{ eV}$) and Sn₂S₃ ($E_g = 2.0 \text{ eV}$) in SnS thin films [7]. Poor crystallinity of the films may also lead to higher optical band gap. Optical band gap decreased with increase in t and reached 1.7 eV, for the film with $t=300\text{nm}$. This value of and gap is comparable with the reported value for SnS thin films [8].

The variation of the refractive index versus wavelength in the range (200-1100nm) for SnS films with different thicknesses (100, 200, and 300nm) prepared at R.T is shown in Fig.(4). We can notice from this figure and Table 2 that the refractive index, increases with increasing of thickness t for prepared samples, moreover n increases from 1.72 to 2.52 for as deposited SnS films when t increases from (100to300)nm, this behavior can be explained on the basic of that increasing of (t) to make SnS more dense (increasing the packing density) which in turn decreases the propagation velocity of light through them which resulting in increasing of n values since n represent the ratio of light velocity through vacuum to velocity through any medium, also this behavior can be explained depending on the fact that refractive index value of bulk material exceeded that of thin film. This behavior is expected and accompanies the increase of thickness (i.e. decreases energy gap value) according to inverse relation between the refractive index and energy gap [9].

The behavior of the extinction coefficient of SnS films for different thicknesses, are shown in Figs.5. We can observe from this figure and Table 2 that the extinction coefficient increases with increasing of thickness for all films. It is clear that for as deposited SnS films k increases from 0.338 to 0.527 when t increases from (100 to300) nm, the behavior explanation is the increases of t increases the absorbance or the absorption coefficient and consequently k will be increases, on the other hand this may be attributed to the same reason mentioned previously in the refractive index, since the increasing of thickness decreases the optical energy gap as a result of absorbance increment [10].

The variation of the real (ϵ_r) and imaginary (ϵ_i) parts of the dielectric constant values versus wavelength in the range(200–1100)nm for SnS films deposited at R.T with different thicknesses (100,200and 300nm), are shown in Figs.(6 and 7). The behavior of ϵ_r is similar to that of the refractive index because of the smaller value of k^2 compared with n^2 according to equation 6, while ϵ_i is mainly depends on the k values. It is found that ϵ_r increases with increasing of thickness. Moreover ϵ_r found to increase from 2.908 to 6.03for as deposited films when thickness increases from (100 to 300) nm, as shown in Table 2.The imaginary part of dielectric constant ϵ_i reveals the same behavior of ϵ_r with thickness. It is clear from Table 2 that ϵ_i for as deposited SnS films increases from 1.16 to 2.56 when t increases from 100 to 300nm .The same explanation of n and k can be given to ϵ_r and ϵ_i [11].

Table.2. the values of n , k , ϵ_r , ϵ_i , T at $\lambda=800\text{nm}$, and E_g^{opt} for SnS thin films with different thickness.

Thickness (nm)	n	k	ϵ_r	ϵ_i	T	E_g^{opt} (eV)
100	1.72	0.338	2.908	1.16	83.88	2.10
200	1.88	0.203	3.55	0.76	80.59	2.02
300	2.52	0.527	6.03	2.56	43.61	1.70

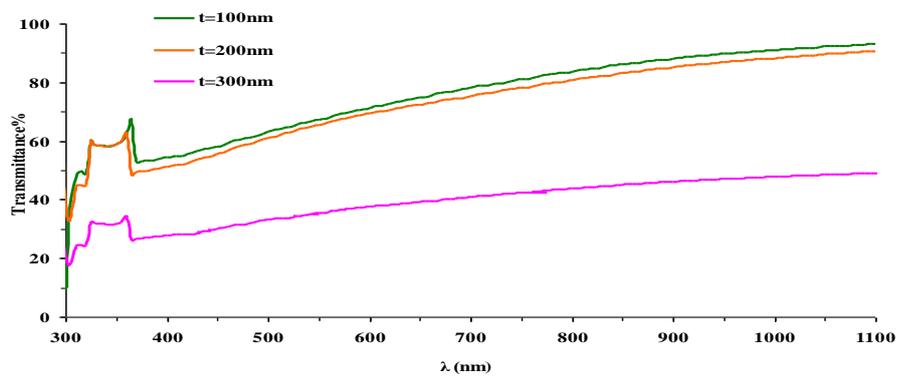


Figure.2. Transmittance spectra of as deposited SnS thin films with different thicknesses.

