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Characterization of Spray Pyrolysised Nano Tin Disulphide Thin Film

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Abstract: Tin disulphide (SnS_2) thin film has been prepared on glass substrate by chemical spray pyrolysis technique using the precursor solutions of tin (IV) chloride and thiourea, which were atomized with compressed air as carrier gas. Thin layer of SnS_2 film has been grown at lower thermal energy of 473 K. The Structural properties have been analyzed by X-ray diffraction (XRD) and surface morphology by SEM micrograph. The optical properties of the thin film deposited were obtained using experimentally recorded transmission spectral data as functions of the wavelength, in the range of 400– 800 nm. Analysis of the spectral absorption of the deposited film revealed optical direct forbidden band gap (2.2 eV) and indirect band gap energy (2.35 eV) respectively for SnS_2 layer. The DC room temperature electrical resistivity of this film is calculated using four probe technique as 4.2 x 10^4 Ω cm in dark and 1.65 x 10^3 Ω cm in light respectively. Activation energy of this thin film was plotted by Arrhenius plot.

Keywords: Thin Film; Diffraction; Optical; Transmittance; Band Gap.

1 Introduction

Metal chalcogenides are synthesized and characterized in thin film form prepared from different techniques have attracted considerable attention for the last few decades of their potential applications in various fields. Tin chalcogenides belonging to the IV–VI group semiconductors are found to be a good candidate for optoelectronic and solar cell applications [1]. Different forms and their properties of several binary sulfides of tin compounds were studied [2]. Due to their electrical and optical properties, these binary compounds have a high potential use in optoelectronic devices and photoconductive cells [3-10]. Among them, tin disulfide (SnS_2) has layered semiconductor with CdI_2 type structure [4]. It is composed of sheets of tin atoms sandwitched between two close-packed sheets of sulphur atoms. It is an n-type semiconductor with wide optical direct band gap of 2.44 eV- 2.6 eV [2,11-17]**.** It has many interesting properties related to electrical switching and conduction mechanism [11], Raman spectral shift [15], and high optical absorption (>10^4 cm^{-1}) in the visible region [2]. Thin films of SnS_2 were fabricated by various techniques using atmospheric pressure chemical vapour deposition [14], successive ionic layer adsorption and reaction [16], chemical deposition [8,17], vacuum evaporation [7,18], chemical vapour transport [19], dip coating [4,6], chemical spray pyrolysis [2,3,20]and solvo thermal process [21]. To reduce the cost of deposition of large uniform coatings, a variety of methods are used. Among them, the spray pyrolysis technique is principal [22]. $SnCl_2.2H_2O$ is much cheaper than $SnCl_4.5H_2O$ [23]. Previous authors had reported the formation of SnS_2 thin film on the glass substrate by spray pyrolysis method using precursor solutions of $SnCl_2.2H_2O$ [2] and $SnCl_4.$ $5H_2O$ [3] at relatively higher temperatures. The formation of nano crystalline SnS_2 thin film reported [4,21] and SnS_2 nano wires [30] using other than spray pyrolysis preparation method. In the present study, an attempt has been made to prepare and characterize light sensitive SnS_2 thin film on the glass substrate with lower thermal energy and spray pyrolysis method using the precursor solutions of $SnCl_2.$ $2H_2O$ and thiourea.

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2 Experimental Details

The precursor solutions of $SnCl_2.2H_2O$ (0.3 M) and thiourea (0.6 M) were prepared using the solvent containing a mixture of deionised water and isopropyl alcohol. 20 ml solutions of each precursor were mixed together and sprayed on the hot glass substrate at the temperature of 473 K. The other deposition parameters are solution flow rate, carrier gas pressure and nozzle to substrate distance were kept as 4 ml/min., 0.7 kg/ cm^2 and 30 cm respectively. After depositing the film, it was allowed to cool to room temperature, cleaned with distilled water, dried and stored in a dessicator. The crystal structural study of the film was examined by the XPERT PRO diffractometer using Cu Kα radiation (λ = 1.5406 Å). The scanning angle 2θ varied in the range of 10° - 80° in steps of 0.05°. The SEM photograph was taken using JEOL-JSM 5300 scanning electron microscope with a magnification of 5 k to study the surface morphology. The thickness of the film sample was found using Mitutoyo- SJ 301 surface roughness profilometer. The absorption coefficient (α) of the optimized thin film was determined in the wavelength range 400 – 800 nm using Shimadzu - UV 410S model double beam spectrophotometer by recording the absorption spectrum in the wavelength range. The spectral data was used to determine the type of optical transition and the band gap present in the sample. The electrical resistivity at room temperature in dark and light was determined using four probe apparatus. The change of DC electrical resistivity with respect to temperature was analyzed using Arrhenius plot and the activation energy of this thin film was found out.

