



**CHAPTER V**  
**SUMMARY AND CONCLUSIONS**

**CHAPTER NO V**  
**SUMMARY AND CONCLUSION**

- 5.1 General
- 5.2 Preparation and Mechanism of Film Formation
- 5.3 Thin Film Properties
- 5.4 Photoelectrochemical (PEC) Properties
- 5.5 Conclusion

**CHAPTER NO V**  
**SUMMARY AND CONCLUSION**

**5.1 General**

Energy crises of last three decades made aware of the fact that there should be an effective alternative source of energy to replace conventional energy sources. The solar energy is one of the best alternative to conventional energy. Solar energy can be converted into electrical energy by using photo electrochemical cell. Its function is economical and simple. The PEC cells have advantages over the conventional solid state devices as (i) easy method of fabrication, (ii) no problem of lattice mismatch, (iii) no need for anti-reflecting coatings etc. Secondly, with a proper choice of an electrolyte redox couple, the Fermi level of an electrolyte could be adjusted to a desired level. High efficiency (> 10%) Photoelectrochemical solar cells using II-VI, IV-VI and III-V group compound single crystals have already been reported. The growth of single crystals is costly because it requires sophisticated instrumentation. Our main purpose is to develop the low cost-high efficient solar cell devices. Polycrystalline thin semiconductor films are exciting option for wide spread utility of the solar energy. The semiconductor material should satisfy the following conditions for its effective use, (i) the grain size should be sufficiently large to absorb almost all the incident light in few of the topmost layers of the grains exposed to the electrolyte, (ii) the space charge width should be comparable or greater than the light absorption depth to ensure rapid carrier separation. (iii) The loss of incident light when passing through

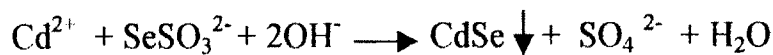
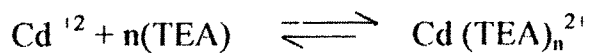
the solution to the semiconductor junction should be negligible and iv) the trap density near the junction should be small so as to minimise the carrier recombination. In PEC cells, an important task is to select, synthesize and characterize a suitable photosensitive semiconductor material. For this II-VI, IV-VI and III-V semiconductors have been rigorously studied due to their proven potential abilities in a variety of applications. A large number of technologies have been developed to deposit these materials in pure, mixed and doped thin film forms. Chemical deposition processes has proved its excellence for preparation of the large area thin films. The method allows for an intimate contact between the reacting species and the substrate material that permits for uniform deposition onto the substrate surfaces of the complex shapes and size. Further, a variety of substrate materials like metals, insulators and semiconductors can be used since the working temperature of the process is quite low. The preparative parameters could easily be controlled and desired orientation of the crystallites can be made possible. Of the above compounds, cadmium chalcogenides have a prominent place in a variety of electronic and optoelectronic devices. Cadmium selenide with an energy gap of 1.7eV is important in this respect. As the chemical composition and structural homogeneity of the crystal have important role in the physical, optical and electrical properties of semi conductor materials, CdSe material was preferred for the present work for investigation.

## 5.2 Preparation and mechanism of Film Formation.

CdSe thin films with a varying Tl- doping concentration were deposited onto glass and stainless steel substrates using a chemical deposition process. Cadmium sulphate and sodium selenosulphate were used as the starting materials. Initially cadmium sulphate was complexed with a sufficient quantity of triethanolamine which controls release of the  $\text{Cd}^{+2}$  ions that, in the presence of  $\text{Se}^{2-}$  ions permit for the reaction to take place slowly so as to obtain uniform deposits onto the substrates. Thallium sulphate was used as a source material for doping and was varied so as to achieve Tl concentration from 0.02 mole % to 2 mole%. The various preparative parameters and deposition conditions optimized are as following.

- 1 pH of the reaction Mixture :  $10.5 \pm 0.1$
- 2 Deposition temperature :  $60^{\circ}\text{C} \pm 2^{\circ}\text{C}$ .
- 3 Speed of the substrate rotation :  $70 \pm 2$  rpm
- 4 Deposition time : 90 min.

The basic reactions could be formulated as :



The as grown samples were thin, uniform, smooth, diffusely reflecting and adherent to the substrate support. The colour of the pure

CdSe was orange-red and became faint when thallium doping concentration was increased from 0 to 2 mole %.

### 5.3 Thin Film Properties

Though considerable improvement in the cell performance was observed with pure CdSe, there is a considerable loss in photoelectrochemical conversion efficiency. This has been partly attributed to the higher resistivity of the photoelectrode material that could effectively be reduced by a suitable donor impurity concentration. Thallium, a third group element, has shown pronounced effects in a number of host lattices and therefore pure CdSe was doped with a diverse concentration of Thallium. The effect due to Tl-doping concentration on various thin film properties were studied.

