

Summary and Conclusions

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5.1 General

All over the world, the energy saving programs and search for new alternatives are in progress of these various alternatives, solar energy which is clean, low cost, harmless and abundantly available source of energy that fulfills the energy demands of the world. The photovoltaic cell converts the solar energy into electrical energy. In order to come to a real breakthrough of PV in the energy market, new low cost polycrystalline compound semiconductor thin film solar cell are exciting option for wide spread utility of solar energy. Most scientists are in search of PEC solar cells which rely on the junction formed between a semiconductor and liquid to accomplish a PV system. An important task in PEC cell 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 PV applications. A single or multicomponent, mixed/ alloyed compound or multilayer coatings on substrate of different sizes and shapes may form a thin film photoelectrode. The polycrystalline metal chalcogenide thin films have found useful in this respect. Therefore the thin film cells have been deposited in variety of configurations such as Schottkey barrier, p-n homojunction, p-n heterojunction and MIS structure.

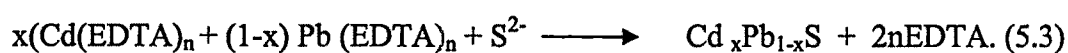
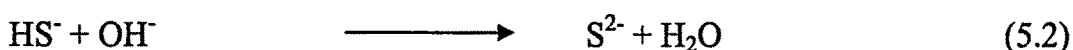
5.2 Preparation of $Cd_xPb_{1-x}S$ thin films

Thin films of $Cd_xPb_{1-x}S$ material were deposited onto glass as well as metal substrate with varying composition parameter 'x' from 0.0 to 1.0. Cadmium sulphate and lead acetate were used as source of Cd^{+2} , Pb^{2+} and S^{-2} ions. Simple chemical bath deposition technique was used for obtaining uniform well adherent PbS, CdS and $Cd_xPb_{1-x}S$ thin films. The various preparative parameters and deposition conditions optimized are as shown in the following table,

Sr. No.	Preparative parameters	Optimum conditions
1.	pH of reaction solution	10.5±10.9
2.	Initial temperature	303±2 K
3.	Deposition temperature	343±2 K
4.	Speed of substrate rotation	45±2 rpm
5.	Deposition time	180 min.

5.3 Mechanism of Cd_xPb_{1-x}S thin film formation

The as grown films were uniform, reflecting and well adherent to the substrate. The colour of pure PbS was grayish black and that of CdS thin film was yellow. The colour changes from black to yellow with increase in composition parameter 'x'. The mechanism of film growth has been accounted in terms of the following reaction mechanism,



5.4 Characterization of Cd_xPb_{1-x}S thin films

The characterization of Cd_xPb_{1-x}S thin films have been made by using various techniques such as XRD, optical absorption measurements, electrical conductivity, SEM, AAS, TEP and PEC cell study etc.

5.4.1 Structural and Morphological study

Structural analysis was done by observing the XRD pattern, recorded by Philips PW-1710 (Holland) X-ray diffractometer in 2θ range from 10⁰-80⁰ using CuKα line (λ= 1.54056 Å). The X-ray diffraction (XRD) spectra of annealed Cd_xPb_{1-x}S thin films deposited on glass substrate is shown in Fig. (4.3). The sulphide of cadmium can be formed with either hexagonal or cubic structure and sulphide of Pb can be formed with cubic structure. In the present investigation we obtained a large number peaks for each time indicating these polycrystalline nature. The deposits are polycrystalline over whole range of the parameter x (0 ≤ x ≤ 1) studied. Pure PbS is the cubic type and the intense reflections have been observed at 2.096, 2.965 and 3.420 Å, while for hexagonal CdS at 3.483, 3.357, 3.60 Å. It has been observed that for films with 0 ≤ x ≤ 0.4 solid solution of the kind Cd_xPb_{1-x}S have been formed and are of cubic type. The most intense peak corresponds to (200) reflection shifts towards lower d values with a corresponding decrease in relative intensity.

The lattice parameter 'a' is calculated from these observations and found to be decreased with increase in 'x' upto 0.4. The variation of 'a' with 'x' is linear. For higher values of 'x' (x > 0.4) more abrupt change is observed which

can be ascribed to the formation of individual phases. Beyond 0.4 ($0.4 \leq x \leq 1$), sample consist of mixture of separate phases of cubic PbS and hexagonal CdS.

