CHAPTER III
EXPERIMENTAL STUDIES

3.1. Introduction

Thin films of semiconducting chalcogenides such as FeSe, FeSe₂, CdSe and Cd₁₋ₓFeₓSe are considered important technological materials because of their wide range of applications in photovoltaic, photodetection, opto-electronic devices, IR detectors, lasers and light emitting diodes [1-8]. This chapter deals with the experimental details relevant to the fabrication of FeSe, FeSe₂, CdSe and Cd₁₋ₓFeₓSe thin films obtained using potentiostatic cathodic electrodeposition technique. Various experiments that are to be carried out for the determination of structural, morphological, compositional, optical, electrical, magnetic and photoelectrochemical properties are also discussed.

In D.C potentiostatic method, the deposition potential is kept constant and is one of important key parameters to be optimized in order to obtain coherent films [9]. There are two methods that are particularly adopted to fix the range of deposition potential. First one is Pourbaix diagram approach and the other is cyclic voltammetric method [10]. The cyclic voltammetric studies for fixing the deposition potential of FeSe, FeSe₂, CdSe and Cd₁₋ₓFeₓSe systems are discussed in this chapter. The vital role of deposition kinetic studies in order to fix the optimum range of deposition parameters are also discussed in detail. FeSe, FeSe₂, CdSe and Cd₁₋ₓFeₓSe thin films are obtained under optimized conditions and subsequent characterizations are carried out for films obtained under optimized conditions.

3.2. Electrochemical cell

It needs to be part of a circuit which contain a voltage source and a means of measuring the current. Although the characteristics of the over all cells are measured, the investigation may be consumed with the electrochemical process at a particular electrode, which is known as working electrode (WE) and the current is supplied by the auxiliary electrode (or) counter electrode (CE). If the working electrode has an area which is significantly smaller (approximately 10 times) than the counter electrode, then the performance of the electrochemical cell is dominated by the process at the working
electrode. Practically, 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 configuration, the voltage is applied between the working electrode (WE) and counter electrode (CE) as in the simple cell arrangement which is 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 gives the reference value. This means that if there is a requirement to control the potential of the working electrode with respect to the reference electrode (RE), which provides the reference value it is achieved by actually adjusting the potential applied between the working and counter electrodes. This is usually achieved by an instrument known as potentiostat. The potentiostat enables the user automatically and accurately controls the potential at the working electrode. This may be fixed 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 principle of operation of potentiostat a detailed investigation of three electrode cells is necessary.

3.3. Experimental details

The schematic representation of experimental set up used for electrodeposition is shown in Fig. 3.2 and the cell is explained in detail with its associated parts. Typically 50 ml glass beaker was used to contain the solution known as electrolytic bath. The magnetic stirrer cum heater set up was used to deposit films by stirring the electrolytic bath as well as raising the temperature. Indium doped tin oxide coated conducting glass (ITO) substrates were used as working electrode and platinum electrode is used as counter electrode. A saturated calomel electrode (SCE) was used as reference electrode in order to measure the potential of the working electrode. The working and counter electrodes were placed at a distance of 1 cm apart and surfaces were kept parallel to ensure attraction of the released ions and to enable the growth of the films exactly perpendicular to the cathode surface [11]. The reference electrode tip is placed very close to the cathode surface so that the exact potential at the surface will be monitored with out getting affects by the solution resistance [12].
Fig. 3.1. Simple cell arrangement
1. Potentiostat/Galvanostat (EG & G, Model 362, PAR, USA)
2. Ammeter- Digital Multimeter
3. Working Electrode
4. Counter Electrode
5. Saturated Calomel Electrode (SCE)
6. Connecting Bridge for SCE
7. 50 ml Beaker
8. Electrolytic Bath
9. Magnetic Stirrer with Temperature control

Fig.3.2. Schematic representation of experimental set-up used for electrodeposition
CHAPTER - III

It is impossible to determine the absolute potential of the individual electrodes and it is common practice to measure the electro motive force of a system comprising the electrode under investigation and some other electrodes 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 reference electrode.

A regulated DC power supply (EG & G, Model 362, Princeton Applied Research, USA) is used to prepare FeSe, FeSe$_2$, CdSe and Cd$_{1-x}$Fe$_x$Se thin films. Before used for deposition, indium doped tin oxide coated conducting glass electrodes are first cleaned well with soap solution followed by smooth application of acetone. Platinum electrode is cleaned with triple distilled water and acetone. The saturated calomel electrode is placed in potassium chloride (KCl) solution kept in a beaker. The potential of the calomel electrode depends on chloride ion concentration. Hence, the saturated condition of KCl is ensured before the start of each deposition.

3.3.1. D.C. Potentiostatic deposition

The electrochemical depositions are carried out potentiostatically at constant deposition potentials. A regulated d.c power supply (EG & G, Model 362, Princeton Applied Research, USA, Potentiostat/Galvanostat) is connected with its negative terminal to working electrode (cathode), positive terminal to counter electrode (anode) and the deposition of FeSe, FeSe$_2$, CdSe and Cd$_{1-x}$Fe$_x$Se thin films are obtained cathodically. The required deposition potential is kept constant using potentiostat and the current during deposition was measured using an ammeter connected in series with the cathode and negative terminal of the power supply. Cathodic deposition of FeSe, FeSe$_2$, CdSe and Cd$_{1-x}$Fe$_x$Se are carried out at various deposition potentials.
3.3.1.1. Electrochemistry of FeSe and FeSe$_2$ thin films

The basic electrochemical reactions for the electrodeposition of FeSe, FeSe$_2$ and their corresponding Nernst relations are:

\[ \text{Fe}^{2+} + 2e^- \rightarrow \text{Fe} \]

\[ E_{Fe}^0 = -0.447V \]  

\[ \text{H}_2\text{O} + \text{SeO}_3 + 4\text{H}^+ + 4e^- \rightarrow \text{Se} + 3\text{H}_2\text{O} \]

\[ E_{Se}^0 = 0.740V \]  

\[ E_{Fe} = E_{Fe}^0 + \left( \frac{RT}{2F} \right) \ln \left( \frac{a_{Fe}^{2+}}{a_{Fe}} \right) \]  (3.1)

\[ E_{Se} = E_{Se}^0 + \left( \frac{RT}{4F} \right) \ln \left( \frac{a_{Se^2-}}{a_{Se}} \right) \]  (3.2)

Here, $a_{Fe}^{2+}$ and $a_{Se^2-}$ are the activities of Fe and SeO$_2$ in the electrolyte, $a_{Fe}$ and $a_{Se}$ are the activities of Fe and Se in FeSe. $E_{Fe}^0$ and $E_{Se}^0$ are the standard reduction potential of Fe and Se, $E_{Fe}$ and $E_{Se}$ are the equilibrium electrode potentials of Fe and Se, F is Faraday constant, R is universal gas constant and T is the absolute temperature of the bath. It has been reported that selenide anion formation from six electron reduction of Se (IV) ions is assumed negligible with the deposition potential used. Hence, the deposit is formed by the solid state reaction of plated Fe and Se atoms rather than the precipitation of H$_2$Se and Fe$^{2+}$. Hence the reaction of formation of FeSe and FeSe$_2$ are described by the following Eq.3.3 (a) and (b)

\[ \text{Fe}^{2+} + \text{Se} + 2e^- \rightarrow \text{FeSe} \]  (3.3 a)

\[ \text{Fe}^{2+} + 2\text{Se} + 2e^- \rightarrow \text{FeSe}_2 \]  (3.3 b)

From the equilibrium electrode potential of Se and Fe, it can be seen that the electrode potential of Se is far more positive than those for Fe deposition. Further, to obtain simultaneous deposition of Fe and Se, the electrolyte concentration should be adjusted so as to bring the electrode potential of both the deposits closer. It is desirable to use a higher concentration of Fe and lower concentration of the noble component Se, so that the deposition potential of Fe shifts towards a positive value approaching the Se deposition potential. The deposition of Se will be diffusion controlled due to a very low concentration of SeO$_2$ (and consequently of H$_2$SeO$_5^-$). Based on these observations, a
higher concentration of Fe and very low concentration of Se have been taken in the bath for the deposition of FeSe and FeSe$_2$ thin films. Since, the electrodeposition of FeSe and FeSe$_2$ 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 this case, all good films, the transferred electrons for the deposition of one molecule of FeSe are found to be close to six.

3.3.1.2. Electrochemistry of CdSe thin films

The basic electrochemical reactions for the electrodeposition of CdSe and their corresponding Nernst relations are:

\[ Cd^{2+} + 2e^- \rightarrow Cd \]
\[ E_{Cd}^{0} = -0.403V \]

\[ E_{Cd} = E_{Cd}^{0} + \left( \frac{RT}{2F} \right) \ln \left( \frac{a_{Cd}^{2+}}{a_{Cd}} \right) \] \hspace{1cm} (3.4)

\[ H_2O + SeO_2 + 4H^+ + 4e^- \rightarrow Se + 3H_2O \]
\[ E_{Se}^{0} = 0.740V \]

\[ E_{Se} = E_{Se}^{0} + \left( \frac{RT}{4F} \right) \ln \left( \frac{a_{Se}^{2+}}{a_{Se}} \right) + \left( \frac{RT}{4F} \right) \ln \left( a_{H^+} \right)^4 \] \hspace{1cm} (3.5)

Here $a_{Cd}^{2+}$ and $a_{Se}^{2+}$ are the activities of Cd and SeO$_2$ in the electrolyte, $a_{Cd}$ and $a_{Se}$ are the activities of Cd and Se in CdSe, $E_{Cd}^{0}$ and $E_{Se}^{0}$ are the standard reduction potential of Cd and Se, $E_{Cd}$ and $E_{Se}$ are the equilibrium electrode potentials of Cd and Se, F is Faraday constant, R is universal gas constant and T is the absolute temperature of the bath. It has been reported that selenide anion formation from six electron reduction of Se (IV) ions is assumed negligible with the deposition potential used. Therefore, the deposit is formed by solid state reaction of plated Cd and Se atoms rather than precipitation of H$_2$Se and Cd$^{2+}$. Hence the formation CdSe is described by the following Eq.(3.6).

\[ Cd^{2+} + Se + 2e^- \rightarrow CdSe \] \hspace{1cm} (3.6)

From the equilibrium electrode potential of Se and Cd, it can be seen that the electrode potential of Se is far more positive than those for Cd deposition. Further, to obtain simultaneous deposition of Cd and Se, the electrolyte concentration should be adjusted so as to bring the electrode potentials of both the deposits closer. It is desirable
to use a higher concentration of Cd and lower concentration of the noble element Se, so
that the deposition potential of Cd shifts towards positive value approaching the Se
deposition potential. The deposition of Se will be diffusion controlled due to a very low
concentration of SeO₂ (and consequently of H₂SeO₂⁻). Based on these results, a higher
concentration (0.25 M) of Cd and very low concentration (0.0025 M) of Se have been
taken in the bath for the deposition of CdSe thin films. Since the electrodeposition of
CdSe 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 case of all
good films, the transferred electrons for the deposition of one molecule of CdSe are
found to close to six.

3.3.1.3. Electrochemistry of Cd₁ₓFeₓSe thin films

The electrodeposition of Cd₁ₓFeₓSe alloy thin films were carried out cathodically
from an aqueous solution bath containing CdSO₄, FeSO₄ and SeO₂. The basic
electrochemical reactions for the electrodeposition of Cd₁ₓFeₓSe alloys and their
corresponding Nemst relations are:

\[
Cd^{2+} + 2e^- \rightarrow Cd
\]

\[
E_{Cd} = E_{Cd}^0 + \frac{RT}{2F} \ln \left( \frac{a_{Cd}^{2+}}{a_{Cd}} \right)
\]

\[
Fe^{2+} + 2e^- \rightarrow Fe
\]

\[
E_{Fe} = E_{Fe}^0 + \frac{RT}{2F} \ln \left( \frac{a_{Fe}^{2+}}{a_{Fe}} \right)
\]

\[
H₂O + SeO₂⁻ + 4H⁺ + 4e^- \rightarrow Se + 3H₂O
\]

\[
E_{Se} = E_{Se}^0 + \frac{RT}{4F} \ln \left( \frac{a_{Se}^{2+}}{a_{Se}} \right) + \frac{RT}{4F} \ln(a_{H}^+)^{4}
\]

Here \(a_{Cd}^{2+}, a_{Fe}^{2+}\) and \(a_{Se}^{2+}\) the activities of Cd, Fe and SeO₂ in the electrolyte,
\(a_{Cd}, a_{Fe} \) and \(a_{Se}\) are the activities of Cd, Fe and Se in Cd₁ₓFeₓSe. \(E_{Cd}^0, E_{Fe}^0\) and \(E_{Se}^0\) are the
standard electrode potential of Cd, Fe and Se, \(F\) is Faraday constant, \(E_{Cd}, E_{Fe}\) and \(E_{Se}\) are the
equilibrium electrode potentials of Cd, Fe and Se, \(R\) is universal gas constant, and
T is the absolute temperature of the electrolytic bath. It has been reported that selenide anion formation from six electron reduction of Se (IV) ions is assumed negligible with deposition potential used. Hence, the deposit is formed by the solid state reaction of plated Cd, Fe and Se rather than precipitation of H₂Se and a²⁺, a²⁺. The deposition of Cd and Fe occurs at potentials more positive than their reduction potential by gaining free energy in the compound formation [9,13] and ternary alloy films of Cd₁₋ₓFeₓSe are formed via the equation [Eq.(3.10)]

\[ xFe^{2+} + (1 - x)Cd^{2+} + Se + 4e^- \rightarrow Cd_{1-x}Fe_xSe \]  

(3.10)

It has been reported that under potential deposition of less noble constituent (here Cd) of a compound (Cd₁₋ₓFeₓSe) is brought about by the gain of free energy by its formation [13]. Hence, in order to acquire the co-deposition of Cd, Fe and Se, we use a higher concentration of (0.006 M) Cd, Fe (0.03M) and lower concentration of noble element Se to fetch the electrode potentials of three deposits closer. Since, the electrodeposition of Cd₁₋ₓFeₓSe is six electron transfer process in each deposition the number of transferred electron is calculated from the total charge and mass of the deposit. In case of all good films the transferred electrons for the deposition of one molecule of Cd₁₋ₓFeₓSe is found to be six. Similar result was obtained for Zn₁₋ₓHgxSe alloy thin films reported earlier [14].

