Chapter III

Sample Preparation and Diagnostic Studies
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3.1 Introduction

Polycrystalline zinc telluride films are of potential interest for the low temperature growth of transparent conductive windows in solar cell fabrication. As electrodeposition from aqueous electrolytes is a low temperature process, this makes it suitable for the above use. This chapter deals with the experimental details pertaining to the fabrication of ZnTe thin films using electrodeposition technique. The various experiments that are performed for the structural, optical, electrical and compositional analysis are discussed.

In D.C potentiostatic method, the deposition potential is kept constant and is one of the main parameters to be optimized to get coherent films [1]. There are two methods that are usually adopted to fix the range of deposition potential. First one is Pourbaix diagram approach and the other is cyclic voltammetric method [2]. In this chapter the cyclic voltammetry method of fixing the deposition potential is discussed. The vital role of deposition kinetic studies in fixing the optimum values for the deposition parameters are also discussed in detail. Under the optimized deposition conditions, the fabrication of ZnTe thin films through potentiostatic and
galvanostatic techniques was performed and subsequent characterization studies were carried out for these films.

3.2 Electrochemical cell

needs to be part of a circuit which includes a voltage source and a means of measuring the current. Although the characteristics of the overall cells are measured, the investigation may be consumed with the electrochemical process at a particular electrode. This is known as the working electrode (WE) and the current is supplied by the counter electrode (CE) or auxiliary electrode. If the working electrode has an area which is significantly less (approximately 10 times) than the counter electrode, then the performance of the electrochemical cell is dominated by the process at the working electrode. In practice, the surface area of the working electrode is usually small so that there is an even distribution of current and potential.

In a three electrode cell, the voltage applied between the working electrode (WE) and counter electrode (CE) is as in the simple cell arrangement shown in Fig.3.1. However, in this case the potential of the working electrode is measured with respect to the third electrode called the reference electrode (RE) which provides the reference value. This means that if there is a need to control the potential of the working electrode with respect to the reference electrode, it is achieved by actually adjusting the voltage applied between the working and the
Fig. 3.1 Simple cell arrangement.
counter electrodes. This is usually achieved by an instrument known as potentiostat. The potentiostat enables the user automatically and accurately to control the potential at the working electrode. This may be fixed potential or it may vary in a controlled manner. Thus a potentiostat provides a source of constant potential, whereas a constant current source is known as a galvanostat. In order to understand the principles of operation of a potentiostat a more detailed examination of the three electrode cell is necessary.

3.3 Experimental details

The schematic representation of the electrodeposition set up is shown in Fig.3.2 and the cell used is explained in detail with its associated parts. Typically 50 ml glass beaker was used to contain the solutions. Magnetic stirrer cum heater set up is used to deposit films by stirring the bath as well as rising the temperature. A Saturated Calomel Electrode (SCE) is used as a reference electrode to measure the potential of the working electrode. Tin oxide coated glass plates were used as working electrodes. The working and counter electrodes were kept at a distance of 1 cm to each other and surfaces were kept 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 is 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].
1. POTENTIOSTAT EC&G
2. AMMETER - DIGITAL MULTIMETER
3. WORKING ELECTRODE
4. COUNTER ELECTRODE
5. SATURATED CALOMEL ELECTRODE (SCE)
6. CONNECTING BRIDGE FOR SCE
7. 50cc BEAKER
8. SOLUTION BATH
9. MAGNETIC STIRRER WITH TEMPERATURE CONTROL.

Fig. 3.2 Schematic representation of the electrodeposition set-up used.
It is impossible to determine the absolute potentials of the individual electrodes and it is common practice to measure the e.m.f of a system comprising the electrode under investigation and some other electrode with the known potential value. Auxiliary electrodes with the known readily reproducible electrode potential values which are used for potential measurements are known as reference electrodes. These electrodes can be used to determine the electrode potentials at temperatures ranging from 0 to 100°C. When these are used, the diffusion potential which arises at the interface of the two solutions is generally small and is frequently neglected. In the present work, the saturated calomel electrode was used as the reference electrode.

A regulated DC power supply EG&G PAR Model 362 Potentiostat is used to prepare the ZnTe semiconducting films. The oxide coated transparent conducting electrodes are first cleaned well with soap solution followed by smooth application of acetone. The substrates are cleaned well with triple distilled water before use. Glassy carbon electrodes are cleaned with acetone and triple distilled water. Graphite counter electrodes are cleaned with triple distilled water. The saturated calomel electrodes are 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 is ensured before the start of each deposition.
D.C. Potentiostatic deposition

The depositions are carried out potentiostatically under constant deposition potentials. A d.c power source (EG&G PAR Potentiostat) is connected with the negative terminal to the working electrode (cathode) and positive terminal to the counter electrode (anode) and the deposition of ZnTe films are achieved cathodically. The required deposition potential is kept constant using potentiostat and the current during deposition was measured by an ammeter connected in series with the cathode and negative terminal of the power supply. Cathodic deposition of ZnTe films are carried out at varies deposition potentials.

D.C. Galvanostatic deposition

The depositions are carried out galvanostatically under constant current densities. The required current is kept constant using EG&G PAR Galvanostat and the depositions were carried out cathodically. The varying voltage during deposition is measured by using a voltmeter between the working electrode and reference electrode (SCE). Cathodic deposition of ZnTe films are carried out at various current densities.

