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Structural, Morphological, Optical and FTIR Analysis of Spray Deposited (040) Oriented Tin Sulphide Thin Film for Photovoltaic Applications

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Abstract: Thin film of tin sulphide (SnS) has been prepared at the substrate temperature 300°C by chemical spray pyrolysis technique on glass substrate. The precursor solutions are tin chloride dehydrate ($SnCl_2 \cdot 2H_2O$) and thiourea in de-ionized water and Isopropyl alcohol in molarity ratio 1:1. The structural, morphological and optical properties were studied using X-ray diffraction (XRD), scanning electron microscope (SEM), UV–Vis spectrophotometer and FTIR. The structure of the film was found to be orthorhombic with preferential orientation along (040) plane. X-ray line profile analysis was used to evaluate the micro structural parameters such as crystallite size, micro strain, dislocation density. The average crystallite size value determined as 27 nm. Thickness of film was found using surface roughness profilometer. Morphological results of the SnS thin film was spherical shaped particles. The compositional analysis of tin sulfide thin film was determined using EDAX spectrum. The optical studies revealed that the direct optical band gap value as 1.53 eV and transmittance spectrum recorded in the wavelength range 400 nm-1100 nm. The bond structure of SnS thin film was determined using FTIR studies in the range of 500 – 3500cm^{-1}.

Keywords: Thin film; transmittance; orthorhombic; composition; bonding; crystallite size.

1. Introduction

The numerous applications in the production of infrared rays and detection, IV–VI group compound semiconductors have attracted the attention of many industrial research and advanced technology. High optical transmittance, absorbance, energy band gap, and electrical properties play a significant role in the synthesis of photovoltaic devices [1]. SnS is a p-type semiconductor and the crystallites in the orthorhombic crystal system [2, 3] adopting GeS structure type [4] and an energy band gap around 1.3 eV [5], being in a range for use as absorbent material in solar cells [6].Beside this, SnS is composed of non-toxic, low cost and abundant elements compared to indium and selenium forming CIGS thin film solar cells. The making SnS material a serious candidate as absorbing layer for thin film solar cells [7] and the theoretical prediction of the solar cell efficiency prepared with SnS layer indicates that a value of 25% can be achieved [8]. Tin sulfide thin films have been prepared by different techniques such as multilayer-based solid-state reaction [9], spray pyrolysis [10], constant-current electro deposition [11], chemical bath deposition [12],radiofrequency sputtering [13], plasma-enhanced chemical vapor deposition [14], chemical vapor deposition [4], sulfurization of metallic precursors [15], dip deposition [16], vacuum thermal evaporation [17], successive ionic layer adsorption and reaction [18], electron beam evaporation [19], and electrochemical deposition [20]. Spray pyrolysis is a process for preparing thin films by forming droplets from a precursor solution, then evaporating and decomposing them in a reactor. This process has proven to be quite useful for the preparation of multi-functional particles, with many reports into the effect of the main variables on particle formation [21]. In the present work, it is intended to investigate the structural, morphological, optical characterizations of tin sulphide thin film by spray pyrolysis method using the precursor solutions of tin chloride dehydrate ($SnCl_2.2H_2O$) and thiourea (CH_4N_2S) with molar ratio 1:1.

2. Experimental procedure

2.1 Precursor solution preparation and conditions

Tin sulphide (SnS) thin film was deposited by spray pyrolysis technique on corning glass substrates with dimensions of 75×25 mm^2. Tin chloride dehydrate ($SnCl_2.2H_2O$) was dissolved in deionized water while thiourea (CH_4N_2S) were dissolved in deionized water. Both the solutions were mixed to prepare precursor solution of 0.2 M with the ratio of 1:1. Some drops of Con.Hclwere added and stirred to produce complete dissolution of the precursor. Compressed air is used as carrier gas to spray the solution with pressure of 0.6 Kg/cm^2. The

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distance between the spray nozzle and substrate was fixed at 25cm. A temperature controller has been employed for controlling the substrate temperature with an accuracy ± 5°C. The spray rate of the solution was 4ml/min and the substrate temperatures of 300°C. After deposition, the film was removed from the heater and cooled down to room temperature for further structural and optical characterizations.

