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Photoelectrochemical investigations of cadmium sulphide (CdS) thin film electrodes prepared by spray pyrolysis

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ABSTRACT

Polycrystalline cadmium sulphide (CdS) thin films have been prepared by spraying a mixture of an equimolar aqueous solutions of cadmium chloride and thiourea on preheated fluorine doped tin oxide (FTO) coated glass substrates at different substrate temperatures. The cell configurations n-CdS/1 M ($NaOH + Na_2S + S$)/C were used for studying the capacitance–voltage (C–V) characteristics in dark, current–voltage (I–V) characteristics in dark and under illumination, photovoltaic power output and spectral response characteristics of the as deposited thin films. Photoelectrochemical study shows that as deposited CdS thin films exhibits n-type of conductivity. The spectral response characteristics of the films at room temperature show a prominent sharp peak at 500 nm leading to optical bandgap energy of 2.48 eV. It is found that fill factor and efficiency are maximum for photoelectrode deposited at 300 °C. This is due to low resistance; high flat band potential, maximum open circuit voltage as well as maximum short-circuit current. The measured values of efficiency (η) and fill factor (FF) are found to be 0.17% and 0.38 respectively for film deposited at 300 °C.

1. Introduction

Solar energy is one of the most promising energy sources in the future. Many researchers have concentrated on its utilization. Since Fujishima and Honda found a TiO_2 anode could split water into H_2 and O_2 under UV irradiation [1], which is considered as an important technique for solar energy storage and conversion, a variety of photoelectrochemical (PEC) solar cells have been fabricated and investigated for transformation of solar energy into electricity [2]. For the PEC solar cell, the primary requirement for good solar energy conversion is that the photocathode or photoanode should have band gap close to the maximum in the visible spectrum of solar light, besides its high stability in the electrolyte [3]. In recent years, considerable interest has been shown in the synthesis and photoelectrochemical test of semiconductor thin films due to the high conversion efficiency and low production cost [4]. The study of PEC solar cells fabricated by polycrystalline thin films of II–VI chalcogenide compound is interesting because of their excellent optoelectronic properties [5,6]. The II–VI semiconductor compounds, particularly CdS, CdSe, CdTe, are of great interest because they are potential candidates in many practical applications like solar cells, optical detectors, dosimeters of ionized radiation, field effect transistors, and optoelectronic devices. The performance of the devices based on CdS thin films depends on the structural and optoelectronic properties of the layers obtained under various experimental conditions [7,8]. Nanocrystalline cadmium sulphide has attracted considerable attention because of its wide use in the fabrication of solar cells and optoelectronic devices [9–11].

Chemically deposited CdS thin films have been widely studied in the last decade due to their potential applications. Most of these studies were devoted to the deposition mechanism and chemistry and only few to the investigations of physical properties. What commonly accepted is that the chemically deposited CdS thin films are nearly stoichiometric and exhibit a high photosensitivity (10^6–10^9) [12]. Thus CdS is a technologically important material, especially for terrestrial utilization of solar energy.

With its n-type semiconductor characteristics [13] and wide band gap ($E_g = 2.44$ eV), thin films of CdS hold promise in photovoltaic applications as window coatings in many types of solar cells with absorber materials. Electron hole pairs generated in CdS are well separated with electrons being highly localized. So it is the most studied nanocrystalline semiconductor because of its suitable bandgap, long lifetimes, important optical properties, excellent stability, easy fabrication and numerous device applications. The performance of polycrystalline semiconductor photoelectrochemical (PEC) solar cell depends to a large extent on the preparation of the thin film semiconductor electrode. Therefore the development of economical and effective synthetic method of CdS film is of importance in solar cell applications. In literature; variety of

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deposition techniques have been used to grow CdS films of desirable optical, electrical and structural properties; such as chemical bath deposition [14], thermal evaporation [15], electrodeposition [16], spray pyrolysis [17,18], etc. Literature survey shows that though the extensive work has been done on the preparation and characterization of CdS thin films, very few workers deposited these films by spray pyrolysis. Spray pyrolysis offers a number of advantages, the main ones being its simplicity, capability to produce large areas of highly sensitive films of uniform thickness and the low energy needs for operation. Doping of semiconductor film is simple, since it is accomplished by mere addition of the dopant to the spray solution.