3.4 Electrochemistry of ZnTe films

The basic electrochemical reactions for the electrodeposition of ZnTe and their corresponding Nernst relations are,

\[ \text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}, \quad E^0_{\text{Zn}} = -1.003 \text{ V (SCE)} \]
$$E_{Zn} = E_{Zn}^0 - \left[ \frac{RT}{2F} \right] \ln \left( \frac{a_{Zn}}{a_{Zn}^2} \right)$$

$$\text{TeO}_2 + 4H^+ + 4e^- \rightarrow \text{Te} + 2H_2O; \quad E_{Te}^0 = 0.351 \text{ V (SCE)}$$

$$E_{Te} = E_{Te}^0 - \left[ \frac{RT}{4F} \right] \ln \left( \frac{a_{Te}}{a_{TeO}_2} \right) + \left[ \frac{RT}{F} \right] \text{pH}$$

Here $a_{Zn}^{2+}$ and $a_{TeO}_2$ are the activities of Zn and TeO$_2$ in the electrolyte, $a_{Zn}$ and $a_{Te}$ are the activities of Zn and Te in ZnTe. $E_{Zn}^0$ and $E_{Te}^0$ are the standard reduction potential of Zn and Te, $E_{Zn}$ and $E_{Te}$ are the equilibrium potential of Zn and Te. F is the Faraday constant, R is the universal gas constant and T is the temperature of the bath. It has been reported that [5] telluride anion formation from the six electron reduction of Te (IV) ions is assumed negligible with the deposition potentials used. So the deposit is formed by solid state reaction of plated Zn and Te atoms rather than precipitation of H$_2$Te and Zn$^{2+}$. Therefore Zn + Te $\rightarrow$ ZnTe with negative free energy formation $\Delta G^0 = -141.6 \text{ kJmol}^{-1}$. From the equilibrium electrode potential of Te and Zn, it can be seen that the potential of Te is far more positive than that for zinc deposition. Further, to obtain simultaneous deposition of Zn and Te, the electrolyte concentration should be adjusted so as to bring the electrode potentials of both the deposits closer. It is desirable to use a high concentration of Zn and low concentration for the nobler component Te, so that the deposition potential of Zn shifts towards a positive value, approaching the Te deposition potential. The deposition of Te will be diffusion controlled due to a very low concentration of TeO$_2$ (and consequently of the HTeO$_2^+$). Based on these
electrode reactions, a higher concentration of 0.15 M of Zn and very low concentration of 0.5 mM of Te have been taken in the bath for the deposition of ZnTe films. Since the electrodeposition of ZnTe is a six electron transfer process, in each deposition, the number of transferred electrons is calculated from the total charge and the mass of the deposit. In the case of all good films the transferred electrons for the deposition of one molecule of ZnTe is found to be close to six.

3.5 Cyclic voltammetry studies

The study of the electrodeposition mechanism is performed using Cyclic Voltammetry (CV) using PAR Scanning Potentiostat (Model 362, USA). A three electrode system is adopted to deposit ZnTe thin films. A magnetic stirrer cum heater set up is used to deposit the films by stirring the bath as well as raising the temperature. A saturated calomel electrode is immersed in to the bath very near to the cathode, which measures the potential of the working electrode. Both working and counter electrodes are kept as close as each other to obtain good results. The two surfaces facing each other are kept parallel, so that the released ions will be attracted and deposited exactly perpendicular to the cathode surface.

Cyclic voltammetry studies are carried out in an aqueous solution containing 0.15 M ZnSO$_4$ and 0.5 mM TeO$_2$ in 12 M H$_2$SO$_4$. Tin oxide coated glass slides are used as working electrodes to study the ZnTe deposition mechanism. Fig.3.3 shows a typical cyclic voltammogram for a tin oxide coated electrode in the
Electrodeposition bath carried out between 0.4 and -1.2 V versus SCE. It is observed that by scanning towards more negative potentials, the first cathodic wave appeared at -0.3 V versus SCE corresponds to the cathodic reduction of HTeO$_2^+$ to Te. Tellurium being nobler, it is expected to deposit first by the following charge transfer reaction:

$$\text{HTeO}_2^+ + 4e^- + 3\text{H}^+ \rightarrow \text{Te} + 2\text{H}_2\text{O}$$

A second cathodic wave observed at -0.80 V versus SCE may be ascribed to the formation of ZnTe on the substrate by the reaction:

$$\text{Zn}^{2+} + \text{Te} + 2e^- \rightarrow \text{ZnTe}$$

The current increased rapidly as the substrate potential increased cathodically more than -0.8 V versus SCE and this observation may be attributed to the high concentration of zinc ions present in the bath. The anodic sweep exhibited a peak at -0.6 V versus SCE corresponds to elemental zinc stripping. The cathodic current increased further, crossed the forward sweep and exhibited a large anodic peak at -0.2 V versus SCE. This corresponds to stripping of tellurium. The results of the CV experiments led us to select a potential range of -0.8 to -1.1 V versus SCE for the preparation of ZnTe thin films.

### 3.6 Preparation of ZnTe thin films

Electrochemical growth experiments are carried out both potentiostatically and galvanostatically, since a single valued cathodic deposition
Fig. 3.3 Cyclic voltammogram on TCO coated glass cathode in the electrodeposition bath.
versus potential curve is obtained. Control of the electrodeposition process is in principle easier in the potentiostatic mode, since the growth process shows a form of cathodic inhibition. Nevertheless, this growth mode can be applied reliably only if low resistance cathodic substrates are employed, which is not the case for many of the semiconducting substrates of interest. Thus both approaches are adopted in this work.

