CHAPTER-V

Properties of ECPV cells formed with Cd-Zn-S and Cd-Bi-S films.

5.1 Introduction :

The semiconductors CdS, ZnS, Bi_2S_3, Cd-Zn-S and Cd-Bi-S films were prpared by electrodeposition technique. The preparative parameters such as optical absorption, variation of compositioin, variation of band gaps, was studied and reported. The variation of band gap with zinc composition and Bismuth composition is described in Chapter III and IV respectively. In Cd-Zn-S semiconductor films prepared by spray pyrolysis technique, it is found that the band gap is dependent on the zinc composition. This results in altering the properties of the ECPV cells (1-6).

In the present investigatioin, the Cd-Zn-S films were electrodeposited on stainless steel substrate. Similarly, a new semiconductor Cd-Bi-S films were deposited on stainless steel substrate by electrodeposition technique with appropriate composition of CdS and Bi_2S_3 solutions. The band gap of Cd-Bi-S film was varied between 2.4 eV (E_g for CdS) and 1.7 eV (E_g for Bi_2S_3). The attempt has been made to prepare the semiconductors of the band gaps between 1.2 eV to 1.8 eV to match with the solar spectrum for effective conversion of solar energy into electrical energy (7). A solar energy conversion device called Electrochemical Photovoltaic (ECPV) cell with the configuration semiconductor photoanode/electrolyte/counter electrode were formed. The Electrical and Optical properties of these cells were studied and reported in this chapter. The photovoltaic output characteristics were determined.

5.2 Experimental :

The performance of the ECPV cells formed with polycrystalline semiconductor photoanodes CdS, ZnS, Bi_2S_3, Cd-Zn-S and Cd-Bi-S was studied. The electrolyte used in the cell was polysulfide 1 M ($NaOH-Na_2S-S$). The carbon rod was used as a counter electrode. The distance between a photoanode and the counter electrode was kept constant at 0.2 cm. The circuit diagram for studing the electrical properties of ECPV cells is as shown in fig. 5.1. The electrical characterization I-V curves in dark and under illumination were recorded with a potentiostat (EG & G) PARC Model-362 for photoanodes. The scan rate was 20 mV/sec. A 500 W tungeston filament lamp was employed to illuminate the cell.

The spectral response of ECPV cells were studied by using a monochromator spekol (Carl Zeiss Jena) in the wave length range varied between 400 nm to 700 nm. The photoresponse of the ECPV cell was studied with intensity by varying the distance between lamp and the cell. The water filter was interposed between lamp and the cell.

5.3 Results and Discussion :

5.3.1 Variation of I_{sc} and V_{oc} of the ECPV cells formed with Cd-Zn-S and Cd-Bi-S films :

When a semiconductor film Cd-Zn-S was dipped into an electrolyte, a voltage called, dark voltage (V_D) and a current called dark current (I_D) develops when the ECPV cell is in dark. The origin of the dark voltage is attributed to the difference between the two half cell potential in a ECPV cell and can write this potential as :

