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Chemical deposition of $CuInSe_2$ thin films by photoelectrochemical applications

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ABSTRACT

Copper indium diselenide films have been synthesized by chemical bath deposition method. The configuration of fabricated cell is n-$CuInSe_2$|NaOH (1 M) + S (1 M) + Na_2S (1 M)|$C_{(graphite)}$. The photoelectrochemical cell characterization of the films is carried out by studying current–voltage characteristics in dark, capacitance–voltage in dark, barrier height measurements, power output, photoresponse and spectral response. The study shows that $CuInSe_2$ thin films are n-type conductivity. The junction ideality factor is found to be 3.81. The flat band potential is found to be 0.763 V. The barrier height value is found to be 0.232 eV. The study of power output characteristic shows open circuit voltage, short circuit current, fill factor and efficiency are found to be 310 mV, 20 μA, 42.12% and 0.82%, respectively. Photoresponse shows lighted ideality factor which is 2.92. Spectral response shows the maximum current observed at 650 nm.

1. Introduction

Copper indium diselenide is a narrow band gap material at room temperature. It is efficiently used in red, and green light emitting diodes, photovoltaics, laser screens, thin film transistor and photoelectrochemical cells [1–5]. In photoelectrochemical cells (PEC), the use is made of the interface which forms by mere dipping the semiconductor into electrolyte solution and the liquid junction potential barrier can be easily established. Polycrystalline semiconductor films can also be used without any drastic decrease in efficiency. This is probably due to the intimate and perfect contact of liquid electrolyte with the crystalline grains. Thus PEC cells provide an economic chemical route for trapping solar energy [6]. Along with PEC the semiconductor–electrolyte interface may be used for photoelectrolysis, photocatalysis and photoelectrochemical power generation [7]. The properties of such systems are mainly dependent on the interface formed between the semiconductor electrode and electrolyte hence from material point of view the microstructure of the photoelectrode surface is of main importance [8]. The advantage of PEC cells is simpler to make as compared to the *p–n* junctions which require highly pure semiconducting material.

We reported the successful deposition of crystalline copper indium diselenide thin films by chemical bath deposition technique. Growth mechanism, structural, morphological, compositional, optical, electrical and thermoelectrical properties are studied [9]. This paper is devoted to the study of photoelectrochemical performance of chemically deposited $CuInSe_2$ photoelectrode, *I–V*, *C–V* characteristics, barrier height measurements, power out curves, photoresponse, and spectral response parameters.

2. Experimental details

2.1. Preparation of $CuInSe_2$ photoelectrode

All the chemicals used for the deposition are of analytical grade. It includes copper sulphate pentahydrate, indium trichloride, tartaric acid, liquor ammonia, hydrazine hydrate, sodium sulfite and selenium powder. All the solutions are prepared in double distilled water. Sodium selenosulphate is prepared by the following method as reported earlier [10]. The deposition of $CuInSe_2$ thin films was made from a reactive solution obtained by mixing 5 mL (0.2 M) copper sulphate, 5 mL (0.2 M) indium trichloride, 2.5 mL (1 M) tartaric acid, 10 mL (2%) hydrazine hydrate and 10 mL (0.25 M) sodium selenosulphate and finally diluted to 80 mL by adding double distilled water. The beaker containing the reactive solution was kept at the room temperature. The pH of the resulting solution was found to be 10 ± 0.05. Four clean stainless steel plates were positioned vertically on a specially designed substrate holder and rotated in a reactive solution with a speed of 50 ± 2 rpm. The temperature of the solution was then allowed to rise slowly to 308 K. After 120 min, the stainless steel plate was removed, washed several times with double distilled water, dried naturally, preserved in dark desiccator over anhydrous $CaCl_2$. The resultant films were homogenous, well adherent to stainless steel substrate.

2.2. Fabrication of PEC cell

Photoelectrochemical cells consist of three electrode configurations which are used in experiment. $CuInSe_2$ as photoanode, CoS-treated graphite rod as a counter electrode. This electrode acts as a photocathode. A calomel electrode is used as reference electrode and sulphide–polysulphide as electrolyte is shown in Fig. 1.

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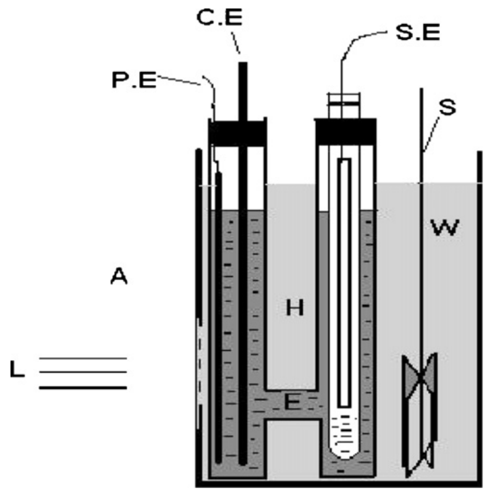

Fig. 1. Fabrication of PEC cell.

