

PHOTOELECTROCHEMICAL STUDY OF SCREEN-PRINTED CADMIUM SULPHIDE ELECTRODES

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Summary

Thin films of CdS have been prepared by the screen-printing technique. Optical absorption studies reveal a band gap of 2.42 eV. Current-voltage studies at the CdS-(1 M NaOH-0.1 M Na₂S-0.1 M S) interface yield an exchange current density of 6×10^{-6} A cm⁻² and a junction ideality factor of 2.8. Mott-Schottky plots at 0.4, 1.0, 2.0 and 4.0 kHz show a flat-band potential of -1.07 V (SCE). At 84.5 mW cm⁻² tungsten-halogen illumination, the photoelectrochemical cell gives an open-circuit voltage of 0.32 V, a short-circuit current density of 0.23 mA cm⁻², and a fill-factor of 0.42.

Introduction

Cadmium sulphide (CdS) belongs to the II-VI group of semiconductors and has a band gap of 2.42 eV at room temperature. The compound has been known to be a photovoltaic material since 1954 when a photovoltaic response was observed [1] in heat treated copper contacts on CdS at photon energies less than the CdS band edge. Cadmium sulphide has also been one of the most extensively investigated semiconductors in thin film form for solar cell use [2]. A wide variety of deposition techniques (e.g., vacuum evaporation, sputtering, screen printing, chemical bath deposition (CBD) and electrodeposition, etc.) have been developed for obtaining low-cost polycrystalline films of CdS. Among them, the processes of spray pyrolysis and CBD have been reviewed by the present authors and others [3 - 6]. Screen printing, the subject of the present investigation, is widely known for its application in thick-film technology. This technique also lends itself to solar-cell technology in the preparation of active semiconductor layers and devices [7]. Compared to other techniques, it is particularly attractive for preparing thicker films in shorter times. The various physical and chemical aspects of screen printing are discussed in detail in ref. 2.

The use of CdS in photoelectrochemical solar cells (PECSC) has been due to a favourable bandgap and a remarkable stability against anodic photo-

decomposition in alkaline sulphide-polysulphide electrolytes [8]. It is also being investigated as a material for generating hydrogen from water by photoelectrolysis [9]. Simplicity of preparation, low cost compared with single crystals, and possibility of obtaining reasonable energy conversion efficiencies are some of the attractive features of polycrystalline film electrodes. Many workers have investigated polycrystalline CdS layers, prepared by various techniques [10 - 22], for PECSC applications. However, literature [23] on screen-printed CdS photoelectrodes is sparse and this has prompted the present investigation.

Experimental

A fine powder of CdS doped with In (0.01 wt.%) was prepared from a solution of 1 M CdCl₂, 1 M NH₂CSNH₂ and 2 M ammonia. A slurry was formed in glycerol with 5 g of CdS and 0.5 g of CdCl₂ (flux). Films of CdS were then deposited on plain and SnO₂-coated glass substrates (10 ohm per square) through a silk screen, mesh size 40 μm. They were initially dried at 100 °C for 3 - 4 h and then sintered at 560 °C for 30 min in air. Finally, the films were annealed at 375 °C for 30 min at a pressure of ~10⁻⁵ Torr.

Compound identification was achieved by conducting X-ray diffraction (XRD) studies using Cu Kα radiation (λ = 1.5418 Å). Bandgap evaluation was made by optical absorption studies using a spectrophotometer.

The PEC cell consisted of a CdS thin-film working electrode and a large-area Pt counter electrode. A saturated calomel electrode (SCE) was used as a reference; all potentials given in this paper are quoted with respect to this electrode. Ohmic contact to CdS was provided through the SnO₂ layer. A small area of the CdS surface was exposed and the rest of the electrode and the contact regions were insulated from the electrolyte with polystyrene. A solution of 1 M NaOH-0.1 M Na₂S-0.1 M S served as the redox electrolyte. Argon was bubbled through the electrolyte before and during measurements to remove dissolved oxygen and to maintain an inert atmosphere.

