

SnS Thin Films Fabricated by Normal Electrochemical Deposition on Aluminum Plate

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Summary: SnS thin films were deposited onto aluminum sheet through electrochemical deposition (ECD) from aqueous solutions containing SnSO_4 and $\text{Na}_2\text{S}_2\text{O}_3$. SnS Deposited was polycrystalline and of orthorhombic structure, and its composition was S-rich in acidic pH while Sn-rich at higher pH values. The relationship between film properties on the deposition parameter was investigated to optimize the deposition condition.

Introduction

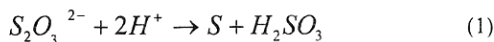
SnS is a p-type semiconducting material and is reported to have a direct band gap of about 1.3 and indirect band gap of about 1.0 eV [1-3]. Moreover both Sn and S are abundant and nontoxic. They are therefore ideally suited for absorption layers in solar cells.

SnS was deposited by electrochemical deposition method which is probably the best method to deposit thin films over large areas because in this method film thickness can be easily controlled by turning on /off the electric current as well as the assembly can be easily scaled up, at low cost. However, only a few attempts of ECD of SnS have been reported. Mishra *et al.*, [4] reported ECD of SnS from organic solutions, while Zainal *et al.*, [5] reported cathodic ECD from aqueous solutions. Recently Ichimura *et al.*, [6] performed pulse electrochemical deposition of SnS from aqueous phase. Aqueous bath consisted of SnSO_4 and $\text{Na}_2\text{S}_2\text{O}_3$ was used in this work. Thiosulphate ($\text{S}_2\text{O}_3^{2-}$) ions were employed as the sulfur source in ECD of SnS. Zainal *et al* and Ichimura *et al.*, used a similar bath for the ECD of SnS. Deposited film have been characterized chemically and structurally and the effect of deposition parameters on the film properties are discussed to optimize the deposition condition.

Results and Discussion

Mechanism of SnS formation on cathode.

The reaction of SnS formation on a cathode is expected to be similar to that reported for other sulfides [7]. Elemental S is released from $\text{S}_2\text{O}_3^{2-}$ by the reaction



and SnS is formed at the cathode according to the apparent reaction



In reality, Sn^{2+} ions are considered to be in the form of a complex, most probably with $\text{S}_2\text{O}_3^{2-}$ ions, because it has been found that solubility of SnSO_4 is enhanced in the presence of $\text{Na}_2\text{S}_2\text{O}_3$.

Figure 1 shows variations in the composition ratio Sn/S with pH. It is evident from the figure that at lower pH the deposit is sulfur-rich, while at higher pH, the deposit becomes Tin-rich. This trend is attributed to the spontaneous release of Sulfur from $\text{S}_2\text{O}_3^{2-}$ ions according to reaction (1). Similar trend of composition ratio with pH are reported elsewhere [6]. This elemental sulfur absorbed on the substrate and made the deposits S-rich. With increase in pH i.e. at pH 6 and 8, release of sulfur from $\text{S}_2\text{O}_3^{2-}$ ions decreases, so Tin content is increased in the deposited film.

Figure 2 shows changes in sulfur to tin ratio with change in the cathodic current density. It can be seen that at low c.c.d the deposit is sulfur-rich, while increase in cathodic current density results in an increase in the Tin content of the deposit. Almost similar results have been reported by M. Ichimura *et al.*[3] for the electrodeposition of SnS on In_2O_3 -coated glass sheet. This could be due to the deposition of elemental Sn, since the deposition potential may be more cathodic than the equilibrium potential of reduction reaction of Sn^{2+} (about -0.4 V vs. SCE).

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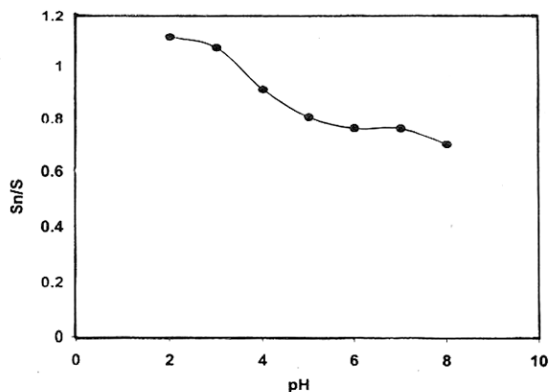


Fig. 1. Effect of pH of the solution on the composition ratio Sn/S.

