Influence of tin precursor concentration on physical properties of nebulized spray deposited tin disulfide thin films

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Abstract

Tin disulfide thin films were prepared with different molarities of tin species (M_Sn) at the optimized substrate temperature using the Nebulized Spray pyrolysis technique to obtain better crystallinity with mono phase thin films. The concentration of Tin IV chloride Penta hydrate precursor is varied from 0.05:0.4 to 0.25:0.4 (SnCl_4·5H_2O; thiourea) to achieve correct stoichiometry and to tune the concentration of Tin ions in the SnS_2 thin films. These films were well adherent, uniform, and shiny. Lower concentrations of Tin yields highly textured SnS_2 thin films with (001) crystalline orientation. On increasing the concentration, the multi-phases (SnS and SnS_2) were found to be present along with SnS_2 material. The platelet-like grains were observed from SEM analysis in these SnS_2 films. Multiple interference effects were predominant in all these thin films in the wavelength region of 600–1100 nm. The direct optical band gap of tin disulfide thin films had decreased from 3.2 eV to 2.75 eV with an increase in M_Sn from 0.05 to 0.2 M, respectively, and further increased to 3.0 eV for 0.25 M concentration. Using Hall Effect measurement, the type of semiconductor is found to be of n-type. A minimum resistivity value of 2.19 × 10^2 Ω cm was obtained for the film grown at M_Sn = 0.2 M.

1. Introduction

Semiconductor thin films have fascinating application in the field of photovoltaic energy conversion [1–3]. Tin sulfide is IV–VI class of compound forming a multiplicity of phases such as SnS, SnS_2, SnS_3, SnS_4, etc. due to their varying coordinating characteristics of tin and sulfur. Amongst these semiconductors, tin disulfide (SnS_2) has CdI_2-type structure. Thin film of tin disulfide is composed of sheets of tin atoms sandwiched between two close-packed sheets of sulfur atoms [4] and has many properties like high optical absorption co-efficient (>10^4 cm^−1) in the visible region [5], n-type electrical conductivity [6,7], wide optical band gap [8], etc. These properties support the use of this material as a window layer in thin film solar cells [9]. Ozin and co-workers [10] reported that excellent gas sensors can be fabricated for sensing NH_3, H_2S, or alcohols with nanoporous SnS_2.

Thin films of SnS_2 were fabricated by various techniques like close-spaced sublimation [11], sulfurization of metallic precursors [12], atmospheric pressure chemical vapor deposition [13], chemical vapor transport [14], chemical deposition [15], vacuum evaporation [16,17], dip coating [18,19], solvothermal process [20], chemical spray pyrolysis [21,22] and each method has its own characteristic advantages and drawbacks in producing homogeneous and defect-free thin film. Among them, nebulized spray pyrolysis method is principal to prepare tin disulfide thin film, which is a low-cost method that can be used to coat uniform deposition on large surface area [23] with less solution wastage. Since this new nebulized spray pyrolysis method is capable of producing mist-like sprayed particles of the precursor solution, nanostructured morphological surface with distinct semiconductor properties were anticipated. In the present study, it is desired to prepare and characterize tin disulfide thin films on amorphous glass substrates at different Tin (M_Sn) precursor concentrations using the precursor solutions of Tin tetra chloride penta hydrate and thiourea by nebulized spray pyrolysis technique. As the substrate temperature was optimized earlier, these films of SnS_2 were prepared at that substrate temperature by changing the concentration of both cation and anion precursor solutions, keeping the ratio of precursors of cation and anion species as 1:2 always.