3.4. Cyclic Voltammetry

Cyclic voltammetry is a commonly used technique that is employed to give qualitative informations about electrochemical reactions. It is an important tool for the study of mechanism of formations in inorganic chemistry. This technique finds utmost important in understanding the mechanism of electrodeposition, in finding the format redox potential, growth pattern of the deposit and the influence of different addition agents in this process. The voltammograms of plating baths in a particular bath composition gave information on the possible range of deposition potentials. The informations about kinetic and thermodynamic considerations can be studied from current-potential curves recorded under the influence of various factors such as electrolyte concentration, solution pH, bath temperature etc. Hence cyclic voltammogram
of FeSe, FeSe₂, CdSe and Cd₁₋ₓFeₓSe thin films were recorded and discussed detail in this chapter.

In cyclic voltammetry, the electrode potential is varied in a desired fashion using a stable reference electrode system. The current flow is measured between the working and counter electrode as in polarography. There are several cyclic voltammetric techniques are available. Among them, in cyclic voltammetry, the voltage is varied from an initial to final and immediately swept back at the same sweep rate to the initial. In Electrochemical Analyzer Bio-Analytical system (ECA BAS-100A) the various techniques of cyclic voltammetry namely, linear sweep voltammetry (LSV), thin layer voltammetry (TLV), multi sweep cyclic voltammetry (MCV), anodic stripping voltammetry (ASV), cathodic stripping voltammetry (CSV), bulk electrolysis (BE) etc., can be performed. This electrochemical analyzer is a self containing integrated and sophisticated system which provides both diverse control and data reduction functions for the study of redox system.

Cyclic voltammetric studies was carried out in a standard electrolytic bath and a data acquisition system. All the voltammograms were first scanned in the cathodic direction and the negative current density indicates cathodic current. Cyclic voltammetric studies were carried out with three compartment cell consists of indium doped tin oxide coated conduct glass (ITO) substrate as working electrode, platinum electrode as counter electrode and saturated calomel electrode (SCE) as reference electrode, respectively. The scan rate employed was 20 mV/sec. The voltammetric curves were scanned in the potential range from -1500 to +1500 mV versus SCE.

3.4.1. Cyclic voltammetric studies on FeSe thin films

Cyclic voltammetric studies on Fe, Se and FeSe thin films were carried out in order to investigate the electrochemical reactions in solutions of FeSO₄, SeO₂ and the solution mixture containing FeSO₄ and SeO₂ to find out the optimum range of potential for the preparation of Fe, Se and FeSe thin films. Cyclic voltammogram of ITO glass electrode in an aqueous acidic bath containing 0.02 M FeSO₄ is shown in Fig.3.3 (a). It is observed from Fig.3.3 (a) that the cathodic current increases gradually upto -720 mV versus SCE, thereafter it increases rapidly upto -900 mV versus SCE. The reduction
peak I' observed at -900 mV versus SCE may be due to the formation of Fe ion according to the following Eq.(3.11). 'Reduction peak II' observed at -1150 mV versus SCE which may due to the reduction of solvent. In the reverse scan, an oxidation potential of metal iron is observed at -310 mV versus SCE as shown in Fig.3.3 (a). A hysteresis is obtained in the potential range between -700 and -1150 mV versus SCE represents that the reduction of Fe ions occurs more easily on the iron surface than on the surface of ITO electrode. The deposition of Fe occurs at a potential -1100 mV versus SCE. Similar behaviour is exhibited for the deposition of Fe ions on stainless steel substrate from an aqueous solution bath containing FeCl3 and TEA reported earlier [2]. A slight shift in deposition potential observed may be due to different substrates and other conditions of experiments such as stirring solution, solution pH, temperature of the electrolytic bath and concentration of the electrolytic solution [15].

\[ Fe^{2+} + 2e^- \rightarrow Fe \]  

(3.11)

Figure 3.3 (b) shows the typical cyclic voltammogram recorded for ITO glass electrode in an aqueous acidic bath containing 0.002 M SeO2. It is observed from Fig.3.3 (b) that a 'reduction wave' observed at - 480 mV versus SCE may be due to the reduction of H2SeO3 to Se according to the following Eq.(3.12). Another 'reduction peak' observed at -1000 mV versus SCE may be responsible for the two electron reduction of Se to H2Se according to the following Eq.(3.13). The formation of reddish elemental selenium layer was observed on the surface of ITO electrode at a deposition potential - 480 mV versus SCE. Similar behaviour is exhibited for metallic selenium on stainless steel substrate reported earlier [2]. Different deposition potentials such as -500,- 400 mV versus SCE have been reported earlier for selenium [16-17]. A slight difference in deposition potential obtained in the present work may be due to different substrates and other conditions of experiments such as electrolyte concentration, stirring solution, solution pH and temperature of the electrolytic bath [15].

\[ H_2SeO_3 + 4H^+ + 4e^- \rightarrow Se + 3H_2O \]  

(3.12)

\[ Se + 2H^+ + 2e^- \rightarrow H_2Se \]  

(3.13)
Fig. 3.3 (a). Cyclic voltammogram of ITO glass electrode in an aqueous acidic bath containing 0.02 M FeSO$_4$

Fig. 3.3 (b). Cyclic voltammogram of ITO glass electrode in an aqueous acidic bath containing 0.002 M SeO$_2$
Fig. 3.3 (c). Cyclic voltammogram of ITO glass electrode in an aqueous acidic bath containing 0.02 M FeSO₄ and 0.002 M SeO₂.

Fig. 3.4 (a). Cyclic voltammogram of ITO glass electrode in an aqueous acidic bath containing 0.02 M FeSO₄ solution.
A typical cyclic voltammogram recorded for ITO glass electrode in an aqueous acidic bath containing 0.02 M FeSO₄ and 0.002 M SeO₂ is shown in Fig.3.3 (c). It is observed from Fig.3.3 (c) that a 'reduction peak' observed at -725 mV versus SCE may be due to the cathodic reduction of H₂SeO₃ to Se. With selenium being nobler, it is expected to be deposited first by the following charge transfer reaction as given in Eq.(3.13). ‘Reduction peak II’ observed at -1100 mV versus SCE may be due to the formation of FeSe on the substrate which is described by the following Eq.(3.14). In the reverse scan, cyclic voltammogram shows cross-over at a potential -1150 mV versus SCE between cathodic current branches represents the characteristic of nucleation and growth process. The oxidation peak observed at -360 mV versus SCE is responsible for superimposed peaks of compound FeSe and element Fe, since this peak is similar to pure solution of FeSO₄ and hence no oxidation peak of FeSe is found. The hysteresis is obtained in the potential region between -700 and -1150 mV versus SCE thus represents the deposition of FeSe occurs more easily on FeSe surface than on ITO surface, since the working electrode was initially covered with FeSe instead of ITO. Hence the formation of FeSe starts at a deposition potential -1100 mV versus SCE on the surface of ITO. Similar behaviour is exhibited for FeSe on stainless substrate reported earlier [2]. The mechanism of formation of FeSe on ITO glass electrode is described as follows. The reduction of H₂SeO₃ to Se is the rate controlling step in the deposition process, the first process is the reduction of Fe²⁺ to Fe on the surface of ITO which is followed by electrochemical reduction of H₂SeO₃ with element Fe according to the following Eq.(3.14). The results of the cyclic voltammetry thus represents that the potential range of -700 to -1300 mV versus SCE may be used for the preparation of FeSe thin films.

\[
Fe^{2+} + Se^{+} + 2e^- \rightarrow FeSe
\]  

(3.14)

3.4.2. Cyclic voltammetric studies on FeSe₂ thin films

Cyclic voltammetric studies on Fe, Se and FeSe₂ thin films were carried out in order to investigate the electrochemical reactions in solutions of FeSO₄, SeO₂ and the solution mixture containing FeSO₄ and SeO₂ in order to find out the optimum range of potential for the preparation of Fe, Se and FeSe₂ thin films. Cyclic voltammogram of ITO glass electrode in an aqueous acidic bath containing 0.02 M FeSO₄ is shown in
Fig. 3.4 (a). It is observed from Fig. 3.4 (a) that the cathodic current increases gradually up to -720 mV versus SCE, thereafter it increases rapidly up to -900 mV versus SCE. The ‘reduction peak I’ observed at -900 mV versus SCE may be due to the formation of Fe ion according to the following Eq.(3.15). ‘Reduction peak II’ observed at -1150 mV versus SCE which may due to the reduction of solvent. In the reverse scan, an oxidation potential of metal iron is observed at -310 mV versus SCE as shown in Fig. 3.4 (a). A hysteresis is obtained in the potential region between -700 and -1150 mV versus SCE represents that the reduction of Fe ions occurs more easily on the iron surface than on the surface of ITO electrode. Hence, once the substrate is covered with metal iron the deposition of Fe occurs more easily on FeSe2 surface than on the surface of ITO at a potential -1100 mV versus SCE. Similar behaviour is exhibited for the deposition of Fe ions on stainless steel substrate from an aqueous solution bath containing FeCl3 and TEA reported earlier [2]. A slight shift in deposition potential observed may be due to different substrates and other conditions of experiment such as stirring solution, solution pH, temperature of the electrolytic bath and concentration of the electrolytic solution [15].

\[ \text{Fe}^{3+} + 2e^- \rightarrow \text{Fe} \]  

(3.15)

Figure 3.4 (b) shows the typical cyclic voltammogram recorded for ITO glass electrode in an aqueous acidic containing 0.01 M SeO2. It is observed from Fig. 3.4 (b) that a ‘reduction wave’ observed at -550 mV versus SCE may be due to the reduction of H2SeO3 to Se according to the following Eq.(3.16). Another ‘reduction peak’ observed at -1000 mV versus SCE which may be responsible for the two electron reduction of Se to H2Se according to the following Eq.(3.17). A reddish elemental selenium layer is appeared on the surface of ITO electrode at a deposition potential -550 mV versus SCE. Similar behaviour is exhibited for metallic Selenium on titanium substrate reported earlier [15]. Different deposition potentials such as - 400, -500 mV versus SCE were reported earlier for selenium deposition [16-17]. A slight difference in deposition potential obtained in the present work may be due to different substrates and other conditions of experiment such as electrolyte concentration, stirring solution, solution pH and temperature of the electrolytic bath [15].
Fig. 3.4 (b). Cyclic voltammogram of ITO glass electrode in an aqueous acidic bath containing 0.01 M SeO$_2$.

Fig. 3.4 (c). Cyclic voltammogram of ITO glass electrode in an aqueous acidic bath containing 0.02 M FeSO$_4$ and 0.01 M SeO$_2$. 
A typical cyclic voltammogram recorded for ITO glass electrode in an aqueous solution bath containing 0.02 M FeSO$_4$ and 0.01 M SeO$_2$ is shown in Fig.3.4 (c). It is observed from Fig.3.4 (c) that a ‘reduction peak’ observed at -600 mV versus SCE may be due to cathodic reduction H$_2$SeO$_3$ to Se. With selenium being nobler, it is expected to be deposited first by the following charge transfer reaction which is indicated in Eq.(3.16). ‘Reduction peak II’ observed at -450 mV versus SCE may be due to the formation of FeSe$_2$ on the substrate according to Eq.(3.17). In the reverse scan, an ‘oxidation peak’ observed at -360 mV versus SCE which is responsible for superimposed peaks of compound FeSe$_2$ and element Fe, since this peak is similar to pure solution of FeSO$_4$ and hence no ‘oxidation peak’ of FeSe$_2$ is found. The hysteresis is obtained in the potential region between -300 and -600 mV versus SCE thus represent that the deposition of FeSe$_2$ occurs more easily on FeSe$_2$ surface than on the surface of ITO, since the working electrode was initially covered with FeSe$_2$ instead of ITO. Hence the formation of FeSe$_2$ starts at a deposition potential -450 mV versus SCE. The results of the cyclic voltammetry represent that the potential range of -300 to -600 mV versus SCE may be used for the preparation of FeSe$_2$ thin films.

