3.1 Introduction

Polycrystalline semiconducting thin films, such as cadmium chalcogenides exhibit great promise as photoelectrodes for the conversion of solar energy into electricity through photoelectrochemical (PEC) solar cells. The studies of preparation conditions and optimization of various deposition parameters are extremely important to fabricate films suitable for device applications. Smooth layers of good quality CdSe, CdTe and CdSe\textsubscript{x}Te\textsubscript{1-x} alloy films are prepared in one step by precisely controlling the electroplating conditions. This chapter deals with the preparation of CdSe, CdTe and CdSe\textsubscript{x}Te\textsubscript{1-x} alloy films by electrodeposition technique.

3.2 Experimental details

The schematic representation of the deposition set up is shown in figure 3.1 where the cell used is explained in detail with its associated parts.

Typically 50 ml glass beaker was used to contain the solutions. Magnetic stirrer cum heater set up is used to deposit films by stirring the bath as well as rising the temperature. A thermometer was used to keep the bath temperature constant. A Saturated Calomel Electrode (SCE) was immersed into the bath. This measures the potential of the working electrode. The electrode spacing should be carefully adjusted to obtain good deposits. Both working and counter electrodes are kept as close as 1 cm to each other and facing surfaces parallel so that released ions will be attracted and deposited exactly perpendicular to the cathode surface. The reference electrode tip is placed very close to the cathode surface so that the exact potential at the surface will be monitored.
Fig. 3.1 Experimental set up for Electrodeposition.

C - Calomel electrode,  L - Lugin capillary,  K - Saturated KCl solution
A - Working solution,  W - Working electrode,  P - Platinum electrode,  S - Stirrer
unaffected by the solution resistance (internal resistance of the cell). The other experimental details used for the preparation of semiconductor films are described below.

3.2.1 Electrodes used

The electrodeposition of semiconducting thin films on transparent conducting substrates like SnO$_2$/ITO coated glass provides the following advantages.

1. Optical properties of electrodeposited films can be analysed easily.
2. Photovoltaic (PV) and photoelectrochemical (PEC) cells can be fabricated either on a front wall or back wall illumination.

An important factor to be considered during the fabrication of a PEC cell is the proper choice of a conducting substrate. The important criterion for the selection of a substrate is its good electrical contact with the cadmium chalcogenide. The conducting substrate is electrochemically relatively inert in the electrolyte used to prevent local shorting of the photoelectrode due to pinholes and other exposed substrate areas. The transition metals Mo, Ti, and Cr are all suitable as substrates and meet the above criterion. Cadmium chalcogenide layers on Ti and to a greater extent, on Cr, have a tendency to peel off from the substrate if suitable precautionary measures are not taken into account. Molybdenum substrates do not have this problem. However, optimum performance of the layers as photoelectrodes is obtained on Ti, compared with either Mo or Cr. On account of the above reasons, tin oxide coated glass slides and titanium substrates are used in this work to prepare semiconductor CdSe, CdTe and alloy CdSeTe thin films.

A platinum foil is used as a counter electrode (anode) to prepare the semiconducting films.
3.2.2 Electrode cleaning

Substrate cleaning must be done with utmost care because the contaminated surfaces would result in poor deposition. The titanium electrodes were etched with 30% hydrofluoric acid. The SnO₂ electrodes were etched with dilute hydrochloric acid. All the electrodes were given a final wash with triple distilled water after etching with acetone.

3.2.3 Reference electrode

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

3.3 Linear sweep voltammetry studies

Voltammetry, the fundamental electrochemical technique is the measurement of current which flows at an electrode as a function of the potential applied to the electrode. The thermodynamic and kinetic information about the electrochemical systems can be determined from the current potential curves recorded under the influence of different factors like sweep rate hydrogen ion concentration, concentration of the species in the electrolysis bath, temperature etc. Various theories are reported to simulate the voltammograms and related current-time transients for different situations, such as two and three dimensional
growth, instantaneous and progressive nucleation constant and changing potentials etc., [1]. Engelken and Van Doren [2] have proposed a kinetic model for the electrodeposition of compound semiconductors from aqueous solutions. Their model is based on the concept of thermodynamical considerations using Butler-Volmer equation [3] for defining current density expression. The model developed for binary compounds is based on a generalised current-potential equation that considers ion transport limitations near the cathode.

3.3.1 CdSe films

Cadmium selenide electrodepositions were initially tried with an electrolyte composition of 0.2 M cadmium sulphate and 2 mM selenium dioxide. The other deposition conditions during the film preparation were:

- pH = 1.8 ± 0.2
- Deposition potential = -0.70 V versus SCE
- Deposition temperature = 70°C.

