CHAPTER 4

DEPOSITION OF SnS THIN FILMS BY ELECTROCHEMICAL DEPOSITION (ECD) AND THEIR CHARACTERIZATION

4.1 INTRODUCTION

Tin sulphide (SnS) is a p-type compound semiconductor with a layered orthorhombic structure. SnS has applications in photovoltaic, photochemical and photoconductive cells as an absorber layer. The direct and indirect bandgap energies were reported to be 1.3-1.5 eV and 1.0 to 1.2 eV, respectively (Lambros et al 1974, Nair et al 1994). There are several binary compounds in tin sulphide such as SnS, SnS$_2$, Sn$_2$S$_3$, and Sn$_3$S$_4$, which are semiconductors. SnS thin film is a p-type semiconductor with bandgap close to that of silicon, and the acceptor levels are created by doubly ionized tin vacancies. Therefore, thin films of SnS can be used as an absorber layer for solar cells with CdS or ZnS window layers.

SnS thin films have been deposited by various techniques, such as vacuum evaporation (Noguchi et al 1994), chemical bath deposition (CBD) (Tanusevski 2003), spray pyrolysis (Koteswara Reddy et al 1999), dip deposition (Lokhande 1990), electrodeposition (Ichimura et al 2000, Subramanian et al 2001), sputtering (Koteswara Reddy et al 1998) and others. Chemical bath deposition and electrochemical deposition techniques have been widely used to deposit thin films because they are cheap and simple compared to other techniques.
For reducing the production cost of solar cells, a new cost effective technique for depositing semiconductor thin films has been strongly desired. On this background, electrochemical deposition (ECD) is a very low cost deposition technique and used for large area deposition. By changing the deposition time, we can easily control the thickness of the depositing films. Therefore ECD seems to be very advantageous to semiconductor thin film deposition for solar cells.

Sn and S have quite low toxicity to human beings and environment. In this work, SnS thin films have been deposited by the electrochemical deposition technique. It is probably the cheapest method to deposit large area thin films, and has been widely used for metal plating. Sn is the most common material for the plating, owing to their abundance and non-toxic nature. Thus, success in fabricating the CdS/SnS solar cells by ECD can lead to real mass production of solar cells.

4.2 PREPARATION OF SnS THIN FILMS BY ELECTROCHEMICAL DEPOSITION

Tin sulphide was deposited by using electrochemical deposition (ECD) technique. ECD setup consists of three electrode cell, saturated calomel electrode (SCE) was used as a reference electrode, platinum sheet as the counter electrode (anode) and indium tin oxide (ITO) coated glass sheet was used as the working electrode (cathode). A typical electrochemical deposition setup is shown in Figure 4.1. The SnS deposition area was about 1 cm². A 50 ml of aqueous solution containing 30 mmol/l SnSO₄ and 100 mmol/l Na₂S₂O₃ was used for the deposition of SnS thin films. The pH of the solution was not adjusted, however, after mixing the chemicals the pH was about 2.7.
Figure 4.1 Schematic of the electrochemical deposition setup

- Working electrode: Glass/ITO
- Counter electrode: Platinum
- Bridge: KCl
- Reference electrode: SCE
- Function generator
- Potentiostat
- SnS film
- Bath concentration: 30 mmol/l SnSO₄, 100 mmol/l Na₂S₂O₃
SnS films were deposited using different applied potential; the potential applied is in the form of two step and three step pulses, which we call as pulsed electrochemical deposition. The reaction for the formation of SnS on ITO coated glass sheet (cathode) is expected to be similar to that of other sulphide semiconductor deposition. Elemental sulphur is released from \( \text{S}_2\text{O}_3^{2-} \) by the following reaction and Sn\(^{2+} \) and S are reduced at the cathode to form SnS (Mishra et al 1989, Omoto et al 2006).

\[
\text{S}_2\text{O}_3^{2-} + 2\text{H}^+ \rightarrow \text{S} + \text{H}_2\text{SO}_3 
\] (4.1)

\[
\text{Sn}^{2+} + \text{S} + 2\text{e}^- \rightarrow \text{SnS} 
\] (4.2)

The cyclic voltammogram for the ITO substrate using the bath concentration 30 mmol/l SnSO\(_4\) and 100 mmol/l Na\(_2\)S\(_2\)O\(_3\) is shown in the Figure 4.2. The potentials were chosen from the cyclic voltammogram and the deposition is carried out by applying two step and three step pulsed potential. Both the ITO substrate and the platinum sheet were washed ultrasonically in an alkylbenzene solution and dried using nitrogen jet before starting the experiments. After the deposition, the SnS thin films were washed softly in pure water and naturally dried in the air.

In case of three step pulse deposition, the applied potential for the deposition are \( V_1=-1.0, V_2=-0.6 \) and \( V_3=0.0 \) V Vs. SCE. The applied potential for the first step \( V_1 \) is -1.0 V Vs. SCE for 6 second, which is the potential used for deposition. The second step \( V_2=-0.6 \) V Vs. SCE applied for 10 second is called as diffusion potential, where the ions migrate near the substrate surface.
Figure 4.2  Cyclic voltammogram for 30 mmol/l SnSO$_4$ : 100 mmol/l Na$_2$S$_2$O$_3$ for ITO substrate