3 Results and discussion

Fig. 1 shows the x ray diffraction profile of the spray pyrolysised SnS_2 thin film on the glass substrate at the substrate temperature 473 K. The corresponding XRD pattern exhibits a single prominent peak at 2θ position 14.45°.The peak is obtained due to the reflections from the miller plane indices (002) which could be assigned hexagonal structure by comparing the JCPDS data [24]. The Interplanar spacing corresponding to this peak is 6.12 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 c is found to be 12.24 Å due to this hexagonal structure. It is found the unit cell of this structure is elongated in c direction comparing with the standard report of 11.80 Å. An elongated strain of 6.49×10^{-3} was calculated [25], which could be attributed to lower thermal energy deposition of this compound with lower concentration solutions of $SnCl_2$ precursor. Previous authors [10, 26] also had observed strain in their SnS_2 thin films prepared by SILAR and plasma – enhanced chemical vapour deposition methods respectively. From the Full Width at Half Maximum (FWHM) value of the peak obtained, the size of the crystallite formed in the nano SnS_2 thin film is calculated to be 65 nm using Debye-Scherrer formula [27]. A little bigger crystallites with sizes of 115 nm [2], 140 nm [4] and 150 nm [31] were reported for SnS_2 thin films prepared by various methods.

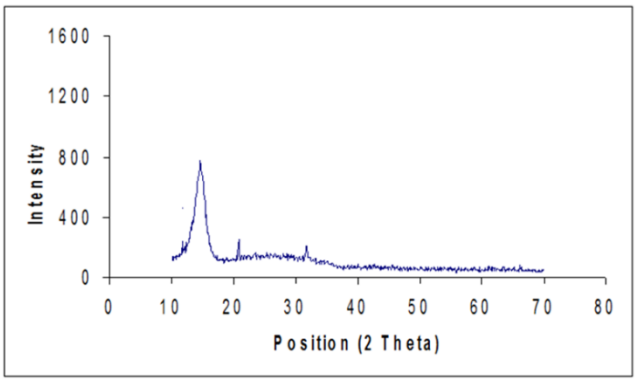

Fig. 1:XRD pattern of nano SnS_2 film at 473 K.

The SEM photograph with a magnification of 5k, recorded on the SnS_2 thin film at temperature 473 K is shown in Fig 2. Fine grained structured surface is observed and the grains are well connected with each other.

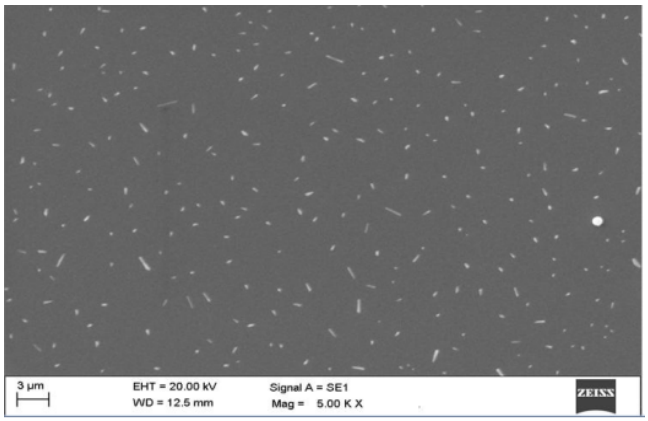

Fig. 2: SEM photograph of nano SnS_2 film at 473 K.

The thickness of the thin film is found using surface roughness profilometer as 780 nm. The optical transmittance (T) versus wavelength (λ) in the wavelength range 400 nm – 800 nm for the nebulized spray pyrolysised SnS_2 thin film is recorded and shown in Fig 3. It was observed a considerable increase in transmittance at the substrate temperature 473 K, which may due to the crystalline nature and the result was attributed by XRD analysis.

