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Electrosynthesis of SnS thin films with pentagon hallow like architectures

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Abstract: SnS thin films were deposited on conducting glass substrates using electro-deposition method. The as-deposited thin films were characterized by Powder X-ray diffraction, Laser Raman spectroscopic technique, Field emission scanning electron spectroscopy and UV-visible spectrophotometer to study the structural, functional, morphological and optical properties respectively. The X-ray diffractogram of as-deposited films reveals the formation of polycrystalline SnS thin films. A detailed growth mechanism is proposed for the formation of SnS thin films. Microstructural properties like crystallite size, dislocation density, microstrain and texture coefficient are calculated. Raman spectroscopic technique indicates A_g Raman active mode of vibration corresponding to SnS phase. FESEM micrographs exhibits pentagon shaped hallow like architectures with random orientations. The band gap was calculated using Tauc's plot from the data obtained using UV-Vis spectrophotometer data. All the results are discussed in detail.

Keywords: SnS; Electrodeposition; Thin films; Optical properties.

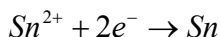
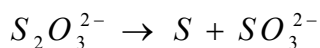
Introduction

Tin monosulphide (SnS) is a p-type semiconducting material with a layered orthorhombic structure and finds wide range of applications in solar photovoltaics, optoelectronic devices like holographic recording system, solar control device and near-infrared detector [1-2]. Its direct and indirect band gap energies were reported to be 1.3 - 1.5 eV and 1.0 - 1.1 eV. High absorption coefficient ($>10^4 \text{ cm}^{-1}$), non toxicity, abundance of its constituents are added advantages [3]. In the present investigation, SnS thin films were deposited on ITO coated glass substrates by Electrodeposition technique and their structural, morphological, functional and optical characteristics were elucidated by powder X-ray diffractometer, scanning electron microscopy, Raman spectroscopy and UV-Vis Spectrophotometer.

Experimental

SnS thin film was potentiostatically deposited using a three cell electrode system. The ITO coated on glass substrate with sheet resistance of $15 \Omega/\text{cm}$ was used as working electrode and graphite was used as

counter electrode. A saturated calomel electrode (SCE) was used as reference electrode. The substrate was ultrasonically cleaned with acetone and finally with distilled water before starting the deposition. The bath solution containing aqueous solution comprises of 30 mM of SnCl_2 and 100 mM of $\text{Na}_2\text{S}_2\text{O}_3$ and the pH of the bath solution were maintained at 2.1 ± 0.2 . The temperature of the bath was kept at 50°C and the deposition was carried out at the potential of -900 mV for about 30 minutes. Uniform, brownish black colored and well adherent film was obtained. The growth mechanism can be explained with the following reactions. The sulphur in $\text{Na}_2\text{S}_2\text{O}_3$ dissociates easily as it is highly unstable in acidic solution. Thus elemental S ion is released from thiosulphate ion by the following reaction



The Sn and S reduces at cathode to form SnS.

Results and Discussion:

Figure 1 (a) depicts XRD pattern of as deposited SnS thin film. The XRD diffractogram reveals that thin film has crystallized with orthorhombic structure. The XRD pattern shows that the thin film is polycrystalline in nature and belongs to Pbnm space group. Peaks were indexed with the standard JCPDS card no # 39-0354 [4]. The preferential orientation is observed along (111) crystallographic plane. The calculated lattice parameters are $a = 4.3\text{ \AA}$, $b = 11.8\text{ \AA}$, and $c = 3.9\text{ \AA}$, which are very closer to the standard values. Perhaps the ITO peaks are well covered by SnS phase. No other secondary phases of Sn and S are detected from the XRD data. The high intensities of the reflections manifests that the film is highly crystalline. Crystallite size evaluated from Debye Scherrer formula was 83 nm approximately. **Figure 1 (b)** shows Raman spectrum of as deposited SnS thin film recorded at room temperature. A broad Raman band observed at 230 cm^{-1} is attributed to the A_g mode of SnS [5]. There are no bands corresponding to the secondary phases of Sn and S observed in the spectrum. Also broad and less intense peaks are manifestations of high crystallinity in Raman spectrum. These observations are in agreement with the XRD data. **Figure 2(a-c)** illustrates FESEM micrographs of as deposited SnS thin film. The micrographs shows pentagon shaped hallow like architectures. Such morphology may be tailored as core shell structures for device fabrication. The particles are well covered with no cracks or pinholes present on the surface revealing good microstructural properties. Surface of the film exhibits no agglomerations or any other pronounced surface defects. Average particle size was estimated to be 435 nm . Further, we can modify the size of the particles by varying the deposition parameters like deposition potential, duration, scan rate etc., to get nanotubes or wire like architectures.

