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Growth and characterization of tin disulphide thin film by spray pyrolysis technique

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An inexpensive spray pyrolysis process has been used to create thin layer of tin disulphide. The concentration, flow rate, and nozzle to substrate distance were tuned as deposition parameters to produce high-quality thin films. Temperature is varied in the range 200˚C to 350˚C. Through physical research, properties such as the structural, electrical and optical were examined. The films generated are SnS_2 with a hexagonal structure, as revealed by X-ray diffraction. EDAX analysis confirms SnS_2 thin films. Scanning electron microscopy indicated uniform stacking and material adherence to the glass substrate. A 2.22 eV straight band gap was found. Two peaks in the photoluminescence spectrum were indicative of the emission of green and yellow fluorescence, respectively. Electrical properties reveal that resistivity decreases from 3.18 x 10^{-2} Ω cm to 3.06 x 10^{-3} Ω cm, carrier concentration & mobility increases to 1.4 x 10^{20}/ cm^3 to 1.8 x 10^{20}/ cm^3, 1.92 cm^2/Vs to 5.3 cm^2/Vs respectively with increases in temperature.

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1. Introduction

In most studies, polycrystalline thin-film solar cells [1] with moduli over 12% have been developed utilizing $CuInSe_2$ [CIS] and CdTe as the absorbent material [2,3]. There are still certain issues with the environmental acceptability of cadmium and the scarcity of gallium and indium, despite the remarkable progress made with these materials [4]. Numerous laboratories are currently working to create novel solar cell materials that will increase conversion efficiency either on their own or in tandem structures without these issues. Constituent element of tin sulphide compounds is Sn and S is one of the promising materials which are non-toxic & abundant in nature [5]. Studies conducted on SnS indicate that it could be used as an optical or holographic data storage media [6, 7]. Also, SnS films have been utilized in photovoltaic systems because of their high absorption coefficient [on the order ~ $10^4 cm^{-1}$] and band gap of ~ 1.2-1.7ev [8,9]. SnS exists in a variety of crystal forms, such as orthorhombic and tetrahedral [10,11], or a highly distorted rock-salt patterns [12]. Tin sulphide thin films were deposited using different technique such as electro deposition [13], vacuum evaporation [14] electro deposition [14], electro less deposition [15], plasma enhanced CVD, spray pyrolysis [16,17,18,19,20], Rf sputtering [20], atomic layer deposition method [21], SILAR method [22], chemical bath method [23,24,25,26], & brush plated technique [27,28]. In this paper we have used spray pyrolysis technique to prepare SnS_2 thin films and their characteristics were discussed.

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2. Experimental

A glass substrate is coated with tin disulphide at temperatures between 200°C and 350°C by maintaining other deposition parameters such as concentration, solution flow rate, gas flow rate, and nozzle to substrate distance as constant 0.1 M $SnCl_2$ and 0.1 M thiourea were combined in methanol to create the solution, which was then sprayed onto the glass substrate. Digital micrometer was used to measure the film's thickness. The film's structural analyses were conducted with [shimad zu l X RD-6000]. EDAX and SEM analysis were carried using JEOL-JSM-5610LV with INCA EDS. Transmittance spectra, which are obtained using a 500 Varian UV-VIS-NIR spectra photometer and cover a wavelength range of 350 to 1350 nm, were used to analyze the optical properties of the material. Electrical properties were carried out using hall measurement system [ECOPIA HMS 5000].

The XRD pattern of SnS_2 thin films were shown in Fig [1]. The hexagonal structure and nanocrystalline nature of SnS_2 films are revealed by an XRD investigation. The peak at 2θ = 15.02˚ corresponds to 001 planes of SnS_2 thin films. The interplanar spacing values that correspond to the peak are 5.90A°, 5.90A°, 5.95A°, and 5.97A°, respectively and these values are quite close to the standard value of 5.90A°.