3.4.3. Cyclic voltammetric studies on CdSe thin films

Cyclic voltammetric studies on Cd, Se and CdSe thin films were carried out in order to determine the electrochemical reactions in solutions of CdSO$_4$, SeO$_2$ and the solution mixture containing CdSO$_4$ and SeO$_2$ to find out the optimum range of potential for the preparation of Cd, Se and CdSe thin films. Cyclic voltammogram of ITO glass electrode in an aqueous acidic bath containing 0.25 M CdSO$_4$ is shown in Fig.3.5 (a). During cathodic scan, visible silver grey films have appeared on the surface of ITO at a potential -690 mV versus SCE. The ‘reduction peak’ observed at -690 mV versus SCE may be due to the reduction of cadmium ions according to the following Eq.(3.18). In the reverse scan, an oxidation potential of metal cadmium is observed at -280 mV versus SCE as shown in Fig.3.5 (a). A hysteresis is obtained in the potential range between -660
and -730 mV versus SCE indicates that the reduction of cadmium ions occurs more easily on the cadmium surface than on the ITO electrode. During cyclic voltammetric studies, the substrate is initially covered with cadmium the deposition occurred at a potential -670 mV versus SCE. Similar behaviour is exhibited for the deposition of Cd ions on titanium substrates reported earlier [15]. A slight difference in deposition potential observed in this work may be due to different substrates and other conditions of experiments such as stirring solution, solution pH, temperature of the electrolytic bath and concentration of the electrolytic solution [15].

\[
Cd^{2+} + 2e^- \rightarrow Cd
\]  

(3.18)

A typical voltammogram of ITO glass electrode in an aqueous acidic bath containing 0.0025 M SeO₂ is shown in Fig.3.5 (b). It is observed from Fig.3.5 (b) that a ‘reduction peak’ observed at - 470 mV versus SCE may be due to reduction of H₂SeO₃ to Se according to the following Eq.(3.19). Another ‘reduction peak’ observed at -980 mV versus SCE may be responsible for the two electron reduction of Se to H₂Se according to the following Eq.(3.20). The formation of reddish elemental Se layer was observed on the surface of ITO at a deposition potential - 470 mV versus SCE. Various deposition potentials such as - 400,- 500 mV versus SCE were reported earlier for selenium deposition [16,17]. A slight shift in deposition potential obtained in the present work may be due to different substrates and other conditions of experiments such as stirring solution, solution pH, bath temperature and concentration of electrolytic solution [15].

\[
H_2SeO_3 + 4H^+ + 4e^- \rightarrow Se + 3H_2O
\]  

(3.19)

\[
Se + 2H^+ + 2e^- \rightarrow H_2Se
\]  

(3.20)

Figure 3.5 (c) shows the cyclic voltammogram recorded of ITO glass electrode in an aqueous acidic bath containing 0.25 M CdSO₄ and 0.0025 M SeO₂. Electrochemical growth of CdSe starts at a potential about -726 mV versus SCE. During cathodic scan, the re-oxidation peak is observed at - 460 mV versus SCE which is responsible for superimposed peaks of compound CdSe and element Cd, since this peak is similar to pure solution of CdSO₄ and hence no oxidation peak of CdSe is found.
Fig. 3.5 (a). Cyclic voltammogram of ITO glass electrode in an aqueous acidic bath containing 0.25 M CdSO₄.

Fig. 3.5 (b). Cyclic voltammogram of ITO glass electrode in an aqueous acidic bath containing 0.0025 M SeO₂.
Fig. 3.5 (c). Cyclic voltammogram of ITO glass electrode in an aqueous acidic bath containing 0.25 M CdSO$_4$ and 0.0025 M SeO$_2$

Fig. 3.6 (a). Cyclic voltammogram of ITO glass electrode in an aqueous acidic bath containing 0.006 M CdSO$_4$
A hysteresis is obtained in the potential range between -726 and -696 mV versus SCE thus represent that the deposition of CdSe occurs more easily on CdSe surface than those on ITO surface, since, the working electrode was initially covered with CdSe instead of ITO. Hence, the formation of CdSe starts at a more positive potential on the surface of ITO electrode [15]. The mechanism of formation of CdSe on ITO glass electrode is described as follows. The reduction of H$_2$SeO$_3$ to Se is the rate controlling step in the deposition process the first process is the reduction of Cd$^{2+}$ to Cd on the surface of ITO electrode (Eq.3.18) which is followed by electrochemical reduction of H$_2$SeO$_3$ with element Cd according to the following Eq.(3.21). The results of the cyclic voltammetry represents that the potential range of -500 to -900 mV versus SCE may be used for the preparation of CdSe thin films.

$$Cd^{2+} + Se + 2e^- \rightarrow CdSe$$ (3.21)

### 3.4.4. Cyclic voltammetric studies on Cd$_{1-x}$Fe$_x$Se thin films

Cyclic voltammetric studies on Cd, Fe, Se and Cd$_{1-x}$Fe$_x$Se thin films were carried out in order to determine the electrochemical reactions in solutions of CdSO$_4$, FeSO$_4$, SeO$_2$ and the solution mixture containing CdSO$_4$, FeSO$_4$ and SeO$_2$ to find out the optimum range of potential for the preparation of Cd, Fe, Se and Cd$_{1-x}$Fe$_x$Se systems. A typical cyclic voltammogram recorded for ITO glass electrode in an aqueous acidic bath containing 0.006 M CdSO$_4$ is shown in Fig.3.6 (a). The ‘reduction peak’ observed at -690 mV versus SCE may be due to the reduction of cadmium ions according to the following Eq.(3.22). In the reverse scan, an oxidation potential of metal cadmium is observed at -110 mV versus SCE as shown in Fig.3.6 (a). A hysteresis is obtained in the potential range between -690 and -660 mV versus SCE indicates that the reduction of cadmium ions occurs more easily on the cadmium surface than on the surface of ITO electrode. During cyclic voltammetric studies, the substrate was initially covered with cadmium the deposition occurred at a potential -660 mV versus SCE. Similar behaviour is exhibited for the deposition of Cd ions on titanium substrates reported earlier. A slight difference in deposition potential obtained in this work may be due to different substrates and other conditions of experiments such as stirring solution, solution pH, temperature of the electrolytic bath and concentration of the electrolytic solution [15].


\[ \text{Cd}^{2+} + 2e^- \rightarrow \text{Cd} \quad (3.22) \]

Figure 3.6 (b) shows the cyclic voltammogram recorded for ITO glass electrode in an aqueous acidic bath containing 0.03 M FeSO\(_4\). It is observed from Fig.3.6 (b) that the cathodic current increases gradually up to -720 mV versus SCE, thereafter it increases rapidly up to -900 mV versus SCE. The ‘reduction peak I’ observed at -900 mV versus SCE may be due to the formation of Fe ion on ITO surface according to the following Eq.(3.23). ‘Reduction peak II’ observed at -1150 mV versus SCE which may due to the reduction of solvent. In the reverse scan, an oxidation potential of metal iron is observed at -310 mV versus SCE as shown in Fig.3.6 (b). A hysteresis is obtained in the potential range between -700 and -1150 mV versus SCE represents that the reduction of Fe ions occurs more easily on the iron surface than on the surface of ITO electrode. The deposition of Fe occurs at a potential -1100 mV versus SCE. Similar behaviour is exhibited for the deposition of Fe ions on stainless steel substrate from an aqueous solution bath containing FeCl\(_3\) and TEA reported earlier [2]. A slight shift in deposition potential observed may be due to different substrates and other conditions of experiments such as stirring solution, solution pH, temperature of the electrolytic bath and concentration of the electrolytic solution [15].

\[ \text{Fe}^{2+} + 2e^- \rightarrow \text{Fe} \quad (3.23) \]

A typical cyclic voltammogram recorded for ITO glass electrode in an aqueous acidic bath containing 0.01 M SeO\(_2\) is shown in Fig.3.6 (c). It is observed from Fig.3.6 (c) that a reduction wave observed at -580 mV versus SCE may be due to the reduction of H\(_2\)SeO\(_3\) to Se according to the following Eq.(3.24). The formation of reddish elemental selenium layer was observed on the surface of ITO electrode at a deposition potential -580 mV versus SCE. Similar behaviour is exhibited for metallic selenium on stainless steel substrate reported earlier [2]. Different deposition potentials such as - 400, -500 mV versus SCE were reported earlier for selenium deposition [16,17]. A small difference in deposition potential obtained in the present work may be due to different substrates and other conditions of experiments such as electrolyte concentration, stirring solution, solution pH and temperature of the electrolytic bath [15].

101
H$_2$SeO$_3$ + 4H$^+$ + 4e$^-$ → Se + 3H$_2$O

(3.24)

The cyclic voltammogram of ITO glass electrode in an aqueous acidic bath containing 0.006 M CdSO$_4$, 0.03 M FeSO$_4$ and 0.01 M SeO$_2$ is shown in Fig.3.6 (d). It is observed from Fig.3.6 (d) that the voltammetric curve shows the reduction of all three precursors. A ‘reduction peak I’ observed at -510 mV versus SCE may be responsible for the reduction of H$_2$SeO$_3$ to Se according to Eq.(3.24). The ‘reduction peak II’ observed at -640 mV versus SCE may be due to the reduction of cadmium ion according to Eq.(3.22). ‘Reduction peak III’ observed at -900 mV versus SCE displays strong (cathodic) photoeffect. This may be ascribed to the formation of Cd$_{1-x}$Fe$_x$Se system according to the following Eq.(3.25). On further decreasing the deposition potential, an oxidation peak observed at -850 mV versus SCE which may be due to the stripping off of the metallic iron layer. The reoxidation of Fe produced during the forward scan would be impossible when covered completely by Cd$_{1-x}$Fe$_x$Se which is only stripped off at more positive potentials such as 400 mV versus SCE. On more positive potential an anodic photoeffect is observed, whereas at more negative potential cathodic photoeffect is observed. The photoeffects observed in the above process produces an intrinsic semiconductor depending upon the deposition potential. No unique element is formed, but sequence of layers corresponding to different compositions is obtained in the potential range between -600 and -1100 mV versus SCE. The results of the cyclic voltammetry on Cd$_{1-x}$Fe$_x$Se thin films represents that the potential range of -600 and -1100 mV versus SCE may be used for the preparation of Cd$_{1-x}$Fe$_x$Se thin films. Similar behaviour is reported earlier for Zn$_{1-x}$Hg$_x$Se alloy systems [14].

$\text{xFe}^{2+} + (1-x)\text{Cd}^{2+} + \text{Se} + 4\text{e}^- \rightarrow \text{Cd}_{1-x}\text{Fe}_x\text{Se}$

(3.25)
Fig.3.6 (b). Cyclic voltammogram of ITO glass electrode in an aqueous acidic bath containing 0.03 M FeSO$_4$

Fig.3.6 (c). Cyclic voltammogram of ITO glass electrode in an aqueous acidic bath containing 0.01 M SeO$_2$
Fig. 3.6 (d). Cyclic voltammogram of ITO glass electrode in an aqueous acidic bath containing 0.006 M CdSO₄, 0.03 M FeSO₄ and 0.01 M SeO₂.
3.5. Preparation of thin films

Recently, electrodeposition is a simple, versatile technique which is utilized for the preparation of thin films. A number of deposition parameters are involved in the preparation of thin films by the electrodeposition technique. The various deposition parameters are fixed using cyclic voltammetric studies. Thin films are prepared using various electrolyte concentrations of the respective species in the range of deposition potential which is fixed using cyclic voltammetric studies.

3.5.1. Preparation of FeSe thin films

All the chemicals used in the present work were of Analytical Grade Reagents (99 % Purity, E-Merck). The first working solution of FeSO₄ was obtained by dissolving 1.39 g of FeSO₄ in 250 ml of deionized water to get 0.02 M FeSO₄ solution. The second working solution of SeO₂ was obtained by dissolving 0.0555 g of SeO₂ in 250 ml of deionized water to get 0.002 M SeO₂ solution. The electrochemical deposition of FeSe thin films are very difficult, because it involves several deposition parameters in the preparation of the films. Cyclic voltammetric studies are performed to fix deposition potential in the range between -700 and -1300 mV versus SCE for the preparation of FeSe thin films. The effect of concentration of the respective species in the solution became evident only after confirmation of the deposited films using X-ray diffraction analysis.