Earlier the structural, optical and electrical properties of spray deposited CdS thin films have been reported [18]. The present paper reports on photoelectrochemical characterization of CdS thin films prepared by spray pyrolysis. The present study examines the photovoltaic characteristics of PEC solar cells based on spray deposited nanocrystalline CdS thin film electrode that are deposited at different substrate temperatures. The films are studied for their photoelectrochemical properties such as type of conductivity; current–voltage characteristics, photovoltaic power output characteristics and capacitance–voltage characteristics. It is observed that, spray deposited CdS thin films are polycrystalline with n-type semiconducting property and show comparable photoelectrochemical properties.

2. Experimental details

2.1. Preparation CdS thin films

The spray pyrolysis method is basically a chemical deposition technique in which fine droplets of the desired material are sprayed onto a preheated substrate. Continuous films are formed on the hot substrate by thermal decomposition of the material droplets. The equimolar (0.025 M) solutions of cadmium chloride ($CdCl_2$) and thiourea ($(NH_2)_2CS$) were prepared in double distilled water by dissolving appropriate amount of these salts. These equimolar solutions were mixed together in 1:1 ratio and sprayed on preheated fluorine doped tin oxide coated glass substrates (sheet resistance $\sim 10\,\Omega/cm^2$) at various substrate temperatures from 275 °C to 350 °C at the interval 25 °C. The substrate temperature was controlled by an iron-constantan thermocouple. The spray rate employed was 3 ml/min and kept constant throughout the experiment. The nozzle to substrate distance was 30 cm. After deposition, the films were allowed to cool at room temperature. The adhesion of the films onto the substrates (obtained by testing the stability of CdS film electrodes in aqueous polysulphide electrolyte) was quite good. In spray the constituent ions form complex in the solution and do not precipitate, on coming into contact with the hot substrate, the complex in the fine spray dissociates and the desired semiconducting film results. Here, $CdCl_2$ and thiourea form a soluble complex ($CdCl_2\,(NH_2)_2CS$) which pyrolysis on the hot substrate to give characteristically yellow and adherent films of CdS.

2.2. Fabrication of solar cell

Photoelectrochemical (PEC) cell was fabricated using a standard three electrode configuration, with n-CdS thin film as active photoanode (area 1 cm^2), graphite as a counter electrode and saturated calomel electrode (SCE) as a reference electrode. The redox electrolyte was 1 M polysulphide ($NaOH + Na_2S + S$). All the used chemicals were of analytical reagent (AR) grade. A 100 W tungsten filament lamp (intensity 20 mW/cm^2) was used as a light source. To avoid direct heating of cell, water lens was interposed between the lamp and the cell. The distance between the photoelectrode and counter electrode was 0.2 cm. The area of the semiconducting thin film other than that in contact with electrolyte was covered by epoxy resin to annul any contribution due to the contact of the base contact oxide material with the electrolyte and its interference in the measured values of the net photocurrent density. For measurement of the power output characteristics, a two electrode configuration consisting of the thin film photoelectrode and graphite as the counter electrode was used. Measurements for the power output characteristics and I–V plots were made at fixed intervals after waiting for sufficient time to equilibrate the system at that setting (both in dark as well as under illumination). The log I against V plots are used to calculate the junction ideality factor in dark and under illumination. Various currents and voltages were measured by the 6(1/2) digit, HP-34401. Mott–Schottky plots were plotted using as LCR meter (Aplab model 4912) at built in frequency 1 kHz.

