Characteristics of CdSe films electrodeposited with microprocessor based pulse plating unit

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Abstract

In this paper we report the results on pulse electrodeposited cadmium selenide thin films using microprocessor control. The as-deposited and heat- treated films were characterized by X-ray diffraction, scanning electron microscope and optical absorption studies. Polycrystalline CdSe films obtained by pulse electrodeposition indicated both cubic and hexagonal structures whose lattice constants agree well with the standard values. An average grain size of 3 μm and an absorption coefficient of 10^4 cm^{-1} were obtained by SEM and optical studies. The power conversion efficiency for an illumination of 80 mW/cm^2 in 1 M polysulphide was in the range of 1.75–2.4% for the films plated at different duty cycles. A peak quantum efficiency of 0.75 was obtained at 725 nm. Acceptor concentration of 1.6×10^{16} cm^{-3}, electron mobility of 5.63 cm^2/V s, and minority carrier diffusion length of 0.185 μm have been obtained. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Pulse plating; Semiconductor; PEC; CdSe thin films

1. Introduction

The II–VI semiconducting compounds, especially the cadmium chalcogenides have been extensively studied due to their potential applications, in semiconductor device technology [1] and solar cells. Metal-Insulator-Semiconductor type solid state solar cells based on CdSe yield respectable efficiencies [2,3]. Solar cells from CdSe single crystal are very expensive, therefore the use of large area semiconductor thin film is a desirable alternative for cost reduction [4]. In this context, CdSe films have been prepared by conventional electrodeposition technique by a number of workers in acidic and alkaline medium [5–8].

The pulse electrodeposition [9] is a modified form of electrodeposition in which either pulse current or pulse potential is applied to the electrode for a given duration of time. Metal deposits obtained by pulse plating show distinct advantages like improved deposit distribution, minimised edge effect, pinhole free deposit, less hydrogen uptake, uniform thickness, better adhesion and lower impurity content compared to conventional dc electrodeposition [10]. The characteristics of the films deposited by pulse electrodeposition are controlled by factors like on-time, off-time and current density [11–13]. Smooth layers of

CdSe on titanium or SnO$_2$ substrates were obtained by pulse plating technique [14]. In this paper, result of a systematic study of pulse electrodeposited CdSe films are reported.

2. Experimental methods

CdSe films of area 2.5 cm^2 were deposited on titanium and conducting glass substrate. The titanium was first degreased with trichloroethylene then etched for 30 s in a solution containing 1:1 HCl and finally treated for 30 s in NaOH and washed with triple-distilled water. Conducting glass substrates were degreased with soap solution and acetone and then washed with triple-distilled water.

The pulse potential / pulse current was generated from a microprocessor and fed into a three electrode electrochemical cell through a potentiostat / galvanostat. The counter electrode, working electrodes and reference electrode were graphite, titanium or conducting glass substrate, and SCE, respectively. The deposition bath consisted of an aqueous solution of 0.5 M CdSO$_4$ and 10^{-2} to 10^{-3} M of SeO$_2$. The pH of electrolyte was adjusted to 2 by adding 10% H$_2$SO$_4$ [14]. The deposition was carried out for a duration of one hour on Ti or SnO$_2$ glass substrates at −870 mV vs. SCE at room temperature. Films were deposited using different duty cycles varying from 6.25 to 50%. The thick-

ness of the as-deposited films was estimated to be 1.6 μm by gravimetric method. The films were heat treated in the air at different temperatures in the range of 450–550°C for a duration of 5 min. The thickness of the films after heat treatment was around 1.4 μm. Reproduciblity of the deposition process was checked by depositing about 15 samples under each condition.

X-ray diffraction measurements were made with a computer controlled JEOL model JDX 30 using Cu K$_\alpha$ radiation. Surface morphology and grain size of the films were determined with a JEOL model JSM-35CF scanning electron microscope. Optical absorption studies were carried out for the films deposited on conducting glass substrate with a Hitachi U3400 UV-VIS-NIR spectrophotometer. Composition analysis of the films were determined by using XRF technique from Coating Measuring Instruments-XRX series (CMI). Conductivity of the films was measured by using the two probe technique.