2. Experimental detail

Tin disulfide thin films were deposited onto amorphous glass substrates with different precursor concentrations of tin species by modified spray pyrolysis technique using the nebulizer (generally used by asthma patients). The ratio of molarities of thiourea solution was kept constant at 0.4 M. A detailed description of the mechanism of nebulized spray...
The pyrolysis method has been given by Raj Mohamed et al. [24]. The precursor solutions of tin tetra chloride penta hydrate (M₅Sn₄) (SnCl₄·5H₂O) and thiourea (M₃) (CS (NH₂)₂) were prepared separately using a solvent containing de-ionized water and isopropyl alcohol in 3:1 ratio, respectively. Two drops of concentrated hydrochloric acid were added for complete dissolution. An equal volume of Tin tetra chloride penta hydrate and thiourea solutions were mixed together and sprayed onto the hot glass substrates with an area of 75 × 24 mm². The deposition parameters like the substrate temperature, carrier gas pressure, volume of the solution, and nozzle to substrate distance were fixed as 523 K, 0.8 Kg/cm², 15 ml, and 1 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 crystal structure of these films was examined by the X-ray diffraction (XRD) pattern recorded using XPERT PRO diffractometer using Cu Kα radiation (k = 1.5406 Å). The scanning angle 2θ was varied in the range of 10–60° in steps of 0.05°. The absorption spectrum was recorded in the wavelength range 350–1100 nm using Shimadzu-UV 1800 model double beam spectrophotometer. Photoluminescence emission spectra of the as-deposited samples were obtained using a HITACHI F 7000 Fluorescence spectrophotometer. The surface morphology of the as-deposited SnS₂ thin films was recorded with a magnification of about 20,000 by CARLZEISS (EV018) scanning electron microscope with a working distance of around 10 mm and the chemical composition of the films was recorded with the same instrument. The room temperature mobility, Hall co-efficient, and effective carrier concentration were determined using an automated Hall Effect system (ECOPIA HMS – 3000) with Van-der paw configuration. The activation energy values were calculated using the conventional four probe method in the temperature range 40–100°C.

### 3. Results and discussion

The color of the thin film prepared with 0.05 M concentration was pale golden yellow with less adhesion to the substrate. Thin films prepared with 0.1 M, 0.15 M, and 0.2 M concentrations had good adherence and were golden yellow in color. These films looked shiny with multiple colors due to internal multiple reflections and golden yellow in color due to transmitted light. For 0.25 M concentration, the film appeared with golden yellow color along the edges of the film and with a dark grey in the middle with good adhesion. This variation in the color may be due to light variation in the temperature of the substrate which may be evident and prominent at higher concentration. The thickness values were determined as 299, 338, 410, 555, and 520 nm for the samples prepared with the tin precursor concentrations of 0.05, 0.1, 0.15, 0.2, and 0.25 M, respectively.

#### 3.1. Structural studies

The XRD profiles of these five samples are shown in Figure 1. From the XRD profiles, all the SnS₂ thin films showed a broad peak around 14.8° with a preferential orientation along (001) plane revealing the polycrystalline nature having the hexagonal structure. The peaks corresponding to other planes of SnS₂ were not observed, indicating these SnS₂ films were highly textured. This (001) orientation was matched well with the JCPDS file no-23-0677. Panda et al. [18] reported similar peak around 14.88° for the nano crystalline SnS₂ thin films prepared by dip-coating method. The low-intensity diffraction peak was observed around 14.8° at the precursor concentration of 0.05 M. The intensity of that (001) diffraction peak with hexagonal phase became more intense and sharp with the increase in precursor concentration up to 0.2 M, which shows an enhancement of the crystallinity of the layers. Above this precursor concentration, the peak intensity of the (001) is reduced and other peaks corresponding to Sn₃S₄ and SnS materials such as 21.33° (130) and 31.53° (111), respectively, started to appear. At higher precursor concentration of tin species, the presence of multi-phases (Sn₃S₄ and SnS) along with SnS₂ phase might be due to less availability of sulfur atoms. These peaks are in good agreement with the standard JCPDS card No-72-0031 (Sn₃S₄) and 39-0354 (SnS). At higher precursor concentration of 0.25 M, the concentration of reactants reaches a saturation point after a linear
growth in the surface of the substrate and leads to the nonlinear growth in this precursor concentration. Further deposition with more concentration leads to the homogenous reaction which in turn leads to peeling of the films, therefore the thickness may reduce. This reduction in film thickness with precursor concentration can be attributed to the decrease in intensity of (001) peak.

