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Archives of Applied Science Research, 2012, 4 (2):951-959
(http://scholarsresearchlibrary.com/archive.html)

ISSN 0975-508X
CODEN (USA) AASRC9

Photo-electrochemical properties of $Zn_{1-x}Hg_xTe$ thin films

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ABSTRACT

The zinc based II-VI group semiconductor compounds and their alloys are considered as potential candidates for solar application purpose. A solar to electrical energy conversion route using semiconductor- electrolyte junction is the easiest way to harness solar energy. In view of this we report the photo-electrochemical properties $Zn_{1-x}Hg_xTe$ ($0<x<1$) thin film photo-electrodes. A carbon rod as counter electrode and potassium ferro-ferricyanide as electrolyte was used. The PEC parameters studied were I-V characteristics, C-V characteristics, Mott Schottky characteristics and power output curves. The analysis of results indicated considerable improvement in the energy conversion efficiency for $Zn_{0.4}Hg_{0.6}Te$ photoanode.

Key words: Semiconductors, Solar Cell, Photo-electrochemical cells, Mott-Schottky plots.

INTRODUCTION

The zinc blende compounds and their alloys obtained by replacement of their cations with other suitable cation are promising semiconductor for various thin film optoelectronic devices such as light emitting diodes, photo-detectors and solar cells [1, 2]. The conversion of photon of light into electrical energy may occur either using solid-solid junction (called Solar cells) or solid -liquid junction (called Photo-electrochemical cell, PEC). A simple type of cell has a semiconductor and an inert metal or another semiconductor as counter electrode in contact with an electrolyte. A semiconductor with proper band gap (matching to maximum of solar spectrum), better conductivity and a reversible electrolyte are essential requirements of a PEC cell. A PEC cell find many advantages over the conventional solar cell such as; i) it is simple to set up, ii) semiconductors of different morphology can be used, iii) special processing on semiconductor is not needed, iv) the cell is not much sensitive toward defects, lattice mismatch etc, v) the Fermi level potential can be adjusted by suitably choosing electrolyte, vi) the potential of working electrode with respect to reference electrode also can be adjusted [3]. Thus a PEC cell seems to be cheaper as no sophistication is required, this also enables a semiconductor chemists to make the study of energetic and chemistry of semiconductor-electrolyte interface easily [4,5]. The efficiency and stability of a PEC are strongly dependent on the nature of the photoelectrode, electrolyte and experimental conditions set during the experimentation [6].

The solar to electrical conversion using semiconductor-electrolyte junction was first demonstrated by Gerischer and Eills [7,8], since then a large number of II-VI and III-VI group metal chalcogenides and oxides have been investigated for solar applications. A solid-liquid junction utilizing polycrystalline material is demonstrated to have efficiency as high as 70% of a single crystal of the same material [9]. The use of nano-structured thin film semiconductor materials also have shown attractive performance [10,11].

The zinc telluride is widely used in modern solid state devices due to its excellent characteristics such as large energy gaps, low resistivity, high transparency in visible spectral domain [12, 13]. The mercury telluride, on the

other hand, is a semimetal with low resistivity and high charge carrier concentration can form a complete range of solid solution with zinc telluride [14]. The resulting solid solution, however, despite of its number of advantages over the similar alloy (e.g. CdHgTe) has received less attention [15]. So far several investigations on PEC properties of II-VI ternary materials [16,17] are available in literature, however the report on use of ZnHgTe for PEC is scare.

In the present paper, we report on the photo-electrochemical properties of $Zn_{1-x}Hg_xTe$ thin film photo-anodes for the first time.

MATERIALS AND METHODS

2.1. Preparation of Photo-electrode

Thin films of $Zn_{1-x}Hg_xTe$ [i.e.$0 \leq x \leq 1$] have been obtained on stainless steel substrates of size 12*50*1mm size. For getting the deposits, the method described in our previous investigations [18] was used.

2.2. PEC Cell Construction

A $Zn_{1-x}Hg_xTe$ photoelectrode with 1 cm^3 unmasked surface and a carbon rod as counter electrode was placed in a square quartz cuvette (50 ml capacity) containing 0.1M potassium ferro-ferricyanide redox solution in 0.1 M KOH. The distance between two electrodes was kept at least 3 mm. The electrical contacts were made by applying silver paste on electrodes.