The photoelectrochemical cell consisted of the CdSe film deposited on Ti substrate as photoanode and graphite as counter electrode with 1 M polysulphide as redox electrolyte. A 100 W tungsten lamp was the light source. The intensity of the source was measured by CEL light intensity meter (Suryamapi). Action spectrum of the films was measured by using a Photophysics monochromator to estimate the bandgap of the material and to estimate the spectral response characteristics.

3. Result and discussions

3.1. Structure

The X-ray diffraction patterns of the pulse electrodeposited films for the as- deposited and annealed films are shown in Fig. 1. The diffractograms indicate the polycrystalline nature of the films with all the major peaks corresponding to CdSe. Some peaks assignable to Cd were also present. After annealing at 550°C in the air, the structure changed to hexagonal with all the major peaks corresponding to CdSe; peaks corresponding to element Se or Cd were not present. Lattice constants were calculated for the films and the values agree well with the standard ASTM ones.

The effect of duty cycle on the deposition of CdSe films were studied. As the duty cycle decreased from 50 to 6.25% the intensity of the peak (100) also decreased. This observation indicates the variation of duty cycle affects the grain size of the film. Surface morphology (Fig. 2)of the annealed and unannealed films prepared under a duty cycle of 9% indicate agglomeration of the particle with an average grain size of 3 μm. Optical absorption studies indicate a bandgap of 1.70 eV for the film annealed at 550°C irrespective of the duty cycle. Absorption coefficient of 1.65×10^4 cm^{-1} and the linearity of the $(\alpha h\nu)^2$ vs. $h\nu$ plot shown in Fig. 3 indicate the direct bandgap nature of the films. The composition was estimated by XRF analysis. From the
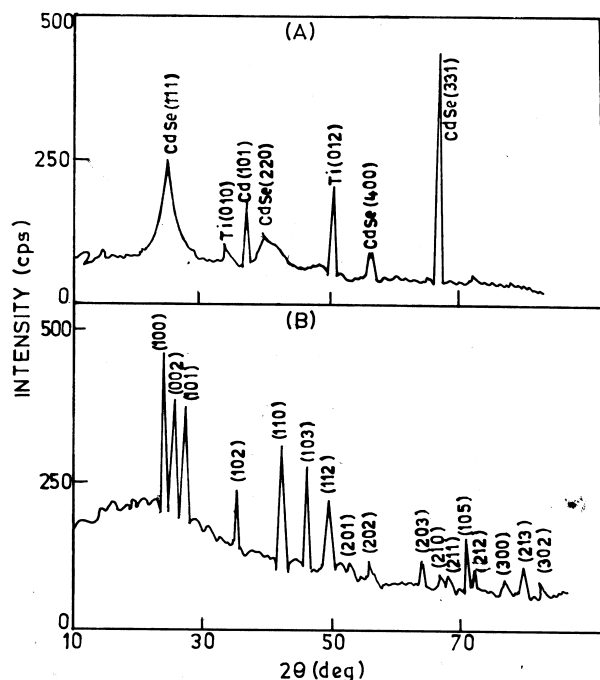

Fig. 1. XRD pattern for CdSe films on a Ti substrate (a) as-deposited and (b) annealed at 550°C.

results given in Table 1, it is clear that Cd-rich films were obtained in all cases. For the films deposited with a duty cycle of 15.15% (1 s on time, 5.6 s off time) the XRF data almost coincides with the data obtained with the commercial Aldrich chemicals CdSe powder that is 58.2% (Cd) and 41.8% (Se).

