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Influence of annealing and etching on the solar power conversion efficiency of thin film n-$CdSe_{0.3}Te_{0.7}$/Polyiodide photoelectrochemical cell

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Abstract: Photoelectrochemical solar cells using vacuum coated (5×10^{-5} torr) thin films of n-$CdSe_{0.3}Te_{0.7}$ of thickness ≈ 4000 Åon In_2O_3 precoated glass slides. The junction was made of semiconducting n-$CdSe_{0.3}Se_{0.7}$ with polyiodide. The composition of freshly prepared redox polyiodide was (aq) 2M KI + 20mM I_2. With counter electrode made of graphite showed photoactivity under white light AM 1.5 illumination. The power conversion efficiency was noted. Another sample of n-$CdSe_{0.3}Te_{0.7}$ thin film was annealed at 200 °C for 30 minutes. followed by etching in HNO_3 for 2 seconds. This showed remarkable improvement in solar power conversion efficiency from 0.5% to 1.5%. The effect of annealing and etching is discussed in this paper.

1. Introduction

The chalcogenide semiconducting alloy, $CdSe_xTe_{(1-x)}$both in bulk form and in thin film form has been studied for various physical properties and applications in possible devices due to its semiconducting nature and the band gap can be tailored by varying the composition parameter "*x*" for photovoltaic applications [1].. The visible spectrum ranges from 350 nm to 750 nm corresponding to the energies between 3.54 eV to 1.65 eV. The semiconducting $CdSe_{0.3}Te_{0.7}$is found to be n-type as per literature with a band gap of $E_g \approx$ 1.6 eV. This opens the semiconductor for potential applications of photoelectrochemical solar cells. A redox electrolyte in conjunction with n-$CdSe_{0.3}Te_{0.7}$ and counter electrode of graphite can be used as a photoelectrochemical solar cell to study the power conversion properties.

2. Experimental

The semiconducting $CdSe_{0.3}Te_{0.7}$alloy was made using99.999% pure Cd, Se and Te granules in stoichiometric proportions and the mixture was heated in a quartz pre-evacuated ampoule at 550°C for 10 hours to obtain a uniform homogenous alloy. This bulk alloy of $CdSe_{0.3}Se_{0.7}$ was ground to a fine power in an agate mortar and pestle till the particles are uniform and homogenous. The powdered alloy was evaporated in a thin film deposition system in a vacuum of $\approx 5 \times 10^{-5}$torr pressure on a pre-coated In_2O_3 glass plates to coat uniformly thin films of $CdSe_{0.3}Te_{0.7}$of thickness ≈ 4000 Å. The as-grown thin films were annealed at 200°C for 30 minutes and etched in dilute nitric acid for 2 seconds. The optical absorption spectrum studied by Joel Optical spectrometer (Made in Japan) in the wavelength range from

350 nm to 750 nm. The structure of the thin films using X-rays was studied using Cu-K_{α}($\lambda \approx$1.542 Å) radiation. The photoelectrochemical solar cell was fabricated in a beaker with rubber cork having photoanode of n-$CdSe_{0.3}Te_{0.7}$ and a graphite counter electrode both of them separated by a distance of 2mm so that only a thin layer of redox electrolyte (polyiodide) can form a junction effectively separating the minority generated carriers on illumination. The freshly prepared redox electrolyte was used comprising of high purity (aq) 2M KI + 20 mM KOH.

The external connections were made using ohmic contacts to the semiconducting photoanode and graphite to prevent any contact losses. While preparing the redoxpolyiodide electrolyte, it was uniformly stirred to make it a homogenous and transparent for use in fabrication of photoelectrochemical solar cell. The photoelectrochemical solar cell was illuminated using a 100 W Tungsten Halogen lamp, simulated as light of AM 1.5 intensity under laboratory conditions. The light intensity in the units of mW/m^2 was measured using SURYAMAPI solar light intensity detector obtained from Central Electronics Engineering Research Institute, Pilani, India.

3. Results and Discussion

3.1 Structural Studies using X-ray diffraction

The powder X-ray diffraction (XRD) studies on $CdSe_{0.3}Te_{0.7}$ were performed using monochromatic Cu-Kα radiation of λ = 1.542 Å. The characteristic peaks corresponding to the CdSe, CdTe and $CdSe_{0.3}Te_{0.7}$ were obtained with the d-values matching with the literature. It is found that the thin films exhibit more cubic structure than hexagonal due to prevalence of Te in the thin film. It is also seen that there are more XRD peaks corresponding to the CdTe obviously due to stoichiometric composition of the $CdSe_{0.3}Te_{0.7}$showing higher prevalence of CdTe.The lattice parameter corresponding to structural zincblende cubic symmetry of the thin filmwas found to bea_o= 6.36 Åwas calculated from the X-ray diffraction pattern. This value too agrees with those obtained from the literature [1]. The thin film on annealing shows appearance of some new peaks which were not exhibited for the as-

