

# Vacuum evaporated CdSe thin films and their characteristics

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Received 10 May 2004; received in revised form 31 August 2004; accepted 11 September 2004

Available online 28 September 2004

## Abstract

CdSe films that were vacuum deposited using the laboratory synthesized CdSe powder as source material were studied. The substrate temperature was varied in the range 30–200 °C. X-ray diffraction (XRD) studies indicated preferential orientation in the (002) direction. SEM studies indicated increase of grain size from 1.9 to 3.9 μm with increase of substrate temperature. The power conversion efficiency was found to be 7.0% under an illumination of 60 mW cm<sup>-2</sup> after photoetching. A peak quantum efficiency of 0.6 was obtained for an incident wavelength of 720 nm. Semiconducting parameters were estimated. Preliminary studies on large area films (25 cm<sup>2</sup>) indicated an efficiency of 5.9%.

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**Keywords:** CdSe; Thin films; Vacuum evaporation; Photoelectrochemistry; PEC cells; Semiconductor; Characteristics; Surface morphology

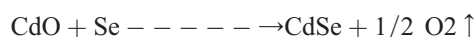
## 1. Introduction

CdSe is the most widely studied semiconductor as a photoanode in photoelectrochemical (PEC) cells. An energy conversion efficiency of 16.7% has been realized with CdSe single crystal photoanodes by employing electrolyte modification [1]. However, for practical applications thin films are preferred owing to their low cost. CdSe films were earlier prepared by electrodeposition [2], spray pyrolysis [3], vacuum evaporation [4], slurry painting [5], etc. In this paper, structural and PEC properties of vacuum evaporated films using the laboratory synthesized CdSe powder as source material are presented and discussed. Earlier CdSe films were vacuum evaporated using the commercial CdSe powder.

## 2. Experimental methods

CdSe powder was synthesized by the reaction of Analar (AR) grade cadmium oxide with AR selenium powder at 80

to 90 °C in the presence of oxalic acid. This technique consists of the reduction of cadmium oxide by oxalic acid and reaction of selenium powder with cadmium. The chemical reaction is as follows.



The mixture was heated for more than 10 h with continuous refluxing. The resulting powder was dried and used for the deposition of films. X-ray diffraction studies on the powder indicated the formation of single phase hexagonal CdSe. Atomic absorption spectroscopy (AAS) analysis indicated that the purity of the powder was comparable with that of Koch light (UK) powder. This powder was used as source for the deposition of films. CdSe films of thickness ranging from 2.0 to 2.5 μm and area 1 cm<sup>2</sup> were evaporated on Ti, conducting glass and glass substrates by vacuum evaporation technique. A vacuum of 10<sup>-5</sup> Torr was maintained during the time of deposition. The substrates were maintained at different temperatures in the range 30–200 °C. Thickness of the films varied from 2.0 to 2.5 μm. Structural characterization of the films were made using JEOL X-ray diffractometer and CuK<sub>α</sub> radiation. Optical studies were made employing a Hitachi U 3400 UV–VIS–NIR spectrophotometer with the films deposited

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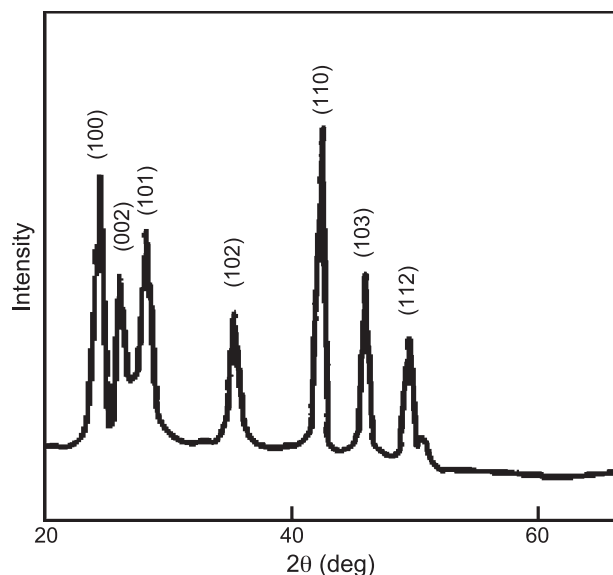


Fig. 1. X-ray diffraction pattern of CdSe powder.

on glass substrates. The PEC cell consisted of the CdSe film and graphite as working counter electrodes, respectively. The electrolyte was a 1 M polysulphide solution (1 M Na<sub>2</sub>S, 1 M NaOH, 1 M S). The light source was a 250 W ORIEL quartz tungsten halogen lamp. The photon flux was measured by a CEL suryamapi intensity measuring system.

