CHAPTER-3
EXPERIMENTAL STUDIES

3.1. INTRODUCTION

This chapter deals with the experimental details pertaining to the preparation of SnS\textsubscript{x}Se\textsubscript{1-x} (x = 0, 0.5 and 1.0) films using electrodeposition and brush plating techniques. The various experiments that are performed for the structural, optical, electrical and compositional characterization for the deposited films are discussed. The dc potentiostatic method is employed throughout this work, i.e., the deposition potential is kept constant and is one of the important parameters to be optimized to get stoichiometric films [1]. In this chapter, the cyclic voltammetry method [2] of fixing the deposition potential is dealt with in detail. Under the optimized conditions, the SnS\textsubscript{x}Se\textsubscript{1-x} films have been deposited and they have been characterized for their materials properties.

3.2. EXPERIMENTAL DETAILS OF ELECTRODEPOSITION

The schematic representation of the deposition set up is shown in Fig. 3.1. A Saturated Calomel Electrode (SCE) and Platinum (Pt) electrode of area 2 cm x 2 cm (99.9\%) were employed as the reference and counter electrode respectively. The films were deposited on tin oxide coated glass plates with the exposed deposition area kept constant at 1.0 cm\textsuperscript{2} throughout the studies. The working and counter electrodes were kept at a distance of 1.0 cm and surfaces were aligned parallel to ensure attraction of the released ions and to enable the growth of the film exactly perpendicular to the cathode surface [3]. The reference electrode tip was placed very close to the cathode surface so that the exact potential at the surface will be monitored without getting affected by the solution resistance [4]. An EG&G Princeton Applied Research (PAR) Model 362
Fig 3.1. Schematic representation of the electrodeposition cell.

1. Potentiostat EG & G (PAR 362)
2. Ammeter - Digital multimeter
3. Working electrode
4. Counter electrode
5. Saturated Calomel Electrode (SCE)
6. Connecting bridge for SCE
7. 50 cc Beaker
8. Solution bath
9. Magnetic stirrer with temperature control
10. Teflon paddle.
potentiostat was employed. The tin oxide coated glass substrates were first cleaned well with triple distilled water followed by the application of acetone. The substrates were cleaned well again with triple distilled water before use. Platinum counter electrodes were kept in hot dilute H₂SO₄ followed by treatment with acetone and triple distilled water. The saturated calomel electrode was placed in potassium chloride (KCl) solution kept in a beaker. The potential of the calomel electrode depends only on chloride ion concentration. Hence the saturated condition of the KCl was ensured before the start of each deposition.

3.3. CYCLIC VOLTAMMETRY (CV)

The electrodeposition technique of semiconductor film is sensitive to the conditions such as current density, electrode potential, concentration of the respective species, pH of the solution and the temperature of the bath. For a single metal deposition, these parameters can be optimized easily. But, codeposition of binary and ternary alloys/semiconductors is difficult because the conditions favourable for deposition of one of the metals may differ from the other constituent metals. Moreover, the electrodeposition technique becomes more complicated for alloys/compounds if one wants to have a desired stoichiometry, a critical condition necessary for semiconductors. In this work, experimental prediction of deposition potential from cyclic voltammetric method is discussed.

In CV, the electrode potential is varied in a desired fashion with respect to a stable reference electrode system. The current flow is measured between the working and counter electrodes as in polarography [4]. The voltage is linearly varied from an initial to final potential value and immediately swept back at the same sweep rate to the initial potential [5,6]. EG&G Instruments PAR Versastat II M278 was used to perform cyclic voltammetry experiments. This is a self contained integrated as well as a sophisticated system which provides both diverse control and data reduction functions for the study of redox systems. Fig. 3.2 shows the photograph of the experimental set up to perform CV studies.
Fig. 3.2. Photograph of the Experimental set up to perform CV studies
3.3.1. Experimental Details

Initially voltammograms for SnCl₂, SeO₂, Na₂S₂O₃ and the background electrolyte water were recorded. The concentration of SnCl₂ was 5.0 mM and the SeO₂ and Na₂S₂O₃ were 2.0 mM and 2.5 mM each respectively. To study the formation of binary compounds, the voltammograms for solution mixtures of SnCl₂ + SeO₂ and SnCl₂ + Na₂S₂O₃ were recorded. To study the formation of the solid solution, the voltammograms were obtained with different concentrations of SeO₂ and Na₂S₂O₃ and keeping SnCl₂ concentration as a fixed one. The experiments were performed at a constant pH of 1.5 and the CV were performed at room temperature. The electrode surface was cleaned with triple distilled water followed by methanol to flush away any entrusted material on the surface. Before recording the voltammograms, the voltammogram for the 0.1 M potassium chloride solution was recorded for standardizing purpose. The CV is characterized by the following six important parameters: (1) Initial potential (2) High potential (3) Low potential (4) Sweep rate (5) Sweep segments and (6) Sensitivity.

