
Studies on the structure and photo electrochemical properties of CdSe thin films grown on In₂O₃ precoated glass substrates

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Abstract: Thin films of CdSe of thickness $\approx 5000 \text{ \AA}$ were coated on a pre-coated In₂O₃ glass plates by vacuum thermal evaporation at a pressure of $\approx 5 \times 10^{-5}$ torr kept at room temperature. The as-grown thin films on powder X-ray diffraction showed formation of CdSe thin films and the miller indices corresponding to different planes were identified. The thin films exhibited hexagonal structure with lattice constants $a_o \approx 4.562 \text{ \AA}$ and $c_o \approx 7.456 \text{ \AA}$. The thin films were characterized by diffuse reflectance studies and using the Kubelka Munk theory there optical band gap was found to be $\approx 1.71 \text{ eV}$. The Mott-Schottky plots in dark for the semiconductor-redox electrolyte junction (aq-Ferro-Ferricyanide) was done and showed a linear variation. Various semiconductor parameters were calculated. The Solar Power studies under white light illumination (AM 1.5) were performed in the laboratory for the semiconductor thin film-(aq) Ferro-Ferricyanide (Redox) electrolyte junction. The calculated power conversion efficiency for the as-grown thin films was found to be $\approx 1.3\%$. The results are discussed and analyzed.

1. Introduction:

There has been a lot of work on the application of Chalcogenide semiconductor like CdSe in conjunction with aqueous redox electrolyte for application towards photoelectrochemical solar cells [1-4]. The CdSe being a direct band gap semiconductor with its band gap in the visible region has potential application towards solar cells. Various researchers have worked in the bulk form of CdSe [5]. The application of CdSe in thin film form grown by thermal vacuum evaporation on conducting In₂O₃ has been found with few workers.

2. Experimental

Before coating of thin films of CdSe, a bulk alloy of CdSe was made by using highly pure (99.999%) and Se (99.999 %). Taking into the account the highly pure Cd and Se by weight in a correct stoichiometric proportion in a quartz ampoule. This ampoule was vacuum sealed to an ambient pressure of $\approx 5 \times 10^{-5}$ torr and the ampoule was sealed by using oxy-acetylene torch. This sealed ampoule was kept in a vertical muffle furnace which is heated from room temperature to the melting point of Se (495 K). by step wise heating for 24 hours and then gradually heated to the melting point of Cd (594 K). The alloy mixture was shaken occasionally. The alloy was heated for another 24 hours and cooled to room temperature by stepwise cooling at the rate of 5°/hour. The cooled alloy was grounded in a pre-cleaned Agate Mortar and Pesle till a fine powder of alloy was realized. This alloy powder was kept in an air tight desiccator for

consideration for thermal evaporation. The vacuum system was cleaned with alcohol and acetone. Highly pure Tantalum boat was used for thermal evaporation. Appropriate sample was taken in the Tantalum boat and the pre-coated In_2O_3 glass plates were kept in sample holders at a distance of 15 cms above the Tantalum boat for thermal evaporation. The vacuum system was operated to final pressure of 5×10^{-5} torr and the system was kept in operation. A current of 15 Amps was passed till the thin films reached the thickness of $\approx 5000 \text{ \AA}$. The thickness of ongoing thin films was monitored by a *in-situ* quartz crystal monitor attached to the vacuum system. A copper $\text{K}\alpha$ radiation was used for structure analysis for powder X-Ray studies. The intensity of the reflected X-ray beams was measured for each step of 0.01° . The optical band was measured using a UV-VIS-IR spectrophotometer for Reflectance (R) vs wavelength (λ) studies in the range of 350 nm to 750 nm. A redox electrolyte of (aq) 0.1 M $\text{K}_4(\text{FeCN})_6$ + 0.3 M $\text{K}_3\text{Fe}(\text{CN})_6$ + 0.3 M KOH was used (pH=10.6). A double distilled and de-ionized water with resistivity of 30 $\text{G}\Omega\text{cm}$ was used to prepare the redox electrolyte. The counter electrode was a highly conducting graphite of 4 mm thickness was used very close to the photoanode. A Bontoon Capacitance meter with a built-in frequency of 1 kHz was used to measure the Capacitance vs Voltage in dark for measuring Mott-Schottky plots. The voltages measured in the dark were with respected to saturated calomel electrode attached close to the thin film electrode in the electrochemical cell set up. A tungsten halogen lamp with an input intensity of 100 mW/cm^2 was used under AM 1.5 conditions at a suitable distance from the photoanode. Care was taken to measure each voltage manually so that a stable state is achieved after every reading.

