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Structural and optical characterization of SnS thin films by electrodeposition technique

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SnS thin films were electrodeposited on ITO (indium tin oxide) glass substrates maintained at different temperatures using aqueous solutions containing 33 mM of $SnCl_2$ and 91 mM of $Na_2S_2O_3 \cdot 5H_2O$. The films were characterized to study the structural, morphological and optical properties. The X-ray diffraction studies of the films show the polycrystalline nature with orthorhombic crystal structure. Microstructural parameters such as crystallite size, microstrain, and dislocation density were calculated with respect to various temperatures. The scanning electron microscope (SEM) studies reveal good surface morphology with a large number of grains at the optimized temperature. The optical band gap of the SnS film was determined from optical transmittance data, in the spectral range 400–1100 nm and the direct band gap energy (E_g) was found to be 1.2 eV, which does agree well with earlier reported values. Fourier transform infrared spectroscopy (FTIR) studies confirm the presence of SnS films in the molecular structure.

Keywords: tin sulphide (SnS) thin films, cathodic electrodeposition, X-ray diffraction, SEM.

1. Introduction

The SnS thin films with band gap energy of 1.3 eV have great potential use in solar photovoltaic applications as an absorber material [1]. It exhibits *p*-type conductivity and the electrical properties can be controlled with different dopants like Ag, Al and Cl [2, 3]. The constituent elements, Sn and S are available in abundance in $SnCl_2$ and $Na_2S_2O_3 \cdot 5H_2O$. Besides, these elements are cheap and non-toxic. Among the many chalcogenides IV–VI semiconductors, SnS, SnSe, GeS and GeSe are promising materials for solar energy conversion [4]. SnS films are highly suitable for many applications in a number of solid state devices, such as photovoltaic [5–8], photo-electrochemical (PEC) [9], photoconductive cells [10], and intercalation battery systems [11]. In addition, SnS thin films have large optical absorption coefficient

($>10^4$ cm^{-1}) and high photoelectric conversion efficiency (>24%) [12] for the fabrication of heterojunction solar cells. Recently, a survey on the ores of tin sulphide by KOTEESWARA REDDY *et al*. [13] also indicates that SnS compound could be used for photovoltaic application as an alternative material. These films can be prepared by different techniques, such as plasma enhanced chemical vapour deposition (PECVD) [14], vacuum evaporation [15], chemical bath deposition [16], spray pyrolysis [17], electrodeposition [18]. The electrodeposition is widely used because it is a simple, economic and viable technique, which produces films of good quality for device applications. However, only very few investigations reported on electrodeposited SnS films in relation to their solar cell application are available. It is therefore essential to have a detailed study on the physical characteristics to estimate the suitability of SnS films for photovoltaic and optoelectronic device applications. In this work, an attempt has been made to prepare electrodeposited SnS films at different temperatures and characterize the same to assess their suitability for device applications.

2. Experiment

Electrochemical experiments were performed using a PAR scanning potentiostat (Model 362, EG & G, Princeton Applied Research, USA) employing three-electrode configuration with ITO substrate as cathode, platinum electrode as anode and saturated calomel electrode (SCE) as reference electrode which controls all experimental potentials. The chemicals used were of analytical reagent grade (99.5% purity from S.D. Fine Chemicals, Mumbai). The SnS thin films were electrodeposited on ITO substrates (sheet resistance 20 Ω/square) immersed in an aqueous electrolytic bath containing 33 mM of $SnCl_2$ and 91 mM of $Na_2S_2O_3{\cdot}5H_2O$ maintained at different temperatures (35 to 85 °C). The working solution of $SnCl_2$ was prepared by dissolving 1.1167 g of $SnCl_2$ in 150 ml of deionized water and the other $Na_2S_2O_3{\cdot}5H_2O$ was prepared by dissolving 3.3844 g of $Na_2S_2O_3{\cdot}5H_2O$ in 150 ml deionized water. The solutions were stirred for 10 minutes using a magnetic stirrer. 15 ml of each solution was taken and mixed well and stirred gently to get the electrolyte for electrodeposition of SnS thin films. The potential was constantly maintained at –1000 mV/SCE for all the depositions conducted at three different temperatures. The potential was so maintained to avoid the film feel out at the other potentials. The pH of the solution was maintained at 2.1 ± 0.1 by adding dilute HCl acid by performing various trials with other pH values. The deposition period was 30 min for

T a b l e. Optimized preparative parameters of electrodeposited SnS thin films.