It shows that the value of absorption coefficient decreases exponentially as the wavelength increases from 400 nm – 800 nm. In the high photon energy region, the energy dependence of the absorption coefficient $\alpha \geq 10^4$ cm^{-1} suggests the occurrence of a direct optical transition is investigated by the relation [28].

$$(ah\nu)^{1/2} = k\,(h\nu - Eg)$$

where k is a proportionality constant and E_g is the direct transition band gap.

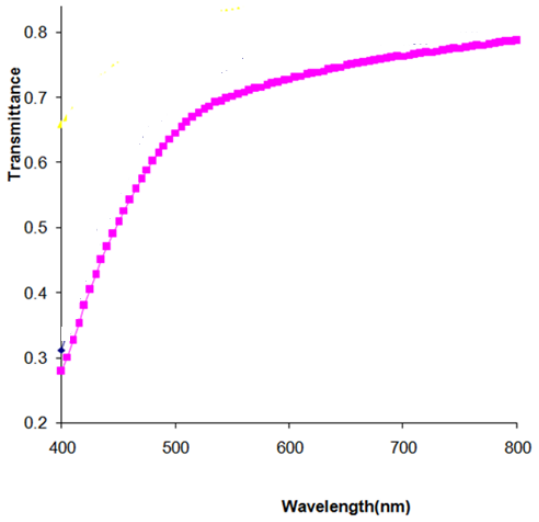

Fig. 3: Transmittance spectrum of nano SnS_2 film at 473 K.

A plot of $(ahv)^{1/2}$ as a function of energy (hv) shown in Fig 4 , yields a straight line portion in the photon energy region extending from 2.5 eV to 3.1 eV. Extrapolation of the straight line to cut the energy axis corresponding to $(ahv)^{1/2} = 0$ gives the band gap of 2.2 eV (fig 4) and $(ahv)^{2/3} = 0$ gives the band gap of 2.35 eV (fig 5) for which agrees with the reported value [3] of indirect and direct forbidden allowed transition.

Previous literatures [2,3,10,16,17,20] had reported the band gap energy of the allowed direct transitions and indirect forbidden in the range 2.2 eV – 2.6 eV of SnS_2 thin film was due to nano particles formation.

In the present study, the optical energy band gap in the ultraviolet region could not be observed due to glass substrate, a band gap of 2.2 eV and 2.35 eV with indirect and direct forbidden transition obtained here can be attributed to the nano crystallite formation of SnS_2, which is evident from XRD spectrum.

The DC room temperature electrical resistivity of this film is calculated using four probe technique as 4.2 x 10^4 Ω cm in dark and 1.65 x 10^3 Ω cm in light respectively. This exhibits the photo conducting nature of the SnS_2 thin film possessing nano grained surface, which could be used as a light sensitive material. The order of magnitude of the resistivity obtained in the present study agree with values of resistivities obtained by [16] and [2]. Joy George and Joseph [18] observed a much higher resistivity of 10^8 - 10^{11} Ω cm for 2 μm thick vacuum deposited films. The variation of resistivity of the as prepared film with respect to temperature was calculated. A decrease in the resistivity is found and the temperature of the sample is increased which predicts the semiconductor nature of the SnS_2 thin film deposited in the present study. The activation energy of SnS_2 thin film is calculated using the formula

$$\rho = \rho_o \exp(-E_a / KT)$$

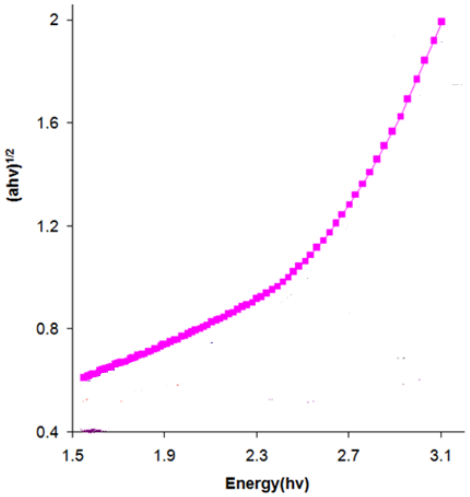

Fig .4: Indirect band gap of nano SnS_2 film at 473 K.

