Optical and structural studies on SnS thin films grown by spray pyrolysis technique

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SnS thin film was grown on a glass substrate by using the spray Pyrolysis technique. This is relatively a new material which exhibits excellent properties to be used as an absorbent layer in solar cells. X-ray diffraction (XRD) measurements indicate that the synthesized samples were grown in two different phases (SnS,SnS_2) in the same deposition conditions but at different temperatures. However, through an extensive parameter study, conditions were found favourable to grow thin films predominantly in the SnS phase with orthorhombic structure at 400°C. Optical properties were analyzed by transmission, extinction coefficient and refractive index spectra. The optical method was used to determine the band gaps of the films. Uniform deposition of the material over the entire glass substrate with pin holes was revealed by scanning electron microscope (SEM).The band gap was found to be varying from 1.3eV to 1.8eV respectively.

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1. Introduction

In recent years, SnS thin films have attracted significant interest owing to their potential application in photovoltaic devices because of its high energy conservation [1], optoelectronic, fabrification of various devices such as holographic recording systems and solar collectors [2]. The factors that should be considered in developing new semiconductor materials include: 1) A suitable energy band gap that matches the solar spectrum to maximize absorption of the incident solar radiation. 2) The ability to deposit the material with an acceptable efficiency using a low-cost deposition method such that the "energy payback time" and "energy ratio" are acceptable. 3) Availability of abundance of elements. 4) There are low "environmental costs" when a "cradle to grave" life cycle analysis is made with respect to the extraction of elements, use of the thin film production methods, operation of the modules and disposal of materials that satisfy the above criteria [3].

SnS belong to the IV –VI group of layered semiconductor and crystallizes in orthorhombic structures where the Sn and S atoms are tightly bounded by weak Vander Waals forces. In addition Sn and S are abundant and non-toxic in nature [4]. SnS has an optical band gap of about 1.3eV, close to the optimum value of 1.5 eV, required for efficient absorption of solar radiation [5]. SnS thin films were deposited using different techniques such as vacuum evaporation [6], electro-deposition [7], electro less deposition [8], chemical melt growth [9], chemical vapour deposition (CVD) [10], plasma enhanced CVD, spray pyrolysis [11,12,13], RF sputtering [14], atomic layer deposition method [15], SILAR method [16], chemical bath method [17,18,19] and brush plated technique. Every technique has its own advantages and disadvantages. Spray pyrolysis technique is economical and highly feasible technique for large area deposition with high reproducibility. In this work, thin films of SnS have been grown and deposited by using spray pyrolysis technique. This paper aims to describe the technique used for the growth of the SnS films and the details of the effect of deposition parameters on the optical properties as well as on the phase and crystalline structure in which the sample was grown.

2. Experimental technique

The samples of the tin sulphide thin films coated at different temperature (300° to 400° C) are shown in Fig. 1. Table 1 shows the deposition parameters under which spray pyrolysis technique was carried out.

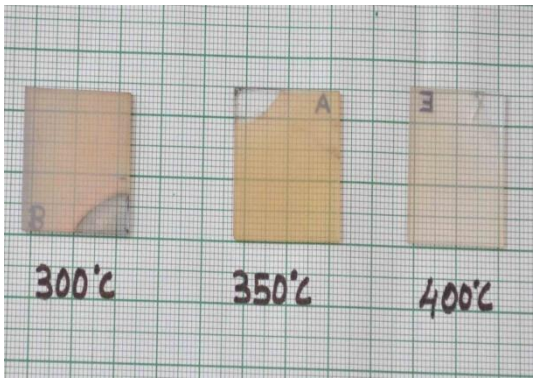


Fig. 1. Photograph of the samples.

Table 1. Deposition parameter and its values.

Deposition Parameter	values
Concentration	0.1M
Solution flow rate	5 ml/min
Gas flow rate	0.2 kg/cm^2
Nozzle to substrate distance	30 cm
Temperature	varied (300° to 400°C)

The starting Precursor solution was prepared by mixing 0.1 M of $SnCl_2$ in methanol and 0.1 M of thiourea in methanol. Both these equimolar precursor solutions were mixed and the final solution was stored in a burette. The burette was connected to one side of the spray head. The carrier gas, compressed air was allowed to flow through the other side of the spray head. The spray head was allowed to move manually in order to achieve uniform coating of the film on the substrate. The substrate temperature was monitored and controlled by a chromealumel thermocouple. The variation in the substrate temperature was controlled with an accuracy of ± 5^0C. The substrate was ultrasonically cleaned first with trichloroethylene and then with acetone and methyl alcohol and rinsed in distilled water.

