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Fabrication And Characterization Of 1% Indium Doped Thin Film Cdse$_{0.3}$Te$_{0.7}$ /Polyiodide Photoelectrochemical Solar Cell

Laxmikant P. Damodare Department of Physics, Hislop College, Temple Road, Civil Lines, Nagpur 440001, India.

Abstract: Photoelectrochemical (PEC) solar cell were fabricated using an aqueous poly-iodide electrolyte in junction with vacuum evaporated 1% Indium doped thin films of CdSe$_{0.3}$Te$_{0.7}$ were coated with thickness of ≈ 400 nm photoanode on conducting glass at a pressure of 5×10^{-5} torr held at room temperature. The as-grown thin films were characterized by X-ray diffraction and optical absorption. It is found that there is a large prevalence of CdTe and a small presence of CdSe leading to an overall cubic structure. The optical band gap of the thin film of 1% Indium doped CdSe$_{0.3}$Te$_{0.7}$ was $E_g \approx 1.55$ eV. The photoelectrochemical solar cells showed a solar power conversion efficiency of $\eta \approx 1.05$ %. The results of the experimental data are explained and discussed.

1. Introduction

Photoelectrochemical (PEC) solar cells based on thin film semiconductor electrode used as a photoanode with graphite as a counter electrode for chalcogende semiconductor family of Cd-Se-Te were widely studied. However influence of doping to the thin film at the bulk alloy level itself can change the properties of the CdSe$_{0.3}$Te$_{0.7}$ making more conducting so that the minority generated carriers on illumination are scattered to a lesser extent. The doping of Indium (In) is very suitable because Indium assists in higher conduction at the semiconductor electrolyte interface and there is larger amount of photocurrent in the external circuit suitable for useful work. Here a doping of 0.1% of Indium is done to CdSe$_{0.3}$Te$_{0.7}$ alloy so that the influence of doping can be studied for the as-grown thin films.

2. Experimental

High purity 99.999% of Cd, Se and Te in the desired quantity were taken with pure 0.1 % Indium were taken in a quartz ampoule and the quartz ampoule was evacuated to a vacuum of 5×10^{-5} torr. The resultant quartz ampoule was sealed and the mixture of the metals was kept in a muffle furnace for 12 hours so that a homogenous alloy was formed with doped Indium. The ingot of the homogenous alloy was broken in an agate mortar and pestle to a fine powder using small quantities of alcohol to obtain a uniform powder. The thoroughly dried powder in a Nitrogen atmosphere was used in vaccum deposition in a Molybdenum boat with currents close to 4 A so that a uniform thermal evaporation is possible. The thickness of the thin film was monitored using quartz crystal monitor to achieve a thickness of ≈ 400 nm on a pre coated Indium Oxide thin film coated glass plate. All the samples were kept in vacuum chamber itself to avoid any surface oxidation of the thin film. The as grown thin film photoanode in conjuction with a freshly prepared redox polyiodide electrolyte of 2 M KI and 20 mM I_2 in double distilled water along with graphite counter electrode was used so that an air tight photoelectrochemical solar cell could be realized. A Tungsten Halogen lamp was used to simulate solar radiation under the AM 1.5 conditions with an intensity of 100 mW/m^2 was kept constant for all the measurements. Mott-Schottky plots were performed in dark with a capacitance bridge at 1 MHz internal frequency. Important parameters like the flat band potential, V_{FB}; depletion width, ω; Donor concentration, N_D were calculated from the Mott-Schottky plots. Saturated calomel electrode (SCE) was used as a standard electrode to specify the voltages in dark for Mott-Schottky measurements. The as-grown thin films of 0.1% In doped $CdSe_{0.3}Te_{0.7}$ were characterized for XRD by using X-ray Cu-K_α radiation and the optical studies were performed using Shimadzu spectrophotometer (Made in Japan) used with scanning range of 350 nm to 750 nm in the visible spectrum for band gap determination.