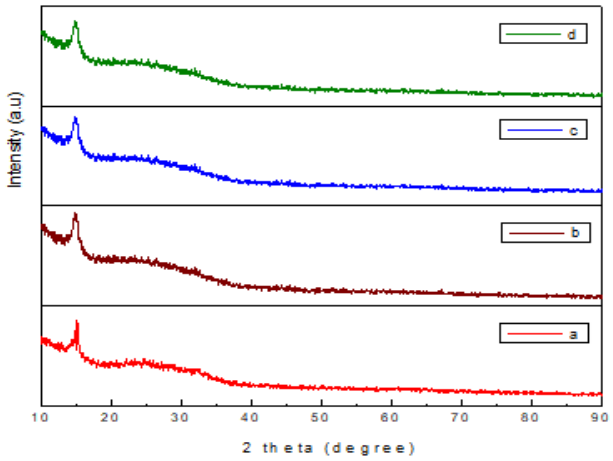

Fig. 1. XRD pattern of SnS_2 films made at the temperatures a) 200°C, b) 250°C, c) 300°C and d) 350°.

Scherer's formula, D=Kλ/βcosθ, is used to compute the grain size [D] of SnS_2 thin films. Where K is the shape factor, which is defined as 0.94, λ is the x-ray wavelength (1.5406 A° for cukα), θ is the Bragg's angle, and β is the full width half maximum. Using Williamson and Smallman's formula, which is $\delta = 1/D^2$ lines/m^2, the dislocation density [δ] has been calculated.

The relation ε= βcosθ/4 is used to calculate the micro strain [ε]. FWHM, micro strain, dislocation density decreases were as grain size increases with increase in temperature. All these parameters were shown in the table [1].

Table 1. Specifications of the SnS_2 thin film's microstructure at various temperatures.

Substrate temperature °C	**[001] Inter planar Distance Å**	**FWHM [degree]**	**Grain size [D] Nm**	**Micro strain [ε] x 10^{-3}**	**Dislocation density x10^{14} cm^{-2}**
200	5.9715	0.8160	10.27	3.4424	0.947
250	5.9824	0.7325	11.44	3.0889	0.764
300	5.9543	0.5538	15.13	2.3330	0.436
350	5.9090	0.1632	43.44	0.6880	0.529

2.1. EDAX analysis

EDAX analysis result conforms the presence of Sn & S of SnS_2 thin films Fig. [2]. Stoichiometry of the film increases with increase of temperature, in spite of Sn and S peaks, lines for Si and Cl are visible, which may originate from the substrate (glass). The "O" line denotes the element's presence in the film or substrate as a result of compressed air. These results suggest that as substrate temperature rises, the atomic ratio rises as well.

