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Influence of Molar Concentration on Nano Tin Disulphide Thin Films Grown by Spray Pyrolysis Technique

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Abstract: Tin disulphide (SnS2) thin films has been prepared on glass substrates by chemical spray pyrolysis technique, using the precursor solutions of SnCl2.2H2O and thiourea with different molar concentration of 0.1 M – 0.4 M in steps of 0.1 M, at the substrate temperature of 548 K. The Structural properties have been determined by X-ray diffraction (XRD), and surface morphology have been observed on the surface of these films using Scanning Electron Microscope (SEM). The optical properties of the thin film deposited was obtained, using experimentally recorded absorption spectral data as functions of the wavelength in the range of 400– 800 nm at different molar concentrations. An analysis of the spectral absorption of the deposited film revealed optical direct and indirect band gap energy for SnS2 layer. A Fourier Transform Infrared Spectroscopy (FTIR) study confirms the presence of Sn–S bonds in SnS2 film in the molecular structure.
Keywords: Thin Flm, Diffraction, Optical, Absorption, Band Gap, Crystallite.

1 Introduction

Metal chalcogenides thin films have been extensively studied due to their potential application in electronic, optical and superconducting devices [1-2]. Tin chalcogenide belonging to IV–VI compound semiconductors has been attracting considerable interest in the field of photovoltaic energy conversion [3-7]. SnS_2 is considered to be one of the most useful group semiconducting tin chalcogenides, which has found applications in opto-electronic devices, a part of solar collectors. The different phases of tin sulfide compounds such as SnS, SnS_2, Sn_2S_3, Sn_3S_4, etc. due to versatile coordinating characteristics of tin and sulfur [8-10]. Each preparation technique has its own characteristics merits and demerits in producing a homogeneous and defect free thin film. Among them, spray pyrolysis method is principal to prepare tin disulphide thin film, which is low cost and can be used to deposit uniform coatings on a large surface area [6,20].Thin films of SnS_2 have been deposited using different techniques such as vacuum evaporation [11], electro- deposition [12], electroless deposition [13,14], chemical melt growth [15], chemical vapour deposition (CVD) [16], plasma-enhanced CVD [17] and spray pyrolysis [18,19]. Each preparation technique has its own characteristics merits and demerits in producing homogeneous and defect free thin film nano materials, and new preparation methods are being evolved to produce controlled size and shape of desired morphology. The intention of this present paper is to prepare and characterize the SnS_2 thin films with different molar concentrations using $SnCl_2$ and thiourea as a starting material by chemical spray pyrolysis technique.

2 Experimental Method

The precursor solutions of $SnCl_2.2H_2O$ and thiourea were dissolved separately in a solution containing deionised water and isopropyl alcohol in a proper ratio. A few drops of concentrated hydrochloric acid were added for a complete dissolution. Equal volume of these two solutions were mixed together and sprayed on the hot glass substrates with an area of 75 x 25 mm^2. The precursor solutions were sprayed at different molar concentration (0.1 M – 0.4 M in steps of 0.1 M) and their films were prepared. The gas pressure monitoring gauge was connected to the other side of the spray head. The spray head was allowed to move

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using the controlled stepper motor system in order to achieve a uniform coating of the film on the substrate. The tin and thiourea solutions were mixed and sprayed on the glass substrate at the substrate temperature 548 K. The solution flow rate is 4 ml/min, carrier gas flow rate is 0.7 kg/cm^2 and nozzle to substrate distance is 30 cm. The golden yellow colour film is obtained with a good adhesion**.** The structural studies of the films were examined using XPERT PRO diffractometer. The SEM photograph is taken with JEOL JSM 5300 scanning microscope. The band gap analysis was studied using UV-VIS NIR X ray spectrophotometer. Fourier Transform Infrared (FTIR, Nicolet Nexus 670) spectrometers of range between 400 and 4000 cm^{-1} is used to study the structural information for possible stretching, bending and vibration modes.

3 Results and Discussions

Figure 1(a–d) shows the XRD diffraction profiles of the spray pyrolysised SnS_2 thin films with different molar concentrations of 0.1 M – 0.4 M. From Fig. 1(a), the obtained film has no definite peaks, which may be attributed to a lower concentration.

