

Photoelectrochemical (PEC) studies on CdSe thin films electrodeposited from non-aqueous bath on different substrates

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Abstract. Thin films of CdSe were deposited by potentiostatic mode on different substrates such as stainless steel, titanium and fluorine tin-oxide (FTO) coated glass using non-aqueous bath. The preparative parameters were optimized to get good quality CdSe thin films. These films were characterized by X-ray diffraction (XRD), optical absorption and photoelectrochemical (PEC) techniques. XRD study revealed that the films were polycrystalline in nature with hexagonal phase. Optical absorption study showed that CdSe films were of direct band gap type semiconductor with a band gap energy of 1.8 eV. PEC study revealed that CdSe film deposited on FTO coated glass exhibited maximum values of fill factor (FF) and efficiency (η) as compared to the films deposited on stainless steel and titanium substrate.

Keywords. Electrodeposition; potentiostatic; XRD; PEC; fill factor; efficiency.

1. Introduction

Cadmium selenide having suitable band gap (1.74 eV) and high photosensitivity in the visible region of the spectrum can be utilized in a number of optoelectronic devices such as PEC cells (Muller and Ginley 1980), photoconductors (Nair *et al* 1993), thin film transistors (Van Cluster *et al* 1998), gamma ray detectors (Roth 1989), etc. A variety of deposition techniques such as electrodeposition (Kutzmutz *et al* 2001), thermal evaporation (Shreekanthan *et al* 2003) and chemical bath deposition (Kale and Lokhande 2000) have been used and among these methods electrodeposition is an isothermal process mainly controlled by electrical parameters, which are easily adjusted to control film thickness, morphology, composition, etc. In the literature, most of the CdSe films electrodeposited from aqueous acidic baths usually contain large concentration of elemental selenium (Pandey *et al* 1991; Gutierrez and Ortega 1989) that weakly crystallizes and the micrographs showed a cauliflower-like appearance, which remained unchanged after annealing. Literature survey shows that extensive work has been done on the preparation and characterization of CdSe thin films electrodeposited from aqueous acidic baths, but very few workers (Baranski and Fawcett 1980; Baranski *et al* 1983; Skyllas-Kazacos and Miller 1980) deposited these films from non-aqueous baths. Compared to water, non-aqueous solvents offer an alternative process with some

advantages. The proclivity of the chalcogen to exist predominantly in low oxidation states in these baths, and the attendant lack of complications in the electrodeposition chemistry have been the principal motivating factors in the evaluation of non-aqueous media (Dongsheng *et al* 2003). However, no literature is found on CdSe thin films deposited by electrodeposition using cadmium acetate as source of Cd²⁺ ions from non-aqueous bath. In addition, the comparative study of PEC cell performance of these films deposited on different substrates from non-aqueous bath is rarely found.

In view of this, the present study deals with preparation of CdSe thin films by electrodeposition method under potentiostatic condition on different substrates such as stainless steel, titanium and FTO coated glass from non-aqueous bath with ethylene glycol as a solvent. The influence of deposition parameters on the performance of PEC cell are of great scientific importance (Pawar *et al* 2006). In view of this, a PEC cell of configuration *n*-CdSe/1M polysulphide/graphite is fabricated. The PEC characterization technique was used to optimize the bath temperature and to determine the conductivity type of the film. The structural, optical and photovoltaic properties of CdSe films deposited on different substrates have been studied and the results are discussed at length.

2. Experimental

CdSe thin films were electrodeposited on different substrates at various bath temperatures using non-aqueous

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bath with saturated calomel (SCE) as reference electrode and graphite as counter electrode (volume, $4 \times 2 \times 0.3 \text{ cm}^3$). Cadmium acetate [$\text{Cd}(\text{CH}_3\text{COO})_2$] and selenium dioxide (SeO_2) were used as sources of Cd and Se, respectively. Tetrasodium salt of ethylene diamine tetraacetic acid (EDTA) was used as a complexing agent. Prior to the deposition, the metallic substrates (stainless steel and titanium) were thoroughly polished using zero fine grade (3/0) polish paper (supplied by Kohinor products, India) and then washed with liquid detergent (labolene) followed by ultrasonic cleaning with double distilled water. In order to remove oily substance from the surface, cleaned substrates were etched in 10% H_2SO_4 for 2 min and finally ultrasonically cleaned with double distilled water. FTO coated glass substrates were boiled in chromic acid for 30 min and ultrasonically cleaned with double distilled water and dried with hot air.