The CdSe deposits obtained were found to be a heterogeneous mixture of amorphous CdSe and selenium. Also, the deposits were not useful for photoelectro-chemical applications without a thorough annealing treatment. Hence a systematic study of the selenium ion concentration and the range of potentials needed to carry out the depositions to obtain stoichiometric CdSe films are extremely important.

Figure 3.2 shows polarization curves for linear sweep voltoammograms for Cd, Se and CdSe for solution compositions of 0.2M CdSO₄, 2 mM SeO₂, and 0.2m CdSO₄, 2mM SeO₂ respectively.

Smooth CdSe depositions were obtained in the central plateau region of the I-V curves. In this plateau region, pure cadmium would be dissolved and pure selenium would form a passivating coating. The plateau current, Iₚ results from the growth rate limitations by the diffusion of selenium ions in the liquid phase.
Fig. 3.2. Linear sweep voltammograms for Cd, Se and CdSe for solution compositions of 0.2M CdSO₄ (a), 2mM SeO₂ (b) and 0.2M CdSO₄, 2mM SeO₂ (c) respectively.
EDAX studies show that the CdSe layer composition is close to the stoichiometry within a potential domain corresponding to the diffusion plateau of the I-V curves.

The best crystallinity is obtained when the films are deposited at a potential \(-0.7\) V versus SCE. When the films are prepared at potentials preceding the plateau region, they are found to be heterogeneous and irregular. X-ray studies revealed that these films contained pure selenium which gave rise to strong compositional inhomogeneities. When the films are deposited beyond the plateau region (\(> -0.75\) V versus SCE) towards the cathodic potentials, pure metallic cadmium is deposited at a fast rate.

### 3.3.2 CdTe films

Figure 3.3 shows the recorded voltammograms for cadmium, tellurium and cadmium telluride. The plateau region of cadmium telluride curve is the underpotential deposition region for cadmium. The higher current value for cadmium telluride curve confirms the presence of currents due to cadmium and tellurium. The steep rise in the cathodic current at potentials more negative than \(-0.85\) V is observed in the figure. This corresponds to the onset of another cathodic process viz., the deposition of metallic cadmium. Since the Gibb's free energy of formation of CdTe is \(0.51\) V/\(\text{mol}\), underpotential deposition of cadmium is expected even at potentials more positive than \(-0.85\) V. Electrodeposition of cadmium telluride with different Cd/Te stoichiometry can thus be accomplished at potentials between \(-0.30\) and \(-0.70\) V. The influence of the deposition potential and bath temperature on the structure and composition of the deposits are therefore, to be investigated.

It is interesting to note that CdTe layers are p-type semiconductors in the beginning of the plateau region and are n-type in the middle and end of the plateau regions. However, their crystalline quality improves when the potential is more negative and also n-type CdTe deposits exhibit good semiconductor properties.
Fig. 3.3. Linear sweep voltammograms for Cd,Te and CdTe for solution compositions of 0.2M CdSO₄ (a), 1mM TeO₂ (b) and 0.2M CdSO₄ ,1mM TeO₂ (c) respectively.
3.3.3 CdSe$_x$Te$_{1-x}$ films

Linear sweep voltammetric studies have been carried out on CdSe$_x$Te$_{1-x}$ films. The deposition of CdSe$_x$Te$_{1-x}$ films are carried out through a two electron reduction for cadmium and four electron reduction for selenium and tellurium. Voltammogram recorded for cadmium (0.2 M cadmium sulphate), selenium (2 mM selenium dioxide), tellurium (1 mM tellurium dioxide) and cadmium selenotelluride (0.2 M cadmium sulphate, 2 mM selenium dioxide and 1 mM tellurium dioxide) depositions are shown in figure 3.4. The plateau region of the cadmium selenotelluride current curve is the underpotential deposition region for cadmium. Co-deposition of cadmium, selenium and tellurium for cadmium selenotelluride has been carried out at the plateau region at a potential less than the reduction potential of cadmium. The large increase in current value for cadmium selenotelluride deposition after -400 mV versus SCE is due to the enormous increase in cadmium current and hydrogen evolution process. Therefore, stoichiometric films of cadmium seleno telluride can be achieved in the plateau region.