2.2 Characterization

The deposited SnS film was characterized to investigate the structural, morphological, compositional and optical properties using XRD, SEM, EDAX, UV, and FTIR studies. X-ray diffractometer (PAN analytical X' Pert PRO) with CuKα radiation in the Bragg angle range of 10–80° with step size 0.0500 was used for structural study. EVO 18 Carl ZEISS scanning electron microscope attached with EDAX was used to analyze the morphology and elements presented in the film. A double- beam UV– Vis–NIR Spectrophotometer (Lambda Perkin Elmer) was used in the range 400–1100 nm to obtain transmittance and absorption spectra of the film and to calculate the optical band gap of the film. Thermo Nicolet 380 FTIR spectrophotometer was used to study the vibrational positions of atoms of thin film.

3. Results and Discussion

3.1 Structural studies

3.1.1 XRD analysis

The X-ray diffraction (XRD) pattern of tin sulphide thin film prepared at the substrate temperature of 300°C is shown (fig.1), the presence of single phase SnS is seen from the Bragg peaks in the XRD pattern recorded over the thin film. From the XRD data, it is found that only one prominent peak (040) is clearly observed that SnS film, and also the (040) plane orientation (JCPDS 75-1803) become narrow and strong crystalline**.** The 2θ value of this plane is 31.92° which is in good agreement for reported values [22].The spectrum also contained another SnS peak that corresponds to (260) orientation (JCPDS 83-1758), however this orientation has very poor intensity.

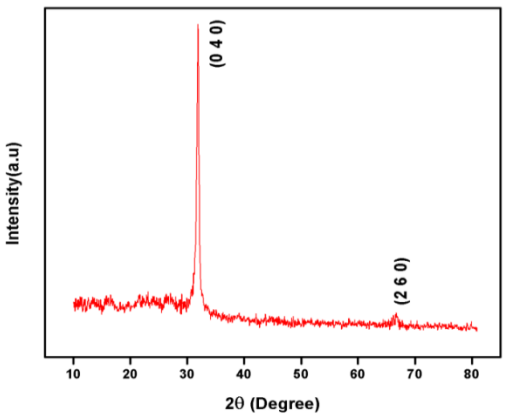

Fig. 1: X-ray diffraction of SnS thin film grown at 300°C

The presence of all the two planes indicated that only SnS phase had the orthorhombic crystal structure. No other phases like SnS, Sn_2S_3, and Sn_3S_4 were observed in the XRD spectrum, so the film has only single (SnS) phase. This is correlated with the author prepared the SnS film with different molarity concentration [23].

The lattice constants 'a' and 'c' for the orthorhombic phase structure are determined by [24] and their average of all the observed X-ray diffraction peaks. The average lattice constant was found to be a = 4.241,b= 11.243 and c = 3.987, and the volume of unit cell V = 190.10 which is slightly lower than the standard value (JCPDS file: V = 193.53) of the orthorhombic structure. This may be caused by the defect in the cell of the crystal, which causes local changes in the lattice parameters. From the full width at half maximum (FWHM) value of the peak obtained, the size of the crystallites formed in the SnS thin film is determined using Debye–Scherrer formula [24]. The micro strain and dislocation density of this film was calculated and the number of crystallites (*N*) per unit volume is calculated using formula [25]. The number of crystallites per unit area of (040) plane of the thin film ispresented, and d-spacing values are compared with standard JCPDS results are shown in Table 1.

Table 1: Structural parameters of SnS thin film

Temperature (°C)	2θ (deg)	Miller indices (h k l)	d-spacing		Thickness (nm)	Crystallite size (nm)	Strain ($\times10^{-3}$ lines^{-2} m^{-4})	Dislocation density ($\times10^{15}$nm^{-2})	Number of crystallite ($\times10^{15}$)
			Observed values	JCPDS value					
300	31.92	0 4 0	2.803	2.800 (75-1803)	638	27	4.50	1.27	2.90
	66.42	2 6 0	1.407	1.406 (83-1758)					

3.2 Morphology Studies:

3.2.1 SEM analysis:

The surface morphology of the SnS thin film prepared at 300°C is shown in figure 2. The surface morphology of thin film was found to be homogeneous. This structure repeats throughout the materials with closely packed to each other indicating good adhesiveness of film with the substrate.