The polarization curves were recorded at various bath temperatures to estimate the deposition potential and the effect of bath temperature on deposition potential was studied. PEC cell was fabricated using 3-electrode configuration, comprising *n*-CdSe thin film as a photoanode (area, 1.5 cm^2), graphite as counter electrode and SCE as reference electrode. The redox electrolyte was 1 M polysulphide ($\text{NaOH-Na}_2\text{S-S}$). A 500-Watt tungsten filament lamp (intensity, 40 mW/cm^2) was used as a light source. To prevent heating of the cell, water filter was interposed between the lamp and the cell. To optimize the bath temperature, the short circuit current (I_{sc}) and the open circuit voltage (V_{oc}) generated in the PEC cell under illumination of light (40 mW/cm^2) were measured at various bath temperatures. To optimize deposition time, the films were deposited at optimized bath temperature for different time intervals. The films deposited using optimized bath temperature and deposition time were used for structural, optical and PEC characterization. XRD patterns of the films were obtained with the help of a Philips X-ray diffractometer (PW-3710) Cr- K_α radiation. The optical absorption studies were carried out with a UV-VIS-NIR spectrophotometer (Systronic, Model 119). PEC characterization of the films was carried out to determine the conductivity type and to study photovoltaic output characteristics.

3. Results and discussion

3.1 Deposition potential

Figures 1 a–c show cathodic polarization curves for stainless steel, titanium and FTO coated glass substrates in 0.01 M $\text{Cd}(\text{CH}_3\text{COO})_2$, 0.005 M SeO_2 and 0.01 M $\text{Cd}(\text{CH}_3\text{COO})_2$ (10 mL) + 0.1 M EDTA (1 mL) + 0.005 M SeO_2 (10 mL) at 80, 75 and 85°C, respectively. Estimated deposition potentials from polarization curves are given in table 1. It is observed that the deposition potentials of Cd and Se are different for different substrates. Also, the deposition

potential of CdSe lies between those of elemental Cd and Se (Yesugade et al 1995). The current density values for stainless steel, titanium and FTO coated glass substrates

