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Photoelectrochemical studies on CdSe thin films grown on precoated SnO_2 coated glass plates with a junction of (aq) Polyiodide

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Abstract: Thin films of CdSe were grown using thermal vacuum evaporation on a precoated SnO_2 glass plates and bare glass plates at a pressure of 5×10^{-5} torr. The thin films of CdSe on glass, SnO_2 on glass and CdSe/SnO_2 structure were characterized by X-ray diffraction for structural analysis. The lattice constants thus obtained for the Hexagonal structure are a_o = 4.312 Å and c_o = 7.034 Å respectively.The SnO_2 being a conducting wide band gap material paves way for proper transmission of white light to be absorbed by semiconducting CdSe. The optical band gap studies of the as-grown CdSe thin films on glass in the UV-VIS-IR region yielded a band of 1.76 eV. The thin film CdSe/SnO_2 structure in junction with a redox electrolyte of polyiodide (2M KI + 20mM I_2) showed photoelectrochemical effects under white AM 1.5 white light illumination. The solar power conversion efficiency was found to be 2.1%. This is due to the some of illuminated optical photon scattering in the SnO_2 thin films and CdSe thin films. The results obtained other photoelectrochemical solar parameters are studied and analysed in this paper.

1. Introduction

There has been a lot of work in the scientific circles on chalcogenide semiconductors using a compounds made from Cd, Se and Te. These compounds exhibit a direct band gap in the visible region and have potential applications in solar cells. When in conjunction with a suitable redox electrolyte they can show solar to power conversion. There has been work related to CdSe grown on various substrates but few of the workers have worked on SnO_2 as a conducting substrate on which CdSe has been grown especially with a junction with polyiodide. The photoelectrochemical solar cell fabricated with the CdSe/SnO_2/(aq) Polyiodide structure has future applications for improvement and public use.

2. Experimental

Highly pure Cd and Se of 99.999% purity were used in appropriate stoichiometric ratio in a quartz crystal ampoule and this ampoule was evacuated to a pressure of 5×10^{-5} torr. The ampoule was sealed by using an oxyacetylene torch so that no air gets into the quartz crystal ampoule. A vertical muffle furnace was used to heat the ampoule. The ampoule was inserted into the muffle furnace such a way that maximum heat reaches the alloy through the ampoule. The alloy is heated in a stepwise fashion to the melting point of Cadmium and kept for nearly 5 hours. Later on the temperature of the furnace is increased to a that of melting

point of Selenium and kept for another 5 hours. The temperature was kept constant for another 5 hours. During the heating process the ampoule was constant shaken so that the constituents are thoroughly mixed and a homogeneous mixture of alloy is obtained. This alloy was cooled gradually to the room temperature. The cooled alloy was ground to a fine powder in a Agate mortar and pestle. The finely grounded powder was used in a Molybdenum boat for thermal evaporation. An AC current of nearly 35 A was passed for 45 seconds to achieve thermal evaporation of the alloy. The thickness of the coated thin film was monitored by quartz crystal monitor. The substrates placed at a distance of 25 cms were bare pre-cleaned glass plates and SnO_2 precoated glass plates. The coated thin films of CdSe on various substrates were kept in a vacuum of 5×10^{-5} torr overnight. The freshly prepared samples were subjected to X-ray diffraction for structure determination. A Copper K_α X-ray radiation was used for diffraction purpose. The angle of scanning (2θ) was varied from 5^o to 85^o by varying the position of the goniometer with a step of 0.01^o. For optical absorption studies, a UV-VIS-NIR spectrophotometer was used to vary wavelengths from 350 nm to 750 nm. To make the photoelectrochemical solar cell, the freshly coated samples were used as photoanode and a thin graphite foil was used as a counter photocathode separated by a distance of 3mm. The photoanode and photocathode were placed such that a thin layer of redox electrolyte (aq) 2M KI + 20 mM I_2 (pH=6.5) is in contact with the semiconducting CdSe. White light under AM 1.5 conditions were created by using a Tungsten Halogen lamp with an incident intensity of 100 mW/cm^2. Ohmic contacts of Pb-Sn alloy were used to make electrical contact with the base SnO_2 thin film material.

