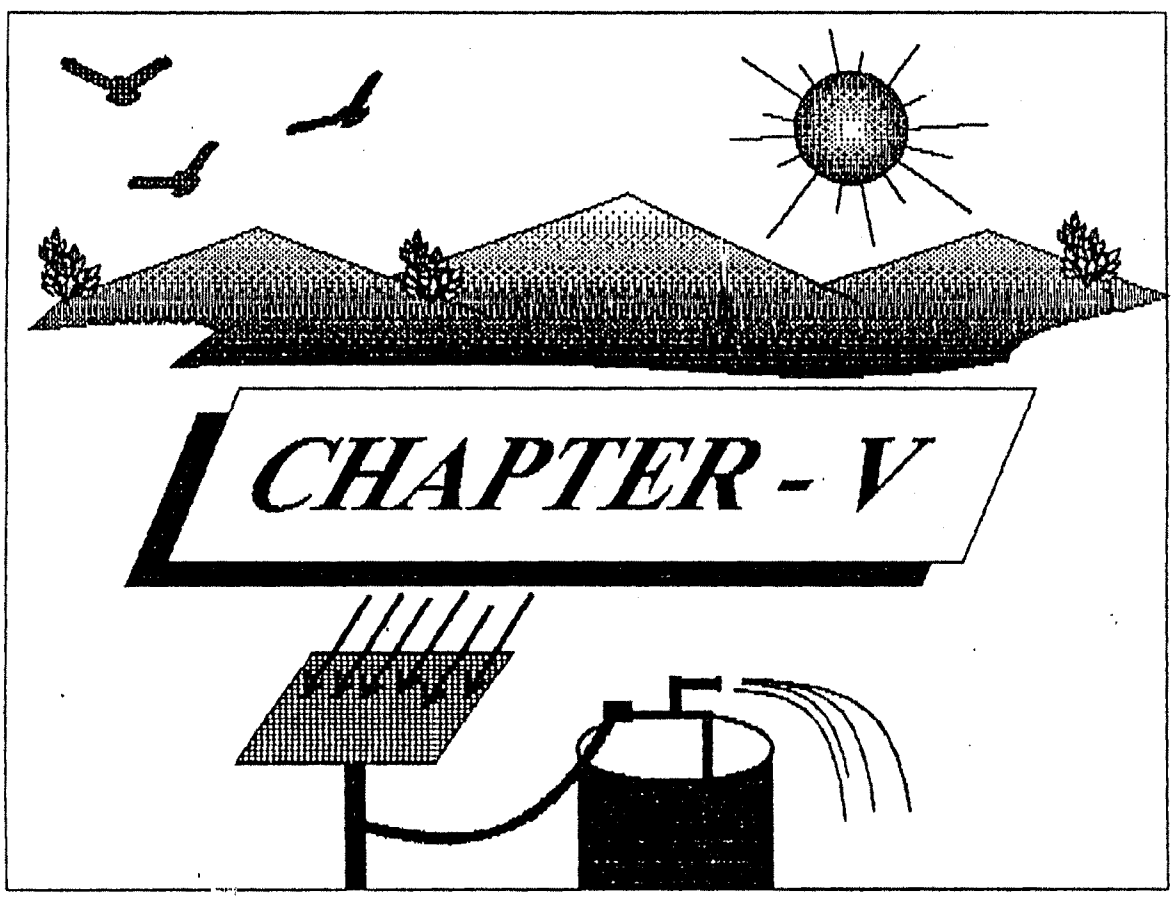

CHAPTER - V

CHAPTER V

SUMMARY AND CONCLUSIONS

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5.1 General

The energy crisis of the last three decades made aware of the fact that there should be an attractive alternative source of energy to replace the dwindling conventional energy sources. The solar energy that is available on the surface of the earth is now treated as one of the alternatives subjected to its efficient conversion into electrical counterpart. Of the various ways predicted for trapping the solar energy, an electrochemical conversion (PEC cells) has been preferred owing to its economic ability and processing simplicity. These cells have such potential advantages over the conventional solid state devices as; i) easy method of fabrication, ii) no problem of lattice mismatch, iii) no need for antireflecting 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. As the growth of single crystal requires sophisticated instrumentation leading to a high process cost and our main intention is to develop the low cost-high efficient solar cell devices, polycrystalline thin semiconductor films seem to be an exciting option for wide spread utility of the solar energy. For efficient conversion, the semiconductor material should at least satisfy the following requisites; 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. In this respect, 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. In general, Chemical Deposition Process (so called Chemical Bath Deposition Technique or Solution Growth Process) 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 sizes. 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 1.7 eV 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 semiconducting materials, I have selected CdSe as my working material.