The test solution was continuously stirred using a magnetic stirrer and left to attain steady state. For every system, preliminary experiments were carried out to evaluate the potential region where the electrochemical process took place. The voltammograms were recorded by changing the sweep rates from 20 mV/sec to 800 mV/sec. The reproducibility of the result was often verified by recording voltammograms under identical conditions at various time intervals. Purified N₂ gas was purged into the electrolyte solution at least for 15 minutes to remove the dissolved oxygen before starting the experiment.

3.3.2. Results and Discussion

(i) CV studies of Sn, Se and S solutions

The voltammograms of plating baths with different compositions give information on the possible range of deposition potentials. The current versus
voltage plot has several characteristics which varies in different species in the test solution.

Many electrochemical information are obtained from the recorded voltammograms. However, only limited number of CV patterns are chosen for our discussion as they are sufficient to the selection of deposition potential range.

The cyclic voltammetry for a tin (II) concentration of 5.0 mM in aqueous bath was carried out at a scan rate of 20 mV/sec using conducting oxide coated as working electrode (Fig. 3.3). The forward scan current remains at a very low value up to \(-0.4\) V\textsubscript{SCE}. The current starts increasing afterwards and a cathodic peak is observed at about \(-0.72\) V\textsubscript{SCE}. This cathodic current flow is associated with Sn(II) reduction process. The reverse scan forms a loop like curve confirming the formation of tin film all over the cathodic surface. This reverse scan crosses the forward scan at \(-0.49\) V. The anodic peak is observed at \(-0.42\) V. This well defined anodic peak confirms the dissolution of the tin layer deposited during the cathodic scan. The reversible nature of the tin deposition mechanism is confirmed by nearly constant potential values of the anodic peaks with the different scan rates [5,7].

Fig. 3.4.a shows the CV pattern obtained for 2.0 mM SeO\textsub{2}{2} solution for the scan rate 20 mV/sec. These patterns are found to be similar to those of the CV patterns reported for SeO\textsub{2}{2} solutions [6]. The current starts increasing beyond \(-0.6\) V revealing the onset of reduction process. It is followed by a broad but small peak at \(-0.75\) V corresponding to the reduction of SeO\textsub{2}{2} to Se. A reddish film formation followed by an increase of cathodic current can be attributed to H\textsub{2} evolution. The deposition reaction is reconfirmed by the reversed scan, showing zero current interception at about \(-0.7\) V. A very small stripping peak starts at \(-0.3\) V and no other anodic process is detected up to 0.0 V. At a scan rate of 100 mV/sec as shown in Fig. 3.4.b, cathodic current starts flowing at \(-0.50\) volt. The strong cathodic peak observed at \(-0.73\) V is the well defined peak associated
Fig. 3.3. Cyclic voltammogram obtained for 5.0 mM SnCl₂ at the scan rate 20 mV/sec.
Fig. 3.4. Cyclic voltammogram obtained for 2.0 mM SeO$_2$ at the scan rates (a) 20 mV/sec  (b) 100 mV/sec
with the reduction of SeO\textsubscript{2} to Se as explained earlier. The zero current interception is shifted correspondingly to −0.55 volt.

The voltammogram at a scan rate of 20 mV/sec obtained for a tin oxide coated working electrode in 2.5 mM Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} in the potential range 0.0 V to −1.0 V is shown in Fig. 3.5.a. The cathodic current starts flowing at about −0.63 V. A shoulder at −0.7 V may be associated with the reduction of thiosulphate ions. This reduction wave may be due to the following reaction, i.e., S\textsubscript{2}O\textsubscript{3}\textsuperscript{2−} ions released during the disproportionation of Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} at the pH of 1.5.

\[
S_{2}O_{3}^{2−} \rightleftharpoons S + SO_{3}^{2−} \quad (3.1)
\]

\[
S + 2e^{-} \rightarrow S^{2−} \quad (3.2)
\]

No significant change in the voltammograms is observed when scanning was performed at different rates, e.g. for 100 mV/sec as shown in Fig. 3.5. b.

