CHEMICALLY DEPOSITED $CdIn_2Se_4$ THIN FILMS: PHOTOELECTROCHEMICAL APPLICATION

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ABSTRACT
Cadmium Indium Selenide films have been synthesized by chemical bath deposition method by using cadmium sulphate, Indium sulphate, tartaric acid, ammonia and sodium selenosulphate onto stainless steel substrate. The cell configuration is n-CdIn2Se4-NaOH (1M)-S (1M) - Na2S (1M) -C (graphite). The photoelectrochemical characterization of the films is carried out by studying electrical and optical characterization. The lighted ideality factor was found to be minimum for $CdIn_2Se_4$ (Cd/In ratio = 0.5) composition. A cell utilizing photoelectrode of composition showed a wider spectral response and high short circuit current. These studies indicates that the $CdIn_2Se_4$ thin films are n-type in conductivity.

KEY WORDS: Chemical bath deposition, Efficiency, Photoelectrochemical cell, Spectral response.

INTRODUCTION

PEC system can be characterized not only by the semiconductors but often also by electrolytic limitations and substantial improvements of the PEC energy conversions which are attained by understanding and optimizing solution phase phenomenon. The properties of such systems are critically dependent on the interface formed between the semiconductor and the electrolyte; hence from the material science point of view, the microstructure of semiconductor surface is of main importance. Since any practical application of solar energy conversion has to rely on polycrystalline semiconductor films, the electrode behavior of such layers developed by soft growth technique like chemical bath deposition has to be determined in detail (Dass , 2004).

In last decade, construction of PEC cells with the aid of active semiconductor-electrolyte junction has been advanced as an alternative to well known method of energy conversion involving the use of solid state semiconductor solar cells. The alternative method was searched because the usual solar cells are manufactured from highly pure and perfect crystalline materials & p-n junction is obtained by using sophisticated technology. For this reason they are quite costly. Simple in construction, absence of lattice mismatch, possibility of adjustment of Fermi level by suitably choosing redox electrolyte, no requirement of coating are the advantage of these cells. Semiconductor electrolyte interface may be used for photoelectrolysis, photocatalysis & photoelectrochemical power generation. (**Kale, 2006).** The direct conversion of solar energy into electrical current using semiconductor-electrolyte interface was first demonstrated by Gerischer & Eills. (Gurierrez, 1990) Since then a large number of metal as well as mixed chalcogenide & oxides have been used as photoelectrode in PEC cells. The stability & efficiency of PEC cells are mainly dependent on preparation conditions for photoelectrode, electrolyte & experimental conditions set during the experiment. The low restitivity of the photoelectrode required to minimize the series resistance of the PEC cell which leads to lower the short circuit current. (Lokhande, 1987) In PEC cells, the use is made of the interface which is formed on merely dipping the semiconductor into electrolyte solution & liquid junction potential barrier can be easily set up. Polycrystalline semiconductor film can be used without any drastic decrease in efficiency. Binary & ternary chalcogenide semiconductors of II-VI have received widespread interest in the field of PEC. Single crystals as well as polycrystalline thin films are giving good response.

This paper deals with photoelectrochemical performance of $CdIn_2Se_4$ thin film. I-V, C-V characteristics in dark, power output curves, barrier height measurements, photoresponse, spectral response study.

Experimental Details

Preparation of $CdIn_2Se_4$ photoelectrode

The deposition of $CdIn_2Se_4$ thin films was made in a reactive solution obtained by mixing 5ml (0.02M) cadmium sulphate, 10 ml (0.02M) indium trichloride, 2.5 ml (1M) tartaric acid, 10 ml (10%) hydrazine hydrate and 20 ml (0.25M) sodium selenosulphate. The total volume of the reactive mixture was made up to 100 ml by adding double distilled water. The beaker containing the reactive solution was transferred to an ice bath at 278 K temperature. The pH of the resulting solution was found to be 11.80±0.05. To obtain the film, four FTO glass substrate were positioned vertically on a specially designed substrate holder and rotated in a reactive solution with a speed of 55±2 rpm. The temperature of the solution was then allowed to rise slowly to 293K. The substrates were subsequently removed from the beaker after 2 hours of deposition. The films obtained were washed with distilled water, dried in air and kept in a desiccator.