From the XRD pattern of all the SnS$_2$ films, a hump between 20° and 40° was observed. The hump slowly decreased with the increase in precursor concentrations. At the precursor concentration of 0.2 M, the hump fully disappeared and started to appear for further increase in precursor concentration. The hump of the SnS$_2$ film was formed due to X-rays reflected from the amorphous glass substrates. It clearly shows that these SnS$_2$ films are thin. Panda et al. [18] and Sankapal et al. [8] also observed broad hump between 20° and 40°. From the XRD profiles, it was concluded that single phase material of SnS$_2$ could be prepared with cation precursor concentrations in the range 0.05–0.2 M. The lattice parameter “c” values of the (001) peak were determined to be 6.008, 5.989, 6.007, 5.959, and 6.027 Å, respectively, due to this hexagonal structure. These “c” values were comparable with the standard data report of 5.899 Å (JCPDS card No-23-0677).

The Peak position (2θ), FWHM values, and stacking fault probability (α*) present in all the samples were calculated and listed in Table 1. The crystallite size was determined using the Debye Scherrer’s formula [25].

\[
D = \frac{k\lambda}{\beta \cos \theta}
\]  
(1)

Where, \(k\) is a constant (0.94), \(\beta\) is the Full Width Half Maximum value, \(\lambda\) is the wavelength of a cu-k$_\alpha$ radiation source (\(\lambda = 1.5418\) Å), and \(\theta\) is the Bragg angle. The strain present in the SnS$_2$ thin films (ε) was calculated using the relation [26].

\[
\varepsilon = \frac{\beta \cos \theta}{4}
\]  
(2)

The dislocation is an irregularity in the crystal structure. It can strongly affect many properties of the materials. Crystalline materials contain a periodic structure with the molecules or atoms placed in repeating fixed positions and this periodicity can be determined by the unit cell parameters. The dislocation or the crystallographic defects interrupt the regular periodic lattice structure. The dislocation density (\(\delta\)) can be evaluated using relation [27].

\[
\delta = \frac{1}{D^2}
\]  
(3)

The stacking fault probability (\(\alpha^*\)) is a fraction of layers that undergo stacking sequence faults in a given crystal. The stacking fault probability affect the optoelectronic properties of the films due to the distorted lattice and was determined using the relation [28]

\[
\alpha^* = \left(\frac{2\pi^2}{45(3 \tan \theta)^{1/2}}\right) \beta
\]  
(4)

The sizes of the crystallites in all the cases are found to be in nano range (5–35 nm) and these nanocrystallites explain that the SnS$_2$ thin films have larger nucleation rate than the growth rate due to more number of nucleation centers that exist on the substrate surface [29]. The size of the SnS$_2$ crystallites found to increase from 5 nm to 35 nm with the increase in precursor concentration from 0.05 to 0.2 M. The increase in crystallite size may be attributed to the improvement of the crystallinity and an increase in the cluster formation owing to increase of precursor concentration leading to agglomeration of small crystallites. These agglomerated crystallites combine together, resulting in the formation of larger crystallites with better crystallinity. The crystallite size decreased to 13 nm when the precursor concentration was increased up to 0.25 M, where the decrease may be due to the lesser thickness corresponding to 0.2 M film thickness and hence less agglomeration among them. Kherarchi et al. [30] had reported the similar crystallite size values (12.35–16.98) on the influence of various tin molarities for SnS$_2$ thin films prepared by an ultrasonic spray technique. The crystallite size of the SnS$_2$ can be affected by so many factors such as impurities, defects, and heating conditions. Figure 2 shows the variation in the crystallite size, strain, and dislocation density of the films as a function of precursor concentrations. The lattice strain, dislocation density, and stacking fault probability of the films decreases with an increase in precursor concentration up to 0.2 M and is increased for further increasing of molar concentration. From