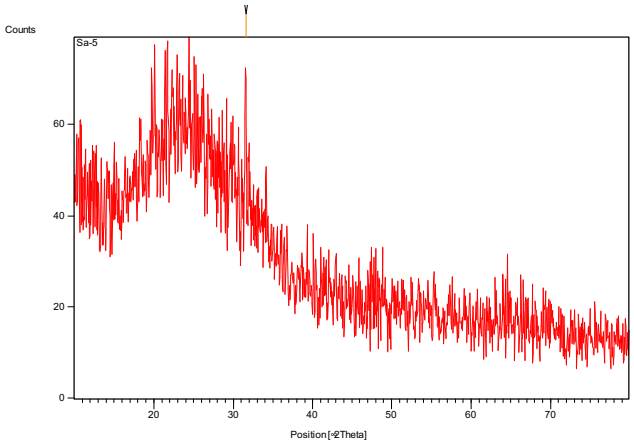


Fig. 1 (a): XRD pattern SnS_2 thin film at 0.1 M.

At a molar concentration of 0.2 M, the peak exhibits SnS_2 compound at the 2θ position of 14.527˚ [(fig 1(b)] reflection from the miller planes having indices (002), which could be assigned hexagonal structure.

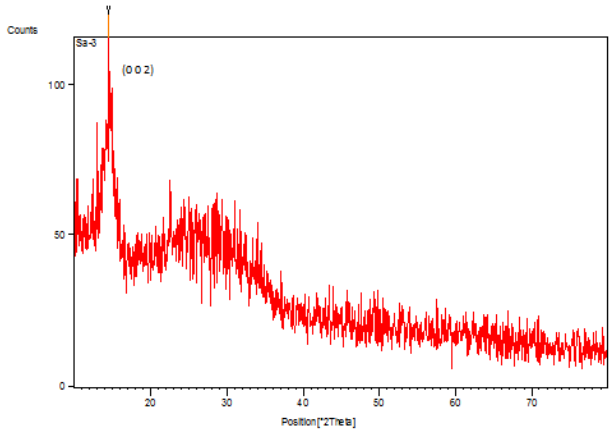


Fig. 1 (b): XRD pattern SnS_2 thin film at 0.2 M.

At 0.3 M, the peak indicates that mixed phases of SnS and SnS_2 are observed with broad Bragg peak value of 31.535˚ and 14.60 [Fig. 1 (c)], respectively. Panda et al. [21] had been observed the broad peak value of for SnS_2 thin film deposited by dip coating technique.

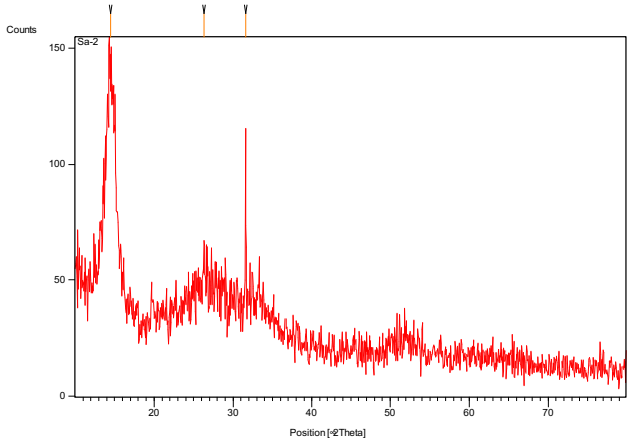


Fig. 1 (c): XRD pattern SnS_2 thin film at 0.3 M.

When the concentration increased to 0.4 M, the crystallanity with the preferential orientation growth of SnS_2 compound having hexagonal structure along (002) plane [(Fig. 1 (d)] diffracted with single prominent Bragg peak at the 2 θ position 14.446˚incresaed. The peak is obtained due to the reflections from the miller planes having indices (002) which could be assigned a hexagonal structure, by comparing JCPDS file no. 89-3198 [22].

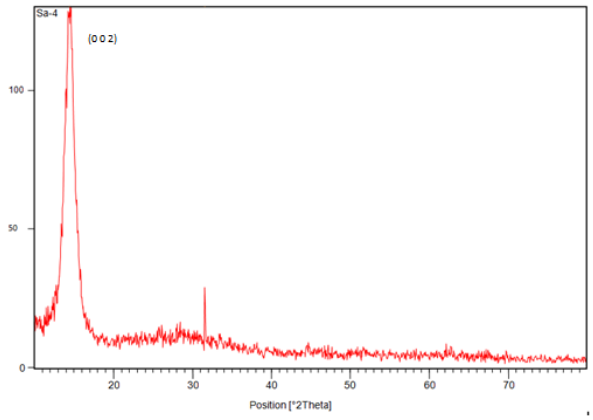


Fig.1: (d): XRD pattern SnS_2 thin film at 0.4 M.