3. Results and Discussion

3.1 Powder X-ray Diffraction

The thin films of CdSe were grown over bare glass, over pre-coated SnO_2 and SnO_2 coated over bare glass plates were subjected to X-ray diffraction. Figure 1 shows the X-ray diffraction pattern of the three situations. It is seen that the bulk CdSe has many peaks as maximum grains are possible with different orientations. Some of the preferred orientations of planes, depending on the deposition conditions are seen in the CdSe thin film over glass. The amorphous nature of glass and the broadening is filtered out so that only peaks concerning our thin films material are displayed. The thin films of SnO_2 too show peaks which are there in the X-ray diffraction pattern of CdSe/SnO_2 structure. The peaks are compared with standard peaks from other researchers

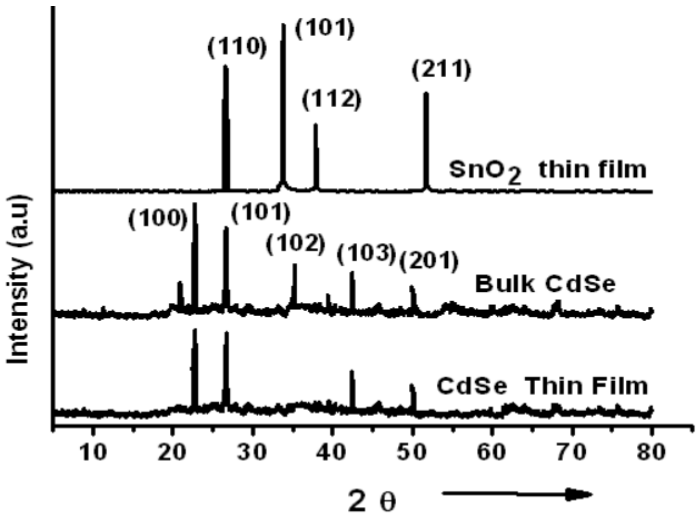

Fig. 1. A typical powder X-Ray diffraction pattern for CdSe thin thin film grown over glass plate, SnO_2 and Bulk CdSe

[1-3] and tally well with their work. The Miller indices of the planes are identified and indexed. From the values of the miller indices of different planes the lattice constants of the Hexagonal structure namely, a_o and c_o are calculated. The obtained values are: a_o = 4.312 Å and c_o = 7.034 Å respectively. This matches well with the other researchers [1].

3.2 Optical Absorption Studies

The thin films of CdSe were subjected to optical absorption studies. In the UV-VIS-IR region the optical absorption constant, α was calculated from the optical density data. As per the Pankov [4] the optical absorption coefficient, $\boldsymbol{\alpha}$, is related to the incident frequency by the following relation:

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

Where $\boldsymbol{\nu}$ 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, $\boldsymbol{c}$ is the speed of light, $\boldsymbol{h}$ is the Planck's constant and $\boldsymbol{n}$ is the refractive index. Therefore, a plot of $(\alpha h\nu)^2$ vs $h\nu$ gives a straight line. The intercept of the plot gives the optical band gap of the CdSe, which is a direct band, $E_g \approx 1.76$ eV which matches with the values obtained from literature [6]. This is shown in Fig. 2.

