CHAPTER-V

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Todays technology requires several types of thin films which are assuming increasingly interest for a variety of applications. Thin films can be single or multicomponent alloy/compound or multilayered coatings on substrates of different dimensions. The properties required of the films can be depending on the applications, high optical reflection/transmission, hardness, wear resistance, single crystal nature etc.

Such versatility in thin films can be brought about by the techniques of thin film deposition. Although the thin films are creating increasingly interest, their structure is complex in view of their applications which demand tailor made properties. As a result, sophisticated characterisation techniques have emerged out for understanding of the multifarious properties of thin films. Depending on the property, interest, a host of characterisation techniques are available for giving some times similar and more often additional and complementary informations. Further, film properties are the strong function of deposition techniques and it is quite obvious that no one technique can deposit the film covering all beneficial aspects. An overview of commonly used thin film deposition techniques is outlined in chapter II (sec.2.2). The semiconducting films of II-VI and III-V compounds are extensively studied because of their proven potential ability in many fold applications.

The Cd-chalcopyrites exihibits excellent electrical, chemical and optical properties which make them one of the promissing candidates in the field of photovoltaic energy conversion. Thus the choice lies both for the method of preparation and the material. We have chosen CdS as semiconductor material owing to its suitability in photovoltaic converters. Further, the technique by which it is prepared is simple and easiest. Section 2.3 focusses some of its inherent advantages over the other preparative methods.

Todays alternative to the solid state devices, in order to come out of the energy crisis, is the semiconductor-electrolyte junction cells as they have certain advantages over the first as stated in chapter-I. The basic requirements of a good PEC cell is also given in Chapter-I. Chapter II lights out the different basic charge transfer processes in light and in dark at semiconductor/electrolyte interface. The basic requirements, essential designs and fabrication of various measurement tools needed to study different aspects of thin film as well as PEC cell are discussed in chapter-III. Chapter IV deals with the measurements, observations and results on both thin films and PEC cells.

The thin film deposition process, developed in our ´Thin Film and Solar Cell Research Laboratory´ for deposition of CdS, alloyed CdS, Bi_2S_3, Sb_2S_3, As_2S_3, Ag_2S, PbS etc., with suitable impurity concentration, is found convenient, easier and reproducible one in which uniform large area and adhesive films on various substrate materials can be prepared. As a part of continuing programm thin films of cadmium sulphide were deposited onto amorphous glass and stainless steel substrate by a chemical deposition process. The basic ingradients used were 1M $CdSO_4$, 1M Thiourea, 14N Liquor ammonia and appropriate $AsCl_3$ solution for doped samples. The various preparative parameters and deposition conditions are finalised in the initial stages of the work. The optimum values of these parameters are: a) time and temperature of the deposition - 30 mins. and 85° C respectively. b) speed of substrate rotation - 75 r.p.m. c) Molar concentration of the basic ingradients = 1M, d) substrate holder geometry. e) Cd:S ion ratio - 1:1. f) In order to reduce the resistivity of these films, arsenic was used as a dopant material and its optimum concentration is searched out both in respect of film and optimum cell properties.The different phases of the work undertaken were as under :

I) <u>The Design and Fabrication Aspects:</u>

For the deposition of contaminent free thin samples of cadmium sulphide, a protective means, called as dustproof chamber was designed, fabricated and whole assembly was put into the chamber. Other essentials related to the work such as bushing arrangements to the constant speed motor, design of substrate holder, design of reaction mixture holder, design and fabrication of special arrangement for thiourea addition, design and fabrication of conductivity and thermoelectric power units, design and fabrication of PEC cell, experimental arrangement for cell properties in dark and in light, were procurred and fabricated.

II) Effect of As-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 with trivalent impurity. Few 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 arsenic (As+++). The doping concentration was changed from 0.01 wt% to 2 wt% and the films were deposited onto amorphous glass substrates. The presence of As+++ was confirmed by semimicro analysis technique. The optical microscopy and x-ray diffraction analysis showed that the films are polycrystalline and crystallinity is improved after 0.25 wt % arsenic 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 As-doped and undoped samples.The transport properties of As-doped and nondoped 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 0.25 wt% CdS:As 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 0.25 wt% CdS:As films |42|than others. Still higher resistivity can be due to the lower mobility of the charge carriers.

2) Optical properties :

The optical absorption measurements were carried out in the wavelength range from 4000 Å to 7800 Å. The results show higher absorption coefficient (10^4 cm^{-1}) for 0.25 wt% CdS:As thin film samples and the bandgap estimation showed decrease in bandgap with As-doping level. Typically it decreases from 2.44ev. to 2.24ev. Further, the As-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 0.25 wt% CdS:As samples found more favourable for using in PEC cell.

III) Effect of As-Doping Concentration on PEC Properties .

The photoelectrochemical cells (PEC) were fabricated with as-deposited and arsenic doped CdS:As photoelectrodes. 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 process across the electrode/electrolyte interface. Considering S/E interface as the analogue of M/E interface, Butler-Volmer relation |59| was used to describe the current transport machanism across the S/E interface. All junctions were found of the rectifying nature and 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 | 93,94,98,112 |. The n_d is smaller for cell formed with 0.25 wt% CdS:As photoelectrode indicating the fewer recombination and trap centres in the space charge region |94|. The flat band potential was determined from the capacitance-voltage measurement studies and is found highest for the cell consisting of CdS:As photoelectrode with 0.25 wt% As-doping 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.|9, 94, 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 improvements for a cell configuration with 0.25 wt% CdS:As photoelectrode |94|. The calculation of R_s,R_{sh}, η and ff also pointed out such improvement with the same cell.

3) Optical properties :

The measurements of photorespose and spectral 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 intensites. n_L is found highest of all, for the above cell indicating direct relationship between n_L and V_{oc} as:

$$V_{oc} = \frac{n_L KT}{q} \ln \frac{I_{sc}}{I_o} \qquad \text{--------------------5.1}$$

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 electrolyte and the surface recombination phenomena. It revealed from spectral response study that relatively less recombination centres and defect levels are associated with 0.25 wt% CdS:As photoelectrode reflecting in greater V_{oc} , lesser I_0 and larger V_{fb} and η. Thus in conclusion the performance has been found improved with arsenic doping and is optimum at 0.25 wt% As-doping level in CdS.

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

IV) Work in Progress and Future Directions : (Beyond the scope of this dissertation):

The thin CdS layer is highly disordered and grain size is probably a function of distance from CdS/substrate interface. The large number of defects in the active region of thinner CdS is the main cause for the deterioration of the collection efficiency. Thus attempts are in progress to increase the photoelectrode thickness and to observe its reflections on cell properties. The technique of etching and annealing will be applied to the photoelectrode and its impact on PEC performance will be examined.

Like the solid state solar cells, earlier methods for the enhancement in the output voltage and current of a PEC cell, have relied on coupling of two separate diodes those respond to two different regimes of the solar spectrum. Thus some efforts will be spent in the direction to convert, in a small gap semiconductor, the light transmitted by a large gap material. The materials whose bandgap is smaller than CdS/CdS:As, will be utilised in this process and the cell performance will be examined | 98,115,116 |.