3. Results and discussion

The as-grown CdS thin films deposited at various substrate temperatures were characterized by the X-ray diffraction (XRD) technique scanned in the 2θ range of 20–80°. X-ray diffractogram of CdS film deposited at optimized substrate temperature 300 °C has been depicted elsewhere [18]. X-ray diffraction patterns reveal that the films of CdS deposited by spray pyrolysis technique are polycrystalline in nature. The diffractogram indicated presence of hexagonal wurtzite crystal structure irrespective of substrate temperature, according to JCPDS Data Card no. 77-2306. Elemental cadmium, sulphur and CdO are not depicted in the diffractograms. The calculated values of lattice constant with hexagonal crystal structure are found to be $a = b = 4.1174$ Å and $c = 6.6991$ Å agreeing well with the standard values CdS [19]. It is observed that as the substrate temperature increases, the intensity of the peaks also increases and the width of the peak decreases due to improved crystallinity up to 300 °C, for further increase in substrate temperature there is decrease in peak intensity. The increase in peak intensity from 275 °C to 300 °C temperature may be attributed to the continuous increase in film thickness. Decrease in peak intensity after 300 °C might be ascribed to the fact that at these substrate temperatures, there is complete thermal decomposition of sprayed droplets before reaching the hot substrates due to unsuitable thermal energy (higher) than required for perfect decomposition and subsequent recrystallization. Crystallite size estimated by using Scherrer's formula has been observed to increase initially with increase in substrate temperature reaching the maximum 13 nm at 300 °C and thereafter it goes on decreasing with increase in substrate temperature. Scanning electron microscopy studies revealed nearly smooth, uniform, crack free dense morphology covering entire substrate surface area. Nearly stoichiometric films are obtained at substrate temperature of 300 °C. The optical bandgap of the films have been determined from absorption spectra of films. The band gap energy is found to lie in the range 2.44–2.58 eV depending on the substrate temperature [18].

3.1. Conductivity type of CdS thin films

Photoelectrochemical cell with configuration CdS/(1 M NaOH + 1 M Na_2S + 1MS)/graphite was formed in order to check the type of conductivity exhibited by CdS thin films. In dark, PEC cell gives some voltage and current and the polarity of this voltage and current is negative towards the CdS electrode. The origin of this voltage is attributed to the difference between two half cell potentials in the PEC cell. When above junction is illuminated both short circuit current I_{sc} and open circuit voltage V_{oc} were increased with negative polarity towards CdS electrode showing that spray deposited CdS is an n-type semiconductor [3,6].

3.2. Current–voltage characteristics

To get deep insight about the behavior of a semiconductor/electrolyte interface, the interfaces formed in this experimental work were analyzed through the current–voltage relations in dark and under illumination of light. The current–voltage characteristics were therefore obtained for a whole series of cells under study. Fig. 1 shows one of its representative plots under forward and reverse bias for CdS film deposited at 300 °C, in dark and under illumination. It is observed that in the dark the forward current increases rapidly with applied bias. The increase in forward current can be attributed to the small contact height and increase in tunneling mechanism [20]. The non symmetric nature of I–V curve in forward and reverse bias shows rectification property of the semiconductor–electrolyte junction. Under illumination shift of I–V curve in IVth quadrant is indication that the cell can work as

