

Influence of Substrate Temperature on Tin Sulphide Thin Films Using Chemical Spray Pyrolysis Technique

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Abstract: Thin films of tin sulphide (SnS) were prepared on glass substrates, using chemical spray pyrolysis technique, using precursor solutions of doubly hydrated stannous chloride and thiourea at, different substrate temperatures varied in the range 548 - 648 K in steps of 25 K. X ray diffraction analysis revealed the crystalline nature of SnS compound having orthorhombic structure along (111) plane. The size of the tin sulphide crystallites with nano dimension was determined using the Full Width Half Maximum values of the Bragg peak at the optimized substrate temperature. The surface morphology have been observed on the surface of these films, using scanning electron microscope and atomic force microscopy. Single-phase, p-type, SnS film with direct allowed band gap of 1.3 eV was determined at the substrate temperature 573 K.

Keywords: thin film, diffraction, band gap, crystallite, Bragg peak.

1 Introduction

Metal chalcogenide nanomaterials are found to have various optoelectronic applications such as photovoltaic devices, display devices and batteries as a result of their good electrical and optical properties [1]. A chalcogenide is a chemical compound consisting of at least one chalcogen anion, such as sulfur (S), selenium (Se), and tellurium (Te) and at least one more electropositive element. In recent years, thin films of SnS have attracted much attention for the photovoltaic applications due to the high absorption coefficient [1,2], and high conductivity SnS belongs to groups IV-VI of compounds formed with Sn as the cation and S as the anion. The constituent elements are inexpensive, nontoxic and abundant in nature leading to the development of devices that are environmentally safe and have public acceptability. SnS is an important optoelectronic material that is found in zinc blend with the lattice constant ($a = 0.5845$ nm) [3], orthorhombic with the lattice constants ($a = 0.385$ nm, $b = 1.142$ nm and $c = 0.438$ nm) [4, 5] and herzenbergite [6] crystal structures. SnS shows a p-type electrical conductivity, and its electrical conductivity can be controlled by using different dopants like Al, Ag and Cl. The optical properties of SnS vary

depending on the synthesizing or fabrication method, but most work agrees with direct and indirect band gap values. These properties enable SnS thin films to be used as an absorption layer in the fabrication of heterojunction solar cell [4, 7]. Due to its interesting structural and optical and electrical properties, SnS has become an important material for optoelectronics and photovoltaics with many promising technological applications [8,9]. Further, properties like high absorption coefficient [10], direct band gap in the range 1.2 to 1.5 eV and indirect band gap in the range 1.0 to 1.2 eV [7, 11] make SnS a more viable material for photovoltaic applications. The author Loferski theoretically proved that a maximum efficiency of 25% is achievable for this material [12]. Electronic structure and structural calculations of SnS were deduced from photoelectron spectra by Ettema et al [13]. In terms of cost and efficiency, thin film solar cells hold an optimistic fervor as a future resource for sustainable energy. Now, the most developed thin film photovoltaic technologies are based on CdTe and CuInSe₂ absorber layers. Recently a maximum efficiency of 19.9 % has been achieved at National Renewable Energy Laboratory, United States of America, using Cu (In,Ga)Se₂ based absorber layers.

SnS thin films could be prepared using different techniques such as vacuum evaporation [14], radio frequency sputtering [15], electrochemical deposition [16-

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[17], atmospheric pressure chemical vapor deposition [18], plasma enhanced chemical vapor deposition [19], brush plating [20], dip deposition [21], chemical bath deposition [22] and chemical spray pyrolysis [23]. Among these, chemical spray pyrolysis is one of the simplest and cost effective means of thin film deposition, especially when large area deposition is required. Moreover, the ease of doping and flexibility of tailoring the stoichiometry make this technique more popular in the field and adapt well to our requirements of photovoltaic device fabrication. Hence, this technique was selected for the deposition of SnS thin films. In the present work, it is intended to prepare the tin sulphide thin film at an optimized substrate temperature, using the precursor solutions of mixtures of doubly hydrated stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) and thiourea ($\text{CS}(\text{NH}_2)_2$). The usage of SnCl_2 instead of SnCl_4 reduces material cost as well as deposition temperature required for the deposition substantially, which is very vital for device level applications.

