6.1. INTRODUCTION

Mixed chalcogenides of II-VI family are the most promising semiconductor materials utilised in IR detectors, optoelectronic, solar cell and heterojunction devices [Cusano (1963), Fuji et al (1988), Hodes et al (1976), Hodes et al (1982), Hodes et al (1984), Loutfy and Ng (1984), Moorthy Babu et al (1991 b), Mirovsky et al (1982)]. Solid solutions of most of the compounds of interest exist over the entire range, although they appear to be somewhat difficult to grow as single crystals. These materials attracted particular interest because of their wide choice of lattice parameters and the energy bandgap values with the composition of the system. The major advantages of these materials are their stability, high optical absorption and optimal bandgap for terrestrial solar energy conversion, detectors and optical communications.

Cadmium seleno telluride (CdSe$_x$Te$_{1-x}$) solid solution attracted particular interest because of its bandgap variation of 1.35 to 1.5 eV at $x$ between 0.4 and 0.8.
Cadmium seleno telluride has been successfully electrodeposited from an aqueous solution for photovoltaic and photoelectrochemical solar cells [Bhattacharya (1986), Gutierrez and Ortega (1989), Gutierrez and Ortega (1990), Kolbasov et al (1986), Kolbasov et al (1990), Loizos et al (1989), Moorthy Babu et al (1991 a), Rosamilla and Miller (1986), Rajalakshmi et al (1990)]. Crystal structure, luminescence, conduction process, isomorphous substitution and photoelectrochemistry of cadmium seleno telluride films have also been reported [Abramovich et al (1985), Belyaev and Kalinkin (1988), Sanitarov et al (1982), Tai et al (1975), Tripathi and Kumar (1990)]. The relative stability of cadmium telluride and cadmium seleno telluride as photoanodes reveal that cadmium seleno telluride is more stable particularly at high values of $x$ and the stability is found to be related to their crystal structures. Cadmium telluride is normally cubic while the usual structure of cadmium selenide is hexagonal. Increase in cubic phase content, paralleling the decrease in stability. Thus the alloy cadmium seleno telluride results in a semiconductor material which combines the output stability of cadmium selenide with optimum bandgap of cadmium telluride. Though extensive research have been done on the preparation and characterisation of cadmium seleno telluride, no report is available on the electrodeposition by periodic pulse technique. Hence cadmium seleno telluride has been
electrodeposited by both potentiostatic and periodic pulse techniques. Applicability and advantages of this technique are explained with the results obtained.

The solid solutions of cadmium sulphide and cadmium selenide are among the most sensitive photoconductors known today for detection of visible and near-infrared radiations at room temperature [Bube (1964), Svechnikov and Kaganovich (1980)]. The high photosensitivity of these materials is associated with the presence of a particular type of sensitizing centre which has a large capture cross section for photoexcited holes when occupied by an electron, but a much smaller cross section for photoexcited electrons when occupied by a hole. Mixed cadmium sulpho selenide crystals are a convenient system for investigating the collective effects at high exciton densities and determining the nature of changes in these effects as a result of continuous variation of the composition from cadmium sulphide via cadmium sulpho selenide to cadmium selenide, since these materials have similar energy structures and the parameters of excitons vary smoothly with the composition. Graded samples of n-cadmium sulpho selenide have been shown to exhibit color coded photoluminescence that permits identification of the spatial origin of electron - hole pair recombination in continuous illumination experiments [Bille et al (1969)]. Cadmium sulpho selenide can be prepared over
the whole range of composition $x$ ranging from 0 to 1. The lattice parameter varies linearly with the composition as $a = 4.11$ to $4.30$ Å and $c = 6.60$ to $7.0$ Å for $x$ varying from 1 to 0. Hence, Vegards law holds good for this material. But the variation in bandgap with composition is slightly nonlinear from $2.41$ to $1.74$ eV. Several methods have been employed to prepare cadmium sulpho selenide films [Feigelson et al (1977), Agnihotri and Raturi (1983), Raturi et al (1982)]. Aqueous electrodeposition of cadmium sulpho selenide has been carried out with the bath containing cadmium sulphate, sodium thio selenate and sodium thio sulphate [Gonzalez-Velasco and Rodriguez (1990)]. Non-aqueous deposition of cadmium sulpho selenide has also been reported from ethylene glycol solution of cadmium chloride, sulphur and selenium dioxide. In the present investigation electrodeposition of cadmium sulpho selenide from an electrolyte bath consisting of cadmium sulphate, selenium dioxide and sodium thio sulphate has been carried out. The deposited materials have been characterised.

