CHAPTER – VI

PHOTO-ELECTROCHEMICAL PROPERTIES OF Zn$_{1-x}$Hg$_x$Te THIN FILMS

6.1 Introduction

The zinc blende compounds and their alloys obtained by replacement of their cations with other suitable cation are considered as promising semiconductor material for various types of thin film devices including solar energy conversion devices [1, 2]. A typical type of solar energy conversion device has a semiconductor in contact with an electrolyte often referred as photoelectrochemical (PEC) cell. An inert metal or another semiconductor may be used as counter electrode. In general, any solar to electrical energy conversion device converts photon of light into electrical energy. This conversion may occur in various systems containing different types of junctions, for example, solid-solid junction (so called Solar cells) and solid-liquid junction (so called photo-electrochemical cells). The cell utilizing solid-liquid junction is also called as electrochemical photovoltaic cell (ECPVC). This ECPV/PEC cell finds many advantages over the conventional solar cells; i) PEC cells are simple and easy to set up, ii) the junction requires a semiconductor either in polycrystalline form or even nano-crystalline, iii) the set up do not require special processing on semiconductor, iv) the cell is not sensitive to defects lattice mismatch etc, v) there is a choice or adjustment of Fermi level potential by suitably choosing electrolyte, vi) unlike conventional solid state device, the potential of working electrode can be varied with respect to reference electrode by means of an external voltage source connected between working and counter electrode [3]. Thus PEC cell seems to be cheaper and needs no sophistication which eliminate several complicated electrode processing, so that one can study energetic and the chemistry of semiconductor-electrolyte interface easily [4,5].
An important aspect regarding PEC is that the efficiency and stability of a cell are strongly dependent on the nature of the photoelectrode, electrolyte and experimental conditions set in the experimentation [6]. A pioneering photoelectrochemical experiment was realized by obtaining photocurrent between two platinum electrode immersed in electrolyte containing metal salts [7]. The solar to electrical conversion using semiconductor-electrolyte junction was first demonstrated by Gerischer and Eills [8, 9]. Since then, a large number of II-VI and III-VI group metal chalcogenide as well as oxides have been used as photoelectrode in the PEC cells. A S-L junction cell utilizing a single crystal, pellets or polycrystalline material can show efficiency as high as 70% [10] instead of the single crystal of the same material. Now a days, dye sensitized nanostructred thin film semiconductor materials have shown an attractive performance [11,12].

The zinc blende compounds and their solid solutions show high absorption coefficient (10^4-10^5 cm\(^{-1}\)) and tunability of their optical and electrical properties [13-18]. So far several investigations on PEC properties of II-VI ternary materials [19-25] are available in literature. In this regard the report on use of ZnHgTe for PEC is scare. However there exist a number of report on use of ZnTe and Hg based ZnTe alloy in photovoltaic devices and solar cells [26-29]. The Mercury Telluride attracts a great deal of attention for use in PEC due to its better absorptivity, conductivity and higher spectral sensitivity over a considerable range of photon energies.

In this chapter, we report on photoelectrochemical properties of Zn\(_{1-x}\)Hg\(_x\)Te thin films.

6.2 Experimental Details

6.2.1 Preparation of Photo-electrode
Thin films of Zn_{1-x}Hg_xTe materials in a whole range of its composition [i.e. 0 ≤ x ≤ 1] have been obtained on suitable size stainless steel substrates. The process of deposition of semiconducting material in thin films form is outlined in experimental section of this thesis.

6.2.2 PEC Cell Construction

For PEC measurements, a special ‘H’ shaped glass vessel was used. Two glass test tubes of 7 cm length each (one having diameter of size 2.7 cm & other 1.5 cm) were joined with a small glass tube admeasuring 2 cm in length. The PEC cell consisting of Zn_{1-x}Hg_xTe thin films as photoelectrode, 0.1M Potassium ferro-ferricyanide redox couple in 0.1 M KOH as an electrolyte and graphite rod as a counter electrode were setup. This ‘H’ shaped glass container was fitted in a copper pot of a suitable size. A window having the dimension of 2 cm x 1.5 cm was made available for illumination of the photoelectrode.