Fabrication of PEC Cell

It consists of H-shaped glass tube. One of the arms of the tube was made from hard glass having diameter of size 2.7 cm and length 7 cm and other is ordinary test tube of inner diameter 1.5 cm and length 7 cm. This H-shaped glass container was fitted in a copper pot. A window having the dimension of 2 cm x 1.5 cm was made available for illumination of the photoelectrode. The cell can be represented as

$$\text{n- }CdIn_2Se_4 \mid NaOH\ (1M) + S\ (1M) + Na_2S\ (1M) \mid C_{(graphite)}$$

Counter electrode is constructed by using a graphite rod sensitized in a medium containing concentrated CoS solution for 24 hours. A rubber cork was used to make the cell air tight and to support both the counter and photoelectrode. The active area of the size 1 x 1 cm^2 was exposed to light. The remaining part of the film was masked by the use of common epoxy resin.

Characterization of PEC Cell

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 & power output characteristics under illumination were studied. A wire wound potentiometer was used to vary the voltage across the junction & current flowing through the junction was measured with a current meter. The same circuit was used to determine the capacitance of the junction. Photoresponse for all the samples were measured to determine the light ideality factor. The short circuit current & open circuit voltage were measured as a function of incident light intensity. Spectral response was determined by measuring the short-circuit current as well as open circuit voltage as a function of incident wavelength. (400-900 nm).

RESULTS AND DISCUSSION

The nature of contact of the photoelectrode with substrate was examined for all samples. The nature of contact of the photoelectrode with substrate was examined for all samples.

Electrical Properties

I-V characteristics in Dark

Current-voltage (I-V) characteristics of PEC have been studied at 303 K. The dark voltage and dark current were found to develop. The dark voltage is developed due to difference between two half-cell potential of a cell **(Darkowski, 1991)**

$$E = E_{CdIn2Se4} - E_{carbon} \text{ ----------------------------------3.1}$$

Where, $E_{CdIn2Se4}$, E_{carbon} are the half-cell potential of photoelectrode and counter electrode respectively. Half-cell potential is developed when the electrode is directly in contact with the electrolyte. But,

$$E_{CdIn2Se4} > E_{carbon} \text{ -----------------------------------3.2}$$

After illumination of the junction, the magnitude of voltage increases with increase in negative polarity towards the thin film. The sign of this photovoltage gives the conductivity type of $CdIn_2Se_4$. This indicates that $CdIn_2Se_4$ is an n-type conductor which has also been proved from TEP measurement studies.

The presence of dark current is an indication of some deterioration of the photoanode in the electrolyte. Considering semiconductor-electrolyte interface analogous to metal-electrolyte interface, the current transport mechanism through the interface can be defined by a Butler-Volmer relation;

$$I = I_0 [\exp (1-\beta) VF/RT] \exp (-\beta VF/RT) \text{ ------------------- 3.3}$$

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 Faraday constant. A value of β equal to 0.5 corresponds to presence of a symmetrical barrier, which yields a symmetrical current-voltage curve. If $\beta > 0.5$, the current versus voltage should not be symmetrical and interface is said to have a rectifying properties called as Faradic rectification. The dynamic current-voltage characteristics were studied for typical samples in dark at room temperature and are shown in Fig.1. The characteristics are non-symmetrical indicating the formation of rectifying type junction. In the present investigation β factor was found to be greater than 0.5 for all compositions suggesting the rectifying nature of the interface.

The junction ideality factor (n_d) can be determined from the plot of log I with voltage (V) and the variation is shown in Figure 2. Linear nature of plot was used for the estimation of junction ideality factor. The ideality factor was found to be minimum for $CdIn_2Se_4$ (Cd/In ratio = 0.5) composition. The higher value of (n_d) suggest the dominance of series resistance as well as the structural imperfection individual by dissimilarities in Cd and In atomic sizes and their resulting arrangement in the solid during lattice construction. The junction ideality has a minimum value for $CdIn_2Se_4$ (Cd/In ratio = 0.5) suggesting lowest trap density at the photoelectrode-electrolyte interface (**Hankare, 2006)**. The junction ideality varies from 2.96 to 3.28.

