# Preparation and Characterization of SnS Thin Films for Solar Cell Application

S.S. Hegde, A.G. Kunjomana, K. Ramesh, K.A. Chandrasekharan, M. Prashantha

***Abstract*— Thin films of tin sulfide (SnS) were prepared by thermal evaporation technique on glass substrates, in the range of substrate temperature 50-300° C and their physical properties were studied with appropriate techniques. The obtained results were discussed in view of testing the suitability of SnS film as an absorber for the fabrication of low-cost and non toxic solar cell. For substrate temperature, $T_s$=300°C, the films showed only the SnS phase with a strong (111) preferred orientation. The films deposited at Ts < 300°C deviated from stoichiometry and additional phases such as $SnS_2$, $Sn_2S_3$ were found to be present. The structural parameters such as crystallite size, strain and dislocation density were estimated from XRD pattern. Studies showed that the crystallite size increased from 18 nm to 42 nm with increase of Ts. The surface morphology of the films was examined using scanning electron microscopy (SEM) and atomic force microscopy (AFM). The average grain size and surface roughness were found to increase with increase in the substrate temperature. The films grown at 300° C have shown blunted grains with an average size of 265 nm and rms roughness of 6.8 nm. Optical transmission spectra were recorded in the wavelength range 400-1200 nm, and the data was used to calculate absorption coefficient and optical band gap. The single-phase film grown at 300°C has shown a direct optical band gap of ~1.36 eV, with an absorption coefficient of $10^5 cm^{-1}$ above the fundamental absorption edge. These poly crystalline, single-phase and highly absorbing SnS thin films are suitable for the fabrication of hetero junction solar cells.**

***Index Terms*— Tin sulfide, Thin films, Photovoltaic materials, Thermal evaporation, Optical properties.**

## I. INTRODUCTION

Providing affordable renewable source of energy is paramount in this century in high energy demand country like India, with abundant sunlight. Affordable solar energy generation will be a key to sustain our economical growth. Solar photovoltaic (PV) is frequently cited as a promising but an economically unrealistic large scale energy supply options. One of the major hurdles for PV cell to become more popular is the fact that price of the electricity (cost/watt) produced by it is not yet competitive. This cost can be reduced by either improving the efficiency and/or reducing the production cost. Solar cell based on the use of $CuIn(Ga)Se_2$, CdTe, GaAs and crystalline silicon (c-Si) as an absorber material have produced with high efficiency (>23%). Problems however remains with these technologies are the lack of abundance of indium and gallium, toxicity of cadmium and high energy processing of silicon. Analysis of PV materials, demonstrated an ample opportunity for fruitful new research and development based on low cost and commonly available materials. It is the fact that, the devices performing below 10% power conversion efficiencies deliver the same lifetime energy output as those above 20% when a 3/4 material reduction is achieved [1]. In this view it is necessary to focus our research on new photo voltaic materials which makes solar cell cheaper, more efficient and produces significantly more energy over its life time. One such material is tin mono sulfide (SnS), which has some desirable properties for photovoltaic application. This is a IV-VI compound semiconductor material having direct optical band gap near to 1.3eV, which is close to optimal band gap (1.5 eV) of solar cells and high absorption coefficient ($\alpha > 10^4$ $cm^{-1}$) [2]. Its constituent elements Sn and S are abundant and are less toxic in nature. SnS has p-type electrical conductivity and it has theoretical light conversion efficiency, greater than 24% according to Loferski diagram [3]. Better understanding of material, and optimized device design may lead to SnS based solar cell with efficiency greater than 10% [4]. In this paper, we report on the preparation and characterization of thermally evaporated SnS thin films in order to study their suitability for the device application.

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## II. EXPERIMENTAL DESCRIPTION

Source material, SnS was prepared by melting high purity elements (99.99%) Sn and S in an evacuated quartz tube at a temperature of 1173 K. Tin sulfide films were deposited on corning 7059 microscopic glass substrate by thermal evaporation technique under high vacuum ($10^{-6}$ Torr) at different substrate temperatures varied from 50° C to 300° C. The distance between source and substrates, the films thickness and rate of deposition have been maintained as constant at 15 cm, 500 nm and 8 Å/s, respectively. A home made electric heater was used to heat the substrates and the film thickness was monitored with the help of digital thickness monitor. The as-deposited thin films of SnS were characterized for morphology, structural, and optical properties. The composition of the films was estimated using energy dispersive analysis of x-rays (EDAX, Model: JSM-840 A) attached with scanning electron microscope (SEM). The structural studies of the films were carried out using x-ray diffraction (XRD, Model: Philips X'Pert Pro) and structure dependent parameters, namely, crystallite size, microstrain and dislocation density have been evaluated. The

surface topology and morphology of the SnS films were examined using SEM and AFM at room temperature. The optical transmittance measurements were made in the wavelength range 400-1200 nm, using FT-IR spectrometer (model: Bruker IFS 66V/s).

