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Characterization of Spray pyrolysised nano Tin disulphide thin films

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ABSTRACT

Tin disulphide thin film on glass substrate is prepared using spray pyrolysis technique at a substrate temperature of 453 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 nano sized crystallites of dimension 5.57 nm having hexagonal structure and a preferential orientation along the (002) plane. The surface morphology has been observed using scanning electron microscope. The thickness of the film is determined as 780 nm. The absorption coefficient α is found to vary between 1.63 x 10^4 cm^{-1} and 0.30 x 10^4 cm^{-1} correspondingly by recording the absorption data in the wavelength range 400 – 800 nm. Band gap value of 2.78 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 7.18 x 10^4 Ω cm in dark and 3.03 x 10^3 Ω cm in light respectively. Activation energy of 0.47 eV is determined using Arrhenius plot.

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 several binary sulfides of tin were studied [3 - 11]. Due to their electrical and optical properties, these binary compounds have a high potential use in optoelectronic devices and photoconductive cells [11]. Among them, tin disulfide (SnS_2) has more than 70 polytype structures [12] and is a 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 [13]. It is an n-type semiconductor having a wide optical direct band gap 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, 3] at relatively higher temperatures. Several authors had reported the formation of nano crystalline SnS_2 thin film [4, 21] and SnS_2 nano wires [30] 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 with lower thermal energy and spray pyrolysis method using the precursor solutions of $SnCl_2.2H_2O$ and thiourea.

Experimental details

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 various substrate temperatures to optimize SnS_2 thin film formation by the same spray setup used by one of the present authors [3]. The other deposition parameters like solution flow rate, carrier gas pressure and nozzle to substrate distance were kept as 3 ml/min., 0.6 kg/ cm^2 and 22 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 crystal structural study of the film was examined by the XPERT PRO diffractometer using Cu K_α radiation (λ = 1.5406 Å). The scanning angle 2θ was varied in the range of 10° - 80° in steps of 0.05°. The SEM photograph was taken using JEOL-JSM 5300 scanning electron microscope to study the surface morphology. The thickness of the sample was determined 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 above 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 variation of DC electrical resistivity with respect to temperature was analyzed using Arrhenius plot and the activation energy of this thin film was found out. The type of conductivity of the semiconductor thin film is determined using the hot probe technique.

Results and discussions

Fig. 1shows the X Ray diffraction profiles of the spray pyrolysised SnS_2 thin film on the glass substrate at the substrate

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temperatures of 453 K,which ia an optimized mono phase SnS_2 thin film is obtained. The corresponding XRD pattern exhibits a single prominent peak at 2θ position 14.28°. The peak is obtained due to the reflections from the miller planes having indices (002) which could be assigned hexagonal structure by comparing the JCPDS data [24]. The interplanar spacing corresponding to this peak is determined to be 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 determined to be 12.24 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 of 6. 49 x 10^{-3} was calculated according to Basheer Ahamed et al.[25], which could be attributed to lower thermal energy deposition of this compound with relatively 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 crystallites formed in the nano SnS_2 thin film is determined to be 5.57 nm using Debye-Scherrer formula [27]. A little bigger crystallites with sizes of 11.5 nm [2], 14 nm [4] and 15 nm [31] were reported for SnS_2 thin films prepared by various methods.