6.3 PEC Cell Characterization

6.3.1 Electrical Properties

In PEC cell, a solid liquid junction is easily established. The charge transfer phenomena occurring across this S-L junction are considered as quite simple as compared to S-S interface. In order to explore the important properties and to optimize the better performance of a PEC, it is highly essential to know the charge transfer mechanism taking place across the semiconductor-electrolyte junction. The important measurements done to know the charge transfer phenomenon occurring in a PEC cell are current voltage characteristics (I-V), capacitance voltage characteristics (C-V) in dark as well as in light, built in potential measurements and power output characteristics (under illumination). A wire wound potentiometer (1000 Ohm, Elico make) was used to vary the voltage across the junction and the current flowing through the junction was measured with a sensitive current meter. The capacitance of the junction was measured using a three
electrode system. The reverse saturation current at different temperature was recorded under a constant illumination intensity of 30 mW/cm² for determination of barrier height. The magnitude of flat band potential was estimated from the MS plots. For PEC cell, a photo active material is deposited on stainless steel plate. The junction formed between the photoactive material and stainless steel should be noninjecting. It should be ohmic, i.e in dark, the current flowing through it should be proportional to voltage applied across.

6.3.2 Optical Properties

The optical properties of electrodes besides electrical properties are important in determining the applicability of material in optoelectronic devices. The lighted ideality factor \( n_l \) determines the ideality of the junction can be determined by measuring photo-response of all the \( \text{Zn}_{1-x}\text{Hg}_x\text{Te} \) thin film samples. The short circuit current \( (I_{sc}) \) and open circuit voltage \( (V_{oc}) \) were measured as a function of incident light intensity.

6.4 Results and Discussion

6.4.1 Electrical Properties

i) Nature of Contacts

An ohmic contact between the photo-electrode and stainless steel substrate (i.e. a linear current-voltage relation) is essential for efficient conversion of light to electricity in both directions [30]. The nature of contact between photo-electrode \( (\text{ZnHgTe}) \) and substrate have been examined in the form of current-voltage relationship (figure 6.1) and found to be almost linear in both the directions indicating that the contact is ohmic.
ii) **Conductivity Type of Cell**

When a photo-electrode semiconductor, dipped in an electrolyte is illuminated with a light having photon energy greater than the optical band gap of the material, the charge carrier are generated within the cell, this lead to development of photopotential and current. The cell is said to be a “converter” of light energy to electrical energy. In absence of light (i.e. in dark), the same cell should not produce any emf. However, a small emf and current is developed in PEC cell in dark condition for all the Zn$_{1-x}$Hg$_x$Te photo-electrodes. This usually happens in case of PEC cell due to residual charge transfer phenomena occurring due to difference in emf potentials of two half cell formed, namely $E_{\text{graphite}}$ (half cell potential of counter electrode) and $E_{\text{ZnHgTe}}$ (half cell potential of photo electrode). These potentials are developed when the electrode come in contact with the
electrolyte. It is observed that the polarity of cell is –ve toward the film electrode indicating n type nature of films. The development of small dark current is indication of some sort of deterioration at the electrodes [31].

**iii) Current-Voltage (I-V) Characteristics of a PEC**

The current voltage characteristics of a PEC cell under forward biased conditions in the voltage range ± 0.5V was measured in the dark as well as under light illumination.

The current flowing through circuit is governed by Butler –Volmer relation [26] as;

\[
I = I_0 \{ \exp (1-\beta) \frac{V}{RT} - \exp [\beta \frac{V}{RT}] \} \quad \ldots (6.1)
\]

Where, \(I_0\) is equilibrium exchange current density, \(V\) is the over voltage, \(\beta\) is a symmetry factor, \(R\) is universal gas constant and \(F\) is Faradays constant. A value of \(\beta = 0.5\) corresponding to presence of a symmetrical barrier, giving a symmetrical current voltage curve. While values of \(\beta > 0.5\), I-V is nonlinear (nonsymmetrical) so that the interface can be called as rectifying nature. The I-V characteristics of few representative films have shown a non symmetrical nature (shown in fig 6.2) in dark indicating that the junction formed is of rectifying type [32]. The presence of unsymmetrical I-V nature (nonohmic/ rectifying) predicts that the junction has been formed between photoelectrode and electrolyte. When this cell is illuminated, the graph shifts to IV\textsuperscript{th} quadrant indicating that the photogenerated carriers are also formed (i.e. the PEC cell is generating an electricity). The photoelectrode becomes more negative confirming n type nature. The current under reverse bias condition, however, was found to increase with the voltage, this type of behavior is usually observed in PEC cell due to the generation of electron-hole pair in depletion layer and onset of electron injection from electrolyte to semiconductor side.
Fig. 6.2. I-V Characteristics in dark for films with $x = 0.2, 0.4, 0.6, 0.8$