The interplanar spacing corresponding to this peak is determined to be 6.10 A˚, which is higher than the standard value (5.90 A˚), which cannot be attributed to any other phase of tin and sulphur. The value of lattice parameter c is determined to be 12.2 A˚ due to this hexagonal structure. It is found that the unit cell of this structure in the present study is elongated in c direction while comparing with the standard report of 11.78 A˚. The elongated strain may be attributed to lower thermal energy deposition of this compound with relatively low- concentration solutions of $SnCl_2$ precursor. The authors [23-24] observed strain in their SnS_2 thin films prepared by SILAR and plasma-enhanced chemical vapor deposition methods, respectively. From the Full Width at Half Maximum (FWHM) values of the peak obtained, the size of the tin disulphide crystallites was determined using Debye–Scherrer formula [25]. The crystallite size was determined as 50.25 **A**˚ for the film grown at 0.2 M and 55.90 **A**˚ for the film grown at 0.4 M. This can be understood with the help of availability of thermal energy at a suitable molar concentration. Amalraj et al. [26] also have reported that the crystallite size of spray pyrolysised SnS_2 thin film is 63.9 A˚ at the substrate temperature of 513 K, using the precursor solutions $SnCl_4$ and thiourea.

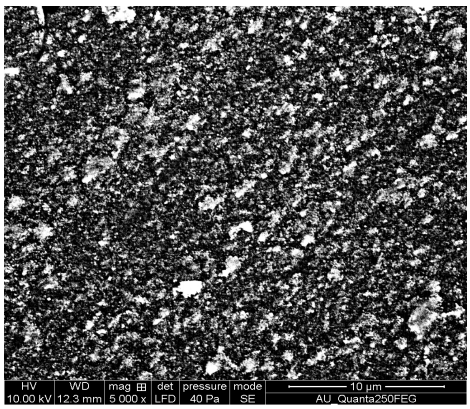


Fig. 2 (a): SEM micrograph of SnS_2 thin film at 0.2 M.

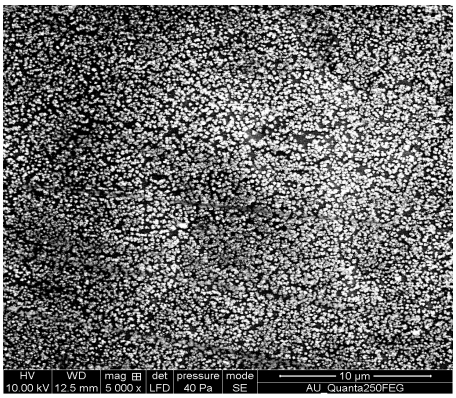


Fig. 2 (b): SEM micrograph of SnS_2 thin film at 0.4 M.

The SEM photograph is recorded on SnS_2 thin film as shown in Fig. 2 (a & b). These SEM pictures were with a same magnification of 5 k for comparison. It is seen from Fig. 2(a) that the random shaped grains with surface morphology of the film (0.2 M) were found to be of a sandy structured nature. As the molar concentration increases to 0.4 M, the nanometer sized particles decrease, which is clearly observed from Fig. 2 (b).

To study the optical properties of the deposited thin film, the optical absorption spectrum is recorded in the wavelength range 400–800 nm, using the double beam spectrometer shown in figure 3. It shows that the film has a high absorption in the range of ultraviolet, and the absorption coefficient reduces rapidly with the increase in the wavelength, when the wavelength is at 400- 700 nm and the absorption is very small, it becomes zero near the wavelength of 800 nm. It shows that the value of absorption coefficient decreases exponentially as the wavelength increases from 400 to 800 nm.

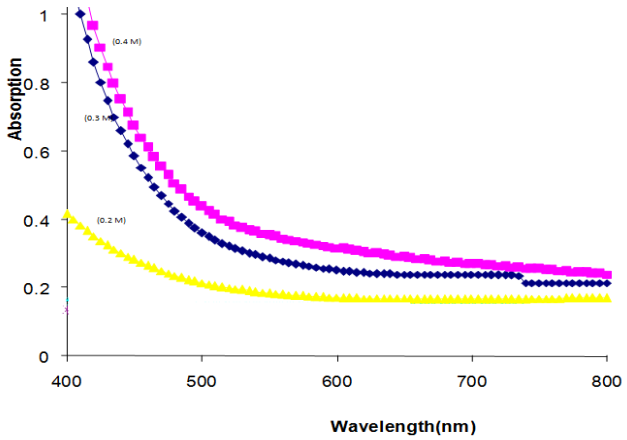


Fig. 3: Variation of absorption spectra of SnS_2 thin film.