Deposition potential	–1000 mV/SCE
Bath compositions	33 mM of $SnCl_2$, 91 mM of $Na_2S_2O_3{\cdot}5H_2O$
Bath temperatures	35, 60 and 85 °C
pH value	2.1 ± 0.1
Deposition time	30 min

all films deposited. The deposited SnS film was washed with deionized water, and dried in air. The optimized preparative parameters of SnS thin films are listed in the Table.

The SnS thin film formation is due to the ionic product of Sn^{2+} and S^{2-} ions. The steps involved in the electrodeposited SnS thin film are as follows:

$$S_2O_3^{2-} \rightarrow S^{2-} + SO_3^{2-} \tag{1}$$

The Sn^{2+} and S^{2-} are reduced at the cathode to form SnS

$$Sn^{2+} + S^{2-} + 2e^- \rightarrow SnS \tag{2}$$

The thickness of the deposited films was estimated using "stylus profilometer". X-ray diffraction data of the electrodeposited SnS samples were recorded with the help of Philips Model PW 1710 diffractometer with Cu Kα radiation (λ = 0.1542 nm). Surface morphological analysis was carried out using a scanning electron microscope (Philips Model XL 30). FTIR spectra of SnS thin films were recorded using Thermo Nicollet V-200 spectrometer. Optical transmittance spectrum was recorded using a JASCO-V-570 spectrophotometer.

3. Results and discussion

3.1. Film thickness

The deposition of SnS thin films was controlled by two independent variables: *i*) thickness and its uniformity, and *ii*) surface morphology [19]. The average thickness of layers deposited can be directly controlled by controlling the plating current and

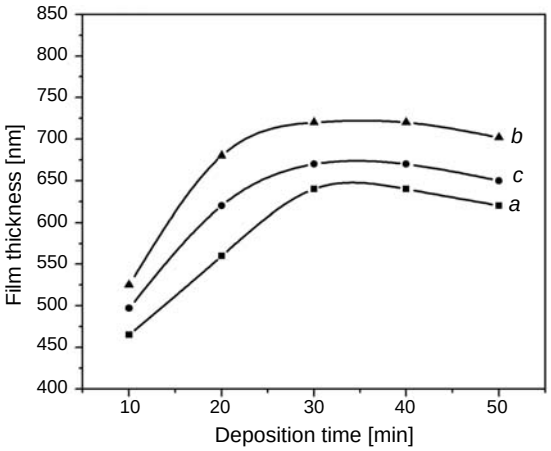

Fig. 1. Variation of film thickness with deposition time for SnS thin films: 35 °C (curve *a*), 60 °C (curve *b*) and 85 °C (curve *c*).

the depositing time. During deposition it was observed that at higher bath temperatures (85 °C and above) the film formation is hindered due to hydrogen evolution. At lower bath temperature (35 °C) irregular film growth with rough surface was obtained. Hence the optimized time was fixed as 30 min and the deposition time variation was fixed between 35 and 85 °C.

The variation of film thickness with deposition time for SnS films obtained under different bath temperatures varying from 35 to 85 °C is shown in Fig. 1. It is observed that the film thickness increases linearly with deposition time and attains a maximum for the deposition time of 30 minutes. Though the deposition time was increased to 40 minutes, the thickness of the deposited films remained constant. Further increase of deposition time (over 50 minutes) caused the thickness to be slightly reduced due to the peel-off of the film from the substrate. It is also observed that a maximum thickness (725 nm) was obtained for the films prepared at a bath temperature of 60 °C. Hence, the deposition path temperature was fixed at 60 °C.

3.2. X-ray diffraction studies

X-ray diffraction patterns of SnS thin film prepared at different bath temperatures of 35, 60 and 85 °C are given in Fig. 2. The XRD patterns reveal that the deposited films are found to have orthorhombic crystal structure and agree well with the earlier reported structure [20, 21]. The observed diffraction peaks of orthorhombic SnS films are found at 2θ values of 27.36, 30.39, 21.42, 32.05, 38.98, 44.65, 45.44, 51.06, 53.09, 56.72, 60.02, 74.03 corresponding to the *hkl* planes (021), (101), (111), (040), (131), (141), (002), (112), (122), (042), (250) and (270), respectively. The different peaks were indexed and the corresponding values of interplanar spacing *d* were calculated and compared with the standard values [22]. From Figure 2, it is observed that

