CHAPTER - V

CHAPTER V

SUMMARY AND CONCLUSIONS

5.1 General

All over the world, the energy saving programmes and search for new alternatives are in progress. Of the various alternatives, solar energy which is a clean, low cost, inexhaustible, harmless and abundantly available source of energy fulfils the energy demands of the world. The solar energy can be converted into an electrical energy by means of a photovoltaic effect. In order to come to a real breakthrough of photovoltaic in the energy market, new low cost options have to be developed. High efficiency and low cost polycrystalline compound semiconductor thin film solar cells are the exciting option for wide spread utility of solar energy. Many researchers are looking towards the electrochemical (PEC) solar cells which rely on the junction formed between a semiconductor and a liquid to accomplish a photovoltaic effect. An important task in PEC cells is to select and prepare a suitable photosensitive semiconductor material of desired properties. Therefore, it is important to investigate the new materials and to explore their possible potential in photovoltaic applications. A single or multicomponent, mixed/alloyed compound or multilayered coatings on substrates of different sizes and shapes may form a thin film photoelectrode. The polycrystalline metal chalcogenide thin films found useful in this repect. The properties of the films have direct bearing on the method of formation and it is quite obvious that no one technique can deposit the films of desired properties. Among the various deposition techniques,chemical deposition process which involves controlled but slow precipitation is presently an attractive means for the preparation of large area II-VI and V-VI compound thin films. The preparative parameters are easily controllable and better orientation of the crystallites can be obtained resulting into the improved grain structure. Since the photovoltaic properties are directly related to the material properties, the choice lies both for the preparation technique and characterisation methods. Considering these observations into account we have deposited various thin films by employing a chemical deposition method since it has certain overriding advatages over the other conventional techniques. The plan of our research work was many fold and the actual work that has been carried out is divided into five chapters. Chapter I is a short survey of the thin film technology and photoelectrochemical cells. Essentially it describes the requirements of the photoelectrochemical (PEC) cell. Chapter II describes the designs, fabrications and experimental techniques for carrying out the proposed work. The growth mechanism and detailed procedure for the deposition of PbS:CuS mixed thin films are also discussed. The electrical, structural and optical properties of PbS and PbS:CuS mixed thin films are included in Chapter III. The electrochemical cells were constructed with these films and the electrical and optical properties of the cells have been examined. The various phases of the work were as follows:

5.2 Preparation and Growth Mechanism of PbS and PbS:CuS Samples

The preparation procedure involved the reaction container consisting of 20 mi(0.5 M) lead acetate, 20 ml(0.5 M) sodium hydroxide and 20 ml(0.5 M) thiourea solutions. The thoroughly cleaned glass slides were kept vertically in the reaction container. The total volume of the solution was made roughly upto two third volume of a reaction container by adding a double distilled water. For the preparation of PbS:CuS thin films, controlled quantity of copper sulphate solution was added directly into the lead acetate solution. The reaction was carried out at room temperature for 20 minute. These samples were used for further studies. All the chemicals used were AR grade.

The preparation of PbS and PbS:CuS mixed thin films is carried out in an alkaline medium. Sodium hydroxide controls the rate of release of sulphur ions. The reaction mixture develops a white precipitate which then gradually turns through yellow to brown and finally greyish black. The deposition of PbS on glass surface takes place during this process. The series of reactions are;

$$\begin{array}{l} H_2N \\ \quad \diagdown \\ \quad\; C = S \\ \quad \diagup \\ H_2N \end{array} + OH^- + \begin{array}{l} H_2N \\ \quad \diagdown \\ \quad\; C = O \\ \quad \diagup \\ H_2N \end{array} \qquad \ldots(5.1)$$

$$HS^- + OH^- \;=====>\; H_2O + S^{2-} \qquad \ldots(5.2)$$

$$Pb(CH_3COO)_2 + S^{2-} \;===========>\; PbS + 2CH_3CO\bar{O} \qquad \ldots(5.3)$$

The controlled quantities of copper sulphate solution were added in the reaction bath for the preparation of PbS:CuS thin layers.

