CHAPTER-VI

CHAPTER VI

SUMMARY AND CONCLUSIONS

Thin films are now assuming increasingly interest because of their possible technological usage in a variety of applications. A thin film structure can be single or multicomponent, mixed/alloyed or multilayered coatings on the substrates of different shapes and sizes. Even though a variety of thin film properties are required for various technological applications, their applicability is limited due to their complex structure. As a result, sophisticated characterisation techniques emerged out for understanding of the multifarious properties of the thin films. A number of characterisation techniques are available depending on the property and interest for giving some times similar and more often additional and complementary informations. Experimentally it has been observed that the properties of the thin films have a direct bearing on the method of formation and it is quite obvious that neither of the available techniques nor the deposition processes can yield a out put product (thin film) which can suffice all the problems. The II-VI and III-V compound semiconductors or hybrides thereof are rigorously studied with an intension that they have proved their potential ability in manyfold applications.

The Cd-Chalcogenides exhibits excellent electrical, optical, chemical, electrochemical, and electro-optical properties which make them one of the promissing candidates

in the fields of photovoltaic and electrochemical energy conversion. Thus the choice lies both for the quality of the material and the process by which it can be prepared. We have chosen cadmium sulphide as an active material owing to its suitability in photovoltaic converters as discussed in earlier chapter. The second important advantage in selecting the cadmium sulphide as a semiconductor active material lies in the fact that the technique by which it is prepared is simple, easier, and less complex. In section 3.3 some of the inherent advantages of a deposition process over the other conventional preparative methods are outlined. In order to come out of the energy crises, solid-liquid junctions are todays alternative to the solid-solid junctions. The solid-liquid junctions have certain favourable advantages over their solid-solid counter part as stated in Chapter I. The basics for a good photoelectrochemical cell is also given. Chapter II describes the various basic charge transfer processes at the electrode electrolyte interface both in dark and under lighted conditions. The details of the basic requirements, essential designs, and fabrication of a chemical deposition process is discussed in Chapter III. The growth mechanism and deposition of CdS and CdS:Sb thin films is also given. Chapter IV deals with the measurements on various compositions of CdS thin films and the necessary fabrications involved therein. The measurements basically involve studies on electrical, optical, and structural properties. Some of the interesting results on

photoelectrochemical cells formed with this material are embodied in Chapter V.

The thin film deposition process developed in our "Thin Film and Solar Cell Research Laboratory" for the deposition of chalcogenides of cadmium, lead, bismuth, antimony, arsenic, silver etc. and some alloyed compositions thereof with suitable impurity concentration is found to be convenient, simple, easier, and reproducible one in which good quality, uniform, large area, and adherent deposits on various substrate materials can be obtained. It has been mentioned earlier that the thin film deposits of pure and doped cadmium sulphide were grown on both the amorphous ground glasses and stainless steel substrates. The basic ingradients used were cadmium sulphate, thiourea and antimony trichloride. The preparative parameters and various deposition conditions are optimised in the initial phases of the work. The optimum values (comparatively selected) of these parameters are:

i) Temperature of the deposition - 85 $\pm$ 2 ^{o}C

ii) Speed of the substrate rotation - 72 r.p.m.

iii) Time for the deposition - 45 min.

iv) Cd:S ion ratio - 1:1

v) pH of the reaction mixture - 8.5

vi) Antimony (III) was used as a dopant material and its optimum concentration is searched out both in respect of film and optimum cell properties.

The work that has been carried out is splitted into various phases as under :

I) The Design and Fabrication Aspects :

For the deposition of contaminent free cadmium sulphide, a protective means called as dustproof chamber was designed and fabricated in our laboratory and the whole working assembly was put into the chamber. Other essentials related to the work (bushing arrangement for motor, substrate holder, reaction mixture holder, design and fabrication of electrical conductivity and thermoelectric power measuring units, design and fabrication of PEC cell and related arrangements etc.) were procurred and fabricated. A solar cell testing chamber of approximately same dimensions as that of the dust proof chamber was designed and all the photoelectrochemical studies have been carried out under contaminent free conditions.

II) Deposition of Cadmium Sulphide Thin Films :

Thin films of cadmium sulphide have been deposited onto the glass substrates by allowing thiourea to react with ammonium complex of cadmium sulphate. The series of reactions involved are :

i) Formation of the complex compound as,

$$CdSO_4 + 4NH_3 \longrightarrow [Cd(NH_3)_4]SO_4.$$

ii) Diffusion of the complex ion, OH^- and thiourea to the catalytic surface of CdS.

iii) Catalytic CdS dissociates thiourea as,

$$(NH_2)_2-C=S + OH^- \longrightarrow CH_2N_2 + H_2O + SH^-$$

iv) Formation of bivalent sulphide ion,

$$SH^- + OH^- \longrightarrow H_2O + S^{--}$$

v) Formation of CdS,

$$Cd(NH_3)_2 + S^{--} \longrightarrow CdS + 2NH_3\uparrow$$

The pH of the solution was maintained around 8.5. The temperature of the reaction mixture was controlled to 85 ± 2 ^{o}C. The film growth takes place by ion-by-ion condensation of the material or by the adsorption of the colloidal particles from the solution on the substrates [43,44].

