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Effect of pulse reversal on the properties of pulse plated $CdSe_xTe_{1-x}$ thin films

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Abstract

$CdSe_xTe_{1-x}$ thin films with $0 < x < 1$ were deposited on titanium and conducting glass substrates by pulse electrodeposition using microprocessor control. Formation of the solid solution takes place for values of $x(0 < x < 1)$. The films were characterized by X-ray diffraction. While the as-deposited films are cubic in nature, those annealed at 475 °C in air indicate hexagonal structure and the lattice parameters increase with increasing value of x. From the optical absorption measurements the band gap of the material was calculated. The value of the band gap varies from 1.42 to 1.70 eV as x varies from 0 to 1. The photoelectrochemical (PEC) characteristics were obtained for all compositions of $CdSe_xTe_{1-x}$ ($x = 0$–1). The output parameters for $CdSe_{0.66}Te_{0.34}$ with 9% duty cycle at an intensity of 80 mW cm^{-2} using 1 M polysulphide as the redox electrolyte, are V_{OC} of 398 mV, J_{SC} of 5.59 mA cm^{-2}, *ff* of 0.45, η of 4.73%, R_s of 13 Ω, R_{sh} of 1.50 kΩ. The output parameters were found to increase with 60 ms pulse reversal. After photoetching for 40 s, a V_{OC} of 481 mV, J_{SC} of 16.00 mA cm^{-2}, *ff* of 0.57, η of 5.46%, R_s of 6 Ω, R_{sh} of 2.16 kΩ were obtained.

1. Introduction

The semiconducting compounds CdSe, Cd(SeTe) are suitable for the conversion of solar energy into useful electric energy through photovoltaic devices. CdSeTe is a promising semiconductor which is used for various applications like optoelectronic devices, solar cells etc. In the case of mixed compounds such as $CdSe_xTe_{1-x}$, the optimal direct bandgap from 1.40 to 1.70 eV can be achieved by changing the value of x which, in turn, changes the optoelectronic properties [1, 2].

These compounds can be obtained as thin films using different techniques such as vacuum evaporation [3], spray pyrolysis [4], chemical bath deposition, electrodeposition [5], pulse electrodeposition [6]. Pulse electrodeposition has several advantages over conventional electrodeposition such as better adhesion, crack free hard deposits, fine grained films with uniformity and lower porosity. By varying the duty cycle, that is, (on time)/(on time + off time), where ‘on time’ is the period during which the potential is applied to the electrode and ‘off time’ is the period during which no potential is applied, changes in deposit structure, mainly grain size can be achieved, because of forced nucleation during each new cathodic pulse. It is clear that adsorption/desorption as well as recrystallization takes place. The main purpose of carrying out pulse reversal plating [7] is to obtain better film thickness with good adherence yielding higher conversion efficiencies for photoelectrochemical cells fabricated using these films. In the present work, $CdSe_xTe_{1-x}$ films were pulse plated from an acidic solution. Films were also deposited by applying pulse reversal for short durations.

2. Experimental details

$CdSe_xTe_{1-x}$ films were deposited using a conventional three-electrode cell with graphite as anode, conducting substrates like titanium or tin oxide on glass as cathode, and SCE as the reference electrode. The deposition bath consisted of an aqueous solution of 0.1 M $CdSO_4$, 10^{-2}–10^{-3} M SeO_2 and TeO_2 [8]. The pH of the solution was adjusted to 2 by adding dilute sulfuric acid. The deposition was carried out at room temperature for one hour at −700 mV vs SCE under potentiostatic conditions. The duty cycle was varied from 50% to 6.25% for all compositions of $CdSe_xTe_{1-x}$. Pulse reversal was done by applying +100 mV vs SCE for different durations in the range 30–90 ms during the ‘off’ period. The thickness of the films was estimated by the gravimetric method. The films were characterized by X-ray diffraction using a Joel model JDX-8030 X-ray diffraction unit with CuK_α radiation. Optical absorption studies were carried out for the films deposited on conducting substrates with a Hitachi u.v.–vis.–n.i.r. spectrophotometer. The conductivity of the films was measured using the two probe technique.