3.4 Preparation of cadmium chaleogenide thin films

The main aim of the present work is to prepare CdSe, CdTe and CdSeTe alloy films which are expected to exhibit better semiconducting properties and in particular high efficiency with regard to photoelectrochemical solar energy conversion. In the present work, we have studied the simultaneous cathodic deposition of cadmium, selenium and tellurium from an aqueous electrolyte. The correlation between the electrochemical properties and the crystal structure, the composition and semiconducting properties of the as-deposited as well as annealed layers are studied.
Fig. 3.4. Linear sweep voltammograms for Cd, Se, Te and CdSeTe for solution compositions of 0.2M CdSO₄ (a), 2mM SeO₂ (b), 1mM TeO₂ (c) and 0.2M CdSO₄, 2mM SeO₂, 1mM TeO₂ (d) respectively.
3.4.1 Cadmium selenide (CdSe) thin films

Large area CdSe photoelectrodes were prepared by electrodeposition /5/. However, the quality of these layers was very sensitive to the deposition rate and agitation of the electrolyte. Literature survey reveals that most of the as-grown electrodeposited CdSe films are heterogeneous and contain weak crystallites with large excess of selenium /6,7/. In order to obtain photoelectrodes suitable for photoelectrochemical solar cell applications, a heat treatment must be applied to increase the grain size and eliminate by sublimation the excess of selenium /8,9/ for the synthesis of cadmium chalcogenide films. The process of Cd-Te alloy formation has been studied by many workers /10,11,12/ and theoretical models are proposed /2,13/. However, the process of Cd-Se alloy formation by electrodeposition has not been studied in detail.

CdSe was obtained by electrodeposition for the first time by Patsauskas et al /14/. The electrolyte was very acidic (pH = 0), aqueous solution of cadmium sulphate and selenous acid. CdSe layers prepared under similar conditions and recrystallized by a heat treatment were first used in a photoelectrochemical solar cell by Hodes et al /8/. The results obtained has created interest in several groups to explore the preparation conditions of electroplated thin films to yield photoelectrodes suitable for photoelectrochemical solar cell applications. As-deposited CdSe layers were quite often amorphous. The effect of heat treatments on CdSe films were carried out by many workers /5,9, 15-17/.

Analytical Reagent (AR) grade chemicals of cadmium sulphate (CdSO₄) and selenium dioxide (SeO₂) were used for the electrodeposition of cadmium selenide thin films. Triple distilled water was used to prepare the molar concentration of the chemicals. The pH of the bath during deposition was maintained in the range 1.0 to 2.2. The low value of pH is essential for deposition, since only at low pH, the hydrogen ion concentration and hence the conductivity of the solution is high /18/. However, few depositions were carried out with very acid electrolytes, for the preparation of pure CdSe.
Depositions were tried at pH values of 4.0 and above. However, it was found that at higher pH values, CdSe film formation did not occur. The optimum range of pH for films formation is found to be in the range 1.5 to 2.2. All the CdSe film depositions were carried out at a pH of 1.8 ± 0.2.

High deposition temperatures result in the following advantages.

a) Deposition of thick deposits suitable for PEC applications.
b) Improvement in the crystallinity of the films.
c) Formation of the desired compound.

Hence, depositions have been carried out in the temperature range 30 to 85°C.

Mixing the different molar solutions were carried out with vigorous stirring to get homogeneous and well mixed bath. The important parameter to be monitored before starting the deposition is the rest potential of the system. The working electrode is kept in the bath for few minutes before the deposition potential is applied. A steady state potential called 'rest potential' would be reached. This shall be of the order of 100 millivolts. If it is higher, the substrate should be cleaned well once again and used for deposition. The depositions were carried out for durations ranging from 10 minutes to 1 hour.

CdSe thin films were electrodeposited onto precleaned tin oxide coated glass (< 20 ohms/square) and titanium substrates. From voltammetry studies, it has been observed that CdSe thin films could be electrodeposited in the potential range -0.4 to -0.75 V versus SCE corresponding to constant current density. The structure and crystal quality of the films depend strongly on the deposition potential, temperature and the total amount of chalcogen species (SeO₂) present in the electrolyte. Since the main objective of the work is to prepare photoelectrochemical solar cells, the optimum conditions required for the deposition of CdSe and Cd(Se,Te) films are to be analysed. Hence, CdSe
thin films are electrodeposited potentiostatically at various deposition potentials ranging from -0.4 to -0.75 V versus SCE at various temperatures (30 to 85°C).

The deposited films were found to be reddish grey in colour and adhered well to the substrates. In addition, the films were found to be uniform and smooth.

Deposition Kinetics

The basic electrochemical reactions for the electrodeposition of CdSe and their corresponding Nernst equations are as follows.

\[
\text{Cd}^{2+} + 2e^- \rightleftharpoons \text{Cd}; \quad E_{\text{Cd}}^\circ = -0.645 \text{ V (SCE)} \quad \text{(3.1)}
\]

\[
E_{\text{Cd}} = -0.645 - \frac{RT}{2F} \ln \left( \frac{a_{\text{Cd}}}{a_{\text{Cd}}^{2+}} \right) \quad \text{(3.2)}
\]

where \( a_{\text{Cd}} \) and \( a_{\text{Cd}}^{2+} \) are the activity coefficients of cadmium atom and cadmium ion respectively and other symbols have their usual meanings.

