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Effect of molar concentration on SnS thin films using chemical spray pyrolysis technique

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Abstract: Thin films of Tin Sulphide (SnS) are deposited on glass substrate at room temperature by chemical spray pyrolysis and reaction method for solar cell application. The structural, morphological and optical properties of tin sulphide thin films are analyzed by X-ray diffraction, SEM, EDAX, FTIR and UV–Vis analysis. The X-ray diffraction studies confirm that the deposited SnS films are polycrystalline structures. From the SEM micrographs, it is clear that the film possesses an almost smooth surface although some particles have been distributed on the film because of the increasing concentration. Various functional groups present in the developed thin film are investigated by FTIR analysis. The band gap energy decreases with increase in molar concentration as observed by UV–Vis studies and also it shows that the band gap decreases with the increasing particle size.

Keywords:diffraction; grain size; thin film; spray pyrolysis; transmittance.

1 Introduction

Binary semiconductors are considered as important technological materials because of their important applications in optoelectronic devices, solar cells and infrared (IR) detectors. In recent years, thin films of SnS have concentrated much attention because of their potential applications in the fabrications of photovoltaics [1] solar cells [2] and devices of optoelectronics. Their constituent elements Sn and S are abundant and are less toxic in nature. Tin monosulphide (SnS) is one of the tin chalcogenides layered semiconductors in groups IV–VI. It has a direct energy band gap of 1.3 eV which is nearer to the optimum value 1.5 eV, the bandgap required for an absorbing layer for efficient light absorption. Its absorption coefficient is comparatively higher than that of presently existing materials like CdTe [3] and CuInSe2 [4]. Its light conversion efficiency predicted from Loferski diagrams is 25% [5]. Tin sulfide (SnS) thin films exhibit p-type conductivity and optical absorption coefficient (α) > 10^4 cm^{-1} in the visible region. The optical band gap (E_g) of SnS films has been reported in the range 1.2–1.8 eV, depending on the deposition methods and crystalline structure of the films [6-9]. Different techniques are used to fabricate its thin films like: CBD [10-12], thermal evaporation [13], ultrasonic spray [14], electro deposition [15, 16], D.C. magnetron sputtering [17], electron beam evaporation [18], atomic layer deposition (ALD) [19], SILAR [20], spray pyrolysis [21] and APCVD [22] and enhanced efficiency has been achieved. Among all methods, we have chosen the chemical spray pyrolysis (CSP) method which is the simplest and has many advantages such as ahigher deposition rate and an easier operation than other methods. In the following sections, we will report a novel growth process in which p-type SnS is deposited by CSP technique using glass as a substrate at different molar concentration. Significant improvements in both the crystallin observed, optoelectronic properties of the materials are observed, and their structural, morphological, optical characterizations will be studied, by chemical spray pyrolysis method using the precursor solutions of Tin chloride dehydrates ($SnCl_2.2H_2O$) and thiourea (CH_4N_2S) with molar precursor concentration of 0.1 and 0.2M.

2 Experimental procedure:

The glass substrates are well cleaned and kept inside the furnace. The furnace was resistively heated with kanthal wire, and the temperature was controlled by a dimmer stat. A chromel–alumel thermocouple-based temperature controller is used to monitor and measure the temperature of the substrates. The inner tube of the spray nozzle was connected to the air compressor and the outer tube to the solution reservoir. The carrier gas pressure was monitored by a valve flow meter. The solution flow rate was determined with the help of a graduated burette as the reservoir. The precursor solution was prepared at two different molarities of 0.1 M and 0.2 M respectively. The precursor solutions of $SnCl_2.2H_2O$ and thiourea were dissolved separately in a solution containing de-ionized water and isopropyl alcohol in proper ratio. A few drops of concentrated hydrochloric acid were added for complete dissolution. Equal volume of these two solutions were mixed together and sprayed on to the hot glass substrates with area of 75 ×25 mm^2. The precursor solutions were

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sprayed at substrate temperature 523K and their films were prepared. The other deposition parameters like solution flow rate, carrier gas pressure and nozzle to substrate distance were kept as 3 ml/min, 0.6 kg/ cm^2 and 25 cm respectively. After deposition of these films, it was allowed to cool to room temperature, cleaned with distilled water, dried and then stored in a desiccator.