(ii) CV studies of SnCl\textsubscript{2} + SeO\textsubscript{2} solutions

In order to fix the deposition potential range for the synthesis of SnSe thin films, CV studies are performed for the Sn\textsuperscript{2+} and SeO\textsubscript{2} in the bath. When 2.0 mM of SeO\textsubscript{2} solution is added to the electrolyte containing Sn(II) ions, changes are observed in the CV pattern as shown in Fig. 3.6. The cathodic current shows a sudden increase at −0.6 V, just slightly negative of the potential is required to plate elemental tin. A clear cathodic wave is observed around −0.7 V which is attributed to the reduction of SeO\textsubscript{2} species followed by hydrogen evolution in the acidic environment. The cathodic peak current is about 120 µA which is higher than the cathodic peak height of 75 µA observed for the Sn reduction peak as in Fig. 3.3. The reaction of formation of tin selenide is attributed to

\[
Sn^{2+} + 2e^{-} \rightleftharpoons Sn(s) \quad (3.3)
\]
Fig. 3.5. Cyclic voltammogram obtained for 2.5 mM Na₂S₂O₃ at the scan rates (a) 20 mV/sec (b) 100 mV/sec
Fig. 3.6. Cyclic voltammogram obtained for 5.0 mM SnCl$_2$ + 2.0 mM SeO$_2$ at the scan rate 20 mV/sec
\[ \text{H}_2\text{SeO}_3 + 4\text{H}^+ + 4e^- \rightleftharpoons \text{HSeO}_2 + 4\text{H}^+ + 4e^- + \text{OH}^- \]
\[ \rightleftharpoons \text{Se(s)} + 3\text{H}_2\text{O} \]  \hspace{1cm} (3.4)

\[ \text{Sn} + \text{Se} \rightarrow \text{SnSe} \]  \hspace{1cm} (3.5)

In the reverse scan, the zero current interception with forward scan occurred at potential of \(-0.85\) V. A stripping peak is observed around \(-0.45\) V beyond this no other anodic process was detected upto \(0.0\) V.

The influence of end negative potential upto which cathodic scan was terminated and then reversed, has been studied. Fig. 3.7.a, b and c show the CV scans performed upto \(-1.0\), \(-0.9\), \(-0.8\) V at a scan rate of 100 mV/sec.

It is observed that the anodic dissolution peak height decreases with reduced negative potential values. The observed anodic peak current values are 94 \(\mu\)A, 60 \(\mu\)A and 45 \(\mu\)A for the scan reversing negative potential of \(-1.0\) V, \(-0.9\) V and \(-0.8\) V respectively. When the negative scan is performed upto \(-1.0\) V, the current density during cathodic scan is large which is associated with the formation of SnSe in addition to elemental Sn. This is confirmed by the higher peak current of the anodic peak which arises due to the dissolution of the excess tin formed alone with SnSe. The anodic peak current values for \(-0.9\) V and \(-0.8\) V are found to reduce which may be due to the formation of stoichiometric SnSe compound along with reduced excess metallic tin content. These observations reveal the fact that stoichiometric SnSe films are formed when the deposition is carried near to the equilibrium potential of the constituent elements under the chosen bath conditions.

In order to study the mechanism involved in the film formation and the nature of the film formed, CV are carried out at different scan rates of 20, 100, 200, 300, 500 and 800 mV/sec. Fig. 3.8 a, b, c,d,e and f shows the CV of Sn\(^{2+}\) +
Fig. 3.7. Cyclic voltammogram obtained for 5.0 mM SnCl₂ + 2.0 mM SeO₂ for different reverse potentials at scan rate 100 mV/sec (a) – 1.0 V, (b) – 0.9 V, (c) – 0.8 V.
Fig. 3.8. Cyclic voltammogram pattern obtained for 5.0 mM SnCl₂ + 2.0 mM SeO₂ at different scan rates
(a) 20 mV/sec  (b) 100 mV/sec  (c) 200 mV/sec
(d) 300 mV/sec  (e) 500 mV/sec  (f) 800 mV/sec
Fig. 3.8. Contd....
Fig. 3.8. Contd....
SeO₂ species at different scan rates. The most noticeable effect observed is the increase in peak separation. The cathodic peak current is found increased while the anodic peak current is reduced. These data are given in Table 3.1 and 3.2. It shows that SnSe films formed during the cathodic scan are highly stable and do not dissolve in the anodic scan.

(iii) CV studies of SnCl₂ + Na₂S₂O₃ solutions

After studying the deposition behaviour of the individual Sn²⁺ and S₂O₃²⁻ species, it is essential to analyse the interaction between the two species as it provides the mechanism underlying the process of SnS formation.

When 2.5 mM S₂O₃²⁻ ions are added to the Sn(II) solution some marked changes occur on the voltammetric curves as shown in Fig. 3.9. The cathodic current onset is shifted to −0.57 V followed by a clear cathodic peak at −0.67 V and a broader peak at about −0.8 V. The presence of thiosulphate ions increases the overpotential for the reduction of Sn(II) ions which may be due to the complex formation ability of S₂O₃²⁻ ions with Sn(II) ions. These two peaks might have been associated with the reduction of Sn(II) and S₂O₃²⁻ ions leading to their codeposition.

A relatively small anodic stripping and broad peak at about −0.4 V is observed. It confirms the formation of a stable tin compound during the cathodic scan. The presence of S₂O₃²⁻ ions dictates the deposition process and the formation of SnS film.