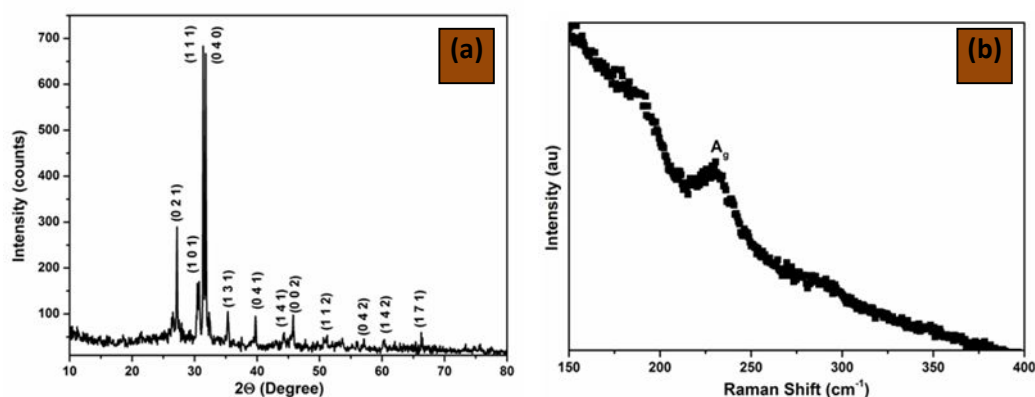
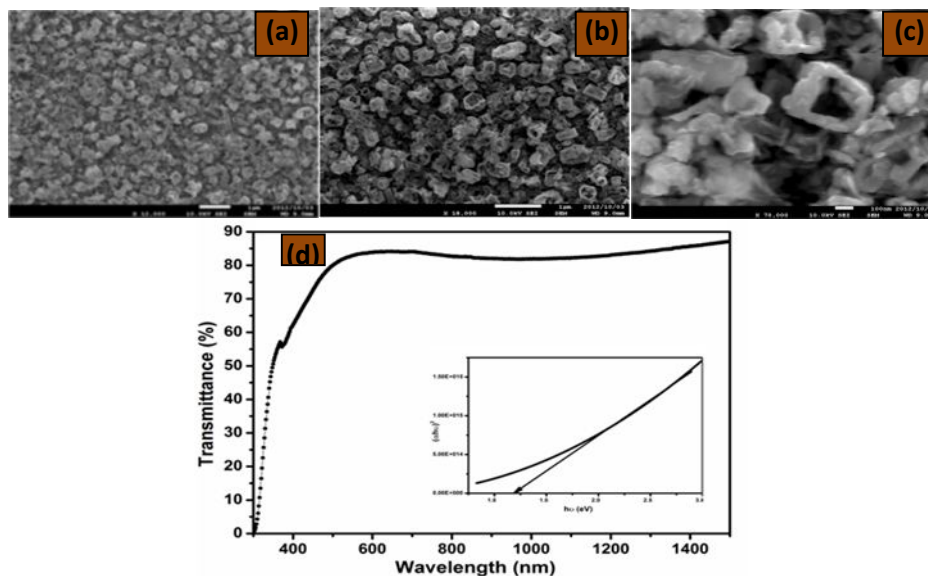


Figure 1 (a) XRD pattern and (b) Raman Spectrum of SnS thin film



**Figure 2 (a-c) FESEM micrograph and (d) Transmittance Spectrum of SnS thin film.
Inset figure is Tauc's Plot**

Figure 2 (d) shows transmittance spectrum of SnS thin film taken at room temperature in air atmosphere. The film exhibits low transmittance in the region 300 to 600 nm of visible spectrum and increases rapidly for wavelength longer than 600 nm. This high transmittance may be attributed to the homogeneous distribution of grains which minimizes the scattering loss. This is supported by FESEM micrographs. The low transmittance in the visible region makes it a suitable candidate as absorber material in solar cells. A good approximation of direct band gap energy can be obtained by extrapolating a straight region of $(\alpha h\nu)^2$ Vs $h\nu$ plot, where α is absorption coefficient. Inset of **figure 2 (d)** shows Tauc's plot. The estimated direct band gap is 1.28 eV, which are in good agreement with earlier reports [5].

Conclusion:

SnS thin film was successfully deposited by cathodic electrodeposition onto ITO coated glass substrates. XRD pattern reveals polycrystalline film with orthorhombic structure belonging to Pbnm space group. No secondary phases of Sn and S were observed in XRD which is further evidenced from Raman spectrum. FESEM micrographs show pentagon shaped hollows with average particle size of 435 nm. The direct band gap was estimated from Tauc's plot to be 1.28 eV. These results show a scope for SnS thin film coated using three electrode cell configurations for optoelectronic device applications.

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