### 3. Results and discussion

Fig. 1 shows the X-ray diffractogram (XRD) of the CdSe powder synthesized in the laboratory. All the peaks corresponding to hexagonal CdSe are observed. Prominent peaks corresponding to (100), (002), (101), (110), (103) and (112) reflections are observed. Elemental selenium or cadmium peaks are not observed indicating the formation of single phase material.

AAS was used for the trace elemental analysis of the synthesized CdSe powder. The determination of the concentration of metallic elements in CdSe powder was done by Perkin Elmer Model 380 AAS unit. For the purpose of analysis, 10 mg of CdSe powder was dissolved in 15 ml of nitric acid. The presence of impurities such as calcium, potassium, sodium, thallium, zinc, lead, cobalt and arsenic were screened and were found to be in the range of 5–10 ppm. This is comparable with the purity of the imported powder. The data are shown in Table 1.

Table 1  
Elemental analysis of CdSe powders

Material	Trace analysis in ppm							
	Tl	Ca	K	Na	Zn	Pb	Co	As
Laboratory synthesized	20	11	10	8	6	—	—	—
Koch light	16	11	7	5	3	—	—	—

The XRD pattern of the CdSe films deposited at different substrate temperature is shown in Fig. 2. The peaks corresponding to hexagonal CdSe are observed. This data compares well with the ASTM data. Elemental Se or Cd peaks were not observed. The intensity of the peak corresponding to (002) orientation increased as the substrate temperature increased, indicating the preferential orientation in this direction.

EDAX measurements were made on the samples deposited at different substrate temperatures. The chemical composition of the films varied from 63.0% to 65.4% for Cd and from 37.0% to 34.6% for Se as the substrate temperature increased from 30 to 200 °C.

The XPS studies were carried out on the CdSe films deposited at different temperatures, the peak energy levels associated with Cd (3d<sub>5/2</sub> and 3d<sub>3/2</sub>) and Se (3d<sub>5/2</sub> and 3d<sub>3/2</sub>) were found at 405.0, 411.7 eV and 53.9, 59.2 eV, respectively. These observations are characteristic of Cd and Se in CdSe as reported in the literature [6]. As the substrate temperature increased there was a small reduction in the area under the Se curves compared to the area of the Se curves for the films deposited at lower substrate temperatures, possibly due to the different sticking coefficient of Cd and Se. Atomic concentration measurements

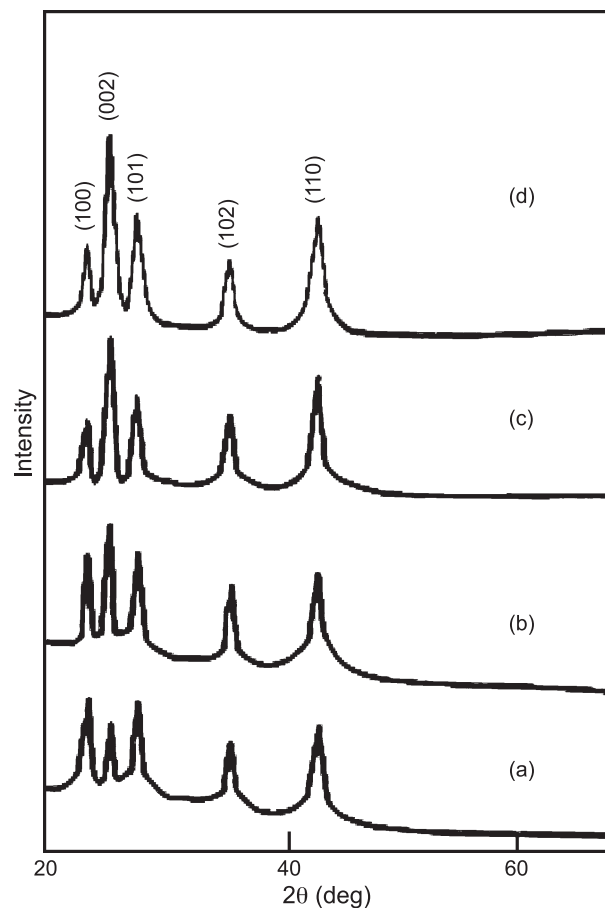


Fig. 2. X-ray diffraction pattern of CdSe films at different substrate temperatures: (a) 30 °C, (b) 100 °C, (c) 150 °C, (d) 200 °C.