3. PEC Cell Characterization

The PEC was characterized by measuring current voltage characteristics (I-V), capacitance voltage characteristics (C-V) in dark as well as in light, built in potential 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 of 30 mW/cm^2 intensity. The flat band potential was estimated from the MS plot. The lighted ideality factor (n_L) which determines the ideality of the junction is determined by measuring photo-response of all the $Zn_{1-x}Hg_xTe$ photo-electrodes. The short circuit current (I_{sc}) and open circuit voltage (V_{oc}) were measured as a function of incident light intensity.

RESULTS AND DISCUSSION

3.1Electrical 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 [19]. The nature of contact between photo-electrodes and substrate has been examined in the form of current-voltage relationship (Fig.1). The plot was found to be almost linear in both the directions indicating that the contact is ohmic.

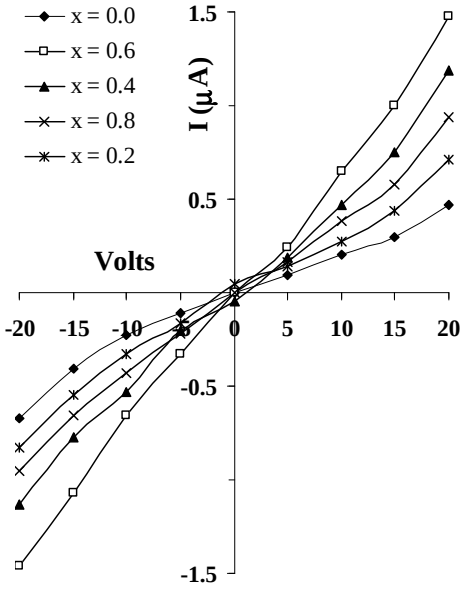

Fig.1: Nature of contact between stainless steel and different photo-electrodes (with x = 0.0, 0.2, 0.4, 0.6 & 0.8)

ii) Conductivity Type of Cell

A photo-electrode semiconductor, dipped in an electrolyte on illumination generates charge carrier within the cell, which lead to development of photo-potential and current (cell is acting as "converter" of light energy to electrical energy). In absence of light the cell should not produce any emf. However, a small emf and current is developed in PEC cell in dark condition for all photo-electrodes. This residual charge transfer is due to difference in emf potentials of two half cell formed, namely $E_{Graphite}$ and E_{ZnHgTe}. The polarity of cell was –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 [20].

iii) Current-Voltage (I-V) Characteristics

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 [21] as;

$$I = I_0\{[\exp (1-\beta) V_f/RT] – \exp [\beta V_F/RT] \} \quad \ldots (1)$$

Where, I_0 is equilibrium exchange current density, V is the over voltage, β is a symmetry factor, R is universal gas constant and F is Faradays constant. A value of β = 0.5 corresponding to presence of a symmetrical barrier, giving a symmetrical current voltage curve. While values of β > 0.5, I-V is nonlinear (nonsymmetrical) so that the interface can be called as rectifying nature. Figure 2 shows I-V characteristics of few representative films. The plot show non symmetrical nature in dark indicating that the junction formed is of rectifying type [22]. The presence of unsymmetrical I-V nature (non-ohmic/ rectifying) predicts that the junction has been formed between photoelectrode and electrolyte. As the cell is illuminated, the I-V characteristics shifts to IV^{th} quadrant indicating that the photogenerated carriers are also formed.. The photo-electrode 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.