A greater number of components in the solid solutions as compared with that in binary compounds facilitates the defect formation and extends the assortment of defects, which can give rise to a number of specific features as against a binary system. Mixed zinc cadmium selenide materials form a number of solid solutions whose
composition can be continuously changed from cadmium selenide to zinc selenide. Their distinguishing feature consists in a lattice symmetry change from hexagonal to cubic. The photoconductivity of zinc cadmium selenide covers a broad spectral region from visible to near infrared. Zinc cadmium selenide was the first mixed semiconductor material in which the resonant Raman scattering of light was observed. In the present work effort has been made to prepare zinc cadmium selenide films from electrodeposition. The deposited material has been characterised.

6.2. Experimental

The primary electrochemical reactions for the deposition of cadmium seleno telluride and their respective Nernst equilibrium potentials are

\[
\begin{align*}
\text{Cd}^{2+} + 2e^- & \rightleftharpoons \text{Cd} ; & E^\circ_{\text{Cd}} = -0.645 \text{ V vs SCE}, \\
\text{SeO}_2 + 4H^+ + 4e^- & \rightleftharpoons \text{Se} + 2H_2O ; & E^\circ_{\text{Se}} = 0.5 \text{ V vs SCE}, \\
\text{TeO}_2 + 4H^+ + 4e^- & \rightleftharpoons \text{Te} + 2H_2O ; & E^\circ_{\text{Te}} = 0.351 \text{ V vs SCE}.
\end{align*}
\]

When a sufficient potential is applied between the electrodes, the ions undergo the discharge process and the deposit of cadmium seleno telluride is formed by the solid state reaction between the plated species as
Cd + Se ⇌ CdSe, 
Cd + Te ⇌ CdTe and 
x CdSe + (1-x) CdTe ⇌ CdSexTe1-x.

Cadmium seleno telluride has been electrodeposited from an aqueous solution containing their respective reducible ionic species (cadmium sulphate, selenium dioxide and tellurium dioxide) by both potentiostatic and periodic pulse techniques [Moorthy Babu et al (1991 a), Moorthy Babu et al (1991 b)]. Deposition has been carried out for different ionic concentrations, pH, deposition potential and pulse to pause width ratio of potential (duty cycle). The pH value and the corresponding deposition potential have been chosen in such a way that they provide a common immunity region for simultaneous codeposition of Cd, Se and Te. A conventional three electrode cell has been used with titanium or graphite substrates as working electrode, platinum being counter electrode and saturated calomel electrode as reference electrode. All depositions were carried out at room temperature. The pulse potential is varied as -0.35 to -0.65 V vs SCE.

Cadmium sulpho selenide has been electrodeposited from an aqueous solution containing cadmium sulphate, sodium thio sulphate and selenium dioxide on titanium substrates by potentiostatic technique. The electrochemical reactions for the deposition of cadmium sulpho selenide are
Deposition was carried out at room temperature with deposition potentials ranging from -0.55 to -0.7 V vs SCE. The pH of the solution was adjusted to 2 with dilute sulphuric acid. The deposition bath has been chosen to have initial composition of x=0.65 for Cd$_x$Se$_{1-x}$ deposition.

The electrolyte bath consists of aqueous solution of cadmium sulphate, zinc sulphate and selenium dioxide for electrodeposition of zinc cadmium selenide.
Deposition has been carried out for different potential range -0.6 to -0.8 V vs SCE at room temperature. The pH of the solution was adjusted to 1.5 with dilute sulphuric acid. Deposition has been carried out on titanium substrates by potentiostatic technique.

6.3. RESULTS AND DISCUSSION

Cadmium seleno telluride has been electrodeposited on titanium and graphite substrates by potentiostatic and periodic pulse techniques. Tellurium and selenium ion concentrations in the deposition bath have been chosen in such a way that the ratio of their concentrations is equal to the composition ratio in the deposits of CdSe$_x$Te$_{1-x}$. The deposition bath has been chosen to have $x$ values 0.65 and 0.8 in the deposits. X-ray powder diffractogram data for the cadmium seleno telluride films on titanium are as shown in Figure 6.1. As deposited cadmium seleno telluride has intensity peaks corresponding to both cubic and hexagonal structures. The lattice constants for the dominant hexagonal structure have been calculated analytically and are $a = 4.45$ Å and $c = 7.19$ Å. From the lattice parameters and using the Vegards law [Stucks and Farrel (1964)], the composition of the film has been confirmed. The pulse to pause width (duty cycle) of potential is varied to have uniform deposit distribution. The pulse to pause width of
Figure 6.1. X-ray diffractogram data of \( \text{CdSe}_{1-x}\text{Te}_x \) films on titanium.
potential applied are 10 min/5 min, 10 min/1 min, 10 min/5 sec, 5 min/10 sec, 5 min/5 sec, 5 min/2 sec, 1 min/10 sec, 1 min/5 sec, 1 min/2 sec etc. Uniform deposits of cadmium seleno telluride were obtained with pulse to pause width ratios of 10 min/5 sec and 5 min/2 sec.