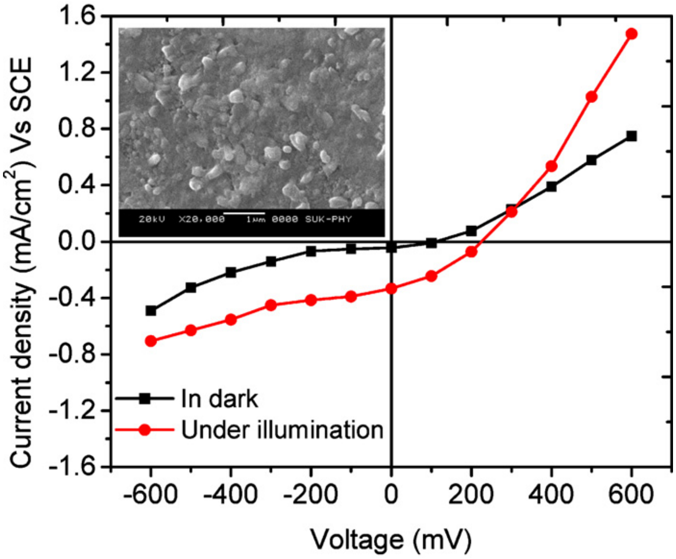

Fig. 1. Current–voltage characteristics of n-CdS thin film/1 M polysulphide/C photoelectrochemical cells in dark and under illumination for film deposited at substrate temperature of 300 °C. Inset shows the SEM image of typical CdS film exhibiting porous structure.

electricity generator. Using famous diode equation junction ideality factor can be calculated as [21],

$$I = I_0(e^{qV/nkT} - 1) \qquad (1)$$

where I is the forward current in dark, I_0 reverse saturation current, V the applied forward bias voltage, q is charge on electron and n is the junction ideality factor.

Fig. 2 shows the plot of log I versus V for CdS thin film deposited at 300 °C in dark. The estimated value of junction ideality factor was found to be 2.01. The higher value of n_d is may be due to the series resistance effect and carrier recombination at the semiconductor electrolyte interface. Under light illumination I and V are replaced by I_L and V_L resp. Then the current I_L is given by [21],

$$I_L = I_0(e^{qV_L/n_LkT} - 1) - I_{ph} \qquad (2)$$

The plot of log I_L against V_L under illumination for CdS thin film deposited at 300 °C is shown in Fig. 3. The graph shows linear behavior, with estimated junction ideality factor n_L to be 1.87. It is seen that the values of junction ideality factor are greater than ideality value. The values of junction ideality factor in dark and under illumination for CdS films deposited at various substrate temperatures are given in Table 1. The I–V characteristic changes significantly under illumination. This might be due to the porous crystal structure as has been seen from the SEM (inset in Fig. 1) micrograph of the deposited material [18].

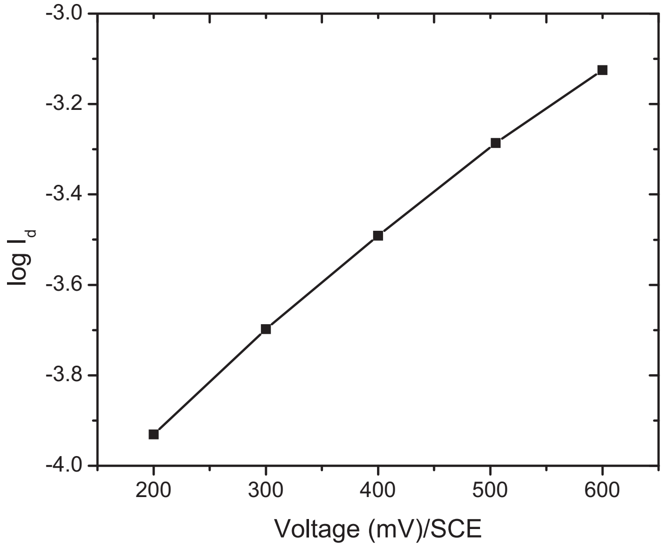

Fig. 2. Plot of log I_d vs. V for n-CdS/1 M polysulphide/C PEC cell in dark for film deposited at 300 °C.