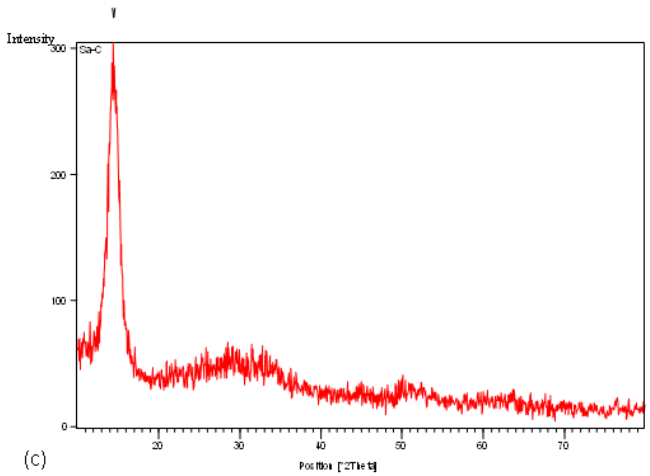

Fig 1 XRD patterns of SnS_2 thin films prepared at 453 K

The SEM photograph with a magnification of 30 k, recorded on the optimized SnS_2 thin film is shown in Fig 2. Fine grained, sandy-like structured surface is observed and the grains are well connected with each other continuously.

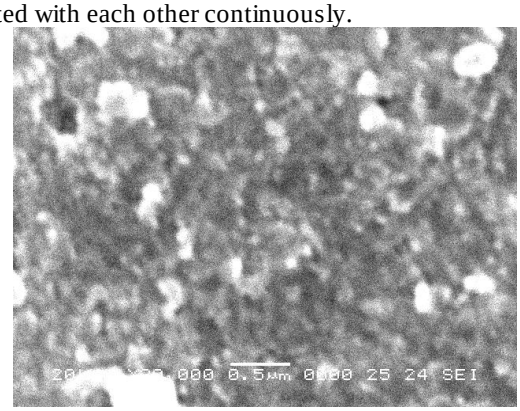

Fig 2 SEM image of optimized SnS_2 thin film with 30 k magnification

The thickness of the film is determined using surface roughness profilometer as 780 nm. The optical transmittance (% T) versus wavelength (λ) in the wavelength range 400 nm – 800 nm for the spray pyrolysised SnS_2 thin film is recorded and shown in Fig.3 from which the variation of the absorption coefficient α with respect to wavelength is calculated and plotted as in Fig 4.

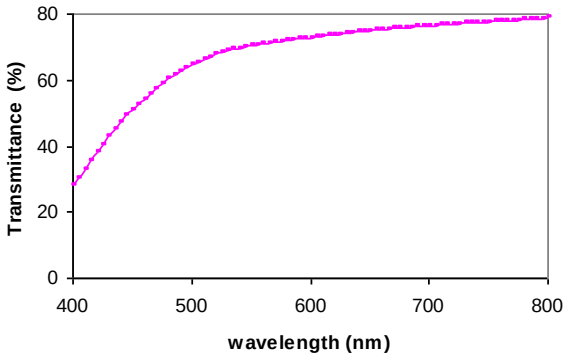

Fig 3 Transmittance spectra of SnS_2 thin film

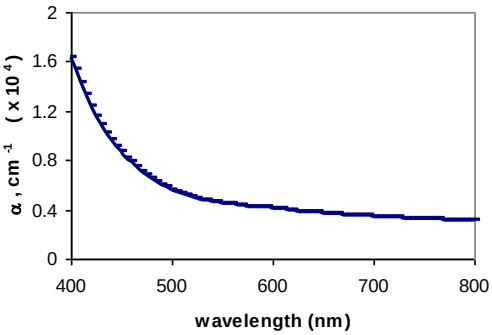

Fig 4 Absorption coefficient versus wavelength for SnS_2 thin film

It shows that the value of absorption coefficient α 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 which is investigated by the relation [28].

$$(\alpha\ h\nu)^2 = k\ (h\nu - E_g) \quad \text{----------} \quad (1)$$

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 5 , yields a straight line portion in the photon energy region extending from 2.7 eV to 3.1 eV indicates a good fit. Extrapolation of the straight line to cut the energy axis corresponding to $(\alpha h\nu)^2 = 0$ gives the band gap of 2.78 eV, which agrees with the reported value of 2.88 eV [29] for direct allowed transition. Previous workers [2, 10, 16, 17, 20] also had reported the band gap energy of the allowed direct transitions in the range 2.2 eV – 2.6 eV. It was reported that the direct optical band gap energy of 3.05 eV [4] and 3.3 eV [30] from SnS_2 thin film were due to the nano particles formation. 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 2.78 eV with direct 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 determined using four probe technique as 7.18 x 10^4 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 variation of resistivity of the as prepared film with respect to temperature was determined. A decrease in the resistivity is found as the temperature of the sample is increased which predicts the semiconductor nature of the nano SnS_2 thin film deposited in the present study. The activation energy of SnS_2 thin film is calculated by the formula