Table 1 Various performance parameter of $CdIn_2Se_4$ photoelectrode

Film	Cd/In ratio	V_{oc} (mV)	I_{sc} (μA)	η %	ff %	Φ_β (eV)	V_{fb} (V)	R_{sh} (Ω)	R_s (Ω)	n_L	n_d
CdSe	-	260	169	0.55	36.91	0.186	0.700	550	823	2.94	**3.28**
In_2Se_3	-	293	180	0.61	37.64	0.196	0.720	500	740	2.78	**3.24**
$CdIn_2Se_4$	0.4	305	225	0.74	38.54	0.199	0.742	482	698	2.69	**3.09**
$CdIn_2Se_4$	0.45	342	232	0.82	38.90	0.200	0.768	458	654	2.50	**3.00**
$CdIn_2Se_4$	**0.5**	**382**	243	**0.94**	**39.65**	**0.205**	**0.789**	**405**	**600**	**2.34**	2.96
$CdIn_2Se_4$	0.55	282	175	0.86	37.75	0.201	0.751	489	694	2.58	**3.07**
$CdIn_2Se_4$	**0.6**	**278**	**170**	**0.62**	**35.87**	**0.191**	**0.710**	**504**	**790**	**2.67**	**3.13**

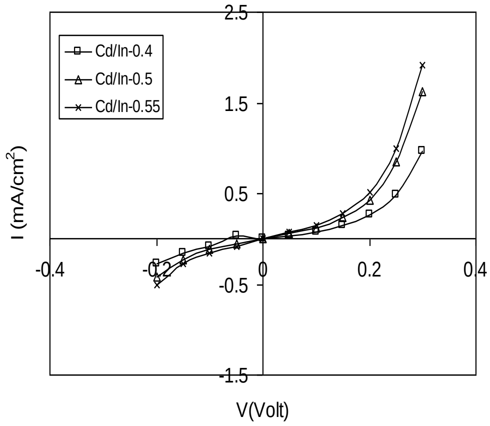

Figure 1. Current-voltage characteristics of $CdIn_2Se_4$photoelectrode (in dark)

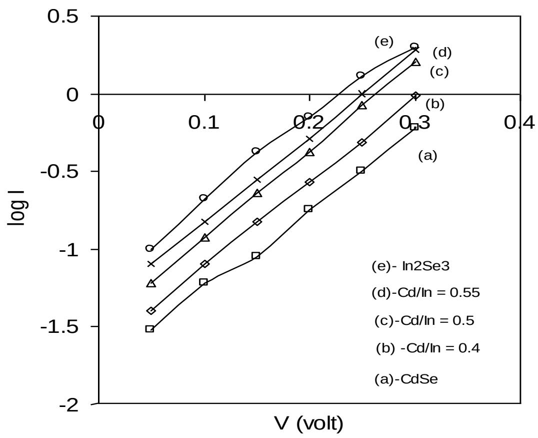

Figure 2. Plot of log I with Voltage of $CdIn_2Se_4$ cells

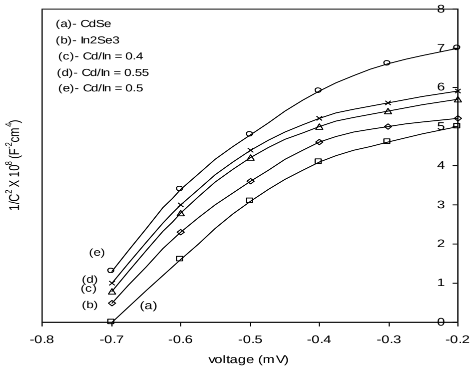

Figure3. 1/C^2 versus d.c.bias voltage of $CdIn_2Se_4$ cells.