The surface micrographs of cadmium seleno telluride deposited on graphite at two different magnifications are as shown in Figures 6.2 and 6.3. The deposit distribution is less porous, adherent and cauliflower like structure. The approximate grain size of the deposits are 2 to 4 μm. Surface micrograph of the deposits on titanium substrate (Figure 6.4) also show smooth, well adhered and cauliflower morphology. According to Abramovich et al (1985) this peculiar morphology (which is not observed to change with heat treatments) is believed to be ideal for a photoanode in the liquid junction solar cell configuration, since it leads to large effective contact area between semiconductor and electrolyte. The relation connecting the amount of charge passed to the mass of the deposits obtained for cadmium seleno telluride on titanium substrate is depicted in Figure 6.5. The deposition process has been proposed to have two electron reductions for cadmium and four electron reductions for selenium and tellurium. Voltammograms recorded for cadmium (0.2M cadmium sulphate), selenium (20 mM selenium dioxide), tellurium (10 mM tellurium dioxide) and cadmium
Figure 6.5. Plot of the amount of charge passed vs the mass of the deposits obtained corresponding to CdSe Te \textsubscript{1-x} deposition.
Seleno telluride (0.2 M cadmium sulphate, 20 mM selenium dioxide and 10 mM tellurium dioxide) depositions are shown in Figure 6.6. The plateau region of the cadmium seleno telluride current curve is the underpotential deposition region for cadmium. Codeposition of cadmium, selenium and tellurium for cadmium seleno telluride has been carried out at the plateau region, at a potential less than the reduction potential of cadmium. The higher current value for cadmium seleno telluride deposition confirms the presence of three different currents due to cadmium, selenium and tellurium. The large increase in current value for cadmium seleno telluride deposition after -0.65 V is due to the enormous increase in cadmium current and hydrogen evolution process. Hence stoichiometric deposition of cadmium seleno telluride can be achieved in the plateau region.

Cadmium sulpho selenide has been electrodeposited from an aqueous solution containing cadmium sulphate, sodium thio sulphate and selenium dioxide on titanium substrates by potentiostatic method. X-ray powder diffractogram data for the cadmium sulpho selenide films deposited on titanium substrate are as shown in Figure 6.7. As deposited films contain intensity peaks corresponding to both wurtzite and zinc blende structures. The lattice parameter for the dominant wurtzite structure has been determined analytically and is \( a = 4.23 \, \text{Å} \) and \( c = 6.86 \, \text{Å} \). The composition of the
Figure 6.6. Linear sweep voltammogram recorded for Cd, Se, Te and CdSe$_x$Te$_{1-x}$. 
Figure 6.7: X-ray powder diffractogram data for CdS$_x$Se$_{1-x}$.
films is confirmed with the lattice parameters and using the Vegards law. The surface micrographs of cadmium sulpho selenide films deposited on titanium are as shown in Figure 6.8.(a, b & c). The scanning electron micrographs show that the layers have irregular morphology being composed mostly of spherical particles (cauliflower morphology) as like cadmium seleno telluride.

Cadmium zinc selenide has been electrodeposited from an aqueous solution on titanium substrates by potentiostatic method. X-ray powder diffractogram data of the cadmium zinc selenide films on titanium substrate have been shown in Figure 6.9 The diffractogram confirms the single phase cadmium zinc selenide and its crystalline nature. Optimising the condition for uniform growth is a major problem. Reducing the cadmium concentration in the bath leads to spongy amorphous films (Figure 6.10). And higher concentration of zinc combined with low current density lead to films with more pinholes and spongy nature (Figure 6.11.(a)). Application of higher current density results in films with dendritic morphology (Figure 6.11.(b)). The uniform deposits on titanium substrate obtained by optimising the conditions are as shown in figure 6.12. The band gap of the material at its fundamental absorption edge has been calculated from the UV-visible spectrum and is found to be $1.96 \text{ eV at } x = 0.8$. 
Figure 6.9. X-ray powder diffractogram data for Cd$_x$Zn$_{1-x}$Se
6.4. CONCLUSION

Cadmium seleno telluride, cadmium sulpho selenide and cadmium zinc selenide have been electrodeposited from an aqueous solution containing their respective reducible ionic species by potentiostatic and periodic pulse techniques. The optimum conditions for codeposition are presented. The deposited materials have been characterised with X-ray powder diffractograms, scanning electron micrographs, electron probe microanalysis and voltammetry to understand the composition of phases, structure, morphology, stoichiometry and kinetics of the system. From the results it is concluded that cadmium seleno telluride deposits obtained by periodic pulse technique have better physical properties. Cauliflower like morphology was observed for cadmium seleno telluride and cadmium sulpho selenide deposits. The surface morphology and the crystalline nature of zinc cadmium selenide deposits very much depends on the value of applied current density. The ratio of Se/Te, S/Se and Cd/Zn in the cadmium seleno telluride, cadmium sulpho selenide and cadmium zinc selenide deposits respectively depends very much on their respective initial composition in the bath.