2 Experimental Details

Films were deposited using the indigenously designed and fabricated spray coating unit. It consists of a base plate in which a heater coil is embedded to facilitate heating upon which the substrates for film deposition are to be placed. Substrate temperature (T_s) was maintained with the help of a feedback circuit which controls the heater supply. During the spray, temperature of the substrate was kept constant with an accuracy of $\pm 5^\circ\text{C}$. Spray head and heater with substrates were kept inside a chamber provided with an exhaust fan for removing gaseous by products and vapors of the solvent. Pressure of the carrier gas can be adjusted manually. With the help of indigenously developed dispensing unit, the spray rate of the solution can also be precisely controlled. Spray rate is an important parameter in controlling different properties of the films and in the automated spray unit, this can be controlled so as to get good repeatability of film properties. Cleaned glass slides with dimensions of $37 \times 12 \times 1.2 \text{ mm}^3$ were used as the substrates. Clear aqueous solution of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CS}(\text{NH}_2)_2$ were used as the starting anionic and cationic precursors, respectively. For the present study, we prepared sets of films at different substrate temperatures from 548 K to 648 K in steps of 25 K. For all the sets, distance of spray head from the substrate was 30 cm and total volume of the solution sprayed was 40 ml, which contained equal volumes (20 ml) of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CS}(\text{NH}_2)_2$. The spray rate was fixed at 3 ml/min, since low spray rate favored formation of films with superior surface morphology. Further lowering of deposition rate would require longer coating durations, which is an undesirable condition. Films were prepared by varying the substrate temperatures 548 K to 648 K with an accuracy of $\pm 5^\circ\text{C}$, while the 'molarity of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ' (M_{Sn}) and 'molarity of $\text{CS}(\text{NH}_2)_2$ ' (M_{S}) were kept constant at 0.1 M, separately. Thickness of the films was measured using Stylus method (Dektak 6 M thickness

profiler). Structural analysis was performed, employing x-ray diffraction (XRD) using Rigaku (D.Max.C) x-ray diffractometer having $\text{CuK}\alpha$ ($\lambda = 1.5405 \text{ \AA}$) radiation and Ni filter operated at 30 kV and 20 mA. All samples were scanned in the range from 10° to 60° with a scan speed of $5^\circ/\text{min}$. Surface studies of the samples were done with the help of atomic force microscopy (AFM) (Nanoscope-E, Digital Instruments, USA, in contact mode) and scanning electron microscopy (SEM) (JEOL, JSM-840). Operating voltage for SEM measurements was 20 kV, and the surface morphology of the sample was compared at $25,000\times$ magnification, at the optimized substrate temperature. Optical absorption studies were carried out using UV-Vis-NIR (190–2500 nm) spectrophotometer (Jasco V-750 model).

3 Results and Discussions

Figure 1 shows the XRD diffraction profiles of the spray pyrolysed SnS thin films with various substrate temperatures from 548 K to 648 K, in steps of 25 K. The role of different substrate temperatures is to determine the optimized temperature to prepare SnS thin film.

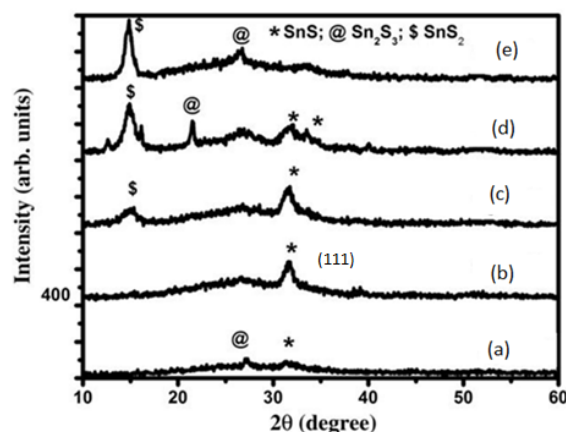


Fig. 1: XRD pattern of SnS thin films at (a) 548 K, (b) 573 K, (c) 598 K, (d) 623 K and (e) 648 K.