3.2. Power output

The power output (current–voltage) characteristics of the PEC cells for the pulse electrodeposited films is shown in Fig. 4. The as-deposited films did not exhibit any photoresponse. However, the films exhibited some photoresponse after heat treatment at 450–550°C in the air. The films heat treated at 550°C exhibited highest photoresponse. The current I–V voltage characteristics of the films deposited at different duty cycles and heat treated at 550°C are presented in Fig. 4. The values of V_{oc}, I_{sc}, η, FF, R_s and R_{sh} are given in the Table 1. The values of R_s and R_{sh} are determined from the inverse of the slope of the linear points of I–V curve near V_{oc} and I_{sc}, respectively. From Table 1 it can be seen that as the duty cycle decreases, there is an increase in V_{oc} and I_{sc} values; but below 9% duty cycle, the I_{sc} values decrease probably due to the change in the stoichiometry of the films. The I_{sc} value is found to be 1.520 mA for a 9% duty cycle and this result is highly reproducible. The efficiency value is low compared to those reported for electrodeposited thin films electrodes. Cocivera et al. [15] reported an efficiency of 5.8% for their electrodeposited films that were chemically etched after heat treatment followed by dipping in 1 N NaCN and treated with ZnCl₂.
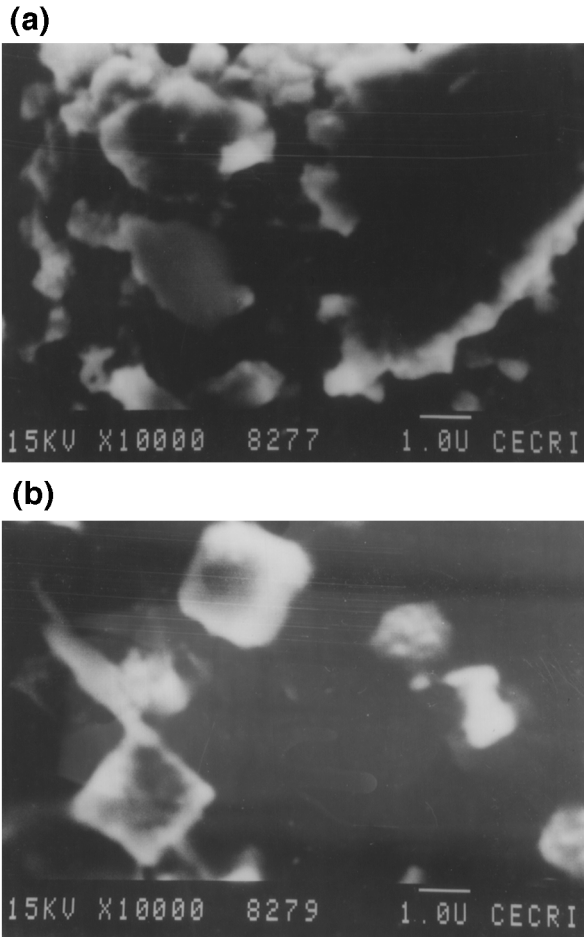
(a)

(b)

Fig. 2. SEM photographs for CdSe films (a) as-deposited and (b) annealed.

Tomkiewicz et al. [16] reported efficiency values in the range of 4.5–5.5% for electrodeposited films heat treated at 750°C for 40 min in an argon atmosphere. For the pulse plated CdSe film, in general, taken at random from different batches, V_{oc} varied from 5 to 10% and I_{sc} from 8 to 13% at 80 mW/cm^2 illumination.

