

STUDIES ON POLYCRYSTALLINE CADMIUM SULPHIDE PHOTOANODES

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Summary

The spectral dependence of absolute quantum efficiency for chemically deposited cadmium sulphide thin-film electrodes in 1 M NaOH: 0.1 M Na₂S:0.1 M S, is reported. A peak quantum efficiency of 1.75×10^{-2} is observed at $\lambda = 560$ nm. The diffusion length of minority carriers has been calculated from Gartner's photocurrent equation. The light intensity dependence of the short-circuit current (J_{sc}) was linear, whereas the open-circuit voltage (V_{oc}) showed a $[\log I_L]^2$ variation. Reasons for observed low values of V_{oc} and J_{sc} are discussed.

Introduction

Cadmium sulphide (CdS, $E_g = 2.42$ eV) has become a prominent solar-cell material following the first reports in 1954 of its photovoltaic behaviour [1, 2]. Furthermore, CdS is one of the most widely studied semiconductors in thin-film form. A variety of techniques has been developed to obtain good quality films for use in solar cells. Among them, the solution-growth procedure is relatively simple and effective. It was first used for the preparation of CdS thin films with dopants such as Ag, In, Cu, and Zn on a variety of substrates for photoelectrochemical (PEC) cell applications [3]. In later years, the technique became popular for the fabrication of CdS photoelectrodes [4-9]. The methods of chemical-bath deposition and of spray pyrolysis [14-18] for the preparation of thin films for solar-cell applications have been recently reviewed [10, 11]. Other preparative methods include electrodeposition [12, 13] and screen printing [19, 20].

A fund of information on CdS as a solar-cell material is available in the literature (e.g., ref. 21). Pioneering studies on the basic principles of PEC cells have been conducted by Gerischer [22]. Ellis *et al.* [23] studied the stability of CdS electrodes in alkaline polysulphide electrolyte. In a

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recent communication, photoelectrochemical investigations into polycrystalline CdS films on SnO₂ substrates prepared by the chemical precipitation technique have been reported [24]. The work reported here is an extension of these studies.

Experimental

Thin films of indium-doped CdS were prepared on tin oxide (SnO₂)-coated glass plates by a chemical precipitation technique at 75 °C using CdCl₂ and thiourea in alkaline medium. The films were vacuum annealed at 375 °C for 30 min. Photoelectrochemical studies were performed on these electrodes using the procedure reported previously [24].

Results and discussion

Scanning electron microscope (SEM) and X-ray diffraction (XRD) studies showed the annealed CdS films to be polycrystalline. The experimental *d* values agreed with standard *d* values for hexagonal CdS. The film on the SnO₂ substrate was 1.5 μm thick and had a darksheet resistance of 25 - 50 ohm per square. By contrast, films on plain glass substrates showed values greater than 20 MΩ.

The variation of forward dark current with voltage was found to be exponential, as verified from the $\log J$ versus *V* plot (Fig. 1). The latter showed two slopes (marked I and II in Fig. 1). Using Schottky barrier theory [25], extrapolation of the two straight-line portions to the $\log J$

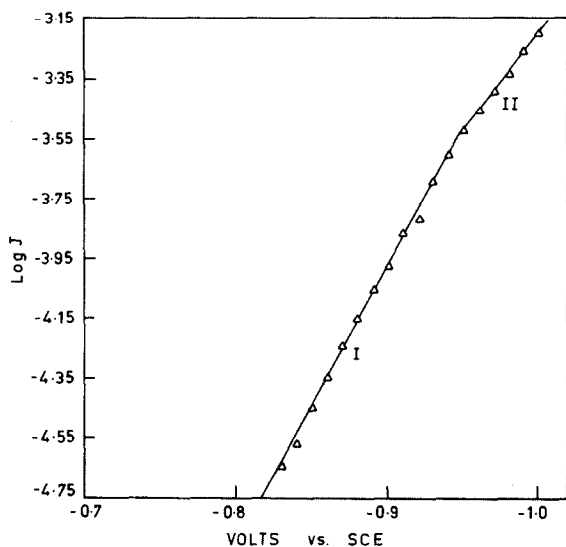


Fig. 1. $\log J$ vs. *V* plot under cathodic bias for CdS PEC cell in the dark.