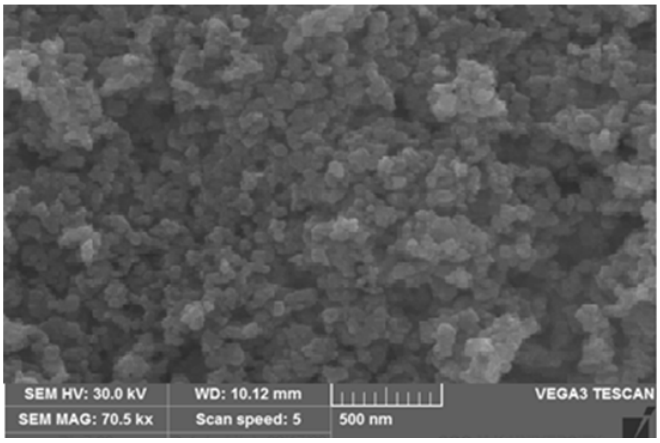

Fig. 2: Scanning electron microscope image of SnS thin film at 300°C

It is clearly seen that there was spherical shape structure, and it was accessed that smaller agglomeration of grains. This is perfectly matched with crystallite size calculated through XRD. The similar behavior of morphological studies with respect to substrate temperature was reported by the author [26].

3.2.2 EDAX studies:

The EDAX profile of the SnS thin film was depicted (fig. 3), the atomic ratio of Sn to S is found to be 0.99, which indicates that Sn is more dominant in the film. Besides the Sn and S peaks, lines for Oxygen, Ca that could come from the glass substrate (not labeled here) are seen. The present film showed p-type conductivity due to high concentration of tin [27].

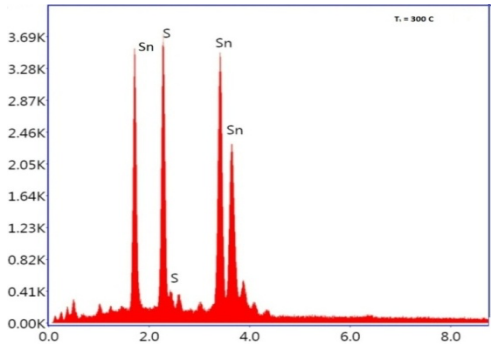

Fig. 3: EDAX spectrum of SnS thin film at 300°C

3.3 Optical studies:

The spectral behavior of Transmittance T(λ) for SnS thin film prepared at the substrate temperature of 300°C is shown on figure 5. The transmittance spectrum was recorded in the wavelength of 400 – 1100 nm at the maximum transmittance of 63%.It is clear that the transmittance of the sample increases with increasing wavelength (λ) beyond the visible region i.e., rear red region, while fig 4 shows the absorption spectrum in the wavelength of 400 – 1100 nm.

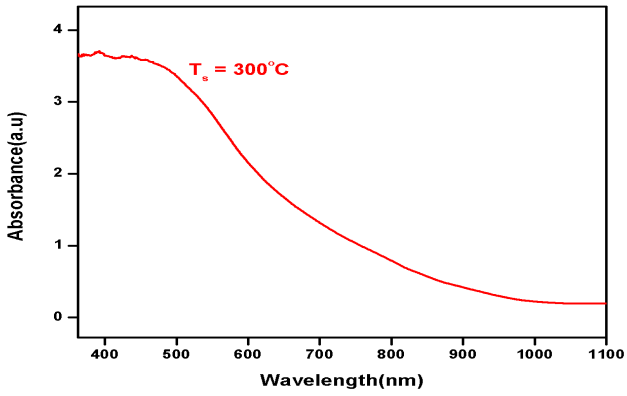

Fig. 4: Absorption spectra for SnS thin film at 300°C

The absorbance value of the SnS thin film shows that it has peak value at the beginning of visible region, and it was gradually decreased while in the increase of wavelength and becomes null value at 950 nm. In order to estimate the optical band gap, the following equation connecting the photon energy (hυ) and absorption coefficient (α) is used: to determine the direct allowed band gap, a graph between $(\alpha h\upsilon)^2$ and (hυ) was plotted and shown in figure 6.

$$(\alpha h\upsilon)^2 = A\,(h\upsilon - E_g)$$

The straight portion of the graph is extrapolated to energy axis to given band gap value is 1.53 eV. i.e., near the optimum needs for photovoltaic solar energy conversion (1.5eV) has the best crystalline structure as it clears from behaviors analysis for XRD pattern [28].

The extinction coefficient (k) was calculated for the sample obtained at substrate temperature of 300°C. An extinction coefficient value for this sample shows a maximum around 500 nm, in which also the wavelength dependence similar to the reported value [29, 30].

