Chapter VII: Summary and Conclusions

Summary and Conclusions

The compound semiconductors of the II–VI family including zinc telluride (ZnTe), mercury tellurides (HgTe) has been the focus of great interest due to their low cost and high absorption coefficients for applications to photovoltaic and photo-electrochemical cells. The pseudo binary or ternary chalcogenide semiconductor thin films belonging to II-VI family, for example, HgZnTe, CdZnTe, etc are potential candidates for the detection of electromagnetic radiations. Zinc mercury telluride (ZnHgTe), a solid solution, has a wide range of band gaps tunability between 0 to 2.25 eV. It offers potential advantages over cadmium based HgCdTe, HgCdSe due to its high bonding nature and stability. The pseudo-binary material synthesized under controlled conditions offer composition-dependent physical, electrical, optical, microscopic and structural characteristics suitable for photovoltaic application purpose.

In the present investigation, we attempted the chemical deposition of Zn$_{1-x}$Hg$_x$Te pseudo-binary thin films on conducting (steel plates) as well as non-conducting (glass) substrates with the composition parameter(x) varying from zero to one. The systematic studies have also been made to characterize the material, to investigate their properties and to find its suitability for solar energy conversion. The various preparative parameters such as temperature, pH, concentrations of ions, rate of addition, rate of stirring etc have been finalized to get good quality thin films. The thin film photoelectrical properties such as I-V characteristics, Power output curves, Barrier height determination, Junction ideality factors etc have been studied in details so as to optimize a good composition. The material have been characterized by using the techniques such as XRD, AAS, SEM, absorbance, electrical, thermo-electrical and photo-electro-chemical properties measurements.

The detailed account of above mentioned investigations are outlined in the form of seven chapters which constitutes the thesis.
**Chapter I**

This chapter describes the general overview of the problem, solar energy, thin films, the present status of the total energy consumption, the future need of energy, available conventional and nonconventional routes, the solar cells, their types, historical developments of solar cells, thin film technology and information about various deposition techniques. The advantages and disadvantages of various preparative methods have also been discussed with special reference to Chemical Bath Deposition Technique. A brief literature survey indicates the scope of chalcogenides films, various methods of preparation of thin films, characterization techniques employed, structure and applications as device in solar energy conversion.

**Chapter II**

This chapter describes a theoretical discussion on the chemistry of semiconductor-electrolyte interface of a PEC cell. The basic charge transfer processes taking place across the semiconductor electrolyte surface in a photo-electrochemical cell, both in light and in dark along with efficiency consideration are discussed.

**Chapter III**

This chapter describes the experimentation, basic requirements for preparation of thin film material, essential designs and fabrication of various instruments for the measurement and characterization procedures. The chapter also includes the essential theoretical back ground and details of the charge transfer phenomena occurring in the photo-electrochemical cells. The details of the chemical deposition system developed for the deposition of the thin films are discussed. A brief theoretical background of each characterization tools used for the characterization, such as x-ray diffraction (XRD), energy dispersive x-ray spectroscopy (EDAX), optical absorption measurements, thickness measurements, scanning electron microscopy (SEM), and electrical conductivity have been discussed.
Chapter IV

This chapter describes the theoretical background of the thin film deposition with reference to ionic product, solubility and solubility product and super saturation in detail so that the mechanism of film formation, the growth of precipitate can be understood. The formation of thin films can be explained on the basis of ion-by-ion condensation on surface of the substrate. The effects of deposition parameters such as super saturation, pH, temperature and composition of reaction bath on the quality of films have been studied and optimized to get the better quality film. The various preparative parameters and deposition conditions optimized to obtain the good quality film are as follows;

1. pH of the reaction Mixture: 10.5.
2. Initial Temperature: 5°C
3. Deposition temperature: 70° ± 2°C.
4. Speed of the substrate rotation: 45 ± 2 rpm, and
5. Deposition time: 3 Hours

The basic reactions have been formulated as:

The formation of Hg and Zn complexes takes place via;
\[ \text{Hg}^{2+} + \text{Zn}^{2+} + \text{NH}_3(aq) \rightleftharpoons [\text{Hg(NH}_3)_4^{2+}] + [\text{Zn(NH}_3)_4^{2+}] \]

The decomposition of \( \text{Na}_2\text{TeSO}_3 \) in an ammonia gives Te\(^{2-}\) ions by;
\[ \text{Na}_2\text{TeSO}_3 + 2\text{OH}^- \rightleftharpoons \text{Te}^{2-} + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} \]

The breaking up of Zn and Hg complexes produce Zn and Hg ions via;
\[ [\text{M} (\text{A})_n]^{2+} \rightleftharpoons \text{M}^{2+} + n \text{A}^{2-}, (\text{M}^{2+} = \text{Zn}^{2+} \text{ or Hg}^{2+} \text{ and A = Ammonia}) \]

The combination of Te\(^{2-}\), Hg\(^{2+}\) and Zn\(^{2+}\) ions forms alloy according to;
\[ [\text{Zn}(\text{A})_n] + [\text{Hg}(\text{A})_n] + \text{Te}^{2-} \rightleftharpoons \text{Zn}_{1-x}\text{Hg}_x\text{Te} + n\text{A} \]
The ‘as grown’ samples were found to be uniform, stiochiometric, cubic, diffusely reflecting, smooth, grey in color and well adherent to the substrates.