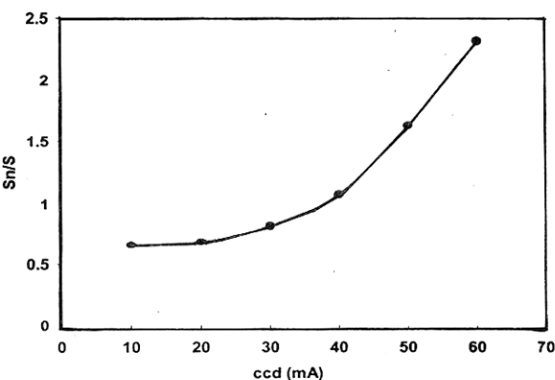


Fig. 2. Effect of cathodic current density on the composition ratio Sn/S.

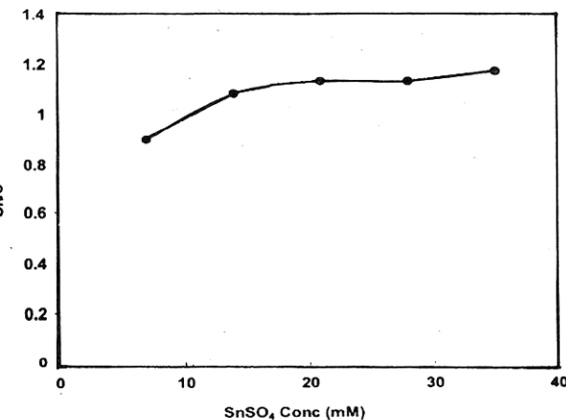


Fig. 3. Effect of Sn^{+2} concentration on the composition ratio Sn/S.

Figure 3 shows that the composition ratio Sn/S does not change drastically with changes in $[\text{Sn}^{2+}]$. This effect was studied at pH 4, cathodic current density ≈ 30 mA and $\text{Na}_2\text{S}_2\text{O}_3$ 100 mM. Almost same results were reported by M. Icimura *et al.* [3] for the effect of tin sulfate concentration on Sn/S composition ratio.

The FTIR spectra of SnS Figure. 4a shows the appearance of bands at 616, 1000-1200, 1400, 1620, 2840, 2920, 3000-3400 and 3700 cm^{-1} . These bands are almost at similar positions, if compared with the bands obtained in Figures 4b for standard SnS. The SnS used as standard was supplied by Merck. The bands, which appear in the spectrum of standard SnS at 619, 1000-1200 and 1400 cm^{-1} , are characteristics of SnS.

In Figure i.e. 4a and 4b the bands appeared at 1624 and $3000\text{-}3400\text{ cm}^{-1}$ are due to OH bending and stretching vibrations, respectively.

Figure 5 shows the XRD pattern of the electrodeposited SnS film. The peaks at about 31° and 47° are consistent with the results reported in the literature [3]. These peaks are of orthorhombic SnS which shows that the deposited film is polycrystalline.

Figure 6. Shows the SEM micrographs of SnS thin film electrodeposited on Aluminum sheet. This Figure also shows that film is polycrystalline and dense with a sub-micron grain size and a uniform thickness. However, surface roughness and porosity of the film is evident from the figure. Similar results for normal electrodeposited SnS film have been reported in the literature [6].

Experimental

A two-electrode cell was used for ECD of SnS. A clean aluminum sheet was used as the working electrode and a stainless steel sheet as the counter electrode. The deposition area was about 1.1 cm^2 . An aqueous bath used for the deposition contained 12 mM SnSO_4 and 100 mM $\text{Na}_2\text{S}_2\text{O}_3$. The pH of the solution was varied between 2-8 by adding dil. H_2SO_4 . In this work we studied the effect of pH, cathodic current density and SnSO_4 concentration on Sn/S ratio. Various parameters giving better results in terms of Sn/S ratio, surface coverage and morphology are presented in this manuscript.