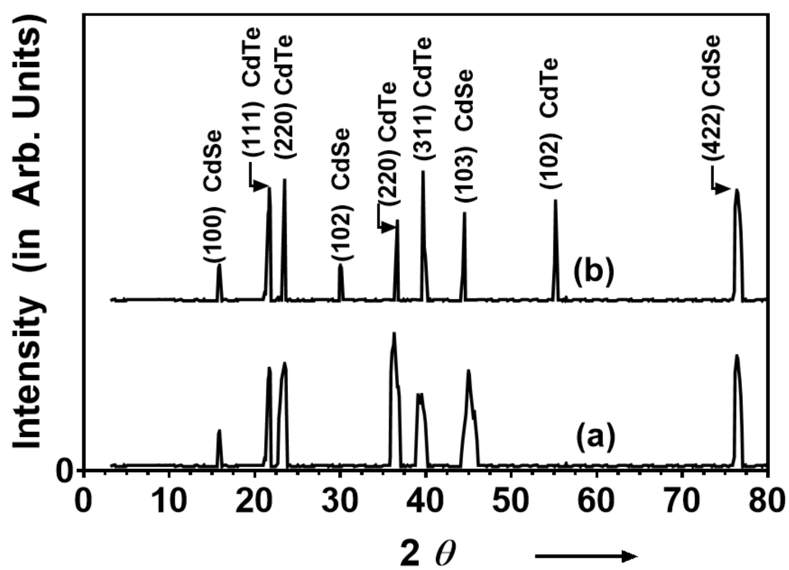

Fig. 1. A typical XRD plot of $CdSe_{0.3}Te_{0.7}$ thin film for (a) as grown and (b) annealed thin film

grown thin film. This is due to the fact that there is some crystallization on annealing which leads to increase of grain size and more prominent peaks appearing in the XRD pattern.

3.2 Optical Absorption Studies

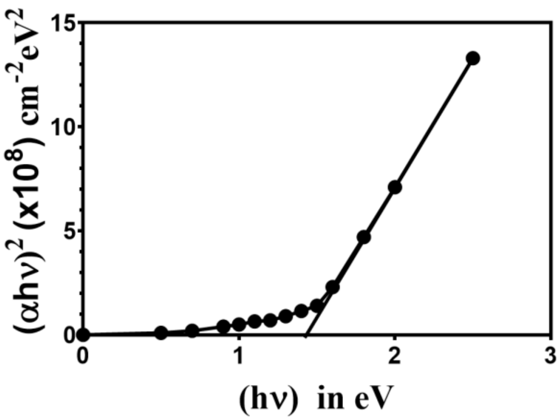

Fig. 2. A plot of $(\alpha h\nu)^2$ *vs* (hν) for an as grown $CdSe_{0.3}Te_{0.7}$ thin film

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 $(h\nu)$. It is a straight line with intercept on the energy axis being the band gap$E_g \approx$ 1.42 eV. For permitted direct transmissions in the optical region the absorption coefficient, α is given by [2]

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

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:

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

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 $h\nu$ will be a straight line plot with intercept on the $h\nu$ axis at $(\alpha h\nu)^2 = 0$ gives the direct optical band gap of the semiconducting $CdSe_{0.3}Te_{0.7}$ was around $E_g \approx$ 1.42 eV [3].

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

The freshly prepared $CdSe_{0.3}Se_{0.7}$ in conjunction with (aq) 2M KI + 20mM I_2 was used to study the Mott-Schottky plots for both as grown thin films and etched thin film of $CdSe_{0.3}Se_{0.7}$. The counter graphite electrode was cleaned using carbon tetrachloride solution followed by double distilled water. It is seen the Mott-Schottky plots for the thin films exhibited straight line profile. The Mott-Schottky plots were thus obtained for the $1/C^2$ vs Voltage(*vs* SCE) was a linear plot. 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:

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

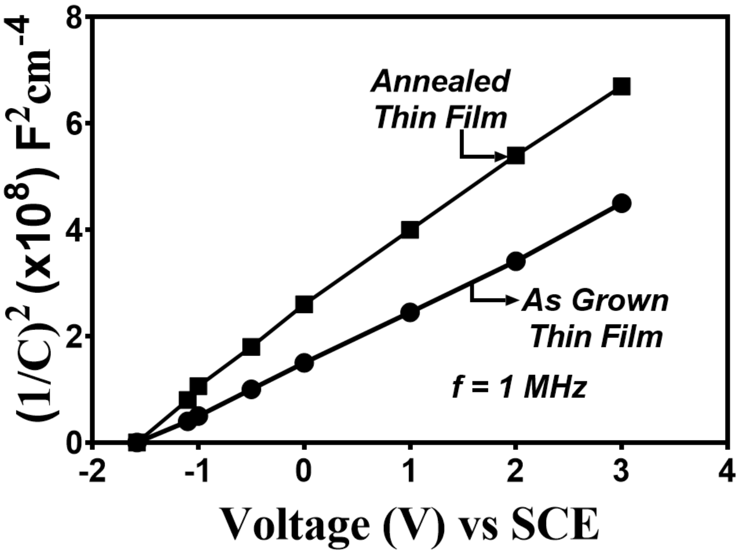

Fig. 3. Mott-Schottky Plots in dark for $CdSe_{0.3}Te_{0.7}$ thin film/(aq) Polyiodide cell

