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Spray pyrolysised tin disulphide thin films at different precursor concentration ratios

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ABSTRACT

Thin films of tin disulphide on glass substrates were prepared by spray pyrolysis technique using precursor solutions of $SnCl_2.2H_2O$ (0.04 M) and n-n dimethyl thiourea (0.02 M - 0.12 M) at different precursor concentration ratios varied in the range 1:0.5 – 1:3, keeping other deposition parameters are constant. The films are found to be n type electrical conduction using hot probe technique. X ray diffraction analysis revealed the polycrystalline nature of tin disulphide thin film with hexagonal structure and a preferential orientation along (002) plane. The size of the tin disulphide crystallites was determined using the Full Width at Half Maximum values of Bragg peaks. The surface morphology had been observed on the surface of these films using scanning electron microscope. The optical absorption and transmittance have been recorded for the films in the wavelength range 400 - 800 nm. From the analysis of the absorption region data both allowed and forbidden optical transition nature was determined for the films in the above wavelength range. The electrical resistivity values in dark and light were determined with respect to the precursor concentration ratio.

Introduction

Semi conducting chalcogenide thin films have been increasing interest in the field of photovoltaic energy conversion [1-3]. Tin sulfide forms a variety of phases such as SnS, SnS_2, Sn_2S_3, Sn_3S_4, etc. due to their versatile coordinating characteristics of tin and sulfur. Amongst these semiconductors, Tin disulfide (SnS_2) is a member of class of compounds having CdI_2 type structure. It is composed of sheets of tin atoms sandwiched between two close-packed sheets of sulfur atoms [4]. It has many important properties like n-type electrical conductivity [5 - 8], high optical absorption coefficient (10^4 cm^{-1}) in the visible region [6], wide optical band gap [6-8]. The results of direct optical band gap and photoconductivity properties support the use of this material as a solar absorber in thin film solar cell and near-infrared detector [9, 10]. Ozin and co-workers [11] reported that excellent sensors might be fabricated for NH_3, H_2S, or alcohols by using nanoporous SnS_2. Thin films of SnS_2 were fabricated by various techniques like successive ionic layer adsorption and reaction [12], Atmospheric pressure chemical vapor deposition [13], chemical deposition [14, 15], vacuum vaporation [16, 17], dip coating [18, 19], chemical spray pyrolysis [5, 6] and solvo thermal process [20]. Each method has its own characteristics merits and demerits in producing homogeneous and defect free thin film [21]. Among them, spray pyrolysis method is principal to prepare tin disulphide thin film, which is low cost that can be used to deposit uniform coatings on large surface area [22]. Previous workers [23] had reported the characterization of sprayed tin sulphide thin films (SnS) at different precursor concentrations. In the present study, it is intended to prepare and characterize tin disulphide thin film on the glass substrate at different precursor concentration ratios using the precursor solutions of $SnCl_2.2H_2O$ and thiourea by spray pyrolysis technique.

Experimental details

Double nozzle sprayer was designed and fabricated by in our laboratory using glass to prepare thin film samples by spray pyrolysis method. It is a coaxial assembly of two corning glass tubes, in which the diameters of inner and outer tubes are 6 and 14 mm, respectively. Both the tubes were tapered at one end with a tapering angle of 30° to form the spray nozzle. 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 valve flow meter. The solution flow rate was determined with the help of a graduated burette as the reservoir. The precursor solutions of $SnCl_2{\cdot}2H_2O$ and thiourea were dissolved separately in a solution containing de-ionised water and isopropyl alcohol in proper ratio. The molarities of $SnCl_2{\cdot}2H_2O$ (0.04 M) and thiourea solutions were 0.02, 0.04, 0.08 and 0.12 M respectively. 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 x 25 mm^2. The precursor solutions were sprayed at different precursor concentration ratio (1:0.5, 1:1, 1:2 and 1:3) and their films were prepared. The other deposition parameters like the substrate temperature, solution flow rate, carrier gas pressure and nozzle to substrate distance were kept as 398 K, 3 ml/min, 0.7 kg/ cm^2 and 24 cm respectively. After deposition of these films, it was allowed to cool at room temperature, cleaned with distilled water, dried and then stored in a dessicator. The colour of the