The electrode potential of Se can be written as

\[
\text{Se (s)} + 2H_2 \rightleftharpoons H_2\text{SeO}_3 + 4H^+ + 4e^- \quad \text{(3.3)}
\]

Electrode potential (V)

\[
= 0.74 (E^\circ) + \frac{RT}{4F} \ln \left( \frac{a_{\text{HSeO}_2^2+}}{a_{\text{Se}}} \right) + \frac{3RT}{4F} \ln \text{OH}^- \quad \text{(3.4)}
\]
\[ V = 0.74 + 0.0148 \ln \left( \frac{a_{\text{HSeO}_2^+}}{a_{\text{Se}}} \right) - 0.0443 \text{pH} \] .......................... (3.5)

where \( a_{\text{HSeO}_2^+} \) and \( a_{\text{Se}} \) are the activity coefficients of \( \text{HSeO}_2^+ \) ion and \( \text{Se} \) respectively.

Cathodic electrodeposition from an aqueous acid bath normally yields CdSe films inherently rich in selenium. The following reactions occur at the cathode during the electroplating process.

\[ \text{H}_2\text{SeO}_3 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{H}_2\text{Se} + 3\text{H}_2\text{O} \] .......................... (3.6)

\[ \text{Cd}^{2+} + \text{H}_2\text{Se} \rightarrow \text{CdSe} + 2\text{H}^+ \] .......................... (3.7)

\[ 2\text{H}_2\text{Se} + \text{H}_2\text{SeO}_3 \rightarrow 3\text{Se} + 3\text{H}_2\text{O} \] .......................... (3.8)

The chemical reaction gives in equation (3.7) leads to the deposition of CdSe whereas the chemical reaction (3.8) causes the deposition of elemental Se at the cathode. Due to a strong competition of the reaction (3.8) with reaction (3.7), CdSe films inherently possesses an excess of selenium.

3.4.2 Cadmium telluride (CdTe) thin films

Cadmium telluride was obtained by electrodeposition from an acidic solution of CdSO\(_4\) saturated in tellurium oxide by Panicker et al /12/. CdTe was obtained at a potential more positive than the cadmium equilibrium potential \( E_{\text{Cd}} \) owing to the gain of Gibb's energy provided by the formation of defined compound /19,20,21/. The electrocrystallization techniques were analysed by various techniques and several models were proposed /2,13,22,23/.

CdTe films were electrodeposited onto tin oxide coated glass and titanium substrates by using Analar grade chemicals of cadmium sulphate (CdSO\(_4\)) and tellurium dioxide (TeO\(_2\)). Tellurium dioxide does not dissolve in water easily. At high
temperatures of deposition bath, a considerable amount of tellurium dioxide can be dissolved and facilitates fast deposition. Tellurium dioxide solution was prepared by dissolving TeO₂ powder in NaOH solution (10% by weight). The initial speciation of TeO₂ with NaOH permits introduction of higher TeO₂ concentration in the deposition bath. The pH of the bath during deposition was maintained to the optimized value of 1.8 ± 0.2. Lower values of pH are favourable for a better solubility of TeO₂, but they are found to promote rapid hydrogen evolution which yielded non-coherent layers. CdTe this films. CdTe this films are deposited at various temperatures (30 to 85°C). The deposition potential was fixed in the range -300 to -700 mV versus SCE as obtained from linear sweep voltammetric studies. The deposited films were smooth, uniform and black in colour. Also, they are found to be well adherent to the substrates.

Deposition kinetics

The basic electrochemical reactions for the electrodeposition of CdTe and their corresponding Nernst relations are.

\[
\text{Cd}^{2+} + 2e^- \rightarrow \text{Cd}; \quad E_{\text{Cd}}^\circ = -0.645 \text{ V (SCE)} \quad (3.9).
\]

\[
E_{\text{Cd}} = -0.645 - \frac{RT}{2F} \ln \left( \frac{a_{\text{Cd}}}{a_{\text{Cd}^{2+}}} \right) \quad \text{.......................... (3.10)}
\]

where \(a_{\text{Cd}}\) and \(a_{\text{Cd}^{2+}}\) are the activity coefficients of Cd atoms and Cd²⁺ ions respectively.