(A) Potentiostatic method

The working solution of tellurium (Te$^{4+}$) is obtained by dissolving 20 mgms of TeO$_2$ (99.99% Merck) in 250 ml deionized demineralized water. Due to the low solubility of TeO$_2$ we need continuous heating and stirring for several hours. In order to avoid this we have introduced, nearly 5 cc of 98% concentrated H$_2$SO$_4$ with the working solution and heated to about 30 minutes to get clear 0.5 mM stock solution of Te$^{4+}$. The second working solution of Zn$^{2+}$ is prepared by dissolving 10.8 gms of ZnSO$_4$ (99.99% Merck) in 250 ml of distilled water to get 0.15 M solution. The Na$_2$SO$_4$ (0.5 M) is used as the supporting electrolyte. The deposition of ZnTe thin films are very difficult as it involves several parameters in the growth of the films. The CV studies performed gave the possible range of potentials for the deposition of ZnTe films as -0.8 to -1.1 V versus SCE. The effect of concentrations of the respective species in the solution became evident only after the XRD studies.

The range of depositions employed is 0.15 to 0.30 M. Initially the concentration of zinc sulphate and tellurium dioxide is taken as 1:1. The films are
deposited with different concentration ratios, and are analyzed by XRD studies. Zinc telluride films are electrodeposited at different concentrations of Zn and Te and their characteristic appearances as shown in table 3.1. The HTeO$_2^+$ concentration is kept at a low value of 0.5 mM during all the depositions and Zn$^{2+}$ concentration is varied from 0.15 to 0.30 M. An approximate stoichiometric composition of 49:51 (Zn/Te) is obtained for a lower zinc concentration of 0.15M. Also it is observed that the peak height of XRD signal of (111) cubic phase increases with decreasing Zn$^{2+}$ concentration, indicating preferred orientation and improved crystallinity of ZnTe films deposited at lower Zn$^{2+}$ concentration. Uniform ZnTe thin films are obtained by blending suitable amount of stock solutions and diluting with water to get a final nominal concentration of Zn/Te as 3×10$^{-8}$. The plating experiments are carried out from room temperature to 90°C with different intervals of time. The various range of deposition parameters used to prepare ZnTe thin films are given in table 3.2. The colour of the films is found to vary from orange to dark brown and the films are well adherent to the substrates.

1. Thickness and rate of deposition

There are two important variables to be controlled during deposition of ZnTe films (i) film thickness and its uniformity and (ii) morphology. The ZnTe films are deposited in the thickness range between 0.1 to 0.7 μm. The thickness of ZnTe films in the range 0.1 to 0.4 μm is estimated using a multiple beam interferometer.
Table 3.1

The characteristic appearances of ZnTe thin films with Solution pH: 3.8 ± 0.1, Deposition potential: -1.1V versus SCE, and Bath temperature: 90°C.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Film thickness (nm)</th>
<th>Zn$^{2+}$ conc: (M)</th>
<th>HTeO$^{2+}$ conc: (mM)</th>
<th>Film appearance</th>
<th>Percentage of Zn:Te</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>680</td>
<td>0.15</td>
<td>0.5</td>
<td>Reddish brown</td>
<td>49:51</td>
</tr>
<tr>
<td>2</td>
<td>695</td>
<td>0.17</td>
<td>0.5</td>
<td>Light brown</td>
<td>48.52</td>
</tr>
<tr>
<td>3</td>
<td>710</td>
<td>0.20</td>
<td>0.5</td>
<td>Orange</td>
<td>47:53</td>
</tr>
<tr>
<td>4</td>
<td>705</td>
<td>0.23</td>
<td>0.5</td>
<td>Light orange</td>
<td>52.58</td>
</tr>
<tr>
<td>5</td>
<td>700</td>
<td>0.25</td>
<td>0.5</td>
<td>Grayish brown</td>
<td>53.57</td>
</tr>
<tr>
<td>6</td>
<td>700</td>
<td>0.27</td>
<td>0.5</td>
<td>Pale brown</td>
<td>45.55</td>
</tr>
<tr>
<td>7</td>
<td>715</td>
<td>0.30</td>
<td>0.5</td>
<td>Dark brown</td>
<td>46.54</td>
</tr>
</tbody>
</table>
Table 3.2