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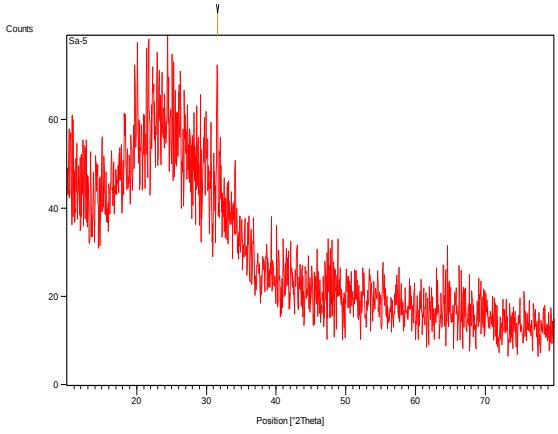
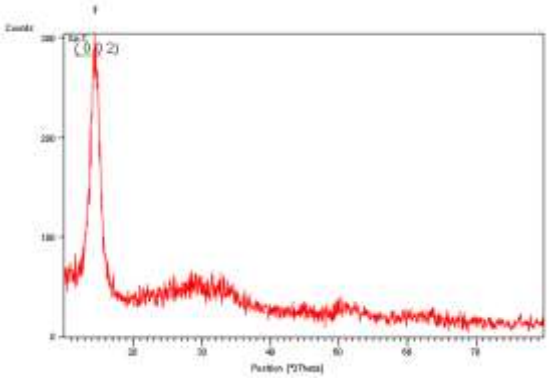
deposited thin films is golden-yellow and adheres well to the substrate. The crystal structural study of these films were examined by the XPERT PRO diffractometer using Cu K_α radiation (k = 1.5406 A°). The scanning angle 2θ was varied in the range of 10–80 in steps of 0.05°. The absorption coefficient (α) of these thin films were determined in the wavelength range 400–800 nm using Shimadzu-UV 410S model double beam spectrophotometer by recording the absorption spectrum in the above wavelength range. The spectral data was used to determine the type of optical transition and the band gap present in the sample. The dark and photo-resistivities of the samples were measured using the four-probe technique with Keithly 2000 electrometer. The type of conductivity of these semiconductor thin films was determined using the hot probe technique.

Result and discussions

Fig 1 (a) – 1 (d) showed the XRD profiles of the spray pyrolysised SnS_2 thin films with various precursor concentration ratios 1:0.5, 1:1, 1:2 and 1:3 respectively. The XRD pattern of the film at 1:0.5, (Fig.1 (a)), has no definite peaks may be attributed to lower molarity ratio. The mixed phases (SnS_2, Sn_2S_3) are observed at 2θ = 14.45° (for SnS_2) and 31.53° (for Sn_2 S_3) at 1:2 (Fig 1 (c)). At the ratio 1:3, the Bragg peaks appear at 14.49° (SnS_2) and at 26.33° and 31.58° (Sn_2S_3) is shown in the fig1 (d). The preferential orientation growth of SnS_2 compound having hexagonal structure along (002) plane at the precursor concentration ratio 1:1 with (002) preferred orientation [(Fig 1(b)] diffracted with single prominent Bragg peak at 14.52°. The Inter planar spacing corresponding to this peak is determined to be 6.09 Å, which is higher than the standard value 5.90 Å which cannot be attributed to any other phase of tin and sulphur. The value of lattice parameter is determined to be 12.18 Å 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 11.80 Å [24]. The elongated strain may be attributed to lower molarity ratio of this compound and this ratio affects the nucleation kinetics resulting in a change of critical nucleus size and the rate of nucleation [25]. Previous authors [7, 26] had 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) value of the peak obtained, size of the tin disulphide crystallites was determined and tabulated in table 1 using Debye Scherrer formula [27].