C-V Characteristics in Dark

The capacitance-voltage measurements were carried out using these cells to evaluate the flat band potential (V_{fb}) parameter which yields in formation about the relative positions of the fermi levels of the semiconducting material as well as the influence of an electrolyte in terms of band bending due to surface interactions. The intrinsic bond bending of the interface is used to determine ability of photoelectrode to operate under the short circuit condition. This is also useful to measure the maximum open circuit voltage (V_{oc}) that can be obtained from a cell. Measured capacitance is the sum of the capacitance due to depletion layers and Helmholtz layer in electrolyte which is neglected by assuming high ionic concentration (**Lade, 2001**). Under such circumstances, V_{fb} can be obtained using Mott-Schottky equation;

$$C^{-2} = [2/q\varepsilon\varepsilon_0 N_d] (V- V_{fb}-kT/q) \text{ ----------------------------3.4}$$

Where symbols have their usual meaning. The charge space layer capacitance was measured under reverse biased condition and the flat band potential is obtained from the Mott-Schottky plot. The variation of C^{-2} with Voltage for representative samples is shown in Fig.3. Intercepts of plots on voltage axis determine the flat band potential value of the junction. The flat band potential value was observed maximum for $CdIn_2Se_4$ (Cd/In ratio = 0.5). The plot suggests presence of two regions and which are attributed to the defect structure and surface state present in the films as shown in Fig. 4. It also suggests that the junctions are graded type.

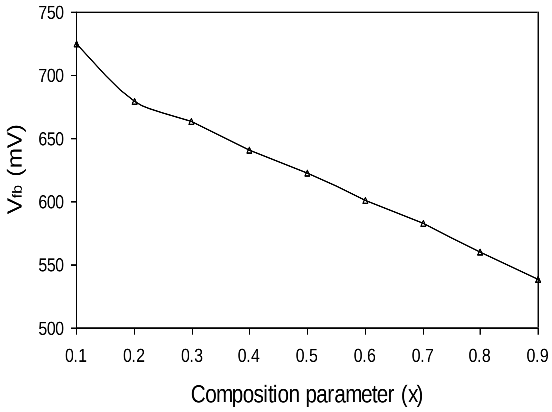

Figure 4. Plot of V_{fb} against composition parameter (x)

Optical Characterization

Photoresponse

The open circuit voltage & short circuit current were measured as function of light intensity. Fig.5 shows variation of Isc as a function of light intensity, whereas, Fig.6 shows the variation of Voc as a function of light intensity. The photoresponse measurements showed a logarithmic variation of open circuit voltage with the incident light intensity. However, at higher intensities, saturation in open circuit voltage was observed, which can be attributed to the saturation of the electrolyte interface, charge transfer & non-equilibrium distribution of electrons & holes in the space charge region of the photoelectrode. But short circuit current follows almost a straight line path. A plot of log Isc against Voc should give a straight line & from the slope of the line the lighted ideality factor can be determined (**Lade S. J., 2001)**. The plot of log Isc with Voc for representative CdIn2Se4 photoelectrode is shown in Fig.7. The junction ideality factor was calculated for all the photoelectrodes & found to be minimum for Cd /In ratio is 0.5 composition. The observed value being 2.94 for x = 0.5 photoelectrode.