\[
\text{TeO}_2 + 4 \text{H}^+ + 4e^- \rightarrow \text{Te} + 2\text{H}_2\text{O}; \quad E_{\text{Te}}^\circ = 0.351 \text{ V(SCE)} \quad (3.11)
\]

\[
E_{\text{Te}} = 0.351 - \frac{RT}{4F} \ln \left( \frac{a_{\text{Te}}}{a_{\text{TeO}_2}} \right) - \frac{RT}{F} \ln \left( \frac{a_{\text{TeO}_2}}{a_{\text{TeO}_2}} \right) + \text{pH} \quad \text{.......................... (3.12)}
\]

where \(a_{\text{Te}}\) and \(a_{\text{TeO}_2}\) are the activity coefficients of Te and TeO₂ respectively.
According to Engelken and Van Doren, telluride or polytelluride anion formation from the six or ten electron reduction of tellurium (IV) ions is assumed negligible with the deposition voltages used. So, the deposit is formed by the solid state reaction of plated cadmium and tellurium atoms rather than the precipitation of \( \text{Te}_2^2^- \), \( \text{Te}^2^- \), \( \text{HTe}^- \) or \( \text{H}_2\text{Te} \) and \( \text{Cd}^{2+} \). The reaction that leads to the deposition of \( \text{CdTe} \) is \( \text{Cd} + \text{Te} \rightarrow \text{CdTe} \); 
\[ \Delta G^o = -9.97 \times 10^4 \text{ J mol}^{-1} \cdot \]

3.4.3 Cadmium seleno telluride (\( \text{CdSe}_{x} \text{Te}_{1-x} \)) alloy thin films

The electronic properties of compound semiconductors are much affected by their stoichiometries. Hence, identifying optimum film preparation conditions is necessary in order to make a good photoelectrode suitable for device applications. The electrochemical properties of \( \text{CdSeTe} \) produced by electrodeposition have been reported in the literature. However, it is not clearly understood how preparation conditions affect the electrochemical properties. In the present work, a number of films were prepared under various conditions and their physical properties were characterized. The optimum conditions were identified for the preparation of thin film electrodes for PEC solar cell applications. The important objectives of deposition of \( \text{CdSeTe} \) are to

1) find the optimum conditions of electrolysis for good quality, reproducible \( \text{CdSeTe} \) alloy films on titanium substrates for PEC applications.

2) optimize the alloy composition and structure to deposit device quality films for applications.

The solution mixture for the electrodeposition of \( \text{CdSeTe} \) consisted of Analar grade chemicals of cadmium sulphate (\( \text{CdSO}_4 \)), selenium dioxide (\( \text{SeO}_2 \)) and tellurium dioxide (\( \text{TeO}_2 \)). The solution pH was maintained at 1.8 ± 0.2 during deposition. Alloy films of \( \text{CdSeTe} \) were electroplated potentiostatically onto tin oxide coated glass and titanium substrates for a duration ranging from 15 minutes to 1 hour. The current densities during deposition were found to vary from 1 mA/cm\(^2\) to 5 mA/cm\(^2\). The deposition potential was in the plateau region of current
-voltage studies observed in the linear sweep voltammetric studies (-0.4 to -0.8 V versus SCE). Depositions were carried at different temperatures, (30° to 85°C). Good quality CdSeTe layers were prepared at high temperatures (>70°C). At high bath temperatures, a large amount of tellurium dioxide was dissolved and the deposition rate was faster. However, the formation of gas bubbles within the bulk of the electrolyte induces hydrodynamic turbulences, which result in large fluctuations of current density. It was found that the CdSeTe deposits prepared at a potential preceding the plateau region contained an excess of non-alloyed chalcogen and have an irregular morphology. It was observed that the films deposited at a high temperature permits the use of baths richer in selenium.

The potential range was well defined in the plateau region to deposit CdSeTe thin films. In the entire plateau region, a single phase of CdSeTe was deposited without any evidence of free crystallized chalcogen. The layers appeared to be dull, compact and homogeneous.

**Reaction Kinetics**

The primary electrochemical reactions for the deposition of CdSeTe and their respective Nemst equilibrium potentials are

\[
\text{Cd}^{2+} + 2e^- \rightarrow \text{Cd} \quad \text{.......................... (3.13)}
\]

\[
E_{\text{Cd}}^0 = -0.645 \text{ V versus SCE}.
\]

\[
\text{SeO}_2 + 4H^+ + 4e^- \rightarrow \text{Se} + 2\text{H}_2\text{O} \quad \text{............... (3.14)}
\]

\[
E_{\text{Se}}^0 = 0.58 \text{ V versus SCE}.
\]

\[
\text{TeO}_2 + 4H^+ + 4e^- \rightarrow \text{Te} + 2\text{H}_2\text{O} \quad \text{.......... (3.15)}
\]

\[
E_{\text{Te}}^0 = 0.351 \text{ V versus SCE}
\]