The deposited SnS film were characterized to investigate the structural property through (XRD, morphological by using SEM with compositional by EDAX, optical property through UV spectrophotometer and FTIR studies. X-ray diffractometer (PAN analytical X' Pert PRO) with CuKα radiation in the Bragg angle range of 10–80° with step size 0.0500 was used for structural study. EVO 18 Carl ZEISS scanning electron microscope attached with EDAX was used to analyze the morphology and elements presented in the film.

A double- beam UV– Vis–NIR Spectrophotometer (Lambda Perkin Elmer) was used in the range 500–1100 nm to obtain transmittance and absorption spectra of the film and to calculate the optical band gap of the film. The IR spectra of the thin films prepared at different temperatures were measured by a Thermo Nicolet 380 FTIR spectrophotometer over the spectral range from 400 to 4000 cm^{-1} wave number to study the vibrational positions of atoms of thin film.

3 Results and discussion

3.1 XRD analysis:

X-ray diffraction (XRD) patterns of SnS films deposited with different molar concentrations such as 0.1and 0.2 M are shown in Fig.1. XRD pattern shows that the strong and dominant peak of (400) for 0.1 M with JCPDS no: 75-2115 and (040) for 0.2 M with JCPDS no: 75-1803 which gives the preferential orientation for the growth of SnS crystallinity with orthorhombic structure. The other SnS diffraction peaks are corresponded to (003), (215) and (260) orientations at 2θ = 22.6°, 66.47° and 66.43° with orthorhombic structure. The corresponding peak (001) indicates the presence of SnS_2 at 2θ = 15.14° and 15.17°, for 0.1 M and 0.2 M, with low peak intensity that shows the agglomeration may be formed. The thickness of the film increases from 785 nm to 924 nm to increase the precursor molar concentration from 0.1 M to 0.2 M. It was noticed that the unit cell volume is increased with increasing molar concentration of precursor that may be determined as development of stress due to non-hydrostatic pressure [23]. The crystallite size (D) of SnS films were investigated using XRD data by utilizing the Debye Scherer's relation [24]:

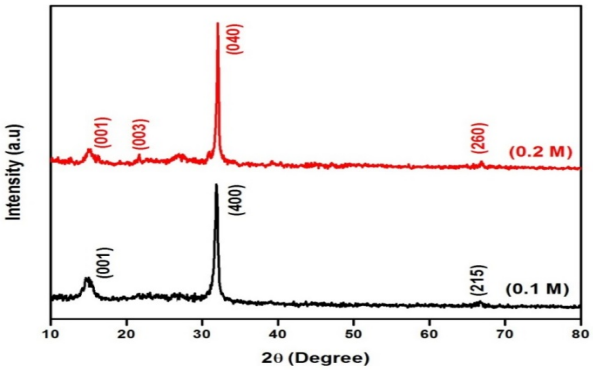

Fig. 1: XRD pattern of SnS thin films prepared at different molar concentration.

$$D = \frac{0.9\lambda}{\beta cos\theta}$$

The dislocation density (δ) of a film can be estimated from crystallite size using Williamson and Smallman's formula [25].

$$\delta = \frac{1}{D^2}$$

Microstrain (ε) of the SnS films can be calculated [26]

$$\varepsilon = \frac{\beta cos\theta}{4}$$

Table 1: Lattice parameter of SnS films in different molar concentration.

Molar concentration (M)	Crystallite size D (nm)	Dislocation density (δ)	Microstrain (ε)
0.1	11.84	18.46	19.94
0.2	17.86	7.28	13.89

Table 1 shows the values of crystallite size D, dislocation density δ and microstrain ε for the prepared SnS thin film at different molar concentration. From the calculated values, it was clearly observed that while the molarity concentration increases, crystallite size was also increased. The dislocation density and microstrain were also reduced for the increase of molar concentration which may produce the good crystallinity for the high-quality films [27].

Table 2: Structural parameters of SnS films deposited at various molar concentration.

Molar concentration (M)	Lattice parameter values (Å)						Unit cell Volume (Å)	
	Observed values			Standard values				
	a	b	c	a	B	c	Observed	Standard
0.1	11.09	3.78	4.21	11.19	3.980	4.330	176.48	192.84
0.2	4.78	11.21	3.49	4.334	11.20	3.987	187.01	193.53

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3.2 SEM analysis:

The surface morphology of the SnS thin films for different molar concentration are shown in fig 2. The effect of molar variation on the surface morphology of SnS thin film can be seen that the surface morphology was found to be affected by molar concentrations. The films are densely packed with crystallites and grown with different sizes in different directions with identified small pores. It is clearly seen that there was petal like structure at low molar concentration and it was converted spherical like structure with larger agglomeration of grains while increased the precursor concentration. This is perfectly matched with crystallite size calculated through XRD. The grain size increased as the molar concentration of precursor increased with the decrease of porous size [27, 28].