(a)



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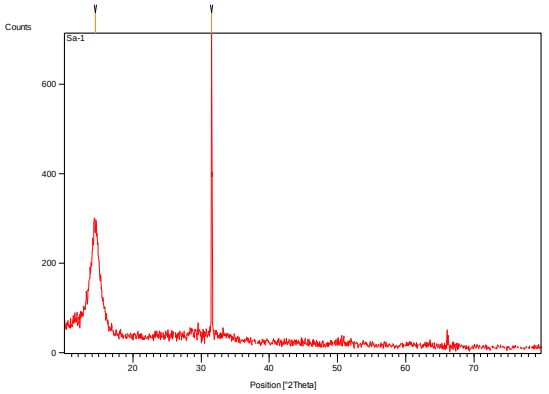
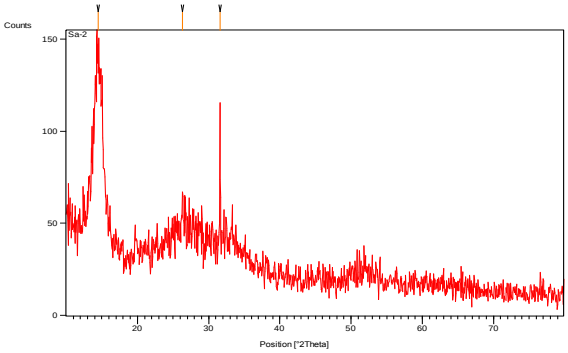


(c)



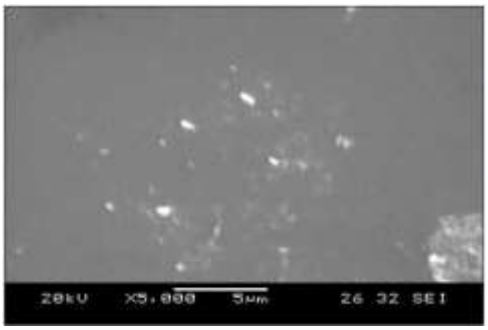
(d)

Fig 1. XRD patterns of tin disulphide thin film at (a) 1:0.5 (b) 1:1 (c) 1:2 (d) 1:3

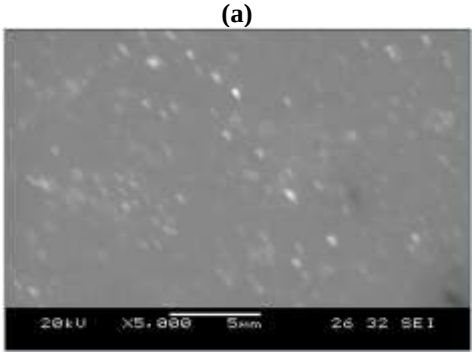
Table 1. Size of the crystallites of SnS_2 thin film at different concentration ratio

Precursor concentration ratio	crystallite size (Å)
1:1	49.5
1:2	70.0
1:3	85.5

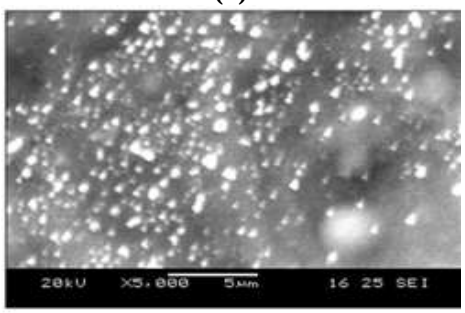
Amalraj et al. [5] also had reported the crystallite size of spray pyrolysised SnS_2 thin film is 63.9 Å using the precursor solutions $SnCl_4.5H_2O$ and thiourea. Thangaraju and kaliannan [6] reported the size of the crystallite is 115 Å and 324 Å using spray pyrolysised SnS_2 thin film on the glass substrate and FTO coated glass substrate respectively, using the same precursor solutions of present study. The present values of crystallite size are agreed closely [5] with the reported data.