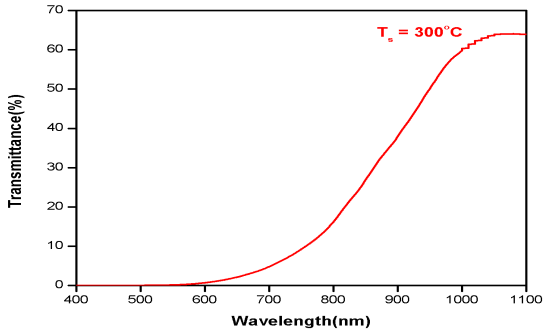

Fig. 5: Transmittance spectra for SnS thin film at 300°C

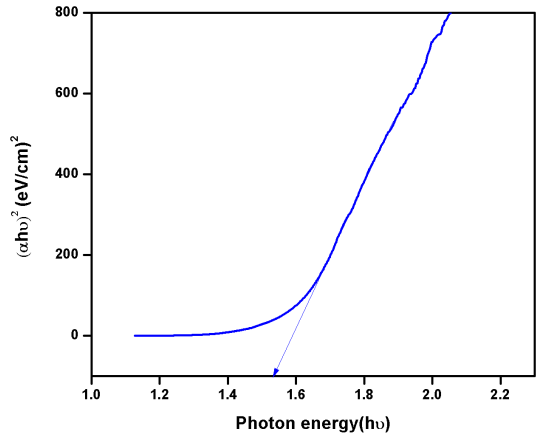

Fig. 6: (αhν) ^{2} vs (hν) plot for SnS thin film prepared at 300°C

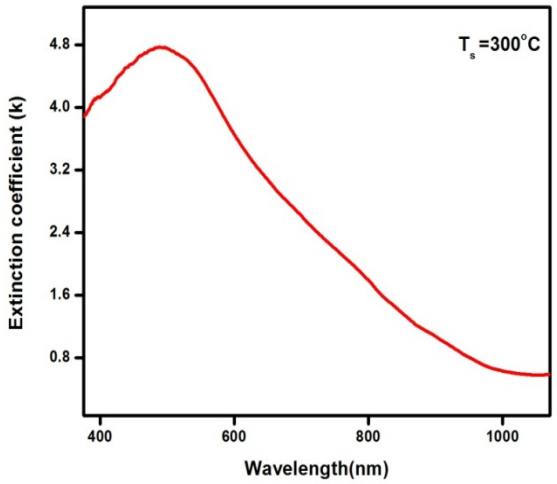

Fig. 7: Extinction coefficient for SnS thin film prepared at 300°C

3.4 FTIR studies:

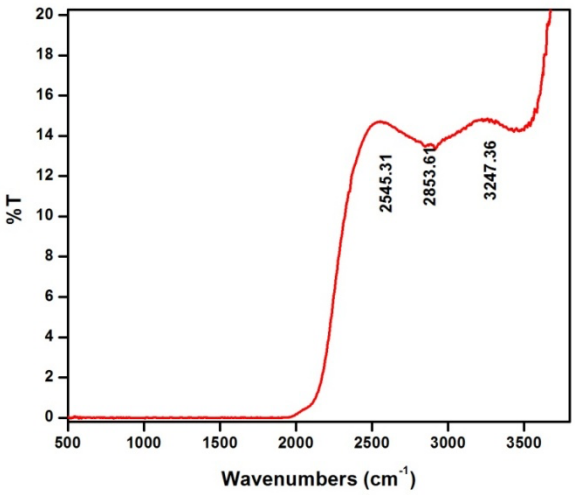

Fig. 8: FT-IR spectrum of SnS thin film at 300°C

The Fourier Transform infrared (FTIR) spectroscopy of the SnS thin film was shown in figure 8. The presence of bonding between Sn and S atoms is estimated from the FTIR spectrum recorded in the range of 500 -3500 cm^{-1}. In the present study of the FTIR spectra of tin sulphideindicates a broad band at 2545.31 cm^{-1}and 3247.36 cm^{-1}which corresponds to the vibration mode of O–H group indicating the presence of small amount of water absorbed on the surface. The presence of strong C–H stretching at 2853.61 cm^{-1} is probably due to atmospheric moisture. The main band corresponding to the formation of vibration band at 2545.31 cm^{-1}attribute to the hydroxyl group, it is good agreement with reported value [31].

4. Conclusion:

Tin sulfide (SnS) thin film has been successfully deposited onto glass substrate using chemical spray pyrolysis technique. XRD studies show formation of pure SnS film with orthorhombic structure is identified with (040) orientation. The morphology of the deposited film has been found as smooth and spherical shaped particle with surface adhesiveness. The chemical constituents and their compositions of the film have been estimated by the energy dispersive X-ray analysis. The optical band gap value with direct allowed transition nature is determined as 1.53 eV. FTIR analysis shows the bonding structure of SnS thin film, from the various results for the properties of prepared thin film conclude that it is a good material for solar cell and photo detector devices also can be tuned.

