Effect of Tin Concentration on SnS_2 Thin films Prepared by Simple Nebulizer Spray Method

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Abstract **- Tin disulfide thin films have been deposited onto glass substrates by Nebulizer Spray Pyrolysis method using tin tetrachloride and thiourea with tin molar concentrations varied from 0.5M to 0.7M at 325ºC. XRD studies show that the films prepared by (0.5M and 0.6M) exhibit the shows the crystalline nature of the thin films with preferred orientation (0 0 2) plane and hexagonal structure, but 0.7M concentration thin film is found in an amorphous form. Atomic force microscopy (AFM) measurements revealed that the surface roughness of the films decreased due to concentration. Uniform deposition of the material over the entire glass substrate was revealed by Scanning Electron Microscopy (SEM). The chemical composition, optical properties of the SnS_2 thin films were characterized by energy disperse X-ray spectroscopy, ultraviolet-visible-near infrared spectrophotometers (UV-Vis-NIR). The atomic ratio, optical constants and band gap of SnS_2 thin film were calculated and analyzed.**

I. INTRODUCTION

Tin sulphide thin films have been premeditated in recent years due to its likely applications in solar cells. Tin sulphides belong to the IV–VI group semiconductors, with a multiplicity of form which contain tin disulfide (SnS_2), Sn_2S_3 and tin sulfide (SnS) [1]. SnS_2 crystallizes in the hexagonal crystal arrangement espouse CdI_2 structure form [2] whereas SnS_2 having a band gap of 2.2 to 2.4eV which is more suitable for photoconductive and photo electrochemical cells. Sn_2S_3 can be classified as a miscellaneous valence multiple with semiconductor behavior, whose optoelectronic properties are needy on the crystalline structure and stiochiometry [3]. SnS can be very interesting for the photovoltaic alteration of solar energy into electrical energy, given that its band gap of 1.2 eV is similar to that of silicon [4]. A number of avowal techniques, which consist of dip coating [4], chemical bath deposition [5], chemical vapour transport [6], spray pyrolysis [7] and Atmospheric Pressure chemical vapor deposition [8] have been used for the preparation of these films.

Development of the nebulizer spray technique for the deposition of SnS and SnS_2 thin films would be of practical interest, since nebulizer spray technique is both very simple and financial, low quantity of spray solution and time saving technique by which minute droplet of particle can be deposited. This technique has already been used for preparation of SnO_2, ZnS and CdSnSe [9, 10].

II. EXPERIMENTAL DETAILS

Analytical grade $SnCl_4\,5(H_2O)$ as a source of tin and CS $(NH_2)_2$ as a source of sulfur used for the film preparation on glass substrates. The glass substrate (glass thickness l.25 mm) which is non-conducting and amorphous in nature was used as the substrate. The solution was prepared with the various concentration of of $SnCl_4.H_2O$ and Thiourea, solved in 1:3 ratio of water and Isopropyl Alcohol. The solution was sprayed with the substrate temperature maintained for 300ºC. The compressed air was used to carry the oxygen gas maintained at 0.5 Kg/cm^2. The distance between nozzle and substrate was kept at 3cm. It does not require high quality target and vacuum. The thickness of the film and rate of deposition can be easily controlled.

A. Characterization

After having developed our layer we have characterized by various methods; Structural, morphological optical and electrical. The structural study was done using the diffractometer conducted a CuKα radiation source with a wavelength λ = 1.5418Å length in the range 10-80°. The double-beam UV / VIS / NIR Spectrometer has been used in the range 300-1200 nm for the calculations for the transmittance and absorption. Keithiely Source Meter Model 2450 used for the I-V characteristics of SnS_2 thin film samples deposited on non conducting glass substrate were determined for silver adhesive contacts by the 'DC' two probe methods.

