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Spray Pyrolytic Deposition and Characterization of Tin Disulphide Thin Films

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Abstract: The chemical spray pyrolysis technique is employed to prepare thin film of tin disulphide (SnS_2) on glass substrate using precursor solutions of $SnCl_2.2H_2O$ and n-n dimethyl - thiourea at a substrate temperature of 548 K. Using the hot probe technique the type of conductivity is found to be n type. X ray diffraction analysis revealed the polycrystalline nature of the SnS_2 thin film with crystallites of dimension 25 nm having hexagonal structure and a preferential orientation along the (002) plane. The surface morphology has been observed using field emission scanning electron microscope (FESEM). The surface composition of the elements is analyzed with EDAX spectrum. The optical absorption and transmittance spectra have been recorded for this film in the wavelength range 400 – 800 nm. Thickness of the film and variation of absorption coefficient with wavelength is determined using these spectral data. Band gap value of 2.48 eV of direct allowed nature is observed for this pyrolysised SnS_2 thin film. The room temperature resistivity of SnS_2 thin film is found to be 5.35 $x10^5$ Ω cm in dark and 3.03 $x10^3$ Ω cm in light respectively. Activation energy of about 0.12 eV is determined by plotting a graph between log ρ (resistivity) versus reciprocal temperature. The photoluminescence (PL) measurements showed the film has an emission peak at approximately 526 nm.

Keywords: chalcogenides;spray pyrolysis; hexagonal ; band gap; resistivity.

1 Introduction

Metal chalcogenides were synthesized and characterized in thin film form prepared via different techniques have attracted considerable attention for the last few decades due to their potential applications in various fields. Tin chalcogenides belonging to the IV–VI group semiconductors are found to be good candidates for optoelectronic and solar cell applications [1, 2]. Different forms and their respective properties of binary sulfides of tin were studied [3 - 10]. Due to their electrical and optical properties, these binary compounds have a high potential use in optoelectronic devices and photoconductive cells [11]. Tin disulfide has layered semiconductor with CdI_2 type structure [4] and it is composed of sheets of tin atoms sand witched between two close-packed sheets of sulphur atoms [13]. It can exist in a number of differen polytypes [12]. It is an n-type semiconductor having a wide optical direct band gap in the range of 2.44 eV- 2.6 eV [2, 16, 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 like 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 solvothermal process [21]. To reduce the cost of deposition of large uniform coatings, a variety of methods are in use and 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 studied 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. Several authors had reported the formation of nano crystalline SnS_2 thin film [4, 21] using methods other than spray pyrolysis. In the present study, it is intended to prepare and characterize nano particle SnS_2 thin film on the glass substrate by spray pyrolysis method using the precursor solutions of $SnCl_2.2H_2O$ and thiourea.

2 Experimental Details

A glass made double nozzle sprayer was designed and fabricated in our laboratory 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

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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 $SnCl_2.2H_2O$ (0.08 M) and thiourea (0.16 M) were prepared using the solvent containing a mixture of deionised water and isopropyl alcohol. 15 ml solutions of each precursor were mixed together and sprayed on to the hot glass substrates at substrate temperature to optimize SnS_2 thin film formation. The other deposition parameters like solution flow rate, carrier gas pressure and nozzle to substrate distance were kept as 3 ml/min., 1.0 kg/ cm^2 and 20 cm respectively. After deposition of the film, it was allowed to cool to room temperature, cleaned with distilled water, dried and then stored in a dessicator. The structural characterization of deposited films was carried out by X-ray diffraction technique on JEOL JDX 803a diffractometer (monochromatic CuKα radiation, λ = 1.5406 Å). The XRD pattern was recorded in 2θ interval from 10˚ to 80˚ with the step of 0.05˚ at room temperature. The surface morphology was studied using FESEM (JEOL JSM-5000). Elemental analysis was used to determine the chemical composition of the films. The thickness of the film was evaluated using the conventional gravimetric method. Optical absorption spectrum was recorded in the range 400-800 nm using Varian-Cary 500 scan double beam spectrophotometer. Electrical resistivity at room temperature was determined using four-probe technique with Keithley 2000 electrometer. The photoluminescence spectrum was studied at room temperature using Varian Cary spectroflurometer in the spectral range 200-700 nm with a wavelength of 255 nm as the excitation source.