Further, the observed increase in cathodic peak height and the reduced anodic peak height with different scanning rate confirms the formation of stable SnS films at pH 1.5. Based on the above discussions, the sequence of reactions leading to deposition of SnS can be written as
Table-3.1  
CV data for SnSe deposition at different scan rates

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Scan rate mV/sec</th>
<th>Cathodic Peak Position</th>
<th>Anodic Peak Position</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Potential (V)</td>
<td>Current (µA)</td>
</tr>
<tr>
<td>1.</td>
<td>20</td>
<td>0.761</td>
<td>120</td>
</tr>
<tr>
<td>2.</td>
<td>100</td>
<td>0.767</td>
<td>150</td>
</tr>
<tr>
<td>3.</td>
<td>200</td>
<td>0.825</td>
<td>155.5</td>
</tr>
<tr>
<td>4.</td>
<td>300</td>
<td>0.845</td>
<td>204</td>
</tr>
<tr>
<td>5.</td>
<td>500</td>
<td>0.877</td>
<td>235.3</td>
</tr>
<tr>
<td>6.</td>
<td>800</td>
<td>0.897</td>
<td>270</td>
</tr>
</tbody>
</table>

Table-3.2  
Anodic peak current values for different reverse negative potentials for SnSe

<table>
<thead>
<tr>
<th>Scan Range (Volt)</th>
<th>Anodic Peak (or Stripping Peak) Current (µA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 → - 1</td>
<td>94</td>
</tr>
<tr>
<td>0 → - 0.9</td>
<td>60</td>
</tr>
<tr>
<td>0 → - 0.8</td>
<td>45</td>
</tr>
</tbody>
</table>
Fig. 3.9. Cyclic voltammogram obtained for 5.0 mM SnCl₂ + 2.5 mM Na₂S₂O₃ at the scan rate 20 mV/sec
\[
\text{Sn}^{2+} + 2e^{-} \rightleftharpoons \text{Sn}(s) \tag{3.6}
\]

\[
(S_{2}O_{3})^{2-} + 6H^{+} + 4e^{-} \rightleftharpoons 2S(s) + 3H_{2}O \tag{3.7}
\]

\[
\text{Sn} + S \rightarrow \text{SnS} \tag{3.8}
\]

At high negative potential, a Sn rich film is formed. When scan rate is increased from 20 to 800 mV/sec, the cathodic peak slightly shifts towards the positive potentials as shown in Fig. 3.10 a, b, c, d, e and f. As the scan rate increases the stripping peak reduces which again indicates the tin rich deposit at low scan rates [8,9].

As in the case of SnSe, the influence of end negative potential upto which cathodic scan is performed, has been studied. Fig. 3.11.a, b, c and d shows CV curves performed upto -1.0, -0.9, -0.8 and -0.7 V at a scan rate of 20 mV/sec. It is observed that the stripping peak height decreases with reduced negative potential values. The observed anodic (stripping) peak current values are 45.16 µA, 43.75 µA, 20.0 µA and 3.70 µA for the scan reversing negative potential of -1.0 V, -0.9 V, -0.8 V and -0.7 V respectively. When the negative scan is performed upto -0.9 V, the current density during the cathodic scan is large which is associated with the formation of SnS in addition to elemental Sn. This is confirmed by the higher peak current of the anodic peak which arises due to the dissolution of the excess tin formed along with SnS. The anodic peak current values for -0.8 V and -0.7 V are found to reduce which may be due to the formation of SnS compound with reduced excess metallic tin content. The CV data at different scan rates for SnS are presented in Table 3.3. Anodic peak current values for different reverse negative potentials are given in Table 3.4.

(iv) CV studies of SnCl₂ + NaS₂O₃ + SeO₂ mixed solutions

To deposit SnSₓSe₁₋ₓ solid solution, the different sulphur and selenium ion concentrations are used. A representative CV for SnS₀.₅Se₀.₅ is discussed here.
Fig. 3.10. Cyclic voltammogram obtained for 5.0 mM SnCl₂ + 2.5 mM Na₂S₂O₃ at different scan rates (a) 20 mV/sec (b) 100 mV/sec (c) 200 mV/sec (d) 300 mV/sec (e) 500 mV/sec (f) 800 mV/sec
Fig. 3.10. Contd...
Fig. 3.10. Contd.....
Fig. 3.11. Cyclic voltammogram obtained for different potential scan range at the scan rate 20 mV/sec (a) 0 to -0.1 V (b) 0 to -0.9 V (c) 0 to -0.8 V (d) 0 to -0.7 V
Fig. 3.11. Contd.…….
Table-3.3
CV data for the SnS deposition at different scan rates