The thickness of the film was measured using a digital micrometer. The structural studies of the films were examined using Shimadzu (XRD- 6000). The optical properties of the film were studied using transmittance spectra and it was recorded by carry 500 Varian UV-VIS-NIR Spectrophotometer with the wavelength range of 450 –2500 nm.

3. Result and discussion

SnS thin films prepared at different temperatures (300 °C, 350 °C and 400°C) were analyzedwith the help of X-ray diffraction pattern and are shown in Fig. 2. The XRD Pattern reveals that the deposited film is found to have orthorhombic crystal structure for 400°C and agrees well with the earlier reported structure [20,21,22]. The observed diffraction peaks of orthorhombic SnS films are found at 2θ values (26.47,33.91,37.97,51.58) corresponding to the hkl planes (120),(040),(131)&(112) respectively. The different peaks were indexed and corresponding value of interplanar spacing d were calculated and compared with the standard values is shown in the table [2], lattice parameter was calculated as a=4.36808 $A°$, b=10.572 $A°$, c=3.9008 $A°$, which was very much close to the reported data [JCPDS card No. 39-354]. The X – ray diffraction patterns for SnS_2 thin film prepared at 300 °C and 350 °C are shown in Fig. 3, 4. It was absorbed from the diffraction pattern that there was only one peak at 2θ = 14.98 °for (substrate temperature) T_s= 300 °C and 2θ = 14.82 °for Ts= 350°C corresponding to the hkl plane (040) with hexagonal crystal structure. The d spacing value is compared with JCPDS data file [23- 677]. These observations are in good agreement with the reports in literature that lower temperatures are more favorable for the growth of SnS_2 thin films [23].

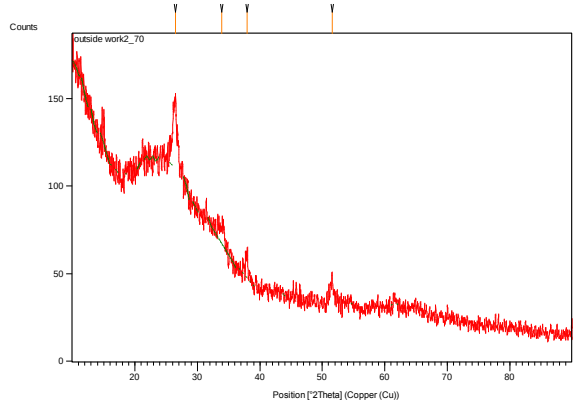


Fig. 2. X – ray diffraction pattern for SnS thin film at 400 ºC.

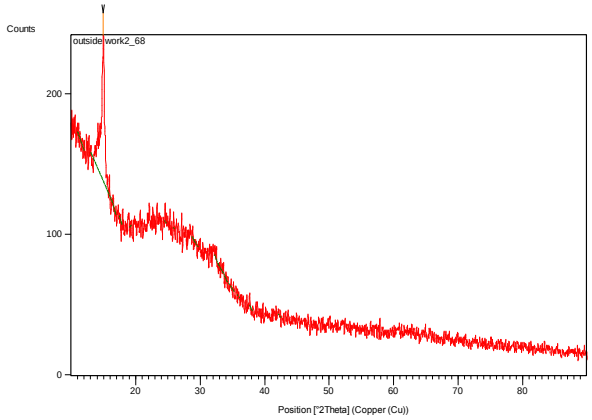


Fig. 3. X – Ray diffraction pattern for Sns_2 thin film at 300 ºC.