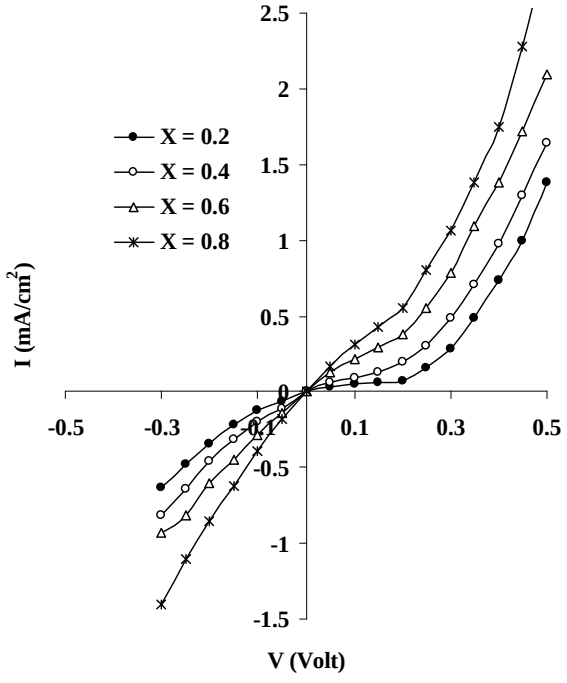

Fig. 2: I-V Characteristics in dark for films with x = 0.2, 0.4, 0.6, 0.8

The semiconductor-electrolyte junction is analogues to a schottky barrier [23], therefore we can represent I-V relation by equation;

$$I = I_0(e^{eV/nKT} - 1) \quad \ldots(2)$$

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 the last term in equation (2) can be neglected and rewritten as;

$$I = I_0(e^{eV/nKT}) \quad \ldots(3)$$

The validity of equation (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 is shown in Fig. 3.

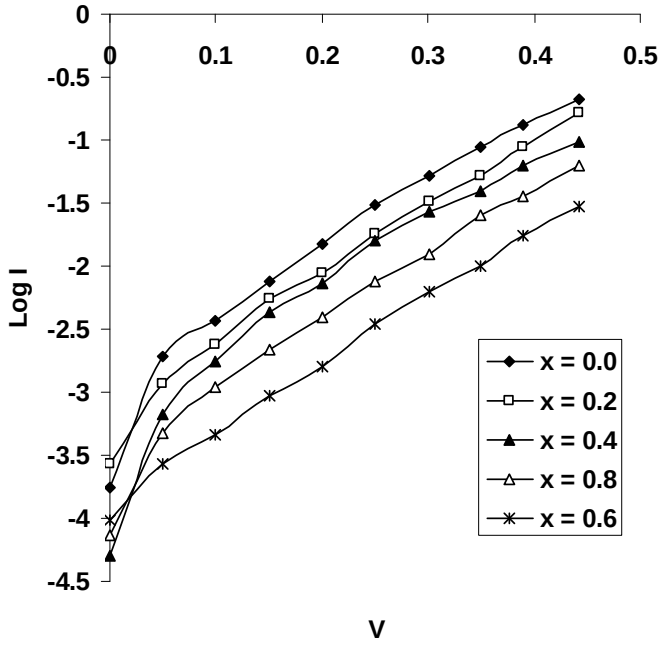

Fig. 3: Log I Vs. V Characteristics for films with x = 0.2, 0.4, 0.6, 0.8

The estimated values for all the compositions are included in table 1. The values of junction ideality factor (in dark often written as n_d) obtained are all higher than ideality value (i.e.1). The values were found to vary systematically with the composition (x) while registering minimum for $Zn_{0.4}Hg_{0.6}Te$ photoanode. A junction ideality factor gives the quality of a junction formed. In general the higher value of n_d 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 [23], 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 giving two type of capacitance. As both are in series, their total capacitance is the sum of their reciprocals. The capacitance due to S-L double layer is small enough to neglect 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 [24]. The measurement of apparent capacitance as a function of potential under depletion condition is based on Mott-Schottky relation;

$$1/C^2_{sc} = 2/e\varepsilon_0\varepsilon_s N\,[V-V_{fb}-(kT/e)] \quad \ldots (4)$$