If we consider the semiconductor–electrolyte junction analogues to a schottky barrier [33], we can represent I-V relation by equation;

$$I = I_0(e^{\frac{V}{nKT}} - 1)$$  \hspace{1cm}  \text{...(6.2)}

Where, $I_0$ is reverse saturation current, $V$ is applied forward bias voltage and $n$ is junction ideality factor. For bias voltage exceeding $3kT/e$, one can neglect the last term in eq. 6.2. and can rewrite;

$$I = I_0(e^{\frac{V}{nKT}})$$  \hspace{1cm}  \text{...(6.3)}

The validity of equation 6.3 can be tested by plotting the graph of Log $I$ versus $V$. The value of junction ideality factor, $n$ can be calculated from the slope of the linear region of the plot. Accordingly the plot for few representative photo electrodes are shown in Fig 6.3.
Fig. 6.3. Log I vs. V Characteristics for films with x = 0.2, 0.4, 0.6, 0.8

The estimated values for all the compositions are included in Table 6.1. It is seen that the values of junction ideality factor (n) are greater than ideality value (i.e. 1). They vary systematically with the composition (x). The value of n was found to be minimum for Zn_{0.4}Hg_{0.6}Te photoanode. In general the higher value of n factor is an indication of the fact that the current transport is under influence of recombination of charge carriers either at interface or in the depletion region [33], this also deviate the I-V characteristics at low applied bias voltage.

iv) Capacitance - Voltage (C-V) Characteristics

A semiconductor-liquid junction of a PEC involve formation of two types of double layers (one at the S-L junction and other in space charge region of the semiconductor) and hence two type of capacitance. As two capacitance are in series, their total capacitance is the sum of their reciprocals. The capacitance due to S-L double layer is small so that in
comparison to space charge capacitance, it can be neglected so that the measured capacitance can be conveniently considered as due to space charge. Thus measurement of capacitance as a function of applied bias under depletion condition provides useful information about values of flat band potential, donor density, magnitude of band bending, width of depletion layer etc. The flat band potential, \( V_{fb} \) of a semiconductor gives information of the relative position of the Fermi level in photo-electrode. The intrinsic band bending at the interface can be used to measure the maximum open circuit voltage (\( V_{oc} \)) attainable from the cell [34]. The measurement of apparent capacitance as a function of potential under depletion condition is based on Mott-Schottky relation;

\[
1/C_{sc}^2 = 2/\varepsilon_0 \varepsilon_r N [V - V_{fb} - (kT/e)] \quad \ldots (6.4)
\]

Where, \( C_{sc} \) is the space charge capacitance per unit area, \( e \) is the electronic charge, \( \varepsilon_r \) is dielectric constant of the semiconductor, \( \varepsilon_0 \) is the permittivity of the free space, \( N \) is the donor density, \( k \) - Boltzmann constant, \( T \)- absolute temperature. The first term in eq.6.3 is constant. Neglecting the term \( kT/e \), the equation 6.4 can be written as;

\[
1/C_{sc}^2 = \text{Constant} \ [V - V_{fb}] \quad \ldots (6.5)
\]

The intercept of linear plot of \( C_{sc}^2 = 0 \) determines the value of flat band potential. The values of band bending, also called built in voltage \( V_b \) can be calculated from;

\[
V_b = V_{F,\text{redox}} - V_{fb} \quad \ldots (6.6)
\]

Where, \( V_{F,\text{redox}} \) is the redox potential of the ferro-ferricyanide electrolyte and is equal to 0.37 V against standard calomel electrode (SCE).