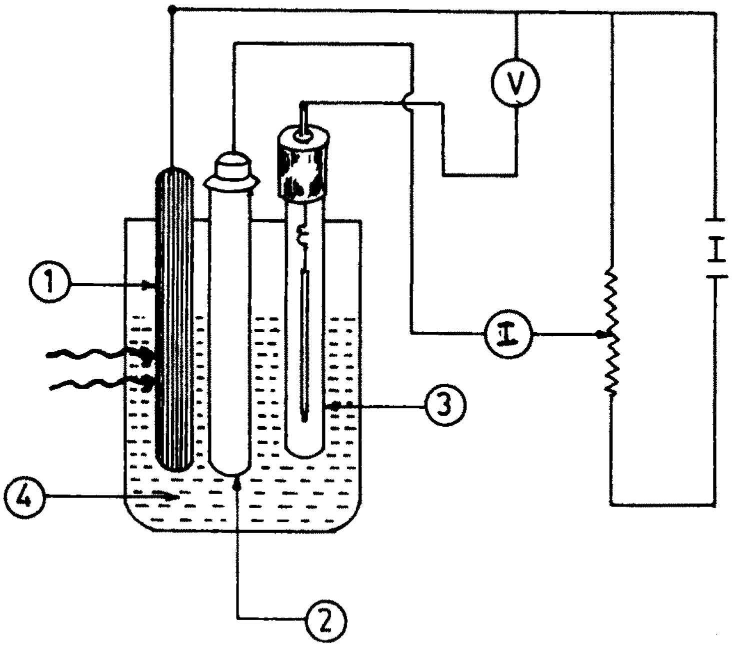

Fig.5·1 - Circuit diagram for current-voltage characteristics of the ECPV cell.
1) Photoanode 2) Counter electrode 3) SCE and 4) Electrolyte.

$$E = E_{Cd-Zn-S} - E_{Carbon} \quad \ldots (5.1)$$

and

$$E = E_{Cd-Bi-S} - E_{Carbon} \quad \ldots (5.2)$$

where $E_{Cd-Bi-S}$ and E_{Carbon} are the half cell potentials of Cd-Bi-S and carbon electrode respectively, when they are dipped into an electrolyte. The dark current is due to the deterioration of the photoanode in dark. The variation of the short circuit current (I_{sc}) and open circuit voltage (V_{oc}) with Zinc composition in Cd-Zn-S photoanode is studied. The open circuit voltage (V_{oc}) was found to be increased with increase of Zn composition upto 0.2 and beyond this value both V_{oc} and I_{sc} decreases. The ECPV cell formed with photoanode Cd-Bi-S under illumination shows the short circuit current (I_{sc}) increases with increase in Bi composition and open circuit voltage (V_{oc}) decreases continuously which may be attributed to decrease in band gap energy. In comparison with films of Cd-Zn-S and Cd-Bi-S observed that the open circuit voltage (V_{oc}) for Cd-Zn-S films was greater than that of the Cd-Zn-S films. It is also found that the short circuit current (I_{sc}) for Cd-Bi-S film was greater than that of the Cd-Zn-S films. The corresponding values of (I_{sc}) and (V_{oc}) are tabulated in table 5.1.

5.3.2 I-V Characteristics :

In order to investigate the charge transfer across the interface between the semiconductor and electrolyte, the current of the ECPV cell as a function of applied voltage was recorded for all cells formed with photoanodes CdS, ZnS, Bi_2S_3, Cd-Zn-S and Cd-Bi-S in dark and in light as shown in fig. 5.2(a-e). The current-voltage (SCE) (I-V) curves for all cells in dark and under light were studied both in the forward and reverse bias. The nature of I-V curves are rectifying for all cells. The current-voltage characteristics of CdS film as photoelectrode in cells are modified when alloyed film of Cd-Zn-S and Cd-Bi-S film photoelectrodes are used. It is observed that by addition of ZnS to CdS increases the barrier height at interface so that the reverse saturation current decreases. The addition of Bi_2S_3 to CdS decreases the barrier height at interface so that the reverse saturation current increases. I-V curves are not passing through origin which means that at zero external voltage; the ECPV cells give some voltage. The polarity of dark voltage is negative towards n-type photoanode Cd-Zn-S and Cd-Bi-S.

After illuminatioin photoanode Cd-Zn-S and Cd-Bi-S in ECPV cell becomes more negative. This predicts that the material of photoanode is of n-type semiconductor. It is seen that I-V curves in light is shifted from I-V curves in dark, which shows that the ECPV cell is the generator of electricity. The maximum power available from the ECPV cell is found from a point on the I-V curve where the product of (I-V) is maximum. The maximum power ($P_m = I_m V_m$) values are estimated from the ECPV cell. The efficiency (n) and fill factor (ff) were computed for all ECPV cells when exposed to white light intensity of 100 mW/cm^2 and values are listed in table 5.1.