3 Results and Discussion

Fig. 1 shows the x ray diffraction profile of spray pyrolysised SnS_2 thin film on the glass substrate at substrate temperature of 548 K. The crystallanity with the preferential orientation growth of this compound having hexagonal structure along (002) plane diffracted with single prominent Bragg peak at the 2θ position 15.23˚. The Interplanar spacing corresponding to this peak is determined to be 5.81 Å, which is lower 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 determined to be 11.62 Å due to this hexagonal structure. It is found that the unit cell of this structure is shrinked strain in the present study in c direction while comparing with the standard report of 11.80 Å [24]. This shrinked strain may be attributed to lower precursor concentration of deposition of this compound with relatively lower concentration solutions of $SnCl_2$ precursor. Previous authors [10, 25] 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 crystallites formed in the SnS_2 thin film is determined to be 25 nm using Debye-Scherrer formula [26].

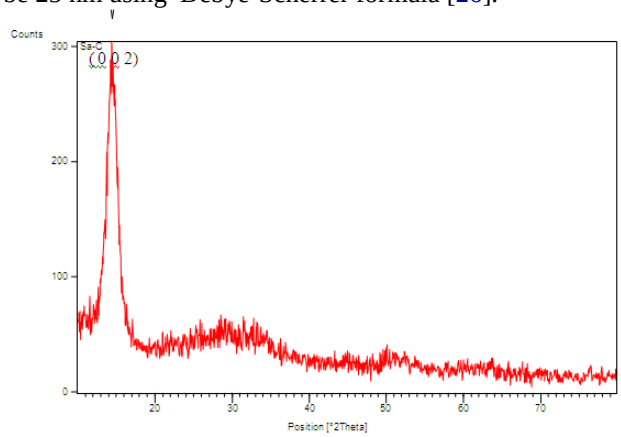

Fig 1. XRD spectra of SnS_2 thin film grown at 548 K.

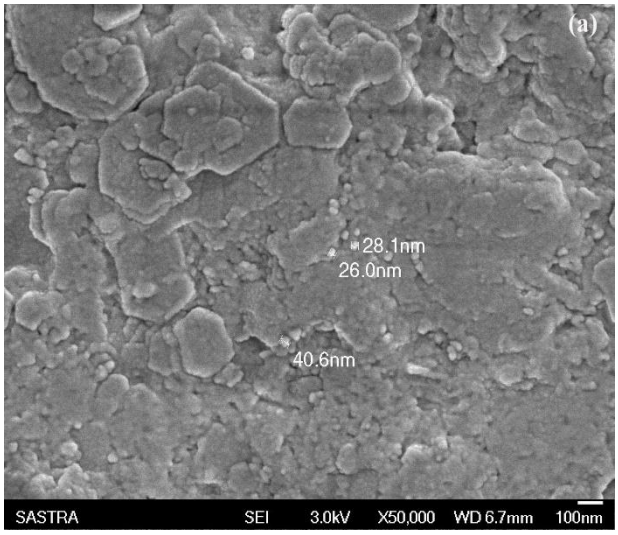

Fig 2. FESEM image of SnS_2 thin film prepared at 548 K.

The FESEM image with a magnification of 50 K was shown in Fig.2. The film deposited at substrate temperature 548 K showed the hexagonal shape grains with size of 26-40 nm. The observed grain size values from SEM image is much larger than the crystallite size measured from XRD peak. This is due to the fact that in SEM image, the grain size is measured by the distance between the visible grain boundaries. Each grain constitutes aggregates of several crystallites [27]. In XRD, the diffraction of X-ray takes place inside the tiny crystallites and hence the measured size is always in the nm range, which is very much less than the grain size measured from SEM image studies. The EDAX analysis showed that the

film formed at 548 K was sulphur rich and nearly stoichiometric as shown in fig.3, consisting of 32.48 % tin and 66.25% of sulphur which was in agreement with the