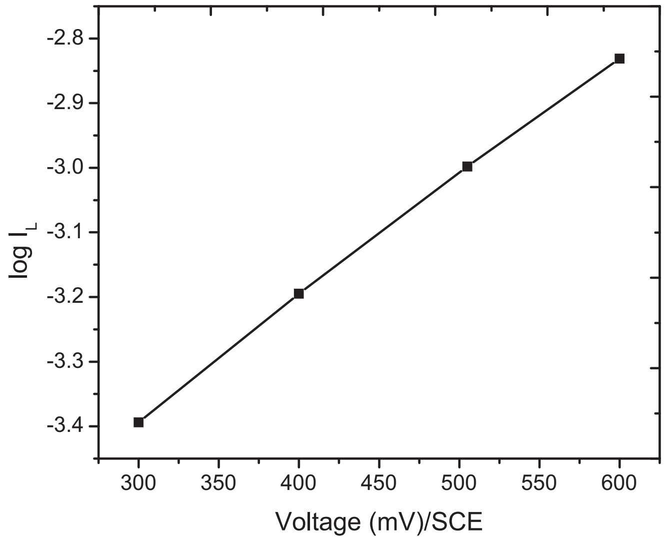

Fig. 3. Plot of log I_L vs. V for n-CdS/1 M polysulphide/C PEC cell under illumination for film deposited at 300 °C.

3.3. Capacitance–voltage characteristics

An interface between a semiconductor electrode and an electrolyte combines the characteristic features of both electrochemical and semiconductor systems. Several reviews on semiconductor/electrolyte interfaces are now available [22] and the mechanism of charge transfer across the interface is now fairly understood. For high bandgap semiconductors, a Schottky barrier with a space charge of ionized donor or acceptor ions is formed within the semiconductor and minority carriers are present in too low concentration. This barrier, typically, is 1 μm thick. The capacitance–voltage measurements give useful information regarding the donor concentration (N_D) and type of conductivity exhibited by the film. In our case n-CdS/sulphide/polysulphide interfaces were fabricated for a series of cells and the Schottky barrier capacitances were measured at a 1 Vpp–1 kHz as a function of the applied d.c. bias from −0.8 to 0.4 V (vs. SCE). Fig. 4 shows the Mott–Schottky (M–S) plots for n-CdS/polysulphide/C electrolyte system in dark for CdS thin film on FTO coated glass substrate at various substrate temperatures. The value of flat band potential V_{fb},

Table 1
Estimated important photoelectrochemical parameters of spray deposited CdS thin films.

Substrate temperature (°C)	n_d	n_L	η (%)	FF	R_s (Ω)	R_{sh} (kΩ)	N_D ($\times 10^{19}$ cm^{-3})	D (nm)
275	2.12	1.92	0.09	0.36	350	2.968	1.09	11
300	2.01	1.87	0.17	0.38	262	3.645	1.48	13
325	2.04	1.89	0.13	0.37	290	3.468	1.21	12
350	2.11	1.91	0.11	0.36	326	3.015	1.15	11

n_d: junction ideality factor in dark; n_L: junction ideality factor under illumination; η: efficiency; FF: fill factor; R_s: series resistance; R_{sh}: shunt resistance; N_D: donor concentration; D: crystallite size.

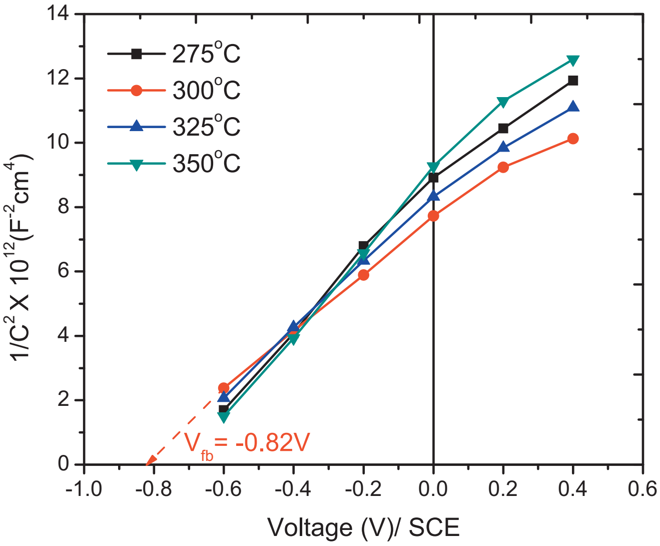

Fig. 4. Mott–Schottky plots for n-CdS/1 M polysulphide/C photoelectrochemical cell at frequency $f = 1$ kHz for films deposited at various substrate temperatures.