The concentration of FeSO₄ for the preparation of FeSe thin films are found to be in the range between 0.01 and 0.025 M. Initially, the concentration of iron sulphate and selenium dioxide is taken as 5:1. The films are deposited with different concentration ratios, and are analyzed using X-ray diffraction analysis. Iron Selenide thin films (FeSe) are electrodeposited at different concentrations of Fe and Se. The concentration of SeO₂ is kept at a low value 0.002 M during all depositions and FeSO₄ concentration is found to be vary in the range between 0.01 and 0.025 M. An approximate stoichiometric composition of 52.55:47.45 (Fe:Se) is observed for films obtained at 0.02 M Fe²⁺ concentration. It is also observed that the peak height of XRD signal for hexagonal (002) plane increases while increasing FeSO₄ concentration, indicating preferred orientation and improved crystallinity of FeSe films deposited at 0.02 M FeSO₄ concentration.
CHAPTER - III

The ratio of concentration of stock solutions (Fe/Se) are found to vary in the range between 5 and 12.5. Uniform FeSe thin films are obtained by blending suitable ratio of stock solutions and diluting with water to get a final nominal concentration of Fe/Se value at 10. The plating experiments are carried out at various bath temperatures from 30 to 90°C with step increment of 20°C with different intervals of time. The range of deposition parameters used for the preparation FeSe thin films are given in Table 3.1.

3.5.2. Preparation of FeSe₂ thin films

The chemicals used in the present work were of Analytical Grade Reagents (99 % Purity, E-Merck). The working solution of FeSO₄ was obtained by dissolving 1.39 g of FeSO₄ in 250 ml of deionized water. The second working solution of SeO₂ was obtained by dissolving 0.277 g of SeO₂ in 250 ml of deionized water. The deposition of FeSe₂ thin films are very difficult as it involves several deposition parameters which control the growth of the films. The cyclic voltammetric studies are carried out in order to fix the deposition potential in the range between -300 and -550 mV versus SCE. The effect of concentration of the respective species in the solution became evident only after confirmation of the deposited films using X-ray diffraction analysis.

The FeSO₄ concentration used for the deposition of FeSe₂ thin films are found to be in the range between 0.01 and 0.025 M. The concentration of SeO₂ is fixed as 0.01 M for all depositions. Initially, the concentration of iron sulphate and selenium dioxide is taken as 1:1. The films are prepared at different concentration ratios and their X-ray diffraction patterns are investigated. An approximate stoichiometric composition of 32.08:67.92 (Fe/Se) is obtained for films prepared at 0.02 M FeSO₄ concentration. The ratio of concentration of Fe/Se stock solutions are found to be in the range between 1 and 2.5. Also it is observed that the XRD peak height of (120) orthorhombic plane increases while increasing FeSO₄ concentration upto 0.02 M, thereafter it decreases slightly indicating preferred orientation of FeSe₂ films deposited at 0.02 M FeSO₄ concentration. The ratio of concentration of stock solution (Fe/Se) is found to be 2:1 in order to obtain uniform FeSe₂ thin films. The depositions are carried out in the temperature range 35 and 95°C. The range of deposition parameters used for the growth of FeSe₂ thin films are given in Table 3.2.
**CHAPTER - III**

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Concentration (M)</th>
<th>Deposition conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeSO₄.7H₂O</td>
<td>0.01 to 0.025</td>
<td>Potential: -700 to -1300 mV versus SCE</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bath temperature: 30 to 90°C</td>
</tr>
<tr>
<td>SeO₂</td>
<td>0.002</td>
<td>Solution pH: (2.0 to 4.0) ± 0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Deposition time: 10 to 60 minutes</td>
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<tr>
<td></td>
<td></td>
<td>Scan rate: 20 mV/sec</td>
</tr>
</tbody>
</table>

Table 3.1. The range of deposition parameters used for the preparation FeSe thin films

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Concentration (M)</th>
<th>Deposition conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeSO₄.7H₂O</td>
<td>0.01 to 0.025</td>
<td>Potential: -300 to -550 mV versus SCE</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bath temperature: 35 to 95°C</td>
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<tr>
<td>SeO₂</td>
<td>0.01</td>
<td>Solution pH: (1.5 to 3.0) ± 0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Deposition time: 10 to 60 minutes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Scan rate: 20 mV/sec</td>
</tr>
</tbody>
</table>

Table 3.2. The range of deposition parameters used for the preparation FeSe₂ thin films
3.5.3. Preparation of CdSe thin films

All the chemicals used in the present work were of Analytical Grade reagents (99% purity, E-Merck). The first working solution of CdSO₄ was obtained by dissolving 48.10 g CdSO₄ in 250 ml of deionized water to get 0.25 M CdSO₄ solution. The second working solution of SeO₂ was obtained by dissolving 0.0694 g of SeO₂ in 250 ml deionized water to get 0.0025 M SeO₂ solution. The preparation of CdSe thin films are difficult, since it involves several deposition parameters which control the formation of CdSe thin films. Cyclic voltammetric studies are carried out in order to fix the deposition potential in the range between -500 and -900 mV versus SCE for the preparation of CdSe thin films. The effect of concentration of the respective species in the electrolytic solution became evident only after confirmation of the deposited films using X-ray diffraction analysis.

The CdSO₄ concentration used for the deposition of CdSe thin films are found to be vary in the range between 0.15 and 0.3 M. Initially, the concentration of cadmium sulphate and selenium dioxide is taken as 60:1. The films are deposited at various concentration ratios and their X-ray diffraction patterns are analyzed. An approximate stoichiometric composition of 49.83:50.17 (Cd/Se) is obtained for 0.25 M CdSO₄ concentration. Also it is observed that the X-ray diffraction peak height of (002) hexagonal plane increases while increasing the concentration of CdSO₄ upto 0.25 M, thereafter the peak height slightly decreases represents the formation preferential orientation and better crystallinity CdSe films obtained at 0.25 M CdSO₄ concentration. The ratio of concentration of stock solutions (Cd/Se) are found to vary in the range between 60 and 120. Uniform CdSe thin films are obtained by mixing suitable amount of stock solutions in order to get a nominal concentration of Cd/Se value at 100/1. The electrochemical depositions are carried at various bath temperatures in the range between 35 and 95°C with step increment of 15°C with different intervals of time. The range of deposition parameters used for the preparation of CdSe thin films are given in Table 3.3.
CHAPTER - III

3.5.4. Preparation of \( \text{Cd}_{1-x}\text{Fe}_x\text{Se} \) thin films

The chemicals used in this work were of Analytical Grade Reagents (99% Purity, E-Merck). The first working solution of CdSO\(_4\) was obtained by dissolving 1.155 g of CdSO\(_4\) in 250 ml of deionized water to get 0.006 M CdSO\(_4\) solution. The second working solution of FeSO\(_4\) was obtained by dissolving 2.09 g of FeSO\(_4\) in 250 ml deionized water in order to get 0.03 M FeSO\(_4\) solution. Third working solution of SeO\(_2\) was obtained by dissolving 0.2774 g of SeO\(_2\) in 250 ml deionized water to get 0.01 M SeO\(_2\) solution. The deposition potential was fixed in the range between -600 and -1100 mV versus SCE using cyclic voltammetric studies. The effect of concentration of the respective species became evident only after confirmation of the deposited films using X-ray diffraction analysis.

The CdSO\(_4\) concentration used for the preparation of \( \text{Cd}_{1-x}\text{Fe}_x\text{Se} \) thin films are found to be vary in the range between 0.002 and 0.008 M. The concentration of FeSO\(_4\) was found to be vary in the range between 0.01 and 0.04 M. Also the range of CdSO\(_4\) and SeO\(_2\) are found to be 0.006:0.01. Initially the range of CdSO\(_4\), FeSO\(_4\) and SeO\(_2\) are found to be 0.002:0.01:0.01 M. Films prepared at various concentration ratios are analyzed using X-ray diffraction analysis. An approximate stoichiometric composition value of 26.95:23.04:50.01 (Cd/Fe/Se) is obtained for 0.006:0.03:0.01 M concentration. It is observed that the X-ray diffraction peak height of (002) hexagonal plane increases while increasing the concentration of FeSO\(_4\) upto 0.03 M. Further increasing concentration above 0.03 M the peak height of (002) plane is found to decrease represent that films with better crystallinity are obtained at 0.03 M FeSO\(_4\) concentration. The ratio of concentration of stock solutions (Cd/Se) and (Fe/Se) are found to be vary in the range between 0.2 and 0.8, 1 and 4. Uniform \( \text{Cd}_{1-x}\text{Fe}_x\text{Se} \) alloy thin films are obtained by mixing suitable amount of stock solutions in order to obtain a nominal concentration of Cd/Fe/Se value at 0.6:3:1. The depositions of \( \text{Cd}_{1-x}\text{Fe}_x\text{Se} \) alloy thin films are carried out at various bath temperatures ranging from 30 to 90°C with step increment of 20°C with different intervals of time. The range of deposition parameters used for the preparation of \( \text{Cd}_{1-x}\text{Fe}_x\text{Se} \) alloy thin films are given in Table 3.4.
### Table 3.3. The range of deposition parameters used for the preparation of CdSe thin films

<table>
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<tr>
<th>Precursor</th>
<th>Concentration (M)</th>
<th>Deposition conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>3CdSO₄ .8H₂O</td>
<td>0.15 to 0.3</td>
<td>Potential: -500 to -900mV versus SCE&lt;br&gt;Bath temperature: 35 to 95°C</td>
</tr>
<tr>
<td>SeO₂</td>
<td>0.0025</td>
<td>Solution pH: (1.5 to 3.0) ± 0.1&lt;br&gt;Deposition time: 10 to 60 minutes&lt;br&gt;Scan rate: 20 mV/sec</td>
</tr>
</tbody>
</table>

### Table 3.4. The range of deposition parameters used for the preparation of Cd₁ₓFeₓSe thin films

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Concentration (M)</th>
<th>Deposition conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>3CdSO₄ 8H₂O</td>
<td>0.002 to 0.008</td>
<td>Potential: -600 to -1050 mV vs SCE&lt;br&gt;Bath temperature: 30 to 90°C</td>
</tr>
<tr>
<td>FeSO₄ 7H₂O</td>
<td>0.01 to 0.04</td>
<td>Solution pH: (1.5 to 3.0) ± 0.1</td>
</tr>
<tr>
<td>SeO₂</td>
<td>0.0025 to 0.02</td>
<td>Deposition time: 10 to 60 minutes&lt;br&gt;Scan rate: 20 mV/sec</td>
</tr>
</tbody>
</table>
3.6. Thickness measurement

Thickness is one of the important film parameters which control the film properties. The reason is that the properties and behaviour of thin films are mainly depend on thickness. The utilization of thin films in optical applications spurred the development of techniques capable of measuring film thickness with high accuracy. Thickness of FeSe, FeSe$_2$, CdSe and Cd$_{1-x}$Fe$_x$Se thin films was measured using stylus profilometer (Mitutoyo SJ 301).

3.6.1. Variation of film thickness in FeSe thin films

The electrodeposition of FeSe thin films was controlled by two independent variables such as (i) film thickness and its uniformity (ii) surface morphology [18]. Thickness of the deposited films was estimated using stylus profilometer. The average thickness of the deposited layers could be directly controlled by controlling the plating potential and plating time. During the process of deposition, it is observed that at more negative potential such as above -1300 mV versus SCE the film formation is hindered due to the process of hydrogen evolution reaction. At lower cathodic potential (such as below -700 mV versus SCE) films with irregular growth and rough surface was obtained. The films deposited in the potential range between -700 and -1300 mV versus SCE are found to be smooth, uniform and well adherent to the substrates. Variation of film thickness with deposition time for FeSe thin films obtained at bath temperature 70°C with different deposition potentials are shown in Fig.3.7. It is observed from Fig.3.7 (a) that the film thickness increases with deposition time and tend to attain saturation after 30 minutes of deposition for films obtained at deposition potential -700 mV versus SCE. Similar behaviour is exhibited for films prepared at different deposition potentials such as -900, -1100 and -1300 mV versus SCE, as shown in Fig.3.7 (b-d). If the deposition potential is increased above -1100 mV versus SCE thickness of the deposited films are found to decrease as shown in Fig.3.7 (d). The maximum value of film thickness was obtained for films prepared at a deposition potential -1100 mV versus SCE and at a deposition time 30 minutes. Hence, the deposition potential and deposition time are fixed as -1100 mV versus SCE and 30 minutes in order to get films with higher thickness.
Fig.3.7. Variation of film thickness with deposition time for FeSe thin films prepared at various deposition potentials: (a) -700 (b) -900 (c) -1100 (d) -1300 mV versus SCE

Fig.3.8. Variation of film thickness with deposition time for FeSe thin films prepared at various bath temperatures: (a) 30 (b) 50 (c) 70 (d) 90°C
Figure 3.8 shows the variation of film thickness with deposition time for FeSe thin films prepared at a deposition potential -1100 mV versus SCE under various bath temperatures in the range between 30 and 90°C. It is observed from Fig.3.8 that the film thickness increases linearly with deposition time and tend to attain saturation after 30 minutes of deposition. The bath temperature is expected to influence the deposition rate by: (i) increasing the solubility of the precursor (ii) increase the diffusion coefficient of the species and decrease of viscosity [18]. Due to increase in solubility with bath temperature higher value of film thickness was obtained for films prepared at higher bath temperature such as 70°C. Further increasing bath temperature above 70°C thickness of the deposited films are found to decrease slightly as shown in Fig.3.8 (d). The studies indicate that an optimum temperature of 70°C is used to prepare FeSe thin films. The maximum value of thickness obtained in the present work for various bath temperatures (30, 50, 70 and 90°C) are found to be in the range between 550 and 1240 nm. It is found that an increase in bath temperature from 30 to 70°C, the rate of release of Fe$^{2+}$ and Se$^{2-}$ ions are faster, enhances the rate of deposition and hence increases the film thickness value while increasing bath temperature from 30 to 70°C. If the temperature of the electrolytic bath is increased above 70°C, the ions are released at relatively faster rate and hence there is no enough time to condense on the substrate surface leading to the precipitation of electrolytic bath. This results decrease in value of film thickness as shown in Fig.3.8 (d) [19-20]. Therefore, the bath temperature and deposition time are fixed as 70°C and 30 minutes, respectively.