By analogy with CdTe, a simple kinetic model may be preposed. Te and Se are first get deposited as follows:

\[
\text{Te}^{4+} + 4e^- \rightarrow \text{Te}_{\text{ads}} \quad \text{.......................... (3.16)}
\]

\[
\text{Se}^{4+} + 4e^- \rightarrow \text{Se}_{\text{ads}} \quad \text{.......................... (3.17)}
\]
In the presence of Se and Te ad-atoms, cadmium can be deposited underpotentially,

\[ \text{Cd}^{2+} + 2e^- \rightarrow \text{Cd}_{\text{ads}} \quad \text{(3.18)} \]

Finally, \( \text{CdSe}_{x} \text{Te}_{1-x} \) film is deposited according to the following reaction.

\[ x \text{Se}_{\text{ads}} + (1-x) \text{Te}_{\text{ads}} + \text{Cd}_{\text{ads}} \rightarrow \text{CdSe}_{x} \text{Te}_{1-x} \quad \text{(3.19)} \]

The electrodeposition process of CdSeTe may be explained in the following manner.

Initially, Te\text{IV} (or) Se\text{VI} ions are reduced to Te\text{0} or Se\text{0} atoms. These atoms are absorbed on the cathodic surface which is already occupied partially by Cd\text{2+} absorbed ions. Consequently, Cd\text{2+} cations are underpotentially reduced to yield Cd\text{0} adatoms. Finally, the cadmium chalcogen compound is formed by crystallization of Cd\text{0} with or Se\text{0} adatoms. However, some Te\text{0} or Se\text{0} adatoms may not have sufficient time to be associated with cadmium ions, are incorporated in the growing crystal. This excess amount of chalcogen result in the deposition of a non-stoichiometric compound. In order to avoid this problem, it is necessary to have a large excess of Cd\text{2+} ions to reduce the surface concentration of adsorbed chalcogen atoms and to increase the reduction of Cd\text{2+} ions. For this purpose, the electrolyte composition and the deposition parameters have to be fixed to control the diffusion of Te\text{IV} and Se\text{VI} ions.

A high deposition temperature facilitates the formation of the defined compounds. As the temperature increases, the probability of reducing one Cd\text{2+} adion for each recently formed chalcogen atom increases resulting in a layer composition closer to the ideal value.

The selenium concentration in the electrolyte of CdSeTe deposition bath plays an important role in the crystal structure and therefore the semiconducting properties of the CdSeTe compound are damaged by an excess of selenium atoms, included in the cubic lattice. For higher concentration of selenium, pure selenium is deposited simultaneously with CdSeTe but it depends completely on the hydrodynamical
considerations. Finally, for a selenium concentration greater than 10mM, the crystallization of a cadmium chalcogenide is totally impeded by the selenium deposition. The CdSeTe thin films prepared in this work belong to the cubic zinc blende crystal structure when the films are deposited at low temperatures less than 65°C. When the films are prepared at temperatures higher than 65°C, they exhibit hexagonal wurtzite structure.

Smooth crystallized CdSeTe films can be prepared in a single step by electrodeposition from an aqueous sulphate solution in a fairly narrow potential domain which corresponds to the underpotential deposition of cadmium. The building of the crystal lattice of the mixed alloy appears to be a slow process and requires a limited concentration of the chalcogen ions in the solution.

3.5 Experimental methods for characterization

The deposited cadmium selenide, cadmium telluride and cadmium selenotelluride films were characterized for their optical, structural, morphological and electrical properties. In this section, the methods used for these studies are discussed in detail.

3.5.1 Thickness measurements

The thickness of the films was measured by a multiple beam interferometer (MBI) /24/. The technique consists of the deposition of a semiconductor film like cadmium selenide over the SnO₂ film in such a way to form a mechanical step as shown in figure 3.5 A SnO₂ coated glass plate with a semiconductor film was held as shown in figure and the step was viewed through a travelling microscope. The experimental set up is illustrated in figure 3.5 An interference pattern as shown in the figure is obtained in the field of view of the microscope. The discontinuity in the fringe pattern is clearly due to the step whose height is identified with the thickness of the semiconductor film and given by
Fig. 3.5 Schematic diagram of multiple beam interferometer.
\[ t = \frac{X}{Y} \times \frac{\lambda}{2} \]  

where \( X \) and \( Y \) are the measured quantities as indicated in the figure 3.5. Normally a sodium vapour lamp (of wavelength 589.3nm) is used as the monochromatic source.

The thickness was also calculated from weight gain method. The substrates (SnO\(_2\) coated glass and titanium) were cleaned thoroughly, dried and its weight was measured before deposition. After carrying out deposition, the weight gain was measured.

Weight gain, \[ M = A t d \]

\[ M = l b t d \]

where \( l \) is the length of the film,
\( b \) is the breadth of the film,
\( t \) is the thickness of the deposit and
\( d \) is the density of the film.

For the estimation of the film thickness, the bulk density of the corresponding material is taken into account.