was obtained at $1/C_s^2 = 0$ on the potential axis according to well known Mott–Schottky relation [23,24],

$$\left(\frac{1}{C_s^2}\right) = \left(\frac{2}{\varepsilon_0 \varepsilon_s q N_D}\right)\left[V - V_{fb} - \left(\frac{kT}{q}\right)\right] \qquad (3)$$

where C_s is the space charge capacitance, V_{fb} is the flat band potential, V is electrode potential, ε_0 is the permittivity of free space, ε_s is the static permittivity of the semiconductor, N_D is donor concentration and q is the charge on electrons. The variation of flat band potential (V_{fb}) with substrate temperature is shown in Fig. 5. It appears that the value of V_{fb} varies from −0.72 to −0.82 V and is highest for the cell with photoelectrode deposited at substrate temperature of 300 °C. The change in V_{fb} with substrate temperature is due to: (i) decreased electron affinity in CdS thin film and (ii) an increased amount of surface adsorption and creation of new donor levels in the bandgap of CdS and hence the amount of band bending at the interface. The values of N_D obtained using M–S plot are given in Table 1. The values of N_D are found to increase with increase in substrate temperature reaches a maximum 1.48×10^{19} cm^{-3} at 300 °C and thereafter go on decreasing with further increase in substrate temperature.

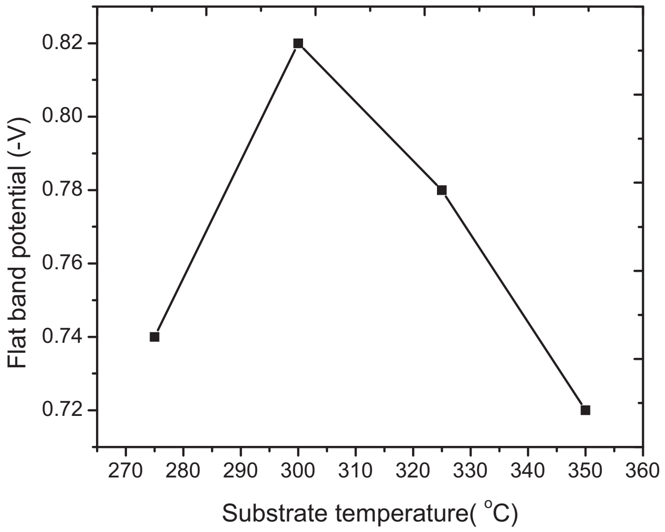

Fig. 5. Variation of flat band potential (V_{fb}) with substrate temperature for spray deposited CdS thin films.

3.4. Photovoltaic power output characteristics

Another useful technique to determine the properties of semiconductor/electrolyte interface involves illumination of the interface with a light of suitable wavelength that shows photovoltaic effect. The photovoltaic output characteristics were studied under light intensity of 20 mW/cm^2 for films deposited at all substrate temperatures. Fig. 6 shows the variation of short-circuit current density (I_{sc}) and open-circuit voltage (V_{oc}) as a function of substrate temperature for spray deposited CdS thin films. It is observed that both the I_{sc} and V_{oc} increase with increase in substrate temperature, attain a maximum values at 300 °C and then decrease with further increase in substrate temperature. Typical photocurrent density versus photo voltage characteristics (power output characteristics) of spray deposited n-CdS films/polysulphide interface deposited at various substrate temperatures under illumination is shown in Fig. 7. The photovoltaic efficiency η (%) was

