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Photoelectrochemical Study of Chemically Deposited Nanocrystalline Indium Selenide Thin Film

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ABSTRACT: *Nanocrystalline In_2Se_3 films have been synthesized by chemical bath deposition method by using Indium sulphate, tartaric acid, ammonia and sodium selenosulphate onto stainless steel substrate. The cell configuration is n-In_2Se_3-NaOH (1M)-S (1M) - Na_2S (1M) -$C_{(graphite)}$. The photoelectrochemical characterization of the films is carried out by studying electrical and optical characterization. These studies indicates that the In_2Se_3 thin films are n-type in conductivity.*

KEYWORDS: *Thin Film, Chemical bath deposition, Photoelectrochemical cell, fill factor, Spectral response.*

I. INTRODUCTION

The Photoelectrochemical 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 [1- 3].

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. [4-5] The direct conversion of solar energy into electrical current using semiconductor-electrolyte interface was first demonstrated by Gerischer & Eills.[6-7] 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. [8] Determination of electronic parameters of these semiconducting thin films is essential in testing their suitability. PEC cell provide an economical chemical route for trapping solar cells. It consists of a photosensitive n-or-p- type semiconductor electrode & a counter electrode dipped in a suitable electrolyte. 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.

In the presentation investigation, we describe the photoelectrochemical performance of In_2Se_3 thin film. I-V, C-V characteristics in dark, power output curves and barrier height measurements study.

II. EXPERIMENTAL DETAILS

2.1 Preparation of In_2Se_3 photoelectrode

The deposition of In_2Se_3 thin films was made in a reactive solution obtained by mixing 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 upto 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 [9]. The temperature of the solution was then allowed to rise slowly to 293**K**. 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.

2.2 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

$$\text{n- }In_2Se_3 \mid NaOH\ (1M) + S\ (1M) + Na_2S\ (1M) \mid C_{\text{(graphite)}}$$

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.

2.3 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. The barrier height was examined from temperature dependence of reverse saturation current at different temperature; the lighted ideality factor was calculated. The junction ideality for all the cells were determined by plotting the graph of log I versus V. Photoelectrochemical activities were studied under 30 mW/cm^2 light illumination. The illumination intensity was measured with Meco Lux meter.

III. RESULT & DISCUSSION

3.1. Conductivity type

A PEC cell with configuration n-In_2Se_3|NaOH (1 M) + S(1 M) +Na_2S(1M)|$C_{\text{(graphite)}}$ was formed. Even in the dark, PEC cell shows dark voltage and dark current. The polarity of this dark voltage was negative towards semiconductor electrode. The sign of the photovoltage gives the conductivity type of In_2Se_3. This suggests that In_2Se_3 is a n-type conductor which has also been proved from TEP measurement studies [10].

3.2. I–V characteristics in dark

Current–voltage (I–V) characteristics of PEC cell in dark have been studied at 303K and shown in Fig. 1. The characteristics are non-symmetrical indicating the formation of rectifying type junction [11]. The junction ideality factor (n_d) can be determined from the plot of log I with voltage and the variation is shown in Fig. 2. The ideality factor was found to be 3.85 which is higher than earlier reported 1.30 [12-13]. 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 [14,15].

3.3. C–V characteristics in dark

The measurements 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 layers and Helmholtz layer in electrolyte which is neglected by assuming high ionic concentration [16-20]. The variation of 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 found to be −0.530V (SCE) for In_2Se_3–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 $In_2Se_3$and polysulphide electrolyte. Non-planar interface, surface roughness, ionic adsorption on the photoelectrode surface may be possible reasons for deviation from linearity in C–V plot.

3.1.3 Barrier-height Measurement

The barrier-height was determined by measuring the reverse saturation current (I_o) through the junction at different temperature from 363 to 303 K. the reverse saturation current flowing through junction is related to temperature as [21, 22];

$$I_o = AT^2 \exp(\Phi_\beta / kT) \text{ ---------------------------------- } 3.5$$

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_o/T^2) with 1000/T was plotted. The plot of log (I_o/T^2) with 1000/T for representative sample is shown in Fig. 4. From the slope of the linear region of plots, the barrier height was determined.

3.1.4 Power Output Characteristics

Fig. 5 shows the photovoltaic power putout characteristics for a cell under illumination of 30 mW/cm2. 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 153mV and 20_A, respectively. The calculation shows the fill factor is 29.41%. The power conversion efficiency is found to be 0.13%. 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 were found to be 1.941 k_ and 1.452 k_, 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. Lu and Kamat [23] 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.

$$\eta_{max} = (V_{redox} - V_{fb})\,(e/E_g) \qquad \text{----------------------3.6}$$

where V_{fb} is flat band potential, V_{redox} is the redox potential and Eg is the energy band gap [24-25].

IV. CONCLUSIONS

Indium selenide photoelectrode can be deposited by using Indium sulphate heptahydrate, tartaric acid, ammonia, hydrazine hydrate and sodium selenosulphite onto stainless steel plate. The photoelectrochemical cell can be easily fabricated using In_2Se_3 photoanode, sulphide–polysulphide as electrolyte, CoS-treated graphite rod as a counter electrode. A saturated calomel electrode was used a reference electrode. The various performance parameters were determined for In_2Se_3 photoelectrode.