The PEC cell consisted of the photoanode as working electrode, graphite as counter electrode and SCE as reference electrode with 1 M alkaline polysulphide as the electrolyte. The light source was an Oriel 250 W tungsten halogen lamp. The photon flux reaching the electrode surface was measured by a CEL (Central Electronics Limited) Suryamapi. After heat treatment the electrodes were used for PEC studies. Photoetching was carried out by shorting the photoelectrode and the counter electrode in 10% HCl for different durations in the range from 10 to 50 s under an illumination of 80 mW cm^{-2}. Capacitance–voltage measurements were carried out with sodium sulphate as the electrolyte using an EG&G PARC impedance analyser at different d.c. bias voltages and at a constant frequency of 10 kHz.

3. Results and discussion

The X-ray diffraction pattern of the as deposited $CdSe_xTe_{1-x}$ films, irrespective of duty cycle, exhibited cubic structure. After heat treatment in argon atmosphere at 475 °C for 10 min, the crystal structure changed to hexagonal. The X-ray diffraction pattern of the as deposited films is shown in Figure 1(a), the XRD pattern of heat treated sample is shown in Figure 1(b) which indicates all the peaks corresponding to hexagonal structure, peaks corresponding to (100), (002), (101), (110), (103), (112) and (210) along with one Cd line and one Ti line are observed. The composition of the films were calculated using Vegard's law. Better crystallinity is observed for the films of composition $CdSe_{0.66}Te_{0.34}$ deposited with 9% duty cycle and with pulse reversal for a period of 60 ms. The potential was reversed to +200 mV vs SCE for different durations ranging from 30 to 90 ms during the 'off' period. The intensity of the peaks corresponding to the reflections (100), (002) and (110) is found to increase with reversal time (Figure 1(c)).

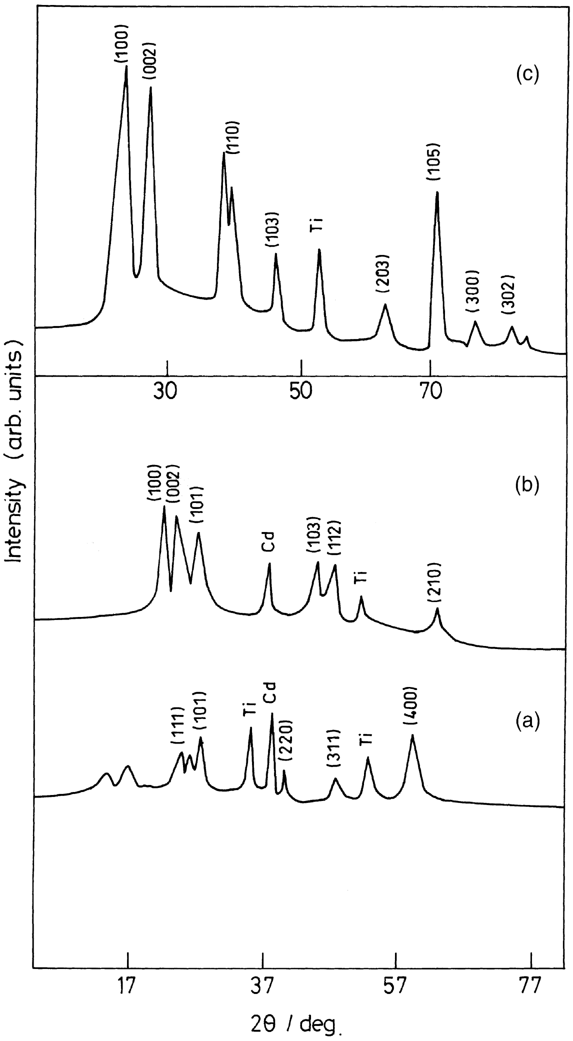

Fig. 1. XRD pattern for $CdSe_{0.66}Te_{0.34}$ film on Ti substrate (a) as deposited (b) heat treated in argon at 475 °C (c) with pulse reversal time of 60 ms.

The optical absorption spectrum (Figure 2) indicated a bandgap shift from 1.42 to 1.70 eV as the composition of the $CdSe_xTe_{1-x}$ varied from $x = 0$ to 1. An absorption coefficient of 10^4 cm^{-1} was obtained for the films. The linearity of the $(\alpha h\nu)^2$ aginst $h\nu$ plot indicated the direct bandgap nature of the films.