2.3. Characterization of PEC cell

The illuminated area of electrode is 3.0 cm^2. The type of conductivity exhibited by the film is determined by noting the polarity of the emf developed in PEC cell under illumination. The Mott–Schottky plot is used to determine the flat band potential 1-kHz frequency is used to determine the flat band potential. The current–voltage (*I*–*V*) characteristic in dark has been plotted. The junction ideality factor has been determined by plotting the graph of log *I* versus *V*. The fill factor and power conversion efficiency of the cell are calculated from photovoltaic power output characteristics. The power output characteristic has been obtained for a PEC cell at a constant illumination of 30 mW/cm^2. The barrier height has been examined from temperature dependence of reverse saturation current at different temperatures. Light ideality factor has been measured from photoresponse. Spectral response has been determined by measuring short circuit current as well as open circuit voltage as function of incident light.

3. Results and discussion

3.1. Conductivity type

A photoelectrochemical cell with configuration n-$CuInSe_2$|NaOH (1 M) + S (1 M) + Na_2S (1 M)|$C_{(graphite)}$ is formed. PEC cell shows dark voltage and dark current even in the dark. The polarity of this dark voltage is negative towards semiconductor electrode. The sign of the photovoltage gives the conductivity type of $CuInSe_2$. This suggests that $CuInSe_2$ is an n-type conductor which has also been proved from TEP measurement studies [11].

3.2. I–V characteristics in dark

Current–voltage (*I*–*V*) characteristics of PEC cell in dark have been studied at 303 K and shown in Fig. 2. The characteristics are non-symmetrical indicating the formation of rectifying type junction [12]. The junction ideality factor (n_d) is determined from the plot of log *I* with voltage and the variation is shown in Fig. 3. The ideality factor is found to be 3.85. The higher value of n_d suggests the dominance of series resistance as well as structural imperfection. It also suggests that average transfer across the semiconductor electrolyte interface with significant contribution from surface states and deep traps [13,14].

3.3. C–V characteristics in dark

The measurement of capacitance as a function of applied voltage provided useful information such as type of conductivity, depletion layer width and flat band potential (V_{fb}). The flat band potential of a semiconductor gives information of the relative position of the Fermi levels in photoelectrode as well as the influence of electrolyte and charge transfer process across the junction. 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 layer and Helmholtz layer in electrolyte which is neglected by assuming high ionic concentration [15]. Under such circumstances, V_{fb} can be obtained using Mott–Schottky relation by standardizing with saturated calomel electrode (SCE).

$$C^{-2} = \left[\frac{2}{q\varepsilon\varepsilon_0 N_d}\right]\left[V - V_{fb} - \frac{kT}{q}\right] \tag{1.1}$$

where symbols have their usual meaning. The variation of C^{-2} with voltage for representative samples is shown in Fig. 4. Intercepts of plots on voltage axis determine the flat band potential value of the junction. The flat band potential value found to be 0.763 V (SCE) for $CuInSe_2$–polysulphide redox electrolyte, which is a measure of electrode potential at which band bending is zero. The non-linear nature of the graph is an indication of graded junction formation between $CuInSe_2$ and polysulphide electrolyte. Non-planar interface, surface roughness, ionic adsorption on the photoelectrode

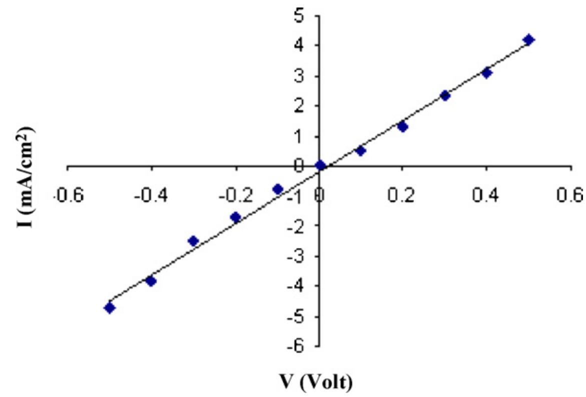

Fig. 2. *I*–*V* characteristics of $CuInSe_2$ photoelectrode (in dark).

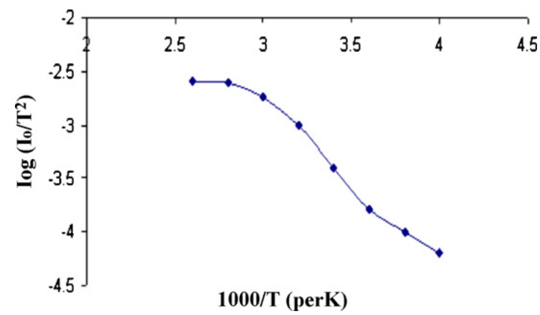

Fig. 3. Determination of junction ideality factor of $CuInSe_2$ photoelectrode.