| Precursor concentration (M$_{Sn}$) | Peak position 2θ (degree) | FWHM | Crystallite size (nm) | Stacking fault (×10$^{-1}$ J/m$^2$) | Sn (at.%), S (at.%) | S/Sn ratio |
|----------------------------------|--------------------------|------|----------------------|------------------------------------|-------------------|------------|
| 0.05                             | 14.7434                  | 1.4400 | 5                    | 17.6                              | 30.98             | 69.02      | 2.22       |
| 0.1                              | 14.7897                  | 0.6000 | 13                   | 7.42                              | 31.4              | 68.6       | 2.18       |
| 0.15                             | 14.7447                  | 0.3600 | 23                   | 4.44                              | 32.5              | 67.5       | 2.07       |
| 0.2                              | 14.8659                  | 0.2400 | 34                   | 2.93                              | 33.5              | 66.5       | 1.98       |
| 0.25                             | 14.6954                  | 0.6396 | 13                   | 7.86                              | 35.05             | 64.95      | 1.85       |
these observations, it is clear that when the precursor concentration of tin increases, the crystallite size increases and this leads to a decrease in grain boundaries, lattice strain, dislocation density, and stacking fault probability. The decrease in grain boundaries at higher precursor concentration (0.2 M) indicates the reduction of crystal lattice imperfections and formation of high-quality films.

3.2. Surface morphology

The surface morphology of tin disulfide thin films was grown by nebulized spray pyrolysis technique with different tin precursor concentrations and was characterized and analyzed by photographing the scanning electron microscope images as shown in Figure 3. These SEM photographs were recorded with magnifications of about 20,000. The SEM images show that the surface morphology strongly depends upon molar concentrations of the tin species solutions. For the films formed with the molar concentrations of 0.05–0.2 M, the solution droplets containing tin chloride and thiourea reach the substrates where the evaporation of solvent occurs thereby forming a solid phase of SnS2 in the form of platelet-like crystallites. The platelet-shaped grains of SnS2 were spread homogeneously over the surface of the films. It has been observed that platelet-shaped SnS2 grains are found to increase in size with an increase in precursor concentrations. The definite and well-grown plate-like formation of grains was observed for the film prepared with the precursor concentration of 0.2 M. Similar platelet-shaped grains for SnS2 films were observed in the earlier reports [13,31,32]. However, the surface morphology of the film prepared

Figure 2. The variation of structural parameters with different tin concentrations of SnS2 thin films.

Figure 3. Scanning electron microscope (SEM) images of SnS2 thin films with different precursor concentrations of tin species.
with the precursor concentration of 0.25 M is distinctly different from other SEM images. The high density of clusters or heaps was randomly distributed on the surface of the film at the higher precursor concentration of tin species due to faster nucleation and their grain boundary not being clearly visible. When increasing the precursor concentration from 0.2 to 0.25 M, there is a lower probability of rearrangement of the arriving material and the inhomogeneity increases inducing the formation of clusters [33]. Such morphology may be due to the presence of multiphase (SnS and Sn$_2$S$_3$) material along with SnS$_2$ material which was evident from the XRD analysis discussed earlier.

Surface microstructures and roughness of SnS$_2$ thin films were analyzed by Atomic Force Microscopy (AFM) instrument. Figure 4(a,b) shows the 3D micrographs of SnS$_2$ films prepared at the concentration of 0.2 and 0.25 M, respectively. The 3D topographic images were recorded in a non-contact mode with an area window of 2.5 $\times$ 2.5 $\mu$m$^2$. Both the films were having vertically aligned grains which are favorable for the multiple internal reflections and led to more optical absorption. Figure 4(a,b) shows the 2D images of the films deposited at the precursor concentration of 0.2 and 0.25 M, respectively. These images agreed well with the SEM images deposited at the precursor concentration of 0.2 and 0.25 M and confirm that film surface changed from platelet-like structure to cluster-like structure. The changes in surface morphology depending on the influence of precursor concentration can clearly be seen. The root mean square roughness values are 9.668 and 11.258 nm for the films prepared at the concentration of 0.2 and 0.25 M, respectively. The SnS$_2$ thin films formed with the precursor concentration of 0.2 M showed lower surface roughness value of 9.668 nm, which leads to less light scattered by the optical surface and hence the better surface quality [34].