The power output characteristics were studied for the photoelectrochemical (PEC) cells made using pulse-plated $CdSe_xTe_{1-x}$ films of different composition with and without pulse reversal at an intensity of 80 mW cm^{-2}. Better V_{oc} and J_{sc} are obtained for the composition $CdSe_{0.66}Te_{0.34}$ compared with all the other compositions, hence pulse reversal as well as photoetching studies were carried out only on films of this composition. The PEC parameters for the pulse-plated $CdSe_{0.66}Te_{0.34}$ film heat treated at 475 °C is shown in Table 1 for various duty cycles. The output characteristics of the films deposited with different pulse reversal times are shown in Figure 3. For the sake of comparison the output characteristic of d.c.-plated films deposited at −700 mV vs SCE and post heated treated at 475 °C for 10 min in argon is also included in Figure 3. The PEC parameters of the d.c.-plated and pulse-plated $CdSe_{0.66}Te_{0.34}$ films heat treated at 475 °C are shown in Table 1. Enhanced output is obtained after pulse reversal. The effect of photoetching time on V_{oc} and J_{sc} of the electrodes deposited with different pulse reversal times are shown in Figures 4 and 5, respectively. Both the current and voltage are found to increase up to a photoetching time of 40 s, beyond which both are found to decrease. Hence, a photoetching time of 40 s was used for studying the load characteristics. The load characteristics of the electrodes after photoetching are shown in Figure 6. After photoetching, the photovoltaic parameters are found to increase (Table 2). The efficiency of the photoetched electrodes is found to double its value for the electrodes deposited using 60 ms pulse reversal. The efficiency of the photoetched electrodes with 90 ms pulse reversal decrease due to a reduction in the output parameters. This can be attributed to the reduction in thickness of the films from 2.5 to 1.9 μm. The pulse reversal time of 90 ms is high enough to remove a few monolayers of the deposited film. To check reproducibility about 20 films were prepared