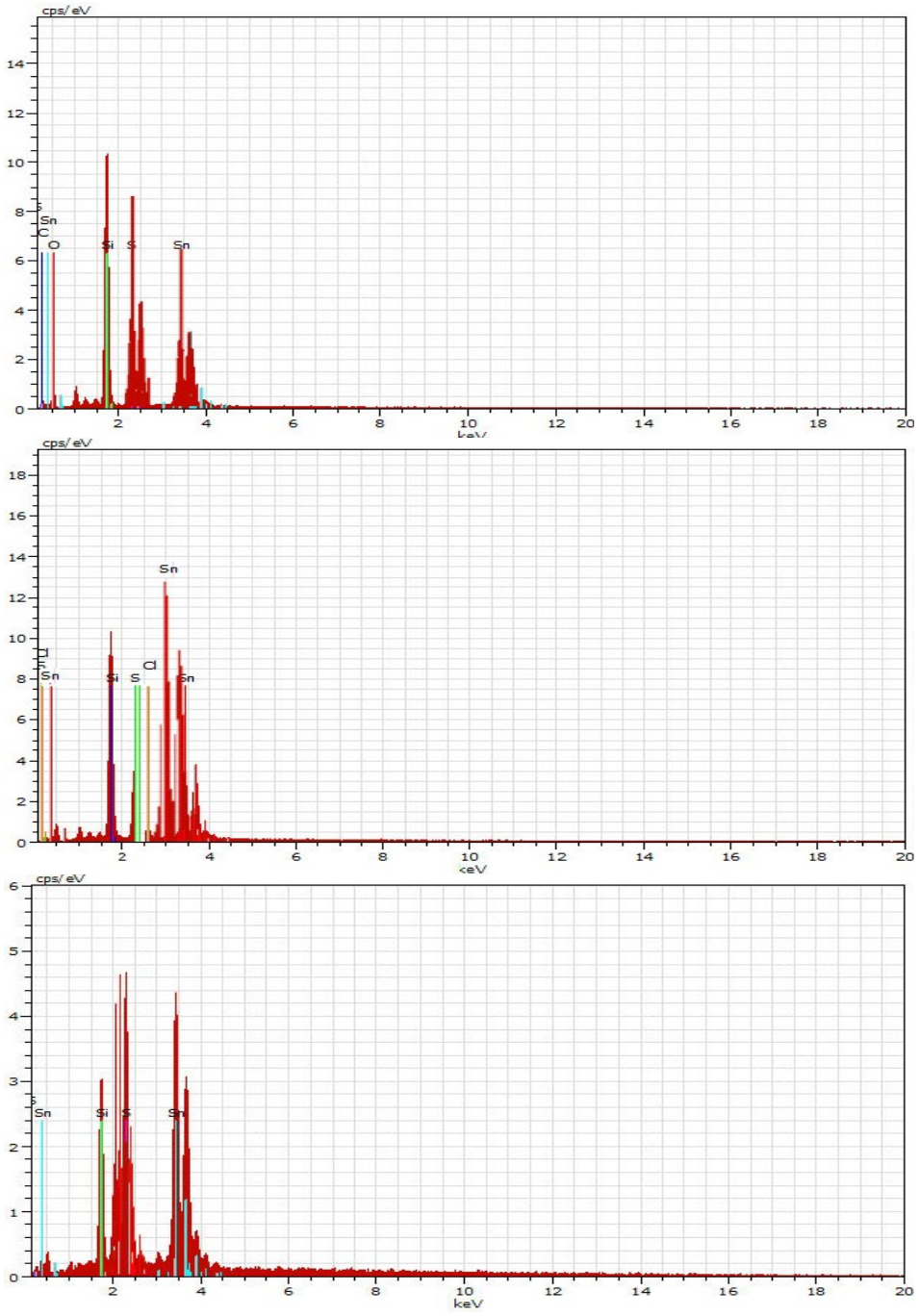

Fig 2. EDAX examination of SnS_2 films produced at the temperatures 200°C, 250°C, 300°C and 350°

2.2. SEM analysis

The SnS_2 thin-film surface morphology after being sprayed on a glass substrate is shown in Figure [3]. These SEM micrographs make it clear that coatings are less bonded to the substrate and less homogenous at lower temperatures. It is observed that fine grains are distributed

randomly throughout the substrate and adherence also increases. It is clear that grains of sample deposited at higher temperature 350°C are relatively larger in size than of films prepared at lower temperature. It is clear that when substrate temperature rises, grain size increases.