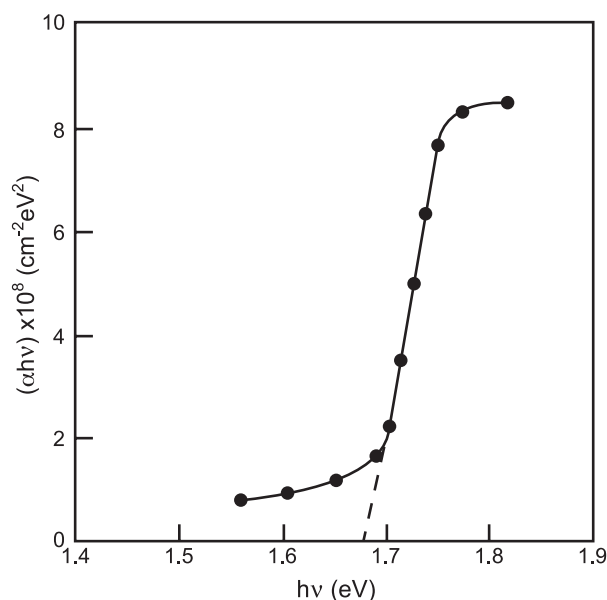


Fig. 3.  $(\alpha h\nu)^2$  vs.  $h\nu$  plot for CdSe films deposited at 200 °C.

made on the films deposited at a substrate temperature of 200 °C yielded an apparent Cd/Se ratio of 1.62, this calculation was based on the consideration of the area sensitivity factors for Cd and Se, respectively, and agrees very well with the composition estimated from EDAX measurements.

CdSe is a direct band gap semiconductor. Hence a plot of  $(\alpha h\nu)^2$  vs.  $h\nu$  should give a straight line and extrapolation gives the energy gap. Fig. 3 shows such a plot for the films deposited at a substrate temperature of 200 °C. A direct band gap value of 1.68 eV was observed. This is comparable with the results obtained earlier on electrodeposited, chemically deposited, slurry painted and

Table 2

PEC parameters of CdSe film electrodes deposited at different substrate temperatures after chemical etching (int: 60 mW cm<sup>-2</sup>)

$T_{\text{sub}}$ (°C)	$V_{\text{oc}}$ (V)	$J_{\text{sc}}$ (mA cm <sup>-2</sup> )	FF	$\eta$ (%)
30	0.30	9.5	0.55	2.62
100	0.34	11.5	0.55	3.60
150	0.37	15.0	0.65	6.00
200	0.42	17.5	0.57	7.00

spray pyrolysed CdSe films. With change of substrate temperature, the band gap was found to vary in the range of 1.66–1.68 eV.

The power output characteristics of the PEC cell employing the films deposited at different substrate temperature are shown in Fig. 4. As deposited films did not exhibit any photoactivity, the films were heat-treated in argon atmosphere at 500 °C for 20 min and cooled at a very slow rate. This results in crystal refinement and hence increased photoactivity. The films were first given a chemical etching treatment followed by PEC etching. Photoetching was done in 1:10 HCl at an illumination of 100 mW cm<sup>-2</sup> white light illumination for different durations up to 80 s by shorting the photo and counter electrodes.

From the figure, it is found that for the chemically etched films, all the output parameters (Table 2) are found to increase with increase of substrate temperature. The PEC parameters are found to increase after photoetching. Photoetching leads to an increase in surface area which gives rise to an enhanced current [7]. Photoetching also leads to selective attack of surface defects not accessible to chemical etchants [8]. Both  $V_{\text{oc}}$  and  $J_{\text{sc}}$  are found to increase with increase of photoetching time up to 60 s, beyond which they decrease. This can be attributed to the separation of grain boundaries due to prolonged photo-

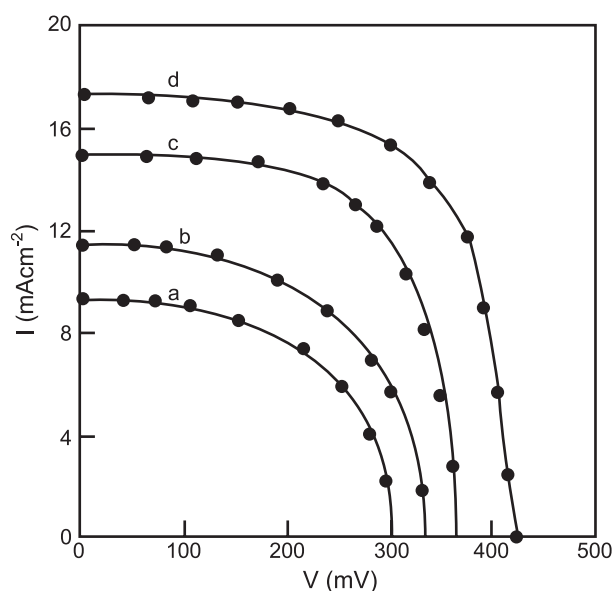


Fig. 4. Power output characteristics of CdSe films deposited at (a) 30 °C, (b) 100 °C, (c) 150 °C, and (d) 200 °C and post annealed in argon at 500 °C for 20 min and slow cooling.