Where, C_{sc} is the space charge capacitance per unit area, e is the electronic charge, ε_s is dielectric constant of the semiconductor, ε_0 is the permittivity of the free space, N is the donor density, k - Boltzmann constant, T- absolute temperature. The first term in equation (4) is constant, neglecting the term kT/e, the equation can be written as;

$$1/C^2_{sc} = \text{Constant}\,[V-V_{fb}] \quad \ldots (5)$$

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

$$V_b = V_{F,redox} - V_{fb} \quad \ldots (6)$$

Where, $V_{F,redox}$ 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, ϕ_B using relation;

$$\phi_B = V_b + (E_c - E_f) \quad \ldots (7)$$

The slope of a Mott-Schottky plot is given by relation;

$$\text{Slope} = [2/e\varepsilon_0\varepsilon_s N] \quad \ldots (8)$$

The impedance measurements were carried out for all the photo-electrodes at 1 kHz frequency. Figure 4 shows Mott Schottky plot for few of the representative film photo-electrodes. The donor concentration, N, for all the photo-electrodes have been calculated from the equation (8) and is included along with other characteristic values in table 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 photo-electrodes indicating that all the films are n-type in nature. The lowering of V_{fb} for other photo-electrodes 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 donor levels [20]. The observed nonlinear variation in Mott Schottky 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 may lead to modification in the potential across Helmoltz layer [25].

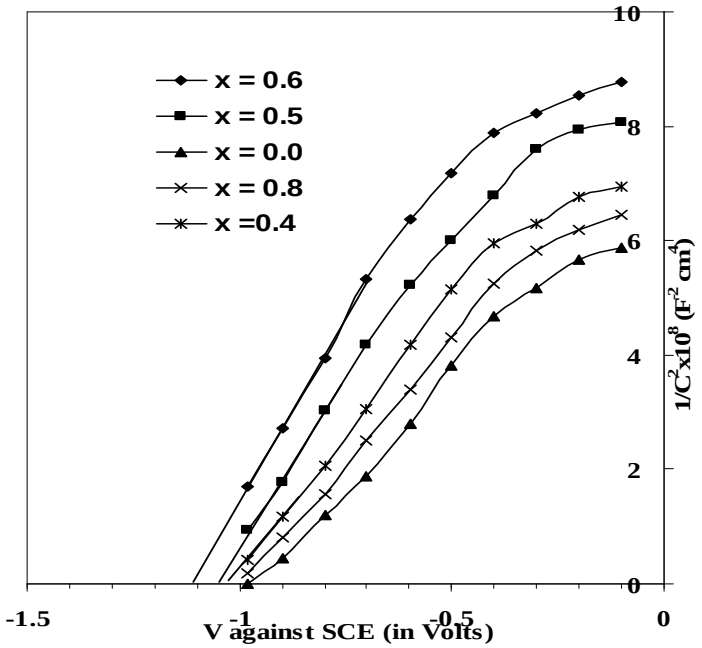

Fig. 4. Mott Schottky plot for films with x = 0.0 ,0.4, 0.5, 0.6, 0.8

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, ϕ_β is determined using relation[26-27];

$$I_0 = AT^2 \exp(-\phi_B/kT) \quad \ldots (9)$$

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 l000/T could give the values of ϕ_B Accordingly figure 5 shows the variation of $\ln(I_0/T^2)$ vs. l000/T for few representative photo-anodes. 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 roughly with those estimated from equation (7).

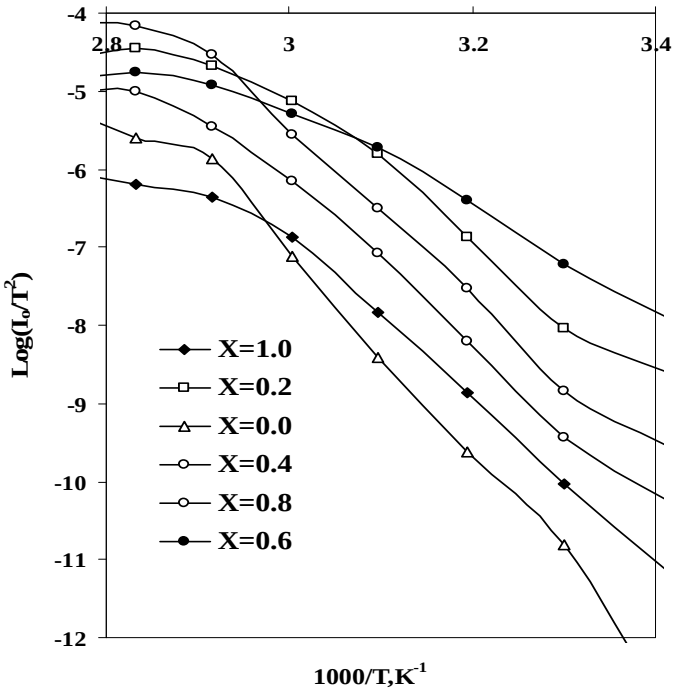

Fig. 5. LogI_0/T^2 Vs $l0^3/T$ plots for x = 0.0, 0.2, 0.4, 0.6, 0.8 & 1.0.