The range of deposition parameters used for the preparation of ZnTe films under potentiostatic mode.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Deposition parameters</th>
<th>Range used</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Concentration of ZnSO₄</td>
<td>0.15 – 0.30 M</td>
</tr>
<tr>
<td>2.</td>
<td>Concentration TeO₂</td>
<td>0.5 mM</td>
</tr>
<tr>
<td>3.</td>
<td>Deposition potential</td>
<td>-0.8 to -1.1 V (SCE)</td>
</tr>
<tr>
<td>4.</td>
<td>Bath temperature</td>
<td>30 – 90°C</td>
</tr>
<tr>
<td>5.</td>
<td>Solution pH</td>
<td>1.5 – 5.5</td>
</tr>
<tr>
<td>6.</td>
<td>Plating duration</td>
<td>10 – 60 minutes</td>
</tr>
</tbody>
</table>
technique. The weight loss method is used to estimate the film thickness in the range 0.4 to 0.7 μm. The average thickness of the layers can be directly controlled by controlling the plating current and the plating time. During deposition, it is observed that at more cathodic potentials (-1.4 V versus SCE and less) the film formation is hindered due to hydrogen evolution. At lower cathodic potentials (-0.75 V versus SCE and more) an irregular growth and a rough surface is obtained. The films deposited between -0.95 to -1.25 V versus SCE are found to be smooth and dense. Fig.3.4 shows the time dependence of the ZnTe thin film deposited onto a F: SnO₂ coated glass substrate. In this case the solution pH and the applied cathodic potential are fixed as 3.8 ± 0.1 and -1.1V versus SCE respectively. It is observed that the thickness of the ZnTe films increases with deposition time and tend to attain saturation. The same trend is noted for films deposited at various bath temperatures (30 to 90°C). The bath temperature is expected to influence the deposition rate by i) increase of precursor solubility and ii) increase of diffusion coefficient and decrease of viscosity. Cheng et al [6] reported that the solubility of TeO₂ increases exponentially with raising temperature and at pH 4.5, a 20-fold increase of solubility from room temperature to 99°C is estimated. Due to increase in solubility of TeO₂ with temperature higher thicknesses are obtained for films deposited at higher temperatures.
Fig. 3.4 Variation of film thickness with time at different bath temperatures for ZnTe films.
It could be observed from the graph that 0.4 to 0.7μm thickness of ZnTe is obtained from a single deposition within 60 minutes for bath temperature varying from 30 to 90°C. Further, at lower pH (3.5 ± 0.1), free tellurium is deposited and at comparatively higher pH (5.5 ± 0.1), the solution became cloudy due to the precipitation of TeO₂. Increasing the tellurium ion concentration in the solution by adding TeO₂ is limited by the solubility of TeO₂ at a given pH and temperature [8]. Since tellurium is less electropositive than zinc, the Te could be more likely to deposit as the element from its ions in an electrochemical bath than Zn from its ions. Hence, very low concentration of Te in the solution must be maintained compared to Zn ions and in the present work the concentration of Zn:Te is maintained at 3×10⁻³.

2. Effect of deposition potential

Deposition potential plays a vital role in the preparation of semiconducting thin films. Hence, deposition potential is an important parameter to be optimized during deposition. Cyclic voltammetric studies revealed the deposition potential region as -0.8 V to -1.1 V versus SCE. Hence further studies were carried out using potentials between -0.8 V to -1.1 V versus SCE. During this study, film thickness variation with deposition time at various constant deposition potentials is recorded and the results obtained are shown in Fig.3.5. From the figure it is found that the variation of film thickness with deposition time is an exponential one. The deposition current during deposition increases rapidly from lower value, reaches a
Fig. 3.5 Variation of film thickness with deposition time for various deposition potentials (potentiostatic mode).
peak and then decreases gradually. The variation of deposition current is caused by the variation in the rate of deposition. Rate of deposition is calculated from the slope of each graph of Fig.3.5 and the variation of rate of deposition with deposition time at constant deposition potential (-1.1V versus SCE) is shown in Fig.3.6. Initially it increases rapidly and then begins to decay gradually, which indicates that the rate of deposition does not remain constant during deposition at constant deposition potential. Hence non-uniform films are obtained in this mode of deposition. Also, the rate of deposition is found to be maximum value at the deposition time of 35 minutes. Hence, in potentiostatic deposition the deposition time of 35 minutes is preferred for the preparation of ZnTe thin films.

The overall rate of deposition (rate of deposition for the whole deposition period) increases as the deposition potential is increased in the negative mode (Fig.3.7). Deposition at -0.95 V (SCE) produces film with a thickness of about 0.35 μm for the deposition time of 70 minutes, whereas a film with thickness of about 0.58 μm can be deposited when the deposition potential is -1.05 V (SCE). This shows that the rate of deposition increases as the deposition potential increases in the negative mode. At the same time, depositions with potential between -0.95 V versus SCE and -1.05 V versus SCE yields films with spotty and porous appearance. The lower rate of deposition observed at lower negative potentials is the main cause for spotty and porous appearance of the films. Hence deposition potential between
Fig. 3.6 Variation of rate of deposition with time (Deposition potential: -1.1 V versus SCE).
Fig. 3.7 Variation of overall rate of deposition with deposition potentials (from Fig. 3.5), Deposition time: 60 minutes.
-1.05 V and -1.15 V (SCE) is preferred to deposit ZnTe films. However, the depositions at -1.1 V versus SCE yielded higher thickness ZnTe films.

3. Effect of temperature

During deposition, bath temperature plays an important role in determining film thickness and also the grain size of the deposits. Variation of film thickness with temperature for various deposition duration at constant deposition potential of -1.1 V (SCE) were recorded and shown in Fig.3.8. The growth rate and hence the film thickness is found to vary for a constant deposition potential and exhibit significant temperature dependence. Also it is noticed that the film deposited at 80°C has higher thickness than the films deposited at other temperatures. Hence, deposition temperature of 80°C is taken as the optimum deposition temperature to synthesize ZnTe thin films by potentiostatic deposition technique.

4. Effect of pH

In electrodeposition of thin films, the rate of deposition depends upon the deposition current. In potentiostatic mode of deposition, the instantaneous rate of deposition does not remain constant. Hence the overall growth rate, which remains almost constant for a particular deposition is calculated and this overall growth rate can be changed by changing the pH of the solution. Increase in pH of the solution increases the conductivity of the electrolyte and hence increases the deposition current passing through solution. This enhances the overall rate of deposition as
Fig. 3.8 Film thickness versus bath temperatures for ZnTe film at various plating time (Deposition potential -1.1 V versus SCE).
shown in Fig.3.9. The overall rate of deposition increases slowly for pH values less than 3.5 and then it begins to increase steeply as shown in Fig.3.9. This increase in rate of deposition above pH 3.8 causes films of lower grain size to be deposited as in the figure (Fig.3.9). Hence a deposition at pH 3.5 is preferred to yield films with higher thicknesses and grain size. For all the subsequent studies, pH of the bath is kept at 3.5 ± 0.1 to prepare ZnTe films. The optimum deposition parameters limit to yield higher thickness ZnTe film in potentiostatic mode of deposition is given in Table 3.3.