The third step $V_3=0.0$ V Vs. SCE for 10 second is used for dissolving the unreacted precursors at the film surface. The three step potential was applied in two forms, one is from negative to positive direction (condition A) and the other is from positive to negative direction (condition B), which are shown in Figures 4.3 and 4.4. In two step pulse deposition two types of potential were applied, which are called as reduction and oxidation potentials. For reduction -1.0 V Vs. SCE and for oxidation 0.0 V Vs. SCE was used at the interval of 6 and 10 seconds, respectively. The deposition time was about 30 minutes and those two potentials were applied alternatively throughout the deposition. The two step applied potential (condition C) is shown in Figure 4.5.
Figure 4.3 Deposition potential applied for the SnS deposition using condition A

Figure 4.4 Deposition potential applied for the SnS deposition using condition B
Figure 4.5 Deposition potential applied for the SnS deposition using condition C

Figure 4.6 shows the current profile for the three step pulse applied for the SnS deposition on ITO substrate. When the first step potential \( V_1 = -1.0 \) V Vs. SCE is applied for the deposition, there is a sudden increase in the current value. This current gradually decreases even when the potential is constant for about 6 seconds, owing to the decrease of Sn\(^{2+}\) ions and S atoms near the substrate surface. The gradual decrease in current shows decrease in the deposition rate of SnS because Sn\(^{2+}\) ions and S atoms near the substrate is not constant.

In the second step there is no such increase or decrease in the current value and it is almost zero. During this step it is expected that the Sn\(^{2+}\) ions and S atoms approach the substrate surface, but do not participate in the deposition. When the third step potential \( V_3 = 0.0 \) V Vs. SCE is applied, there is a current increase in positive direction. This current is responsible for dissolving of unreacted metal ion or weekly bonded SnS layer near the film solution interface. The deposited SnS thin film is shown in Figure 4.7.
The deposited films were subjected to various characterization studies: XRD studies for the identification of its crystal structure, SEM for the surface morphology, PEC to confirm the conductivity type, I-V studies for finding the resistivity etc.,

Figure 4.6 Applied potential and the observed current for the SnS deposition using three step pulse: (a) applied potential (b) observed current for the applied potential

Figure 4.7 SnS thin film deposited using electrochemical deposition method
4.3 RESULTS AND DISCUSSION

4.3.1 Thickness, surface morphology and optical studies

The thickness of the as deposited SnS film deposited for 30 minutes is around 1.75 μm and it is measured using the step height measurement. Figure 4.8 shows the thickness of the deposited SnS film. The SEM photographs of the as deposited and 300°C annealed films are shown in Figures 4.9 and 4.10, respectively. The film surface is composed of fine grains and has smooth surface. Whereas for the DC deposited films the grains are large and the two step deposited films also have grain size higher than that of the three step deposited film. For the present investigation the three step deposited films were used for studies. The bandgap of the deposited films were estimated from the optical transmission spectra. In the case of two step deposited samples, the direct bandgap was calculated as 1.4 to 1.5 eV. It was not possible to obtain clear absorption edge for the samples deposited under the three step pulse condition, which may be due to amorphous nature of the films. The resistivity of the films deposited for all the three conditions vary from 130 to 230 Ω cm.

4.3.2 X-ray diffraction studies

X-ray diffraction spectrum was recorded for the SnS film (thickness = 1.75μm) deposited for 30 minutes using electrochemical deposition method. The XRD spectrum shows that the deposited SnS thin film is of orthorhombic crystal structure (Nabi et al 2003). The X-ray diffraction patterns for the films of SnS deposited at different conditions are shown in Figure 4.11. The peak at 30.6° corresponds to the diffraction of the ITO substrate. The peaks at about 26.9°, 32.1°, 39.8°, 44.1° and 45.05° correspond to (120), (040), (131), (141) and (002). The SnS peak at 31.5° corresponding
to (111) plane nearly overlaps with the ITO signal. The deposited films are polycrystalline in nature. The diffraction pattern does not exhibit clear dependence on the deposition conditions.

Figure 4.8  Thickness of the SnS film measured using step height measurement
Figure 4.9  SEM photograph of as deposited SnS thin film

Figure 4.10  SEM photograph of 300°C annealed SnS thin film
Figure 4.11 XRD patterns for the SnS films deposited with different applied potentials

4.3.3 Photoelectrochemical (PEC) studies

Figure 4.12 shows the result of the PEC measurement for the as deposited SnS thin film with a chopped light illuminating under the linearly increasing cathodic bias (0 to -1 V Vs. SCE). The value of the current changes due to chopping of the light. But under the anodic bias (0 to +1 V Vs. SCE), the value of the current does not change by illumination. Under chopping light the carriers are excited in the illuminated region in the SnS thin film, and excited minority carriers diffuse to the surface during their life time to participate in the electrochemical reaction at the film/electrolyte interface. Hence, this phenomenon is observed under the cathodic biasing;
this means the reduction reaction at the film surface is enhanced under illuminating condition. This shows that the minority carriers generated here are electrons (Omoto et al 2006). This result proves that the SnS thin film is of p-type and shows photoconduction behavior.

![Figure 4.12 Photosensitivity plot for SnS thin film](image)

**Figure 4.12 Photosensitivity plot for SnS thin film**

### 4.4 CONCLUSIONS

SnS thin films were deposited on ITO substrates from the aqueous solution containing SnSO₄ and Na₂S₂O₃ by electrochemical deposition. Films were deposited for different applied potentials and their properties were studied. The deposited SnS is polycrystalline and orthorhombic in structure. The bandgap was estimated as 1.4 to 1.5 eV from the transmittance measurement. The surface morphology of the deposited films is smooth and they have good adherence with the substrate. The SnS thin films exhibit photoconducting behavior under the cathodic bias, which is the characteristic behaviour of p-type semiconductor.