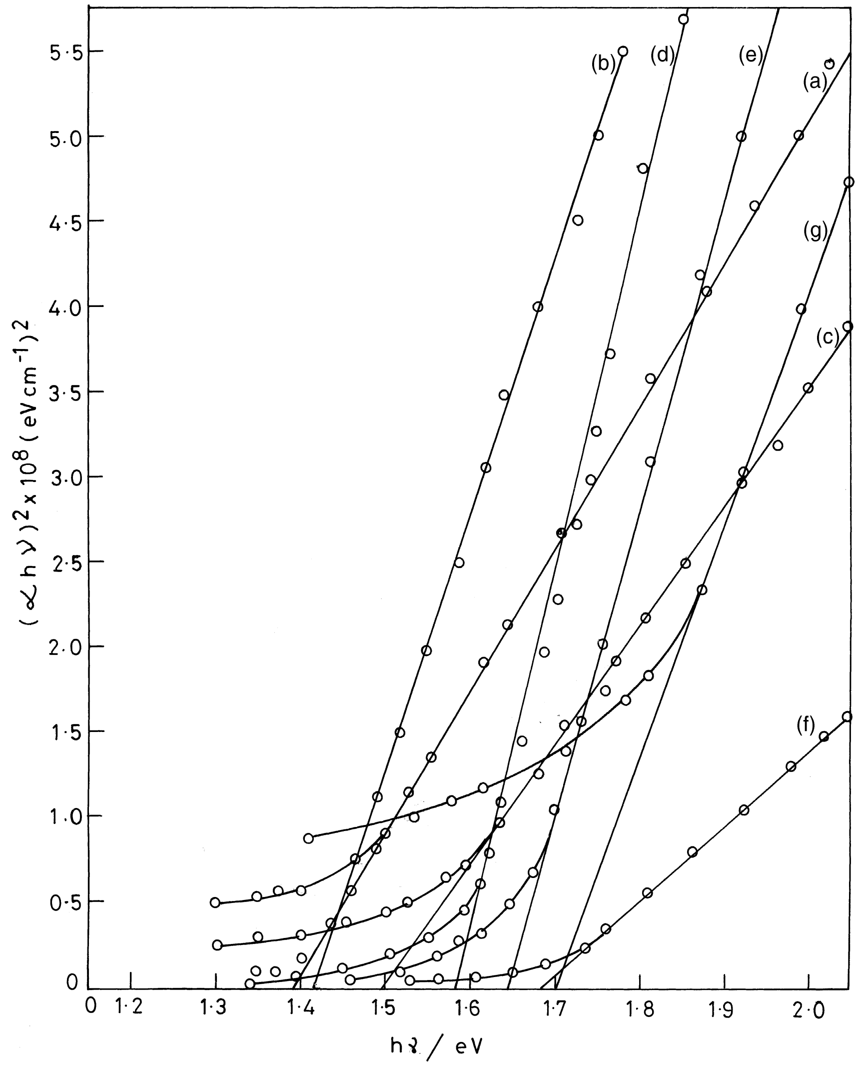

Fig. 2. $(\alpha h\nu)^2$ against $h\nu$ plot for films heat treated at 475 °C (a) $CdSe_{0.1}Te_{0.9}$, (b) $CdSe_{0.2}Te_{0.8}$, (c) $CdSe_{0.3}Te_{0.7}$, (d) $CdSe_{0.66}Te_{0.34}$, (e) $CdSe_{0.8}Te_{0.2}$ and (f) $CdSe_{0.9}Te_{0.1}$.

Table 1. PEC parameters of $CdSe_{0.66}Te_{0.34}$ films deposited at different duty cycles
Intensity of illumination 80 mW cm^{-2}

On time /s	Off time /s	V_{oc} /mV	J_{sc} /mA cm^{-2}	*ff*	η /%	R_s /Ω	R_{sh} /kΩ
d.c. Plated		340	3.75	0.45	0.72	45	0.90
1	1	365	4.14	0.43	0.81	21	0.92
1	2	373	4.32	0.44	1.09	20	1.06
1	5.6	382	5.19	0.44	1.12	17	1.15
1	10	398	5.59	0.45	1.25	13	1.52
1	15	374	5.01	0.42	0.98	15	1.50

under each condition. For the pulse plated $CdSe_xTe_{1-x}$ films, in general, taken at random from different batches, V_{oc} varied from 10% to 13% and J_{sc} from 6% to 16% at 80 mW cm^{-2} illumination.

The voltage and efficiency values obtained with the cells studied in this investigation are lower than those reported for slurry coated ones [9] due to the lower thickness in this case. The values are comparable with data reported on electrodes prepared by conventional electrodeposition. The efficiency and current density values are higher than those in earlier reports. In the present study, the output parameters were measured under sunlight illumination. The values for the current and voltage were found to vary within 2% of the values obtained with illumination from a tungsten halogen lamp of the same intensity of illumination.

The capacitance of the films was of the order of 10^{-6} F. Using the Mott–Schottky relation [10], a plot of between $1/C^2$ against V was made for films prepared at a duty cycle of 9% (Figure 7). A linear variation is observed which indicates that the impurities are uniformly ionized and extrapolation of the line to the X-axis yields a flat band potential of −980 mV vs SCE. The Mott–Schottky plots indicate 'n' type behaviour. From the slope of the plot, a carrier density of 4×10^{16} cm^{-3} is obtained.