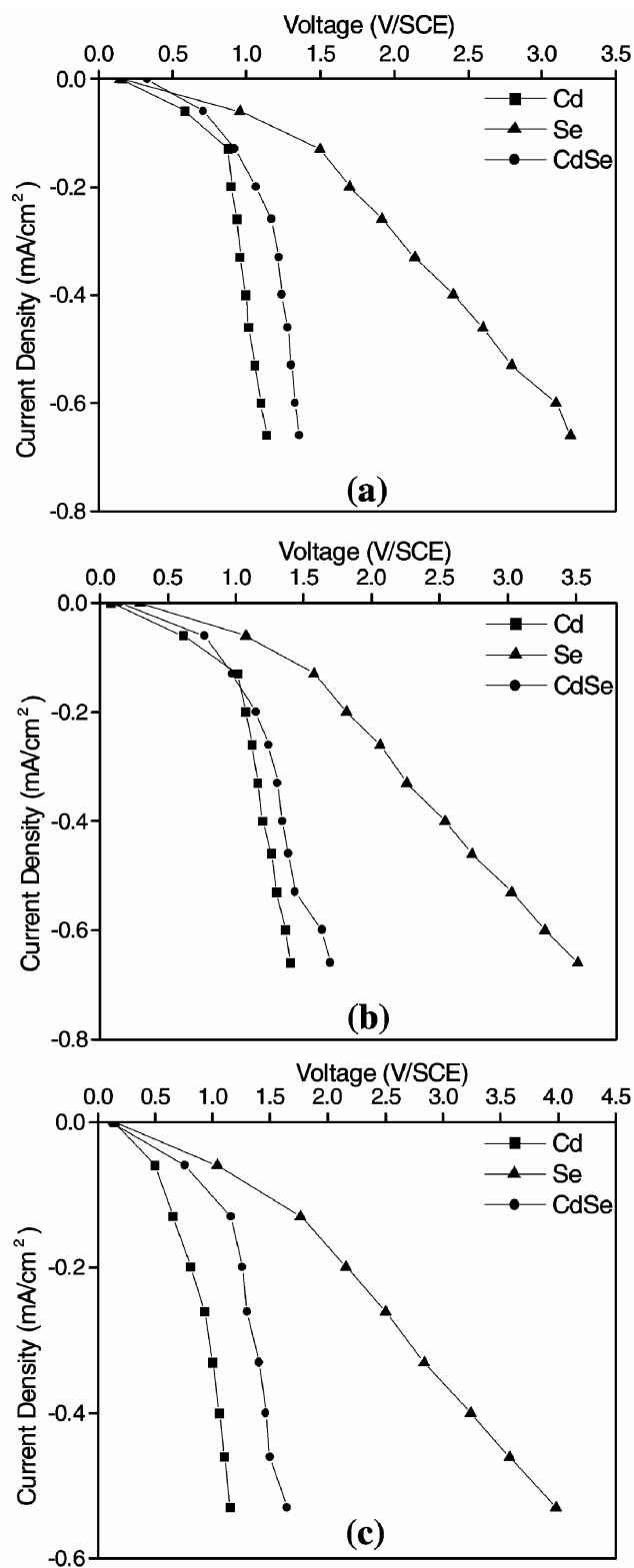


Figure 1. Cathodic polarization curves for Cd, Se and CdSe at (a) 80°C on SS, (b) 75°C on Ti and (c) 85°C on FTO coated glass.

Table 1. Estimated deposition potentials from the polarization curves for the films deposited on SS, Ti and FTO coated glass at bath temperatures 80, 75 and 85°C, respectively.

Sl. no.	Bath composition	Deposition potential (V/SCE)		
		SS (80°C)	Ti (75°C)	FTO (85°C)
1	0.01 M Cd(CH ₃ COO) ₂	-0.85	-0.99	-1.14
2	0.005 M SeO ₂	-1.44	-1.49	-1.64
3	0.01 M Cd(CH ₃ COO) ₂ (10 mL) + 0.1 M EDTA (1 mL) + 0.005 M SeO ₂ (10 mL)	-1.14	-1.18	-1.36

Note: SS = Stainless steel; Ti = titanium; FTO = FTO coated glass.

for bath composition 3 given in table 1 are 0.3, 0.35 and 0.4 mA/cm² and the corresponding values of current efficiency are 75.62, 72.13 and 70.11%, respectively.

3.2 Effect of temperature

Effect of bath temperature on deposition potential in the temperature range 70–90°C was studied. Figures 2a–c show cathodic polarization curves for stainless steel, titanium and FTO coated glass substrates in 0.01 M Cd(CH₃COO)₂ (10 mL) + 0.1 M EDTA (1 mL) + 0.005 M SeO₂ (10 mL) at different bath temperatures, respectively and the corresponding deposition potentials are given in table 2. It is observed that the deposition potential decreases with increase in the bath temperature. Generally, increase in temperature increases the grain size. The increase in grain size corresponds to a decrease in polarization potential at higher temperature (Brenner 1963). The increase in temperature dissociates the complex (Marcus 1952) and hence the concentration of simple metal ions increases, leading to the discharge of ions at a lower potential. Also, the rise in temperature of the bath enhances the rate of diffusion and increases the ionic mobilities and hence the conductivity of the bath (Jundale and Lokhande 1994).

3.3 Effect of temperature on PEC properties

A PEC cell of configuration, CdSe/1 M polysulphide/graphite, was formed in order to check the conductivity type exhibited by CdSe thin films. In light (40 mW/cm²), cathodic behaviour of photovoltage of CdSe thin films is observed, indicating that the electrodeposited CdSe thin films are of *n*-type. The origin of this voltage is attributed to the difference between two half cell potentials in the PEC cell and can be written as

$$E = E_{\text{graphite}} - E_{\text{CdSe}}, \quad (1)$$

where E_{graphite} and E_{CdSe} are the half cell potentials when dipped in the redox electrolyte.