Current-voltage curves were obtained with a Wenking Potential Control Amplifier (PCA 72 L) driven by a PARC 175 Universal Programmer and a Philips (PH 8120) X-Y recorder. Illumination was provided from a 250 W Oriel 6432 tungsten-halogen lamp. The light emerging from the lamp was passed through a 5 cm pathlength circulating-water filter and an Oriel 7165 infrared absorbing filter and then focused on the photoelectrode by an Oriel 7169 condensing lens assembly. The intensity of illumination (I_L) at the photoelectrode (uncorrected for absorption losses due to the glass window and the redox solution) was measured by an Oriel 7102 thermopile detector and found to be 84.5 mW cm⁻². Intensity dependence of power characteristics was studied using neutral density filters.

Space charge capacitance was measured at 0.4, 1.0, 2.0 and 4.0 kHz using a Solartron 1170 Frequency Response Analyser coupled with an 1186

Electrochemical Interface. The applied d.c. voltage across the junction was varied from -0.55 to $+0.70$ V. The superimposed a.c. signal was 10 mV_{pp}. The capacitance was calculated from the measured reactance in ohms.

Spectral response studies were carried out using an Oriel 7155 monochromator (slit width 1 mm) over the wavelength range $400 - 700$ nm. The response was normalized for the incident intensity variations. An Si photodiode of known spectral response was used for this purpose.

Results and discussion

The sheet resistance of CdS layers on SnO₂ substrates was found to be in the range $40 - 50$ ohms per square, while on plain glass substrates it was greater than 10^6 ohms per square. XRD patterns exhibited prominent peaks corresponding to hexagonal CdS. The experimental and the standard d values for CdS are compared in Table 1.

TABLE 1
Experimental and Standard d values for CdS

Intensity	d (Å)	
	Standard	Experimental
75	3.580	3.575
60	3.360	3.351
100	3.160	3.153
25	2.450	2.442
55	2.068	2.066
40	1.898	1.895
45	1.761	1.758
16	1.398	1.398

Figure 1 shows the current-voltage curves obtained at 1 mV s⁻¹ scan rate for a CdS thin-film electrode both in dark and with illumination. The photocurrent (I_{ph}) was obtained after subtracting the dark current (I_d) from the total current (I). The onset of photocurrent occurred at a potential of -0.89 V. This indicates that the flat-band potential (V_{fb}) is approximately of the same value. The variation of forward cathodic dark current with electrode potential (V) is shown in Fig. 2. It shows a slope of 150 mV ($\log J$)⁻¹, as against 60 mV ($\log J$)⁻¹ expected for semiconductor electrodes [24]. Treating the CdS-electrolyte interface as a Schottky barrier, an exchange current density, J_o , of 6×10^{-6} A cm⁻² and a junction ideality factor, n , of 2.8 were obtained from Fig. 2. An ideality factor of 2 is known to indicate that generation-recombination processes in the space-charge region predominate over other current-transport mechanisms in solid state p-n junction diodes [25]. Values of n far in excess of 2 have also been reported by Vainas *et al.*

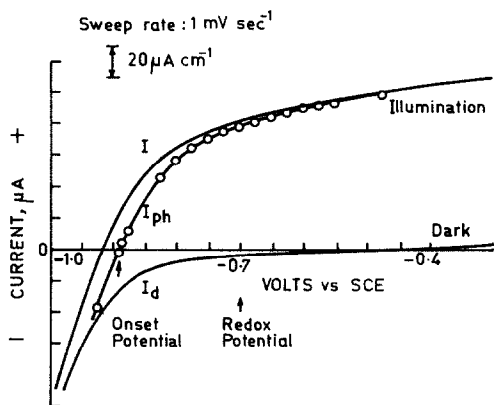


Fig. 1. Current-voltage relationship for CdS-(1 M NaOH-0.1 M Na₂S-0.1 M S) junction in dark and with illumination. I = total current; I_d = dark current; I_{ph} = photocurrent = $I - I_d$.

