Effect of Substrate Temperature on Tin Disulphide Thin Films

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Effect of Substrate Temperature on Tin Disulphide Thin Films

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Abstract: Thin films of tin disulphide (SnS_2) were deposited on glass substrates by spray pyrolysis technique using precursor solutions of $SnCl_2.2H_2O$ and n-n dimethyl thiourea at different substrate temperatures varied in the range 473 – 573 K. Using the hot probe technique the type of conductivity is found to be n type. X ray diffraction revealed the polycrystalline nature with increasing crystallinity with respect to the different substrate temperature. The preferrential orientation growth of compound having (002) plane belongs to the hexagonal crystal structure. The size of the crystallites was determined using FWHM values of the Bragg peaks and found to increase with the substrate temperature. The direct energy band gap values are found to be increased with the increasing substrate temperature. The room temperature resistivity values are decreased with increasing substrate temperature in order of 10^5 Ω-cm.

Keywords: thin film; band gap; resistivity; hexagonal; crystallite.

1 Introduction

Metal chalcogenides are great importance for researchers because they are potential candidates for optoelectronic applications such as photo detectors, solar cells, thin film transistors etc., [1-5]. SnS_2 is considered to be one of the most useful IV-VI group semiconducting tin chalcogenides, which has found applications in opto-electronic devices, a part of solar collectors, etc., SnS_2 was first synthesized some 200 years ago [6] and has more than 70 polytype structures [7]. It is a layered semiconductor with CdI_2 type structure composed of sheets of tin atoms sandwiched between two close-packed sheets of sulphur atoms. The optical band gap values of this film vary from 0.81 to 3.38 eV [8].

The typical direct band gap is about 2.9 eV and indirect energy band gap is 2.0 eV [9]. SnS_2 thin films have large optical absorption coefficient ($>10^4$ cm^{-1}) [10], wide band gap [9], n-type electrical conduction and possession of strong photo conducting behaviour [9, 11, 12, 13]. These characteristics make this compound suitable for a solar collecting material in a thin film solar cell [10]. In addition, the elemental constituents of this compound are non-toxic and abundant in nature.

Many techniques have been reported for the deposition of SnS_2 thin films. These include chemical deposition [14, 15], vacuum evaporation [16, 17], chemical vapour transport [18], dip deposition [11] and chemical spray pyrolysis [10]. Every technique of thin film deposition has its own merits and demerits. Owing to simplicity and inexpensiveness, the chemical spray pyrolysis is a better method at a lower cost for the preparation of thin films with a large area and also for preparing pin hole free, homogeneous thin films with the required thickness. Some of the present authors at studied the formation of SnS_2 monophase at higher thermal energy with lower concentration of precursor solutions of $SnCl_2.2H_2O$ and n-n dimethyl thiourea. Thus it is indented to analyze the formation of SnS_2 thin film in the same precursors with different thermal energy with lower concentrations.

2 Experimental Details

Tin disulphide films were deposited on microscopic glass substrate with different substrate temperature (T_s= 473 – 573 K) using spray pyrolysis technique. The precursor solutions of $SnCl_2.2H_2O$ (0.1M) and n-n dimethyl thiourea (0.2M) were dissolved separately in a solution containing deionised water and isoprophyl alcohol in proper ratio. A few drops of concentrated hydrochloric acid were added for complete dissolution. Equal volume of these two solutions were mixed together and sprayed on to microscopic glass substrates with dimensions of 75x25 mm^2. The substrates were cleaned with acetone, ethanol and deionised water.

Films were deposited using microprocessor based spray unit, consists of substrate heater, temperature controller, dispenser container, spray nozzle, spray head and air compressor. The

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spray head was allowed to move in the X-Y plane using the microcontroller stepper motor in order to achieve a uniform coating on the substrate. A temperature controller has been employed for controlling the substrate temperature with an accuracy ± 5°C. Spray head and heater with substrates were kept inside a chamber provided with an exhaust fan for removing gaseous by-products and vapours of the solvent. For the preparation of good quality films, various parameters such as nozzle to substrate distance (20 cm), flow rate of air (1 kg/cm^2), Solution flow rate (3 ml/min) etc.