Figures 3a–c show the variation in I_{sc} and V_{oc} with respect to bath temperature for CdSe film deposited on

stainless steel, titanium and FTO coated glass substrates, respectively. It is seen that I_{sc} and V_{oc} increases initially with increase in bath temperature, becomes maximum at a particular temperature (80, 75 and 85°C for the film deposited on stainless steel, titanium and FTO coated glass substrates, respectively) and then decreases with further increase in temperature (Bhardwaj *et al* 1984). This variation in I_{sc} and V_{oc} at lower and higher values of bath temperature other than optimized one is attributed to the resistivity of CdSe thin films (Pawar *et al* 2006).

3.4 Thickness measurement

The thickness of the film was measured by weight difference method assuming the density of the deposited film to be same as that of the bulk. The variation of film thickness with deposition time is shown in figure 4. It is observed that as deposition time increases, film thickness increases, attains maximum thickness and thereafter, decreases slightly with further increase in deposition time. This is attributed to the increase in the rate of dissolution than the rate of deposition after attaining the maximum thickness (Lade *et al* 2000).

3.5 XRD studies

Structural properties of CdSe thin films were studied by X-ray diffraction. CdSe can form the hexagonal, wurtzite-type structure or the cubic, zincblend-type structure. Figures 5a–c show XRD patterns of CdSe films deposited on stainless steel, titanium and FTO coated glass substrates, respectively. XRD patterns revealed that the films are polycrystalline in nature with hexagonal (JCPDS card number 77-2307) phase. Table 3 shows a comparison of observed '*d*' values of CdSe films with standard '*d*' values from JCPDS data files. Plane (002) at $2\theta \sim 38^\circ$ of hexagonal phase is observed in all the XRD patterns. Some peaks of substrates (JCPDS card number 33-0397, 34-0396, 44-1294 and 77-0448) were also observed in all the XRD patterns. Elemental selenium (JCPDS card number 73-2121) was observed for the film deposited on stainless

steel and titanium substrates, however, it was not observed in case of the film deposited on FTO coated glass substrate.

Crystallite size of CdSe film was calculated by using Scherrer's formula,

$$D = \frac{K\lambda}{\beta \cos\theta}, \quad (2)$$

where D is the crystallite size, λ the X-ray wavelength used, β the angular line width of half maximum intensity, θ the Bragg's diffraction angle and K some constant with a value of 0.9. The D values are also given in table 3. It shows that the crystallite size of CdSe films deposited on FTO coated glass substrate is large as compared to the films deposited on stainless steel and titanium substrate for (002) plane of hexagonal phase. Generally, 'efficient' electrocrystallization means obtaining of compact, crystallized layers. However, high crystallinity may not always be the main objective, at least in view of a high PEC solar cell efficiency. The substrate state deposition plays an important role in this matter, since, together with potential, it determines the outcome of the process in terms of grain size and structure (Bouroushian *et al* 2000). In our case, deposition potential is more negative for CdSe thin film deposited on FTO coated glass than stainless steel and titanium substrates (table 1). When deposition potential becomes more negative, larger current densities lead to growth of larger particle sizes (Shen *et al* 2005). The other possible reason might be the value of optimized bath temperature, which is greater (85°C) for FTO coated glass substrate as compared to stainless steel (80°C) and titanium (75°C) substrates (Brenner 1963; Mahalingam *et al* 2002).

3.6 Optical studies

Optical study of CdSe film was carried out in the wavelength range 350–850 nm at room temperature for the film deposited on FTO coated glass substrate. The transmittance data was used to calculate the absorption coefficient (α) using Tauc's relation (Manificier *et al* 1977):

$$\alpha h\nu = A(h\nu - E_g)^{1/2}, \quad (3)$$

Table 2. Effect of bath temperature on deposition potential for bath composition, 0.01 M Cd(CH₃COO)₂ (10 mL) + 0.1 M EDTA (1 mL) + 0.005 M SeO₂ (10 mL) used on different substrates.

Sl. no.	Bath temperature (°C)	Deposition potential (V/SCE)		
		SS	Ti	FTO
1	27	-1.77	-1.78	-1.81
2	70	-1.26	-1.28	-1.47
3	75	-1.18	-1.18	-1.40
4	80	-1.14	-1.12	-1.38
5	85	-1.12	-1.06	-1.36
6	90	-1.10	-1.01	-1.33

Note: SS = Stainless steel; Ti = titanium; FTO = FTO coated glass.