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Scan rate mV/sec</th>
<th>Cathodic Peak Position</th>
<th>Anodic Peak Position</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Potential (V)</td>
<td>Current (µA)</td>
</tr>
<tr>
<td>1.</td>
<td>20</td>
<td>0.819</td>
<td>424</td>
</tr>
<tr>
<td>2.</td>
<td>100</td>
<td>0.858</td>
<td>572</td>
</tr>
<tr>
<td>3.</td>
<td>200</td>
<td>0.890</td>
<td>700</td>
</tr>
<tr>
<td>4.</td>
<td>300</td>
<td>0.929</td>
<td>867</td>
</tr>
<tr>
<td>5.</td>
<td>500</td>
<td>0.967</td>
<td>1041.2</td>
</tr>
<tr>
<td>6.</td>
<td>800</td>
<td>0.980</td>
<td>1065.1</td>
</tr>
</tbody>
</table>

Table-3.4
Anodic peak current values for different reverse negative potentials for SnS

<table>
<thead>
<tr>
<th>Scan Range (Volt)</th>
<th>Anodic Peak (or Stripping Peak) Current (µA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 → - 1</td>
<td>119.0</td>
</tr>
<tr>
<td>0 → - 0.9</td>
<td>53.8</td>
</tr>
<tr>
<td>0 → - 0.8</td>
<td>37.5</td>
</tr>
<tr>
<td>0 → - 0.7</td>
<td>7.4</td>
</tr>
</tbody>
</table>
Fig. 3.12 shows the curves obtained for 5 mM of SnCl₂ + 2.5 mM Na₂S₂O₃ + 2.0 mM of SeO₂ solution keeping pH 1.5. During the cathodic scan the current starts increasing first at about −0.4 V and then a peak is observed at about −0.75 V. The broad peak may be due to the deposition of tin sulphoselenide compound. When the scan reverses, no anodic peak is observed. This confirms the formation of stable SnSₓSe₁ₓ (x = 0.5) compound alone without any individual species deposited along with the compound. The compound is highly stable and it does not dissolve in the potential range engaged for the scan.

Fig. 3.13 shows the cyclic voltammograms obtained at the scan rates of 20, 100, 200, 300, 500 and 800 mV/sec. As the scan rate increases, the cathodic peak height increases. However, there is no dissolution peak observed for all the scan rates. This confirms the stable compound formation and the irreversible nature of the SnS₀.₅Se₀.₅ formed. The optimized deposition parameters are presented in Table 3.5.

(v) Electrochemistry of Sn, Se and S

The inherent problem associated with the deposition of binary or ternary compounds is the widely varying individual deposition potential of the ions taking part in electrochemical reactions. If the individual potentials are much separated; to obtain co-deposition and stoichiometric compounds, one should bring their deposition potentials very close to both ions. In the case of electrodeposition of SnSe, the electrode potential for the deposition of selenium (Se) is more positive than that for tin (Sn). The individual electrochemical reaction steps involved in the deposition of Sn and Se are given as follows:

(a) Sn reduction: it involves a two electron transfer reaction.

$$Sn^{2+} + 2e^- \rightleftharpoons Sn(s)$$

$$= E^\circ (Sn^{2+} / Sn) + (RT/2F) \ln (a_{Sn^{2+}} / a_{Sn})$$

$$= -0.38 \, V_{SCE} + 0.0295 \log (a_{Sn^{2+}} / a_{Sn}) \quad (3.9)$$
Fig. 3.12. Cyclic voltammogram pattern obtained for 5.0 mM SnCl$_2$ + 2.5 m Na$_2$S$_2$O$_3$ + 2.0 mM SeO$_2$ at the scan rate of 20 mV/sec
Fig. 3.13. Cyclic voltammogram pattern obtained for 5.0 mM SnCl₂ + 2.5 mM Na₂S₂O₃ + 2.0 mM SeO₂ at different scan rates (a) 20 mV/sec  (b) 100 mV/sec  (c) 200 mV/sec  (d) 300 mV/sec  (e) 500 mV/sec  (f) 800 mV/sec
Fig. 3.13. Contd....
Fig. 3.13. Contd......
Table 3.5

Optimized parameters for the preparation of electrodeposited SnS$_{x}$Se$_{1-x}$ films (x = 0, 0.5 and 1)