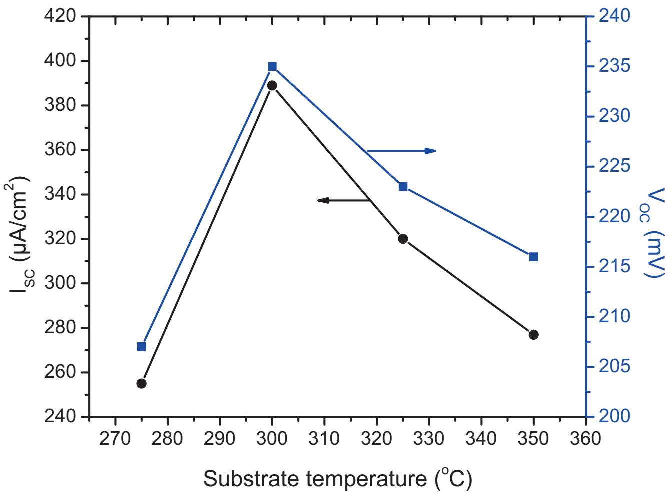

Fig. 6. Variation of I_{sc} and V_{oc} with substrate temperature for spray deposited CdS thin films.

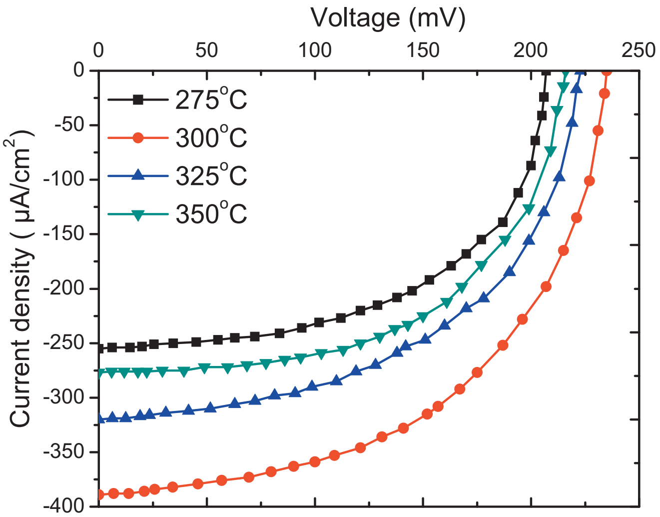

Fig. 7. Plot of power output characteristics for CdS thin films deposited at various substrate temperatures.

calculated from the relation [25].

$$\eta = \frac{V_{oc} \times I_{sc} \times FF}{P_{input}} \times 100 \tag{4}$$

where P_{input} is the power density of incident radiation. I_{sc}, V_{oc} are short circuit current and open circuit voltage, respectively.

The fill factor (FF) was calculated from the relation [26]

$$FF = \frac{V_m \times I_m}{V_{oc} \times I_{sc}} \tag{5}$$

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

Series resistance R_s and the shunt resistance R_{sh} where evaluated from the slopes of power output characteristics using the relation [26],

$$\left(\frac{dI}{dV}\right)_{I=0} \cong \left(\frac{1}{R_s}\right) \tag{6}$$

$$\left(\frac{dI}{dV}\right)_{V=0} \cong \left(\frac{1}{R_{sh}}\right) \tag{7}$$

The parameters estimated from power output plots for CdS thin film deposited at different substrate temperature are given in Table 1. The maximum power conversion efficiency (η) is found to be 0.17% for CdS thin film deposited on FTO coated glass substrate at substrate temperature of 300 °C, while it was less for other substrate temperatures. This efficiency is comparable with 0.21% reported for as deposited CdS thin films by chemical bath deposition by Hilal et al. [27] and Sankir et al. [28] and 0.29% reported for as deposited CdSe thin films by electrodeposition [29]. The increase in efficiency with increase in substrate temperature from 275 °C to 300 °C may be attributed to increase in crystallinity and grain size of the film at 300 °C than other temperatures. The decrease in efficiency after 300 °C can be attributed decrease in crystallinity and thickness due to re-evaporation of the film after decomposition or thermal convection of the sprayed droplets during the deposition process or both. Though the obtained conversion efficiency is very less, there is a scope for the improvement of the efficiency. The series and shunt resistances are found to be 262 and 3.645 kΩ from the slope of the power characteristic at $I = 0$ and $V = 0$, respectively. The micro crystallites are in general normal to the film plane, which makes leakage of current across the semiconductor surface [30]. Ideally, the shunt resistance should be infinite so that there will not be leakage current.