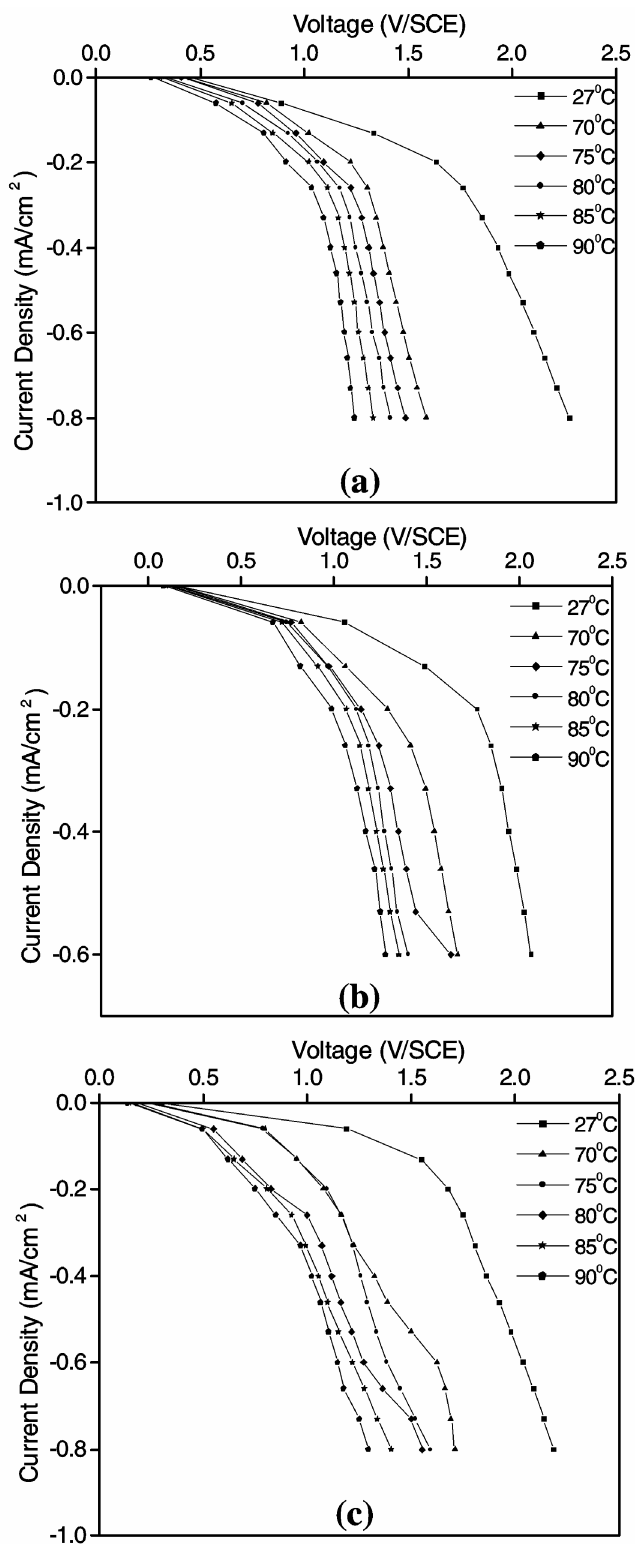


Figure 2. Cathodic polarization curves for CdSe at various bath temperatures on (a) SS, (b) Ti and (c) FTO coated glass.

where $h\nu$ is the photon energy, E_g the band gap and A a constant.

Further, absorption coefficient (α) can be simplified as,

$$\alpha = \frac{-\ln T}{t}, \tag{4}$$

where T is the transmission and t the thickness of the film which is $0.72 \mu\text{m}$.