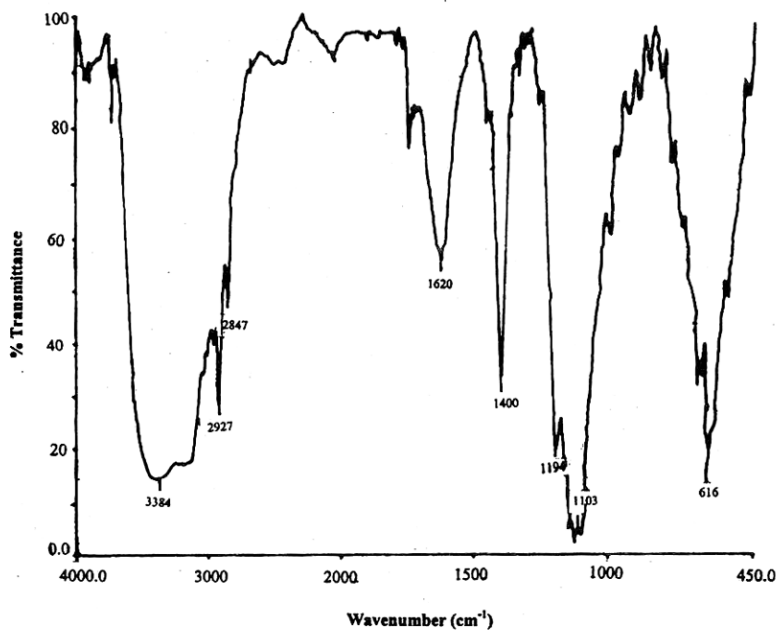


Fig. 4a. FTIR spectrum of SnS sample.

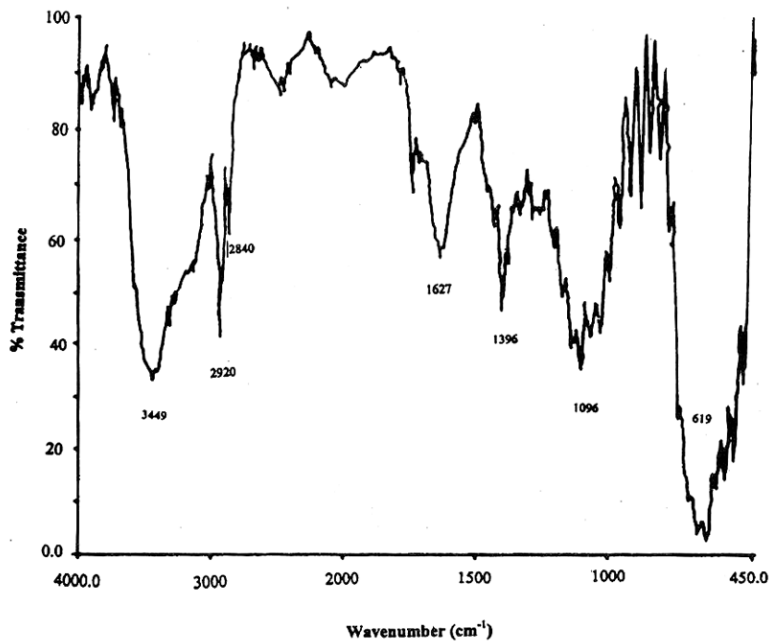


Fig. 4.b FTIR spectrum of standard SnS.