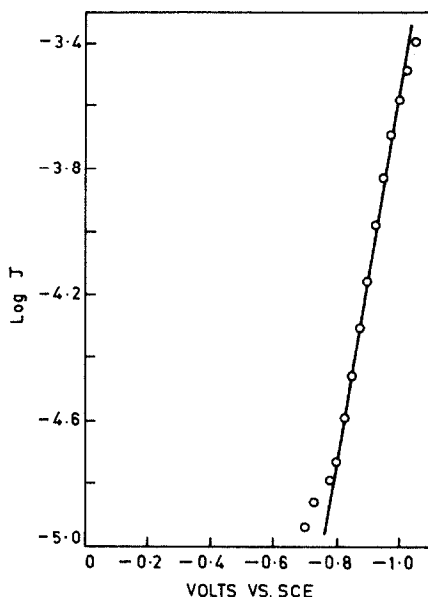
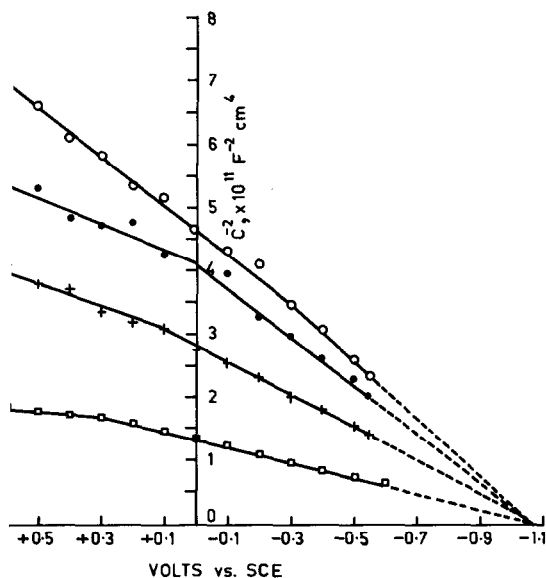


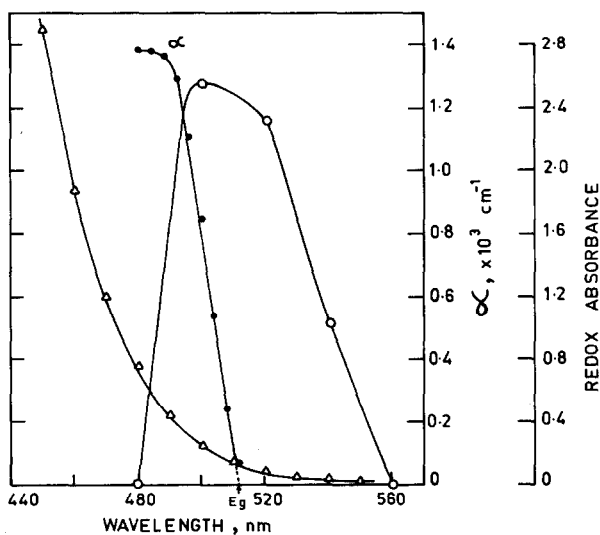
Fig. 2. Log J vs. V plot.

[26] on mechanically damaged CdS electrodes. These authors observed that a high density of surface states was mainly responsible for the non-ideal behaviour of the junction. However, satisfactory explanations for the occurrence of high ideality factors in semiconductor-electrolyte junctions have yet to be reported.

Mott-Schottky plots at four different frequencies (f) are given in Fig. 3. Each of the plots shows two linear regions corresponding to different extents of band bending. The higher values of C^{-2} correspond to a larger band bending and lower values to a smaller band bending at the interface. The linearity of the plots suggests that both the shallow and deep donor levels are uniformly ionized. From the extrapolated intercepts of the V -axis (Fig. 3) a V_{fb} of -1.07 V was obtained; this value was independent of f . V_{fb} obtained from the onset of photocurrent is -0.89 V. Thus, there is a difference of 0.18 V between the values obtained by the two methods. It is pertinent to remember that the V_{fb} determination from the photocurrent onset is approximate and is strongly influenced by the presence of hole traps in the space charge region of the CdS photoanode [27]. Figure 3 depicts a frequency dependence of $d(C^{-2})/dV$. Such a behaviour has been observed with CdS [28] and it is mainly due to the frequency dependence of the static dielectric constant (ϵ_s) in the space-charge region. Assuming $\epsilon_s = 10.3$ [2] and using the Mott-Schottky relation [27], a donor density, N_D , of $2.65 \times 10^{19} \text{ cm}^{-3}$ is obtained from the slope of the plot at $f = 1$ kHz.



3. Mott-Schottky plot for CdS-electrolyte junction; frequency (Hz): ●, 400; ○, 2000; □, 4000; +, 4000.



4. ○, Normalized spectral response for PEC cell; ●, optical absorption coefficient (α) with λ for film on plain glass substrate; △, absorbance of 0.1 M Na_2S -0.1 M S l cm path length of light.