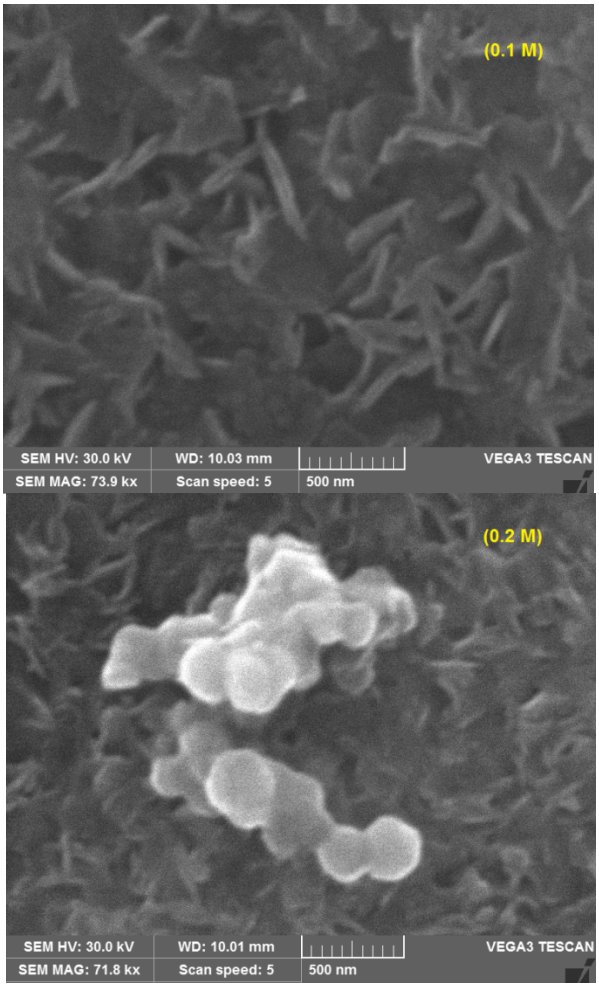

Fig. 2: SEM images of SnS film on glass substrate for different molar concentration

3.3 Composition analysis:

The EDAX profiles of the SnS thin films are depicted in Fig. 3. The results of the EDAX study given in Table 3 show the existence of Sn and S elements in the layers. The atomic ratio of Sn to S is found to be 0.99, which indicates that S is more dominant in the low molar concentrated films. Besides the Sn and S peaks, lines for Oxygen, Ca that could come from the glass substrate (not labeled here) are seen. When the molar concentration increases Sn/S ratio also increases. The present film showed p-type conductivity due tareetarehigh concentration of tin [29].