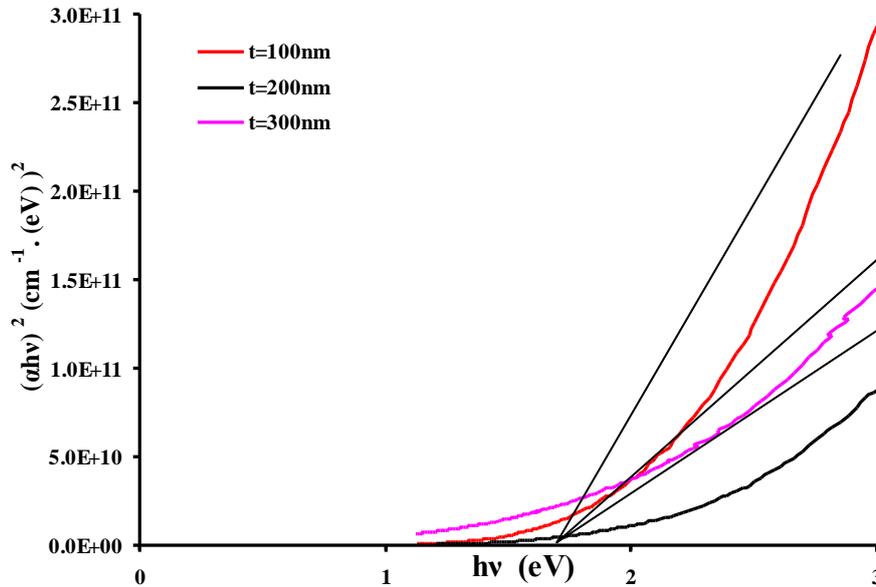


Figure.3. Variation of $(\alpha hv)^2$ with (hv) of as deposited SnS thin films with different thicknesses.

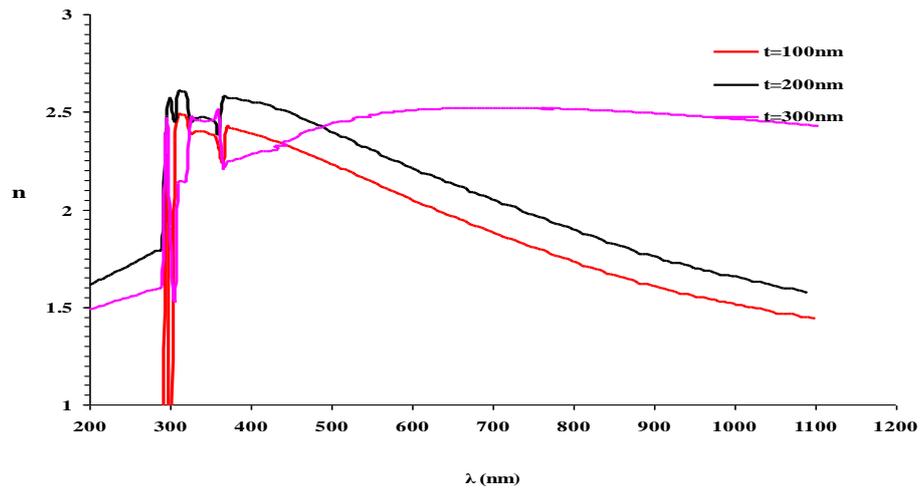


Figure.4. Variation of n with wavelength of as deposited SnS thin films with different thicknesses.