3.3. C–V Measurements

Mott–Schottky plot at a frequency of 10 kHz in sodium sulphate as the electrolyte is shown in Fig. 5. The linearity of the plot suggests that the impurities are uniformly ionised. From the extrapolated intercepts on x-axis a flat
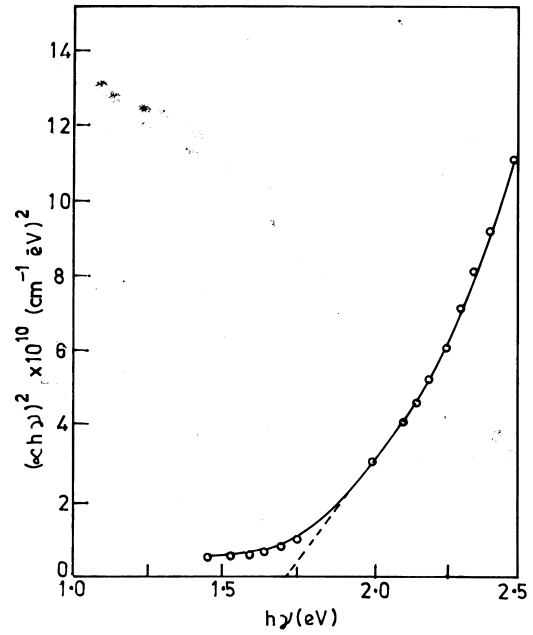

Fig. 3. $(\alpha h\nu)^2$ vs. curve for CdSe films heat treated at 550°C.

band potential (V_{fb}) of 1.20 V vs. SCE was obtained, agreeing well with the value reported earlier [17]. The plot indicated 'p' type behaviour of the film. 'p' type behaviour has also been reported earlier [18] and the reason for this behaviour has not been well understood. From the slope of the plot a value of 1.6×10^{16} cm^{-3} has been calculated for carrier density N_a.

3.4. Quantum efficiency

Quantum efficiency (ϕ) was evaluated from the spectral response measurements by employing the following expression

$$\phi = \frac{1239 J_{sc}}{\lambda P} \tag{1}$$

where J_{sc} is the current density expressed in A/cm^2, λ is the wavelength expressed in nm, P is the radiant power absorbed in photo active region in W/cm^2 [19]. Fig. 6. shows the quantum efficiency in the wavelength range 500–850 nm. A peak quantum efficiency of 0.75 is observed in the region of 725 nm. The maximum at 725 nm compared

Table 1
Composition and PEC characteristics of pulse plated CdSe films heat treated at 550°C

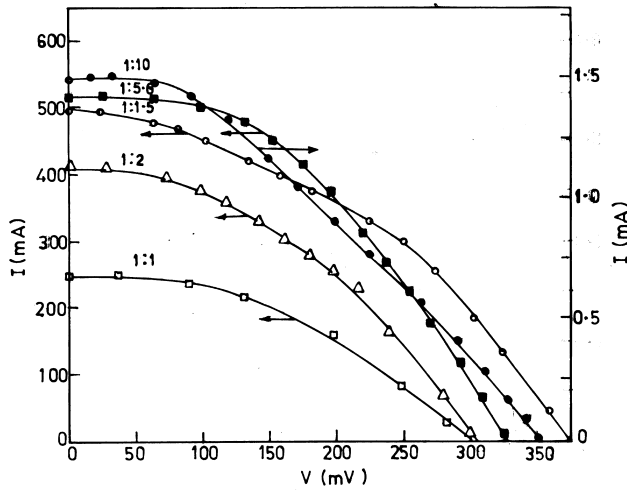| Duty cycle (%)	Compositions (%)		V_{oc}(mV)	I_{sc}(mA)	FF	η (%)	R_s (Ω)	R_{sh} (kΩ)
	Cd	Se						
50.00	58.2	41.8	295	0.250	0.33	1.75	280	3.61
33.33	70.2	29.8	305	0.410	0.34	1.78	185	3.94
15.15	66.4	33.6	325	0.515	0.35	1.80	165	4.04
9.99	62.3	37.7	350	1.520	0.38	2.42	105	4.15
6.25	61.8	38.2	380	0.500	0.38	2.14	140	4.10

Fig. 4. Power output characteristics of the CdSe films for different on:off timings, (□) 1:1 s; (△) 1:2 s; (■) 1:5.6 s; (●) 1:10 s; (○) 1:15 s.

very well with the bandgap of 1.71 eV determined from optical absorption measurements.