To determine the energy band gap E_g and the type of optical transition responsible for this intense optical absorption, the absorption spectrum is analyzed using the equation for the near-edge absorption.

$$(ahv)^n = A\,(hv - E_g)$$

where A is a constant, n characterizes the transition process. We can see that n = 2 for direct allowed and n = ½ for indirect allowed transitions.

The best fit of $(ahv)^2$ versus hν and its extrapolation to $(ahv)^2=0$ given a band gap for this thin film. With the increase in of molar concentration, the direct allowed band gap values increased from 2.6 eV to 2.75 eV and indirect allowed band gap values increased from 2.25 eV to 2.45 eV. The author Domingo et.al [27] reported the wide optical direct band gap of tin disulfide thin film as 2.8 eV is in good agreement with deposited SnS_2 film.

The direct allowed band gap value have been reported by [27] for 2.8 eV and [3] for 2.6 eV. In the present study, even though the above such band gap in the ultraviolet region could not be observed due to glass substrate, a higher band gap of 2.75 eV at the molar concentration 0.4 M with direct transition obtained here can be attributed to the nano crystallite formation of SnS_2, which is evident from XRD spectrum.

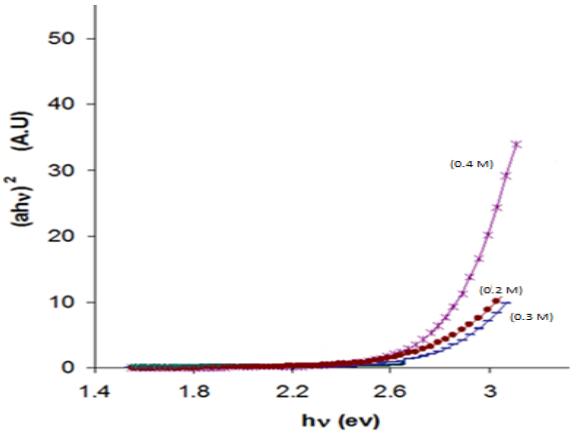


Fig. 4: A typical plot of $(ahv)^2$ against (hν) for SnS_2 thin film.

Figures 6 (a & b) represent the FTIR spectra of SnS_2 thin film with different molar concentrations. At 0.2 M, it is observed that the O-H stretching mode is represented [Fig. 6 (a)] by the absorption band at 3710.56 cm^{-1} and 1994.82 cm^{-1}. Absorption bands belong to O-H bending mode, and the stretching is represented by absorption bands at 477.45 cm^{-1}.

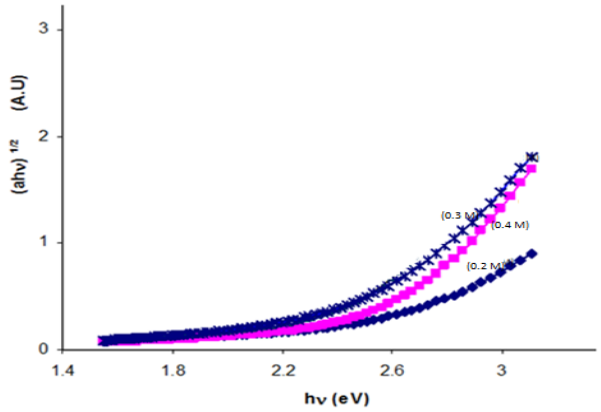
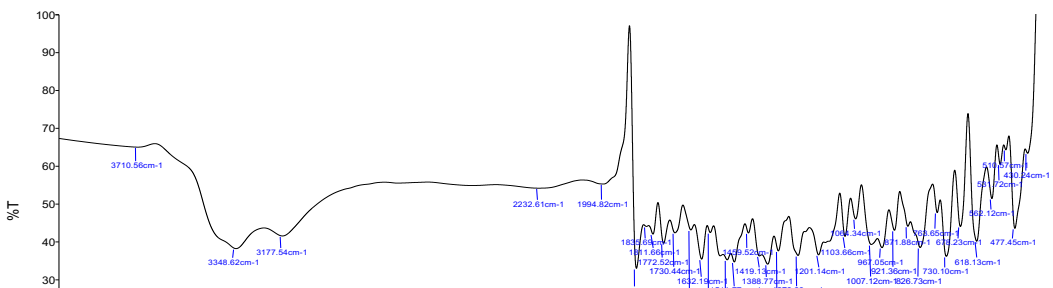