5.3.3 <u>Spectral Response</u> :

The spectral response study of the ECPV cell is important as it is directly related to the solar spectrum utilization. It contains the

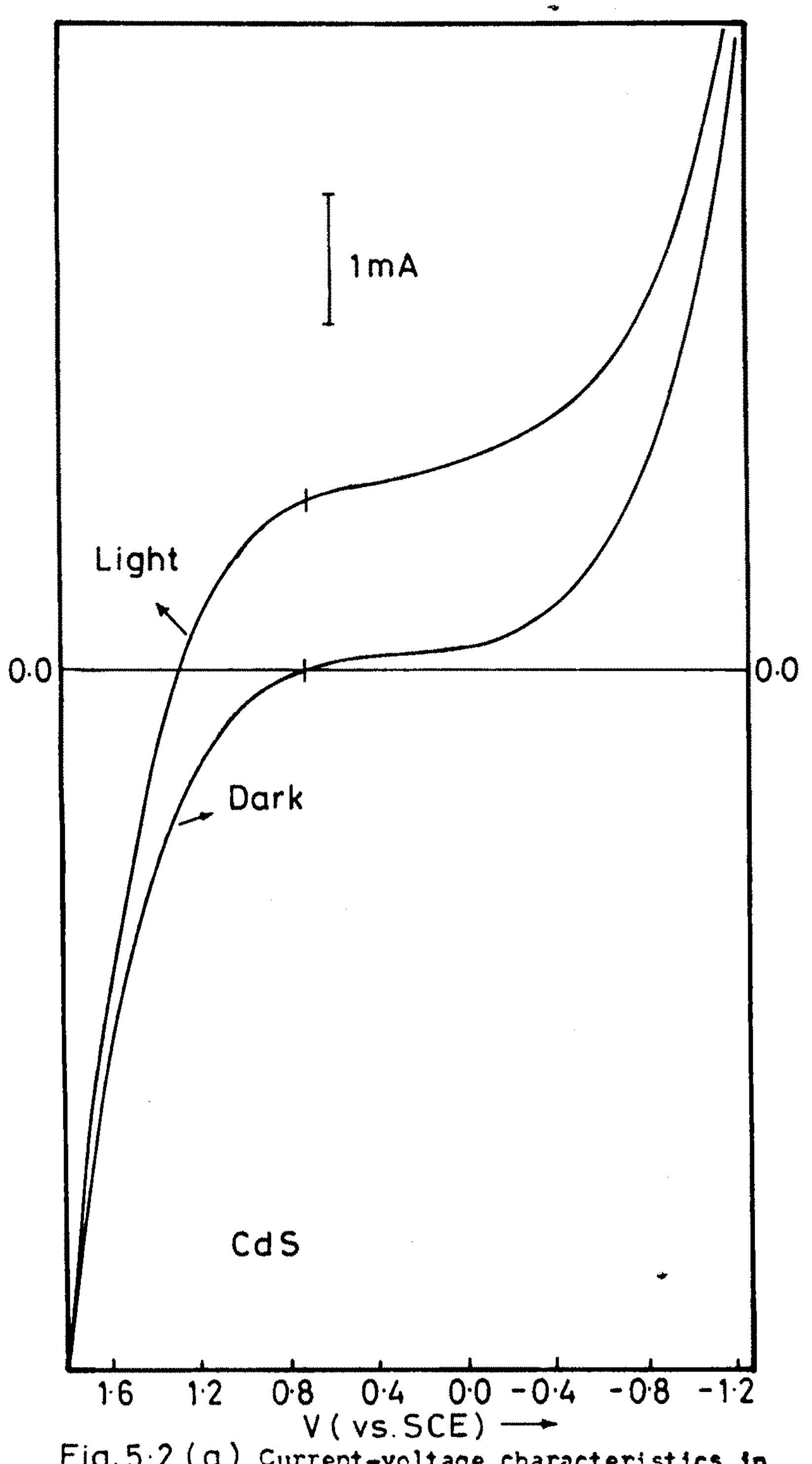

Fig. 5·2 (a) Current-voltage characteristics in dark and under illumination for CdS film.