(B) Galvanostatic method

Zinc telluride thin films with reddish brown appearance are deposited onto F : SnO₂ substrates under deposition conditions shown in Table 3.4. All the films are found to be polycrystalline in nature with good adherence. The various deposition parameters used for the preparation of ZnTe thin film under galvanostatic mode is discussed in detail.

1. Effect of current density

The variation of thickness with deposition time is measured by knowing the amount of material deposited after certain intervals of time. For this study, the film is taken out of the solution after 45 minutes. Film thicknesses are measured from the mass and apparent area of the films using a density of 6.34 gm cm⁻³ for zinc telluride films. The variations of film thickness with deposition time at
Fig. 3.9 Variation of overall rate of deposition and grain size with solution pH. Deposition time: 60 minutes, Deposition temperature: 80°C, Deposition potential: -1.1 V (SCE).
Table 3.3

The optimum deposition parameters used to yield high thickness ZnTe films under potentiostatic mode.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Deposition parameters</th>
<th>Range used</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Concentration of ZnSO4</td>
<td>0.15 M</td>
</tr>
<tr>
<td>2.</td>
<td>Concentration TeO2</td>
<td>0.5 mM</td>
</tr>
<tr>
<td>3.</td>
<td>Deposition potential</td>
<td>-1.1 V (SCE)</td>
</tr>
<tr>
<td>4.</td>
<td>Bath temperature</td>
<td>80°C</td>
</tr>
<tr>
<td>5.</td>
<td>Solution pH</td>
<td>3.8 ± 0.1</td>
</tr>
<tr>
<td>6.</td>
<td>Plating duration</td>
<td>35 minutes.</td>
</tr>
</tbody>
</table>
Table 3.4

The range of deposition parameters used for the preparation of ZnTe films under galvanostatic mode.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Deposition parameters</th>
<th>Range used</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Concentration of ZnSO₄</td>
<td>0.15 – 0.30 M</td>
</tr>
<tr>
<td>2</td>
<td>Concentration TeO₂</td>
<td>0.5 mM</td>
</tr>
<tr>
<td>3</td>
<td>Deposition current density</td>
<td>1.2 – 1.7 mAcm⁻²</td>
</tr>
<tr>
<td>4</td>
<td>Bath temperature</td>
<td>30 – 90°C</td>
</tr>
<tr>
<td>5</td>
<td>Solution pH</td>
<td>1.5 – 5.5</td>
</tr>
<tr>
<td>6</td>
<td>Plating duration</td>
<td>15 – 75 minutes.</td>
</tr>
</tbody>
</table>
various constant current densities are measured and are shown in Fig.3.10. The figure shows a linear increase in film thickness with deposition time, which indicates that, the rate of deposition remains constant for a constant density. An important point to be noted is that above a certain value of film thickness the rate of deposition does not remain constant but dropped to a lower value. The variation of rate of deposition with the current density is shown in Fig.3.11, which reveals that the rate of deposition varies linearly with current density.

2. Film uniformity

Film uniformity is an important parameter for an electrodeposited thin film. The deposited films having thickness below the dotted line (Fig.3.10) are found to be uniform, whereas spotty films are obtained above this dotted line. Also it is clear that uniform films with good adherence can be deposited in the region below the dotted line using current densities in the range 1.2 to 1.7 mA cm$^{-2}$. The variation of maximum obtainable uniform thickness as a function of current density is shown in Fig.3.12, which reveals that a uniform film with higher thickness of 1.05 μm can be deposited at a current of 1.6 mA cm$^{-2}$. Hence the deposition at a current density of 1.6 mA cm$^{-2}$ for the deposition time of 45 minutes is preferred for the preparation of higher thickness films.

3. Effect of bath temperature

The variations of film thickness with deposition time at various bath temperatures for various current densities are studied. The data found in Fig.3.13
Fig. 3.10 Variation of film thickness with deposition time at various current densities. Solution pH 3.5 ± 0.1, Bath temperature 80°C.
Fig. 3.11 Variation of rate of deposition with current densities.
Fig. 3.12 Maximum uniform thickness obtained for various current densities.
Fig. 3.13 Film thickness versus deposition time for various current densities at three deposition temperatures (70°C, 80°C and 90°C).
reveals a linear increase in film thickness with deposition time at three different bath temperatures for three different current densities. The growth rate is found to be constant for a particular current density and it does not exhibit any significant temperature dependence. Film thickness variation with current density is also found to be linear and independent of deposition temperature. Constant growth rate leads to the formation of ZnTe films with uniform thickness. Hence, depositions at the temperature between 70°C and 90°C are preferred to prepare ZnTe films.