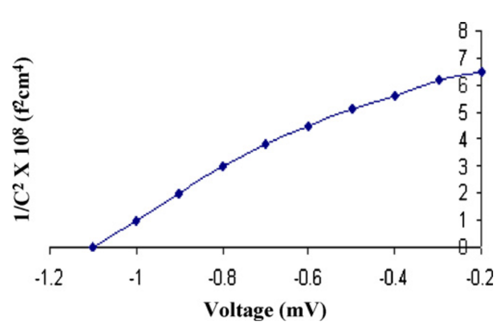

Fig. 4. *C*–*V* characteristics of $CuInSe_2$ photoelectrode.

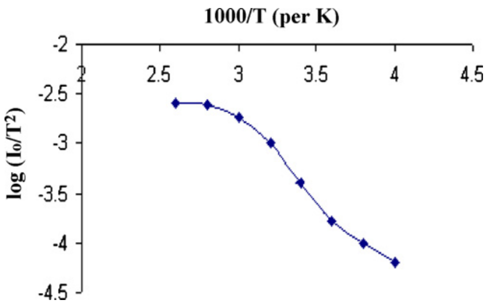

Fig. 5. Determination of barrier height measurement of $CuInSe_2$ photoelectrode.

surface may be possible reasons for deviation from linearity in $C–V$ plot.

3.4. Barrier height measurements

The barrier height is determined by measuring the reverse saturation current (I_0) through the junction at different temperatures from 365 to 305 K. The reverse saturation current flowing through junction is related to temperature as [16,17],

$$I_0 = AT^2 \ \exp\left(\frac{\Phi_\beta}{kT}\right) \tag{1.2}$$

where A is Richardson constant, k is Boltzmann constant, Φ_β is the barrier height in eV. To determine the barrier height of the photoelectrode, a graph of $\log(I_0/T^2)$ with $1000/T$ was plotted. The plot of $\log(I_0/T^2)$ with $1000/T$ for representative sample is shown in Fig. 5. From the slope of the linear region of plot, the barrier height was determined. The barrier height value is found to be 0.232 eV.

3.5. Power out put characteristics

Fig. 6 shows the photovoltaic power output characteristics for a cell under illumination of 30 mW/cm^2. The maximum power output of the cell is given by the largest rectangle that can be drawn inside the curve. The open circuit voltage and short circuit current are found to be 310 mV and 20 μA, respectively. The calculation shows the fill factor is 42.12%. The power conversion efficiency is found to be 0.82%. The low efficiency may be due high series resistance and interface states which are responsible for recombination mechanism. The value of series resistance and shunt resistance are found to be 1.945 (kΩ) and 1.460 (kΩ), respectively. The main drawback in utilizing PEC cell is the absence of space change region at the photoelectrode–electrolyte interface. In this situation, the photogenerated charge carriers can move in both the direction. Kamat [18] reported that the photogenerated electrons in n-type material either recombine readily with holes or leak out into the electrolyte, instead of flowing through external circuit

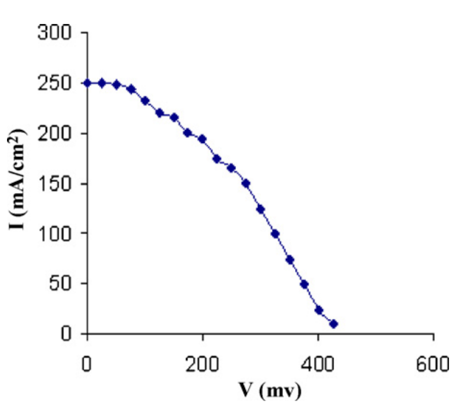

Fig. 6. Power output curves for $CuInSe_2$ photoelectrode.

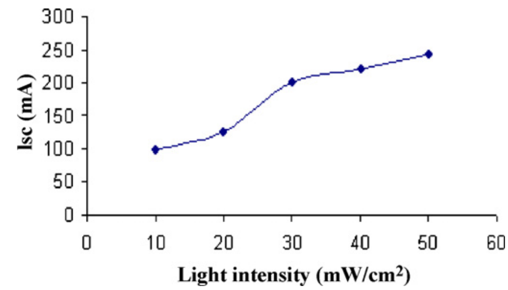

Fig. 7. Photoresponse as a function of short circuit current for $CuInSe_2$ photoelectrode.