3. Results and Discussion

3.1 Powder X-ray diffraction ((XRD) studies for the bulk CdSe and Thin film of CdSe

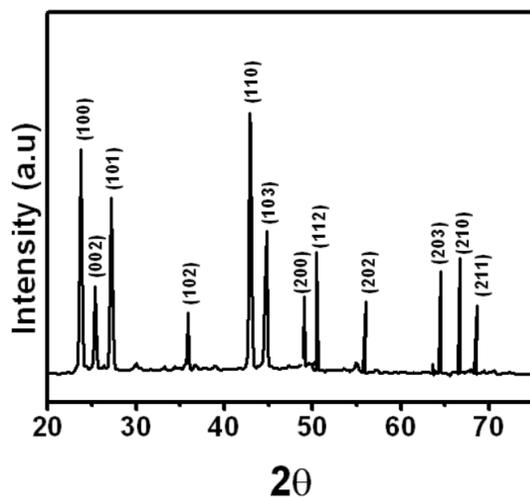


Fig. 1. A typical powder XRD plot of bulk CdSe Powder

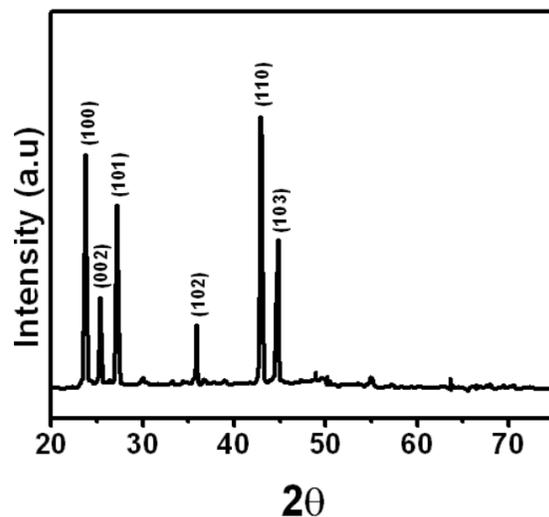


Fig. 2. A powder X-ray Diffraction pattern of a CdSe thin film.

The bulk XRD studies for a sample powder of CdSe was studied by taking a the sample on a bare glass plate.

The background XRD pattern of the glass plate was eliminated in the powder XRD plots for identifying the CdSe peaks properly. It is seen from Fig. 1 that the bulk powder XRD has more number of peaks and the d-values tally well with those of the literature and JCPDS card. The Miller Indices corresponding to diffracting planes are found from the JCPDS cards. The thin films exhibited a X-ray powder diffraction pattern (Fig. 2) with little bit less number of peaks due to the fact that the growth of the thin films by thermal evaporation is in a single direction towards the sample. The as-grown thin films XRD peaks which are lesser in number than the bulk but are found at the same location as the bulk confirming the formation of the CdSe thin films. Also the lattice constants of the thin films were calculated by using the following equations:

$$\text{or} \quad \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a_o^2} \right) + \frac{l^2}{c_o^2} = \frac{1}{d^2} \quad \because \text{for hexagonal lattice } a_o = b_o$$

Sr. No.	2θ degrees	d-values from XRD pattern (Å)	JCPDS d-values (Å)
1.	23.60	3.759	3.720
2.	25.40	3.501	3.500
3.	27.15	3.285	3.290
4.	35.80	2.500	2.550
5.	42.80	2.156	2.149
6.	45.80	2.017	1.970
7.	49.02	1.857	1.8300
8.	50.05	1.860	1.863
9.	55.90	1.640	1.645
10.	64.00	1.440	1.457
11.	66.00	1.405	1.407
12.	68.50	1.368	1.380

Table 1: d-values from bulk powder XRD & Comparison with JCPDS values for CdSe

Sr. No.	2θ degrees	d-values from XRD pattern (Å)	JCPDS d-values (Å)
1.	23.60	3.725	3.720
2.	25.40	3.501	3.500
3.	27.15	3.286	3.290
4.	35.80	2.501	2.550
5.	42.80	2.100	2.149
6.	45.80	2.021	1.970

Table 2: d-values from thin film XRD & Comparison with JCPDS values for CdSe

Table 1 shows the XRD d-values for the bulk CdSe powder. The values obtained were compared with JCPDS Data Card No. 77-2307 for both the thin films and bulk. It was found that the d-values tally fairly with the JCPDS values. The lattice constants calculated taking into account the miller indices as found from the Fig. 2 are $a_o \approx 4.562 \text{ \AA}$ and $c_o \approx 7.456 \text{ \AA}$.

3.2 Diffuse Reflectance Studies of thin film CdSe

Figure 3.0 shows the diffuse reflectance studies for the as grown thin films of CdSe. It is seen from Fig. 3 that the thin films have luster and found to exhibit diffuse reflectance in the optical region of light in the wavelength range 370 nm to 750 nm. The diffuse reflectance studies shows there is a large amount of reflection at the wavelength of $\lambda \approx 725 \text{ nm}$. This corresponds to the band gap of CdSe and is found to tally with many other workers [5]. Kubelka-Munk model [7] was applied to the diffuse reflectance studies to find the band gap of the semiconducting CdSe.