axis at $V = -0.7$ V (zero bias) gave exchange current densities (J_0) of 1.38×10^{-6} A cm $^{-2}$ and 7.76×10^{-6} A cm $^{-2}$ for the low-voltage (region I) and high-voltage (region II) regions, respectively. The corresponding values of the junction ideality factor (n) were 1.86 (region I) and 2.62 (region II). The barrier height at the CdS–electrolyte interface was found to be 0.67 eV and was obtained using the equation:

$$J_0 = A^*T^2 \exp(-V\phi_B/kT) \quad (1)$$

where A^* is the Richardson constant, 20 A cm $^{-2}$ K $^{-1}$ [26].

Log J versus V curves with two slopes have been reported earlier [27] for spray-deposited Cu $_2$ S/CdS heterojunction cells and it was observed that the high-voltage slopes were temperature independent, while the low-voltage slopes showed only a weak dependence on temperature. The present data, however, are insufficient to explain the temperature-dependent behaviour. Further, the rise of forward dark current with electrode potential in Fig. 1 is 244 mV ($\log J$) $^{-1}$ over region I and 187 mV ($\log J$) $^{-1}$ over region II. This is far from the ideal (*viz.*, 60 mV ($\log J$) $^{-1}$) behaviour expected for semiconductor electrodes [28]. The non-ideal behaviour of the junction is also evident from the high values obtained for n . $n = 1$ denotes an ideal Schottky junction formation; $n = 2$ suggests that generation–recombination processes are dominating the current transport in p–n junctions [25]. In semiconductor–electrolyte junctions, n can be >1 due to the presence of thin insulating films at the electrode surface [29]. Indeed, ideality factors as high as 14 have been reported on mechanically damaged CdS electrodes due to the presence of a high density of surface states [30].

The spectral distribution of absolute quantum efficiency (determined from the photocurrent measured at each wavelength) is shown in Fig. 2. The quantum efficiencies are poor, and the peak value occurs at $\lambda = 560$ nm. The results also indicate considerably better response for $\lambda > 540$ nm in the sub-bandgap region. The data of Fig. 2 can be used to determine the value of the diffusion length of the holes according to the following theory.

From Gartner's photocurrent equation [31] for a metal/semiconductor junction, and neglecting the term contributing to the dark current, one can arrive at the following simple equation:

$$(\text{Q.E.})^{-1} = (\alpha L_p)^{-1} + 1 \quad (\text{for } \alpha W \ll 1) \quad (2)$$

where: Q.E. is the quantum efficiency, which is defined as the number of electron–hole pairs collected per incident photon; α is the optical absorption coefficient in cm $^{-1}$; L_p is the diffusion length of holes in cm; W is the depletion width in cm.

In the present case, W (from capacitance measurements) was found to be 44.34 Å for a band bending of 1 V with respect to the dark equilibrium potential [$V_R = -800$ mV (SCE)] of the electrode. From optical absorption studies, the absorption coefficient α was found to be $\sim 10^3$ cm $^{-1}$ over a range of 500 - 600 nm. Hence, the product αW was very much less than 1 and the required condition for eqn. (2) was satisfied. A plot of

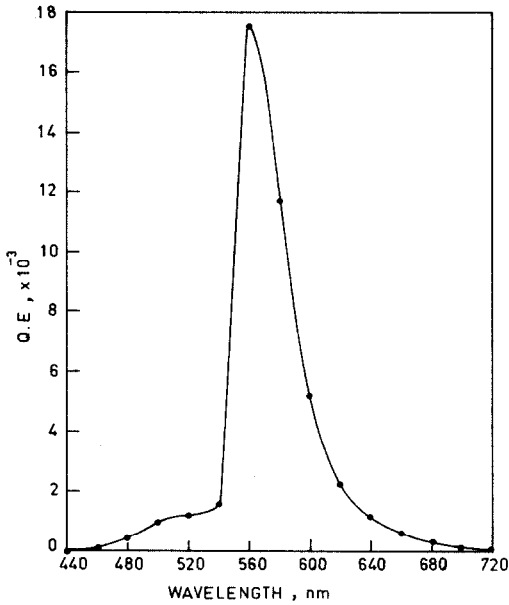


Fig. 2. Variation of absolute quantum efficiency with wavelength of incident light for CdS PEC cell.