The normalized spectral response for the PEC cell, the absorption curve of the CdS film on a plain glass substrate, and the redox (0.1 M Na_2S -0.1 M S) absorbance for 1 cm path length of light are presented in Fig. 4. From the optical absorption curve, E_g was found to be 2.42 eV. The spectral response

showed an onset of response at $\lambda = 480$ nm, where the absorbance due to sulphide-polysulphide is only 25%. The maximum response occurred at 500 nm (or 2.48 eV) which is slightly higher than the bandgap of CdS. The response has a cut-off at 560 nm corresponding to an energy of 2.21 eV. The nature of the spectral response *i.e.*, the onset of response, the wavelength of maximum response, and the cut-off, etc., all suggest that the observed photocurrent is due mainly to the light absorption and electron-hole generation in CdS. The response at energies less than the band gap of CdS is attributed to charge capture and transfer via the surface states.

Figure 5 gives the variation of $\log J_{sc}$ (where J_{sc} denotes short-circuit current density) with the open-circuit voltage (V_{oc}) of the cell at different illumination intensities. The slope yields a value of $n = 1.8$, which is less than the value of 2.8 obtained from the $I-V$ plot (Fig. 2). Under illumination, there will be a decrease in the series resistance of the PEC cell on account of the photoconductivity of CdS which ultimately results in a lowering of the ideality factor.

Two output power curves at 84.5 and 45.5 mW cm^{-2} illumination are given in Fig. 6. Values of V_{oc} , J_{sc} , fill-factor (ff), output power (P_{out}) and conversion efficiency (η) obtained from the two curves are listed in Table 2.

The open-circuit voltage of 0.31 V seems to be a reasonable value from a consideration of V_{fb} and the redox potential (V_o) of the sulphide-polysulphide redox couple. The maximum obtainable cell voltage ($V_{oc(max)}$) is limited to the difference between the two [27]. With $V_o = -0.70$ V and

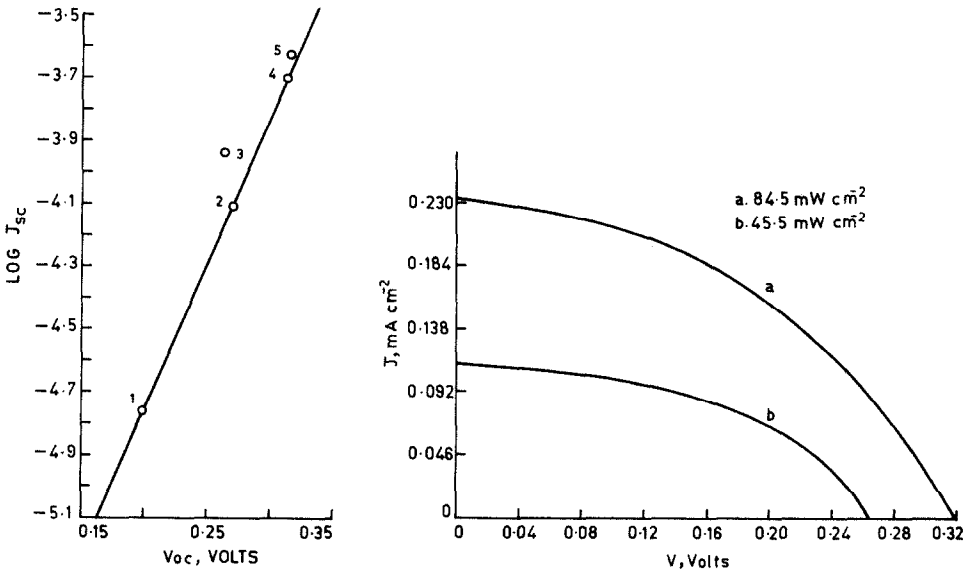


Fig. 5. Intensity dependence of short-circuit current density (J_{sc}) and open-circuit voltage (V_{oc}). Illumination intensity (mW cm^{-2}): 1, 5.5; 2, 27.5; 3, 45.5; 4, 72.0; 5, 84.5.

Fig. 6. Output power curves for the PEC cell at (a) 84.5 and (b) 45.5 mW cm^{-2} tungsten-halogen illumination.