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

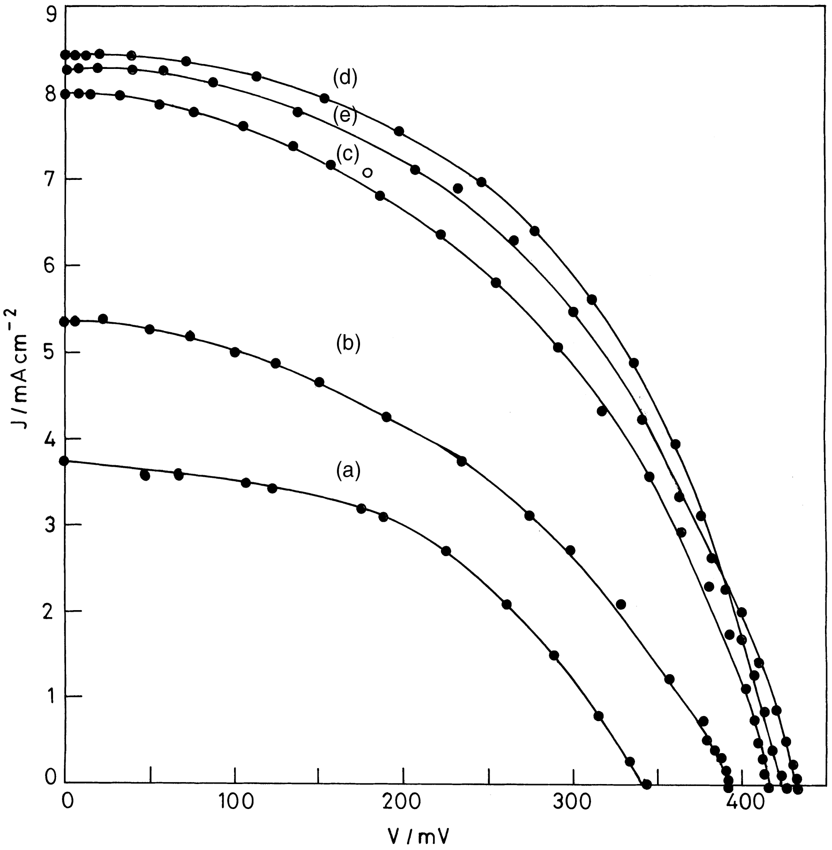

Fig. 3. Power output characteristics of the $CdSe_{0.66}Te_{0.34}$ films deposited at a duty cycle of 9% and with different pulse reversal timings: (a) d.c. plated, (b) 0 ms, (c) 30 ms, (d) 60 ms and (e) 90 ms.

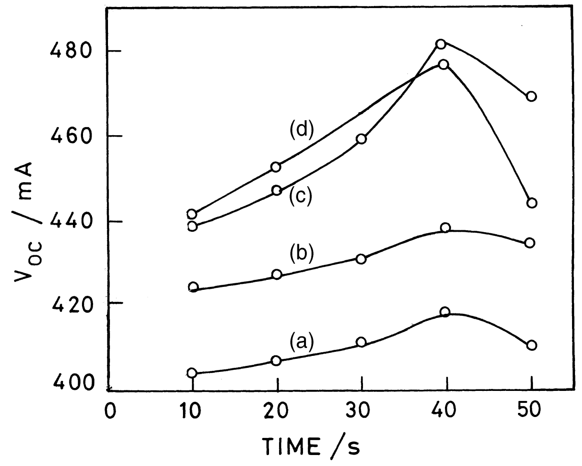

Fig. 4. Effect of photoetching time on the V_{oc} of $CdSe_{0.66}Te_{0.34}$ films deposited at a duty cycle of 9% and with different pulse reversal timings: (a) 0 ms, (b) 30 ms, (c) 60 ms and (d) 90 ms.

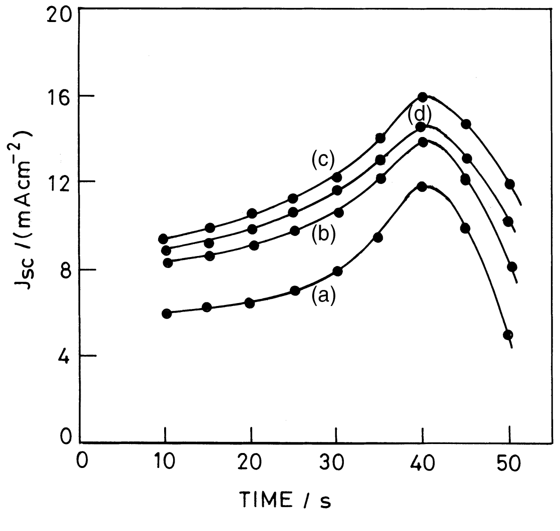

Fig. 5. Effect of photoetching time on the J_{sc} of $CdSe_{0.66}Te_{0.34}$ films deposited at a duty cycle of 9% and with different pulse reversal timings: (a) 0 ms, (b) 30 ms, (c) 60 ms and (d) 90 ms.

$$\phi = \frac{1240}{\lambda P} \tag{1}$$

where J_{sc} is current density (A cm^{-2}), λ is the wavelength (nm), P is the radiant power absorbed in the photoactive region (W cm^{-2}) [11]. Figure 8 shows the variation of quantum efficiency in the wavelength range 500–800 nm. A peak quantum efficiency of 0.51 and 0.71 was obtained for the electrodes without and with pulse reversal at 1.60 eV, agreeing well with the bandgap of the film obtained from optical absorption measurements.