EDAX spectrum of tin disulfide thin film prepared with the precursor concentrations of 0.1–0.5 M was recorded in the binding energy region of 0.5–13.0 KeV as shown in Figure 5. The atomic percentage of tin and sulfur was observed as 30.98% and 69.02%, respectively, for the first sample (0.05 M). The atomic percentage of sulfur had decreased from 69.02% to 64.95% when increasing the precursor concentrations from 0.05 to 0.25 M, respectively. The nearly correct stoichiometric ratio of 33.5:66.5% was observed for tin and sulfur at the precursor concentration of 0.2 M. Panda et al. [18] reported similar stoichiometric ratio for the nano crystalline SnS$_2$. For 0.25 M precursor concentration, the atomic percentage of tin and sulfur was observed as 35.05 and 64.95%, respectively, which predicts the mixed phases of SnS, Sn$_2$S$_3$, and SnS$_2$ present in this film prepared with a precursor concentration of 0.25 M. The changes observed in the stoichiometric ratio with precursor concentration were also supported by the structure analysis and surface morphology. Variations of tin and sulfur percentage with different precursor concentrations were listed in Table 1. The deviation of S/Sn ratio from 2 is due to the incomplete reaction of all the tin atoms in the precursor solution with that of the sulfur ions present in the same precursor solution.

Figure 4. AFM images of SnS$_2$ films prepared at the tin precursor concentration of (A, a) 0.2 M$_{Sn}$, (B, b) 0.25 M$_{Sn}$. 
3.3. Optical properties

The optical transmittance spectra obtained from the recorded absorption spectra of the as-grown SnS$_2$ thin films prepared with different tin precursor concentrations are shown in Figure 6. The multiple interference effect was observed for all the five samples in the wavelength region of 600–1100 nm, which confirms the formation of uniform and smooth films. Below 600 nm, multiple interference effect was not predominant in all the films, which may be due to the absorption of such photons and hence the absence of coherence [6].

The transmittance value of all the SnS$_2$ films in the visible region and it decreased with an increase in precursor concentration from 0.05 M to 0.2 M and with further increase in the precursor concentration to 0.25 M, the transmittance had increased. The decrease in transmittance may be attributed to the increase in film thickness which leads to an inversion in loss of intensity due to absorption and scattering.

Thus the absorption coefficient “$\alpha$” of the SnS$_2$ thin film was calculated in the visible region using thickness “$t$” and the absorption spectrum. The variation of “$\alpha$” with wavelength is plotted for these SnS$_2$ thin films as shown in Figure 7. The calculated absorption coefficient value for SnS$_2$ films exceeds $10^4$ cm$^{-1}$, which indicates that the layers were with high absorption value. Hence, the layers might be suitable for photo voltaic devices [35]. The absorption is more for high-energy photons in the recorded region for this SnS$_2$ material. A similar absorption co-efficient value had been reported by Wang et al. [31].

The optical band gap ($E_g$) can be determined from the absorption co-efficient ($\alpha$) and photon energy ($h\nu$) by the equation.

Figure 5. Energy dispersive spectrum of SnS$_2$ thin films with different precursor concentrations of tin species.