$(Q.E.)^{-1}$ versus α^{-1} is shown in Fig. 3. The diffusion length of the holes, L_p , was calculated from the slope and was found to be $0.0022 \mu\text{m}$ or 22 \AA . This value is very much lower than the $0.13 \mu\text{m}$ (1300 \AA) reported for vacuum evaporated films or $0.41 \mu\text{m}$ (4100 \AA) for spray deposited films

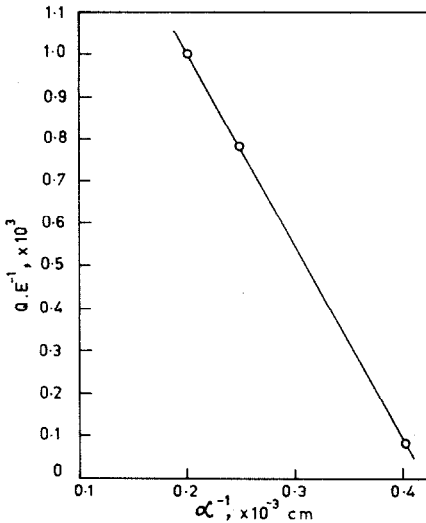


Fig. 3. Variation of inverse quantum efficiency ($Q.E.$) with reciprocal of optical absorption coefficient (α) of the CdS film.

[32]. Jastrzebski *et al.* [33] reported that in the event of a high order of surface recombination, the effective diffusion length is reduced from the bulk value, L_0 , to L_{eff} according to the following equation:

$$L_{\text{eff}}^2 = L_0^2 \left(1 - \frac{s}{s+1} \right) \exp(-Z/L_0) \quad (3)$$

where s is the reduced surface recombination velocity and is equal to SL_0/D , where D is the diffusion coefficient and S is the surface recombination velocity.

For excitation at the surface, Z will be 0. Assuming $L_0 = 0.41 \mu\text{m}$ [32], and $L_{\text{eff}} = 22 \text{ \AA}$ (Fig. 3), s was found to be $3.47 \times 10^4 \text{ cm s}^{-1}$. The actual value of the parameter, S , in the absence of reduced diffusion length would be $1.27 \times 10^4 \text{ cm s}^{-1}$, assuming the value of D to be $0.15 \text{ cm}^2 \text{ s}^{-1}$ [34].

The intensity variation of the short-circuit current density (J_{sc}) is shown in Fig. 4 in terms of a plot of $\log J_{\text{sc}}$ versus I_L , where I_L is expressed in mW cm^{-2} . It can be seen that the relationship is linear with a slope of 0.40. The dependence of the open-circuit voltage (V_{oc}) on $\log I_L$ is shown in Fig. 5. The slope $d V_{\text{oc}}/d \log I_L$ is less than $60 \text{ mV} (\log I_L)^{-1}$ and is not constant over the intensity range studied. V_{oc} is proportional to I_L at very low intensities and to $\log I_L$ at moderate intensities according to the following equation [29]:

$$(d V_{\text{oc}}/d \ln I_L) \left[1 + \frac{nkT}{2q} (V_{\text{oc}} - V_{\text{fb}})^{-1} \right] = - \frac{nkT}{q} \quad (4)$$

Equation (4) shows that if $V_{\text{oc}} - V_{\text{fb}} \gg nkT/2q$, V_{oc} is expected to vary linearly with $\log I_L$, the slope $d V_{\text{oc}}/d \log I_L$ being $-2.3 nkT/q$ or 60 mV

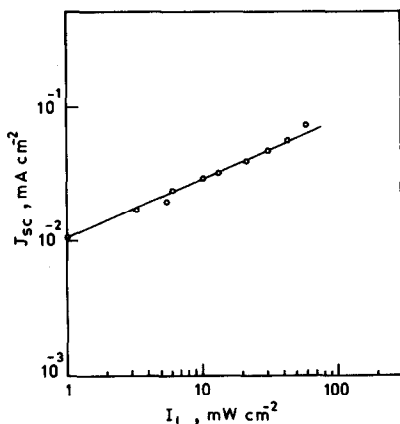


Fig. 4. Dependence of short-circuit current (J_{sc}) over light intensity (I_L) range 1 - 60 mW cm^{-2} .

