Photoelectrochemical Study of Chemically Deposited Nanocrystalline Indium Selenide Thin Film

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ABSTRACT: Nanocrystalline In₃Se₃ 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-In₃Se₃-NaOH (1M)-S (1M) - Na₂S (1M) - C(graphite). The photoelectrochemical characterization of the films is carried out by studying electrical and optical characterization. These studies indicates that the In₃Se₃ 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 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].

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In the presentation investigation, we describe the photoelectrochemical performance of In₃Se₃ thin film. I-V, C-V characteristics in dark, power output curves and barrier height measurements study.

II. EXPERIMENTAL DETAILS

2.1 Preparation of In₃Se₃ photoelectrode

The deposition of In₃Se₃ 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 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 [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

\[ n-In_{2}Se_{3} | NaOH (1 M) + S (1 M) + Na_{2}S (1 M) | C_{(graphite)} \]

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.

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.

### III. RESULT & DISCUSSION

3.1. Conductivity type

A PEC cell with configuration \( n-In_{2}Se_{3}|NaOH (1 M) + S(1 M) + Na_{2}S(1M)|C_{(graphite)} \) 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 \( In_{2}Se_{3} \). This suggests that \( In_{2}Se_{3} \) 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 (\( \eta \)) 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 \( \eta \) 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 (\( V_{bs} \)). 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_{2}Se_{3}–poly sulphide 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 \( In_{2}Se_{3} \) 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]:

\[ I_{o} = AT^2 \exp (\Phi_{b} / kT) \]

\[ \Phi_{b} = \frac{3.5}{kT} \]
Where $A$ is Richardson constant, $k$ is Boltzmann constant, $\Phi$ is the barrier height in eV. To determine the barrier-height of the photoelectrode, a graph of $\log \left( I_0/T^2 \right)$ with $1000/T$ was plotted. The plot of $\log \left( I_0/T^2 \right)$ 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 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 153mV and 20 $\mu$A, respectively. The calculation shows the fill factor is 29.41%. From the slope of the linear region of plots, the barier height was determined.

\[ \eta_{max} = \frac{(V_{redox} - V_{fb}) (e/E_g)}{3.6} \]

where $V_{fb}$ is flat band potential, $V_{redox}$ is the redox potential and $E_g$ 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$_2$Se$_3$ 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$_2$Se$_3$ photoelectrode.

REFERENCES


Figure Caption:

Fig. 1. $I$–$V$ characteristics of In$_2$Se$_3$ photoelectrode (in dark).
Fig. 2. Determination of junction ideality factor of In$_2$Se$_3$ photoelectrode.
Fig. 3. $C$–$V$ characteristics of In$_2$Se$_3$ photoelectrode.
Fig. 4. Determination of barrier height measurement of In$_2$Se$_3$ photoelectrode.
Fig. 5. Power output curves for In$_2$Se$_3$ photoelectrode.
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Fig. 2. Determination of junction ideality factor of $\text{In}_2\text{Se}_3$ photoelectrode.

Fig. 3. $C–V$ characteristics of $\text{In}_2\text{Se}_3$ photoelectrode.
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Fig. 4. Determination of barrier height measurement of In$_2$Se$_3$ photoelectrode.

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