From Gartner's photocurrent equation for a metal / semiconductor junction [20] the quantum efficiency follows the relation

$$\phi = 1 - e^{-\alpha W(1 + \alpha L_n)} \qquad (2)$$
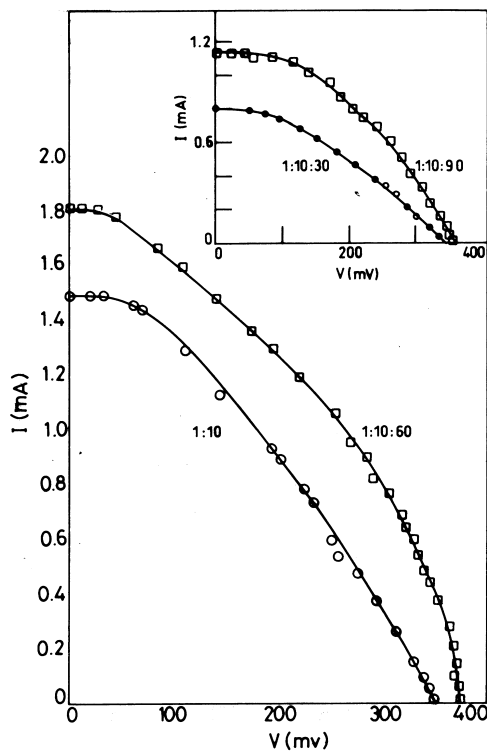
where 'W' is the depletion layer width, given by

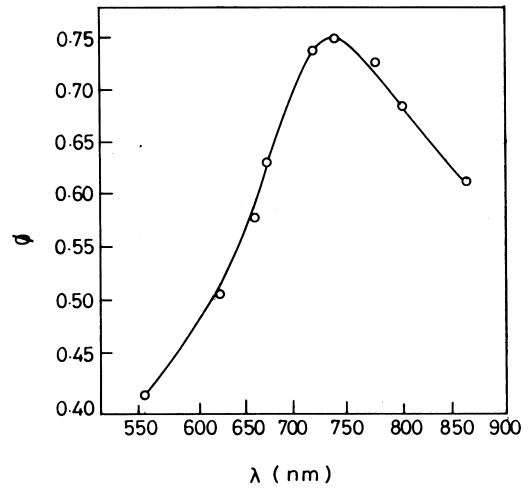Fig. 5. Mott–Schottky plot of pulse plated CdSe films in 1 M sodium sulphate at 10 kHz.

Fig. 6. Variation of quantum efficiency (ϕ) with wavelength (λ) for the PEC cell employing pulse plated CdSe films.

$$W = [(2\varepsilon\varepsilon_0/qN_a)(V - V_{fb})]^{\frac{1}{2}} \qquad (3)$$

where ϕ is the quantum efficiency, q is the electronic charge, α is the absorption- coefficient, L_n is the diffusion length of the minority carriers, ε is the dielectric constant, $\varepsilon_0 = 8.85 \times 10^{14}$ cm^{-1} is the permittivity of free space, V is the electric potential, V_{fb} is the flat band potential, and N_a is the carrier density. Choosing a wavelength 'λ' of relatively weak absorption so that $L_n << 1$ and $\alpha W << 1$ [21], the following relation is obtained

$$\phi = L_n \qquad (4)$$

$$\phi^{-1} = (L_n)^{-1} \qquad (5)$$

A plot of ϕ^{-1} vs. α^{-1} is shown in Fig. 7. L_n is obtained from the inverse of the slope and is found to be 0.109 μm. The low value of quantum efficiency obtained in the present study is probably due to the low L_n values.