After deposition, the film was allowed to cool slowly to room temperature, washed with distilled water and then dried. 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 patterns were recorded in 2θ interval from 10° upto 80° with the step 0.05° at room temperature. The thickness of the film was evaluated using the conventional gravimetric method. Optical absorption spectrum was recorded in the range 400-1200 nm using Varian-Cary 500 scan double beam spectrophotometer. Electrical resistivity at room temperature was determined using four-probe technique with Keithley 2000 electrometer.

3 Result and Discussions

The X ray diffraction spectrum were recorded for the films deposited at the different substrate temperature range 473 – 573 K as shown in Fig (1). The film formed at the substrate temperature 473 K (Fig.1 (a)) exhibited diffraction peak at d= 2.611 Å indicated the presence of the Sn_2S_3 phase, while those at 5.437, 3.143, 2.716 and 1.816 Å were due to the SnS_2 phase. The above observed reflections were in agreement with the JCPDS files for Sn_2S_3 and SnS_2 (JCPDS file no. 720031, 893198). At 498 K (Fig.1 (b)), the intense peak was observed at d =5.815 Å corresponding to (002) plane indicate the hexagonal SnS_2 phase with lattice parameters a = 3.646 Å, c =11.810 Å (JCPDS file no. 893198).

The other smaller peaks at d =2.905 and 3.034 Å were corresponding to (004) and (101) planes respectively. Film formed at 523 K (Fig.1(c)) showed a mixture of phases SnS at d = 2.825 Å (JCPDS 752115) and SnS_2 at d=5.85 Å (JCPDS 893198) with a preferential orientation along the (111) & (002) direction. The reflections of the film formed at 548 K can be indexed at d = 2.822 Å (JCPDS 752115) with the orthorhombic phase of SnS (Fig. 1(d)). The spectrum related to the film formed at 573 K (Fig. 1(e)) showed the diffraction peaks corresponding to a mixture of SnS at d=2.822 Å (JCPDS 752115) and SnO_2 at d=1.410 Å (JCPDS 880287) with (111) & (301) planes respectively.

These observations were in agreement with the reports in the literature that higher temperatures are more favorable for the growth of SnS_2 and Sn_2S_3 than SnS [19, 20]. The average size of the SnS_2 crystallites is estimated by the Scherrer's formula [21].

$$D = k \lambda / \beta \cos \theta$$

where K=0.9 is the shape factor, λ is the X-ray wavelength of CuKα radiation (1.5406 Å), θ is the Bragg's angle and β is the full width half maximum of the peaks. The crystallite size was found to increase with increase of substrate temperature as shown in table (1). The relation between the absorption coefficient (α) and the incident photon energy hυ is given by

$$(\alpha h\upsilon)^2 = A (h\upsilon - E_g)$$
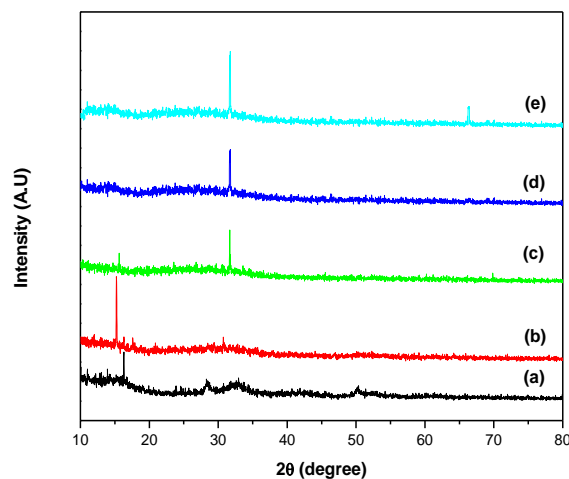
where A is a constant and E_g is the band gap energy.