$\rho = \rho_o \exp(-E_a/KT)$ ---------- (2)

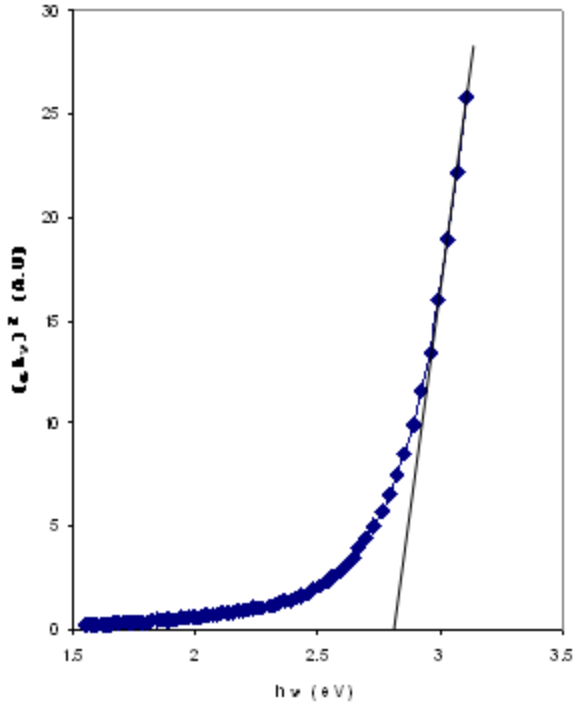

Fig 5 A typical plot of $(\alpha h\nu)^2$ against (hν) for SnS_2 thin film

where ρ_o is a pre-exponential factor and E_a is the activation energy. Both of which are determined by the best fit of the experimental data to equation (2).

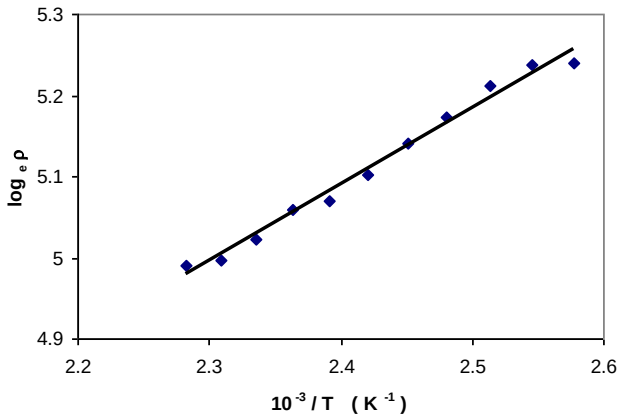

Fig 6 Arrhenius plot of SnS_2 thin film

The Arrhenius plot is drawn with this experimental data as shown in Fig .6, which can predict the variation of resistivity of this SnS_2 film is being assisted by a single activation process with activation energy of 0.47 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. [32] 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. 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 determined using hot probe technique and found to exhibit n- type electrical conductivity, which agrees well with the reported literatures [2, 3, 17, 27, 29].

Conclusion

Nano SnS_2 thin film with golden yellow coloured whose crystallite size is 5.57 nm. Tin disulphide thin film 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 relatively lower substrate temperature of 453 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 found to exhibit n-type electrical conduction. This spray pyrolysised thin film shows direct allowed optical transition nature with a band gap value of 2.78 eV. The room temperature resistivity values are determined in dark and light respectively and found to have photo conducting nature, which suggest that this nano SnS_2 thin film could be a potential candidate for opto- electronic devices.