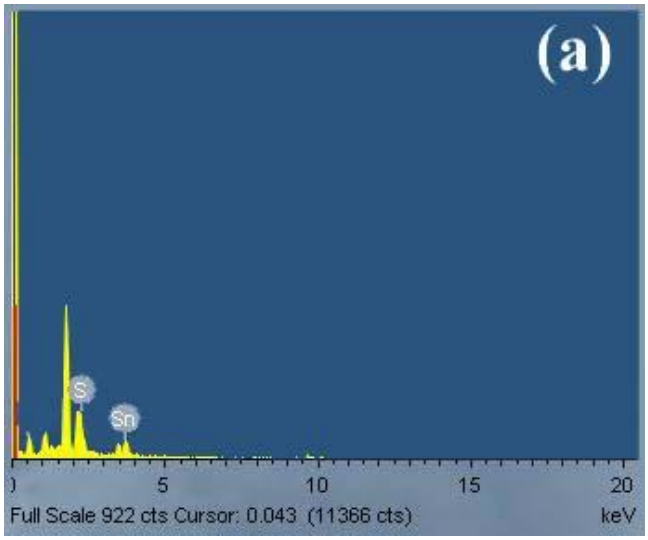

Fig 3. EDAX spectrum of the film prepared at 548 K

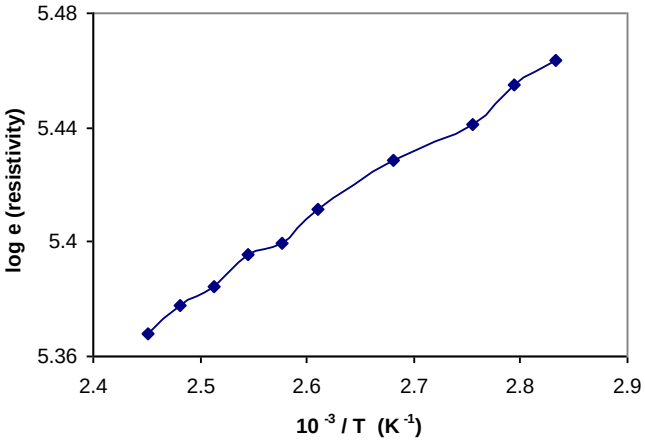

Fig 4. Variation of electrical resistivity of SnS_2 thin film at 548 K.

reported values of Amalraj et al., [3]. The film had a thickness of 474nm, measured by gravimetric method

The DC room temperature electrical resistivity of this film is determined using four probe technique as 5.35 x 10^5 Ω cm in dark and 3.03 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 agrees with the values of resistivities obtained by Sankapal et.al [16] and Thangaraju and Kaliannan [2]. Joy George and Joseph [18] observed a much higher resistivity of 10^9 - 10^{11} Ω cm for 2 μm thick vacuum deposited films.

The activation energy of SnS_2 thin film can be calculated by the formula

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

Where ρ_o is a pre-exponential factor and E_a is the activation energy, which are determined by the best fit of the experimental data to the above equation. The Arrhenius plot is drawn with this experimental data as shown in Fig 4, which it can be predicted that the variation of resistivity of this SnS_2 film is being assisted by a single activation process with activation energy is 0.12 eV, which are determined by the best fit of the experimental data. Sankapal [16] also had reported the activation energy of SnS_2 film is 0.37 eV at ambient temperature. Amalraj et al. [3] had reported a similar single step activation process with activation energy of 0.25 eV at the substrate temperature 458 K 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 SnS2 thin film. They found activation energy of 0.26 eV below 242 K and 0.47 eV above 242 K with pre-exponential values of 0.041x 10^2 and 4.34 x 10^{-2} ohm cm respectively. Lokhande [17] also had observed a two-step activation process with activation energies of 0.43 and 1.52 eV in two different temperature regions for his amorphous SnS_2 films. Such differences in activation energies may be due to varying preparation parameters and the presence of different defect states during the growth of SnS_2 thin film. The obtained activation energy of the sns_2 thin film at the substrate temperature 548 K is well agreed with the reported values [3, 7, 16, 17].

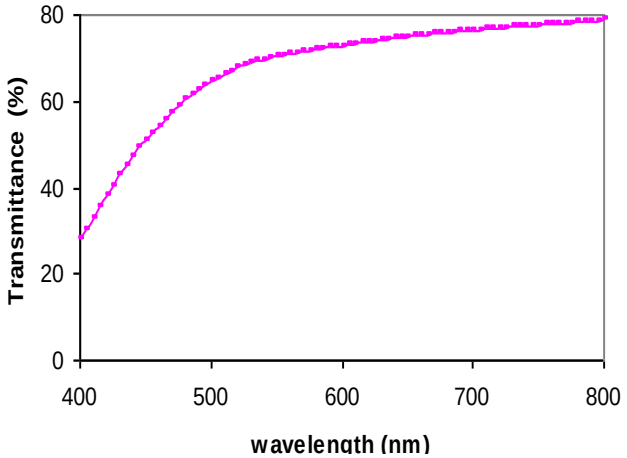

Fig 5. Transmittance spectra of SnS_2 thin film at 548 K

To study the optical properties of the materials, the optical absorption spectra of this spray pyrolysised SnS_2 thin film is recorded in the wavelength range 400–800 nm. Hence the optical transmittance (T) with respect to wavelength of

spray pyrolysised SnS_2 thin film at 548 K, which is observed that, was a considerable transmittance of 80 % (Fig 5). From the absorbance spectrum the variation of the absorption coefficient a with respect to wavelength is calculated and plotted as shown in Fig 6. It shows that the value of absorption coefficient a decreases exponentially as the wavelength increases from 400 to 800 nm. In the high photon energy region, the energy dependence of the absorption coefficient α (10^4 cm^{-1}) suggests the occurrence of direct optical transition, which is investigated by the relation [28]. The dependence of absorption coefficient on photon energy is of importance in studying energy band gap and the type of transition of electrons. The relation between the absorption coefficient (α) and the incident photon energy hν is given by $(\alpha h\nu)^2 = k (h\nu - E_g)$