(a)



(b)



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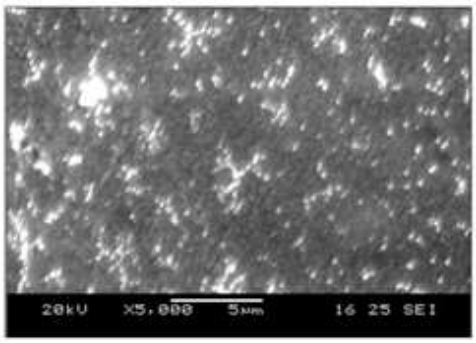

(d)

Fig 2. SEM images of tin disulphide thin film at (a) 1:0.5 (b) 1:1 (c) 1:2 (d) 1:3

The surface morphology of the thin films deposited at different precursor concentration ratios were studied and analyzed by photographing the scanning electron microscope images of the samples shown in Fig 2. These SEM pictures were recorded with a magnification 5000x. From the photograph it is clearly seen that the film composed fine grains with nanometer sized particles. The grain size is measured by the average distance between the visible grain boundaries. Each grain constitutes aggregates of several crystallites [28].

To study the optical properties of the materials, the optical absorption spectra of the film is recorded in wavelength range 400 nm – 800 nm from which the absorption coefficient is calculated and plotted (Fig 3). It varies from the value of 1.1 x 10^4 cm^{-1}. The optical transmittance spectra indicate a smooth increase and almost saturate at 85 % transmittance. This smooth increase is due to high crystalline nature of the prepared film (Fig 4).

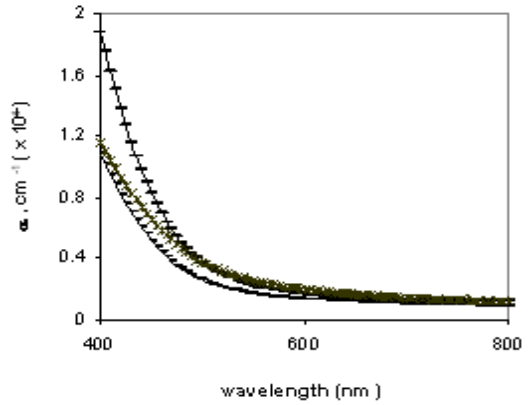

Fig 3. A plot of absorption coefficient with wavelength of SnS_2 film

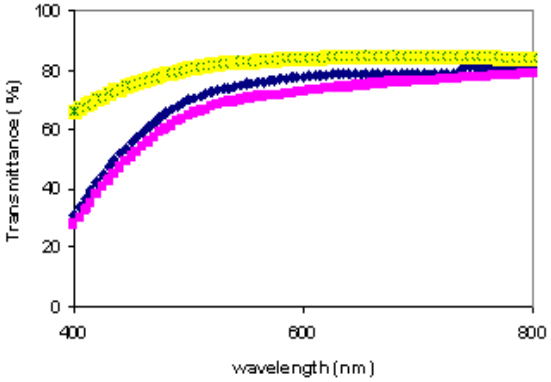

Fig 4. Transmittance spectra of SnS_2 thin film

The optical absorption spectra of tin disulphide thin film have been investigated for the evidence of either allowed or forbidden direct transition in accordance with the theory of Bardeen et al [29]

$$(\alpha h\nu)^{n} = k(h\nu - E_g \pm E_p) \quad (1)$$

An analysis of eqn.1 which relates the absorption coefficient α, with the band gap E_g as provides the information about the type of optical transition takes place in semiconductor thin films. Allowed direct transition and forbidden direct transitions are assigned when eqn (1) is substituted with n = 2 and 2/3 respectively. E_g is the direct band gap and E_p the absorbed (+) or emitted (□) phonon energy. Both $(\alpha h\nu)^2$ and $(\alpha h\nu)^{2/3}$ versus photon energy hν have been plotted in fig 5 and fig 6 respectively. The plot yields a straight line which indicates a good fit, extrapolation of the straight line to $(\alpha h\nu)^2$ and $(\alpha h\nu)^{2/3}$ = 0 gives the optical band gap values for different precursor concentration ratios and is tabulated in table 2 and 3 respectively.