Good quality deposition of PbS and PbS:CuS thin films with less consumption of active materials and electrical energy is made possible. Samples with changing pleasant colours have been obtained for varying concentration of Cu in PbS and are smooth, uniform, diffusely reflecting, crackfree and strongly adherent to the substrates.

5.3 Studies on Thin Film Properties

The structure and crystallinity of the PbS and PbS:CuS mixed samples were tested by XRD and SEM techniques. Both PbS and PbS:CuS samples are crystalline in nature and pure PbS is structurally cubic while mixed samples contain both cubic PbS and hexagonal CuS phases. The observed d values are in excellent agreement with the standard. The SEM micrographs show that there is a little decrease in the grain size, however, Cu concentration has no marked effect on the crystallite size. Electrical conductivity measurements of the samples showed the semiconducting nature of the samples. The activation energy did not varied much with the Cu-concentration but variation of logarithmic conductivity with Cu concentration is notable. TEP measurements revealed p-type conduction of the samples. Carrier concentration at room temperature is found to be of the order of 10^{19} cm^{-3}. The data on electrical conductivity and thermoelectric power have been utilised to calculate the carrier mobility (μ). The study of variation of mobility with the Cu-concentration in PbS showed that, for low doping levels, the behaviour of mobility is similar to the electrical conductivity. Initially the mobility decreases due to the increased carrier concentration and for higher Cu-levels, the carrier density decreases reducing the scattering of the carriers and thereby increasing the carrier mobility. The mobility increases sharply as the temperature is increased. Height of the potential barrier, ($\emptyset_B$), at the grain boundary is determined. For pure PbS, $\varnothing_B$ is of the order of 0.10 eV and it is 0.068 eV for 0.075 mol% PbS:CuS sample.

Optical scanning was done in the 5000 A° to 26000 A° wavelength range. The optical absorption coefficient was determined from these observations and its wavelength dependence has been examined. The absorption spectra show clearly three well defined absorption edges for pure PbS and two for PbS:CuS samples. There is no continuous change in the optical energy gap and the lattice constants as a result of the introduction of Cu in PbS indicating that the samples are of the mixed composite type.

5.4 Studies on Photoelectrochemical (PEC) Properties

The PEC cells were constructed with PbS and PbS:CuS as the photoelectrode dipped in an electrolyte consisting of a mixture of equimolar NaOH-S-N_2S. A sensitised graphite rod was used as a counter electrode. Studies on I-V and C-V characteristics have been carried out to know about the charge transfer process across the electrode/ electrolyte interface.

The junction quality factors (n_d) have been calculated from the variation of log I vs V for all the cells. The values of n_d are greater than unity indicating recombination mechanism effect. Capacitance-Voltage measurements were performed under reverse biased condition to determine the flat band potential from the Mott-Schottky variation. Barrier heights, ($\varnothing_B$) have been determined for all the cells from the variation of reverse saturation current (I_o) as a function of temperature.

The properties of the cells under lighted condition were examined. The short circuit current (I_{sc}) and open circuit voltage (V_{oc}) have been determined. Power output curves are obtained and the various cell parameters such as R_s, R_{sh}, η% and ff% have been computed.

5.5 Conclusions

Although PbS and PbS:CuS thin films deposited using a chemical deposition process are uniform, very adherent, smooth, diffusely reflecting etc their resistivity is quite high and inturn it has reflected on its several electrochemical properties when it is utilised in a photoelectrochemical solar cell. The observed solar cell performance is below the expectation and this is because of i) high electrode resistivity, ii) thinness of the sample, iii) absence of the thorough pre and post preparative treatments, iv) absorption of the light in the electrolyte and v) reflection losses from the glass and that from the photoelectrode surfaces. Secondly, though absorption coefficient of PbS is high, its optical bandgap (0.4 eV) is well out of the active region of the solar spectrum. Therefore it has a poor performance at visible range. Addition of copper improves this performance by improving the film properties such as optical absorption, electrical conductivity, carrier mobility etc.

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