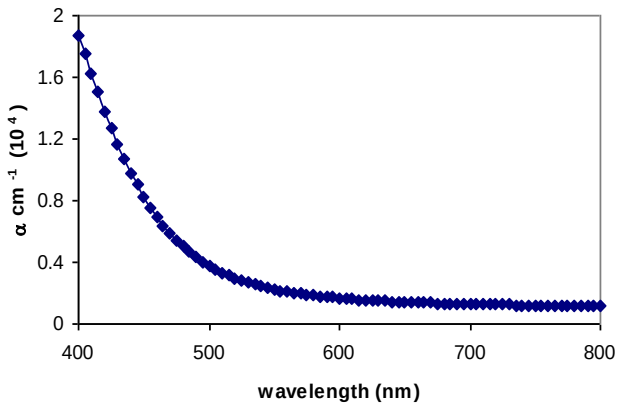

Fig 6. Absorption coefficient spectra of SnS_2 thin film at 548 K

Where k is a proportionality constant and E_g is the direct transition band gap. A plot of $(\alpha h\nu)^2$ as a function of energy (hν) shown in Fig 7, yields a straight line portion in the photon energy region extending from 2.3 eV to 2.75 eV indicates a good fit.

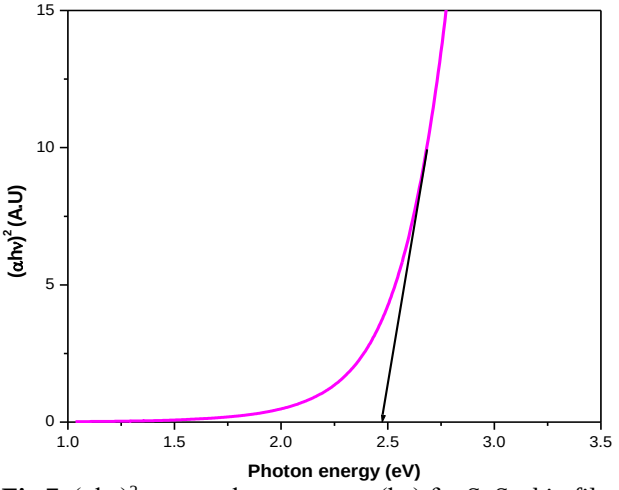

Fig 7. $(\alpha h\nu)^2$ versus photon energy (hν) for SnS_2 thin film at 548 K

Extrapolation of the straight line to cut the energy axis corresponding to $(\alpha h\nu)^2 = 0$ gives the band gap of 2.48 eV, which agrees with the reported value of 2.44 eV [2] for direct allowed transition. Previous workers [2, 10, 16, 17, 20] also had reported the band gap energy of the allowed direct transition in the range 2.2 eV – 2.6 eV. In Fig 8, the PL spectrum of the film at T_s=548 K, exhibit a luminescence peak near band emission at 526 nm due to recombination of bound excitons, whereas the occurrence of other peaks are due to impurities and defects. The PL spectrum also used to measure the energy band gap in a direct way. The value of energy band gap (E_g) obtained from PL spectrum was in agreement with the value obtained through UV- absorption spectrum.