#### a) The structural properties

The as deposited CdSe and CdSe : Tl samples were characterised by an X-ray diffraction technique using  $\text{CuK}\alpha$  line. The range of  $2\theta$  angles was from  $10^\circ$  to  $100^\circ$ . From the diffractograms, it is found that films are crystalline in nature. Pure CdSe exhibits cubic zinc blende structures. The grain size is increased with Tl – doping concentration and is maximum at 0.07 mole % doping level. For higher concentration of thallium, sample tends towards amorphous. The SEM studies also support these observations.

**b) Optical Properties**

The optical studies were performed in the wavelength range from 350 nm to 850 nm and the absorption spectra analyzed to determine the absorption coefficient ( $\alpha$ ), optical energy gap ( $E_g$ ) and the mode of optical transition. The absorption coefficient is of the order of  $10^4 - 10^5 \text{ cm}^{-1}$ . A shift in the absorption edge from 550 nm to 650 nm with a band to band type of transition have been observed for the change of thallium doping concentration from 0.02 to 0.07 mole %. The optical gap is decreased from 1.75 to 1.55 eV as the thallium content in the film was increased from 0 to 0.07 mole %. The decreased band gap could be attributed to the improved grain structure due to segregation of the impurity atoms along the grain boundaries. The mode of optical transitions in these film is found to be direct allowed type.

**c) Electrical Transport Properties :**

The electrical conductivity of good quality sample was measured in the temperature range of 350 to 500<sup>0</sup> K. The observed electrical conductivity at 458 K was calculated in terms of specific conductivity for all the samples and found in the range of  $10^{-5}$  to  $10^{-6} (\Omega \text{ cm}^{-1})$ . The low value of conductivity can be due to small grain size, grain boundary discontinuity effect, lack of stoichiometry and an increased amount of disorder during growth process. The variation of electrical conductivity with temperature is studied. The activation energy of an electrical conduction has been determined and found to be 0.82 eV for pure CdSe film. Activation energy decreases as doping concentration is increased

upto 0.07 mole % and then increases for higher concentration of thallium doping. Slight increase in conductivity with Tl doping concentration can be considered due to improvement in the grain size, that reduces the height of the grain boundary potentials there by increasing the carrier concentration, mobility, electric conductivity. The fact that the conductivity did not vary much can be understood by considering the poor donor action of substitutional Tl atoms in the sample.

#### **5.4 Photoelectrochemical (PEC) properties**

The photoelectrochemical cells were constructed with the CdSe Tl photoelectrodes and various performance parameters were determined.

##### **a) The electrical properties**

The various performance parameters viz  $n_d$ ,  $V_{oc}$ ,  $I_{sc}$ ,  $\eta\%$ ,  $FF\%$ ,  $R_s$  and  $R_{sh}$  etc. were determined for all the cells. The result suggests that a considerable improvement in the energy conversion efficiency has been observed at 0.07 mole % Tl doping concentration. This enhancement is caused mainly due to the enhancements in  $I_{sc}$  and  $V_{oc}$ . The increase in  $I_{sc}$  can be ascribed to the decreased photoelectrode resistance due to the incorporation of Tl and an increased absorption of the incident light by the material itself. The enhancement in  $V_{oc}$  can be correlated to the increased flat band potential ( $V_{fb}$ ) and the built in potential ( $\phi_p$ ).



**b) The optical properties**

The measurement on photoresponse showed that the short circuit current varies almost linearly with the incident light intensity where as the open circuit voltage deviates from the linearity at high levels of illumination.

The spectral response was also examined. A cell with photoelectrode doping concentration at 0.07 mole % showed wider response.

**5.5 Conclusion**

From the investigations done so far it appears that the structural, optical and electrical transport properties of CdSe – Tl films are strongly dependent on the various parameters and Tl doping concentration. The analysis of the PEC properties showed improvement in the cell performance measured in term of the short circuit current ( $I_{sc}$ ), open circuit voltage ( $V_{oc}$ ), efficiency ( $\eta\%$ ) form factor (FF %). The improvement in the cell performance has been observed at 0.07 mole % Tl doping concentration.

Although the performance of a PEC cell has been found to be improved, the observed low efficiency can be attributed to the following reasons

- 1) low density, polycrystalline film morphology which causes high concentration of the lattice and boundary defects.
- 2) The low shunt resistance which is a direct consequence of micropores present in the films.
- 3) Absence of the post deposition treatments.
- 4) The deep colour of the electrolyte that absorbs a significant fraction of the input power
- 5) Reflection of light from the glass and the photoelectrode surfaces.