III. RESULT AND DISCUSSION

A. X-ray Diffraction Studies

Fig.1 shows the X-ray diffraction profile of Nebulized sprayed pyrolysised SnS_2 thin film on the glass substrate at substrate temperature of 300ºC. The crystallinity with the preferential orientation growth of this compound having the plane diffracted with prominent Bragg peak at the 2θ such as 13.90°, 14.60°, and 14.69° of SnS_2 with hexagonal phase; and a preferred orientation along (002) plane (JCPDS card No. 89-3198) was appeared. The sharp peaks also indicated that the tin disulfide thin films were well crystallized. It is worth pointing out that crystalline films were obtained at without recourse to annealing. It was concluded that the tin disulfide thin films consisted only of the pure SnS_2 phase at the source of the tin sulfide thin films prepared at different tin (Sn) concentration are 0.5, 0.6 and 0.7M for 300ºC respectively.

The texture coefficients for preferential orientation of crystals in polycrystalline material were determined. The X-ray diffraction result helps to find the texture coefficient by using equation, [11]

$$TC(hkl) = \frac{I(hkl)/I_0(hkl)}{N_r^{-1}\sum I(hkl)/I_0(hkl)} \quad \ldots\ldots (1)$$

Where $T_{c\,(h\,k\,l)}$ is the texture coefficient of (h k l) plane, I (h k l) is the intensity measured for (h k l) plane, I_o (h k l) is the intensity of (h k l) plane taken from standard data in PDF card fitting in X-ray diffraction pattern of material, and N_r is the number of diffraction peaks. For the preferred orientation at any (h k l) plane, the texture coefficient at least must one .The calculated texture coefficient values of SnS_2 thin film for different (hkl) planes are shown in Table 1. The texture coefficient express that the orientation of the films with different pressure rates was in (0 0 2) plane and found increasing for decrease in tin concentration. The crystallites size of the tin disulphide from the Full Width at Half Maximum (FWHM) value of the peak obtained was determined and tabulated in Table 1

The crystallite size is calculated using Scherrer's formula [12]

$$D = \frac{k\lambda}{\beta\cos\theta} \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Where k is a constant (0.94), λ is the wavelength of the X-ray (1.5406 Å), β is the full width at half maximum (FWHM) of the peak, θ is the Bragg's angle. It was found that by decreasing the tin concentration from 0.7M to 0.5M the grain size increased from 20 nm to 41 nm.

The dislocation density of the crystallite (δ) has been evaluated using the following equation [11,13].

$$\delta = \frac{1}{D^2} \quad \text{---------(3)}$$

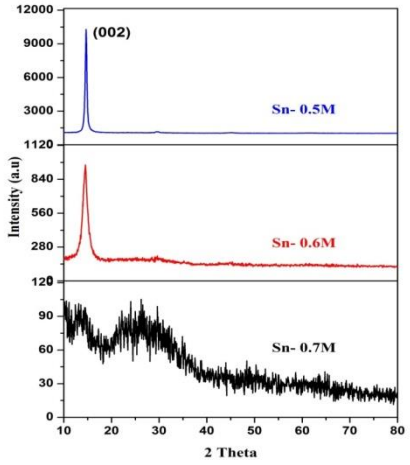


Fig 2. XRD pattern of SnS_2 thin films prepared at different tin concentration.

Deposited films dislocation density (δ) values are listed in table 1. The dislocation density of the deposited films in 0.7M was $5.74x10^{16}$ lines/m^2, it decreases to 2.40 $x10^{15}$ lines/m^2 for 0.6M. Further, decrease in molar concentration to 0.5M the dislocation density and strain decreases gradually as in Table 1, also there is a increase in crystallite size .The results of calculation shows that the decreases in the dislocation density with increasing quality of deposited films. The strain (ε) developed in the film was estimated using the following relation [11]

$$\varepsilon = \frac{\beta\times\cos\theta}{4} \text{---------(4)}$$

The variation of crystallite size and the strain are reported in table.1, the increase in crystallite size of the thin layer of SnS_2 film decreases the stress.