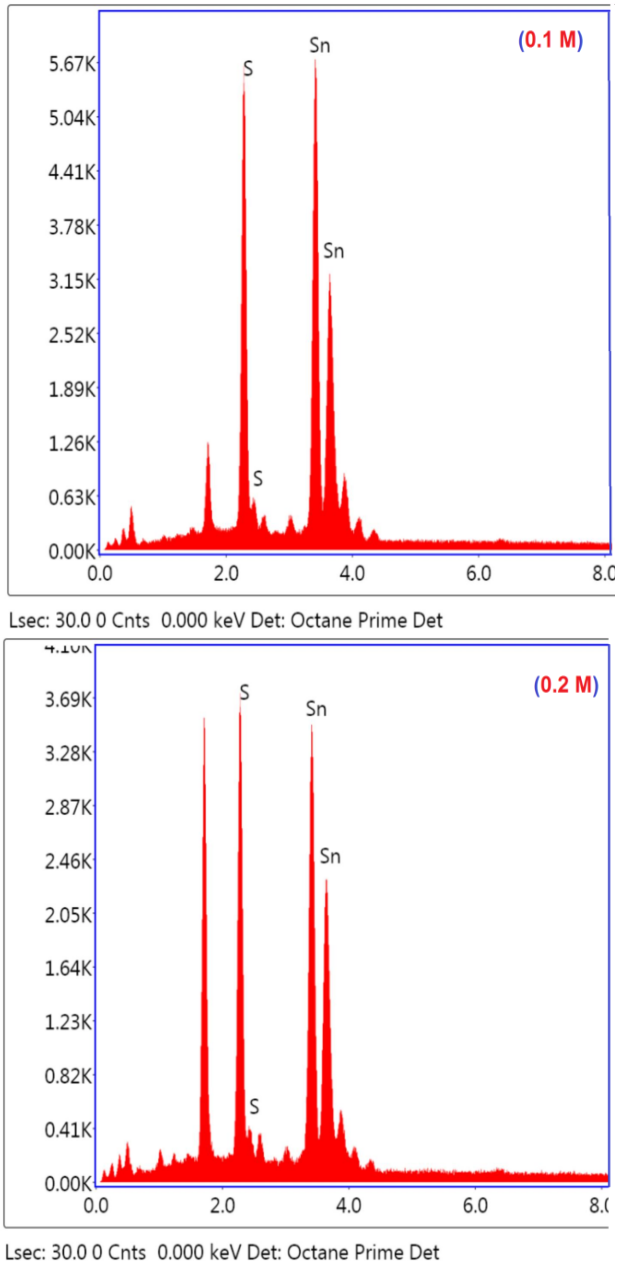

Fig. 3: EDAX spectrum of SnS thin film at different molar concentration

Table 3: Composition of SnS films by EDS at different molar concentration

Molar concentration (M)	Sn	S	Sn/S
0.1	49.87	50.13	0.99
0.2	51.48	48.52	1.06

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3.4 UV analysis:

We have used absorption spectroscopic study to characterize the optical properties of 0.1 M and 0.2 M SnS thin films. The optical absorption spectra of the SnS thin films are recorded in wavelength range 400–1000 nm shown in Fig. 4. are shown in Fig.4. The absorption analysis showed that at the starting of visible region both the samples of SnS thin films have high absorption peaks. Near the IR region, the absorption of the SnS thin films is very low. Hence the molar concentration plays a vital role to increase the absorbance property of a material in the visible region. When the molar concentration of the film increases, absorption also increases.

The optical transmittance of SnS thin films deposited by CSP onto simple glass taken in the range of 500–1100 nm is displayed in Fig. 5. We noted a high transmittance at 0.1 M precursor concentration and an decrease of the transmittance on 0.2 M concentration.

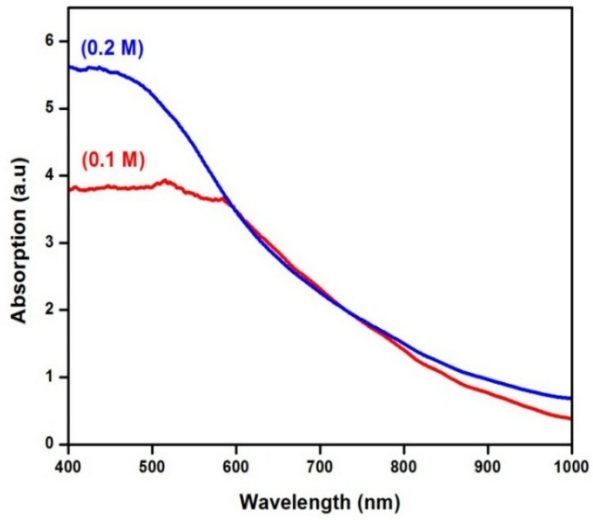

Fig. 4: Absorption spectra of SnS thin films for different molar concentration.

For all films, the transmittance starts to increase gradually at 700 nm, as characteristic for an SnS absorber layer. It is observed that transmission decreases for the increasing molar concentrations. The values are having good agreement with the reported value [30].

Band gap analysis:

The band gap energy of the thin film samples is calculated using the equation below.

$(\alpha h\nu)^n = k\,(h\nu - E_g)$

The bandgap energies for SnS thin films were obtained from optical transmission data plotting $(\alpha h\nu)^2$ versus hν at various temperatures, where αthe absorbance and hν is the photon energy. The calculated optical bandgap for both samples appears in Fig. 6. From the plotted bandgap values, the bandgap for 0.1 M and 0.2 M is 1.78 eV and 1.66 eV respectively. While the molar concentration increases, the bandgap of SnS thin films decreases [31].