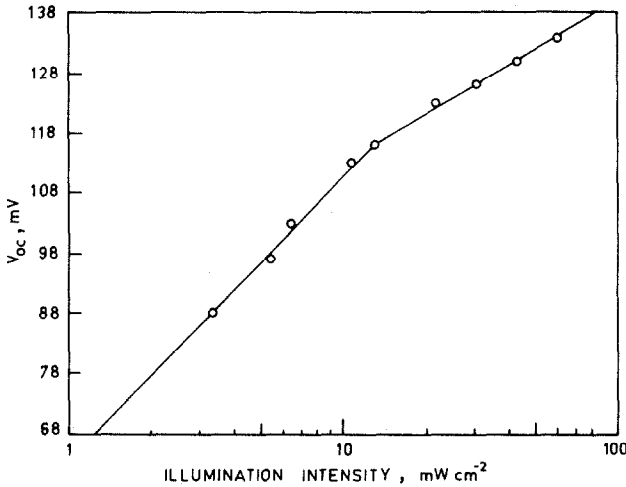


Fig. 5. Variation of open-circuit voltage (V_{oc}) with $\log I_L$ over intensity range 1 - 60 mW cm^{-2} .

for $n = 1$. For a single crystal CdX ($X = \text{S, Se or Te}$)/liquid junction, values in the range 60 - 120 $\text{mV} (\log I_L)^{-1}$ have been reported [23], whereas with polycrystalline CdS films, values as high as 230 $\text{mV} (\log I_L)^{-1}$ [12] and 750 $\text{mV} (\log I_L)^{-1}$ [15] have been cited.

The intensity dependence of J_{sc} and V_{oc} can be combined to form Fig. 6 which shows a plot of V_{oc} against $\log J_{sc}$ according to eqn. (5):

$$J_{sc} = J_0 \exp\left(\frac{qV_{oc}}{nkT} - 1\right) \quad (5)$$

The slope of Fig. 6 gave a value of n of 1.21. Compared with the ideality factors obtained from Fig. 1, the decrease in value may be ascribed to an overall decrease in the series resistance of the cell contributed by the photoconductivity of CdS.

The data of Fig. 5 are replotted in Fig. 7 as V_{oc} versus $(\log I_L)^2$ where I_L is in W cm^{-2} . According to Reiss [35], the photovoltage for an illuminated reverse biased semiconductor ($E_g \geq 3 \text{ eV}$) is given by

$$V_{oc} \approx -V_{fb} + U_{redox}^0 - \frac{2\pi q N_D}{\epsilon_0 \epsilon_s} \left[\ln \frac{K^* I_L}{D_n N_D (1 + \alpha L_D)} \right]^2 \quad (6)$$

That is, V_{oc} is proportional to $(\ln I_L)^2$. The present results (Fig. 7) obeyed the above relation although the band gap is smaller than the specified value of 3 eV. The deviation from the usual logarithmic relationship (and according to which V_{oc} is proportional to I_L at moderate light intensities) is due to the dependence of the depletion width (W) on I_L , namely,

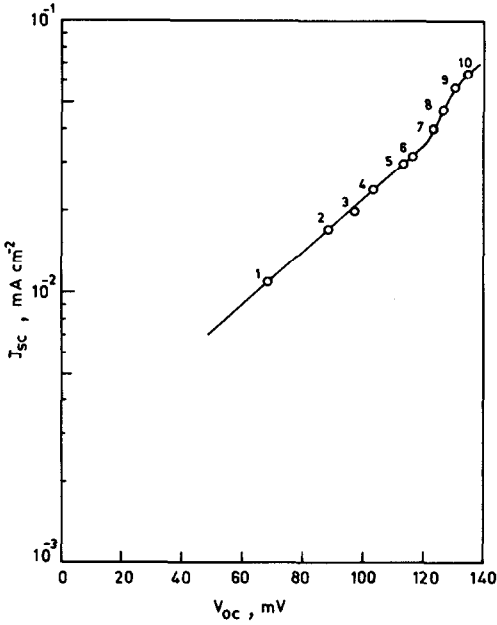


Fig. 6. Intensity dependence of short-circuit current (J_{sc}) and open-circuit voltage (V_{oc}) where V_{oc} varies according to:

$$V_{oc} = \frac{nkT}{q} \ln\left(\frac{J_{sc}}{J_0} + 1\right)$$

Illumination intensity (mW cm^{-2}): 1, 10; 2, 3.3; 3, 5.4; 4, 6.3; 5, 10.5; 6, 12.8; 7, 21.0; 8, 30.0; 9, 42.0; 10, 58.3.

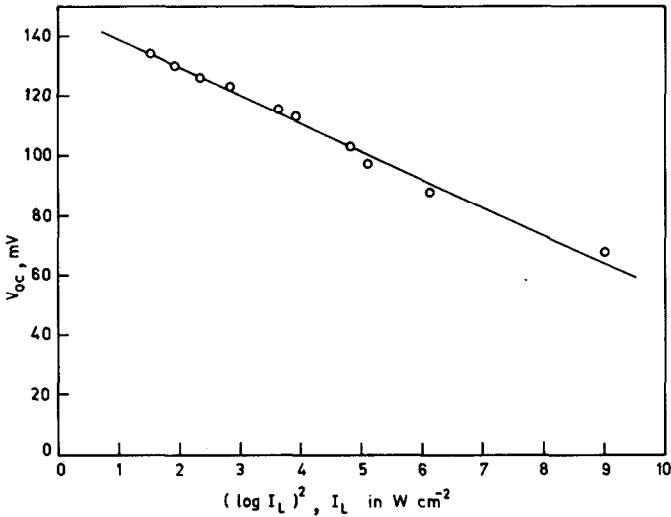


Fig. 7. Data of Fig. 5 replotted to show variation of V_{oc} with $(\log I_L)^2$, thus demonstrating the validity of Reiss's law (see text).

TABLE 1
Comparison of performance data for CdS photoanodes

Substrate	Dopant	Redox composition	Illumination intensity, I_L (mW cm^{-2})	Open-circuit voltage, V_{oc} (mV)	Short-circuit current, J_{sc} (mA cm^{-2})	Fill factor, FF	Reference
SnO_2 -glass	In	a	58.35	175	0.08	0.25	Present work
NESA-glass	Undoped	b	75 ^x	590	0.14	—	4
	Li	b	75 ^x	550	0.24	—	4
	Cu	c	75 ^x	300	0.33	—	4
Ti	Undoped	c	70 ^y	580	0.19	0.27	7
	Cu	c	70 ^y	580	0.58	0.40	7
	Al	c	70 ^y	530	0.18	0.21	7
Ni	Undoped	c	70 ^y	150	0.06	—	7
	Cu	c	70 ^y	160	0.06	—	7
Ti	Undoped	d	—	455	0.90	0.42	8
Stainless steel	In	b	100 ^z	230	0.40	0.53	6
	Undoped	b	35 ^z	185	1.70	0.25	36
	Li	b	35 ^z	254	3.40	0.28	36

a = 1.0 M NaOH-0.1 M Na_2S -0.1 M S.

b = 1.0 M NaOH-1.0 M Na_2S -1.0 M S.

c = 0.1 M NaOH-0.1 M Na_2S -0.1 M S.

d = 1.0 M NaOH-0.5 M Na_2S -0.5 M S.

^xSolar simulator.

^ySunlight.

^zTungsten lamp.

$$W = \ln \frac{K^* I_L}{D_n N_D (1 + \alpha L_p)} \quad (7)$$

where K^* is a constant. According to eqn. (7), V_{oc} versus $\ln I_L$ goes through a maximum at the flat-band potential. At the highest intensity used in the present studies (*i.e.*, 58.35 mW cm^{-2}), however, no such maximum was observed (Fig. 5). On the other hand, the slope of $dV_{oc}/d(\log I_L)^2$ (Fig. 7) was found to be $75 \text{ mV} (\log I_L)^{-1}$ and is in good agreement with the value of $71 \text{ mV} (\log I_L)^{-1}$ calculated from eqn. (4) using $n = 1.21$.