Fig. 2 shows the variation of crystallite thickness with the tin concentration. From the figure it was observed that the increase in tin concentration increases the thickness continuously and its varied with the values in the range from 1.08 to 2.94 µm, similar variation of crystallite size with the thickness reported as Kotte Tulasi Ramakrishna Reddy et al [14].

Table 1. Structural parameters of deposited SnS_2 thin films in various Tin concentration

Various tin (sn) concentration	Crystallite size (nm)	Dislocation density (δ x 10^{15} lines. m^{-2})	Strain (ε x 10^{-3} lines^{-2}.m^{-4})	Texture Coefficient TC (*hkl*)
0.5 M	41	1.35 x10^{15}	0.9	3.28
0.6 M	27	2.40 x10^{15}	1.3	1.07
0.7 M	20	5.74x10^{16}	6.8	-

B. Optical Properties

The optical transmittance versus wavelength spectrum of the SnS_2 films was measured in the wavelength range of 400-1100 nm and is shown in Fig. 3. The presence of interferences fringes in films transmittance spectra indicates that they have a smooth surface. The films deposited with low tin concentration reveal higher transparency due to their low thickness. Fig.5 illustrates the variance of absorbance in the range of 400 to 1100 nm. It is evident that the absorption coefficient decreases with an increase in wavelength and a sharp decrease in absorption coefficient near the band edge indicate better crystallinity of the films. The absorption of figure 4 clearly shows that the absorption spectrum decrease with the tin concentration also decreasing the absorption.

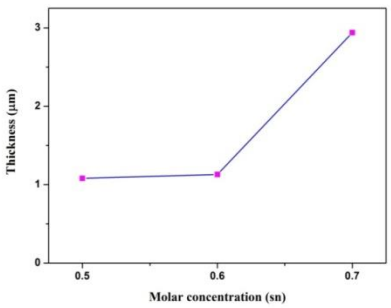


Fig 2. Tin concentration vs thickness

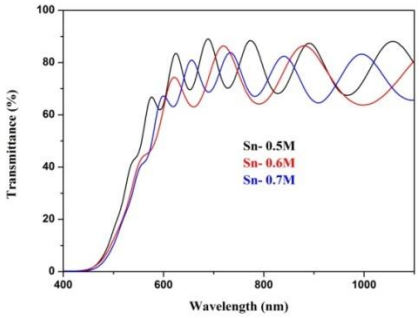


Fig.3 Transmittance spectra for SnS_2 thin films

The optical band gap of the films is calculated from the following relation [15].

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad \text{---------- (5)}$$

Where α is the absorption coefficient, A is the constant independent of photon energy (hv), h is the Planck constant and E_g is he optical band gap. In Fig.5 the plot is linear and indicated to a direct band gap of the films is varied from 2.5 eV to 2.8 eV for the different tin (Sn) concentrations. The optical band gap decrease with increasing the tin concentration can be attributed mainly by the decrease in the film thicknes. Imen Bouhaf Kherchachi et al [15] also had reported the wide optical direct band gap of SnS_2 thin films are 2.70 to 2.97 eV. Chengwu Shi et al [16] reported the direct band gap of 2.41 eV. The refractive index (n) was calculate from the transmission spectrum using the modified envelope method proposed by Swanepoel [17,18].

$$n = \left[N_1 \left(N_1^2 + s^2\right)^{1/2}\right]^{1/2} \quad \text{..... (6)}$$

$$N_1 = 2s\frac{T_M - T_m}{T_M T_m} + \frac{(s^2+1)}{2} \quad \text{..... (7)}$$

T_M and T_m are the values of maximum and minimum transmission values at a particular wavelength's' is the refractive index of the substrate. Refractive index can be estimated by extrapolating envelops corresponding to T_M and Tm. The extinction coefficient was calculated using the relation [17, 19]

$$k = \frac{\alpha\lambda}{4\pi} \quad \text{..... (8)}$$

Where, α, λ are the absorption coefficient and wavelength.