Fig.1 XRD spectra of the SnS_2 films grown at (a) T_s= 473 K (b) T_s= 498 K (c) T_s= 523 K   (d) T_s= 548 K and (e) T_s= 573 K

Table 1: Variation of crystallite size of SnS_2 thin films

Substrate temperature (K)	Crystallite Size (nm)
473	96.1
498	120.0
523	135.2
548	164.9
573	170.3

To determine the direct allowed band gap, a graph between $(\alpha h\upsilon)^2$ and hυ was plotted and the straight portion of the graph was extrapolated to energy axis to give E_g and is shown in Fig 2. It was observed that the band gap increases from 2.28 to 2.9 eV with increase in substrate temperature (table (2)), The evaluated band gap energy is 2.4 eV at 498 K which is in good agreement with the reported values of Thangaraju et al., [20].

Table 2: Direct band gap values of tin disulphide thin films

Substrate Temperature (K)	Direct band gap (eV)
473	2.28
498	2.45
523	2.7
548	2.85
573	2.9

The higher energy band gap of the films grown at substrate temperatures 548 K and 573 K might be due to the presence

of a mixed phase involving amorphous SnS_2 (due to higher concentration of sulphur in the precursor solution) and SnO_2 in addition to SnS phase.
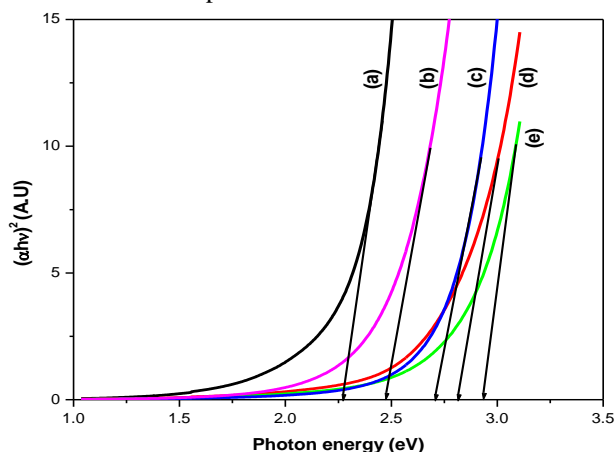

Fig 2. $(\alpha h\nu)^2$ versus photon energy $(h\nu)$ for films grown at (a) T_s= 473 K (b) T_s= 498 K

(c) T_s= 523 K (d) T_s= 548 K and (e) T_s= 573 K

Accordance with the semiconducting nature, the electrical resistivity values of the tin disulphide films decreased from 5.75 to 2.35 $x10^5$ Ω-cm with the increasing of substrate temperature (table (3)).

Table 3: Resistivity values of SnS_2 thin films

Substrate Temperature (K)	Resistivity ($x10^5\Omega$cm)
473	5.75
498	5.35
523	4.6
548	3.5
573	2.35

The observed high resistivity of the films formed at lower temperatures was due to the presence of Sn_2S_3 and SnS_2, which were highly resistive. The low resistivity observed in the film formed at substrate temperature 573 K correlated to the presence of SnO_2. The room temperature resistivity was of the order of 10^5 Ω-cm, which is in good agreement with the reported values of Nair et al [1].

4 Conclusion

The golden yellow colored thin films of tin disulphide were deposited onto glass substrates at different substrate temperature range 473 – 573 K. X ray diffraction studies showed that the best crystallinity of the SnS_2 thin film was obtained at 498 K. The optical direct band gap values are increased with increasing substrate temperature. The electrical resistivity was of the order of $10^5\Omega$-cm. From the above experimental results, it can be inferred that SnS_2 thin film with nano crystallites can be deposited with spray pyrolysis method using $SnCl_2 . 2H_2O$ as one of the precursor which could be a potential candidate for opto- electronic thin film devices.

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