The power output characteristics of the electrode at an illumination of 58.35 mW cm^{-2} are shown in Fig. 8. The results give: $V_{oc} = 175 \text{ mV}$, $J_{sc} = 0.08 \text{ mA cm}^{-2}$, and a fill factor (FF) = 0.25. These values are compared with those of other studies in Table 1. The data include the PEC parameters of chemically precipitated CdS on SnO_2 , Ti, and stainless steel substrates, though under different experimental conditions of redox concentration, incident light intensity, and doping level.

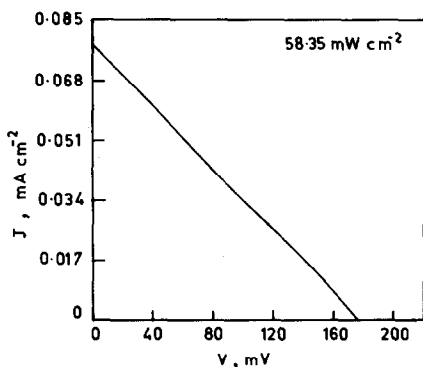


Fig. 8. Output power curve of CdS PEC cell obtained at 58.35 mW cm^{-2} tungsten-halogen illumination.

(i) The value for V_{oc} (175 mV) is close to that (154 mV) calculated from eqn. (5).

(ii) The low value of J_{sc} is largely due to the extremely small hole diffusion length (L_p), *viz.*, 22 \AA . As a consequence, even though the penetration depth of light ($\sim 10 \mu\text{m}$ or 10^5 \AA) is much larger than the depletion width ($\sim 44 \text{ \AA}$), the carriers generated beyond 66 \AA (*i.e.*, a distance of $W + L_p$) do not contribute to the photocurrent. Diffusion lengths in single crystal CdS are in the region $3 - 7 \mu\text{m}$ ($3 - 7 \times 10^4 \text{ \AA}$) [8]. Considering this, the present value of diffusion length, *i.e.*, 22 \AA , is extremely low.

Conclusions

For chemically deposited cadmium sulphide, the dark J - V characteristics showed a non-ideal junction formation, as witnessed by large values

for the exchange current and the ideality factor. Spectral response studies indicated a low hole-diffusion length and a large surface recombination velocity. As a consequence, the photocurrent is small. The open-circuit voltage (V_{oc}) is low because of the high exchange current density. The light intensity dependence of V_{oc} on $(\log I_L)^2$ was found to be in accordance with Reiss's law.

Acknowledgement

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List of symbols

A^*	Richardson constant for the dark current in Schottky barriers
D	Diffusion coefficient
D_n	Diffusion coefficient of electrons in p-type material
d	Interplanar spacing
E_g	Bandgap energy
FF	Fill factor
I	Current
I_L	Intensity of illumination
J	Current density
J_0	Exchange current density (reverse leakage current density in Schottky barriers)
J_{sc}	Short-circuit current density
k	Boltzmann constant
kT	Thermal energy
L_p	Hole diffusion length in n-type material
L_0	Bulk diffusion length of holes in n-type material
L_{eff}	Effective diffusion length for holes in n-type material in presence of surface recombination
n	Ideality factor in dark current of Schottky barriers
N_D	Donor impurity density
q	Magnitude of electronic charge
Q.E.	Quantum efficiency defined as the number of electron-hole pairs collected per incident photon
S	Surface recombination velocity
s	Reduced surface recombination velocity
T	Absolute temperature
U_{redox}^0	Standard redox potential
V	Voltage
V_{oc}	Open-circuit voltage
V_{fb}	Flat-band potential

W	Depletion layer width
Z	Range parameter, usually occurring in the measurements of electron beam induced currents in semiconductor junctions
α	Optical absorption coefficient
λ	Wavelength
ϕ_B	Barrier height in Schottky barriers
ϵ_0	Permittivity of free space
ϵ_s	Static dielectric constant
μm	Micrometre

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