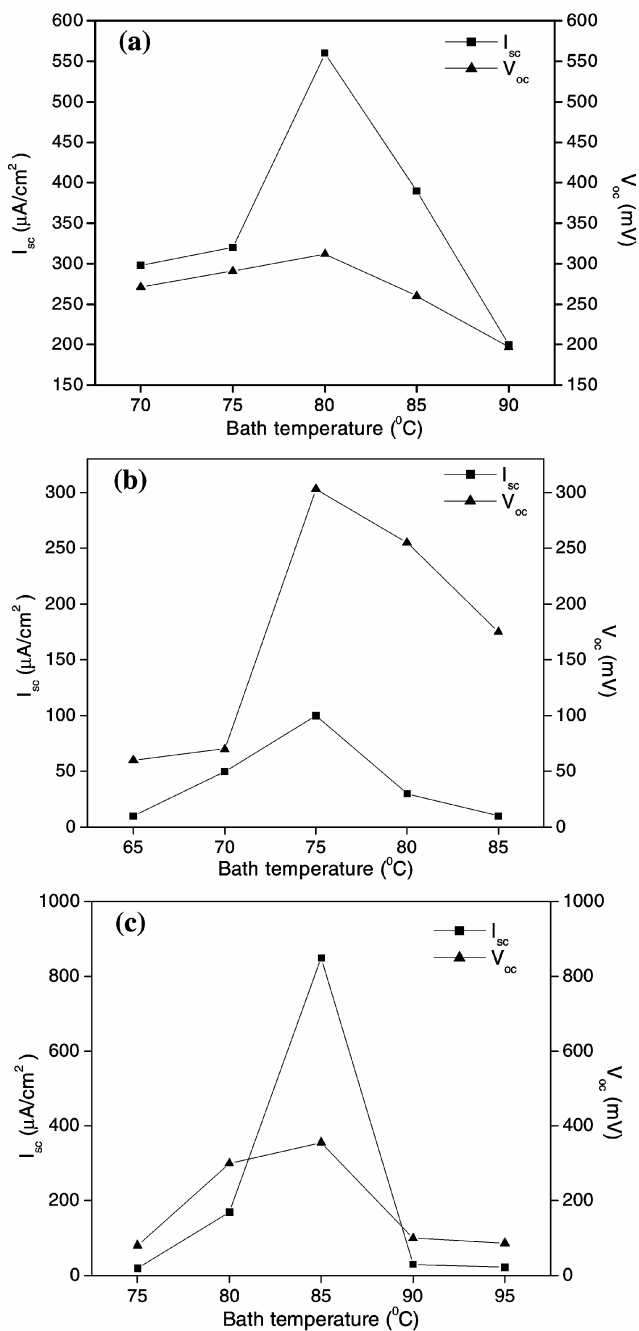


Figure 3. Plots of variation of short circuit current density (I_{sc}) and open circuit voltage (V_{oc}) vs bath temperature for CdSe film deposited on (a) SS, (b) Ti and (c) FTO coated glass.

The variation of $(\alpha h\nu)^2$ vs $(h\nu)$ for CdSe is linear at the absorption edge (figure 6), which confirms that CdSe is a

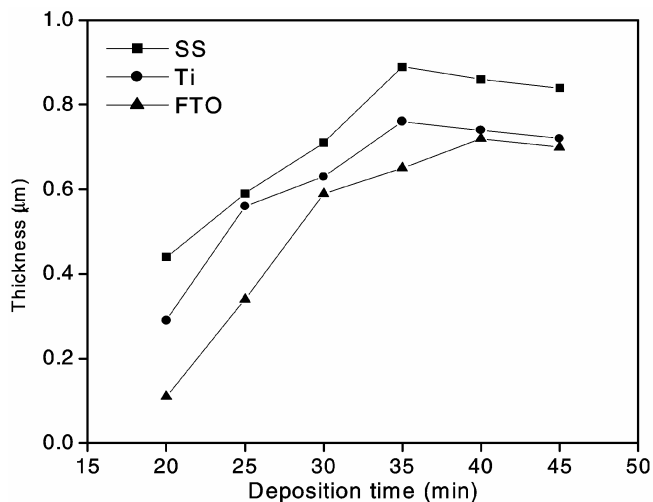


Figure 4. Plot of variation of film thickness vs deposition time.