References:

[1] KTR Reddy, P Prathap, RW Miles (2010), Nova Science, New York, pp 1–27.

[2] Visakh V. Mohan,K.P. Vijayakumar , materials today, doi.org/10.1016/j.mat , 104 (2023).

[3] KT Ramakrishna Reddy, P Purandhara Reddy, PK Datta, RW Miles (2002) Thin Solid Films 403–404:116

[4] LS Price, IP Parkin, AME Hardy, RJH Clark, TG Hibbert, KC Molloy (1999) Chem Mater 11:1792

[5] S Lo´pez, AOrtiz (1994) Semicond Sci Technol 9:2130.

[6] Rohini Neendoor Mohan, Oscar Gomez Daza, Ana Rosa García-
Angelmo, AngelicaLizbeth , M.T.S. Nair, P.K. Nair
Journal of Alloys and Compounds, 892 (2022).

[7] M. Gunasekaran, M. Ichimura, Sol. Energy Mater. Sol. Cells **91**, 774 (2007).

[8] J. J. Loferski, J. Appl. Phys. **27**, 777 (1956).

[9] Z Xu, Y Chen (2012) Semicond Sci Technol 27:035007

[10] TH Sajeesh, AR Warrier, CS Kartha, KP Vijayakumar (2010) Thin Solid Films 518:4370

[11] S Cheng, Y Chen, C Huang, G Chen (2006) Thin Solid Films 500:96

[12] C Gao, H Shen (2012) Thin Solid Films 520:3523

[13] K Hartman, JL Johnson, MI Bertoni, D Recht, MJ Aziz, MA Scarpulla, T Buonassisi (2011) Thin Solid Films 519:7421

[14] A Sa´nchez-Jua´rez, AOrtiz (2002) Semicond Sci Technol 17:931

[15] J Malaquias, PA Fernandes, PMP Salome´, AF da Cunha (2011) Thin Solid Films 519:7416

[16] SK Panda, A Antonakos, E Liarokapis, S Bhattacharya, S Chaudhuri (2007) Mater Res Bull 42:576

[17] C Shi, Z Chen, G Shi, R Sun, X Zhan, X Shen (2012) Thin Solid Films 520:4898

[18] NG Deshpande, AA Sagade, YG Gudage, CD Lokhande, R Sharma (2007) J Alloy Compd 436:421

[19] A Tanusevski, D Poelman (2003) Sol Energy Mater Sol Cells 80:297

[20] Sunil H. Chaki, Mahesh D. Chaudhary , M. P. Deshpande, J.semi conductors, 37,5 (2016).

[21] W.Y. Teoh, R. Amal, L. Mädler, Nanoscale, 2 (2010) 1324–1347.

[22] Thierno Sall, Miguel Mollar, and Bernabe.J. mat.sci. Vol. 51, Issue 16, 2016.

[23] A.M. S. Arulanantham, S. Valanarasu,· A. Kathalingam, K. Jeyadheepan, Journal of Materials Science: Materials in Electronics (2018) 29:12899–12909.

[24] B.D. Cullity, *Elements of X-ray Diffraction*, (2011).

[25] R. Mariappan, M. Ragavendar, V. Ponnuswamy, J. Alloys Compd. **509**, 7337–7343 (2011)

[26] S. Dhanapandian, C.Manoharan, K. SanthoshKumar, T.Mahalingam, Materials Science in Semiconductor Processing18(2014)65–70.

[27] V. Robles, J. F. Trigo, C. Guille´n, J. Herrero, J Mater Sci (2013) 48:3943–3949.

[28] Anis Akkari , Meriem Reghima, Cathy Guasch , Najoua Kamoun-Turki, J Mater Sci (2012) 47:1365–1371.

[29] MM El-Nahass, HM Zeyada, MS Aziz, NA El-Ghamaz (2002) Opt Mater 20:159.

[30] M Khadraoui, N Benramdane, C Mathieu, ABouzidi, R Miloua, Z Kebbab, K Sahraoui, R Desfeux (2010) Solid State Commun150:297

[31] M. Kamalanathan, S. Karuppusamy, R. Sivakumar, R. Gopalakrishnan, Journal of Materials Science, **50**, 8029–8037 (2015).