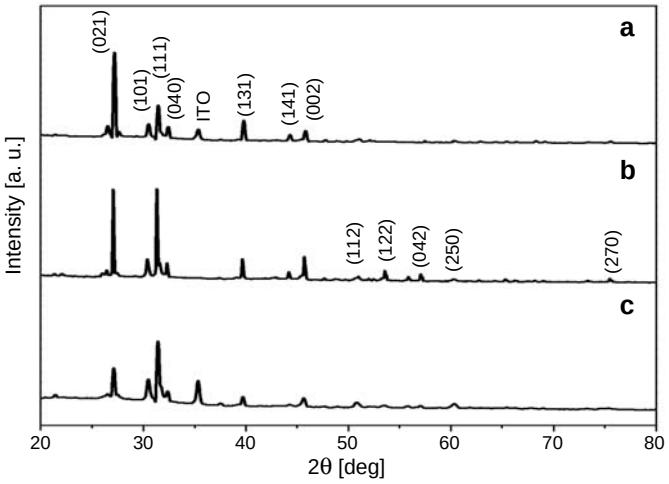

Fig. 2. XRD patterns of SnS films deposited at different bath temperatures: 35 °C (**a**), 60 °C (**b**) and 85 °C (**c**).

the films prepared at 60 °C have increased intensity along with additional peaks (Fig. 2**b**). The SnS films deposited at 60 °C are found to have good crystalline nature.

The height of (021) peak in X-ray diffraction pattern for SnS thin films prepared at bath temperature of 60 °C are found to have sharper peaks with small FWHM data. The average crystallite size has been calculated the Debye–Scherrer formula

$$D = \frac{k\lambda}{\beta \cos\theta} \tag{3}$$

where D is the mean crystallite size, β is the full width at half maximum (FWHM) of the diffraction line, θ is the diffraction angle, and λ is the wavelength of the X-ray radiation. The dislocation density δ can be evaluated from Williamson and Smallman's formula,

$$\delta = \frac{1}{D^2} \quad [\text{lines/m}^2] \tag{4}$$

The microstrain ε can be obtained using the relation

$$\varepsilon = \frac{\beta \cos\theta}{4} \tag{5}$$

The crystallite size and strain ε were calculated from Eqs. (3) and (4). The variation in crystallite size and strain with bath temperature for SnS thin films deposited at bath temperatures of 35, 60 and 85 °C is shown in Fig. 3**a**. It is observed from Fig. 3**a**, that the crystallite size increases with bath temperatures and the film deposited at 60 °C is found to have maximum crystallite size. The dislocation density δ can be evaluated from Eq. (5). Figure 3**b** represents the variation of dislocation density with bath temperature for SnS thin films. It is observed from Fig. 3**b** that the dislocation density decreases with increasing bath temperatures from 35 to 60 °C, and thereafter it slightly increases.

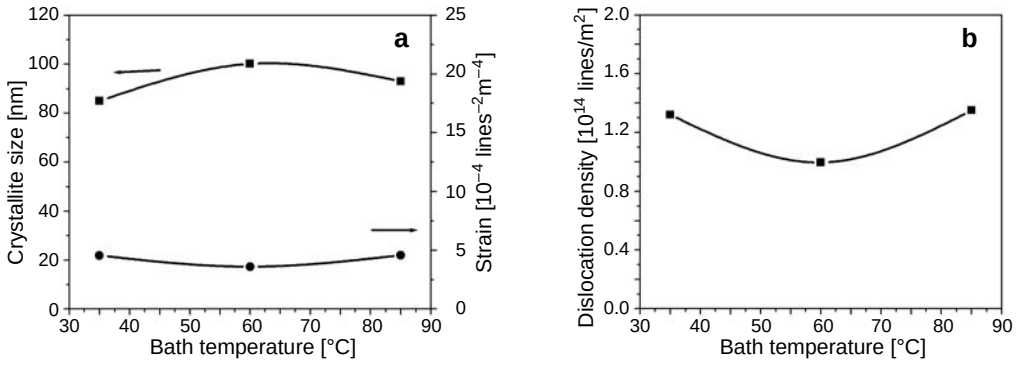

Fig. 3. Variation of crystallite size and strain with bath temperature of SnS thin films (**a**). Variation of dislocation density with bath temperature of SnS thin films (**b**).

3.3. Surface morphology studies

The surface morphology of SnS thin films electrodeposited at bath temperature of 60 °C, and deposition time of 30 min is shown in Fig. 4. Surface morphological studies of the SnS thin films have been carried out using scanning electron microscopy. The SnS film has a granular morphology with good surface coverage and good pyramid-like crystallinity. No cracks (pinhole) on the surface of the film are found. The crystallites are also oriented uniformly and are all of equal size.