The slope of the Mott-Schottky plot for the annealed and etched $CdSe_{0.3}Te_{0.7}$ was higher than the slope of the as-grown $CdSe_{0.3}Te_{0.7}$/(aq) KI + KOH system at 1 MHz frequency in dark. This is due to the fact that the as-grown thin film had a lot of frozen in defects at the time of growth. These defects create surface states which lie within the band gap of the semiconductor thereby producing additional effects in the Mott-Schottky plots. As the thin film is annealed, these frozen in defects get annealed out, reducing the grain boundaries in the thin films thereby reducing the capacitance and thus increasing the value of $1/C^2$ and therefore the slope. As the thin film is etched for a time of 2 seconds, all the impurities at the surface and the dangling bonds get etched out thereby decreasing the capacitance further. This leads to a higher slope. The Mott-Schottky plots in dark give a vital information about the donor concentration, the depletion width and other physical parameters of the semiconducting $CdSe_{0.3}Te_{0.7}$ were calculated. The depletion width was found to be, $\omega \approx 0.45$ μm. The donor concentration was found to be, $N_D \approx 2.5 \times 10^{18} /m^3$. The flat band potential, V_{FB} was found to be ≈ -1.65 $V versus SCE$ for the as-grown thin film. The flat band potential remained same for both the annealed thin film and etched thin film.

3.3 Solar Power characteristics of the $CdSe_{0.3}Te_{0.7}$ / (aq) Polyiodide PEC cell

The solar power characteristics of the as grown, annealed and etched $CdSe_{0.3}Te_{0.7}$ / (aq) Polyiodide PEC cellunder white light AM 1.5 were studied. Figure 4 shows the power output characteristic of $CdSe_{0.3}Te_{0.7}$ / (aq) Polyiodide PEC solar cell. It is seen from the plots that the as-grown thin films of $CdSe_{0.3}Te_{0.7}$ in contact with (aq) Polyiodide when illuminated by white light of intensity of 100 mW/cm^2 under AM 1.5 illumination conditions showed lesser efficiency of 0.4 % [6] with fill factor of ≈ 0.3. On annealing the thin filmsand

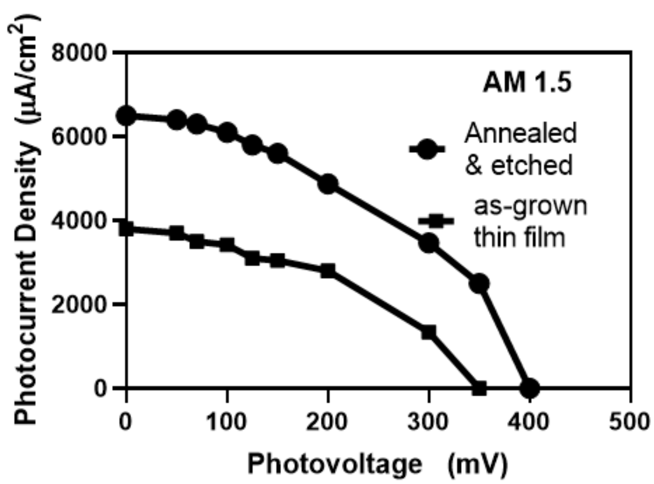

Fig. 4. Power Output Characteristic of $CdSe_{0.3}Te_{0.7}$/(aq)Polyiodide PEC Solar Cell

further etching the thin films we have obtained an efficiency of ≈1.5% with fill factor≈0.6. An improvement in the efficiency and fill factor is due to the fact that on annealing the thin films we have improvement in grain size and reduction of grain boundaries. This leads to less scattering of the minority carriers and the efficiency is seen to improve. This also leads to improvement of shunt resistance and decrement of series resistance [7]..

4. Conclusions

The thin films of $CdSe_{0.3}Te_{0.7}$ in vacuum using thermal evaporation showed cubic structure.The photoelectrochemical cells fabricated using $CdSe_{0.3}Te_{0.7}$ in contact with (aq) Polyiodide have shown improvement in its solar power conversion efficiency from 0.5% to 1.5% due to the fact that the semiconducting $CdSe_{0.3}Te_{0.7}$ is a direct band gap semiconductor and the as grown thin film had a lot of *ab-initio* defects leading to a lower solar power conversion efficiency. On annealing the thin films at a temperature of 200 °C for 30 minutes in a vacuum of $\approx 5 \times 10^{-5}$torrpressure the efficiency improved to 0.8 %. On further etching the thin films, the efficiency improved to 1.5 %. Process of etching removes all impurities on the surface which form minority carrier scattering centres[8]. Additional impurities which get deposited on the surface while coating the thin film are removed by etching and making the surface fresh for device fabrication.

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