The hexagonal phase of CdS is little bit increased as 'x' is increased from 0.4 to 1. The lattice constants fit well with their ASTM data. This clearly indicates that the thin films deposited for various 'x' values (0.4 to 1) are mixtures or composites of the type $(\text{CdS})_x(\text{PbS})_{1-x}$ and not to be $\text{Cd}_x\text{Pb}_{1-x}\text{S}$ ($0.4 \leq x \leq 1$) solid solutions.

The morphological studies were carried out by using scanning election microscopy. The $\text{Cd}_x\text{Pb}_{1-x}\text{S}$ thin films are homogenous, crack free and uniform, well adherent to substrate. The average grain size was measured from SEM. The grain size was found to be in the range of 209 Å⁰ to 600 Å⁰.

5.4.2 Compositional analysis

The composition of cadmium and lead in the sample was determined by atomic absorption studies Perkin-Elmer 3030. Atomic absorption spectrophotometer was used for this purpose. The weighted film sample was dissolved in minimum quantity of concentrated AR grade HNO_3 . The ratio of [Pb/Cd] ion concentration in the films were calculated, which matches with the ions concentration taken in bath. The concentrations and ratio of [Pb/Cd] obtained by measurements were shown in the form of table (1) in section 4.4.

5.4.3 Optical properties

The spectra were utilized for calculation of absorption coefficient (α), nature of transition involved and band gap. The optical absorption spectra of various $\text{Cd}_x\text{Pb}_{1-x}\text{S}$ films deposited onto glass substrate were studied in the wavelength range of 800nm to 1600 nm. A plot of $(\alpha h\nu)^2$ versus $h\nu$ should be straight line whose intercept to the X-axis gives the optical band gap. The band gap of PbS and CdS were found to be 0.9 eV and 2.4eV respectively which matches well with reported values.

5.4.4 Electrical Properties

The graphs show the presence of two conduction mechanism viz intrinsic and extrinsic. The trend of decrease in electrical conductivity may be due to widening of band gap and decrease of grain size with increase in

composition parameter 'x'. The activation energies calculated from the slope of straight lines of $\log \sigma$ vs. $1000/T$. The values were found to be between 0.035 eV to 0.600 eV. The values obtained for activation energy well matches with previously reported values for PbS and CdS.

The type of conduction mechanism was often observed by observing the nature of terminal connected to either positive or negative end in TEP. The $\text{Cd}_x\text{Pb}_{1-x}\text{S}$ films shows the n-type of conductivity.

5.4.5 PEC cell study

The cell fabrication is described in section to study the charge transfer mechanism occurring across the semiconductor, electrolyte interface, the electrical characterization of the PEC cell was tested I-V, C-V characteristics in dark, measurement of built in potential and power output characteristics were studied. The PEC cell were fabricated using $\text{Cd}_x\text{Pb}_{1-x}\text{S}$ thin film as photoelectrode and performance parameters viz n_d , I_{sc} , V_{oc} , $\eta\%$, $ff\%$, ϕ_β , etc were measured.

5.5 Conclusions

The simple chemical bath deposition technique was used for obtaining ternary $\text{Cd}_x\text{Pb}_{1-x}\text{S}$ thin films. The films obtained were uniform and grayish black to yellow in colour. All the samples obtained show large number of peaks indicating presence of polycrystalline nature. From XRD data it is observed that the lattice parameter 'a' is decreased with increase in 'x' upto 0.4. The variation of 'a' with 'x' is linear. For higher values of 'x' ($x \geq 0.4$) more abrupt change is observed which can be ascribed to the formation of individual phases. Beyond 0.4 ($0.5 \leq x < 1$), sample consist of mixture of separate phases of cubic PbS and hexagonal CdS. The values of band gap obtained are in the range of 0.9eV to 2.4 eV. The temperature dependence of TEP is measured for all samples. It is observed that the TEP increases up to $x = 0.4$ and thereafter it decreases as composition parameter (x) increase from 0.5 to 1. In PEC the different cell performance parameters were studied with respect to the composition parameter (x). The photoanode film with $x=0.4$ composition shows better PEC performance characteristics.