### 3.5.2 Optical measurements

Development of semiconductors with controlled energy gap is necessary for the increased applications of alloys in the solar cell fabrication and other optoelectronic devices. The optical properties of CdSe\(_x\)Te\(_{1-x}\) films are of much interest due to their alloying nature. Hence, the absorption and transmission properties were studied using spectrophotometer to calculate their bandgap variations. The basic principle of the method is given below.
Since the generation of both free electron and free holes is essential to produce a photovoltaic current, intrinsic absorption of a single photon across the bandgap of the semiconductor is the dominant optical absorption process in a solar cell. Extrinsic absorption by deep, localised states in the bandgap may act to affect charge transport (by charging states to change a function profile or by empty traps), but it produces negligible net current since the absorption coefficients associated with extrinsic absorption are many order of magnitude smaller than for the intrinsic process.

The magnitude of absorption is described in terms of an absorption constant $\alpha(\lambda)$ which is a function of the wavelength of light. If a photon flux $\varphi_o(\lambda)$ is present at $x = 0$ in the absorbing medium then

$$\varphi(\lambda, x) = \varphi_o(\lambda) \exp[-\alpha(\lambda)x] \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldOTS
photon energy axis equal to the direct bandgap of the material. At the onset of a
direct optical absorption, the absorption constant \( \alpha \) increases rapidly with increasing
photon energy to the values in the range of \( 10^4 \) to \( 10^6 \) \( \text{cm}^{-1} \). For higher photon energies,
the absorption constant \( \alpha \) remains high and varies only slight with photon energy
depending on transitions to states well above the bottom of the conduction band or
to the higher lying bands. The optical characterization of the films are studied using
a uv VIS-NIR Hitachi spectrophotometer model 200-20.

The deposited CdSe\(_x\)Te\(_{1-x}\) films on SnO\(_2\) substrates were kept in the main
light beam. The recording gives only the absorption and transmission curves
corresponding to the semiconductor film from which the bandgap (E\(_g\)) values
were calculated.

### 3.5.3 Structural studies

X-ray diffraction studies become the most important and reliable tool to
analyse the structure of the deposited films. Also the formation of solid solution
(CdSe with CdTe) can be analysed by X-ray diffraction studies. Moreover X-ray
studies yields an estimation of the grain size of the crystallites. X-ray diffraction
measurement were carried out using a JEOL JSM 35 diffractometer with CuK\(\alpha\)
radiation (\( \lambda = 1.5418 \) Å).

The peaks were identified using ASTM index to study the crystalline
nature and structure of the films. The lattice parameters 'a' and 'c' for the
hexagonal structure were calculated using the formula,

\[
d^2 = \frac{1}{4} \frac{1}{(h^2 + k^2 + h) + \frac{I^2}{c^2}} \quad \text{......... (3.24)}
\]

where \( h, k \) and \( l \) represent the lattice planes and \( d \), the interplanar distance.
In the case of cubic structure, the lattice parameter ‘a’ is estimated using the following relation.

\[ d^2 = \frac{a^2}{h^2 + k^2 + l^2} \]  

(3.25)

where h, k and l represent the lattice planes. The observed ‘d’ values are compared with ASTM index to identify the crystal structure.

3.5.4 Photoelectrochemical (PEC) solar cell studies

The photoelectrochemical (PEC) cells based on semiconductor (SC) / electrolyte interfaces have been extensively studied over the last 20 years for possible application to solar energy conversion. The fundamental understanding of the semiconductor / electrolyte interface has been greatly improved and several innovations have been evolved.

Semiconductor based photoelectrochemical cells have been identified as an important class of system. They offer a simple and efficient means of converting light into dc electricity and can compete, in principle, with the photovoltaic solar cells.

A PEC cell is based on the photoelectrochemical effect that is exhibited by the semiconductor (SC) electrolyte junction (interface) in a cell consisting of a photoresponsive n-type SC electrode, an electrolyte and a suitable counter electrode. The counter electrode may also be a photoresponse p type SC electrode. Semiconductor-electrolyte interface, formed by immersing the SC electrode into the electrolytic solution, is similar to a metal - SC (Schottky) junction in effecting a charge separation, when the SC / electrolyte junction is formed, the Fermi energies of the two phases adjust and an equilibrium is reached. (Figure 3.6a,b). Due to the transfer of charge carriers across the two
Fig. 3.6. Schematic energy band diagram of the SC/electrolyte interface: a) before and (b) after junction formation, c) under irradiation with $h\gamma \geq E_g$. * indicates the steady state situation under illumination.
phases upon contact, the bands are bent i.e. a potential barrier is developed. The SC part of the potential barrier is called the space charge or depletion region and it extends into the SC over a significant depth (~ 0.5 m). The potential barrier is such that the majority carriers find a barrier to reach the surface of SC. When light (photons) of energy (hν > Fg, the band gap of the SC) falls on the junction, it is absorbed by the SC and electron-hole pairs are created. The electrons are excited into the conduction band (CB) whereas holes are left behind in the valence band (VB) of the semiconductor. Due to the potential barrier (space charge layer), the electrons and holes are separated and they move in opposite directions and they can be utilized to produce electricity or bring about chemical reactions.