From Gartner's photocurrent equation for a metal–semiconductor junction, quantum efficiency [12] follows the relation

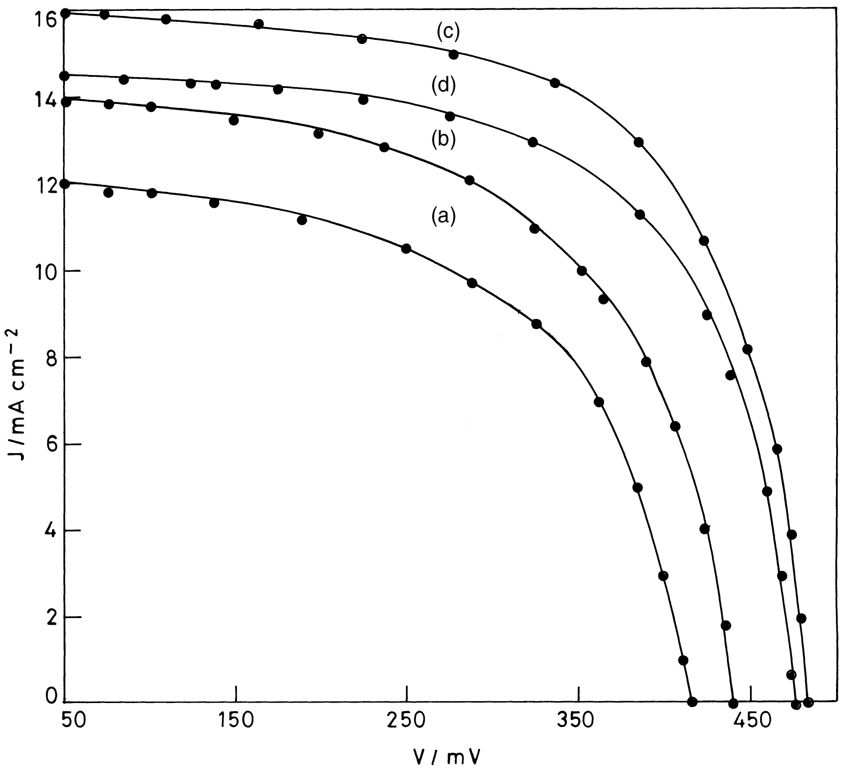

Fig. 6. Power output characteristics of $CdSe_{0.66}Te_{0.34}$ films deposited at a duty cycle of 9% and with different pulse reversal timings after a photoetching time of 40 s: (a) 0 ms, (b) 30 ms, (c) 60 ms and (d) 90 ms.

Table 2. PEC parameters of $CdSe_{0.66}Te_{0.34}$ films deposited with pulse reversal and photoetching

On time /s	Off time /s	reversal time /ms	V_{oc} /mV	J_{sc} /mA cm^{-2}	*ff*	η /%	R_s /Ω	R_{sh} /kΩ
Pulse reversal								
1	10	30	421	7.99	0.45	1.90	12	1.52
1	10	60	434	8.46	0.50	2.30	10	1.58
1	10	90	440	8.26	0.45	2.04	9	1.63
After photoetching								
1	10	0	418	12.00	0.57	3.57	11	1.65
1	10	30	438	14.00	0.58	4.44	10	1.94
1	10	60	481	16.00	0.57	5.46	6	2.16
1	10	90	476	14.50	0.61	5.26	9	2.01

Intensity of illumination −80 mW cm^{-2}.

$$\phi = 1 - e^{-\alpha W/(1+\alpha L_P)} \qquad (2)$$

where W is the depletion layer width given by

$$W = \left[\left(\frac{2\varepsilon\varepsilon_o}{qN_d}\right)(V - V_{fb})\right]^{\frac{1}{2}} \qquad (3)$$

where q is the electronic charge, α is the absorption coefficient, L_p is the diffusion length of the minority carriers, ε is the dielectric constant of the semiconductor, ε_o is the permittivity of free space, V is the applied potential, V_{fb} is the flat-band potential and N_d is the