Fig. 6 and 7. shows the variation of both k and n with wavelength for the layers grown with different tin concentration. The refractive index of the films varied in the range 2.27-2.89 with the change of increase tin concentration from 0.5M to 0.7M. The extinction coefficient of the films increases the range of 0.31 to 0.48 with the increase of tin concentration. An extinction coefficient value shows a maximum around 400 nm, which is similar to that obtained by El-Nahass et al [6].

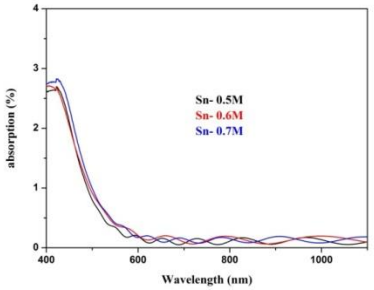


Fig. 4 Absorption spectra for SnS_2 thin films

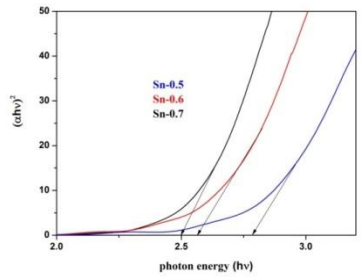


Fig. 5 $(\alpha h\nu)^2$ vs (hν) plot for SnS_2 thin films.

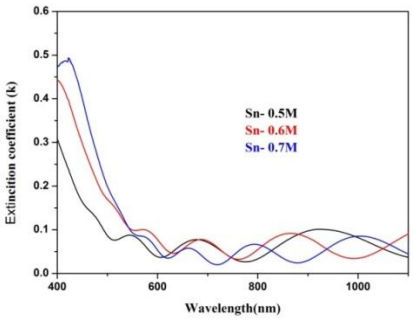


Fig.6 Extinction coefficient of SnS_2 thin films

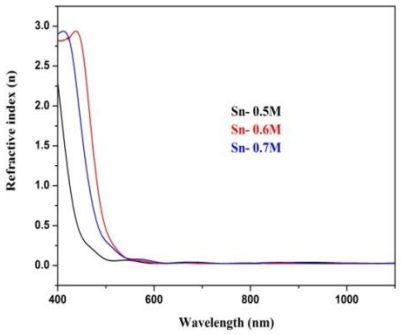


Fig.7 Refractive index (n) of SnS_2 thin films

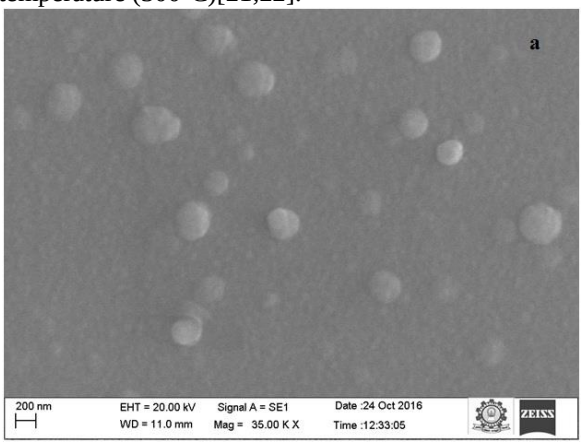
C. Surface Morphology

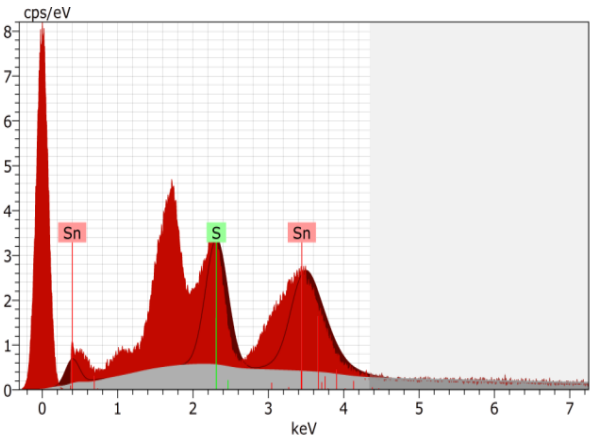
Fig 8. Shows scanning electron micrographs of SnS_2 films deposited at different tin concentration in the range, 0.5M, 0.6M and 0.7M on glass substrate. It can be observed that the grains were clearly spherical in shape and were randomly distributed over the substrate surface. The