The plot of ln (I_0/T^2) Vs 1000/T is nonlinear at high temperature regions indicating that the conduction is influenced by Pool-Frankel type conduction mechanism.

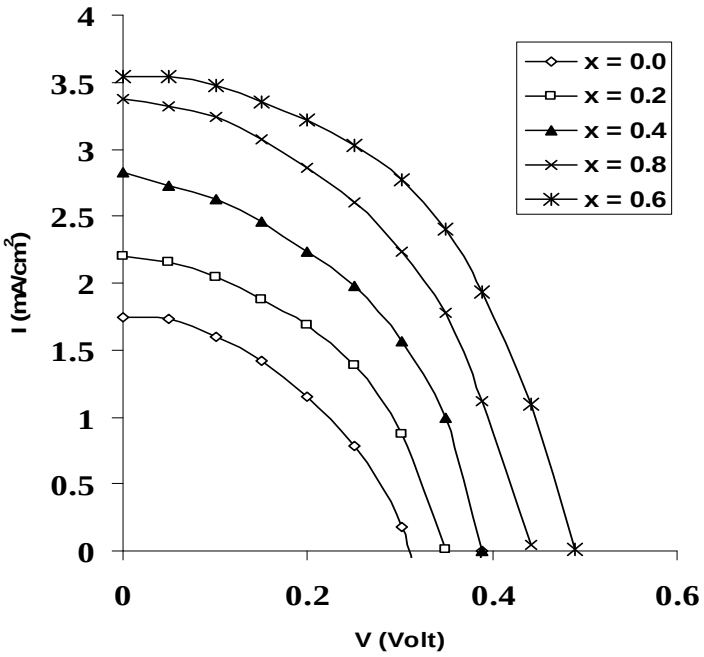

Fig. 6. Power output curve for PEC cells with x= 0.2, 0.4, 0.6, 0.8.

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 band gap 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. 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.

The various open circuit photo-voltage (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 (η) 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.

$$\eta = \text{Power out put / Input power} = V_m.I_m/ \text{Input power} \quad \ldots(10)$$

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

$$FF = I_m V_m / I_{sc} V_{oc} \quad \ldots(11)$$

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 (E_{sh}) were evaluated from the slope of the power output curve at I_o and V_o. They are defined by relation;

$$1/ R_s = [\, dI/dV]_{I=0} \quad \ldots(12)$$
$$1/ R_{sh} = [\, dI/dV]_{v=0} \quad \ldots(13)$$

All the PEC parameters have been determined and are included in Table 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. 7).

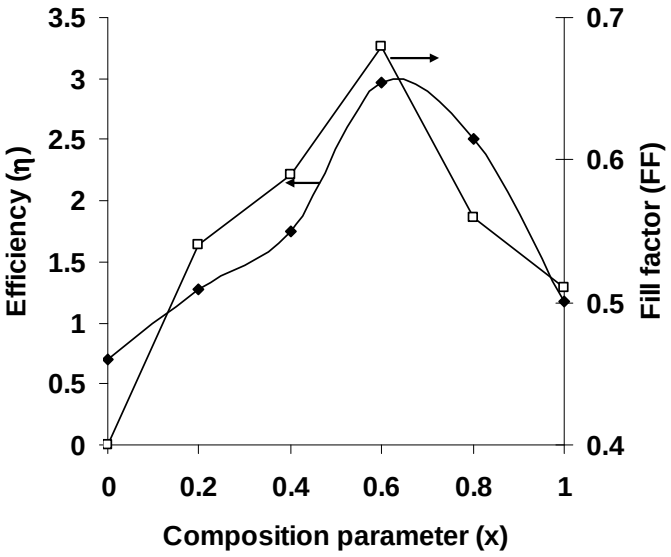

Fig. 7. Efficiency plot for ZnHgTe PEC cells

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_{fb}, higher is the value of open circuit photo-potential 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 electro chemical 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.