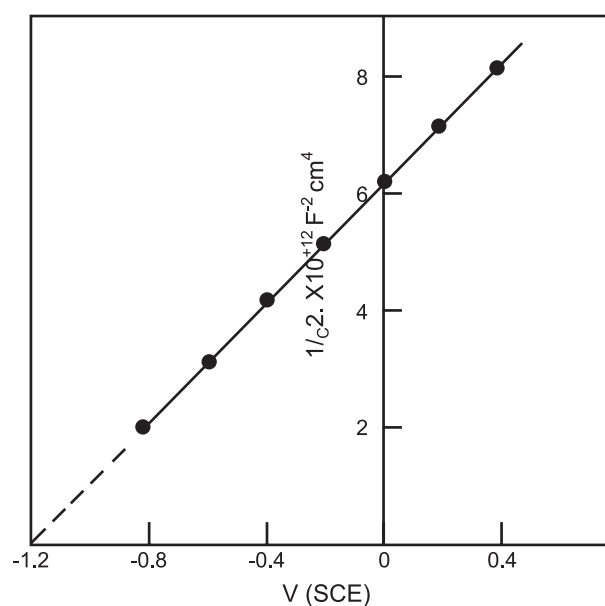


Fig. 5. Mott–Schottky plot of CdSe electrodes deposited at 200 °C and post annealed at 500 °C for 20 min and slow cooling.

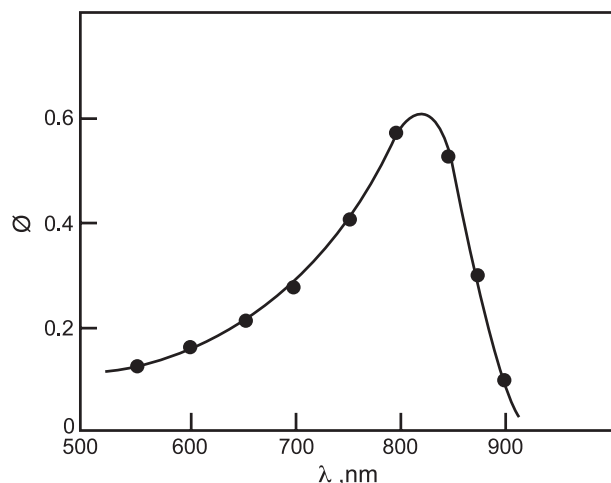


Fig. 6. Variation of quantum efficiency versus wavelength for the electrodes deposited at a substrate temperature of 200 °C and post annealed at 500 °C for 20 min and slow cooling.

etching. The efficiency values obtained with these photoelectrodes are higher than the results obtained in earlier studies [9]. Large area films were deposited on titanium substrates, 25 cm<sup>2</sup> area films have yielded an open circuit voltage of 0.56 V, a short circuit current density of 12 mA cm<sup>-2</sup>, fill factor of 0.52 and a conversion efficiency of 5.9% at an illumination of 60 mW cm<sup>-2</sup>.

Mott–Schottky plot at 500 Hz in 1 M polysulphide solution is shown in Fig. 5. The plot is linear. Extrapolation yields a flat band potential ( $V_{fb}$ ) of -1.2 V (SCE). The nature of the plot indicates n-type behaviour. This value agrees well with the value obtained from the  $I_{ph}^2$  vs.  $V$  plot. A value of 10<sup>17</sup> cm<sup>-3</sup> was obtained for the donor density from the slope of the linear plot. This value is in good agreement with the value of carrier density obtained from Hall measurements.

The quantum efficiency ( $\phi$ ) is influenced by the depletion layer width in the semiconductor, which in turn, is dependent on the conductivity [10]. This has been evaluated by employing the following expression [11,12]:  $\phi (\pi \eta l) = 1240 J_{sc} / \lambda P$ , where  $\phi$  is the quantum efficiency,  $J_{sc}$  is the photocurrent density expressed in A cm<sup>-2</sup>,  $\lambda$  (lambda) is the wavelength expressed in nm and  $P$  is the light absorbed in the photoactive region expressed in W cm<sup>-2</sup>. Fig. 6 shows the variation in quantum efficiency with

wavelength in the range 550–825 nm. A peak quantum efficiency of 0.60 is observed at 720 nm. This wavelength value corresponds to the band gap of the semiconductor.

The cross plane resistivity was found to be 10 Ω cm and the in plane resistivity was found to be 5 Ω cm. This shows that the surface contains more donors than the bulk. Employing the cross plane resistivity value, the mobility of electrons was found to be 66 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. This value is in agreement with the range of values reported recently [13] for CdSe films obtained by the conventional electrodeposition technique. The low value of resistivity may be due to the excess Cd present in the films as evident from the XPS measurements (Cd/Se ratio 1.62).

#### 4. Conclusions

The present study indicates that vacuum evaporation technique can be successfully employed for the preparation of device quality CdSe films. The quantum efficiency as well as the power conversion efficiency can be enhanced further by optimizing the annealing parameters and the etching steps.

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