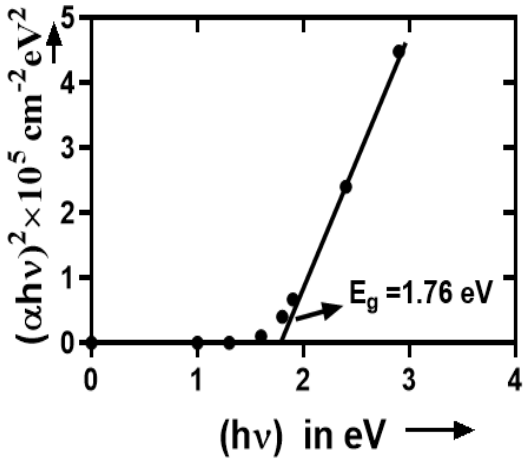

Fig.2. Optical Absorption Tauc Plot for CdSe thin film.

3.3 Energy Dispersive Analysis of X-rays Studies of CdSe Thin Films

The as-grown thin films of CdSe were analysed by Energy Dispersive Analysis of X-rays (EDAX) for compositional analysis. The EDAX spectrum is shown in Fig. 3 The integrated counts for Cd L_α and Se L_α were analyzed by a micro ZAP software program which is in the EDAX set up. The atomic percentage composition of the as-grown thin films obtained from EDAX analysis was Cd $\approx 49.4 \pm 1.4\%$ and Se $\approx 49.5 \pm 1.5\%$. An electron beam at 120 kV was incident on the sample which generated characteristic X-rays corresponding to the atoms in the sample thin film.

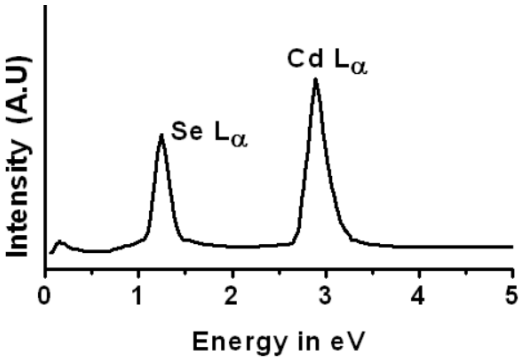

Fig. 3. Energy Dispersive Analysis of X-Rays studies of CdSe thin film

3.4 Quantum Efficiency Studies of the CdSe/SnO_2/(aq) Polyiodide under illumination

The thin film CdSe/SnO_2/(aq) polyiodide junction was subjected to monochromatic light illumination with an optical monochormator. Figure 4. Shows that a plot of photocurrent density with wavelength of incident light. It is seen that the variation peaks at 620 nm. The quantum efficiency is calculated from the formula [7]:

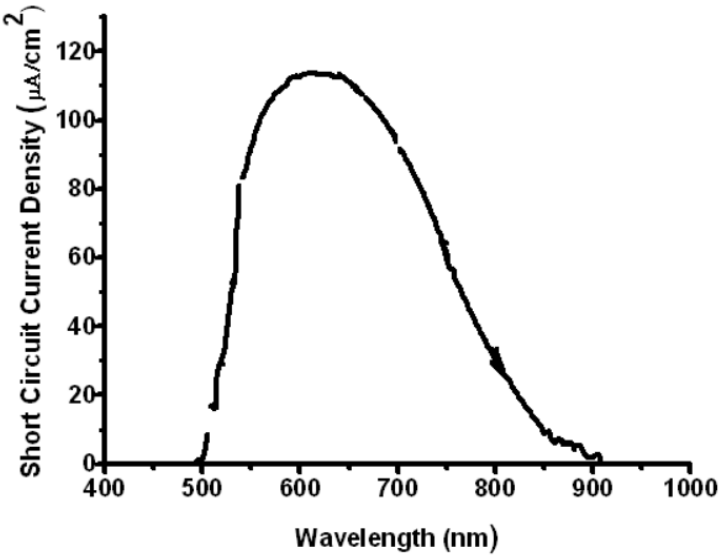

Fig. 4. The variation of Short Circuit Current Density with Wavelength for a typical CdSe/SnO2/(aq) Polyiodide Photoelectrochemical Solar Cell

$$\mathbf{Q_F} = \frac{\mathbf{J_{SC}(A/cm^2)} \times \boldsymbol{h\nu}\ \mathbf{(eV)}}{\boldsymbol{q} \times\ \mathbf{Intensity\ of\ light\ (W/cm^2)}}$$

The quantum efficiency as calculated from the above formula for the highest peak is ≈ 52%. This low quantum efficiency is due to the fact that as white light is passed a monochoromator to access each wavelength, there is a lot of loss of intensity. The intensity corresponding to each colour was separately measured and inserted into the above formula. The shortcircuit current density was measured with no external load.