Chapter V

This chapter describes the characterization of Zn\textsubscript{1-x}Hg\textsubscript{x}Te thin films by using the techniques like XRD, EDAX, AAS, SEM, absorption spectroscopy, electrical resistance measurements and thermoelectric techniques. A summary of the results is outlined below.

a) The Structural and Morphological Properties

The ‘as deposited’ ZnTe, HgTe and Zn\textsubscript{1-x}Hg\textsubscript{x}Te thin film samples were characterized by an X-ray diffraction technique using CuK\textsubscript{α1} line (wave length 1.54056 Å\textsuperscript{0}). The range of 2θ angles was from 10° to 80°. The study of diffractograms indicated that all the films are polycrystalline in nature. Pure ZnTe as well as HgTe show the peaks corresponding to cubic (zinc blende) structures. The XRD pattern of pure ZnTe and HgTe matches well with those pattern given in JCPDS card No 80-0022 and 77-2014.

The films of composition Zn\textsubscript{1-x}Hg\textsubscript{x}Te show the cubic pattern. The peaks observed are 111, 200 & 220. The peak pattern for all ternary films fall intermediate to the extremes. The XRD pattern of ternary films, show no peaks corresponding to hexagonal or individual phases. The cell size was found to increase linearly with inclusion of mercury in ZnTe. The grains are nano-crystalline with an average size of 280 Å. The cell size calculated using Bragg’s law for the intense 111 peak roughly follows Vegards law of composition. The intensity of peaks observed increases with the composition parameter(x) indicating the enhancement in the crystallinity. The theoretical intensity and peak pattern of the ZnTe and HgTe were of the same order of magnitude may be because of similar cell constants. All films show a compact granular structure with uniform texture. The grains are spherical in shape with the size, as calculated using
Scherrer’s equation \( t = 0.9 \lambda / \beta \cos \theta \) fall between 250 to 350 Angstrom. The grain size was found to increase with increase in mercury content. The increase in grain size can be correlated to increase in cell size as Hg is added.

\textbf{b) Optical Properties}

The measurements of absorption edge were carried out in the wavelength range from 800 to 2100 nm at room temperature. The absorption spectra were analyzed on the basis of three dimensional model (theory). The spectra showed a sharp edge at room temperature corresponding to presence of a single band gap. The absorption coefficients found to be of the order of \( 10^4-10^5 \) cm\(^{-1}\). The absorption edge was found to shift towards longer wavelength side with increasing mercury content. The dependence of absorption coefficient in the vicinity of band edge is governed by:

\[\alpha h \nu = A (h \nu - E_g)^n\]

Where, \( A \) is absorption coefficient, \( h \nu \) is photon energy (eV), \( E_g \) is the band gap and \( n \) is a pure number that depends on the type of transition involved. For valid \( n \), the equation, can be rearranged to show linear dependence for \( h \nu > E_g \); in the plot of \((\alpha h \nu)^{1/n}\) versus \( h \nu \). We could obtain a best fit at \( n = \frac{1}{2} \) indicating that the transition involved is the direct allowed type. The \((\alpha h \nu)^2\) versus \( h \nu \) plot with a linear variation for photon energies \( (h \nu) \) greater than band gap \( (E_g) \). The extrapolation of the linear portion of plot to the x-axis corresponds to optical band gap. The band gap for various compositions decreases monotonically from 2.33 to 0.81 eV with increase in mole fraction of mercury(x). All the transitions are found to be direct band to band type.

\textbf{c) Electrical Properties}

The electrical resistance and thermoelectric measurements of good quality samples were carried out in the temperature range of 350 to 500 K. The observed specific conductivity for all the samples is found to be in the
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range of 1.3x10^4 to 2.8x10^6 (Ω⁻¹ cm⁻¹). The conductivity increases nonlinearly with the increase in mercury content. The increase in conductivity is associated with decrease in band gap of the compound. The study of variation of electrical conductivity with temperature indicated a two type conduction mechanism for all the films. The activation energies calculated are 0.505 eV to 0.106 eV (for high temp.) and 0.188 eV to 0.066 eV (for low temp.). The magnitude of activation energy was observed to decrease with increase in mercury concentration. The increase in conductivity may be attributed to increase in the carrier concentration as well as the mobility. All the samples were found to be n-type in nature.

Chapter VI

This chapter describes the features of photo-electrochemical (PEC) cell and the study of photo-electrochemical properties of Zn_{1-x}Hg_xTe thin films. A PEC cell was constructed using the Zn_{1-x}Hg_xTe as photo anode (electrodes) potassium ferro-ferricyanide couple as electrolyte and graphite rod as counter (cathode) electrode.

The current-voltage characteristic of the cell in dark and in light have been studied to know the basic charge transfer processes taking place across the interface and the nature of the junction formed. The junction ideality factors (η_d) for all the photo-anode have been computed from the variation of Log I versus V plots. The barrier height was determined from the temperature dependence of the reverse saturation current. The power output characteristics of the various cells were recorded at 30 mW/cm² illumination intensity. The various performance parameters viz V_{oc}, I_{sc}, η%, FF% etc were determined for all the PEC cells. The results suggest that a considerable improvement in the energy conversion efficiency is achieved for the composition as Zn_{0.4}Hg_{0.6}Te.
ORIGINAL WORK

The chemical deposition technique is considered to be the most suitable method for the deposition of low cost large area thin film materials. Thin films of Zn$_{1-x}$Hg$_x$Te have been prepared for the first time by using chemical deposition techniques. A meta-stable source of Na$_2$TeSO$_3$ was used. The chemical deposition method is free from difficulties and clumsy mechanical processes it do not requires sophistication. The various preparative parameters such as temperature, pH, ingredient concentrations, rate of addition, rate of stirring etc have been finalized to get good quality thin films. The films are characterized by by sophisticated techniques such as XRD, AAS, SEM, EDAX, Absorbance, Electrical measurements. A PEC cell was constructed using films carbon rod and potassium ferri-ferrocyanide as an electrolyte.

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