3.4. FTIR studies

The FTIR spectra of SnS thin films prepared at bath temperatures of 35, 60, and 85 °C are presented in Fig. 5. Figure 5 shows SnS characteristic vibration bands at 2350 cm^{-1} and 930 cm^{-1} attributed to the hydroxyl groups and SnS groups. Transmittance decrease is observed at the vibration bands centered at 2350 cm^{-1} and 930 cm^{-1} with increasing bath temperature. All the absorption peaks are found to appear at the wave number (930 cm^{-1}) in the spectra of SnS (Fig. 5). These peaks are

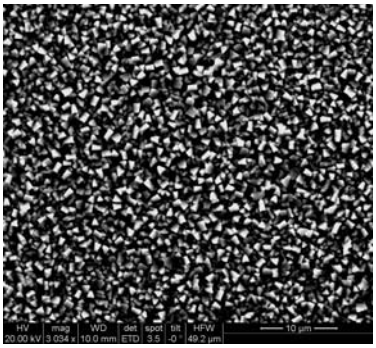

Fig. 4. SEM image of the electrodeposited SnS thin film at bath temperature of 60 °C.

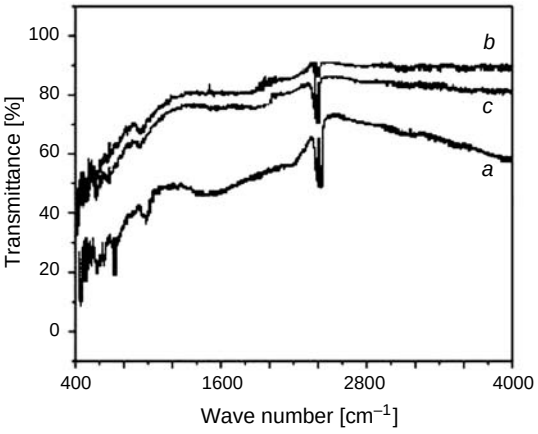

Fig. 5. FTIR spectra of SnS films at different bath temperatures: 35 °C (curve *a*), 60 °C (curve *b*), and 85 °C (curve *c*).

ascribed to the stretching vibration of Sn–S bonds, indicating the formation of SnS film. The results of FTIR analysis are in good agreement with XRD results.

3.5. Optical studies

Optical transmittance of the films was used to estimate the band gap energy. The absorption coefficient can be calculated using the relation

$$\left(\alpha h\nu\right)^n = A\left(h\nu - E_g\right) \tag{6}$$

where A is a constant (slope), E_g is the band gap energy and n characterizes the transition process (n takes the values 2 and 1/2 for direct allowed and indirect allowed transitions, respectively). From the calculated values of the absorption coefficients a plot has been drawn with $(\alpha h\nu)^2$ and $h\nu$ (Tauc's plot). α is the optical

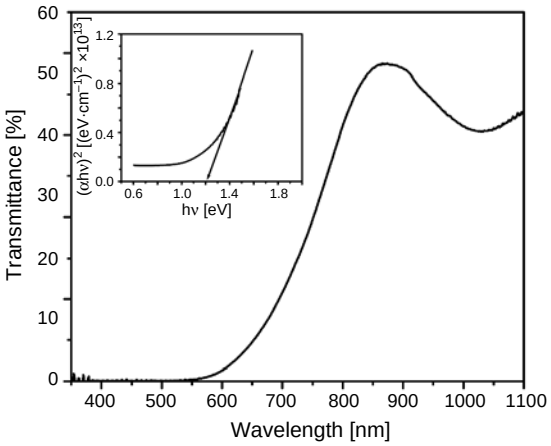

Fig. 6. Transmittance spectra of SnS thin film (inset: the curves of $(\alpha h\nu)^2$ versus $h\nu$ for the SnS film) deposited at 60 °C.

absorption coefficient of the material and $h\nu$ is the photon energy. Extrapolation of the plot to the x-axis gives the band gap energy of the SnS films deposited at 60 °C (inset, Fig. 6). This indicates that the direct band gap absorption in not dominant for the samples prepared. The direct band gap of SnS calculated is 1.2 eV, which compares well with the reported value of 1.34 eV [23].

4. Conclusions

Electrodeposited SnS thin films have been prepared with a deposition potential –1000 mV/SCE and pH value of 2.1±0.1 using a bath maintained at temperatures of 35, 65 and 85 °C. The XRD pattern indexed to the orthorhombic structure estimates

the maximum crystallite size as 99 nm from the Debye–Scherrer formula. The SnS film shows a granular morphology with good pyramid-like crystal structure and tightly bonded well formed dense network. These grains are oriented uniformly with nearly equal size. The optical band gap energy of 1.2 eV obtained from the transmittance data confirms the formation of well-crystallized SnS films.

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