3.5 Solar Power studies CdSe/Polyiodide junction under white illumination

The thin film CdSe/SnO_2/(aq) polyiodide junction was used to fabricate a photoelectrochemical solar cell. The illuminated junction showed photovoltaic effects. Electrical power was generated under white light illumination. The Fill factor (FF) in % was calculated as per the formula [8] :

$$FF = \frac{V_{OC}\ J_{SC}}{V_{MP}\ J_{MP}} \times 100$$

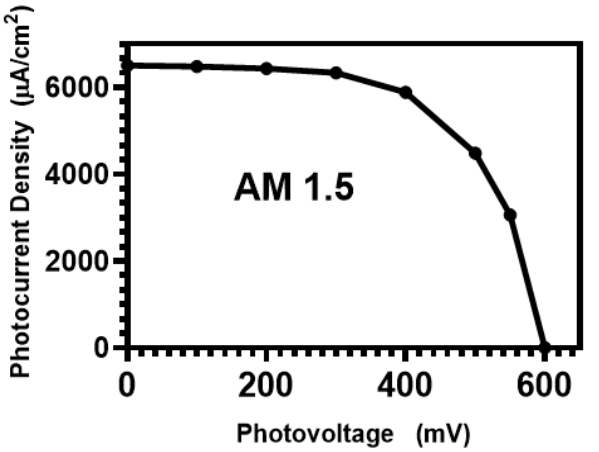

Fig. 5. Solar Output plot of CdSe/SnO_2/(aq) Poly-iodide Photoelectrochemical Solar Cell

Where V_{OC} is the open circuit voltage, J_{SC} is the short circuit current density and V_{MP} is the voltage at maximum power and J_{MP} is the current density at maximum power. Assuming for a normal incidence the solar white light irradiation intensity or the input power is 100 mW/cm^2, it was found from the plot that the fill factor is ≈ 58.5% and the Solar Power conversion efficiency, η in % is calculated as per the following formula [8]:

$$\eta = \frac{V_{MP} J_{MP}}{Input\ Power} \times 100$$

Figure 5 shows a typical plot of Photocurrent density vs Photovoltage obtained for the photoelectrochemical solar cell. For a direct solar illumination, the input power is taken as 100 mW/cm^2. It is seen that on putting the values of the V_{MP} and J_{MP} from the plot in the above formula we have obtained a conversion efficiency of 2.1 %.

4. Conclusion

The thin films of CdSe/SnO_2 were characterized by X-Ray diffraction and it was found that the thin films exhibited hexagonal symmetry. The lattice constants calculated were found to earlier workers. The optical absorption studies showed that the semiconducting CdSe thin film over glass had a direct band gap and the band gap also tallied with earlier workers. The thin films were studied by EDAX and were found to be stoichiometric. The atomic percentage composition was found for Cd ≈ $49.4 \pm 1.4\%$ and Se ≈ $49.5 \pm 1.5\%$. The quantum efficiency for the as-grown CdSe/SnO_2/(aq) Polyiodide photoelectrochemical solar cell was found to be ≈ 56%. This low quantum efficiency for the photoelectrochemical solar cell was due to the frozen in defects in the thin film while performing thermal evaporation. There are agglomerations and dislocations in the thin film which act as scattering centres for the minority generated charge carriers. The solar power conversion efficiency for the as grown photoelectrochemical solar cell was ≈ 2.1 %. This is also due to same reasons.

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