Variation of film thickness with deposition time for FeSe thin films prepared at deposition potential -1100 mV versus SCE, bath temperature 70°C at various solution pH values from 2.0 to 2.5 ± 0.1 are shown in Fig.3.9. It is observed from Fig.3.9 (c) that the film thickness increases while increasing the deposition time up to 30 minutes, thereafter thickness of the deposited films remains constant. If the deposition time is increased above 60 minutes thickness of the deposited films are found to decrease not shown in Fig.3.9. At lower pH value such as 2.0, 2.5 ± 0.1 thickness of the deposited films is low which may be due to low conductivity of the electrolytic solution. The films prepared at
Fig. 3.9. Variation of film thickness with deposition time for FeSe thin films prepared at various solution pH values: (a) 2.0 (b) 2.5 (c) 3.0 (d) 4.0

Fig. 3.10. Variation of film thickness with deposition time for FeSe thin films prepared at various FeSO₄ concentrations: (a) 0.01 (b) 0.015 (c) 0.02 (d) 0.025 M
higher pH value such as $3.0 \pm 0.1$ thickness of the deposited films is high which may be due to high conductivity of the electrolytic solution. As a result, the conductivity in the solution increases which in turn increases the deposition current passing through the solution. This enhances the overall rate of deposition which in turn increases the thickness value of films prepared at solution pH value around $3.0 \pm 0.1$. If the solution pH value is increased above, thickness of the film decreases as shown in Fig.3.9 (d). The decrease in value of film thickness at solution pH value around $4.0 \pm 0.1$ may be due to the precipitation of electrolytic bath. Hence, an optimum solution pH value of $3.0 \pm 0.1$ may be used to attain films with higher thickness.

The variation of film thickness with deposition time for FeSe thin films deposited with concentrations around (0.01-0.025) M FeSO$_4$ and 0.002 M SeO$_2$ at bath temperature, deposition potential and solution pH values such as $70^\circ$C, -1100 mV versus SCE and $3.0 \pm 0.1$ are recorded. In case of electrodeposition of FeSe thin films, the use of low concentration of selenous acid and high concentration iron salt is the usual approach, since the iron is a less noble constituent of the compound [21-23]. In this way, the rate of the following reaction $H_2O + SeO_2 + 4H^+ + 4e^- \rightarrow Se + 3H_2O$ can be lowered, which is one of the paths for the incorporation of excess elemental Se in the deposited films. The influence of FeSO$_4$ concentration on film thickness are studied and shown in Fig.3.10. It is observed from Fig.3.10 that the film thickness increases with deposition time and attained its maximum vale after 30 minutes of deposition. If the deposition time is increased above 60 minutes thickness of the film decreases not shown in Fig.3.10. It is also observed that the film thickness increases while increasing the concentration of FeSO$_4$ upto 0.02 M as shown in Fig.3.10 (a-c). Further increasing concentration above 0.02 M thickness of the film decreases as shown in Fig.3.10 (d). The maximum value of film thickness was obtained for films prepared at 0.02 M FeSO$_4$ concentration and at a deposition time of 30 minutes.

3.6.2. Variation of film thickness in FeSe$_2$ thin films

The electrochemical growth of FeSe$_2$ thin films were controlled by two separate variables such as :(i) film thickness and its uniformity (ii) morphology of the surface
Film thickness was measured using stylus profilometer. By controlling the plating potential and plating time, the average thickness of the deposited films could be controlled. During deposition process, it is observed that at more negative potential such as above -550 mV versus SCE the formation of films may be hindered due to the process of hydrogen evolution. The films prepared at deposition potential below -300 mV versus SCE are found to be less uniform with rough surface. FeSe$_2$ thin films prepared in the potential range between -300 and -550 mV versus SCE are found to be smooth, uniform and well adherent to the substrate. The variation of film thickness with deposition time for FeSe$_2$ thin films prepared at bath temperature 80°C with various deposition potentials are shown in Fig.3.11. It is found that the deposition current decreases monotonically with increasing film thickness. This result is due to increase in rate of deposition with time as observed in Fig.3.11. The same trend is observed for films prepared at various deposition potentials. It is also observed that maximum value of thickness (1580 nm) is obtained for typical FeSe$_2$ film deposited at -450 mV versus SCE and at a deposition time of 40 minutes. Further increasing deposition potential towards the negative side results poor quality films with spotty appearance. This studies indicate that an optimum deposition potential of -450 mV versus SCE may be used for the preparation of FeSe$_2$ thin films. The maximum value of film thickness obtained in the present work for various deposition potentials (-300,-375,-450,-550 mV versus SCE) are found to be in the range between 320 nm and 1580 nm. It is observed that the rate of deposition increases rapidly upto a deposition time of 40 minutes and then decaying gradually and attained almost constant value at 40 minutes for the deposition potential -450 mV versus SCE. Similar trend is observed for films prepared at various deposition potentials. Hence, the deposition potential and deposition time are fixed as -450 mV versus SCE and 40 minutes for further depositions.

The variation of film thickness with deposition time for FeSe$_2$ thin films prepared at deposition potential -450 mV versus SCE at various bath temperatures ranging from 35 to 95°C are shown in Fig.3.12. It is found that the film thickness increases with deposition time and tend to attain almost constant value. The temperature of the electrolytic bath is found to influence the deposition rate by increasing the solubility of
Fig. 3.11. Variation of film thickness with deposition time for FeSe$_2$ thin films prepared at various deposition potentials: (a) -300 (b) -375 (c) -450 (d) -550 mV versus SCE

Fig. 3.12. Variation of film thickness with deposition time for FeSe$_2$ thin films prepared at various bath temperatures: (a) 35 (b) 50 (c) 65 (d) 80°C
the electrolytic bath, increasing the diffusion coefficient of the species and decrease in value of viscosity [18]. Increase in solubility with bath temperature results in increase in film thickness as shown in Fig.3.12. The films with higher thickness are obtained at bath temperature 80°C. Further increasing bath temperature above 80°C thickness of the deposited films decreases slightly not shown in Fig.3.12. The maximum value of film thickness obtained in the present work for various bath temperatures (35, 50, 65, 80°C) at a deposition time 40 minutes are found to be in the range between 660 and 1580 nm. It is found that an increase in bath temperature from 35 to 80°C the rate of release of ions are faster. This enhances the rate of deposition and increases the film thickness while increasing bath temperature upto 80°C. If the temperature of the electrolytic bath is increased above 80°C, the ions are released at relatively faster rate and hence there is no sufficient time to condense on the substrate surface leading to the precipitation of electrolytic bath [19,20]. Hence, the bath temperature and deposition time are fixed as 80°C, 40 minutes, respectively.

Figure 3.13 shows the variation of film thickness with deposition time for FeSe$_2$ thin films prepared at a deposition potential -450 mV versus SCE, bath temperature 80°C at various solution pH values from 1.5 to 3.0 ± 0.1. It is found that the film thickness increases linearly with deposition time and attained its maximum value at a deposition time of 40 minutes for films prepared at solution pH values 1.5, 2.0, 2.5 and 3.0 ± 0.1. If the deposition time is increased above 40 minutes thickness of the deposited films remains constant upto 60 minutes, thereafter the film thickness decreases slightly not shown in Fig.3.13. The films deposited at lower pH values such as 1.5, 2.0 ± 0.1, thickness of the deposited films are low which may be due to low conductivity of the electrolytic solution. The films prepared at higher pH value such as 2.5 ± 0.1, thickness of the deposited films are high which may be due high conductivity of the electrolytic solution. Increase is conductivity results increase in value of deposition current passing through the electrolytic solution. This enhances the overall rate of deposition which in turn increases the thickness of films prepared at solution pH value around 2.5 ± 0.1. Further increasing solution pH value above 2.5 ± 0.1, thickness of the film
Fig. 3.13. Variation of film thickness with deposition time for FeSe$_2$ thin films prepared at various solution pH values: (a) 1.5 (b) 2.0 (c) 2.5 (d) 3.0

Fig. 3.14. Variation of film thickness with deposition time for FeSe$_2$ thin films prepared at various FeSO$_4$ concentrations: (a) 0.01 (b) 0.015 (c) 0.02 (d) 0.025 M
decreases as shown in Fig.3.13 (d). The decrease in value of film thickness with solution pH value 3.0 ± 0.1 may be due to the precipitation of electrolytic bath.

The variation of film thickness with deposition time for FeSe₂ thin films electrodeposited with FeSO₄ concentration around (0.01-0.025) M and 0.01 M SeO₂ concentration at bath temperature, deposition potential and solution pH values such as 80°C, -450 mV versus SCE and 2.5 ± 0.1 are recorded. In case of electrodeposition of FeSe₂ thin films, the use of low concentration of selenous acid and high concentration iron salt is the usual approach, since the iron is a less noble constituent of the compound [21-23]. In this way, the rate of the following reaction
\[ H_2O + SeO_2 + 4H^+ + 4e^- \rightarrow Se + 3H_2O \]
can be lowered, which is one of the paths for the incorporation of excess elemental Se in the deposited films. The influence of FeSO₄ concentration on film thickness for FeSe₂ thin films are studied and shown in Fig.3.14. It is observed from Fig.3.14 that the film thickness increases with deposition time and attained saturation after 40 minutes of deposition. If the deposition time is increased above 60 minutes thickness of the deposited film decreases not shown in Fig.3.14. It is also observed that the film thickness increases while increasing the concentration of FeSO₄ up to 0.02 M [Fig.3.14 (a-c)] thereafter thickness of the deposited films are found to decrease as shown in Fig.3.14 (d). The maximum value of film thickness was obtained for films prepared at 0.02 M FeSO₄ concentration and at a deposition time of 40 minutes.

3.6.3. Variation of film thickness in CdSe thin films

Electrochemical deposition of CdSe thin films were controlled by two individual variables such as (i) film thickness and its uniformity (ii) surface morphology [18]. Thickness of CdSe thin films was measured using stylus profilometer. The average thickness of the deposited films could be controlled by controlling the plating potential and plating time. During electrochemical growth, it is found that at more negative potential such as -1000 mV versus SCE, the growth of the film is hindered due to hydrogen evolution reaction. At lower cathodic potential such as below -500 mV versus SCE an irregular growth with rough surface was obtained. The films prepared in the potential range between -500 and -800 mV versus SCE are found to uniform, smooth and
well adherent to the substrate. Figure 3.15 shows the variation of film thickness with deposition time for films prepared at bath temperature 80°C with deposition potential ranging from -500 to -800 mV versus SCE. It is found that the film thickness increases with deposition time and tend to attain saturation after 40 minutes of deposition for films obtained at a deposition potential -700 mV versus SCE. Similar behaviour is observed for films prepared at different deposition potentials such as -500, -600 mV versus SCE. If the deposition potential is increased above -700 mV versus SCE thickness of the film is found to decrease as shown in Fig.3.15 (d). The maximum value of film thickness was obtained for films prepared at a deposition potential -700 mV versus SCE. Hence, the deposition potential is fixed as -700 mV versus SCE in order to obtain films with higher thickness.

Variation of film thickness with deposition time for CdSe thin films prepared at a deposition potential -700 mV versus SCE at various bath temperatures ranging from 35 to 95°C are shown in Fig.3.16. It is observed from Fig.3.16 that the film thickness increases linearly with deposition time and tend to attain saturation after 40 minutes of deposition for films prepared at all temperatures. The bath temperature is expected to influence the deposition rate by: (i) increase the solubility of the precursor (ii) increasing the diffusion coefficient of the species and decrease in value of viscosity [19-20]. Due to increase in solubility with bath temperature higher value of film thickness was obtained for films prepared at higher bath temperature such as 80°C. Further increasing bath temperature above 80°C thickness of the deposited films decreases slightly as shown in Fig.3.16 (e). These studies indicate that an optimum bath temperature of 80°C is used to prepare CdSe thin films. The maximum value of thickness obtained in the present work for various bath temperatures (35, 50, 65, 80, 95°C) are found to be in the range between 760 and 1350 nm. It is found that an increase in bath temperature from 35 to 80°C the rate of release of Cd$^{2+}$ and Se$^{2-}$ ions are faster. This enhances the rate of deposition and increases the film thickness while increasing bath temperature upto 80°C. If the bath temperature is increased above 80°C, the ions are released at relatively faster rate and hence there is no enough time to condense on the substrate surface leading to the
Fig. 3.15. Variation of film thickness with deposition time for CdSe thin films prepared at various deposition potentials: (a) -500 (b) -600 (c) -700 (d) -800 mV versus SCE

Fig. 3.16. Variation of film thickness with deposition time for CdSe thin films prepared at various bath temperatures: (a) 35 (b) 50 (c) 65 (d) 80 (e) 95°C
precipitation of electrolytic bath [19-20]. Therefore, the bath temperature and deposition time are fixed as 80°C and 40 minutes, respectively.