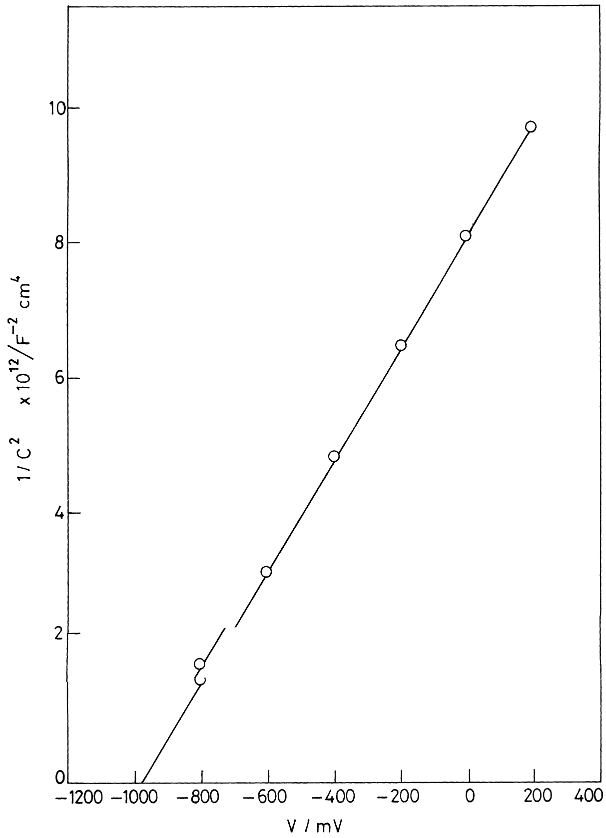

Fig. 7. Mott–Schottky plot of $CdSe_{0.66}Te_{0.34}$ films deposited at a duty cycle of 9% in 1 M sodium sulphate solution at 10 kHz (a) without pulse reversal (b) with pulse reversal (60 ms).

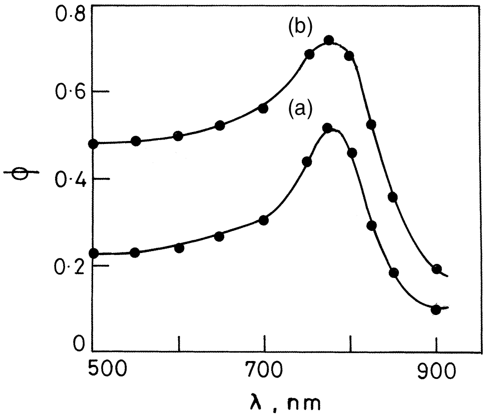

Fig. 8. Variation of quantum efficiency (ϕ) with wavelength (λ) for the PEC cell fabricated employing $CdSe_{0.66}Te_{0.34}$ films pulse plated (a) without and (b) with pulse reversal.

doping density. By choosing a wavelength of relatively weak absorption so that $L_p \ll 1'$ and $W \ll 1$, the following relationship is obtained [13]:

$$\phi = \alpha L_p \quad (4)$$

Hence,

$$\phi^{-1} = (\alpha L_p)^{-1} \quad (5)$$

L_p is obtained from the inverse of the slope of the plot between $(\phi)^{-1}$ against $(\alpha)^{-1}$ and is found to be 0.109 and 0.588 μm for films deposited with and without pulse reversal. The value of W was estimated from Equation 3, by substituting the value of V_{fb} and N_d obtained from the Mott–Schottky plot. 0.243 and 0.160 μm were obtained for films deposited without and with pulse reversal.

4. Conclusions

Semiconducting films with improved characteristics can be obtained by applying pulse reversal for a short duration during the 'off' time. The output parameters are found to be better than those obtained using electrodes prepared without pulse reversal. The values of the output parameters obtained with illumination from sunlight are found to be similar to those obtained with tungsten halogen lamp using the same intensity of illumination. This points to the possibility of obtaining efficient electrodes for application in photoelectrochemical cells.

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