3.6. Photoresponse

To study the response of the PEC cell towards light, the cell is illuminated with light of different intensities. The open circuit voltage and short circuit current are measured as function of light intensity. Fig. 7 shows variation of short circuit current (I_{sc}) as a function of light intensity, whereas, Fig. 8 shows the variation of open circuit voltage as a function of light intensity. The photoresponse measurement shows a logarithmic variation of open circuit voltage with the incident light intensity. However, at higher intensities, saturation in open circuit voltage is observed, which can be attributed to the saturation of the electrolyte interface, charge transfer and non-equilibrium distribution of electrons and holes in the space charge region of the photoelectrode. But short circuit current follows almost a straight line path. The photoelectrode–electrolyte interface can be modeled as a Schottky barrier solar cell [19] and it is therefore possible to represent the current–voltage relationship as;

$$I = I_{ph} - I_d = I_{ph} - \left[I_0 \exp\left(\frac{qV}{n_d kT}\right)\right] - 1 \tag{1.3}$$

where I is the net current density, I_{ph} is the photocurrent densities, I_d is the dark current density, I_0 is the reverse saturation current density, V is the applied bias voltage and n_d is the junction ideality factor. In bias voltage condition $V > 3kT/q$ and at equilibrium open circuit conditions:

$$I_{ph} = I_d \text{ and } V = V_{oc} \text{ thus,} \quad V_{oc} = \left(\frac{n_L kT}{q}\right) \ln\left(\frac{I_{sc}}{I_0}\right) \tag{1.4}$$

where V_{oc} is the open circuit voltage and I_{sc} is the short circuit current. As $I_{sc} \gg I_0$, a plot of $\log I_{sc}$ against V_{oc} should give a straight line and from the slope of the line the lighted ideality factor can be determined. The plot of $\log I_{sc}$ with V_{oc} for $CuInSe_2$ photoelectrode

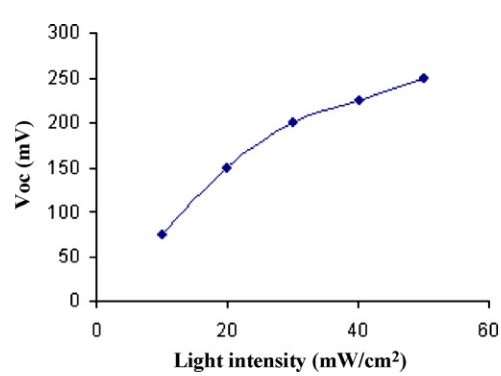

Fig. 8. Photoresponse as a function of open circuit voltage for $CuInSe_2$ photoelectrode.

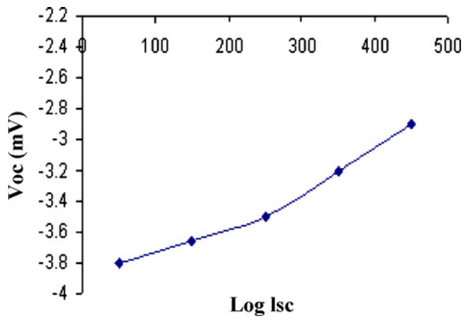

Fig. 9. Determination of lighted ideality factor for $CuInSe_2$ photoelectrode.

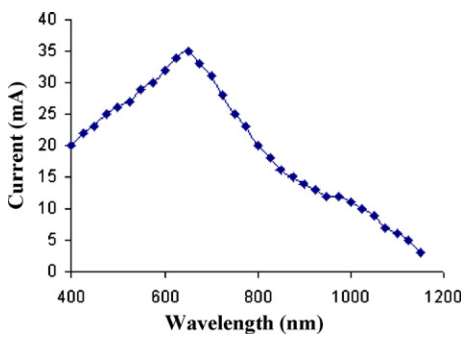

Fig. 10. Determination of spectral response for $CuInSe_2$ photoelectrode.

is shown in Fig. 9. The lighted ideality factor is calculated and found to be 2.92.

3.7. Spectral response

Photoelectrochemical cell is one of the most powerful techniques to measure the performance of the spectral response cell qualitatively. Therefore, the spectral response of a cell has been recorded in the 400–1200 nm wavelength range. The photocurrent action spectra are examined and are shown in Fig. 10. It is seen that spectra attain maximum value of current at $\lambda = 650$ nm and decrease with increase in wavelength. The decrease in current on longer wavelength side may be attributed to non-optimized thickness and transition between defect levels. The maximum current is obtained corresponding to $\lambda = 650$ nm gives band gap value 1.1 eV for agreeing with the results of optical absorption studies [2,9].

4. Conclusions

Copper indium diselenide photoelectrode can be deposited by using copper sulphate pentahydrate, indium trichloride, tartaric acid, ammonia, and hydrazine hydrate and sodium selenosulphate onto stainless steel plate. The photoelectrochemical cell can be easily fabricated using $CuInSe_2$ photoanode, sulphide–polysulphide as electrolyte, CoS-treated graphite rod as a counter electrode. A saturated calomel electrode is used as a reference electrode. The various performance parameters are determined for $CuInSe_2$ photoelectrode.

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