It is also possible to determine barrier height, \( \phi_B \) using relation;

\[
\phi_B = V_{b^+}(E_c - E_d) \quad \ldots (6.7)
\]

The slope of a Mott-Schottky plot is given by relation;
Slope = \[ \frac{2}{\varepsilon_0 \varepsilon_r N} \] \hspace{1cm} \text{...(6.8)}

The impedance measurements were carried out for all the photoelectrodes at 1kHz frequency. The fig 6.4 shows Mott Schottky plot for few of the representative film photoelectrodes. The donar concentration, N, for all the photoelectrodes have been calculated from the eq 6.8 and is included in table 6.1. The flat band potential was found to be highest for Zn_{0.4}Hg_{0.6}Te photo-electrode. The nature of plot suggest a positive slope for all ternary photoelectrodes indicating that all the films are n-type in nature. The lowering of \( V_n \) for other photoelectrodes is an indication of the fact that introduction of Hg\(^{2+}\) ions in the lattice of ZnTe might be increasing surface adsorption to certain extent, increasing shallow donar levels [31]. The observed nonlinear variation in Mott Schootky plot suggests that the junctions are of ‘graded type’ and are attributed to the presence of both shallow and deep donor levels (density of interface state), this behavior usually occur in polycrystalline film. The presence of surface states and a small deviation in homogeneity modify the potential across Helmoltz layer [24].

![Mott Schottky plot for films with x = 0.0, 0.4, 0.5, 0.6, 0.8](image_url)

\textbf{Fig. 6.3. Mott Schottky plot for films with x = 0.0, 0.4, 0.5, 0.6, 0.8}
v) Barrier-Height Measurement

The difference between the edge of conduction band and the redox fermi level of electrolyte is called barrier height built in potential, $\phi_B$ is determined using relation[36-37]:

$$I_0 = AT^2 \exp \left( -\frac{\phi_B}{kT} \right) \quad \ldots (6.9)$$

Where, $A$ is Richardson constant, $k$ is Boltzmann constant. The reverse saturation current flowing through circuit is dependent on the temperature ($T$) exponentially. Thus the barrier height can be determined by measuring the reverse saturation current ($I_0$) of a junction at different temperatures. The plot of $\ln(I_0/T^2)$ versus $1000/T$ could give the values of $\phi_B$ Accordingly Figure 6.4 shows the variation of $\ln(I_0/T^2)$ vs. 1000/T for few representative photoanodes. All the plots exhibited linear variation. The values of flat band were found to between 411-715 mV. The ZnHgTe electrode with $x=0.6$ has shown maximum magnitude for barrier height. The value agrees well with those estimated from Eq. 6.7.

![Graph](image_url)

**Fig. 6.4. Log$I_0/T^2$ Vs $10^3/T$ plots for x = 0.0, 0.2, 0.4, 0.6, 0.8 & 1.0.**
The plot of \( \ln \left( \frac{I_0}{T^2} \right) \) Vs \( 1000/T \) is nonlinear at high temperature regions indicating that the conduction is influenced by Pool-Frankel type conduction mechanism.

vi) Power Output Characteristics

A PEC cell consisting ZnHgTe as photoanode, carbon rod as cathode and ferro-ferricyanide as electrolyte when illuminated with a light of constant intensity greater that the bandgap of the photoelectrode, the cell develops a potential across an external load and a current flows through it. The I-V characteristic shifts in the fourth quadrant and the cell act as generator of electricity. The output characteristics of all the cells were recorded under a constant illumination of 30 mW/cm\(^2\), few of them are shown in Fig. 6.5. The area under the I-V curve gives the total power available to a PEC cell. The maximum power available is determined by a point on the curve where a product of I-V is maximum (usually done by drawing a square, the edge of it touches a point where I-V is maximum). The values of I and V corresponding to this points are called as \( I_m \) and \( V_m \) respectively.

![Power output curve for PEC cells with x= 0.2, 0.4, 0.6, 0.8.](image)

Fig. 6.5. Power output curve for PEC cells with x= 0.2, 0.4, 0.6, 0.8.
The various open circuit photovoltage ($V_{oc}$) is the cell voltage at $I = 0$ and short circuit photocurrent ($I_{sc}$) is the cell current at $V = 0$. The conversion efficiency ($\eta$) is defined as the ratio of power output to power input. The power output is the product of $V_m I_m$. As power input is known (i.e. 30 mW) the efficiency can be calculated.