Variation of film thickness with deposition time for CdSe thin films prepared at a deposition potential, bath temperature -700 mV versus SCE, 80°C at different solution pH values from 1.5 to 3.0 ± 0.1 are shown in Fig.3.17. It is found that the film thickness increases linearly with deposition time and attained its maximum value at a deposition time of 40 minutes for films prepared at all solution pH values from 1.5 to 3.0 ± 0.1. If the deposition time is increased above 40 minutes thickness of the deposited films remains constant upto 60 minutes, thereafter the film thickness decreases slightly not shown in Fig.3.17. The films deposited at lower pH value such as 1.5, 2.0 ± 0.1, thickness of the deposited films are low which may be due to low conductivity of the electrolytic solution. The films prepared at higher pH value such as 2.5 ± 0.1, thickness of the deposited films are high which may be due high conductivity of the electrolytic solution. Increase is conductivity results increase in value of deposition current passing through the electrolytic solution. This enhances the overall rate of deposition which in turn increases thickness of film prepared at solution pH value 2.5 ± 0.1. Further increasing solution pH value above 2.5 ± 0.1 thickness of the film decreases as shown in Fig.3.17 (d). The decrease in value of film thickness with solution pH value 3.0 ± 0.1 may be due to the precipitation of electrolytic bath. Hence, an optimum solution pH value of 2.5 ± 0.1 may be selected to get better quality films with higher thickness.

Variation of film thickness with deposition time for CdSe thin films electrodeposited with CdSO₄ concentrations around (0.15-0.3) M and 0.0025 M SeO₂ concentration at a bath temperature, deposition potential and solution pH values such as 80°C, -700 mV versus SCE and 2.5 ± 0.1 are recorded. In case of electrodeposition of CdSe thin films, the use of low concentration of selenous acid and high concentration cadmium salt is the usual approach, since the cadmium is a less noble constituent of the compound [21-23]. In this way, the rate of the following reaction $H_2O + SeO_2^- + 4H^+ + 4e^- \rightarrow Se + 3H_2O$ can be lowered, which is one of the paths for the incorporation of excess elemental Se in the deposited films. The influence of CdSO₄
Fig. 3.17. Variation of film thickness with deposition time for CdSe thin films prepared at various solution pH values: (a) 1.5 (b) 2.0 (c) 2.5 (d) 3.0

Fig. 3.18. Variation of film thickness with deposition time for CdSe thin films prepared at various CdSO₄ concentrations: (a) 0.15 (b) 0.20 (c) 0.25 (d) 0.30 M
concentration on film thickness is studied and shown in Fig.3.18. It is observed from Fig.3.18 that the film thickness increases with deposition time and attained saturation after 40 minutes of deposition. If the deposition time is increased above 60 minutes thickness of the film decreases not shown in Fig.3.18. It is also observed that the film thickness increases while increasing the concentration of CdSO₄ upto 0.25 M [Fig. 3.18 (a-c)]. If the concentration of CdSO₄ is increased to 0.3 M thickness of the deposited films are found to decrease as shown in Fig.3.18 (d). The films with higher thickness value are obtained at 0.25 M CdSO₄ concentration and at a deposition time 40 minutes.

3.6.4. Variation of film thickness in Cd₁₋ₓFeₓSe thin films

The electrodeposition of Cd₁₋ₓFeₓSe thin films was controlled by two independent variables such as (i) film thickness and its uniformity (ii) surface morphology [18]. Thickness of the deposited films was estimated using stylus profilometer. The average thickness of the deposited layers could be controlled directly by controlling the plating current and plating time. During the process of deposition, it is observed that at more negative potential such as above -1050 mV versus SCE the film formation is hindered due to the process of hydrogen evolution reaction. At lower cathodic potential (such as below -600 mV versus SCE) films with irregular growth and rough surface were obtained. The films deposited in the potential range between -600 and -1050 mV versus SCE are found to be smooth, uniform and well adherent to the substrates. The variation of film thickness with deposition time for Cd₁₋ₓFeₓSe thin films obtained at bath temperature 70°C with different deposition potentials are shown in Fig.3.19. It is observed from Fig.3.19 (a) that the film thickness increases with deposition time and tend to attain saturation after 30 minutes of deposition for films obtained at a deposition potential -600 mV versus SCE. Similar behaviour is exhibited for films obtained at different deposition potentials such as-750,-900 versus SCE as shown in Fig.3.19 (b-c). If the deposition potential is increased above -900 mV versus SCE thickness of the film is found to decrease as shown in Fig.3.19 (d). The maximum value of film thickness was obtained for films prepared at a deposition potential -900 mV versus SCE. Hence, the potential is fixed as -900 mV versus SCE, in order to get films with higher thickness.
Fig. 3.19. Variation of film thickness with deposition time for Cd$_{1-x}$Fe$_x$Se thin films prepared at various deposition potentials: (a) -600 (b) -750 (c) -900 (d) -1050 mV versus SCE.

Fig. 3.20. Variation of film thickness with deposition time for Cd$_{1-x}$Fe$_x$Se thin films prepared at various bath temperatures: (a) 30 (b) 50 (c) 70 (d) 90°C.
CHAPTER - III

Variation of film thickness with deposition time for Cd$_{1-x}$Fe$_x$Se thin films prepared at a deposition potential -900 mV versus SCE under various bath temperatures from 30 to 90°C are shown in Fig.3.20. It is observed from Fig.3.20 that film thickness increases linearly with deposition time and tend to attain saturation after 30 minutes of deposition for films prepared at all temperatures. The bath temperature is expected to influence the deposition rate by: (i) increasing the solubility of the precursor (ii) increasing the diffusion coefficient of the species and decrease of viscosity [19,20]. Due to increase in solubility with bath temperature, higher value of film thickness was obtained for films prepared at higher bath temperature such as 70°C. Further increasing bath temperature above 70°C thickness of the deposited films are found to decrease slightly as shown in Fig.3.20. This study indicates that an optimum temperature of 70°C is used to prepare Cd$_{1-x}$Fe$_x$Se thin films. The maximum value of film thickness obtained in the present work for films obtained at various bath temperatures (35, 50, 70, 95°C) are found to be in the range between 680 and 1480 nm. It is found that increase in bath temperature from 30 to 90°C the rate of release of Cd$^{2+}$, Fe$^{2+}$ and Se$^{4-}$ ions are faster. This enhances the rate of deposition and increases the film thickness value while increasing bath temperature upto 70°C. If the bath temperature is increased above 80°C, the ions are released at relatively faster rate and hence there is no enough time to condense on the substrate surface leading to the precipitation of electrolytic bath [19-20]. Hence, the bath temperature and deposition time are fixed as 70°C and 40 minutes, respectively.

The variation of film thickness with deposition time for Cd$_{1-x}$Fe$_x$Se thin films prepared at a deposition potential -900 mV versus SCE, bath temperature 70°C with different solution pH values from 1.5 to 3.0 ± 0.1 are shown in Fig.3.21. It is found that the film thickness increases linearly with deposition time and attained its maximum value at a deposition time of 40 minutes for films prepared at solution pH values 1.5, 2.0, 2.5, 3.0 ± 0.1. If the deposition time is increased above 40 minutes thickness of the deposited films remains constant upto 60 minutes, thereafter the film thickness decreases slightly not shown in Fig.3.21. The films deposited at lower pH values such as 1.5, 2.0 ± 0.1, thickness of the deposited film are low which may be due to low conductivity of the electrolytic solution. The films prepared at higher pH value 2.5 ± 0.1, thickness of the
Fig. 3.21. Variation of film thickness with deposition time for $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$ thin films prepared at various solution pH values: (a) 1.5 (b) 2.0 (c) 2.5 (d) 3.0

Fig. 3.22. Variation of film thickness with deposition time for $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$ thin films prepared at various $\text{CdSO}_4$ concentrations: (a) 0.002 (b) 0.004 (c) 0.006 (d) 0.008 M
deposited films are high which may be due to higher conductivity of the electrolytic solution. This increase is conductivity results increase in value of deposition current passing through the electrolytic solution. This enhances the overall rate of deposition which in turn increases the value of film thickness for films prepared at solution pH value 2.5 ± 0.1. Further increasing solution pH value above 2.5 ± 0.1, thickness of the film decreases as shown in Fig.3.21 (d). The decrease in value of film thickness with solution pH value at 3.0 ± 0.1 may be due to the precipitation of electrolytic bath. Hence an optimum solution pH value of 2.5 ± 0.1 may be used to obtain good quality films with higher thickness.

Variation of film thickness with deposition time for Cd$_{1-x}$Fe$_x$Se thin films electrodeposited with concentrations around (0.002-0.008) M CdSO$_4$, 0.03 M FeSO$_4$ and 0.01 M SeO$_2$ at bath temperature, deposition potential and solution pH value such as 70°C, -900 mV versus SCE and 2.5 ± 0.1 are recorded. In this case, the use of low concentration of selenous acid and high concentration of cadmium, iron salt is the usual approach, since the cadmium, iron are less noble constituent of the compound [21-23]. In this way, the rate of the following reaction $H_2O + SeO_2 + 4H^+ + 4e^- \rightarrow Se + 3H_2O$ can be lowered, which is one of the paths for the incorporation of excess elemental Se in the deposited films. The effect of CdSO$_4$ concentration on film thickness are studied and shown in Fig.3.22. It is observed from Fig.3.22 that the film thickness increases with deposition time and tend to attain saturation after 40 minutes of deposition. Deposition time is increased above 60 minutes thickness of the film decreases not shown in Fig.3.22. It is also observed that the film thickness increases while increasing the concentration of CdSO$_4$ up to 0.006 M [Fig.3.22 (a-c)]. Further increasing CdSO$_4$ concentration above 0.006 M thickness of the film decreases as shown in Fig.3.22 (d). The maximum value of film thickness was obtained for films prepared at 0.006 M CdSO$_4$ concentration and at a deposition time of 30 minutes.

Variation of film thickness with deposition time for Cd$_{1-x}$Fe$_x$Se thin films electrodeposited with concentrations around 0.006 M CdSO$_4$, (0.01-0.04) M FeSO$_4$ and 0.01 M SeO$_2$ at deposition potential, bath temperature and solution pH values such as
-900 mV versus SCE, 70°C and 2.5 ± 0.1 are recorded. In case of electrodeposition of Cd$_{1-x}$Fe$_x$Se thin films, the use of low concentration of selenous acid and high concentration iron, cadmium salt is the usual approach, since the iron, cadmium are less noble constituents of the compound [21-23]. In this way, the rate of the following reaction $\text{H}_2\text{O} + \text{SeO}_2 + 4\text{H}^+ + 4e^- \rightarrow \text{Se} + 3\text{H}_2\text{O}$ can be lowered, which is one of the paths for the incorporation of excess elemental Se in the deposited films. The influence of FeSO$_4$ concentration on film thickness are studied and shown in Fig.3.23. It is observed from Fig.3.23 that the film thickness increases with deposition time and tend to attain saturation after 40 minutes of deposition. If the deposition time is increased above 60 minutes thickness of the film decreases not shown in Fig.3.23. It is also observed that the film thickness increases while increasing the concentration of FeSO$_4$ upto 0.03 M [Fig.3.23 (a-c)], thereafter thickness of the film decreases as shown in Fig.3.23 (d). The maximum value of film thickness was obtained for films prepared at 0.03 M FeSO$_4$ concentration and at a deposition time of 40 minutes.

![Graph showing variation of film thickness with deposition time](image)

Fig.3.23. Variation of film thickness with deposition time for Cd$_{1-x}$Fe$_x$Se thin films prepared at various FeSO$_4$ concentrations: (a) 0.01 (b) 0.02 (c) 0.03 (d) 0.04 M
3.7. Experimental methods for characterization

Scientific disciplines are identified and differentiated by the experimental equipment and measurement techniques they employ. The same is true for thin film science and technology. The role played by thin film technology 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 deals with the experimental techniques and applications associated with determination of film thickness, structure, morphology, composition and magnetic properties. Within each of these three categories, only the most important techniques viable to us are discussed. Beyond these broad categories there are a host of individual properties like electrical conductivity, reflectivity and microstructural parameters that are specific to particular applications such as photoelectrochemical solar cells. In addition to this, photoelectrochemical properties are also discussed. The associated measurement techniques will therefore be addressed in the appropriate context.