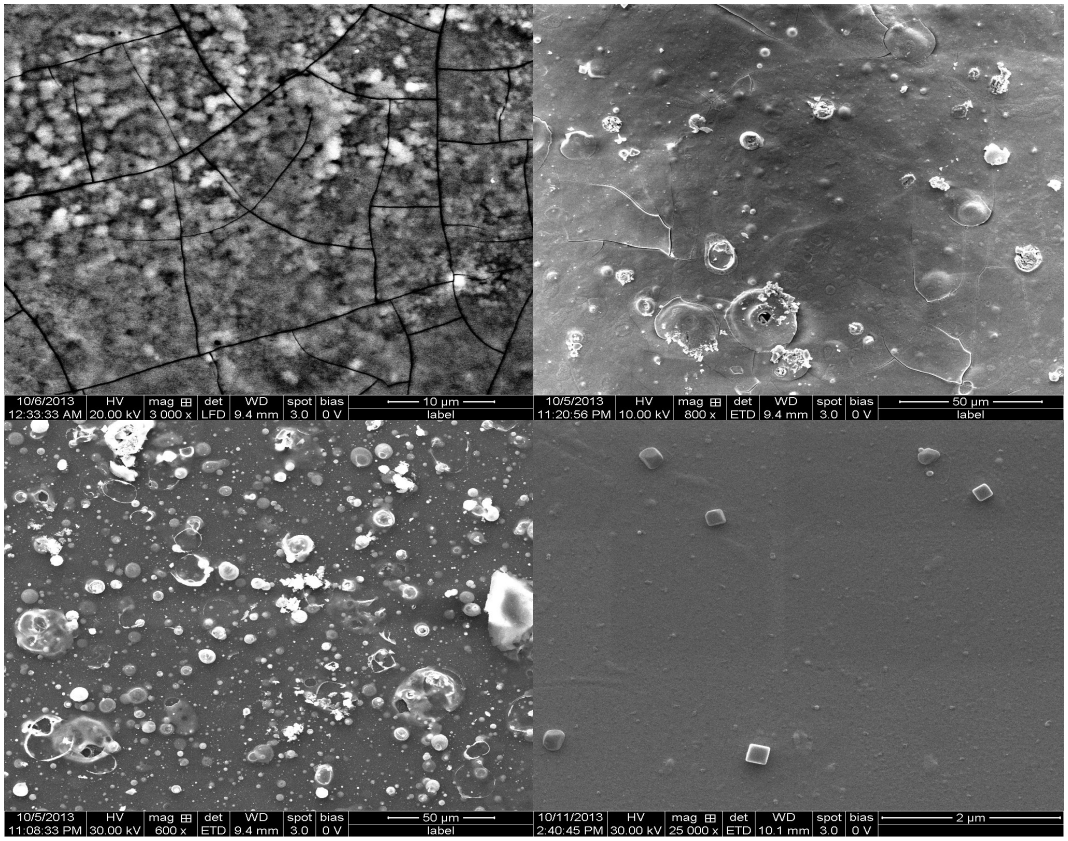

Fig. 3. SEM analysis of SnS_2 films made at the temperatures 200°C, 250°C, 300°C and 350°C.

2.3. Optical properties

Fig [4] shows the optical transmittance spectra of SnS_2 thin films. It was determined that all the films behaved as transparent material in the wavelength range 400-1450 nm. The transmittance value decreases sharply at 500 nm. Based on XRD and SEM analysis, it can be inferred that the wavelength range in question corresponds to the fundamental absorption region. Transmittance increases from 27% to 79% when substrate temperature rises from 200°C to 350°C. These findings may be the result of the film's high crystalline nature, well adherence, and homogeneity. Fig. [5] shows the Optical band gap of SnS2 thin. At 350°C, the band gap drops to 2.1 eV, possibly as a result of sulfur re-evaporating at a higher temperature. Film band gap increases from 2 to 2.30 eV, this is evident from EDAX analysis. Fig [6] displays the photoluminescence spectra of samples that were deposited at various temperature. As the substrate temperature rises in the 200°C to 350°C region, it is evident that the UV emission peak's intensity increases. The films exhibit three prominent peaks at 519,550,575 nm which shows green and yellow fluorescence emission. The direct band gap obtained from the photoluminescence spectra is 2.22eV.

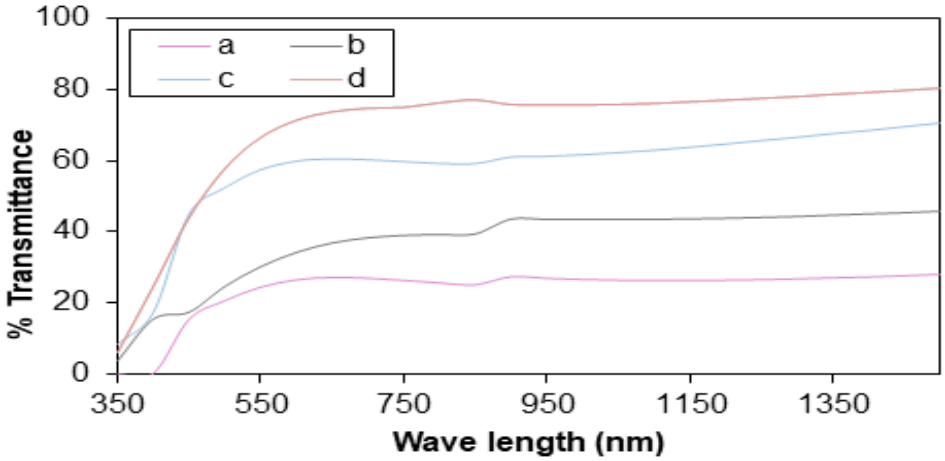

Fig. 4. Transmission spectra of SnS_2 films made at the temperatures: a) 200°C, b) 250°C, c) 300°C and d) 350°C.