Figure 6. A plot of transmittance spectra of SnS$_2$ thin films with different concentrations of tin species.
where $A$ is a constant, $h$ is plank's constant, $\nu$ is the frequency and $p$ has 2, 3, $\frac{1}{2}$, and $\frac{3}{2}$ values for allowed indirect, forbidden indirect, allowed direct, and forbidden direct transitions, respectively. A graph was plotted against $(\alpha h \nu)^2$ and photon energy $(h \nu)$ as shown in Figure 8. The straight line portion was extrapolated to photon energy axis to give $E_g$. The direct optical band gaps of SnS$_2$ thin films were found to be 3.02, 2.98, 2.78, 2.75, and 2.8 eV, respectively, corresponding to increase in precursor concentrations from 0.05 M to 0.25 M. Fadavieslam et al. [36] had reported similar direct optical band gap values from 2.41 to 3.05 eV for SnS$_2$ thin films as a function of deposition conditions on the physical properties by spray pyrolysis method. Kherchachi [30] had studied the same band gap value ranged from 2.53 to 2.88 eV for SnS$_2$ thin films grown by ultrasonic spray pyrolysis method. The direct optical band gap values decreased to a minimum of 2.75 eV at 0.2 M with an increase in precursor concentration from 0.05 M and with the further increase in the precursor concentration to 0.25 M, the band gap value had increased to 2.8 eV. Generally, the decrease in optical band gap may be attributed to the increase in crystallite size [37], thickness and crystallinity [38], roughness, and grain size. In the present study, it is believed that the increase in crystallite size and crystallinity is accountable for the decrease in the band gap, which is evidenced by XRD results. The increase in band gap at 0.25 M can be attributed to the decrease in thickness as well as the crystallite size at that concentration comparing to 0.2 M, leading to its corresponding electronic structure. Since, the peak heights corresponding to Sn$_2$S$_3$ and SnS phases are very small compared to that of SnS$_2$, the presence of those materials corresponding to those two phases other than SnS$_2$ will be very small. The band gap of values of Sn$_2$S$_3$ and SnS are of the order of 1.64 eV [39] and 1.51 eV [40], respectively. The 2.8 eV band gap of 0.25 M film is more than that of 0.2 M film (2.75 eV). This shows that the presence of other two phases does not have any influence on the band gap of SnS$_2$.

In general, the luminescence property of the films has a close relation with the film crystallinity because the density of defects in film reduces with an improvement of the crystallinity. The PL emission spectrum for all the samples was measured in the wavelength range of 400–550 nm at an excitation wavelength of 255 nm. PL spectra of the SnS$_2$ thin films deposited at various Sn molarities are shown in Figure 9. All the SnS$_2$ films exhibit a strong luminescence peak near band edge emissions (NBE) at 455 nm (2.75 eV) (blue) due to recombination of bound excitons. All the films show only the NBE peak in the visible region and IR and UV emission peaks were not observed in these films indicating a good optical quality of the SnS$_2$ thin films.
films. It is seen from the figure that the NBE emission peak very slightly shifted toward higher wavelength side when the precursor concentration is increased up to 0.2 M and with further increasing the precursor concentration it shifted toward lower wavelength side. This result is well matched with the optical band gap values. This result reveals that the peak is maximum for the sample prepared with the precursor concentration of 0.2 M. The single emission peak in the present study may indicate the compound SnS\(_2\) prepared by this nebulized spray pyrolysis technique is free from above defects like sulfur vacancies and interstitials tin atoms. It reveals the fact that no impurity levels or defect levels were present within the forbidden band gap. Wang et al. [41] had reported the PL emission peak at 420 nm for the SnS\(_2\) nanocrystallites. The gradual increase in peak intensity was observed with increasing the precursor concentration up to 0.2 M. The increase in peak intensity with an increase in precursor concentrations indicated the development in crystalline quality and hence an increase in density of free excitons [42]. The decrease in peak intensity was observed in PL spectra when the precursor concentration increased up to 0.25 M. As the thickness decreases, the number of molecules and hence the population will decrease which in turn decreases the peak height.

3.4. Electrical properties

The electrical resistivity, carrier concentration, and Hall coefficient of SnS\(_2\) thin films grown at different precursor concentrations were determined by Hall Effect measuring instrument at room temperature and the corresponding values are given in Table 2. The resistivity of the SnS\(_2\) thin films decreases from 585 \(\times 10^3\) \(\Omega\) cm to 2 \(\times 10^5\) \(\Omega\) cm with the increase in precursor concentration from 0.05 M to 0.2 M. The decrease in resistivity may be attributed to the increase in crystallite size which leads to a decrement in the trapping states at grain boundary [43]. The grain boundary plays an important role between the crystallites and the carrier transport. It can act as a trap center in an incomplete atomic bonding, which depletes the free charge carriers and as a resultant, more number of free carriers become immobilized as trapping state increase. The resistivity again increases to 9 \(\times 10^5\) \(\Omega\) cm, while the precursor concentration had increased to 0.25 M. These thin films are found to exhibit n-type electrical conduction. The Hall mobility and bulk carrier concentration increases with increase in precursor concentration up to 0.2 M and decreases with the further increase in precursor concentration.