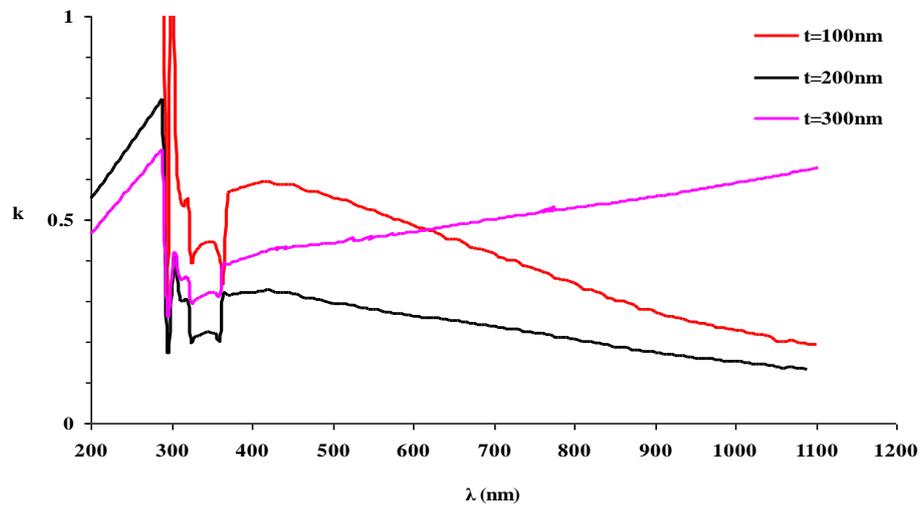


Figure.5. Variation of k with wavelength of as deposited SnS thin films with different thicknesses.

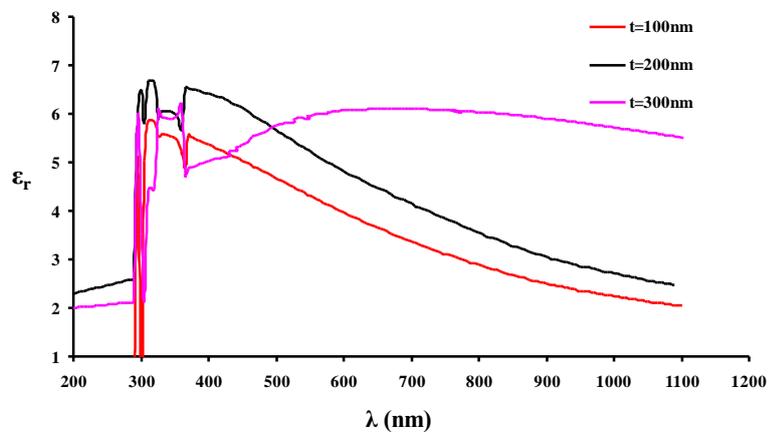


Figure.6. Variation of ϵ_r with wavelength of as deposited SnS thin films with different thicknesses.

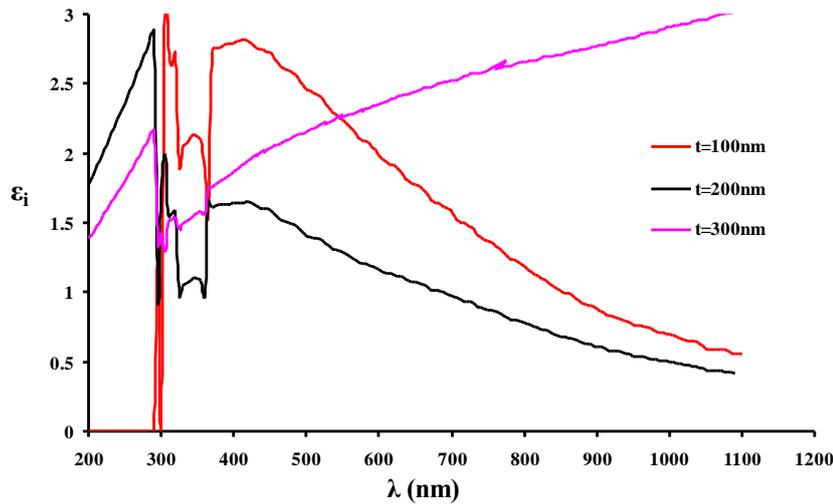


Figure.7. Variation of ϵ_i with wavelength of as deposited SnS thin films with different thicknesses.

4. CONCLUSION

Tin sulfide films were grown by a thermal evaporation technique with different thicknesses on glass substrates. All the films had good adherence to the substrate. Grain size was increased substantially with increase in thickness. Films grown with lower thicknesses exhibited a dominant SnS phase along with minor Sn₂S₃ phase. Films deposited with $t=300\text{nm}$ were highly crystalline, nearly stoichiometric and showed only SnS phase. From the FWHM of XRD spectra, the dislocation density and crystallite size were evaluated. The dislocation density of the deposited films were diminished with increase in thickness. All the deposited SnS films have shown high absorption coefficient, $> 105\text{ cm}^{-1}$, above the fundamental absorption edge. Single phase SnS thin films deposited with $t=300\text{nm}$ has showed the presence of direct optical band gap at 1.7 eV. These nearly stoichiometric, single-phase and highly absorbing SnS films with a direct optical band gap could be used as an absorber in the fabrication of thin film heterojunction photovoltaic devices.

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