## III. RESULT AND DISCUSSION

All the thin films deposited were well adherent to the substrate, pin-hole free and dark brown in colour. The adherence of the films increased with the increase of substrate temperature.

### *A. Surface morphology and compositional analysis*

The composition analysis of the SnS films showed that the tin and sulfur content in the films gradually varied with the increase of Ts. The films grown at lower substrate temperatures are sulfur rich, where as films deposited at 300$^o$ C was nearly stochiometric. Fig.1 shows SEM micrograph of SnS thin film deposited at two typical substrate temperatures, 50$^o$ C and 300$^o$ C. SEM images revealed the growth of randomly oriented, worm-like grains, which are uniformly distributed over the surface. From the micrograph it is clearly seen that grain size is increased with increase of Ts, which is clearly observed in AFM studies. The formation of bigger grains is due to coalescence of smaller grains. AFM pictures (2D view) of SnS thin films grown at two typical Ts are shown in fig.2. The average grain size and rms value of surface roughness were found to increase with increase in the substrate temperature. Availability of thermal energy at higher Ts is responsible for increased grain size [5]. The variation of grain size and surface roughness, with Ts is indicated in Table 1.

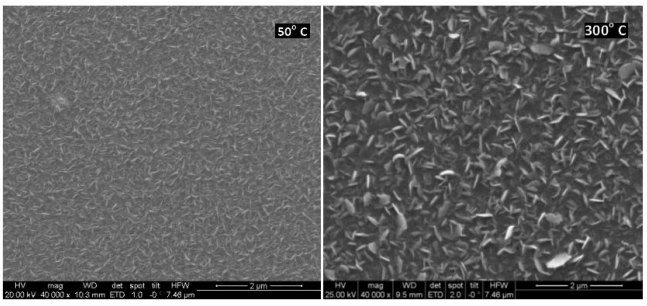


Fig. 1 SEM micrographs of SnS thin film deposited at Ts = 50$^o$ C and 300$^o$ C

### *B. Structural studies*

Fig.3 depicts XRD spectra of SnS thin films deposited at different substrate temperatures in the range 50-300$^o$C. The spectra reveal the presence of traces of other phases along with predominant SnS phase. Degree of crystallinity was also found to increase with substrate temperature. The XRD spectra of films grown at lower substrate temperatures (Ts $\leq$ 100$^o$ C) showed presence of both $SnS_2$ and $Sn_2S_3$ phases, along with dominant SnS phase. The films deposited at Ts = 200$^o$ C showed peaks mainly of SnS phase along with minor peaks corresponding to $Sn_2S_3$. No peaks are observed corresponding to $SnS_2$. However, the films deposited at Ts = 300$^o$ C exhibited only SnS phase. Structural parameters such as crystallite size, strain, lattice parameter, dislocation density and texture coefficient were calculated from XRD pattern. The crystallite size of the film was calculated from the Debye Scherer's formula, $D = 0.94\lambda/(\beta \cos\theta)$, where $\beta$ is the FWHM intensity in radians. The strain and dislocation density values were estimated using following standard relations. Strain ($\varepsilon$) = ($\beta \cos\theta$) / 4, dislocation density ($\delta$) = ($5\varepsilon$/D)( h/a + k/b + l/c). Crystallite size was increased from 18 nm- 42 nm with increase of substrate temperature. Generally the microstrain is indirectly proportional to crystallite size. It was observed that lattice strain and dislocation density decreased with increase of Ts (Table 1). This is an essential property for the fabrication of good quality thin film to use in optical devices. It is to be noted here that, crystallite size estimated from Scherer's formula is much is much smaller than the grain size estimated from AFM study. This indicated that grain is made up of several different crystallites.