3. Results and Discussion

3.1 X-ray Diffraction Studies (XRD)

The Fig. 1 shows a typical X-ray diffraction pattern of the as grown 0.1% Indium doped $CdSe_{0.3}Te_{0.7}$ thin films grown at room temperature. It is seen that the XRD pattern consists of a number of sharp peaks indicating the thin film is a polycrystalline in nature. The XRD pattern of the bulk alloy was also taken. It is seen that there are more peaks than the thin films. There is also a peak corresponding to InTe in the bulk and thin film form. The Indium atom has a tendency to occupy the vacant Cadmium (Cd) sites, thus enhancing the conduction process. Another reason is that the atomic radius of Cd is larger (144 pm) than the Indium atom radius (142 pm) thus a stress free occupation of Indium (In) at Cd vacant sites is possible in both the bulk and thin film states. From the XRD pattern the lattice constant of the Indium doped $CdSe_{0.3}Te_{0.7}$ thin film structure was $a_o \approx 4.21$ Å. This value well agrees with the literature.

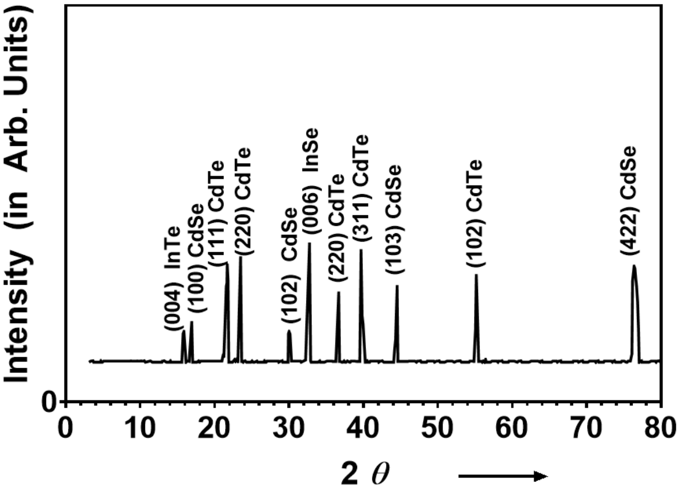

Fig. 1. A typical XRD plot of 1% In doped $CdSe_{0.3}Te_{0.7}$ thin film for the as grown thin film.

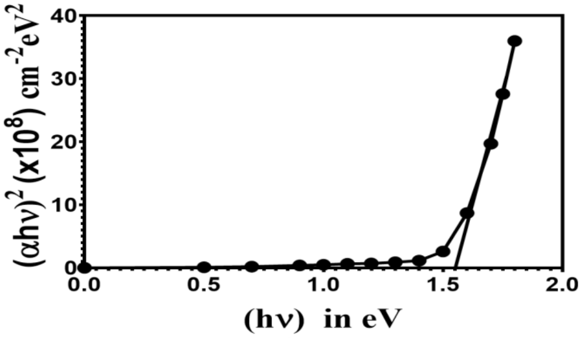

Fig. 2. A plot of $(\alpha h\nu)^2$ *vs* (hν) for an as grown 1% Indium doped $CdSe_{0.3}Te_{0.7}$ thin film

3.2 Optical Absorption Studies

The optical absorption studies were done using an optical absorption spectrophotometer, Joel (Made in Japan) in the wavelength range of $\lambda = 350$ nm to 750 nm. Figure 2 shows a typical plot of $(\alpha h\nu)^2$ vs $(h\nu)$. Here α is the absoption coefficient, h is the Planck's constant and ν is the frequency of the incident light. It is seen that the curve rises at an energy of ≈ 1.55 eV indicating that the straight line intercept on the energy axis is the band gap $E_g \approx$ 1.55 eV. For permitted direct transmissions in the optical region the absorption coefficient, α is given by [2]

$$\boldsymbol{\alpha} \approx \frac{\mathbf{A^*}}{\mathbf{h\nu}}\left(\mathbf{h\nu - E_g}\right)^{\frac{1}{2}}$$