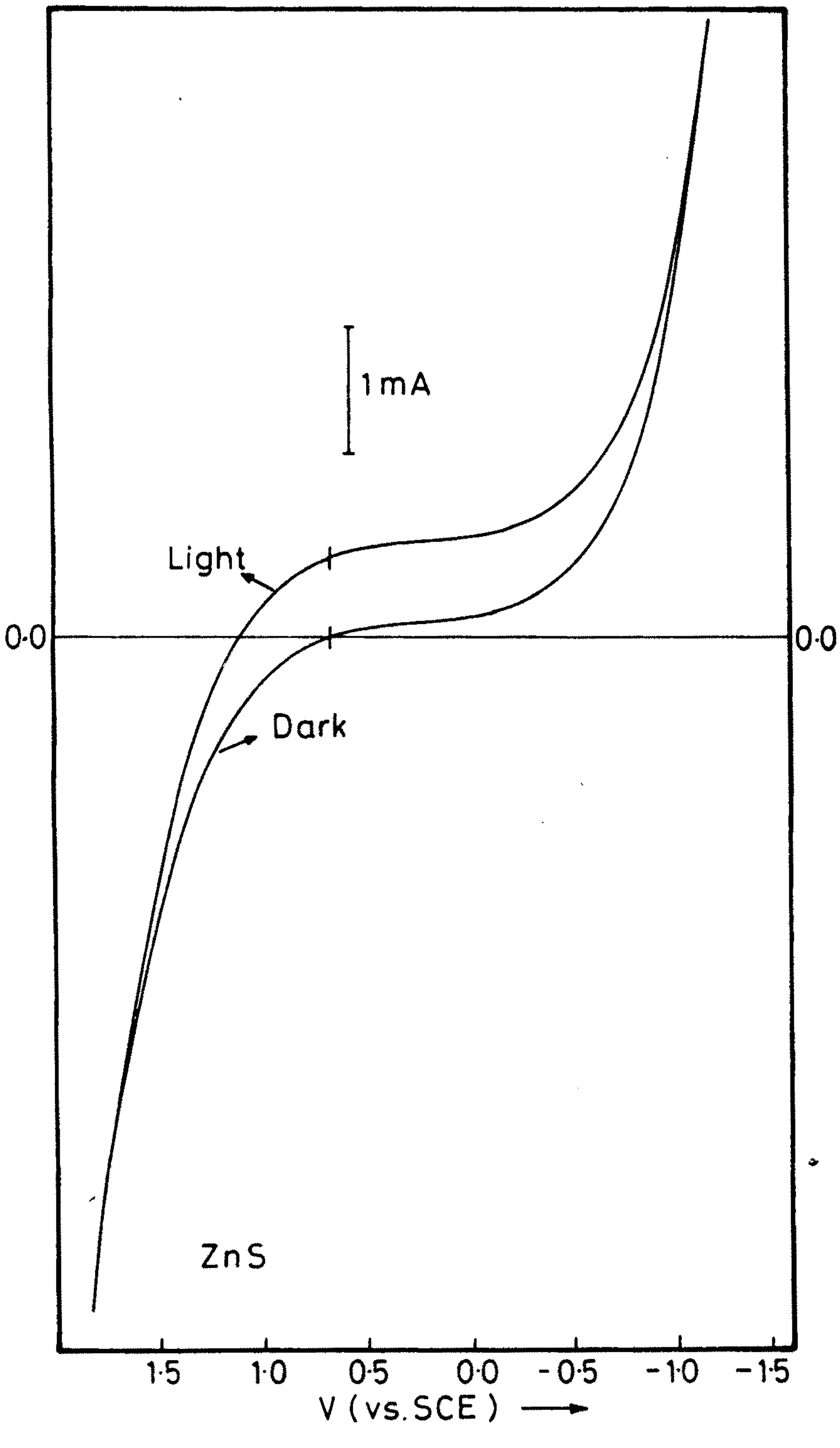

Fig. 5·2 (b) Current-voltage characteristics in dark and under illumination for ZnS film