<table>
<thead>
<tr>
<th>Deposition Parameters</th>
<th>SnSe</th>
<th>SnS</th>
<th>SnS$<em>{0.5}$Se$</em>{0.5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration of SnCl$_2$</td>
<td>5.0 mM</td>
<td>5.0 mM</td>
<td>5.0 mM</td>
</tr>
<tr>
<td>Concentration of SeO$_2$</td>
<td>2.0 mM</td>
<td>---</td>
<td>2.0 mM</td>
</tr>
<tr>
<td>Concentration of S$_2$O$_3$</td>
<td>---</td>
<td>2.5 mM</td>
<td>2.5 mM</td>
</tr>
<tr>
<td>Deposition Potential</td>
<td>-800 mV</td>
<td>-900 mV</td>
<td>-900 mV</td>
</tr>
<tr>
<td>Bath Temperature</td>
<td>55°C</td>
<td>60°C</td>
<td>60°C</td>
</tr>
<tr>
<td>Bath pH</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Deposition Time</td>
<td>15 min</td>
<td>15 min</td>
<td>15 min</td>
</tr>
</tbody>
</table>
(b) Se reduction: selenous acid is formed on dissolving SeO₂ in water.

\[
\text{SeO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{SeO}_3
\]
\[
\text{H}_2\text{SeO}_3 + 4\text{H}^+ + 4\text{e}^- = \text{HSeO}_2^- + 4\text{H}^+ + 4\text{e}^- + \text{OH}^- \\
= \text{Se(s)} + 3\text{H}_2\text{O}
\]

\[
= E^0(\text{H}_2\text{SeO}_3/\text{Se}) + (RT/4F) \ln (a_{\text{HSeO}_2^+} / a_{\text{Se}}) + (3RT/4F) \ln C_{\text{H}^+} \\
= 0.50 \text{ V}_{\text{SCE}} + 0.0148 \log (a_{\text{HSeO}_2^+} / a_{\text{Se}}) - 0.0443 \text{ pH} \quad (3.10)
\]

Here, \( E^0 \) are the equilibrium potentials expressed with reference to SCE, ‘a’ are activities of ions in the bulk solution and the deposit (a = 1, for an ion in the solid deposit) and \( C_{\text{H}^+} \) is the concentration of hydrogen ions. Sn(s) and Se(s) are the respective species in the deposit.

Similarly in the case of electrodeposition of SnS, the electrode potential of sulphur (S) is more positive than tin (Sn). The individual deposition equation of Sn and S is given as follows:

(a) Sn reduction

\[
\text{Sn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Sn(s)} \\
= E^0(\text{Sn}^{2+}/\text{Sn}) + (RT/2F) \ln (a_{\text{Sn}^{2+}} / a_{\text{Sn}}) \\
= -0.38 \text{ V}_{\text{SCE}} + 0.0295 \log a_{\text{Sn}^{2+}} / a_{\text{Sn}} \quad (3.11)
\]

(b) S reduction

\[
(\text{S}_2\text{O}_3)^{2-} + 6\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{S(s)} + 3\text{H}_2\text{O} \\
E = E^0(\text{S}^{2+/S}) + (RT/4F) \ln (a_{\text{S}_2\text{O}_3^{2-}} / a_{\text{e}^+}) + (3RT/4F) \ln \text{OH}^+ \\
= +0.26 \text{ V}_{\text{SCE}} + 0.0148 \quad (3.12)
\]
For simultaneous deposition of Sn and S or Sn and Se, the concentrations and pH of the electrolyte should be so adjusted that the electrode potentials of the individual species come closer to each other.

3.4. PRELIMINARY OBSERVATIONS ON BRUSH PLATED SnSe AND SnS FILMS

The optimised plating parameters for the preparation of SnSe and SnS and SnS\textsubscript{0.5}Se\textsubscript{0.5} films by the brush plating technique are presented in Table 3.6. In order to confirm the formation of stoichiometric films, their colours have been observed as a first hand information at different plating parameters like concentration, plating potential and time.

3.4.1. Tin Selenide Thin Films

A low concentration of 5.0 mM of SnCl\textsubscript{2} is taken in the bath. When the deposition is performed with the addition of 1.0 mM of SeO\textsubscript{2}, a pale red coloured film is obtained. Addition of 2.0 mM of SeO\textsubscript{2} yields a steel gray film, the typical colour of tin selenide thin films. When the concentration is increased to 3.0 mM of SeO\textsubscript{2}, the film is formed with the reddish coloured one. These are indicated in Fig. 3.14 (a).

The plating potential is varied between 2.0 and 8.0 V. The optimum plating potential is found to be 5.0 volt at which steel gray film is obtained as shown in Fig. 3.14 (b). At higher potentials a thick gray colour film indicates the tin rich film. The effect of plating time is studied by varying the plating time from 2.0 to 8.0 minutes. The typical colour of tin selenide films (steel gray) is obtained at about 4 min. as shown in Fig. 3.14 (c). The results of XRD analysis also show good agreement with these initial observations.
Table-3.6
Optimized parameters for the preparation of brush plated SnSₓSe₁₋ₓ films (x = 0, 0.5 and 1)