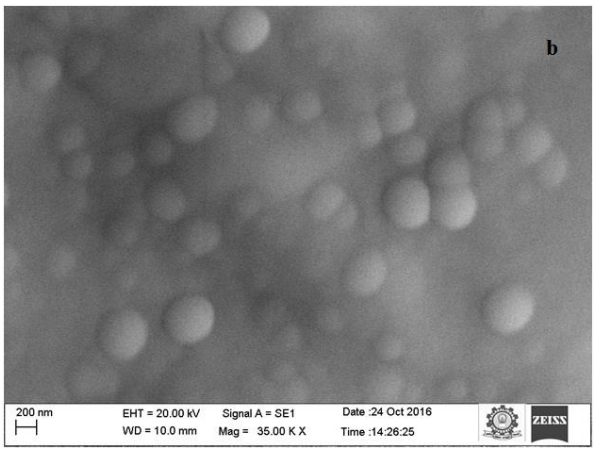
evaluated grain size increased with the increase of tin concentration. This resulted in the holding together of SnS_2 layers by van der Waals forces, which allowed the crystals to get easily cleaved perpendicular to the c-axis producing atomically smooth surfaces [13, 16]. In order to understand the distribution of size of the particles SnS_2, SEM pictures were testimony with a same magnification of 50000 x for comparison. Films seem dense with smooth and soft surface are visible [20]. The number and diameter of particle size increase with respected to tin concentration (Fig. 8a, b and c). It can be observed that SnS_2 thin films are uniform, homogeneous and cover the substrate well without any pinhole or cracks.

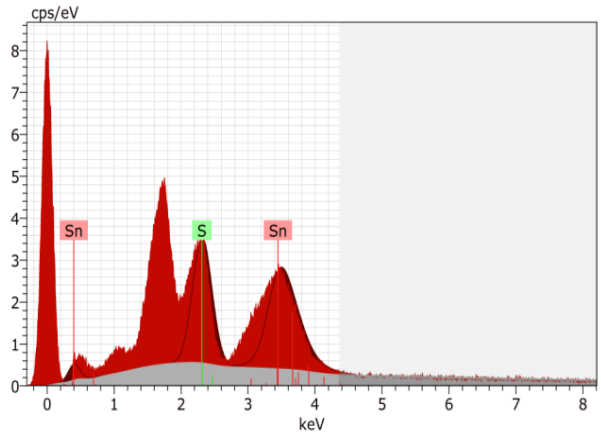
D. Chemical composition analysis

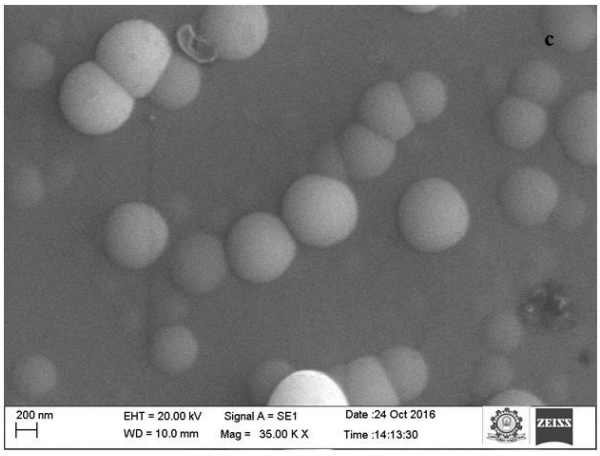
The composition of sprayed SnS thin films was estimated by EDX. The EDX spectra revealed the presence of sulfur and tin in all films. The variation of the Sn to S atomic ratio with the films were calculated from Fig. 9 and presented in Table 2. For the deposited SnS_2 thin film, its chemical composition was non stiochiometry ratio with slightly Sn-rich. The result exposed that the S content slightly decreased with the increase of the tin molar concentration in the concentration range from 0.5M to 0.7M. It was worthy of notice that the S content obviously decreased due to either Sn^{+2} vacancies or excess tin atoms generating deep acceptor states with activation energy in wide range between 0.22 and the sulfur deficiency can be explained by the evaporation of sulfur due to the substrate temperature (300°C)[21,22].