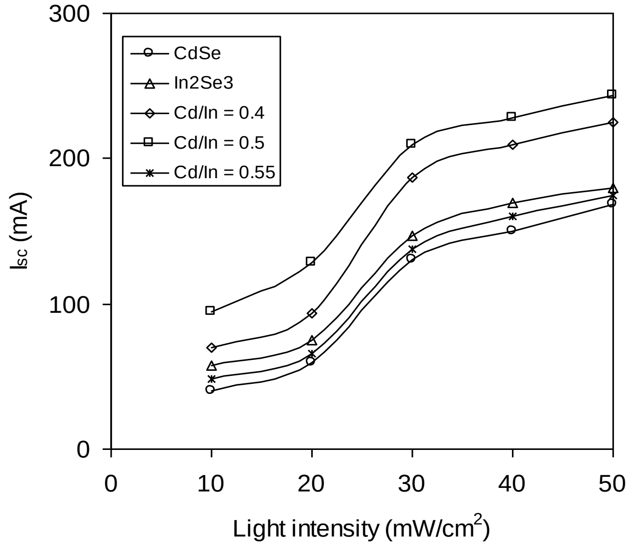

Figure 5. Plot of I_{sc} with light intensity of $CdIn_2Se_4$ photoelectrode

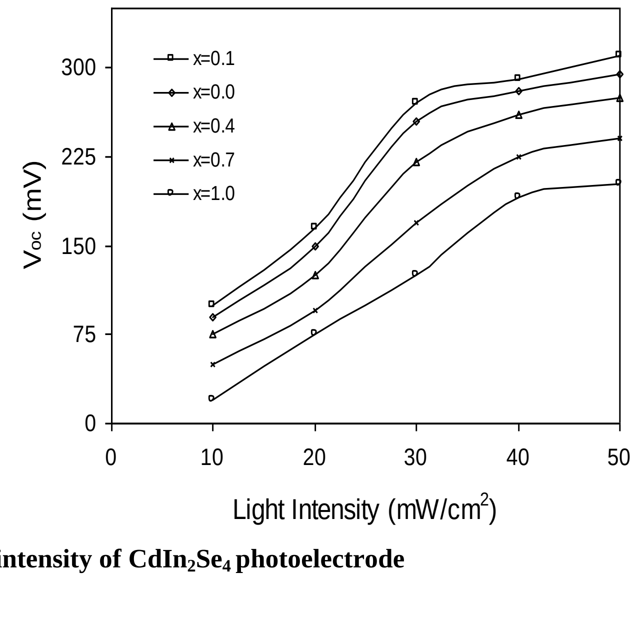

Figure 6. Plot of V_{oc} with light intensity of $CdIn_2Se_4$ photoelectrode

Spectral Response

The spectral response of a cell has been recorded in the 400 to 900 nm wavelength range. The photocurrent action spectra were examined and are shown in Fig. 8. It is seen that spectra attains maximum value of current at λ = 730 nm for CdSe ,527, nm for In_2Se_3 .and $CdIn_2Se_4$

The decrease of current on shorter wavelength side may be due to absorption of light in the electrolyte and high surface recombination of photogenerated minority carriers. The decrease in current on longer wavelength side may be attributed to non-optimized thickness and transition between defect levels (**Lade, 2001)**. The various cell characteristics such as V_{oc}, I_{sc}, η%, ff%, Φ_β, V_{fb}, R_s, R_{sh}, n_L, n_d are cited in Table 1 for photoelectrode.

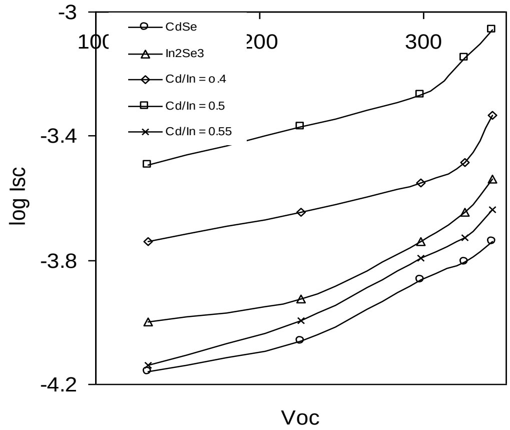

Figure 7. Plot of log Isc with Voc for $CdIn_2Se_4$ photoelectrode

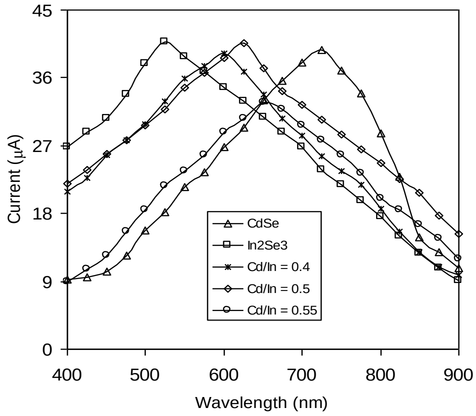

Figure 8. Plot of Isc with wavelength for $CdIn_2Se_4$ photoelectrode

CONCLUSIONS

The PEC cell can be easily fabricated using $CdIn_2Se_4$ photoanode sulphide-polysulphide as electrolyte, CoS treated graphite rod as a counter electrode. A saturated calomel electrode was used as reference electrode. The various performance parameters were determined for all the photoanode. It is found that the fill factor and efficiency is maximum for $CdIn_2Se_4$ (Cd/In ratio = 0.5) composition. This is due to low resistance, high flat band potential, maximum open circuit voltage as well as maximum short circuit current. A cell utilizing photoelectrode of composition showed a wider spectral response and high short circuit current.

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