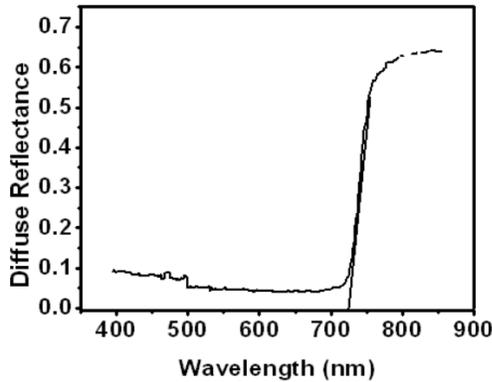


Fig. 3. Variation of Diffuse Reflectance with Wavelength for a thin film of CdSe

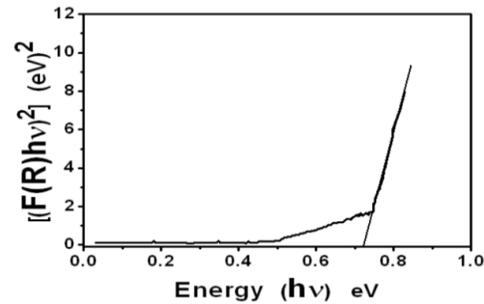


Fig. 4. Shows the variation of $(F(R)hv)^2$ vs hv

As per Kubelka Munk model considered a sample of infinite thickness where the entire absorption is from the thickness of the thin film and no substrate effect plays a part in the absorption process, then if k is the absorption coefficient and s is the scattering coefficient then

$$\frac{k}{s} = \frac{(1-R)^2}{2R} = F(R)$$

where $F(R)$ is the Kubelka Munk function. As per the Kubelka Munk model applied to a semiconducting thin film, the variation of $((F(R)hv)^2$ vs (hv) is linear. Here h is the Planck's constant, ν is the incident frequency of optical radiation. This variation is similar to a Tauc Plot. Therefore the intercept of the above plot on the energy axis hv gives the optical band gap of the semiconductor material, CdSe. Figure 4 shows the $((F(R)hv)^2$ vs (hv) variation. The band gap as calculated is found be $E_g \approx 1.71$ eV. This value is also confirmed from the diffuse reflectance vs wavelength plot.

3.3 Mott-Schottky Plots for the CdSe/(aq) Fe²⁺/Fe³⁺ junction in dark

It is found that the semiconducting CdSe and (aq) Fe²⁺/Fe³⁺ form a depletion width in the semiconductor side. This depletion width (Space Charge) exhibits capacitance (C) in the dark. So on application of potential (V) with respect to Saturated Calomel Electrode (SCE) shows the typical variation of a semiconductor electrolyte junction in dark. On taking inverse square of Capacitance with potential (V) variation at a fixed frequency of 1 kHz we have a linear plot called Mott-Schottky plot as per the following equation [8,9] is:

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

Where C is the capacitance measured in Farads, A is the area of the exposed semiconductor, ϵ_o is the absolute permittivity, ϵ_s is the permittivity of space charge, q is the charge in Farads, N_D is the Donor concentration, V_{FB} is the flat band potential, k_B is the Boltzmann's constant and T is the absolute temperature.