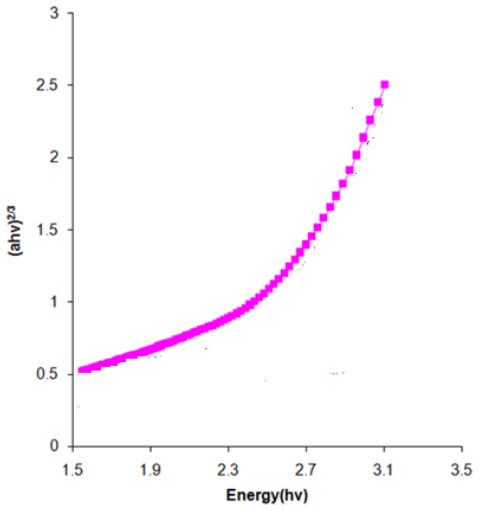

Fig. 5: Direct forbidden band gap of nano SnS_2 film at 473 K.

where ρ_o is a pre-exponential factor and E_a is the activation energy. Both are determined by the best fit of the experimental data to equation . The Arrhenius plot is drawn with this experimental data as shown in Fig 6, which can found the variation of resistivity of this SnS_2 film is being assisted by a single activation process with an activation

energy of 0.49 eV, which is equal to one-sixth of the optical band gap determined from the optical analysis. This indicates the presence of a shallow donor level, which might have been situated close to the conduction band. Amalraj et al. [3] had already reported a similar single step activation process with activation energy of 0.25 eV for the SnS_2 thin film prepared by the same method using $SnCl_4.5H_2O$ as one of the precursors. Kawano et al. [7] had observed a two- step process of activation for their vacuum deposited amorphous SnS_2 thin film.

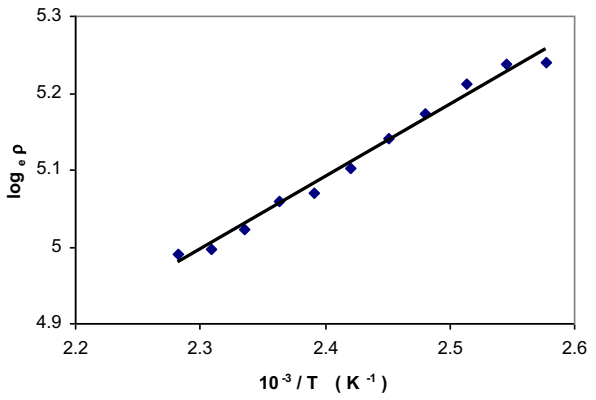

Fig.6: Arrhenius plot of nano SnS_2 thin film at 473 K.

They found activation energy of 0.26 eV below 242 K and 0.47 eV above 242 K with pre-exponential values of 0.041 x 10^2 Ωcm and 4.34 x 10^{-2} Ωcm respectively. Lokhande [17] also had observed a two-step activation process with activation energies of 0.43 eV and 1.52 eV in two different temperature regions for his amorphous SnS_2 films. The type of conductivity of the SnS_2 thin film prepared in the present study is measured using hot probe technique and it exhibit n- type electrical conductivity, which agree to the reported literatures [2, 3, 17, 27].

4 Conclusion

Golden yellow coloured thin film of nano SnS_2 with crystallite size of 65 nm has been deposited on to glass substrate by spray pyrolysis using the precursor solutions of $SnCl_2$. $2H_2O$ and n-n dimethyl- thiourea at the substrate temperature of 473 K. Polycrystalline nature of the film with hexagonal structure grown with high preferential orientation of (002) miller plane with strain is identified. A fine grained structure is observed on the surface of this thin film from the scanning electron microscopic photograph. This film is exhibit n-type electrical conduction. The thickness of the thin film is measured using stylus profilometer. This spray pyrolysised thin film shows indirect and direct forbidden optical transition nature with a band gap value of 2.2 eV and 2.35 eV. The room temperature resistivity values are determined in dark and light respectively. The photo conducting nature, which suggest that this nano SnS_2 thin film could be a potential candidate for opto- electronic as well as thin film solar cell devices.

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