<table>
<thead>
<tr>
<th>Plating Parameters</th>
<th>SnSe</th>
<th>SnS</th>
<th>SnS₀.₅Se₀.₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration of SnCl₂</td>
<td>5.0 mM</td>
<td>5.0 mM</td>
<td>5.0 mM</td>
</tr>
<tr>
<td>Concentration of SeO₂</td>
<td>2.0 mM</td>
<td>---</td>
<td>2.0 mM</td>
</tr>
<tr>
<td>Concentration of S₂O₃</td>
<td>---</td>
<td>2.5 mM</td>
<td>2.5 mM</td>
</tr>
<tr>
<td>Plating Potential</td>
<td>5.0 V</td>
<td>4.0 V</td>
<td>5.0 V</td>
</tr>
<tr>
<td>Current Density</td>
<td>0.01 amp.hr.</td>
<td>0.01 amp.hr.</td>
<td>0.1 amp.hr.</td>
</tr>
<tr>
<td>Plating Time</td>
<td>4.0 min</td>
<td>5.0 min</td>
<td>5.0 min</td>
</tr>
<tr>
<td>Bath Temperature</td>
<td>55°C</td>
<td>50°C</td>
<td>55°C</td>
</tr>
<tr>
<td>Bath pH</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>
Fig. 3.14. Preliminary colour observations for different plating parameters on brush plated SnSe films (a) concentration of SeO₂ (b) plating potential (c) plating time.
3.4.2. Tin Sulphide Thin Films

A similar observation for the formation of tin sulphide thin film is carried out. A 5.0 mM of SnCl₂ is taken for brush plating of SnS. The effect of addition of Na₂S₂O₃ is studied. At very low concentration of 1.0 mM, a pale yellow coloured film showing the sulphur rich film is obtained. At 2.5 mM of S₂O₃²⁻, a gray black film is obtained which is the typical colour of tin sulphide film. At higher concentrations, tin rich films are observed. These observations are shown in Fig. 3.15 (a).

The effect of plating potential is studied by varying it between 2.0 and 8.0 V. The optimum potential is found to be 4.0 V which is shown in Fig. 3.15 (b). Plating time is varied between 2.0 and 8.0 minutes. The gray black colour of SnS film is deposited when plating time is 5.0 min (Fig. 3.15 c). The XRD results also confirm these visual observations. Since the optimized parameters of binary compounds are closely matching, the parameters are the same for solid solutions as confirmed by XRD studies.

3.5. EXPERIMENTAL METHODS FOR CHARACTERIZATION

3.5.1. Thickness Measurements

The thickness of the films is measured by a multiple beam interferometer (MBI) [10,11]. The technique consists of the deposition of a semiconductor film like tin selenide over the SnO₂ film in such a way to form a mechanical step which is held as shown in Fig. 3.16 (a). And the step is viewed through a travelling microscope. The experimental set up is illustrated in Fig. 3.16 (a). An interference pattern as shown in the figure is obtained in the field of view of the microscope. The discontinuity in the fringe pattern is clearly due to the step whose height is identified with the thickness of the semiconductor film and given by
Fig. 3.15. Preliminary colour observations for different plating parameters on brush plated SnS films (a) concentration of $S_2O_3$ (b) plating potential (c) plating time
Fig. 3.16. Schematic diagram of multiple beam interferometer
70

\[ t = \frac{x \lambda}{y \sqrt{2}} \]  

(3.13)

where \( x \) and \( y \) are the measured quantities as indicated in the Fig. 3.16 (b).

Normally a sodium vapour lamp (of wavelength \( \lambda = 589.3 \text{ nm} \)) is used as the monochromatic source. For higher thickness, weight loss method is an easy and efficient method. The substrates are weighed before and after deposition and the difference in weight corresponds to the weight of the film deposited. Knowing the area of the film formation and density of the material, the thickness may be determined. The thickness of the films has also been calculated from the interference patterns observed in the transmittance curves using the relation [12],

\[ t = \frac{\lambda_1 \lambda_2}{2(n_2 \lambda_1 - n_1 \lambda_2)} \]  

(3.14)

Where \( n_1 \) and \( n_2 \) are the refractive indices at two adjacent maxima (or minima) \( \lambda_1 \) and \( \lambda_2 \). In this work, thickness of the films is determined by using these techniques. The thickness values calculated from these techniques are nearly the same as shown in Table 3.7.