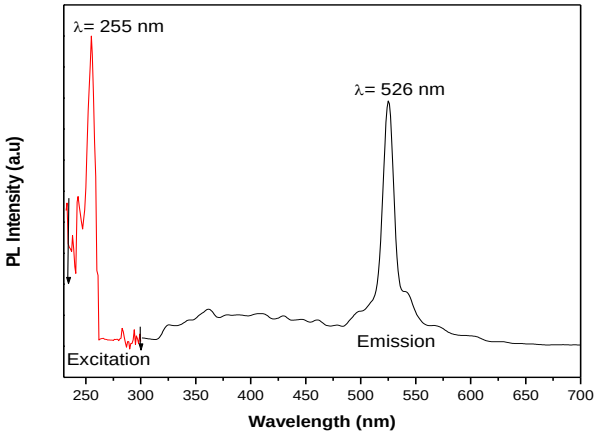

Fig 8. PL spectrum of SnS_2 film deposited at 548 K

4 Conclusion

Golden yellow coloured thin film of SnS_2 with crystallite size of 25 nm has been deposited onto glass substrate by spray pyrolysis using the precursor solutions of $SnCl_2$. $2H_2O$ and n-n dimethyl- thiourea at substrate temperature of 548 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 Field Emission Scanning Electron Microscopic photograph. This film is found to exhibit n-type electrical conduction. This spray pyrolysised thin film shows direct allowed optical transition nature with a band gap value of 2.48 eV. PL showed emission peak at 526 nm which exhibit the potential application for photovoltaic material. The room temperature resistivity values are determined in dark and light respectively and found to have photo conducting nature, which suggest that SnS_2 thin film could be a potential candidate for opto-electronic as well as thin film solar cell devices.

References

[1] H. Noguchi , A. Setiyadi , H. Tanamura , T. Nagamoto , O. Omoto , Sol. Energy Mater. Sol. Cells. **35**, 325 (1994)

[2] B. Thangaraju, P. Kaliannan, J. Phys. D: Appl. Phys. **33**, 1054 (2000)

[3] L. Amalraj, C. Sanjeeviraja, M. Ramachandran, J.Cryst. Growth. **234**, 683 (2002)

[4] S. K. Panda, A. Antonakos, Mat. Research Bulletin. **42**, 576 (2007)

[5] S. Bucchia, J. Jumas, M. Maurir, Acta Crystallogr. **B 37**, 1903 (1981)

[6] S. C. Ray, Malay K. Karanjai, D. Das Gupta, Thin solid films. **350** , 72 (1999)

[7] K. Kawano , R. Nakata , M. Sumita , J. Phys. D: Appl. Phys. **22** , 136 (1989)

[8]R.D. Engelken, H.E. Mc Claud, C. Lee, M. Slayton H. Ghoreishi , J. Electochem. Soc. **134**, 2696 (1987)

[9] N. K. Reddy, K. T. R. Reddy, Mat.Che. Phys. **102**, 13 (2007)

[10] N. G. Deshpande, A A Sagade, Y G Gudage, C.D. Lokhande, J. Alloy.Compouds **436**, 421 (2007)

[11] G. Said, P.A. Lee, Phys. Status Solidi A 15, 99 (1973)

[12] S. Acharya, O.N. Srinivasa, Physica Status Solidi A 56, K1 (1979)

[13] T. Jaing, G.A. Ozin, J. Mater. Chem. 8 , 1099 (1998)

[14] L.S.Price, I.P. Parkin, A.M.E. Hardy R.J.H. Clark, Chem.Mater.**11 ,** 1792 (1999)

[15] D.C. Mead, J.C. Irwin, Solid State Commun. **20,** 885 (1976)

[16] B.R. Sankapal, R.S. Mane and C.D. Lokhande, Mater. Res. Bull. 35, 2027 (2000)

[17] C.D. Lokhande, J. Phys. D: Appl. Phys **23**, 703 (1990)

[18] J. George and K.S. Joseph, J. Phys. D: Appl. Phys. **15,** 1109 (1982)

[19] K. Matsumoto , K. Tagaki, J. Cryst. Growth **63,** 202 **(**1983)

[20] A.K. Abass, K.J. Majeid, H.A. Jassim and W.A. Murad, Solid State Commun. **57,** 805 (1986)

[21] B. Hai,K.Tang,C.Wang,J.crystal growth **225 ,** 92 (2001)

[22] B. Thangaraju, P. Kaliannan , Cryst. Res. Technol. **35**, 71 (2000)

[23] Gordille , L C Moreno,de la Cruz W , P Teheran Thin solid films **252 ,** 61 (1994)

[24] X ray powder diffraction JCPDS file reference no. 21 – 1231.

[25] A.ortiz, A.Sanchez-juarez, J.Elec.chem.Soc, **147,** 3708 (2000)

[26] P. H. Klug, L. E. Alexander X-Ray Diff. Procedures (Wiley, New York, 1954)

[27] R.N. Panda, M.F. Hsieh, R.J. Chung, T.S. Chin, J. Phys. Chem. Solids 64, 193–199 (2003)

[28] J. Bardeen, F.J,Blatt, L.H. Hall, Proceedings of the photoconductivity conference, Atlantic city, **146** , (Wiley, New York , 1956).