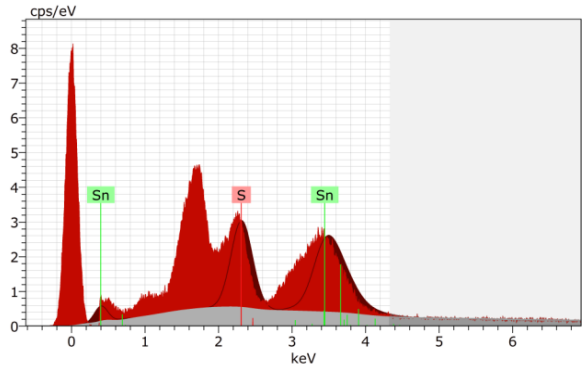


Fig. 8 Surface morphological image of SnS_2 thin films in different tin concentration a) 0.7M, b) 0.6M and c) 0.5M
Fig.9 EDAX spectrum of SnS_2 thin films in different deposited in various tin concentration

Table 2. Composition of SnS_2 films deposited at different concentration

Tin concentration	Sn (%)	S (%)	S/Sn
0.5M	40.48	59.52	1.47
0.6M	40.75	59.25	1.45
0.7M	42.70	57.30	1.34

IV I–V CHARACTERISTICS OF DEPOSITED SNS_2 FILMS

Fig 10 shows the I–V characteristics of coated SnS_2 films. It is mandatory to study the electrical properties for photovoltaic applications. The I-V characteristics of SnS_2 films were determined using 'DC' two probe method where Ag contacts was used since the substrate is non-conducting . The voltage -5 to +5V was applied which showed the ohmic nature of the film. From these plots the observed electrical resistivity of SnS_2 thin films was decreased for the tin concentration also decrease. The conductivity varies on the basis of the some criteria such as the film thickness, crystallite size and composition. The crystallite size was from 20 nm to 41 nm for various Sn concentration. The decrease in resistivity with decreased in tin concentration due to increasing in crystallite size. The electrical resistivity decreases with increase in annealing temperature reported by G.H. Tariq et al [23].

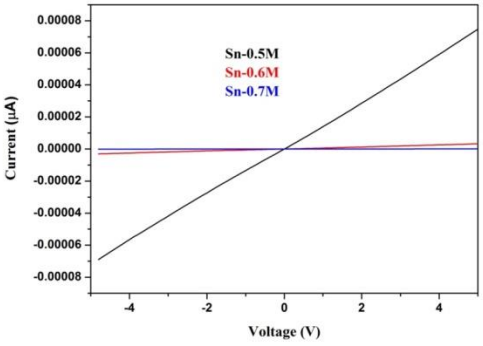


Fig 11. I–V characteristics of deposited SnS_2 films with various tin concentrations

V. CONCLUSION

Tin disulfide (SnS_2) thin films were grown by Nebulized Spray Pyrolysis (NSP) technique on glass substrate at 300°C with various tin concentrations (0.5M, 0.6M, and 0.7M). XRD study indicated that at low 0.5M concentration films are mainly composed with single phase Hexagonal SnS_2 films. The optical transmittance and the energy band gap of the layers decreased with the increase tin concentration. The films had a direct band gap that varied in the range of 2.7 to 2.97 eV. SEM study reveals that films surfaces are smooth and contain bubbles due to atom blowing up from the bulk. Surface explosion followed by material ejection are seen. The decrease in concentration of tin decreases the films resistivity which also increases the crystallite size.

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