Where ν is the frequency of incident light, h is the Planck's constant, E_g is the bandgap of the semiconductor and the coefficient, A^* is given by:

$$A^* \approx \mathbf{q^2}\left(\frac{\mathbf{2m_e^* m_h^*}}{\mathbf{m_e^* + m_h^*}}\right)(\mathbf{nch^2 m_e^*})^{-1}$$

Where m_e^* and m_h^* are the effective electron and hole masses respectively, c is the speed of light, h is the Planck's constant and n is the refractive index. Therefore, the variation of $(\alpha h\nu)^2$ vs hν will be a straight line plot with intercept on the hν axis at $(\alpha h\nu)^2 = 0$ gives the direct optical band gap of the semiconducting $CdSe_{0.3}Te_{0.7}$ was around $E_g \approx$ 1.55 eV [3].

3.3 Mott-Schottky Plots of 1% Indium doped $CdSe_{0.3}Te_{0.7}$ / (aq) 2M KI + 20 mM KOH system in dark

A fresh prepared 1% Indium doped $CdSe_{0.3}Se_{0.7}$ in conjunction with (aq) 2M KI + 20mM I_2 was used to study in dark the Mott-Schottky plots for semiconductor-Redox electrolyte junction. The counter graphite electrode was cleaned using carbon tetrachloride solution followed by rinsing in double distilled water. It is seen the Mott-Schottky plots for the thin film/electrolyte junction exhibited linear profile (Fig.3). The Mott-Schottky plot was thus obtained for the $1/C^2$ vs Voltage(vs SCE) as a straight line. The intercept of the plot on the Voltage axis for which $1/C^2 = 0$ is the flat band potential, V_{FB}. The Mott-Schottky equation [4,5] is:

$$\frac{1}{C^2} = \left[\frac{2}{\epsilon_o \epsilon_s q N_D}\right]\left[V - V_{FB} - \left(\frac{k_B T}{q}\right)\right]$$

Where ϵ_o is the permittivity of free space, ϵ_s is the dielectric constant of the semiconductor, q is the charge, N_D is the donor concentration, k_B is the Boltzmann's constant, T is the absolute temperature.

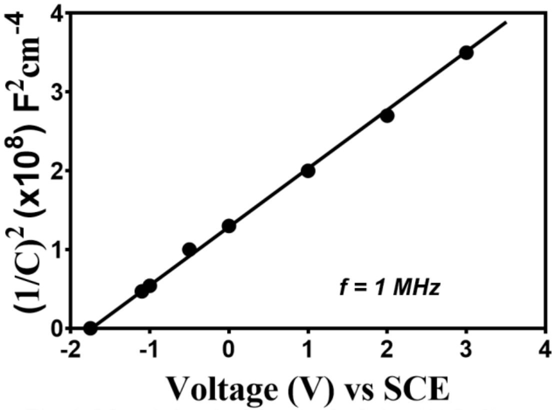

Fig. 3. Mott-Schottky Plots in dark for 1% Indium doped $CdSe_{0.3}Te_{0.7}$ thin film/(aq) Polyiodide cell

The Mott-Schottky plot for the 1% Indium doped $CdSe_{0.3}Se_{0.7}$ was at 1 MHz frequency in dark. The Mott-Schottky plots in dark give an array of vital parameters of semiconductor like the donor concentration, the depletion width and other physical parameters of the semiconducting 1% Indium doped $CdSe_{0.3}Te_{0.7}$ were calculated. The depletion width was found to be, $\omega \approx 0.55$ μm. The donor concentration was found to be, $N_D \approx 4.5 \times 10^{20}$ /m^3. The flat band potential, V_{FB} was found to be ≈ −1.75 V versus SCE for the as-grown thin film.

3.4 Solar power conversion efficiency Plots of 1% Indium doped $CdSe_{0.3}Te_{0.7}$ / (aq) 2M KI + 20 mM KOH system under AM 1.5 white light illumination.