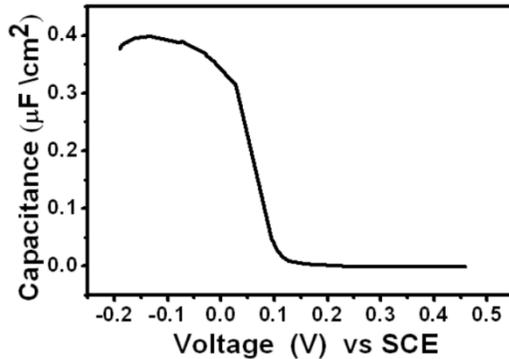


Fig. 5. C - V plots for CdSe/Fe²⁺/Fe³⁺ system in dark

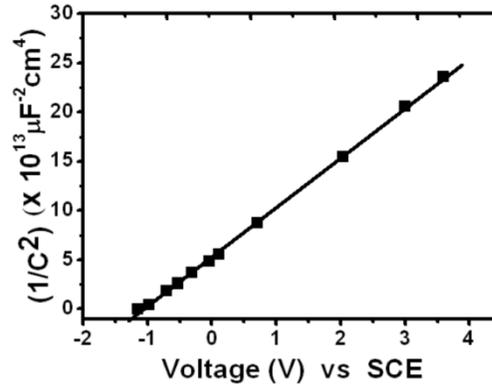


Fig. 6 Mott-Schottky Plots for CdSe/Fe²⁺/Fe³⁺ System

The plot of Capacitance (C) vs Voltage curve is shown in Fig. 5. Mott-Schottky plot is shown in Fig. 6. It is seen that the plot is linear. The intercept on the voltage axis of the plot in Fig. 6 gives the value of Flat Band potential, V_{FB} . It is found to be ≈ -0.13 V vs SCE. This negative value shows that the semiconductor is an *n*-type semiconductor. On taking the room temperature to be 300 K (27 °C), the slope of the linear plot gives the donor concentration, $N_D \approx 5 \times 10^{15} \text{ cm}^{-3}$, depletion width on the semiconductor side, $\omega \approx 0.045 \mu\text{m}$. The less value of the depletion width is due to the as-grown defects on the surface of the semiconductor CdSe thin film during the vacuum evaporation. These defects like grain boundaries prevent larger depletion width. The increase in the depletion width will give rise to the increase in band bending at the surface of the semiconductor and also generation of more number of minority carriers on illumination of the CdSe/Fe²⁺/Fe³⁺ junction in the photoelectrochemical solar cell.

3.4 Power Output characteristic of a CdSe/(aq) Ferro-Ferricyanide photoelectrochemical solar cell.

The power output characteristics of a CdSe/(aq) Ferro-Ferricyanide photoelectrochemical solar cell were studied under white light illumination at an intensity of 100 mW/cm². The Fig.7 gives the power output characteristics plot of the CdSe/(aq) Fe²⁺/Fe³⁺ photoelectrochemical solar cell. It is found from the curve (Fig. 7) that the open circuit voltage $V_{OC} \approx 0.45$ V and the Short Circuit Current Density, $J_{SC} \approx 6500 \mu\text{A}/\text{cm}^2$. The efficiency was calculated from the formula [10-11]:

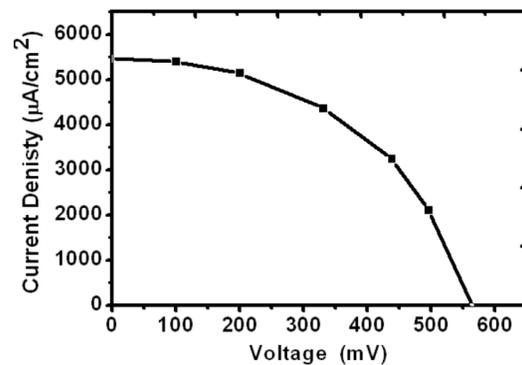


Fig. 7. Power Output Characteristics of a CdSe/Fe²⁺/Fe³⁺ Photoelectrochemical Solar Cell

$$\eta = \frac{J_{MP} \times V_{MP}}{P_{input}}$$

The efficiency of the photoelectrochemical solar cell as calculated from the above formula was nearly, $\eta \approx 1.3 \%$.

4. Conclusions

The thin films of CdSe were grown on a pre-coated conducting In₂O₃ glass plates. The In₂O₃ thin films were transparent and there was no absorption of light by the In₂O₃ material. The thin films of CdSe were characterized by powder X-ray diffraction for both bulk and the thin film. It was found that the thin films exhibited a hexagonal structure. The d-values obtained from the XRD pattern were found to tally with the values given in the literature JCPDS. The lattice parameters were found to be $a_o \approx 4.562 \text{ \AA}$ and $c_o \approx 7.456 \text{ \AA}$. This was also confirmed from the values as obtained from the literature (JCPDS-77-2307). The optical studies of the CdSe thin films were done by studying diffuse reflectance studies between the wavelength 350 nm to 750 nm using a UV-VIS-IR spectrophotometer. The optical band gap was calculated from the Kubelka-Munk theory by plotting the $((F(R)hv)^2 \text{ vs } (hv)$ variation. It was found that that the semiconducting CdSe thin film exhibited a direct band gap of $E_g \approx 1.71 \text{ eV}$. The Capacitance vs Voltage variation was studied in dark for the CdSe/(aq) $\text{Fe}^{2+}/\text{Fe}^{3+}$ junction. The Mott-Schottky plots exhibited a linear plot. The intercept on the voltage axis gave us vital parameters of the semiconductor junction. The flat band potential, V_{FB} was $\approx 0.13 \text{ V vs SCE}$. This low value of the flat band potential was due to the fact the surface of the semiconductor has a lot of grain boundaries. These grain boundaries in turn generate surface states in the band gap. These surface states lead to lower flat band potential. The power output characteristics of the photoelectrochemical solar cell was studied. The obtained low efficiency of 1.3% was due to the fact small grains lead to large grain boundaries. Also these grain boundaries scatter the minority generated carriers in the depletion width when the semiconductor CdSe electrolyte junction is illuminated, thus in turn effecting the lower solar power conversion efficiency.

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