References

[1] Noguchi H, Setiyadi A, Tanamura H, Nagamoto T, Omoto O, (1994) Sol. Energy Mater. Sol.Cells. 35, 325
[2] Thangaraju B, Kaliannan P, J. Phys. D: Appl. Phys. (2000) 33, 1054
[3] Vijayakumar K, , Sanjeeviraja C, Jayachandran M, Amalraj L J.Mat.Sci.(2011) 22,939
[4] Panda S K, Antonakos A, Mat. Research Bulletin. (2007) 42 , 576
[5] Bucchia S, Jumas J, Maurir M, Acta Crystallogr. B (1981) 37,1903
[6] Ray S C, Malay K. Karanjai , Das Gupta D, Thin solid films. (1999) 350, 72
[7] Kawano K, Nakata R, Sumita M, J. Phys. D: Appl. Phys. (1989) 22, 136
[8] Engelken R D, Mc Claud H E, Lee C, Slayton M, Ghoreishi H, J. Electochem. Soc. (1987) 134, 2696
[9] Reddy N K, Reddy K T R, Mat.Che. Phys. (2007) 102, 13
[10] Deshpande N, Sagade A , Gudage Y G, Lokhande C D, J. Alloy. Compouds (2007) 436, 421
[11] Said G, Lee P A, Phys. Status Solidi A (1973) 15, 99
[12] Polosz B, Steurer W, Schultz H, Acta Crystallogr. Sec. B (1990) 46 , 449
[13] Jaing T, Ozin G A, J. Mater. Chem. (1998) 8, 1099
[14] Price L S, Parkin I P, Hardy A M E, Clark R J H, Chem.Mater.(1999)11 , 1792
[15] Mead D C, Irwin J C, Solid State Commun. (1976) 20 , 885

[16] Sankapal B R, Mane R S, Lokhande C D, Mater. Res. Bull. (2000)35 , 2027
[17] Lokhande C D, J. Phys. D: Appl. Phys (1990) 23 , 703
[18] George J, Joseph K S, J. Phys. D: Appl. Phys. (1982) 15 , 1109
[19] Matsumoto K, Tagaki K, J. Cryst. Growth (1983) 63 , 202
[20] Abass A K,Majeid K J,Jassim H A,Murad W A, Solid State Commn.(1986) 57, 805
[21] Hai B, Tang K, Wang C, J.crystal growth (2001) 225 , 92
[22] Thangaraju B, Kaliannan P, Cryst. Res. Technol. (2000) 35 , 71
[23] Gordille , L C Moreno,de la Cruz W , P Teheran Thin solid films (1994)252 , 61
[24] X ray powder diffraction JCPDS file reference no. 21 – 1231.
[25] Basheer Ahamed M.G, Balu A R, Murali K R, Sanjeeviraja C, Jayachandran M, Cryst.Res.Technol. (2010) 45 , 387
[26] Ortiz A, Sanchez-juarez A, J.Elec.chem.Soc, (2000) 147 , 3708
[27] Klug P H , Alexander L E, X-Ray Diff. Procedures Wiley (1954), New York
[28] Bardeen F J, Blatt, L.H. Hall, Proceedings of the photoconductivity conference, Atlantic city, (1956) 146 , Wiley, New York
[29] Domingo G, Itoga R S, Kannerwurf C R , Phys.Rev (1966) 143 , 536
[30] Ya Ting Lin , Jen Bin Shi , Yu – Cheng Chen , Nanoscale Res Lett. (2009) 4 , 694
[31] Sanchez Juarez A, Tiburcio silver A, Ortiz A, Thin solid films (2005) 480, 452
[32] Amalraj L, Sanjeeviraja C, Jayachandran M, J.Cry.growth (2002) 234,683.