Solar power conversion efficiency studies were performed for the 1% In-$CdSe_{0.3}Te_{0.7}$ / (aq) 2M KI + 20 mM KOH system under AM 1.5 white light illumination. A plot of photocurrent vs photovoltage (Fig.4) showed that the efficiency of solar power conversion was ≈ 1.05%. The V_{oc} was found to be ≈ 0.48 V and the I_{sc} was found to be ≈ 5000 μA/cm² calculated as per the formula provided in the literature [6-8]. The low value of efficiency is due to several reasons. The as-grown thin films of 1% In-$CdSe_{0.3}Te_{0.7}$ had a lot of frozen in defects. When a thin film is grown by thermal vacuum evaporation, clusters are formed on the surface of the thin film with high separation between clusters leading to large grain boundaries [9]. The minority generated charge carriers under illumination get scattered at these locations till they reach the terminals to travel in the external circuit to do useful work. So scattering of minority carriers leads to high series resistance and low shunt resistance. For an ideal solar cell, the shunt resistance should be ≈ ∞ and series resistance should be ≈0. However in real thin film photoelectrochemical solar cells, there are plenty of grain boundaries on the surface of the thin film. The as-grown thin films show a large penetration of the electrolyte into the interior of the thin film due to defects, vacancies and non uniformity. This also gives rise to combination of minority generated carriers with ions in the liquid even though doping with 1% Indium should generate additional carriers and also make the semiconducting photoanode more receptive to solar radiation to do useful work.

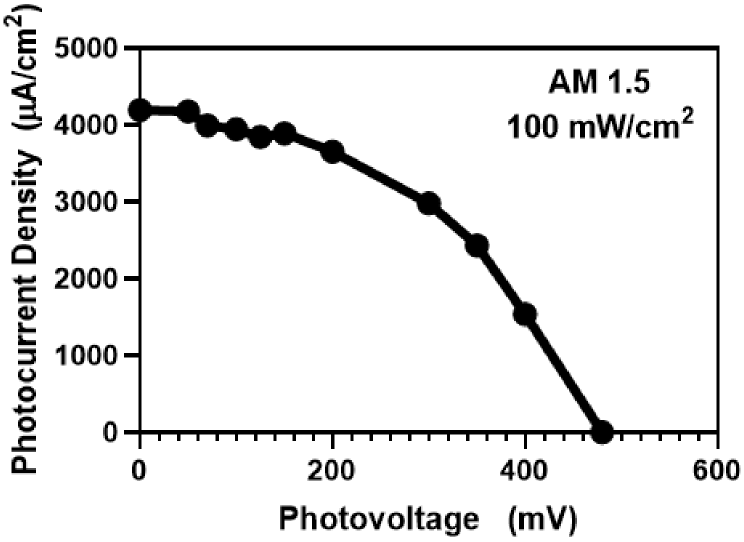

Fig. 4. Power Output Characteristic of 1% Indium doped $CdSe_{0.3}Te_{0.7}$/ (aq)Polyiodide PEC Solar Cell

Conclusion:

The thin films of 1% Indium doped $CdSe_{0.3}Te_{0.7}$ were characterized using X-ray diffraction, Optical absorption to ascertain the structure and band gap of semiconducting 1% Indium doped $CdSe_{0.3}Te_{0.7}$ thin films. The XRD pattern showed that the given composition showed cubic symmetry with lattice constant a_o≈ 4.21 Å. The peaks obtained match well with those of the literature. The optical band gap of the 1% Indium doped $CdSe_{0.3}Te_{0.7}$ was found to be E_g≈ 1.55 eV. The doping of Indium enhances the donor concentration, $N_D \approx 4.5 \times 10^{20}$ /m³ in the thin film as seen from the Mott-Schottky plots in the dark. The metallic Indium doping to the extent of 1% atomic percent helps in better conductivity of the thin film leading to less scattering of solar generated minority carriers and thus the solar power conversion efficiency is seen to be ≈ 1.95%. The doping of conducting metals like Indium can work as an efficiency enhancer for photoelectrochemical solar cells as the doping concentration upto certain extent is increased.

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