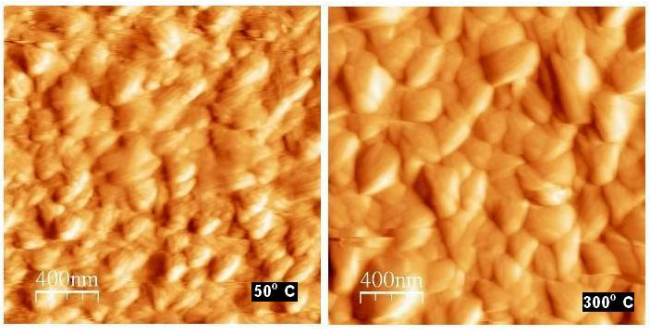


Fig. 2 AFM pictures of SnS thin films deposited at Ts = 50$^o$ C and 300$^o$ C

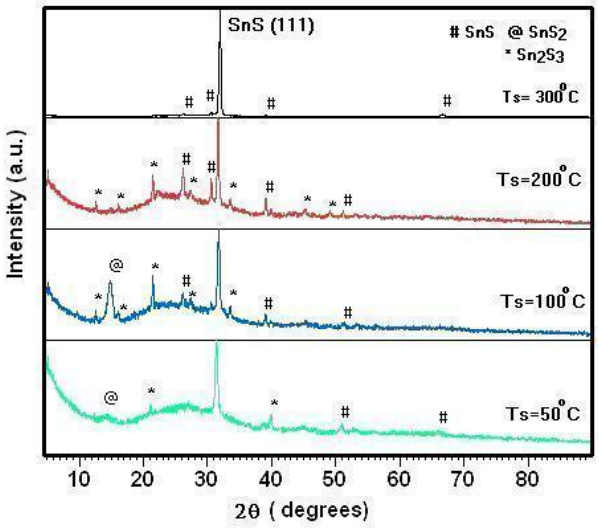


Fig. 3 XRD spectra of SnS thin films deposited at different values of substrate temperature.

Table 1 Micro structural properties of SnS thin films

| Substrate temp. (°C) | Grain Size (nm) | rms surface roughness (nm) | Crystallite size (nm) | Micro Strain ($10^{-3}$) Lines$^{-2}$m$^{-4}$ | Dislocation density ($10^{15}$) Lines m$^{-2}$ |
|---|---|---|---|---|---|
| 50 | 51 | 2.3 | 18.5 | 1.80 | 2.79 |
| 100 | 62 | 2.8 | 21.5 | 1.56 | 2.08 |
| 200 | 220 | 6.4 | 30.1 | 1.11 | 1.06 |
| 300 | 265 | 6.8 | 42.4 | 0.82 | 0.55 |

### C. *Optical properties*

Optical transmittance spectra recorded showed a sharp fall in transmittance at different wavelengths, which corresponds to fundamental absorption edge. The absorption coefficient (α) was calculated using the relations $\alpha = (1/t)\ \ln(1/T)$, where t is the thickness of the film. All the SnS films had high absorption coefficient, ( $> 10^5$ cm$^{-1}$) above the fundamental absorption edge.The direct optical band gap (Eg) , estimated from the $(\alpha h\nu)^2$ versus photon energy (hν) plot is shown in fig.4. Films grown at 50$^o$ C have shown high optical band gap value of 1.7 eV. This large band gap value may be due to presence $SnS_2$ ($E_g$ = 2.44 eV ) and $Sn_2S_3$ ($E_g$ = 2.0 eV) in SnS thin films [6]. Poor crystallinity of the films may also lead to higher optical band gap. Optical band gap decreased with increase in Ts and reached 1.36 eV, for the film deposited at 300$^o$ C. This value of band gap is comparable with the reported value for SnS thin films [7].

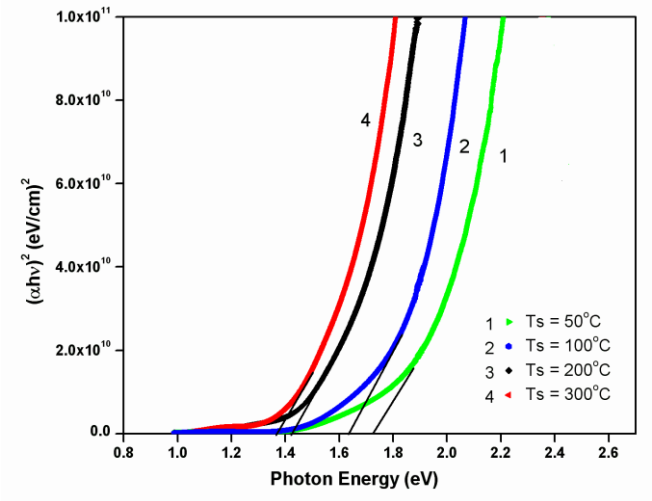


Fig. 4 $(\alpha h\nu)^2$ versus photon energy plot of SnS thin films

## IV. CONCLUSION

Tin sulfide films were grown by a thermal evaporation technique at different substrate temperatures on glass substrates. All the films had good adherence to the substrate and were free of pinholes. Grain size was increased substantially with increase in substrate temperature; where as increase in surface roughness is marginal. Films grown at lower substrate temperature exhibited a dominant SnS phase along with minor $SnS_2$ and $Sn_2S_3$ phases. Films deposited at 300$^o$ C were highly crystalline, nearly stoichiometric and showed only SnS phase. From the FWHM of XRD spectra, the respective strain, dislocation density and crystallite size were evaluated. The microstrain and dislocation density of the deposited films were diminished with increase in substrate temperature. All the deposited SnS films have shown high absorption coefficient, $> 10^5$ cm$^{-1}$, above the fundamental absorption edge. Single phase SnS thin films deposited at 300$^o$ C has showed the presence of direct optical band gap at 1.36 eV. These nearly stoichiometric, single-phase and highly absorbing SnS films with a direct optical band gap of 1.36 eV could be used as an absorber in the fabrication of thin film heterojunction photovoltaic devices.

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