The activation energy of the SnS\(_2\) thin films was calculated as a function of precursor concentration of tin species in the range of 0.05 M to 0.25 M by determining the resistivity of each sample at different temperatures and using the equation.

\[
\rho = \rho_0 \exp \left(\frac{E_a}{KT}\right)
\]

Where \(\rho_0\) is a pre-exponential factor and \(E_a\) is the activation energy. The Arrhenius plot was drawn with these data as shown in Figure 10. The activation energy for SnS\(_2\) thin films were calculated as 0.6 eV, 0.38 eV, 0.26 eV, 0.11 eV, and 0.13 eV corresponding to 0.05 M, 0.1 M, 0.15 M, 0.2 M, and 0.25 M precursor concentrations, respectively. Vijayakumar et al. [22] also had reported the activation energy of 1.12 eV for amorphous SnS\(_2\) film. The present result shows deeper donor impurity level similar to the previous author [22]. It was found that the activation energy values decreases with increase in precursor concentration up to 0.2 M and then increases for the further increase in precursor concentrations. The decrease in activation energy with the increase in precursor concentration may be attributed to the change in the electronic structure corresponding to the increase in thickness values [44]. These values suggest that the deep donor levels in lower precursor concentrations change to shallow donor levels for higher precursor concentrations in accordance with the results in the literature [6,45]. Similar activation energy values were reported by Voznyi et al. [32]. Vijayakumar et al. [22] also reported the activation energy of SnS\(_2\) film as 0.47 eV and 0.12 eV for the samples prepared at the substrate temperature of 398 K and 423 K, respectively, using spray pyrolytic method.

4. Conclusion

SnS\(_2\) thin films were prepared with different precursor concentrations of tin species from 0.05 M to 0.25 M (in steps of 0.05 M) by nebulized spray pyrolysis technique successfully. The ratio of Thiourea solution was kept constant at 0.4 M. The as-deposited SnS\(_2\) thin films were smooth, shiny, adherent, and

| Precursor concentration (M\(_{Sn}\)) | Thickness (nm) | Band gap (eV) | Resistivity (\(\times 10^3\) \(\Omega\) cm) | Carrier concentration (\(\times 10^{13}\) cm\(^{-2}\)) | Mobility (cm\(^2\)/Vs) | Hall coefficient (\(\times 10^2\) cm/Vc) |
|----------------------------------|-------------|--------------|--------------------------------------|---------------------------------|----------------------|-------------------------|
| 0.05                            | 299         | 3.02         | 90.82                                | 1.124                           | 6.114                | -5.55                   |
| 0.1                             | 338         | 2.98         | 18.24                                | 1.974                           | 17.33                | -3.16                   |
| 0.15                            | 410         | 2.78         | 10.08                                | 2.600                           | 23.82                | -2.41                   |
| 0.2                             | 555         | 2.75         | 2.192                                | 7.683                           | 37.15                | -0.82                   |
| 0.25                            | 520         | 2.8          | 9.027                                | 2.172                           | 31.83                | -2.87                   |
golden yellow in color. XRD studies showed polycrystalline nature of the films having hexagonal structured crystallites with the preferential orientation of (001) plane for the above precursor concentrations. For the precursor concentration of 0.25 M, mixed phases of Hexagonal and Orthorhombic were present. Direct allowed optical band gap was found to be present in all these SnS\textsubscript{2} thin films, which may be suitable for preparing better quality solar cells. The surface morphology of SnS\textsubscript{2} thin films was defined with platelet-like structure. The EDAX result revealed the exact stoichiometry for the SnS\textsubscript{2} film prepared with the precursor concentration of 0.2 M. The electrical resistivity of SnS\textsubscript{2} thin films had been decreased by increasing the precursor concentration from 0.05 to 0.2 M. A minimum electrical resistivity was observed as 2.19 × 10\textsuperscript{3} Ω cm for the precursor concentration of 0.2 M. These thin films were found to exhibit n-type electrical conduction. From the above results, it can be concluded that this tin disulfide thin film is a good candidate for the fabrication of solar cell and photo detector devices.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

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