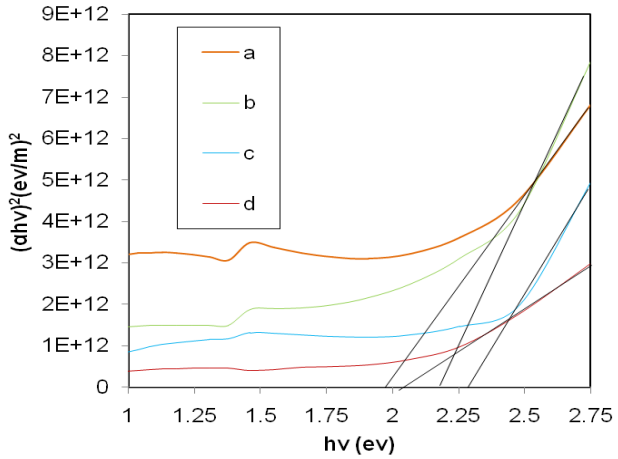

Fig. 5. Band gap of SnS_2 films made at various temperatures a) 200°C, b) 250°C, c) 300°C and d) 350°C.

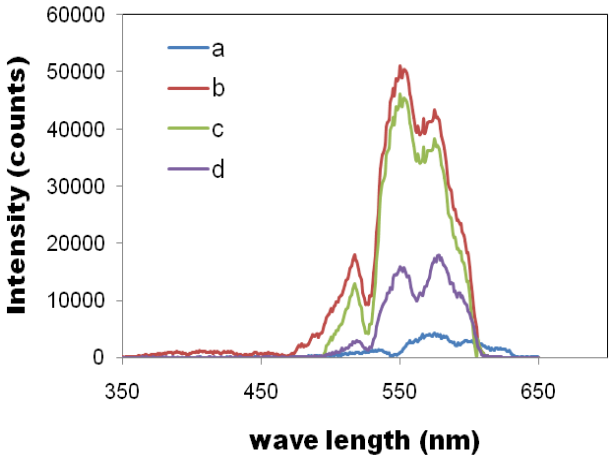

Fig.6. Photoluminescence spectra of SnS_2 films prepared at the temperatures: a) 200°C, b) 250°C, c) 300°C and d) 350°C.

2.3. Electrical property

A silver electrode was applied to the films in order to assess the conductivity for electrical measurements. The deposited films were found to have p-type conductivity from the hall measurement. SnS_2 carrier concentration and mobility increased from 1.92 cm^2/Vs to 5.3 cm^2/Vs, and from 1.4 x $10^{20}/cm^3$ to 1.8 x $10^{20}/cm^3$, respectively. At 350°C, the electrical resistivity drops from 3.18 x 10^{-2} Ω cm to a minimum of 3.06 x 10^{-3} Ω cm. Table [1] makes it clear that the produced films' strain and grain size have a significant impact on the resistivity drop. The resistivity, carrier concentration, and mobility of SnS_2 films formed at various temperatures change, as seen in Fig. [7].