The minority carriers (holes in the case of n type) reach the surface of the SC via valence band whereas the majority carriers (electrons) flow towards the counter electrode and effect an electrochemical reaction. The net effect is to produce a decrease of the potential barrier and the band bending (figure 3.6c). When the light intensity is sufficiently high, the band bending is completely eliminated and the ‘flat-band’ condition is reached. The flat band potential is defined as the potential where the bands are not bent or where there is no field in the semiconductor. Usually Vfb is measured relative to a reference electrode such as saturated calomel electrode (SCE). Under irradiation and when the cell is not ‘shorted’ (open circuit condition), the electrochemical potentials of the SC and electrolyte phases are no longer in equilibrium and tend to reach their original positions before the contact. (ie. before junction formation). The difference in fermi levels of the two phases can now be measured as the open circuit photopotential (Voc, volts). Therefore, the maximum value of the photopotential (in volts) obtainable for a given SC/electrolyte junction on illumination (with hν > Eg) is given by,

\[ V_{\text{oc}}(\text{max}) = E_b = |(E_F - E^\circ)| \]  

.........(3.26)

where E^\circ is the redox potential of the electrolyte and E_b is the magnitude of the height of the potential barrier (extent of band bending). From the point of
view of energy conversion, it would be desirable to select electrolytes where $E^\circ$ 's lie very close to the $E_{VB}$ (VB-edge) for an n-type SC or $E_{CB}$ (CB-edge) for a p-type SC) so that the ratio $EB/E_g$ is high. For the utilization of solar energy, a SC with an $E_g$ in the range 1.2 - 2.5 ev is ideal, since solar irradiance has larger values in this region (visible and near-infrared). It can be shown that the semiconductors produce a maximum photovoltage of 55% of its energy gap /25/.

Depending on the type of electrochemical reaction occurring at the SC electrode, PEC cells can be classified into the following three categories

i. Liquid junction solar cells
ii. Photoassisted electrolysis cells
iii. Photoassisted electrosynthesis cells.

**Liquid junction solar cells**

When the electrochemical oxidation reaction at the anode is balanced by a reduction of the same species at the cathode (counter) electrode, there is no net change in the chemical composition of the electrolyte. Thus the change in Gibbs free energy ($\Delta G$) is zero and hence the light energy is converted into dc electricity. This is an example of the Liquid Junction Solar Cells (LJSC) and the nomenclature was first proposed by Gerischer /26/ and wrington /27/. For example, in the cell, n - CdSe / Na$_2$S + S + Naoh (aq) (1M)/pt, ($E_g$ of SC = 1.7 eV; $E_{redox}$ = - 0.752 V vs SCE; $\Delta G = 0$) the chemical reactions are

- at anode (SC): $S_x^{2-} + S^{2-} + 2H^+$ $\longrightarrow$ $S_{x+1}^{2-}$ (oxidation)
- at cathode (pt): $S_{x+1}^{2-} + Ze^-$ $\longrightarrow$ $S_x^{2-} + S^2$ (reduction)

The energetics of the cells are shown in fig 3.7.

Light - to - electricity conversion efficiencies ($\eta$) of 12-13% have been achieved and an efficiency of 20% has been claimed /28/.
Fig. 3.7. Energy band diagram representation of the functioning of a liquid junction solar cell. * indicates the steady state situation under illumination.
3.6 Conclusions

Linear sweep voltammetric studies are carried out on CdSe, CdTe and CdSe\textsubscript{x}Te\textsubscript{1-x} systems. The potential range required to deposit stoichiometric films of CdSe, CdTe and CdSe\textsubscript{x}Te\textsubscript{1-x} are analysed. Thin films of CdSe, CdTe and alloys of CdSe\textsubscript{x}Te\textsubscript{1-x} are deposited onto tin oxide coated glass and titanium substrates. The reaction kinetics for the deposition of CdSe, CdTe and CdSe\textsubscript{x}Te\textsubscript{1-x} are studied. The effect of various preparation conditions (viz, pH, temperature, selenium ion concentration etc.,) in the deposition of chalcogenide films are studied. Studies revealed that smooth, crystallized films of single phase are successfully electroplated in a single step electrodeposition in a fairly narrow potential domain 400 to -800 mV versus SCE. However, the films require annealing treatment to increase solar energy conversion efficiencies.
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