$$\eta = \frac{\text{Power output}}{\text{Input power}} = \frac{V_m I_m}{\text{Input power}} \quad \ldots(6.10)$$

Another important parameter is fill factor (FF), which is defined by relation;

$$\text{FF} = \frac{I_m V_m}{I_{sc} V_{oc}} \quad \ldots(6.11)$$

For an ideal device the I-V curve under suitable load should exhibit a rectangular form so that FF should be as large as possible. The series resistance ($R_s$) and shunt resistance ($R_{sh}$) were evaluated from the slope of the power output curve at $I_o$ and $V_o$. They are defined by relation;

$$\frac{1}{R_s} = \left[ \frac{dI}{dV} \right]_{I=0} \quad \ldots(6.12)$$
$$\frac{1}{R_{sh}} = \left[ \frac{dI}{dV} \right]_{V=0} \quad \ldots(6.13)$$

All the PEC parameters have been determined and are included in Table 6.1. It is observed that $V_{oc}$ and $I_{sc}$ have been boosted significantly at $x = 0.6$, but decreased thereafter. The cell efficiency was maximum for $x = 0.6$. 
Fig. 6.6. Efficiency plot for ZnHgTe PEC cells

It is observed that films with x = 0.6 showed highest efficiency of ~3.0%.

The values of FF increases with composition parameter ‘x’ with maximum at x = 0.6, thereafter decreases. For a cell with n type photo-electrode, larger the values of $V_{th}$, higher is the value of open circuit photovoltaic contributing to power conversion efficiency. The increase in photocurrent in the present case for x= 0.6 can be attributed to approaching of the magnitude of band gap (to match the maximum of solar cell spectrum), enhanced photosensitivity due to increased absorption and lower electrical resistivity. Although we have improved the photo electrochemical performance at x = 0.6, the observed conversion efficiencies are quite smaller than those reported for binary systems. It is to be noted that no previous reports are available for the PEC study of chemically deposited films. A lower performance is attributed to current leakages across semiconductor surface, presence of grain boundaries, high values of series resistance and lack of post depositional treatments.
6.4.2 Optical properties- Photo-response

The lighted junction ideality factors were determined for all cell configurations under various white light intensities in forward biased condition (V<0). The PEC cell under illumination can be modeled as a Shottky-Barrier solar cell and therefore I-V characteristic can be approximated as:

\[ I = I_{ph} - I_0 \exp \left( \frac{qV}{n_d kT} \right) + 1 \]  \hspace{1cm} (6.14)

Where, \( I, I_{ph}, I_d, I_0, V, n_d \) are net current density, photocurrent density, dark current density, reverse saturation current density, applied bias voltage and junction ideality factor respectively. The \( I_{ph} \) is opposite in sign to dark current and is equal to the product of the absorption flux and the charge on electron. The open circuit voltage is a measure of the maximum Gibbs free energy that can be obtained from the cell. At open circuit voltage, the net current \( I \) is zero, therefore putting \( I = 0 \) and treating \( V \) as \( V_{oc} \), we can rearrange equation 6.14 to:

\[ V_{oc} = \left( n_o kT/q \right) \ln \left( \frac{I_{sc}}{I_0} \right) \]  \hspace{1cm} (6.15)

Where, \( V_{oc} \) is open circuit voltage, \( I_{sc} \) is short circuit current. As \( I_{sc} \gg I_0 \), a plot of \( \ln I_{sc} \) Vs \( V_{oc} \) should give a straight line and from the slope of the line, the junction lighted ideality factor can be obtained. For an ideal device the lighted junction ideality factor should be unity. Figure 6.7 shows the plot of \( \ln I_{sc} \) vs. \( V_{oc} \) for few representative photo-electrodes. The calculated values of \( n_o \) are depicted in Table 6.1. The short circuit current is seen to be an approximate linear function of light intensity.
Fig. 6.7 shows the plot of log I Vs V for few ZnHgTe photo-electrodes

6.5 Conclusion

A PEC cell was constructed using the Zn$_{1-x}$Hg$_x$Te 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 ($\eta_a$) 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/cm$^2$ illumination intensity. The various performance parameters viz $V_{oc}$, $I_{sc}$, $\eta\%$, 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.
Chapter VI: Photoelectrochemical Properties of Zn$_{1-x}$Hg$_x$Te Thin Films
References