3.5. Spectral response studies

The spectral response study of the CdS thin film electrode/polysulphide/C photoelectrochemical solar cell was carried out by measuring short circuit current I_{sc} as a function of wavelength 'λ'. Before measurement, the cell was kept in dark for some time and the response was measured using progression from longer wavelength to shorter wavelengths. Fig. 8 shows the variation of I_{sc} with wavelength 'λ'. The spectral response curve shows a sharp peak at 500 nm. It is observed that the position of this peak is independent of intensity of light. The maximum spectral sensitivity of CdS films at 500 nm corresponds to an optical energy gap of 2.48 eV which is close to the band gap energy 2.44 eV of CdS at room temperature for a single crystal. This is due to a direct transition of electrons form valance band to conduction band [31]. It is observed that there is decrease in photocurrent for both wavelength, shorter and longer wavelength than band edge wavelength. For longer wavelengths it may be explained on the basis of high transmittance and low absorbance of light. The decrease in photocurrent on longer wavelengths side may also be attributed to the non optimized thickness and the transition between the defect levels [32]. Shorter wavelengths have higher photon energy that's why they are strongly absorbed and they produce excitation only near the surface layer of the thin film. As the volume of this layer is small, the concentration of free carries in this layer becomes too high which causes sharp increase in recombination rate and hence decreases the surface life time. Thus due to surface recombination of the photo generated charge carriers by surface states photocurrent is smaller [33,34]. Overall, the relatively low current is due to monochromatic light obtained from filters is of low intensity.

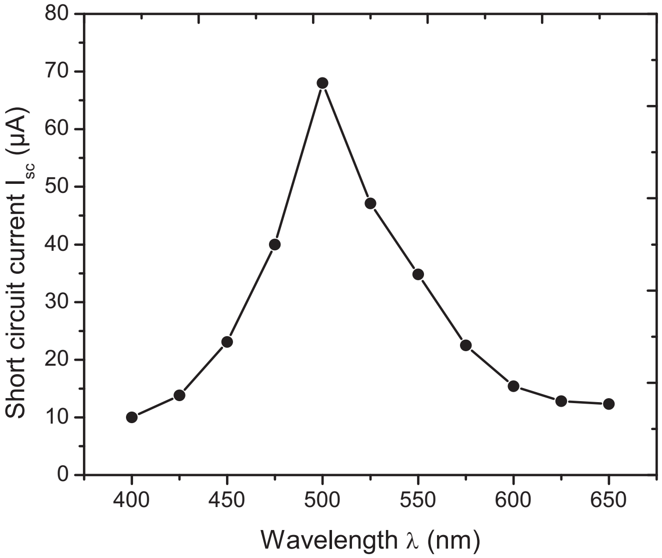

Fig. 8. Spectral response curve of n-CdS/1 M polysulphide/C PEC cell for film deposited at 300 °C.

4. Conclusions

The spray deposition of n-CdS thin film on conducting FTO coated glass substrate is possible by simple and inexpensive spray pyrolysis technique. As deposited CdS thin films are n-type polycrystalline and photoactive. The conversion efficiency (η) and fill factor (FF) for n-CdS/1 M (NaOH + Na_2S + S)/C PEC cell configuration are found to be 0.17% and 0.38 respectively for film deposited at 300 °C, as the deposited films have high series resistance. The spectral response curve shows a sharp peak at 500 nm. The value of flat band potential is found to be −0.82 V/SCE for film deposited at 300 °C.

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