3.5.2. Structural Studies

Tin selenide, tin sulphide and their solid solution SnS\(_x\)Se\(_{1-x}\) are known to exist in orthorhombic structure [13-15]. The multifaceted properties of thin films have forced the emergence of sophisticated characterization techniques, the chief one being X-ray diffraction. X-ray diffraction methods are suitable for estimating the crystallographic parameters.
Table-3.7

Thickness of optimized SnS$_x$Se$_{1-x}$ (x = 0, 0.5 and 1.0) thin films calculated from different methods

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Compound</th>
<th>M.B.I.</th>
<th>Weight Loss Method</th>
<th>Optical Transmission Curves</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Electro-deposited</td>
<td>Brush plated</td>
<td>Electro-deposited</td>
</tr>
<tr>
<td></td>
<td></td>
<td>μm</td>
<td>μm</td>
<td>μm</td>
</tr>
<tr>
<td>1.</td>
<td>SnSe</td>
<td>1.05</td>
<td>1.6</td>
<td>1.0</td>
</tr>
<tr>
<td>2.</td>
<td>SnS</td>
<td>0.90</td>
<td>1.8</td>
<td>1.0</td>
</tr>
<tr>
<td>3.</td>
<td>SnS$<em>{0.5}$Se$</em>{0.5}$</td>
<td>1.0</td>
<td>1.75</td>
<td>1.0</td>
</tr>
</tbody>
</table>
The X-ray diffraction patterns for all films are recorded using JEOL JDX 803a by employing CuK$_x$ radiation of wavelength 0.15418 nm. The diffraction peaks obtained are identified with ASTM index to study the crystalline nature and structure of the films. The lattice parameters ‘a’ ‘b’ and ‘c’ for the orthorhombic structure are calculated.

3.5.3. Optical Properties

Optical properties are of much importance for the semiconductor compound films. The measurement of the transmission or reflection of a sample provides a satisfactory way to determine the form of the absorption edge. The absorption edge and energy bandgap can be determined from the transmission measurement [16]. Hence, absorption and transmission properties are studied using spectrophotometer UV-VIS-NIR Hitachi U-3400-20. The thin films of SnSe, SnS and SnS$_x$Se$_{1-x}$ are mounted normally to the beam in the spectrophotometer. The transmission and absorption spectra are recorded for the normal incidence. The reflectance of the films is also determined in the near normal incidence position.

The absorption coefficient $\alpha$ is given by

$$\alpha \nu = \beta (\nu - E_g)^x$$  \hspace{1cm} (3.15)

where $x = \frac{1}{2}$ for a direct allowed transition and $x = \frac{3}{2}$ for a direct forbidden transition. Apparently the plot of $(\alpha \nu)^{1/2}$ versus $\nu$ yielded a straight line and the intercept of the plots yielded bandgap values. The details are fed into a computer and by employing the CDD algorithm (explained in Chapter 2) the optical constants ‘$n$’ and ‘$k$’ are evaluated for SnSe, SnS and SnS$_x$Se$_{1-x}$ films prepared by electrodeposition and brush plating methods. The variation of bandgap has also been evaluated from the plot of $dT/d\nu$ versus $\nu$ (differential transmittance vs energy plot).
3.5.4. Electrical Studies

Resistivity of the samples is measured by employing both Van der Pauw's geometry and two probe method. Using 40 gauge wire, contact leads are made from the silver surface evaporated on electrodeposited films. The samples are kept inside a vacuum chamber fitted with a heater. The details of the experiment are already discussed in Chapter 2. The resistance and resistivity of the samples are obtained using equation (2.44). A constant current source is used in conjunction with a Keithley 2000 multimeter. The schematic diagram of a typical resistivity measurement system is shown in Fig.2.13 [17].

3.5.5. Morphology and Composition

A Scanning Electron Microscope (Stereoscan 440) is used in the present work to study the surface topography of various samples prepared by brush plating and electrodeposition. The instrument is operated in the secondary emission mode and micrographs are recorded at suitable magnifications between 1 K and 10 K that reveals the topographic features. The Nanoscope E scanning Probe Microscopy Systems Model No. 3138 J has been used to study the surface morphology of SnSₓSe₁₋ₓ films.

X-ray photoelectron spectroscopy (XPS) spectra are taken using VG MKII ESCA spectrometer. The ESCA measurements are performed over the surface of the as prepared film and sputtered film to estimate the relative presence of various species in the samples.

3.6. SUMMARY AND CONCLUSION

The results discussed indicate that SnSₓSe₁₋ₓ solid solution semiconductor films can be deposited from aqueous solutions containing different proportions of
Sn$^{2+}$, S$^{2-}$, and SeO$_2^{2-}$ ions at pH 1.5. The various parameters used and optimum conditions to get the stoichiometric semiconducting compound films of SnSe, SnS and SnS$_{0.5}$Se$_{0.5}$ are presented. The reaction kinetics for the deposition of SnSe, SnS and SnS$_{0.5}$Se$_{0.5}$ are presented. Preliminary colour observations are made to optimize the deposition parameters in the brush plating method. Optimized conditions are given in Tables 3.1 and 3.2. The various characterization experiments performed for structural, microstructural, optical, morphological and transport properties are also briefly discussed.
REFERENCES