Fig. 5: A typical plot of (ahν)1/2 against (hν) for SnS2 thin film

molar concentration	Energy band gap (eV) (direct allowed)	Energy band gap (eV) (indirect allowed)
0.2 M	2.6	2.25
0.3 M	2.65	2.3
0.4 M	2.75	2.45



At 0.4 M, it is observed that the O-H stretching mode is represented [Fig 6(b)] by the absorption band at 3344.36 cm^{-1} and 1859.78 cm^{-1}. Absorption bands belonging to O-H bending mode, and the stretching is represented by absorption bands at 478.79 cm^{-1}. A good agreement of results of spectra is produced by 3350 cm^{-1} for O-H stretching mode and 1657 cm^{-1} absorption bands [28].

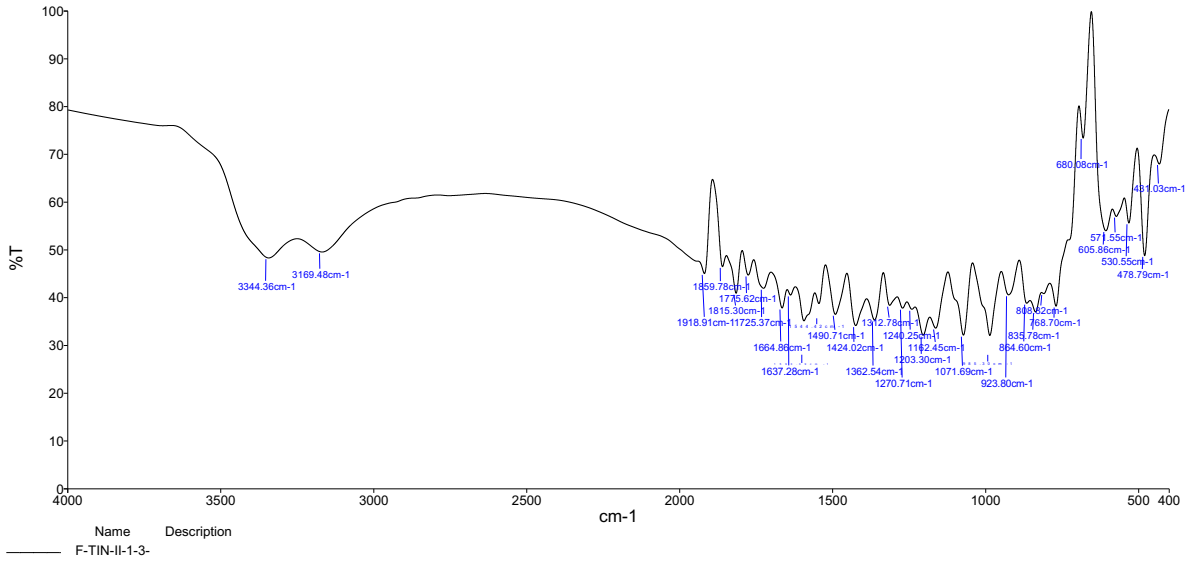


Fig. 6 (b): FTIR spectrum of SnS_2 thin film at 0.4 M.

4 Conclusions

Tin disulphide thin films have been deposited by chemical spray pyrolysis method, using tin chloride and thiourea alcoholic solution at different molar concentrations of 0.1 M – 0.4 M, in steps of 0.1 M. Polycrystalline nature of the film has a hexagonal structure grown with high preferential orientation of (002) miller plane at 0.4 M. From the full width at half maximum value of the XRD peak obtained, the size of the tin disulphide crystallites were determined. The optical absorbance spectra have been recorded for the deposited film in the visible wavelength range. The spray pyrolysised thin film shows direct allowed and indirect optical transition nature with a higher band gap values. FTIR spectrum peaks as the stretching vibration of Sn–S bonds, indicating the formation of SnS_2 film. These experimental results on the film can concluded that the materials are potential candidates for the photo detectors and thin film solar cell devices.

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