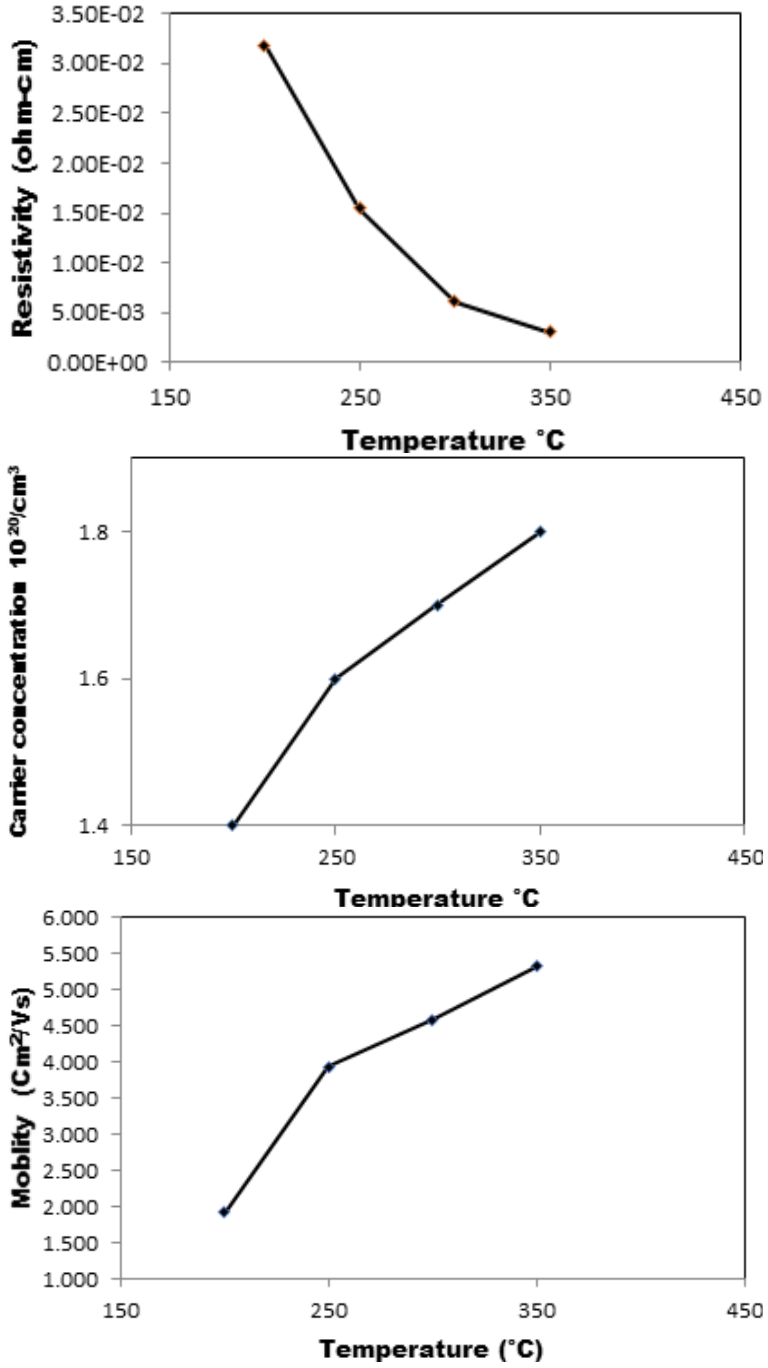

Fig. 7. Variation in SnS_2 films made at the temperatures in terms of (a) resistivity (b) carrier concentration (c) and mobility.

3. Conclusion

Spray pyrolysis technique were used to generate tin disulphide films on glass substrates at varying substrate temperatures. The thin films polycrystalline composition and hexagonal structure have been revealed by XRD investigations. Utilizing the XRD pattern, the structural characteristics such as dislocation density, micro strain, and grain size were computed. EDAX analysis confirms the existence of Sn and S elements. SEM studies reveal that film adherence increases with substrate temperature. Transmission of SnS_2 is found vary from 27-79% and the energy band gap of these is between 2 to 2.30 eV. The P-type conductivity is present in the films, with carrier concentration ranging from 1.4 x $10^{20}/cm^3$ to 1.8 x $102^{0}/cm^3$, mobility from 1.92 cm^2/Vs to 5.3 $cm^{2/}Vs$, and electrical resistivity between 3.18 x 10^{-2} Ω cm and 3.06 x 10^{-3} Ω cm. Photoluminescence spectra shows peaks at 519, 550, 575 nm which shows green and yellow fluorescence emission with direct band gap of 2.22eV. SnS_2 thin films are therefore appropriate for the absorber layer in solar cells.

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