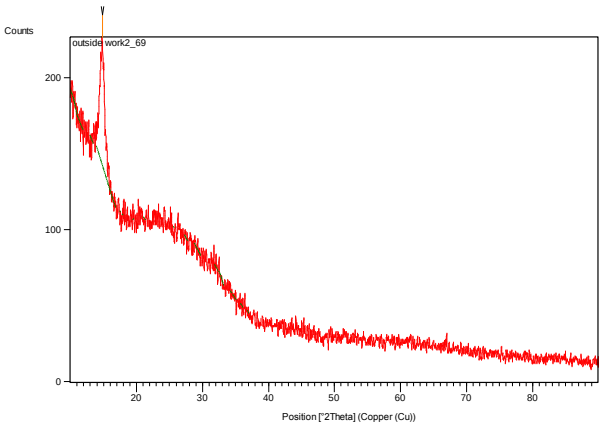


Fig. 4. X – ray diffraction pattern for SnS_2 thin film at 350 ºC.

Table 2. Comparison of characteristics of XRD peaks between standard ASTM data and experimental data for the temperature 400 °C.

Standard JCPDS data			Data from the deposited SnS film	
2 θ	d A°	hkl	2 θ	d A°
26.01	3.423	120	26.47	3.367
31.95	2.797	040	33.91	2.643
39.09	2.305	131	37.97	2.369
51.31	1.779	112	51.58	1.770

3.1 Optical properties

The optical spectra of SnS film showed that the transmittance of the film increased with increase in substrate temperature (T_s). The film coated at 400°C showed a maximum transmittance of ~ 80% at wave length of 2450 nm as shown in Fig. 5. It can be observed that an increase in the temperature improves the transmission which can be due to either decrease in thickness or stoichiometry of the films. The absorption co-efficient (α = (2.303 × A)/t) where 'A' is the optical absorption &'t' is the film thickness.

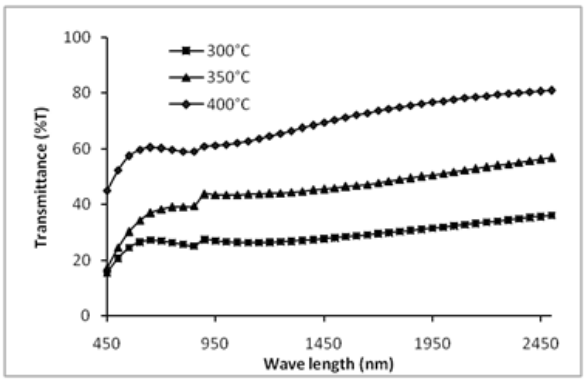


Fig. 5.Transmittance Vs Wavelength Spectra.

Table 3. Optical parameters of SnS Thin filims at different temperature.

Temperature (°C)	Maximum transmittance value in (%)	Refractive index	Band gap energy (eV)
300 °C	80	2.37	1.6
350 °C	56	2.5	1.8
400 °C	36	2.2	1.3

From the absorption co-efficient (α) the extinction co-efficient (k) is calculated using the relation $k = \alpha\lambda/4\pi$ [24] where 'λ' is wavelength of the incident light. The evaluated extinction coefficient k changes from 0.04 to 0.45 with the change of wavelength in the range 450- 2450 nm. The variation of k with λ in the film grown at different substrate temperature is shown in Fig. 6. It is seen that the fall in the k appears for all the films at critical wavelength (λ_c) above which the value of k increases gradually. The value of λ_c was different for films grown at different substrate temperature.

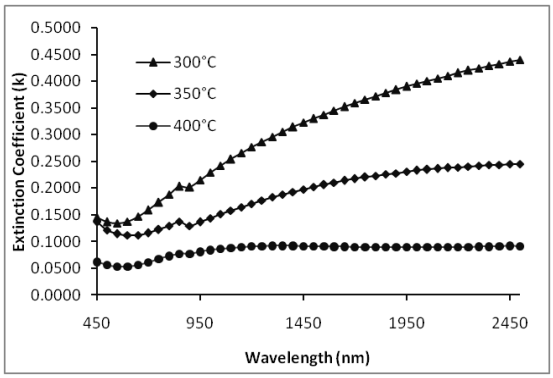


Fig. 6. Variation of extinction co-efficient with Wave length.

The refractive index of the film was calculated from optical reflection. Fig. 7 shows the variation of refractive index with the wavelength (λ). The refractive index of film at different temperature is shown in Table 3 whose value is little lower the reported value of Subramanian et.al. From the calculated value of absorption co-efficient (k) a plot has been drawn with $(\alpha h\nu)^2$&hν(photon energy). The extrapolation of the plotto the x- axis gives the band gap energy of SnS thin film as shown in Fig. 8. Band gap energy of chemically deposited thin film varies from 1.3 to 1.8eV. These values are very much closer to the earlier reported value [25, 26, 27].