III) Role of Sb Doping Concentration on Thin Film Properties:

1) Electrical transport properties :

As stated earlier the films prepared by this method are relatively resistive than the other sophisticated preparation techniques. This initial high resistivity can be reduced considerably by doping these thin films with trivalent impurity. Some reports are available in the literature in this respect. On the similar lines and following closely the similar approximations we have tried here the dopant material as a trivalent antimony (Sb^{+++}). The doping concentration was changed from 0.005 wt% to 1 wt% and the films were deposited onto amorphous glass substrates. The Scanning Electron Microscopy (SEM) and X-Ray Diffraction analysis showed that the films are polycrystalline and crystallinity is improved after 0.075

wt% antimony doping. Since these films were supposed to be utilised as the photoelectrode in PEC cells, it was worth to study the structural, electrical transport, and optical properties of Sb-doped and undoped CdS samples. The transport properties of Sb-doped and undoped samples were studied in the temperature range 300K to 600K using electrical conductivity (6) and thermoelectric power (P) techniques. The conductivity (6) and TEP (P) were found higher for 0.075 wt% CdS:Sb samples. The carrier density was calculated both for pure and doped samples. The order of carrier density is 10^{19} cm^{-3} however, it is considerably higher for 0.075 wt% CdS:Sb films than others. Still higher resistivity can be due to the lower mobility of the charge carriers.

2) Optical properties :

The optical absorption measurments were carried out in the wavelength range from 400 nm to 900 nm. The result shows higher absorption coefficient (10^{4} cm^{-1}) for 0.075 wt% CdS:Sb thin film samples and the bandgap estimation showed decrease in bandgap with Sb-doping level. Typically it decreases from 2.47 eV to 1.7 eV. Further, the Sb-doping has shifted the cutoff towards the lower energy side. This has helped in using the relatively maximum span of the solar spectrum. Thus the 0.075 wt% CdS:Sb samples found more favourable for using in PEC cells.

IV) Role of Sb-doping concentration on PEC properties :

The photoelectrochemical cells (PEC) were fabricated with as-deposited and antimony doped CdS phtoelectrodes. A mixture of equimolar NaOH-Na_2S-S was used as an electrolyte and CoS treated graphite rod as a counter electrode. The cell properties in dark and under 100 $mW.cm^{-2}$ illumination intensity were recorded.

1.) I-V and C-V properties in dark :

These are studied in view to understand the basic charge transfer processes across the electrode/electrolyte interface. Considering S/E interface as the analogue of M/E interface, Butler-Volmer relation [60] can be used to describe the current transport mechanism across the S/E interface. All junctions were found of the rectifying nature and are analogous to the schottky barrier junction. The junction quality factor in dark (n_d) was calculated and it seems that the dark I-V characteristics are often influenced by recombination and series resistance effects [45,93,95]. The n_d is smaller for cell formed with 0.075 wt% CdS:Sb photoelectrode indicating the fewer recombination and trap centres in the space charge region [45]. The flat band potential was determined from the capacitance-voltage measurement studies and is found highest for the cell consisting of CdS:Sb photoelectrode with 0.075 wt% CdS:Sb level. A slight deviation from the straight line behaviour has been observed for all the cells which is indicative of presence of surface states, non-uniform doping etc. [11,45,72].

2) Photovoltaic properties :

The power output curves were obtained for different cell configurations under 100 mW.cm^{-2} intensity and the various cell parameters such as series and shunt resistances (R_S and R_{sh}), fill factor (ff), efficiency (η), short circuit current (I_{sc}), and open circuit voltage (V_{oc}) were examined. Both I_{sc} and V_{oc} showed considerable improvement for a cell configuration with 0.075 wt% CdS:Sb photoelectrode [45]. The calculation of R_S, R_{sh}, η and ff also pointed out such improvement with the same cell.

3) Optical properties :

The measurement of photoresponse, spectral response, and speed of response were carried out. The lighted ideality factor (n_L) was calculated from variation of ln.I_{sc} .vs.V_{oc}, measured under different illumination intensities. n_L is found highest of all for the above cell indicating direct relationship between n_L and V_{oc} as :

$$V_{oc} = \frac{n_L KT}{q} \ln \frac{I_{sc}}{I_o} \qquad \ldots (6.1)$$

The spectral response study observed for different wavelength clearly indicated the higher magnitude of I_{sc} and some peak shifting towards longer wavelength side. This is supported by optical absorption studies. The decrease in I_{sc} on shorter wavelength side is attributed to the absorption of light in the electarolyte and the surface recombination phenomena. It revealed from spectral response study that

relatively less recombination centres and defect levels are associated with 0.075 wt% CdS:Sb photoelectrode, reflecting in greater V_{oc}, lesser I_o and larger V_{fb} and η. The optimum values of the various cell parameters for a typical 0.075 wt% CdS:Sb photoelectrode are :

i) V_{oc} = 220 mV
ii) I_{sc} = 0.460 mA/cm^2
iii) R_s = 192 Ω
iv) R_{sh} = 1.714 KΩ
v) ff = 45.4%
vi) η = 0.046%
vii) n_d = 2.17
viii) n_L = 2.97
ix) V_{fb} = - 0.74 V
x) ϕ_B = 0.41 eV.

Thus in conclusion the performance has been found improved after antimony (III) doping and is optimum at 0.075 wt% CdS:Sb doping level in CdS.

4) Conclusions :

It is clear from the above studies that the efficiency so far obtained is well below the expectation. The major reasons are: i) thickness of the sample, ii) absence of the thorough post preparative treatements, iii) absorption of light by the electrolyte, and iv) reflection from the glass and the photoelectrode surface etc. Attempts are in progress to overcome these difficulties.