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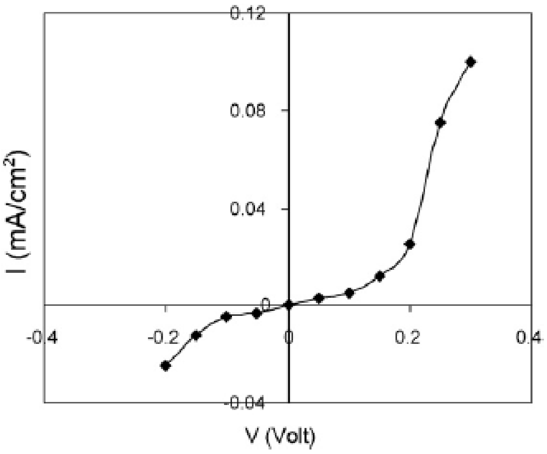
Figure Caption:

Fig. 1. *I–V* characteristics of In_2Se_3 photoelectrode (in dark).
Fig. 2. Determination of junction ideality factor of In_2Se_3 photoelectrode.
Fig. 3. *C–V* characteristics of In_2Se_3 photoelectrode.
Fig. 4. Determination of barrier height measurement of In_2Se_3 photoelectrode.
Fig. 5. Power output curves for In_2Se_3 photoelectrode.



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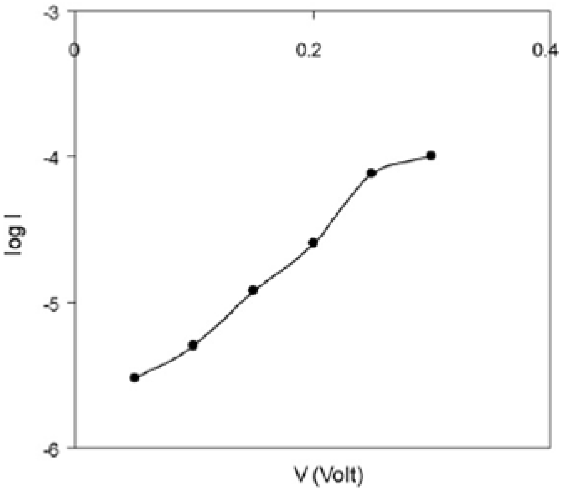

Fig. 2. Determination of junction ideality factor of In_2Se_3 photoelectrode.

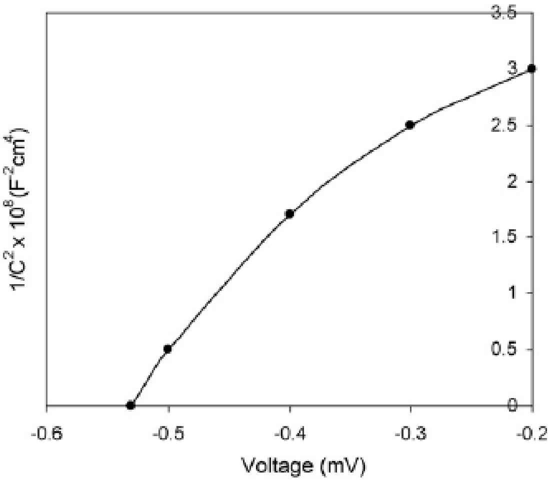

Fig. 3. *C–V* characteristics of In_2Se_3 photoelectrode.

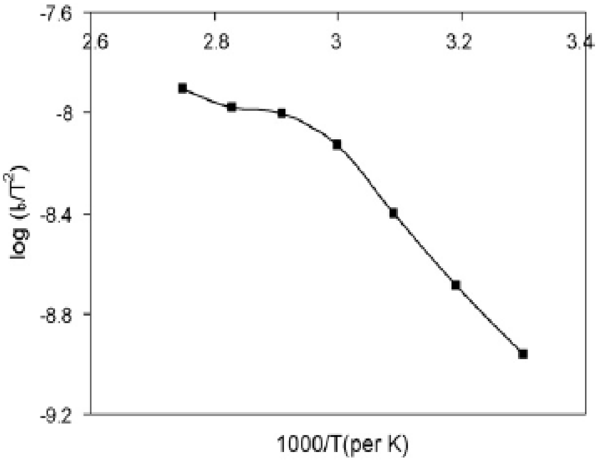

Fig. 4. Determination of barrier height measurement of In_2Se_3 photoelectrode.

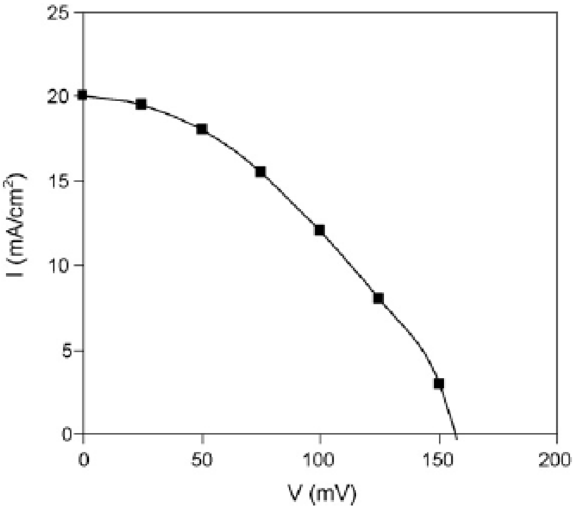

Fig. 5. Power output curves for In_2Se_3 photoelectrode.