At the temperature of 548 K, the obtained film has two peaks of tin phases, Sn_2S_3 and SnS, with lower intensity [fig 1(a)], which may be attributed to less availability of sulfur atoms. When the substrate temperature increases to 573 K, the intensity of diffraction peak shows that the polycrystalline phase becomes more intense and an increase of crystallinity with the preferential orientation growth of SnS compound, having an orthorhombic structure along (111) plane [fig. 1(b)], diffracted with a single prominent Bragg peak at the 2θ position, 31.493° . A similar kind of an orthorhombic structure of SnS with a single phase of (111) plane of thin film is well agreed with reported literature [25]. At 598 K, the mixed phases of tin species are observed with Bragg peak values of SnS and SnS_2 at 31.592° and 14.4° , respectively [fig.1 (c)]. At a higher

temperature of 623 K, the intensity of SnS₂ peak is more (14.94°) along with other phases of SnS and Sn₂S₃, is shown in Fig. 1 (d). Furthermore, at a relative higher temperature of 648 K, the SnS peak is fully disappeared, and binary sulfide phases of tin compound SnS₂ and Sn₂S₃ are also obtained, as clearly indicated in Fig. 1 (e). From this observed results of XRD analysis, which clearly indicate the optimized substrate temperature for the growing of a single phase SnS thin film is 573 K. In this optimization temperature of SnS thin film at 573 K, the size of the crystallites of film is determined as 74.5 nm from the peak at $2\theta = 31.493^\circ$ using the Debye–Scherer formula, $D = 0.9\lambda/(\beta \cos\theta)$, where D is the diameter of the crystallites forming the film, λ is the wavelength of CuK α line ($\lambda = 1.5406 \text{ \AA}$), β is the full width at half maximum in radians and θ is the Bragg angle. The observed crystallite size of SnS film is in good agreement with the reported values of 79.8 nm [24].

The surface morphology of tin sulfide thin film is grown by spray pyrolysis technique and analyzed by the scanning electron microscope image, as shown in fig 2 at the optimized substrate temperature 573 K.

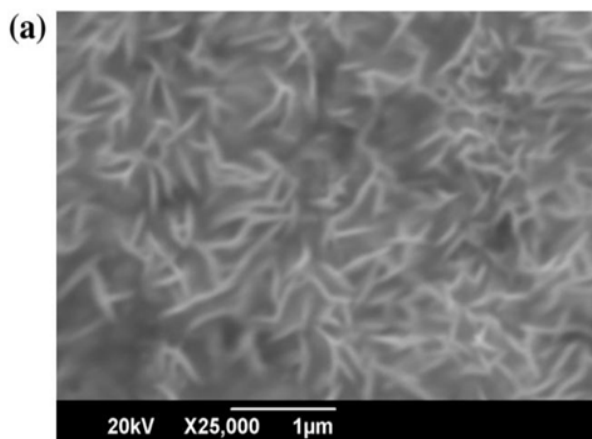


Fig. 2: SEM image of SnS film prepared at 573 K.

This SEM photograph was recorded with magnification of 25 k. It is seen that the film has a needle shape grain structure without cracks on the surface. The grains crystallization was relatively good, grain sizes were almost near and the surface was uniformly covered. Surface properties observed have a strong effect on the optical properties of the thin film such as optical transition, absorption and reflection. Similar needle-shaped grains for SnS films were observed in the earlier reports [25, 26]. This is the atomic force microscopy image (Fig 3) of SnS thin film deposited at 573 K on microscope glass slide.

The study of the AFM image indicates that these small

grains gradually combine and make larger grains (1 μ m). There are large numbers of Sn, and an S ion gets adsorbed

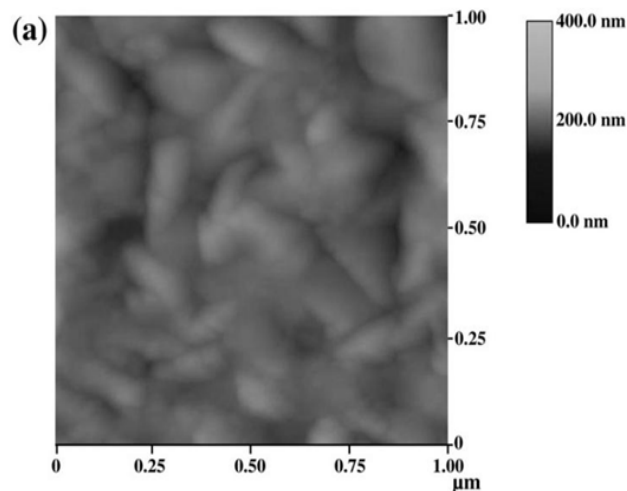


Fig. 3: AFM image of SnS film prepared at 573 K.

on the substrate which leads to crystallization. This film shows a very uniform and a complete coverage of material over the surface of substrate.