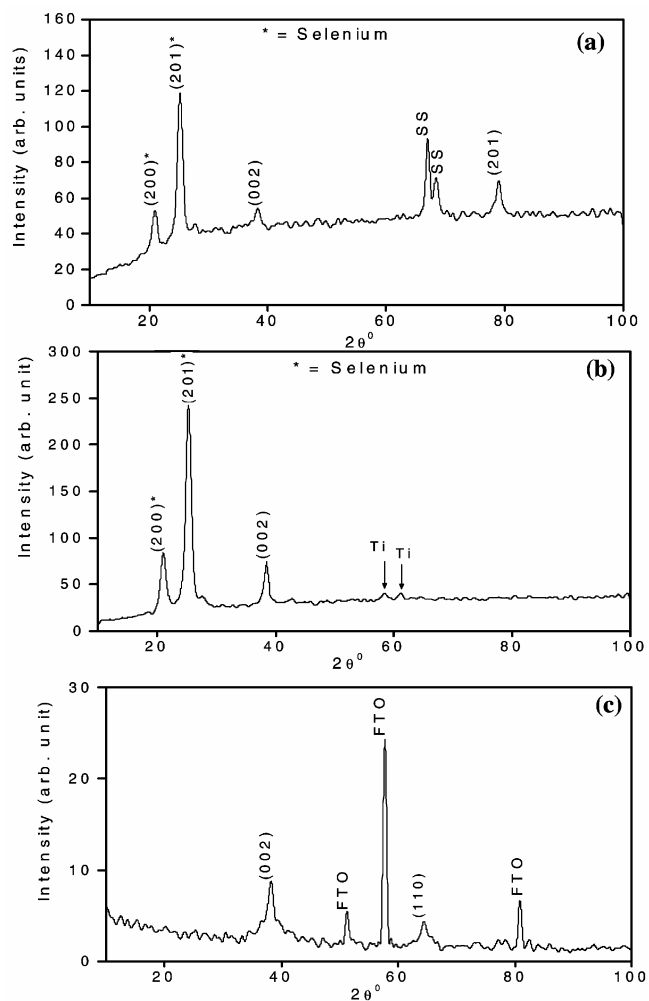
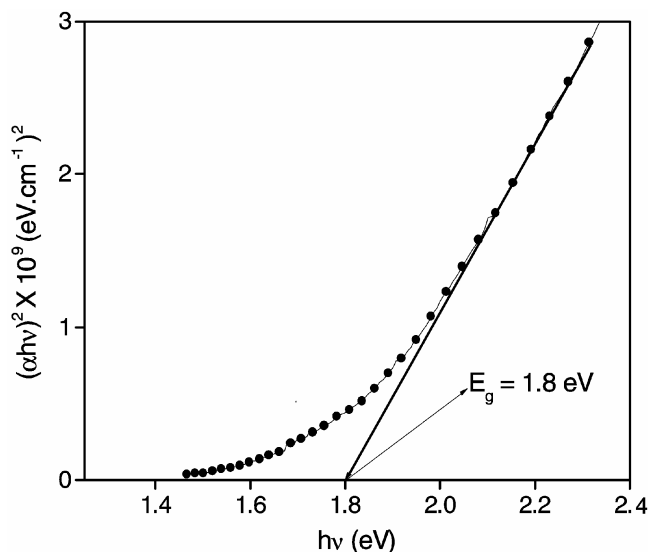


Figure 5. X-ray diffraction patterns of CdSe film deposited on (a) SS, (b) Ti and (c) FTO coated glass.

Table 3. Comparison of observed and standard 'd' values for CdSe films deposited on different substrates.

Sl. no.	Substrate	Observed 'd' (Å)	Standard 'd' (Å)	Plane (h k l)	FWHM	Crystallite size 'D' (nm)
1	SS	3.5002	3.5050	0 0 2	0.5905	11.53
		1.7995	1.7992	2 0 1	0.7452	11.18
2	Ti	3.5015	3.5050	0 0 2	0.7315	10.20
3	FTO	3.5060	3.5050	0 0 2	0.5723	14.55
		2.1498	2.1495	1 1 0	0.7401	11.26

Note: SS = Stainless steel; Ti = titanium; FTO = FTO coated glass.