5.2 Preparation and Mechanism of Film Formation

CdSe thin films with a varying In - doping concentration were deposited onto the 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 ensures controlled release of the cd^{2+} ions that, in the presence of se^{2-} ions permit for

the reaction to take place slowly so as to obtain uniform deposits onto the substrates. Indium trichloride was used as a source material for doping and was varied so as to achieve In^{3+} concentration from 0.005 mole % to 0.5 mole %. The various preparation parameters and deposition conditions which were optimised so as to obtain good quality films are;

1. Deposition temperature : 55 ± 2^0C
2. Speed of the substrate rotation : 70 ± 2 r p m
3. pH of the reaction mixture :10.5 ± 0.1
4. Deposition time : 75 min.

The fundamental reactions could be formulated as;

$$CdSO_4 + 2\,NaOH \rightarrow Cd(OH)_2 + Na_2SO_4 \quad \ldots (5.1)$$

$$Cd(OH)_2 + n(TEA) \rightarrow [Cd(TEA)_n]^{2+} + 2\,OH^- \quad \ldots (5.2)$$

$$[Cd(TEA)_n]^{2+} + Na_2SeO_3 + 2\,OH^- \rightarrow CdSe + Na_2SO_4 + H_2O + n(TEA) \quad \ldots (5.3)$$

The as - grown samples were thin, uniform, smooth, diffusely reflecting and adhered tightly to the substrate support. The colour of the pure CdSe was dark orange-red and went on faint when indium doping concentration was increased from 0.005 mole % to 0.5 mole %.

5.3 Studies on Thin Film Properties

Although 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. Indium, 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 indium. The effects due to In - doping concentration on various thin film properties were studied.

a) The structural properties

The as-deposited and CdSe : In samples were characterised by an X-ray diffraction technique using CuK_{α} line. The range of 2θ angles was from 10^0 to 80^0. From the diffractograms, it is found that films are crystalline in nature. Pure CdSe exhibits hexagonal wurtzite and cubic zinc blend structures. The grain size is increased with In - doping concentration and is maximum at 0.025 mole % doping level. For higher concentration of indium, samples tend towards amorphous. The SEM studies also support these observations.

b) The optical properties

The optical studies were performed in the wavelength range from 350 nm to 950 nm and the absorption spectra were analysed to determine the absorption coefficient (α), optical energy gap (E_g) and the mode of optical transition. The absorption coefficient is of the order of 10^4 - 10^5 cm^{-1}. A shift in the absorption edge from 560 nm to 660 nm with a band to band type of transition have been observed for the change of indium doping concentration from 0.005 mole % to 0.025 mole %. The optical gap is decreased a little typically from 1.82 eV to 1.69 eV as the indium content in the film was increased from 0 to 0.25 mole %. The decreased bandgap could be attributed to the improved grain structure due to segregation of the impurity atoms along the grain boundries.

c) The electrical transport properties

The temperature dependence of an electrical conductivity showed increase in conductivity after indium doping and is maximum at 0.025 mole % In - doping level.

Thermoelectric power measurements showed n-type conduction of the samples. The carrier concentration (n) and mobility (μ) were calculated from the conductivity and thermoelectric data. Both the carrier concentration and mobility are maximum at 0.025 mole % In - doping concentration. The increased conductivity at 0.025 mole % doping concentration could be ascribed to the increased carrier concentration, mobility and decreased bandgap.

5.4 Studies on Photoelectrochemical (PEC) Properties

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

a) The electrical properties

The various performance parameters viz. n_d, ϕ_B, V_{fb}, V_{oc}, I_{sc}, n_L, η%, FF%, R_s, R_{sh} etc were determined for all the cells. The results suggest that a considerable improvement in the energy convervsion efficiency has been observed at 0.025 mol % In-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 indium 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 (ϕ_B).

b) The optical properties

The measurements on photoresponse showed that the short circuit current varies almost linearly with the incident light intensity where as the open circuit volatge deviates from the linearity at high levels of illumination. The lighted ideality factor (n_L) was calculated for all the cell configurations. n_L and V_{oc} are related as under;

$$V_{oc} = (n_L KT/q) / \ln(I_{sc}/ I_o) \qquad \ldots(5.4)$$

where, $I_{sc} \propto I_L$ ...(5.5)

The spectral response was also examined. A cell with photoelethode doping concentration of 0.025 mole % showed wider response.

5.5 Conclusions

From the investigations done so far it appears that the structural, optical and electrical transport properties of the CdSe : In thin films are strongly dependent on the method of preparation and In - doping concentration. The analysis of the PEC properties showed improvement in the cell performance measured in terms of the short circuit current (I_{sc}), open circuit voltage(V_{oc}), efficiency (η %) from factor (FF %) and barrier height (ϕ_B). The improvement in the cell performance has been observed at 0.025 mole % In - 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,

i) The low density polycrystalline film morphology which causes a high concentration of the lattice and boundary defects.

ii) The low shunt resistance which is a direct consequence of the micropores present in the films.

iii) Absence of the post deposition treatments.

iv) The deep colour of the electrolyte that absorbs a significant fraction of the input power (incident light).

v) Reflection of light from the glass and the photoelectrode surfaces.