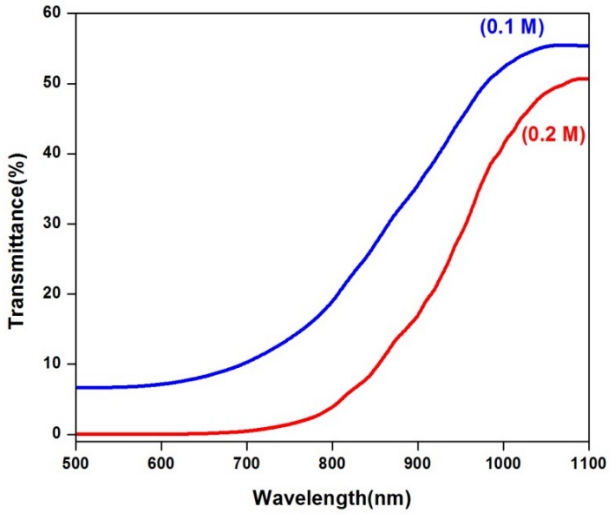

Fig. 5: Transmittance spectra of SnS thin films for different molar concentration.

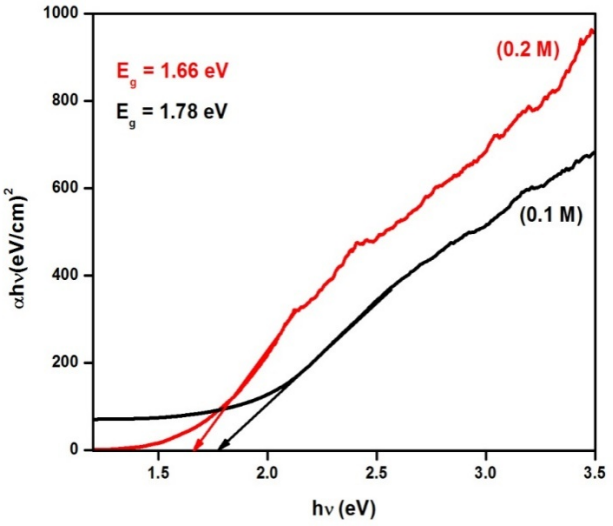

Fig. 6: $(\alpha h\nu)^2$ versus hν of SnS thin films for different molar concentration.

3.5 FTIR analysis:

FTIR spectra of SnS films of different molar concentration grown by CSP method are shown in figure 7and it was obtained in the range of 400–4000 cm^{-1}. Strong and sharp bands appear in the spectrum at 2564.53 cm^{-1}at hydroxyl group and 2915.26 cm^{-1} M at strong C-H stretching for 0.1 M and 0.2 respectively, which are due to the characteristic's peaks of SnS.FTIR spectra of tin sulphide indicate a broad band at 3743.33$cm^{-1}$and 3849.44cm^{-1} for 0.1 M and 0.2 M which corresponds to the vibration mode of O–H group [32].

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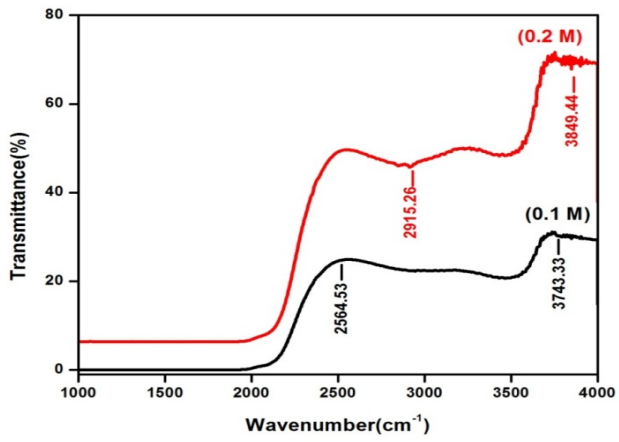

Fig. 7: FTIR spectra of SnS thin film prepared at different molar concentration

4 Conclusion:

Chemical spray pyrolysis technique has been successfully employed to fabricate SnS thin films from precursor solutions having different molar concentrations. From the structural studies, it has been found that the film coated with molar concentration had better crystalline quality. SEM images confirmed that the precursor molar concentration altered the film morphology to a large extent and the film coated with 0.2 molar concentration had better surface morphology. Optical band gap was red shifted with an increase in precursor molar concentration which may be attributed to quantum size effect. The band gap energy decreases from 1.78 to 1.66 eV for increasing molar concentration from 0.1 to 0.2 M.FTIR spectra reveals that the bonding nature of the SnS thin films. From the Results, it shows the SnS thin film is one of the potential candidates for solar cell applications.

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