4. Effect of pH

In thin film electrodeposition, the type of surface depends upon the rate of deposition which, in turn is proportional to the deposition current. In galvanostatic deposition the rate of deposition remains constant. Hence, the growth rate, \( R \) could be changed by changing the \( pH \) of the solution. The conductivity of the electrolyte increases with solution \( pH \), which in turn enhances the rate of deposition \( R \) as shown in Fig.3.14. From this figure it is found that \( R \) increases gradually up to \( pH 3 \) and then begins to increase steeply due to large increase in conductivity of the solution about \( pH 3.0 \). Hence deposition of ZnTe thin films at \( pH \geq 3.0 \) is preferred. However grain size measurement shows higher grain size (0.05 \( \mu m \)) at \( pH 3.7 \) (see Fig.3.14). Hence deposition at solution \( pH 3.7 \) is preferred to deposit ZnTe thin films under galvanostatic mode. The optimum deposition parameters limit to yield higher thickness ZnTe film in galvanostatic mode of deposition is given in table 3.5.
Fig. 3.14 Variation of overall rate of deposition and grain size with solution pH.
Table 3.5

The optimum deposition parameters used to yield high thickness of ZnTe films under galvanostatic mode.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Deposition parameters</th>
<th>Range used</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Concentration of ZnSO$_4$</td>
<td>0.15 M</td>
</tr>
<tr>
<td>2.</td>
<td>Concentration TeO$_2$</td>
<td>0.5 mM</td>
</tr>
<tr>
<td>3.</td>
<td>Deposition current density</td>
<td>1.6 mA cm$^{-2}$</td>
</tr>
<tr>
<td>4.</td>
<td>Bath temperature</td>
<td>90°C</td>
</tr>
<tr>
<td>5.</td>
<td>Solution pH</td>
<td>3.7 ± 0.1</td>
</tr>
<tr>
<td>6.</td>
<td>Plating duration</td>
<td>45 minutes.</td>
</tr>
</tbody>
</table>
3.7 Experimental methods of characterization

Scientific disciplines are identified and differentiated by the experimental equipment and measurement techniques they employ. The same is true of thin film science and technology. The role played by films is largely a utilization one, necessitating measurement of film thickness, and optical properties. General testing and analysis of thin film is carried out with equipment and instruments which are wonderfully diverse in character. This section addresses the experimental techniques and applications associated with determination of film thickness, film morphology and structure and film composition. Within each of these three categories, only the most important techniques viable to us are discussed. Beyond these broad characteristics there are a host of individual properties like electrical conductivity, reflectivity and micro structural parameters that are specific to the particular application. The associated measurement techniques will therefore be addressed in the appropriate context.

3.7.1 Film thickness

The thickness of a film is among the first quoted attributes of its nature. The reason is that thin film properties and behaviours depend on thickness. The use of films in optical applications spurred the development of techniques capable of measuring film thickness with high accuracy. In contrast, other important film attributes, such as structure and chemical composition, are only characterized in
the most rudimentary way recently. Since film thickness is generally of the order of a wavelength of light, various types of optical interference phenomena have been found to be most useful for the measurement of film thickness. In addition to interference phenomena, there are other optical techniques which can be used to measure thickness. Examples are ellipsometry and absorption spectroscopy. In addition to the optical techniques, there are mechanical, electrical and magnetic techniques which have been used for film-thickness measurements [8, 9]. In this work, thickness of the films is determined by using the following techniques in the appropriate ranges.

(i) Ellipsometry measurement

The method consists of measuring and interpreting the change of polarization state that occurs when a polarized light beam is reflecting at non-normal incidence from a film surface. The experimental arrangement for ellipsometer measurements is shown in Fig. 3.15. The light source is first made monochromatic, collimated and then linearly polarized. Upon passing through the compensator (usually a quarter-wave plate), the light is circularly polarized and then impinges on the specimen surface. After reflection, the light is transmitted through a second polarizer that serves as the analyzer. Finally the light intensity is judged by eye or measured quantitatively by a photomultiplier detector. The polarizer and analyzer are rotated until light extinction occurs. The extinction readings enable the phase
Fig. 3.15  Experimental arrangement in ellipsometry.
difference and amplitude ratio of the two components of reflected light to be determined.

(ii) Multiple beam interferometers

The thickness of the films is also measured by a multiple beam interferometer [10]. The technique consists of the deposition of a semiconductor film like ZnTe over the SnO₂ coated glass plate in such a way to form a mechanical step as shown in Fig. 3.16 and the step is viewed through a traveling microscope. An interference pattern as shown in (Fig. 3.16) 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,

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

where \( x \) and \( y \) are the measured quantities as indicated in the figure. Normally a sodium vapour lamp is used as the monochromatic source.

(iii) Gravimetric measurement

Measurement of the weight of the film deposits appears, at first glance, to be an easy direct way to determine film thickness \( d \). Knowing the film mass \( m \), the deposit area \( A \), and film density \( \rho \), we have \( d = \frac{m}{A\rho} \). This simple method has been often used in ill-equipment laboratories, where precision mass balances are more common than interferometers or stylus instruments. Values of \( d \) so obtained are the film packing factor \( p \), a measure of the void content, can be quite low.
Fig. 3.16  Schematic diagram of multiple beam interferometer.
Furthermore, in cases where the substrate contains a great deal of relief in the form of roughness, cleavage steps, patterned topography, etc., the effective deposit area will be larger than the assumed projected area. In this case film thickness may be over estimated. For ultra thin films processing an island structure, this method, as well as others noted previously, is problematical.

Eventhough gravimetric techniques have disadvantages, very delicate and novel microbalances have been constructed and widely employed to monitor film thickness during deposition. In actual laboratory practice the gravimetric technique is more useful for determining the density of a deposited film rather than its thickness. If the film thickness is not constant, extreme precautions must be taken to obtain the proper average thickness for a density determination.