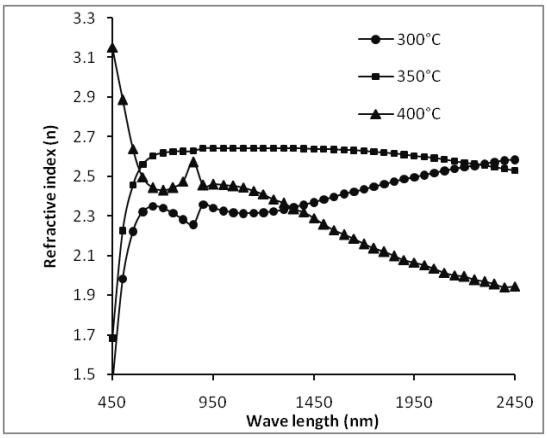


Fig. 7. Variation of refractive index with wave length.

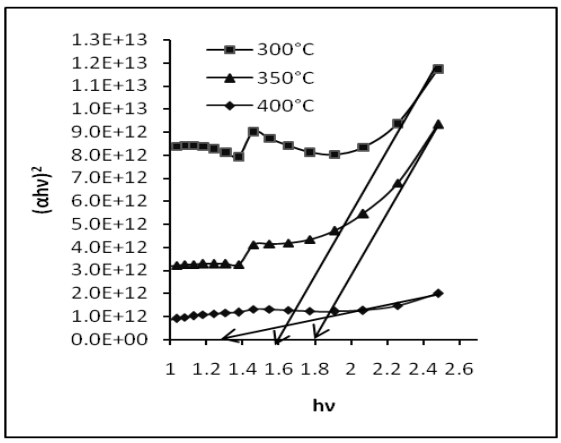
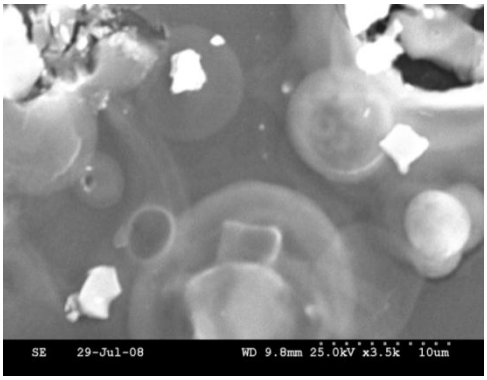


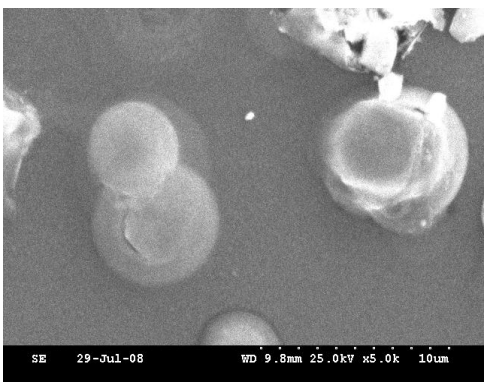
Fig. 8. $(\alpha hv)^2$ Vs (hv).

3.2 SEM analysis

SEM is a convenient and versatile method to study the microstructure of the film. The surface morphology of SnS thin film prepared at 400°C is shown in Fig. 9(a),(b). From the micrograph, it is clear that the agglomeration of spherical grains led to the formation of relatively big island with pin holes. The cluster of theSnS particle was found to be 10µm.



(a)



(b)

Fig. 9. (a), (b) SEM pictures of SnS thin film formed at 400°C.

4. Conclusions

The condition to prepare SnS thin films with adequate properties to be used as an observer layer in thin film solar cells was found with the help of spray pyrolysis technique. Characterization of sprayed thin film carried out through XRD indicates that tin sulphide films grows in SnS phase with orthoromic structure at 400°C and SnS_2 phase with hexagonal structure at 300ºC and 350°C depending on the deposition condition. The optical constants (extension co-efficient (k), refractive index (n) and optical band gap (Eg) were determined by simple calculation using transmission and absorption spectrum. The optical band gap was found to be varying from 1.3eVto 1.8eV respectively. From the SEM analysis the particle size of the film was found to be 10µm.

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