**Figure 6.** Plot of variation of $(\alpha h\nu)^2$ vs $(h\nu)$ for CdSe film deposited on FTO coated glass.

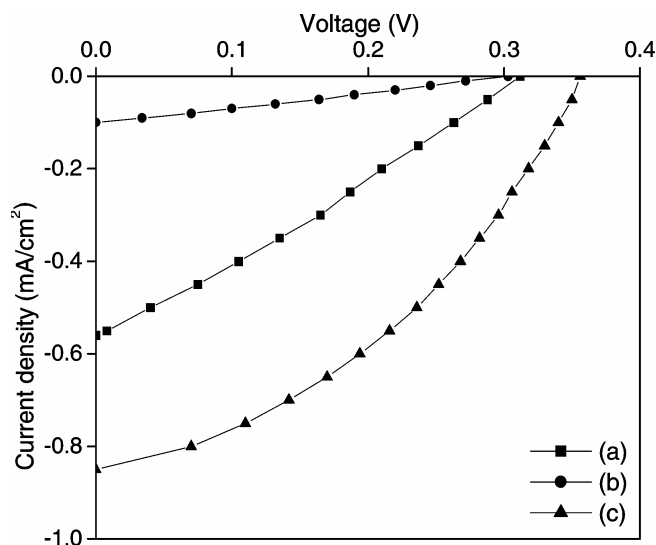
semiconductor with a direct band gap. Extrapolating the straight-line portion of the plot of $(\alpha h\nu)^2$ vs $(h\nu)$ for zero absorption coefficient value gives the band gap, which is found to be 1.8 eV. The optical band gap of CdSe thin film in the present case is higher than the value for single crystals which is in accordance with the earlier observation on chemically deposited CdSe thin films (Nair *et al* 1993).

3.7 Photoelectrochemical (PEC) characterization

The photovoltaic output characteristics were studied under light intensity of 40 mW/cm². Figure 7 shows photovoltaic power output curves for CdSe film deposited on different substrates. The photovoltaic efficiency ($\eta\%$) was calculated from the relation (Dasand and Damodare 1997),

$$\eta = \left[\frac{(I_{sc} V_{oc} FF)}{P_{hv}} \right] \times 100\%, \quad (5)$$

where P_{hv} is the power density of the incident radiation.

**Figure 7.** Plot of power output characteristics for CdSe film deposited on (a) SS, (b) Ti and (c) FTO coated glass.

The fill factor (FF) was calculated from the relation (Coutts 1978)

$$FF = \left[\frac{(I_m V_m)}{I_{sc} V_{oc}} \right] \times 100\%, \quad (6)$$

where I_m and V_m are, respectively the current density and voltage obtained at maximum power point on the photovoltaic power output curve.

Series resistance (R_s) and shunt resistance (R_{sh}) were evaluated from the slopes of the power output characteristics using the relation (Coutts 1978),

$$R_s = \left[\frac{dV}{dI} \right]_{I=0}, \quad (7)$$

$$R_{sh} = \left[\frac{dV}{dI} \right]_{V=0}. \quad (8)$$

The parameters estimated from power output plots are shown in table 4. The maximum efficiency was obtained from CdSe film deposited on FTO coated glass substrate, while it was less for stainless steel and titanium substrate.

Table 4. Estimated important parameters from photovoltaic power output curves of CdSe PEC cells.

Sl. no.	Substrate	I_{sc} (mA/cm ²)	V_{oc} (mV)	Fill factor (FF%)	Efficiency (η %)	R_s (Ω)	R_{sh} (Ω)
1	SS	0.560	312	28.81	0.1237	500	676
2	Ti	0.100	303	27.06	0.0205	2867	3600
3	FTO	0.850	356	39.25	0.2970	1600	2400

Note: SS = Stainless steel; Ti = titanium; FTO = FTO coated glass.

This result is supported by the fact that, films deposited on FTO coated glass have better crystallinity as compared to the films deposited on stainless steel and titanium substrate.

4. Conclusions

CdSe films can be electrodeposited onto various substrates from non-aqueous bath using ethylene glycol as a solvent. Decrease in deposition potential with increase in bath temperature was observed for all the substrates. From PEC studies it is clear that CdSe is an *n*-type material. X-ray diffraction study revealed the polycrystalline nature of the films with hexagonal phase. In addition, the crystallite size for hexagonal (002) plane is large for the film deposited on FTO coated glass, while it is less for stainless steel and titanium substrates. An optical absorption study showed that CdSe is a direct band gap material having a band gap energy of 1.8 eV. Photovoltaic power output characteristics showed better performance of the film deposited on FTO coated glass as compared to films deposited on stainless steel and titanium substrate.

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