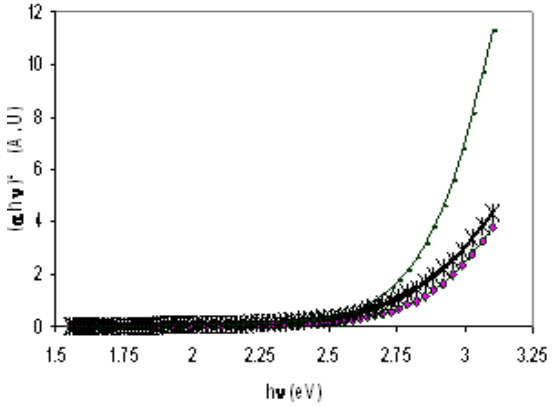

Fig 5. A typical plot of $(\alpha h\nu)^2$ against (hν) for SnS_2 thin film

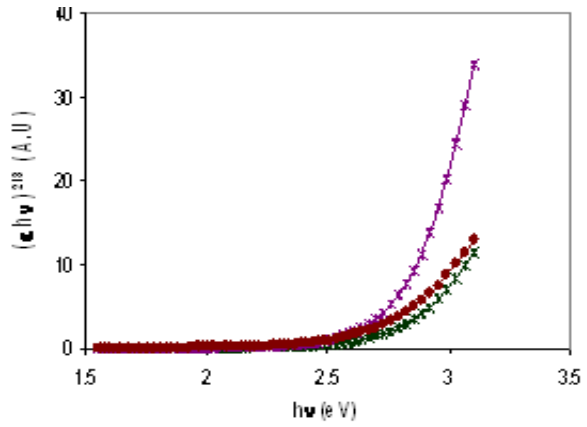

Fig 6. A typical plot of $(\alpha h\nu)^{2/3}$ against (hv) for SnS_2 thin film

Table 2. Direct allowed band gap values at different precursor concentration ratio

Precursor concentration ratio	direct allowed band gap (eV)
1:1	2.80
1:2	2.75
1:3	2.72

Optical band gap measurements on SnS_2 single crystal [30, 31] and thin film [6, 8, 14, 15, 32] have been reported by previous workers. Domingo et al [30] also had reported the wide optical direct band gap of SnS_2 thin film is 2.88 eV. Sankapal et al [8] reported the direct band gap of 2.6 eV using the precursor solutions of $SnCl_2$ and H_2S. 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 2.80 and 2.75 eV with direct allowed and forbidden optical transition obtained here can be attributed to crystallite formation of SnS_2, which is evident from XRD spectrum.

Table 3. Forbidden Direct band gap values at different precursor concentration ratio

Precursor concentration ratio	direct forbidden band gap (eV)
1:1	2.75
1:2	2.70
1:3	2.68

The type of conductivity of SnS_2 thin film prepared in the present study show n- type electrical conductivity, which agrees well with the reported literatures [5 - 8]. The DC room temperature electrical resistivity of SnS_2 thin film is determined using four probe technique at the different precursor concentration ratio and their values are tabulated in table 4.

Table 4. Electrical resistivity with respect to different precursor concentration ratio

Concentration ratio	electrical resistivity in dark ($x10^3\ \Omega-cm$)	electrical resistivity in light ($x10^3\ \Omega-cm$)
1:1	11.20	2.96
1:2	9.60	2.52
1:3	6.95	1.90

This shows the photo conducting nature of the n-type SnS_2 thin film, which could be used as a light sensitive material. The variation of resistivity of the as prepared film with respect to precursor concentration ratio was determined. A decrease in the resistivity is found as the temperature of the sample is increased which predicts the semiconductor nature in the present study. Thangaraju and kaliannan [6] had reported the dark resistivity values of spray pyrolysised SnS_2 thin film on the glass substrate is four times greater than the value of photo resistivity. Sankapal et al [8] had observed the dark resistivity of SnS_2 thin film is in the order of 10^3 Ω-cm. The reported values lie in the same range with the present data.

Conclusion

Tin disulphide thin films had been deposited onto glass substrates by spray pyrolysis technique using the precursor solutions of $SnCl_2$. $2H_2O$ and n-n dimethyl- thiourea. Film quality depends on the preparative parameters. X ray diffraction studies showed that the SnS_2 films have hexagonal crystal structure with strain are identified. The optical band gap values both allowed and forbidden transition nature are good agreement with the reported values. The dark and photo resistivity values are determined with respect to the precursor concentration ratio. These films are found exhibit n-type electrical conduction. From the above experimental results, it can be concluded that the properties of tin disulphide thin film, which are good candidate for solar cell and photo detector devices.

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