3.2 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 ;

$$I = I_{ph} - I_o [\exp (qV/n_dkT) - 1] \quad \ldots (14)$$

Where, I, $I_{ph,}$ $I_{d,}$ $I_{o,}$ 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 (14) to;

$$V_{oc} = (n_LkT/q) \ln[(I_{sc}/I_o)+1) \quad \ldots(15)$$

Where, V_{oc} is open circuit voltage, Isc is short circuit current. As I_{sc} >> I_o, 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 8 shows the plot of ln I_{sc} vs. V_{oc} for few representative photo-electrodes. The calculated values of n_L are depicted in Table 1.The short circuit current is seen to be an approximate linear function of light intensity.

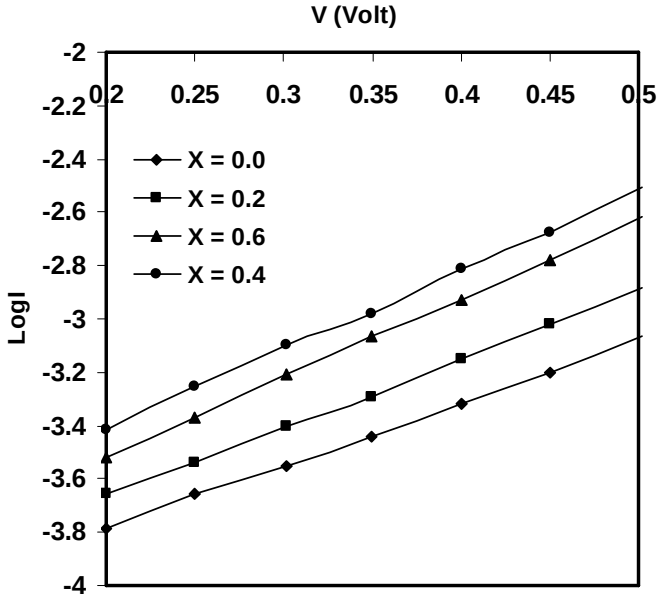

Fig. 8 The plot of log I Vs V for few ZnHgTe photo-electrodes

Table 1 Various performance characteristics of $Zn_{1-x}Hg_xTe$ photoelectrode based PEC cell

Sr. No	(x)	V_{oc} (mV)	I_{sc} (mA)	η %	ff %	Φ_B (meV)	V_{fb} (V)	V_b (V)	R_{sh} (kΩ)	R_s (Ω)	n_d
1	0	320	1.75	0.7	0.4	457	0.910	0.54	1.34	532	3.7
2	0.1	338	2.07	1.1	0.42	501	0.984	0.614	1.61	524	3.4
3	0.2	348	2.21	1.28	0.54	589	0.991	0.621	1.54	511	3.1
4	0.3	367	2.55	1.4	0.56	621	1.019	0.649	1.47	491	2.7
5	0.4	389	2.84	1.75	0.59	658	1.029	0.659	1.41	485	2.1
6	0.5	426	3.47	2.1	0.65	700	1.062	0.692	1.52	465	1.9
7	0.6	489	3.52	2.97	0.68	715	1.115	0.745	1.66	451	2.7
8	0.7	470	3.41	2.8	0.59	654	1.068	0.698	1.52	461	2.9
9	0.8	450	3.37	2.5	0.56	569	1.038	0.668	1.41	475	3.2
10	0.9	423	2.98	2.2	0.54	541	0.914	0.544	1.32	486	3.8
11	1	411	2.65	1.17	0.51	411	0.838	0.468	1.12	511	4.1

CONCLUSION

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. For $Zn_{1-x}Hg_xTe$ cell with composition x=0.6, the junction ideality factors (n_d) of 1.9 was found with conversion efficiency of ~3%. The result suggests that a considerable improvement in the energy conversion efficiency is achieved for the composition as $Zn_{0.4}Hg_{0.6}Te$.

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