In order to obtain , Eq. (2) can be rearranged as

$$W = -\ln[(1 - \phi)(1 + \alpha L_n)]\alpha^{-1} \qquad (6)$$

Substituting the corresponding values of α and ϕ, when $W << 1$, we obtain the depletion layer width 'W' as 0.185 μm. Earlier reports indicate a value of 0.5 μm for the elec-
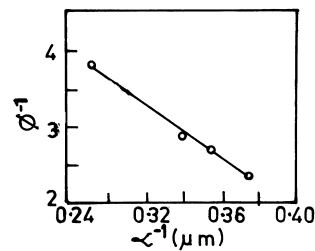

Fig. 7. Variation of inverse quantum efficiency (ϕ^{-1}) with inverse absorption efficient (γ^{-1}) for the cell.

Table 2
PEC characteristics of pulse plated CdSe deposited on different substrate

Substrate no.	Substrate used	V_{oc} (mV)	I_{sc} (mA)	n	I_0, ($\times 10^{-3}$ A)
1	Ti	341	1.485	1.42	0.0032
2	Mo	201	0.099	5.70	1.3504
3	SS	163	0.333	5.44	0.8191
4	Gold	051	0.009	–	–

trodeposited CdSe films [16]. This difference is due to lower thickness of the pulse plated films. The conductivity and mobility of the CdSe films have been found to be 0.51 Ω^{-1} cm^{-1} and 5.63 cm^2/V s, respectively.

3.5. Effect of different substrates

CdSe films were deposited on different substrates like Mo, Stainless Steel, Ti and gold by pulse electrodeposition under identical conditions (9% duty cycle). The PEC characteristics for the samples were measured and given in Table 2. For different light intensities, V_{oc} and I_{sc} values were measured and a plot of V_{oc} against ln I_{sc}, as shown in Fig. 8. obeys the well known equation

$$I_{sc} = I_0 \exp[(qV_{oc}/nkT) - 1] \tag{7}$$

where V_{oc} is the open circuit voltage, where I_{sc} is the short circuit current, I_0 is the reverse saturation current, n is the ideality factor, q is the electronic charge, T is the room temperature and k is the Boltzmann's constant. From the equation, n and I_0 for the electrodes deposited on different substrates are calculated and are given in Table 2. From the observations, substrates like gold, which forms a rectifying contact to CdSe, give lower values of V_{oc} and I_{sc} in the PEC mode in 1 M polysulphide. The value of V_{oc} and I_{sc} for films prepared with substrate like Mo, SS and Ti were found to increase as the resistivity of the material changes. The value of 'n' is very close to the ideal junction for Ti substrates and n_0 is also lower, which indicates that the junction formation is better for these films deposited on Ti.

4. Conclusions

The present study indicates that the simple pulse electrodeposition technique can be successfully employed for the preparation of device quality CdSe films. The V_{oc} and I_{sc} of the films deposited at each duty cycle, varied from 5 to 10% and from 8 to 13%, respectively, indicating the reproducibility.

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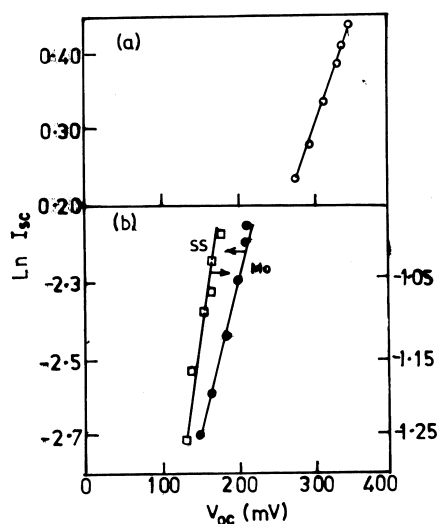[21] R.K. Pandey, S.R. Kumar, A.J.N. Rooz, S. Chandra, Thin Solid Films 200 (1991) 1.

Fig. 8. Ln I_{sc} vs. V_{oc} plot for pulse plated CdSe films on different substrate (a) Ti and (b) (●) Mo, (□) SS.