3.7.2 Structural characterization

X-ray diffraction is very important experimental technique that has long been used to address all issues related to the crystal structure of bulk solids, including lattice constants and geometry, identification of unknown materials, preferred orientation of poly-crystals, defects, etc. Extension of x-ray diffraction methods to thin films has not been pursued with vigor for two many reasons: First the great penetrating power of x-rays means that with typical incident angles, their path length through films is too short to produce diffracted beams of sufficient intensity. Under such conditions the substrate, rather than the film, dominates the
scattered x-ray signal, thus, the diffraction peaks from films require long counting times. Second, the TEM provides similar diffraction information with the added capability of performing analysis over very small selected areas. Nevertheless, x-ray methods have advantages because they are non-destructive and do not require elaborate sample preparation or film removal from the substrate. What is required for workable x-ray method is to make the film appear to be thicker to the beam that it actually is. This can be done by employing a grazing angle of incidence $\gamma = 5^\circ$, then the film is effectively 12 times thicker. In thin films of polymorphic materials either or both the phases can be obtained at room temperature depending on the deposition conditions [11-14]. Thin films of compound semiconductors have been assuming complex structures in view of their applications. The multi-faced properties of thin films have forced the emergence of sophisticated characterization techniques, the chief one being x-ray diffraction methods are best for estimating the crystallographic parameters.

The x-ray diffraction patterns for the electrodeposited ZnTe thin films are carried out using a JEOL-JDX 8030 diffractometer, employing CuK$_\alpha$ radiation of wavelength 1.5418 Å using a scan speed of 1°/min. the diffraction peaks obtained are identified with ASTM index to study the crystalline nature and structure of the films. For the calculation of cubic cell edge $a$ prominent peaks are taken. The formula employed for the cubical cell edge $a$ is,
where \( h, k, l \) represents the lattice planes and \( d \) represents the inter-atomic distance.

3.7.3 Microstructural characterization

The process of measuring a lattice parameter is very indirect one, and is fortunately of such a nature that high precision is fairly easily obtainable. The parameter \( a \) of cubic substance is directly proportional to the spacing \( d \) of any particular set of lattice planes. If we measure the Bragg angle \( \theta \) for this set of planes, we can use the Bragg law to determine \( d \) and, knowing \( d \) we can calculate \( a \). But it is \( \sin \theta \), not \( \theta \), which appears in the Bragg law. Precision in \( d \), or \( a \), therefore depends on precision in \( \sin \theta \), a derived quantity, and not on precision in \( \theta \), the measured quantity. This is fortunate because the values of \( \sin \theta \) changes very slowly with \( \theta \) in the neighborhood of 90°C. For this reason, a very accurate value of \( \sin \theta \) can be obtained from a measurement of \( \theta \) which is not particularly precise, provided that \( \theta \) is near 90°C. Stated in another way, the angular position of a diffracted beam is much more sensitive to a given change in plane spacing when \( \theta \) is large than when it is small.

Another x-ray diffraction study based on precise measurements of the position, broadening and shape of x-ray profiles of the polycrystalline thin films gives information about the microstructural changes in a film. The diffracted intensities from the films are found to be polycrystalline type and the line profiles
are subjected to variance analysis for calculating the crystalline size and micro strain. Because the method is sensitive to the variation of x-ray intensity near the tails, the peaks are carefully corrected for background radiation by the method given by Mitra and Misra [15]. As the variance are additive, the profiles are corrected for instrumental broadening by subtracting the variance of the corresponding profile for standard well annealed ZnTe samples.

The absorption of XRD signal in ZnTe thin film causes a fractional error in $d$. The lattice parameters for different films are calculated from the Nelson Riley plots [16]. Dislocation densities are calculated using the method given by Williamson and Smallman [17]. The stacking fault probabilities are estimated from the peak shift of the x-ray lines with reference to that from well-annealed samples, using the method given by Warren and Warekois [18].

3.7.4 Optical properties

Development of semiconductors with controlled energy gap is necessary for the increased application of alloys in the solar cell fabrication and other optoelectronic devices. The optical properties of ZnTe films are of much interest due to their semiconducting nature. Hence, the absorption and transmission properties are studied using spectrophotometer to calculate their band gap variations. Since the generation of both free electrons and free holes is essential to produce a photovoltaic current, intrinsic absorption of a single photon across the band gap of
the semiconductor is the dominant optical absorption in a solar cell. Extrinsic absorption by deep, localized states in the band gap may act to affect charge transport, but it produces negligible net current, because the absorption coefficients associated with extrinsic absorption are many orders of magnitude smaller than for intrinsic process. The magnitude of absorption is described in terms of a absorption constant $\alpha(t)$ which is the formation of the wavelength of light. If a photon flux $\phi(\lambda)$ is present at $x = 0$ in the absorbing medium then,

$$\phi (\lambda, x) = \phi_0 (\lambda) \exp [-\alpha (\lambda)]$$

The flux $\phi$ may be measured in units of photons cm$^{-2}$ sec$^{-1}$ or in mWcm$^{-2}$. The rate of free carrier generation $G(x)$ by intrinsic absorption is,

$$G (\lambda, x \, dx = -d\phi (\lambda) = \alpha (\lambda) \phi(\lambda, x) \, dx$$

There are two major types of intrinsic absorption process involved in determining $\alpha$ and they are called direct and indirect absorption. Direct optical absorption is a first order process involving only the absorbed photon and can be represented approximately as a vertical line on energy versus wave vector plot. The absorption transition converses energy so that $E = h\nu$ (where $h\nu$ is the photon energy) and there is no change in $k$ between initial and final states except for the small momentum of the photon. The expected variation of $\alpha$ with the photon energy near the minimum energy for absorption $E_g^{d}$ is given by,

$$\alpha = \tau (E - E_g^{d})^n$$
where $\tau$ is a constant, $E$ is photon energy, $E_g^d$ is the direct band gap and $n$ is a constant, which can be assigned values 1/2, 3/2, and 2 for allowed direct transitions, forbidden direct transitions and allowed indirect transitions respectively.