In the high photon energy region, the energy dependence of the absorption coefficient 10^4 cm^{-1} suggests the occurrence of a direct optical transition, which is investigated by the relation [27]

$$(\alpha h\nu)^n = k(h\nu - E_g)$$

where k is the proportionality constant, E_g is the optical band gap and $n = 2$ for a direct allowed transition. The band gap estimation of tin sulphide thin film is achieved by plotting $(\alpha h\nu)^2$ as a function of $(h\nu)$, as shown in Fig 4. The plot yields a straight line which indicates a good fit, extrapolation of the straight line to $(\alpha h\nu)^2 = 0$ gives the optical direct band gap values for different substrate temperatures and is tabulated in table 1.

With the increase of substrate temperature, the direct allowed band gap values are increased from 1.2 to 2.3 eV. A similar behavior of increasing of direct band gap values with the increase of substrate temperature was reported by [28]. The direct allowed band gap value for SnS thin film (1.3 eV) has been reported by the author [29]. In the present study, direct allowed transition band gap values are exactly evidenced with nano crystallite formation of SnS thin film of XRD spectrum, i.e., at the substrate temperature of 573 K, the direct allowed band gap value 1.3 eV is well agreed with single Bragg peak of SnS thin film at 31.493° [Fig. 1 (b)], and at 623 K, the direct allowed band gap value 2.3 eV also matches with the more intense Bragg peak of SnS₂ thin film at 14.94° [Fig. 1 (d)].

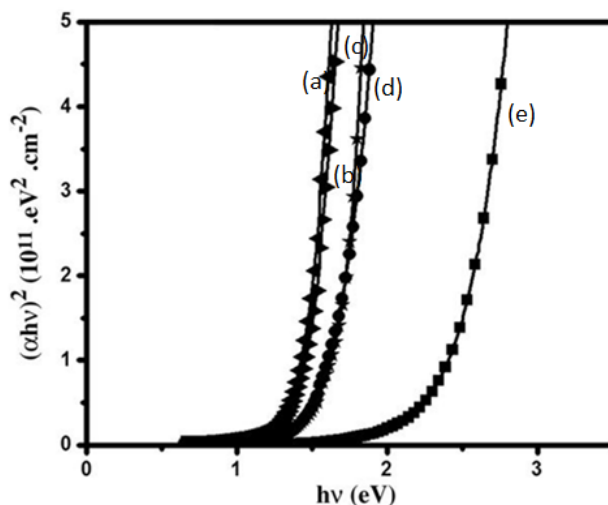


Fig. 4: $(\alpha hv)^2$ versus $h\nu$ for SnS thin films at (a) 548 K, (b) 573 K, (c) 598 K, (d) 623 K and (e) 648 K.

Table 1: Direct band gap values of SnS films with respect to substrate temperature.

Substrate Temperature (K)	Direct Band gap (eV)
548	1.2
573	1.3
598	1.55
623	1.6
648	2.3

4 Conclusions

Spray pyrolysed thin films of SnS crystallite with nano dimension had been deposited on to glass substrate using the precursor solutions of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and n - n dimethylthiourea at different substrate temperatures. From XRD spectrum, it revealed the crystalline nature of the thin film having an orthorhombic structure grown at preferential orientation of (111) miller plane at the optimized substrate temperature of 573 K. The film is found to exhibit p-type electrical conduction. The spray pyrolysed thin film shows direct allowed optical transition nature with band gap values. From this structural and optical analysis, which suggest that this SnS thin film could be a potential candidate for optoelectronic as well as thin film solar cell devices.

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