TABLE 2

 V_{oc} , J_{sc} , ff, P_{out} and η at two different illumination levels

I_L (mW cm ⁻²)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	ff	P_{out} (mW cm ⁻²)	η (%)
84.5	0.31	0.23	0.42	0.03	0.035
45.5	0.26	0.11	0.46	0.01	0.022

$V_{fb} = -1.07$ V (Fig. 3), $V_{oc(max)} = -0.37$ V. The photocurrents are very low due to the combined effects of grain-boundary recombination and a large series resistance ($\sim 685 \Omega$) associated with the cell. The performance (in terms of $I-V$ output) of PECSCs based on polycrystalline CdS film electrodes reported by various workers is listed in Table 3. A close examination of the data reveals wide variations in the experimental conditions.

TABLE 3

Photoelectrochemical cell performance data of various CdS film electrodes

Deposition technique	Doping, substrate	Concentration of NaOH, Na ₂ S and S (M)	Light source, I_L (mW cm ⁻²)	V_{oc} (mV)	J_{sc} (mA cm ⁻²)	Fill-factor (ff)	η (%)	Reference
Screen printing	In doped; SnO ₂	1.0 0.1 0.1	250 W tungsten-halogen 84.5	310	0.23	0.42	0.035	Present results
Slurry-painting	Undoped; Ti	0.1 0.1 0.1	Sunlight 70	200	0.10	—	—	15
Chemical bath deposition	In doped; SnO ₂	1.0 0.1 0.1	250 W tungsten-halogen 60	216	0.58	0.25	0.052	29
	Undoped; Ti	1.0 0.5 0.5	—	455	0.90	0.42	—	16
	CuI doped; Ti	0.1 0.1 0.1	Sunlight 70	580	0.58	0.40	0.192	15
	Ni	0.1 0.1 0.1	Sunlight 70	160	0.06	—	—	15
	AlCl ₃ doped; Ti	0.1 0.1 0.1	Sunlight 70	530	0.18	—	—	15
	In doped; Stainless steel	1.0 1.0 1.0	500 W tungsten lamp 100	230	0.40	0.53	0.048	14

(continued)

TABLE 3 (continued)

Deposition technique	Doping, substrate	Concentration of NaOH, Na ₂ S and S (M)	Light source, I_L (mW cm ⁻²)	V_{oc} (mV)	J_{sc} (mA cm ⁻²)	Fill-factor (ff)	η (%)	Reference	
Spray pyrolysis	In doped; SnO ₂	1.0	250 W tungsten-halogen 100	510	0.82	0.30	0.125	22	
		0.1							
	Undoped; SnO ₂	1.0	500 W Xenon; 100	525	0.50	—	—	30	
		1.0							
	Al doped; SnO ₂	1.0	500 W Xenon; 100	562	1.40	—	—	30	
		1.0							
	Undoped; SnO ₂	1.0	Xenon	510	0.40	—	—	20	
1.0									
Undoped plain glass	1.0	Xenon	500	0.30	—	—	20		
	1.0								
Undoped plain glass	1.25	Tungsten 0.595	600	1.8 × 10 ⁻³	0.21	0.038	21		
	0.2								
— plain glass	0.1	—	400	0.20	—	—	31		
	0.1								
Electro-deposition	— Ti	0.1	Sunlight 70	410	0.22	0.30	0.038	15	
		0.1							
		0.1							
— Ni	0.1	0.1	Sunlight 70	200	0.18	0.17	0.008	15	
									0.1
									0.1
— Ti	1.0	1.0	100 W tungsten 100	600	0.47	0.36	0.101	19	
									1.0
									1.0

From V_{oc} , J_{sc} , ff and I_L , a calculation of efficiencies (η), wherever possible, has been made and the values are also included in Table 3. A comparison of the present results with these will, however, have limited relevance. Nevertheless, it can be said that in terms of efficiency, spray pyrolysed and electrodeposited films appear to show better performance compared with the CBD and screen-printed films. It must also be noted that the screen-printing method offers the advantage of greater manipulation of the preparative parameters and, hence, has greater potential for obtaining films with improved properties.

Conclusions

The screen-printed CdS-electrolyte junction has shown ideality factors greater than 2. Capacitance-voltage behaviour is in accordance with the

t-Schottky theory. Further, the flat-band potential is independent of frequency of measurement. Spectral response is found to be governed by absorption characteristics of CdS. The cell shows reasonable open-circuit voltage, but low photocurrents due to grain-boundary recombination.

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