3.7.1. Cyclic Voltammetry

Cyclic voltammetry is an electrolytic method that used microelectrodes and an unstirred solution so that the measured current is limited by analytic diffusion at the surface of electrode. The electrode potential is ramped linearly to a more negative potential and then ramped in reverse back to the starting voltage. The forward scan produces a current peak for any analytes that can be reduced through the range of the potential scan. The current will increase as the potential reaches the reduction potential of the analyte, but then falls off as the concentration of the analyte is depleted close to the electrode surface. As the applied potential is reversed, it will reach a potential that will be re-oxidize the product formed in the first reduction reaction, and produces a current of reverse polarity from the forward scan. This oxidation peak will usually have a similar shape to the reduction peak.

The study of electrodeposition mechanism is performed using cyclic voltammetry with the help of Electrochemical Analyzer System (AUTOLAB 12 FRA 2). The various techniques of cyclic voltammetry namely, linear sweep voltammetry (LSV), thin layer
voltammetry (TLV), multi sweep cyclic voltammetry (MSV), anodic stripping voltammetry (ASV), cathodic stripping voltammetry (CSV) etc., can be performed. This electrochemical analyzer is a self contained integrated system which provides both diverse control and data reduction for the study of the redox systems. Electrochemical Analyzer System (AUTOLAB 12 FRA 2) exploits the power of the microprocessor to make available within a single unit and extensive many of electrochemical techniques. Each technique is quickly and easily accessible using the display monitor, a key board and simple commands with the experimental arrangements.

A three electrode system is adopted to prepare FeSe, FeSe₂, CdSe and Cd₁₋ₓFeₓSe thin films. A magnetic stirrer cum heater set up is used to deposit films by stirring the bath as well as raising the temperature. A saturated calomel electrode is immersed into the solution and kept closer to the cathode which measures the potential of the working electrode. Both working and counter electrodes are kept closer to each other to obtain good quality films. The two surfaces facing each other, so that the released ions will be attracted and deposited exactly perpendicular to the cathode surface. During deposition, the scan rate was fixed as 20 mV/sec. Indium doped tin oxide coated conducting glass (ITO) substrate was used as working electrode and platinum electrode was used as counter electrode. The redox (oxidation + reduction) potentials of the systems are analyzed by the method of cyclic voltammetry using an Electrochemical Analyzer System (AUTOLAB 12 FRA 2, Micro Devices Metro-Ohm Ltd., Chennai). Its technical specifications are:

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compliance Voltage</td>
<td>±12 V</td>
</tr>
<tr>
<td>Current capability</td>
<td>0.25 A</td>
</tr>
<tr>
<td>Current ranges</td>
<td>8 ranges</td>
</tr>
<tr>
<td>Potentiostatic rise time</td>
<td>&lt;500 ns</td>
</tr>
<tr>
<td>Input Bias current</td>
<td>&lt;1 pA</td>
</tr>
<tr>
<td>Potential range</td>
<td>±10 V</td>
</tr>
<tr>
<td>Bandwidth</td>
<td>500 kHz</td>
</tr>
<tr>
<td>Data accuracy</td>
<td>16 bits</td>
</tr>
<tr>
<td>Power supply</td>
<td>100-240 V_{AC}/12 V_{DC}</td>
</tr>
</tbody>
</table>

132
3.7.2. Film thickness

Thickness is the most important film parameter which controls the film properties. The reason is that the properties and behaviour of thin films depend on thickness. The utilization of thin 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 the film thickness is generally of the order of 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 film thickness. Examples are ellipsometry and spectroscopy. In addition to the optical techniques, there are mechanical, electrical and magnetic techniques which have been used for film thickness measurements [24,25]. In this work, thickness of the film is determined by using the following technique in the appropriate ranges.

The Mitutoyo Surftest SJ-301 is a stylus type surface roughness and thickness measuring instrument. It can be used to measure thickness of thin film coatings on any uniform surface. Stylus of SJ-301 detector unit traces the minute irregularities of the vertical displacement of the fine needle, when the detector traversing over the film surface irregularities. For measuring film thickness, the stylus is placed over the uncoated surface and made to move towards the coating. Then it step over the coating surface and moves over it. The vertical displacement gives the thickness of the coating. Thickness of the deposited thin film samples were measured using this technique. It is a non-destructive technique and the coatings may be used for further studies without any damage. Its technical specifications are given below:

<table>
<thead>
<tr>
<th>Model</th>
<th>Mitutoyo SJ-301 mN type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measuring range</td>
<td></td>
</tr>
<tr>
<td>x-axis</td>
<td>: 12.5 µm</td>
</tr>
<tr>
<td>z-axis</td>
<td>: 350 µm</td>
</tr>
<tr>
<td>Measuring speed</td>
<td>: 0.5 mm/sec</td>
</tr>
<tr>
<td>Stylus tip radius</td>
<td>: 5 µm</td>
</tr>
</tbody>
</table>
3.7.3. Structural characterization

X-ray diffraction (XRD) is very important analytical technique that has been used to address all issues related to phase identification of crystalline materials, crystal structure of bulk solids, including lattice constants and geometry, identification of unknown materials, preferred orientation of polycrystals, defects etc. A typical wavelength used for XRD experiments is 1.540 Å. Extension of X-ray diffraction methods to thin films have not been pursued with vigor for two main 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 diffracted X-ray signal, thus the diffraction peaks from films require long counting times and 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 methods are to make the film appear to be thicker to the beam that is actually is. This can be done by employing a glancing angle of incidence $\gamma = 5^\circ$ then the film is effectively 12 times thicker. In thin films of polymorphic materials either or both phases can be obtained at room temperature depending on the deposition conditions. 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 properties.

In the present work, X-ray diffraction pattern of electrodeposited FeSe, FeSe$_2$, CdSe and Cd$_{1-x}$Fe$_x$Se thin films are analyzed using an XPERTPRO PANalytical,
Netherlands X-ray diffractometer with scanning speed of 0.02° per minute. The technical details about X-ray diffractometer used in the present study are:

<table>
<thead>
<tr>
<th>Model</th>
<th>XPERT PRO PANalytical</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray source</td>
<td>2.2 kW ceramic copper tube</td>
</tr>
<tr>
<td>Operation potential</td>
<td>20 kV, 30 mA</td>
</tr>
<tr>
<td>Filter</td>
<td>Nickel</td>
</tr>
<tr>
<td>Radiation used</td>
<td>CuKα with λ=1.54056 Å</td>
</tr>
<tr>
<td>Detector</td>
<td>Solid state detector (X’celerator)</td>
</tr>
</tbody>
</table>

The obtained X-ray diffraction peaks are identified with Joined Council for Powder Diffracted System- International Centre for Diffraction Data, 2003 (JCPDS-ICDD,2003) in order to investigate the crystalline nature and structure of the deposited films.

3.7.4. Microstructural characterization

The process of measuring a lattice parameter is very indirect one, and is fortunately of such as nature that high precision is fairly easily obtainable. The parameter ‘a’ and ‘c’ of hexagonal substance is directly proportional to the lattice spacing ‘d’ if any particular set of lattice planes. If we measure the Bragg angle ‘θ’ for this set of planes, we can use the Bragg’s law to determine ‘d’. Knowing ‘d’ values we can calculate ‘a’ and ‘c’. But it is sin θ, not θ, which appear in the Bragg’s law. Precision in ‘d’ or ‘a’, ‘c’ therefore depends on precision in sin θ, a derived quantity, and not on precision in θ, measured quantity. This is fortunate because the values of sin θ changes very slowly with θ in the neighbourhood of optimized temperature. For this reason, very accurate values of sin θ can be obtained from a measurement of θ which is not particularly precise, provided that θ is nearly optimized temperature. Stated in another way, the angular position of a diffracted beam is much more sensitive to a given change in plane spacing when θ is larger than when it is small.

Another X-ray diffraction study based on precise measurements upon the position broadening and shape of X-ray profiles of polycrystalline thin films give information about the microstructural variations 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 crystallite size and microstrain. Because the method is sensitive to variation of X-ray diffraction intensity near the tails, the peaks are carefully corrected for background radiation by the method given by Mitra and Misra [26]. As the variances are additive, the profiles are corrected for instrumental broadening by subtracting the variance of the corresponding profile, for standard well annealed sample. The value of dislocation density is calculated using the method given by Williamson and Smallman [27]. The stacking fault probability is calculated by measuring the peak shift of X-ray line with reference to that of fault free well-annealed sample given by Warren and Warekois [28].

3.7.5. Surface morphology and compositional analysis

3.7.5.1. Scanning Electron Microscope

Scanning electron microscope is one of the most versatile instruments available for the direct observation of surfaces because they offer better resolution and depth of field than optical microscopes. The resolution approaches that attainable with conventional electron microscopes and surface-replica samples. In addition, in situ observation of surface morphology changes during heat treatment, etc., of specimen is possible. In a SEM, the area to be investigated (or) to be analyzed is irradiated with a finely focused electron beam which may be static or swept in a raster across the surface of the specimen. The types of signals produced when the electron beam impinges on the specimen surface include secondary electrons, back scattered electrons, auger electrons, characteristic X-rays and photons of various energies. These signals are obtained from specific emission involvement within the sample and can be used to examine many characteristics of the sample (surface topography, crystallography etc.). If the sample is not electrically conducting, it is usually necessary to coat it with carbon, gold or some other metals to provide conducting surface. The surface morphology of all the deposited films is examined using JSM 35 CF JEOL SEM operating at 20 KV using normal incidence. The instrument is operated in the secondary emission mode and micrographs are recorded at suitable magnification between 1000 K and 20,000 K that gives some topographic features. Energy dispersive analysis by X-rays (EDX) system is interfaced to SEM, where the electron beam serves to excite characteristic X-rays from the area of the
specimen being probed. An incoming X-rays generates a photoelectron that eventually
dissipated its energy by creating an electron-hole pairs. Using the Energy dispersive
analysis by X-rays the composition of the deposited films are estimated. EDX
measurements are done with Scanning electron microscope (JSM 35 CF JEOL). The
percentage of atoms of different species present in the films are measured using EDX
studies for FeSe, FeSe₂, CdSe and Cd₁₋ₓFeₓSe thin films prepared using potentiostatic
electrodeposition technique. The technical specifications of SEM used in the present
work are given below:

<table>
<thead>
<tr>
<th>Model</th>
<th>JSM 35 CF JEOL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scanning probe diameter</td>
<td>20 Å</td>
</tr>
<tr>
<td>Resolution</td>
<td>60 Å at 20 kV</td>
</tr>
<tr>
<td>Magnification</td>
<td>1000-20,000 X</td>
</tr>
<tr>
<td>Voltage</td>
<td>20 kV</td>
</tr>
<tr>
<td>Required specimen size</td>
<td>5 mm x 5 mm with 1 mm thickness</td>
</tr>
</tbody>
</table>

3.7.5.2. Atomic Force Microscope

Atomic Force Microscope (AFM) is being used to solve processing material
problems in a wide range of technologies affecting the electronics, telecommunications,
biological, chemical, automotive, aerospace and energy industries. The materials being
investigated include thick and thin film coatings, ceramics, composites, glasses, synthetic
and biological membranes, metals, polymers and semiconductors. The AFM is used to
study phenomenon such as abrasion, adhesion, cleaning, corrosion, etching, friction,
lubrication, plating and polishing. By using AFM, the surface image can be viewed in
atomic resolution but also measured the force in nano-newton scale.

Atomic force microscopy is a useful technique for deriving atomic resolution
information about the surface morphology in our electrodeposited samples. In this
technique an atomically sharp tip mounted at the end of a cantilever is scanned across the
surface of the sample. A laser light is reflected off at the top of the cantilever, and the
position of the reflected laser spot on a position sensitive to photodetector (PSPD) can be
used to very precise measurement of amount of deflection in the cantilever and thus the
contours of the surface. This can either be done at a constant height above the sample and
the force is measured, as in the case of non-contact mode, or using a fixed force measuring the deflection of the cantilever. Other scanning probe microscopes extend the utility of this technique to include the interaction with other forces. For example, magnetic force microscopy is useful for imaging the domain structure of magnetic materials using the deflection base on the strength of a magnetic force. The surface morphology of FeSe, FeSe$_2$, CdSe and Cd$_{1-x}$Fe$_x$Se thin films obtained in this work were analyzed using an ex-situ experimental AFM in a PSIA XE$^{100}$ in both contact and non-contact modes. The technical features of the instrument are listed below:

- **Model**: PSIA XE$^{100}$
- **Mode of operation**: Contact mode
- **Resolution**:
  - In contact mode – atomic level
  - In tapping mode – nm scale laterally
  - Å scale vertically
- **Scanning frequency**: 0-5 – 1 Hz
- **Scan area**: 150 x 150 µm
- **Probe diameter**: 20 Å
- **Spring constant**: 4 N/m
- **Sample size**: 12 mm x 12 mm, 4 mm thick

### 3.7.6. Optical properties

Development of semiconductors with controlled energy gap is necessary for increased applications of alloys in solar cell fabrication and other optoelectronic devices. The optical properties of FeSe, FeSe$_2$, CdSe and Cd$_{1-x}$Fe$_x$Se thin films are of much interest due to their alloying nature. Hence, the absorption and transmission measurements have been carried out using spectrophotometer in order to evaluate the band gap variations. The basic principle of the method is given below.