**Optical constants**

The optical performance of thin films is determined by the thickness and optical constants of the layers. Thus knowledge of the optical constants and thickness of the deposited layers is necessary for effective coating design. It is well known that the optical properties of materials in thin film form greatly depend on the film microstructure and are usually different from the known bulk properties. Microstructure is in turn depends on the method of deposition and various conditions prevailing during deposition.

Polycrystalline thin films of ZnTe have been electrosynthesized onto F:SnO$_2$ plates of thickness nearly 0.1 $\mu$m. the thickness of the electrodeposited ZnTe thin films are determined by the weight loss method. For calculating $n$ and $k$ for the deposited films, the reflectance $R$ and transmittance $T$ are measured at normal incidence using a spectrophotometer. The sample is placed in the path of the reference beam and measurements are carried out in the range of 400 to 1200 nm with respect to the reference plate (SnO$_2$). The values obtained are fed to the computer as data in the program along with the values of wavelength, thickness and refractive indices of air and substrate. The initial approximate values are chosen
from the literature and the value of refractive index and extinction coefficient are obtained. The various values obtained by CDD method for electroplated ZnTe films are presented in chapter VI. The optical constants, the dielectric constants and the optical conductivity of the films were determined for ZnTe films deposited by potentiostatic and galvanostatic electrodeposition techniques. The packing density of the film was obtained using the relation: 

\[ n_f = n_b P + (I-P) n_v, \]

where \( n_f \) is the refractive index of the film, \( n_b \) is the refractive index of the bulk material and \( n_v \) is the refractive index of the void. Since voids in the films were usually filled with moisture \( n_v \) may be taken as 1.33.

3.7.5 Electrical studies

The electrical studies of electrodeposited thin film materials by Hall effect or resistance measurements is complicated by the fact that the sample must be removed from the conducting substrate before measurement. Previously, Baranski et al [19] and Takahashi et al [20] presented limited results for peeled samples of electrodeposited CdS and CdTe, respectively.

Using hot probe method (Fig.3.17), the type of conductivity of the films may be determined. This is a simple method which gives the direction of the electron flow, which makes it possible to determine the nature of semiconductor [21]. The semiconductor is placed on a plate and a metal heater is connected to the conducting substrate base through a multimeter. While the hot probe is momentarily
Fig. 3.17 Hot probe method.

a - HOT PROBE
b - SEMICONDUCTOR POWER
c - METAL BASE
d - MULTIMETER
e - COLD JUNCTION
touched over the semiconductor, current flows from cold junction to the hot junction for n-type and the reverse for p-type. For one group of deposits the initial potential difference is negative, changing to positive after a few seconds. For another group the potential difference is positive at all times. It is believed that the former behaviour indicates p-type, the later n-type semiconductivity. The ZnTe films are found to be p-type.

A very convenient way to measure the sheet resistance of a film is to lightly press a four-point metal-tip probe assembly in to the surface as shown in Fig.3.18. The outer probes are connected to the current source, and the inner probes detect the voltage drop. Electrostatic analysis of the electric potential and field distributions within the film yields, $R_s = KV/I$, where $K$ is a constant depends on the configuration and spacing of the contacts. If the film is larger in extent compared with the probe assembly and the probe spacing large compared with the film thickness, $K = \pi/ln2 = 4.53$. Otherwise correction factors must be applied [22]. Four-point probe assemblies are available commercially with square as well as the more common linear contact arrays.

3.7.6 Morphological and compositional studies

Scanning electron microscopes are becoming more and more useful and popular for the direct observation of surfaces because they offer better resolution and depth of field than optical microscopes. The resolution approaches that
Fig. 3.18 Schematic diagram of a four probe apparatus.
attainable with conventional electron microscopes and surface-replica samples. In addition, \textit{in situ} observation of surface morphology changes during heat treatment, etc., of specimens is possible. The surface morphology of electrodeposited ZnTe films is estimated by a JEOL JSM 840 SEM operating at 20 KV using normal incidence. The instrument is operated in the secondary emission mode and micrographs are recorded at suitable magnifications between 1K and 20K that reveals the topographic features. Most energy dispersive x-ray analysis systems are interfaced to SEMs, where the electron beam serves to excite characteristic x-rays from the area of the specimen being probed. An incoming x-ray generates a photoelectron that eventually dissipates its energy by creating electron-hole pairs. Using the energy dispersive analysis using x-rays (EDAX) the compositions of the film are estimated. EDAX measurements are done with scanning electron microscope (JEOL JSM 840). The percentage of atoms of different species present in the films is measured using the EDAX studies for ZnTe thin films prepared by electrodeposition technique by potentiostatic and galvanostatic methods. The microscopic surface composition of Zn and Te is investigated by x-ray photoelectron spectrometry (XPS) using a VGESCALAB MKII spectrometer with Mg K$_\alpha$ radiation.
3.8 Conclusion

The preparation of thin films of semiconductors requires proper choice of various parameters involved in the experiment. The reaction kinetics and the cyclic voltammetric studies were explained. The deposition parameters were adjusted to get stoichiometric films. The various experimental techniques performed for structural, microstructural, optical, electrical, morphological and compositional analysis were also briefly discussed.
References