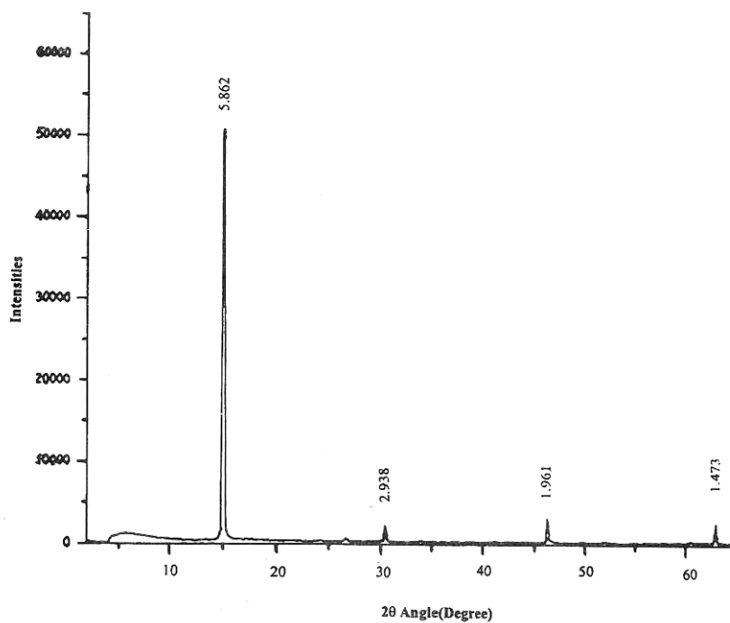


Fig. 5. XRD pattern of electrodeposited SnS film.

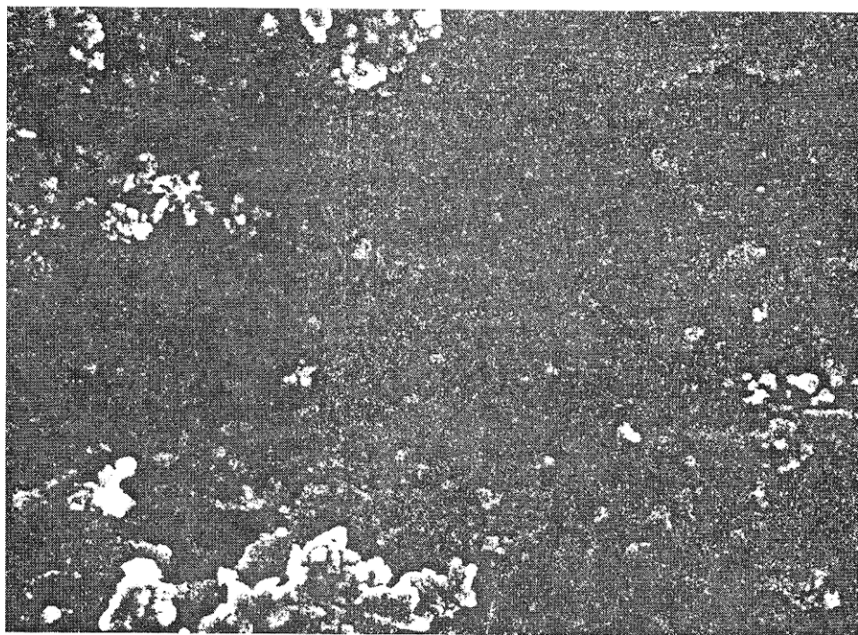


Fig. 6. Scanning electron micrograph of electrodeposited SnS film.

EDX analysis were performed for the composition of electrodeposited film. Surface morphology was observed by a scanning electron microscope (SEM). FTIR spectra were recorded using Parkin Elmer pc16 for comparison with standard tin sulfide. X-ray diffraction (XRD) was recorded for the electrodeposited film using Cu-K α radiation as an X-ray source.

Conclusions

The following conclusions can be drawn from the foregoing discussions.

SnS, a p-type semiconductor, was successfully deposited on aluminum sheet using the well known electrodeposition technique.

The composition ratio Sn/S is highly reluctant to pH and Cathodic Current Density and is weakly dependent upon the respective metal ion concentration.

The FTIR spectra for the electrodeposited SnS layers on Aluminum is consistent with the spectra obtained for standard SnS.

Electrodeposition has been found to be a very useful method for compound semiconductor deposition and the conditions for this technique can be further optimized to get better results.

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