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 process in a solar cell. Extrinsic absorption by deep, localized states in the band gap may be act to affect charge transport, but it produces negligible net current, because the absorption coefficient associated with...
extrinsic absorption are many orders of magnitude smaller than for intrinsic process. The magnitude of absorption is described in terms of an absorption constant $\alpha (\lambda)$ which is the function of wavelength of light. If a photon flux $\phi (\lambda)$ is present at $x = 0$ in the absorbing medium then

$$\phi (\lambda, x) = \phi_0 (\lambda) \exp[-\alpha (\lambda)]$$  \hspace{1cm} (3.26)

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

$$G(\lambda, x) dx = -d\phi (\lambda) = \alpha (\lambda) \phi (\lambda, x) dx$$  \hspace{1cm} (3.27)

There are two major types of intrinsic absorption process involved in determining ‘$\alpha$’ and they are called direct and indirect absorption. Direct 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 change in momentum of the position. The expected variation of $\alpha$ with the photon energy near the minimum energy for absorption $E_g^d$ is given by Eq.(3.28)

$$\alpha = T(E - E_g^d)^n$$  \hspace{1cm} (3.28)

where $T$ is a constant, $E$ is photon energy, $E_g^d$ is the direct band gap and $n$ is a constant which can be assigned to $1/2$, $3/2$, and $2$ for allowed direct transition, forbidden transitions and allowed indirect transitions, respectively.

A plot of $h\nu$ versus $(ah\nu)^2$ yields a straight line for direct absorption with an intercept on the photon energy axis equal to the direct band gap of the material. The absorption coefficient $\alpha$ increases rapidly with increasing photon energy. For higher photon energies, the absorption coefficient $\alpha$ remains high and varies only slightly with lower photon energies depending on transitions to states well above the bottom of the conduction band or to the higher lying bands. The optical characterizations of the films are studied using an Hitachi-3400 UV-Vis-NIR spectrophotometer. The technical specifications of the instrument are given below:
CHAPTER - III

Model : Hitachi-3400 (double beam)
Wavelength range : 300-2500 nm

Using $\alpha$ and $E$ the band gap of the films can be obtained for all the films. The optical constants such as refractive index ‘$n$’ and extinction coefficient ‘$k$’ are calculated using the formulas given in previous section. Real and imaginary part of the dielectric constant $\varepsilon_1$ and $\varepsilon_2$ are determined using the relationship $\varepsilon_1 = n^2 - k^2$ and $\varepsilon_2 = 2nk$. The optical conductivity $\sigma$ is obtained using relation given in chapter II. The optical constants such as refractive index, extinction coefficient, real and imaginary dielectric constants, and dielectric susceptibility are determined for FeSe, FeSe$_2$, CdSe and Cd$_{1-x}$Fe$_x$Se thin films prepared by potentiostatic electrodeposition technique.

3.7.7. Electrical properties

Using hot probe method the type of conductivity of the deposited films may be determined. This is a simple method which gives the direction of current flow, which makes it possible to determine the nature of the semiconductor. The semiconductor is placed on a plate and a metal heater is connected to conducting substrate through a multimeter. While the hot probe is momentarily 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 after a few seconds. It is believed that the former behaviour indicates p-type whereas the later behaviour represents n-type conductivity. Cd$_{1-x}$Fe$_x$Se and CdSe thin films obtained in this work are found to exhibit n-type conductivity whereas FeSe and FeSe$_2$ thin films are found to exhibit p-type conductivity.

The electrical conductivity of intrinsic semiconductors at low temperature is due to intrinsic charge carriers (electrons and holes). Such conductivity is sometimes termed as intrinsic conductivity. Since, there are two types of carriers in the intrinsic semiconductor, electrons and holes, its specific conductance is the sum of their conductivities $\sigma = e_n \mu_e$ due to free electrons, with the concentration $n$ and mobility $\mu_e$ and the conductivity $\sigma_h = e_p \mu_h$ due to the presence of holes, with the concentration $p$ and mobility $\mu_h$. The mobility is the magnitude of the drift velocity per unit electrical
field (i.e) \( \mu = |V|E \). The mobility is defined to be positive for both electrons and holes, although their drift velocities are opposite. In an ideal intrinsic semiconductor, the mobility is determined by collisions between electrons and photons, the electrical conductivity of an intrinsic semiconductor is \( \sigma = |e|(n\mu_e + p\mu_h) \) and for an intrinsic semiconductor \( n = p \), we have \( \sigma_i = |e|(n\mu_e + p\mu_h) \), where \( \sigma_i \) denotes the intrinsic conductivity. But the values of \( n \) is given by Eq.(3.29)

\[
n_e = n_h = \left( \frac{2\pi K_B T}{h^2} \right)^{3/2} \left( m_e^* m_h^* \right)^{1/4} e^{-E_g/2K_BT} \tag{3.29}
\]

\[
\sigma_i = 2|e| \left( \frac{2\pi K_B T}{h^2} \right)^{3/2} \left( m_e^* m_h^* \right)^{1/4} e^{-E_g/2K_BT} (\mu_e + \mu_h) \tag{3.30}
\]

The exponential term \( \exp \left[-E_g/2K_BT\right] \) dominates all other temperature dependence, as it is seen by writing the above equation as

\[
\log \sigma_i = \left( -\frac{E_g}{2K_BT} \right) + \log \left[ 2|e| \left( \frac{2\pi K_B T}{h^2} \right)^{3/2} \left( m_e^* m_h^* \right)^{1/4} e^{-E_g/2K_BT} (\mu_e + \mu_h) \right] \quad \text{or}
\]

\[
\log \rho = \log \sigma_i = \frac{E_g}{- \log \left[ 2|e| \left( \frac{2\pi K_B T}{h^2} \right)^{3/2} \left( m_e^* m_h^* \right)^{1/4} e^{-E_g/2K_BT} (\mu_e + \mu_h) \right]} \tag{3.31}
\]

where \( \sigma \) is the conductivity. If we plot \( 1/T \) along X-axis and \( \ln \sigma \) along the Y-axis, we will obtained a straight line. The slope of straight line determines \( E_g \).

3.7.8. Magnetic properties

In order to investigate the macroscopic magnetic properties of the two materials in question, two forms of magnetometry were performed. Measurements were taken on FeSe and Cd_{1-x}Fe_{x}Se samples using these two techniques.

3.7.8.1. SQUID Magnetometer

Superconducting Quantum Mechanical Interference Devices (SQUID) magnetometry is the standard measurement technique for highly sensitive magnetization studies. In this form of magnetometry, a magnetic sample is drawn through a coil of superconducting wire in the presence of magnetic field. The moving magnetic field from
the sample induces a current in the wire, which through signal processing can be analyzed and converted to a signal proportional to the magnetization of the sample. The noise floor on this technique can be as low as $10^{-8}$ emu, which would make it ideal for studies of dilute magnetic systems. In addition, the superconducting magnet and coil must be cooled to cryogenic temperatures, as the critical temperature for the superconducting wire coil is 20 K. Thus, for the measurement of low curie temperature materials this technique is ideal because this apparatus already requires liquid helium. Moreover, it is easy to perform high sensitivity field cooling and zero field cooling experiments with a need for an additional oven or cryostat which degrades the sensitivity. In these experiments, SQUID measurements are performed using Quantum Design MPMS-5 magnetic property measurement system. In a majority of experiments, the magnetic field of the sample was applied in the plane of the sample. The technical specifications of MPMS-5 are:

- Operating range: 1.8 K to 200 K
- Magnetic field range: - 70 k Oe to + 70 k Oe
- Remanent field: ~ 5 Oe
- Maximum dc moment: 10 emu
- Sensitivity: $< 1 \times 10^{-8}$ to $8 \times 10^{-8}$ emu

### 3.7.8.2. Vibrating Sample Magnetometer

Another form of magnetometry used in these studies are vibrating sample magnetometer (VSM). In this set up, the sample is mounted on a sample tail and places between the coils of an electromagnet. The magnet supplies a field, in which the sample is oscillated at a known low frequency. The moving magnetic field from the sample induces a current in the pick up coils, which is sent, amplified and converted to a known magnetic signal. This technique is nice, because it is inexpensive and fast for routine measurement. However, it is much more difficult to perform low temperature studies, as it needs an additional cryostat. In addition, with these dilute samples, the magnetization of the sample is very often much less than that of the sample holder, such that the data must be background corrected in order to pull out the data from the sample from the measurement of noise. In addition, the noise floor on this measurement technique is two
orders of magnitude greater than what it is for the SQUID measurement technique, so it is difficult to measure very weakly magnetic samples. In this work, measurements are performed using a VersaLab™ Tesla Cryogen-free Vibrating Sample Magnetometer, with the magnetic field applied in both parallel and perpendicular to the plane of thin film.

The vibrating sample magnetometer (VSM) is an important method for studying magnetic properties of thin films. Vibrating sample magnetometer has been used to study the magnetic properties of FeSe thin films. The VSM includes a computer controlled magnetic measurement system accurately determine the magnetic properties of the materials such as single phase, bi-phase, anisotropic, diamagnetic, paramagnetic, ferromagnetic materials. It is an reliable, user friendly technique which can be used to measure low and high coercivity materials make it defacto standard measurement system used by almost all hard disk manufacturers and magnetic recording research groups. Software control provides an automatic sequence of different types of magnetic measurements including field-ranging capability. Testing can be customized for specific applications based on sample size, test fields, measurement planes and temperatures.

The VSM supports all known magnetic measurements such as hysteresis and minor loops, IRM and DCD remanence loops, SFD, delta M and henkel plots, angular and AC remanence loops. Any series of measurements can be run without used intervention, with flexible easy VSM software. The technical specifications of VSM used in the present work are:

<table>
<thead>
<tr>
<th>Model</th>
<th>VersaLab™</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimensions</td>
<td>48 cm wide x 76 cm deep x 131 cm high</td>
</tr>
<tr>
<td>Temperature range</td>
<td>50-400 K</td>
</tr>
<tr>
<td>Field range</td>
<td>± 3 Tesla</td>
</tr>
<tr>
<td>Field homogeneity</td>
<td>0.1 % over 2.4 cm</td>
</tr>
<tr>
<td>Slew rate</td>
<td>0.1 to 300 Oe/S</td>
</tr>
<tr>
<td>Field setting resolution</td>
<td>60 m Oe</td>
</tr>
<tr>
<td>Rms sensitivity</td>
<td>$10^{-6}$ emu</td>
</tr>
<tr>
<td>Accuracy</td>
<td>$6 \times 10^{-6}$ emu</td>
</tr>
</tbody>
</table>
The VSM has a vector coil system, allowing to measure magnetic moment along the field direction as well as perpendicular to it. The VSM can measure samples at different angles with respect to the field direction. In a VSM, a magnetic sample is vibrating at the centre of a set of detection coils. The vibrations of the sample cause the flux through the coils to charge, which include a voltage on the termination of the set of coils. This voltage is proportional to the magnetic moment of the sample, and thus can be determined by calibration. An electromagnet is used to supply a magnetic field on the sample, which allows measuring the magnetic moment of the sample at various values of applied field.

3.7.9. Photoelectrochemical solar cell studies

Photoelectrochemical solar cell (PEC cell) is based on the photoelectrochemical effect that is exhibited by semiconductor-electrolyte junctions in a cell consisting of photoresponsive semiconductor electrodes, an electrolyte and a suitable counter electrode. A proper study on material preparation, evaluation, etching treatment and determination of PEC parameters are essential before starting the experiment. The basic requirements are:

1. The band gap of the materials should be such that the maximum part of the solar spectrum is used.
2. The efficiency of the cell should be high.
3. The electrodes must be stable against corrosion.
4. The resistivity of films must be in the order which could aid good charge collection characteristics.
5. Proper etching is essential for the absorption of light by semiconductor.
6. The counter electrode should be chemically inert and must have good conductivity.
7. The electrolyte must have good ionic conductivity [29,30].

The experimental set up and various studies made on the photoelectrochemical properties of Cd$_{1-x}$Fe$_x$Se films are discussed detail in Chapter VI.
3.8. Conclusions

Cyclic voltammetric studies are carried out on FeSe, FeSe₂, CdSe and Cd₁₋ₓFeₓSe systems in order to find out the optimum range of potential for the preparation of thin films. Thin films of FeSe, FeSe₂, CdSe and Cd₁₋ₓFeₓSe are deposited on indium doped tin oxide (ITO) coated conducting glass substrates using potentiostatic electrodeposition technique. The electrochemical growth of FeSe, FeSe₂, CdSe and Cd₁₋ₓFeₓSe thin films are studied. The effect of various deposition parameters (such as deposition potential, bath temperature, solution pH and electrolyte concentration) in the deposition of chalcogenide films are investigated. Studies revealed that smooth, crystallized films of single phase can be successfully prepared by this technique. However, the films require annealing treatment to increase photoelectrochemical solar energy conversion.
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