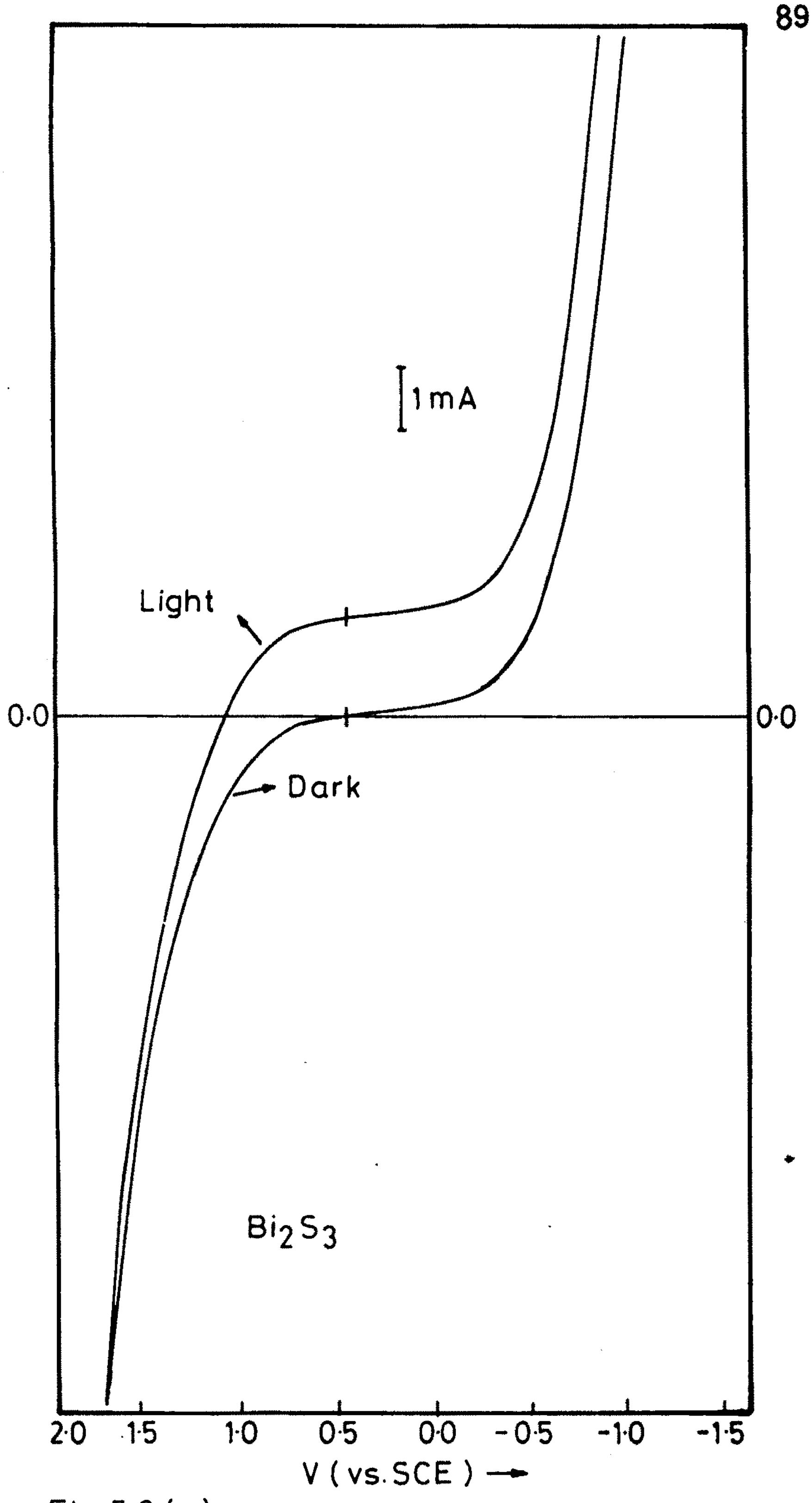

Fig. 5·2 (c) Current-voltage characteristics in dark and under illumination for Bi_2S_3 film

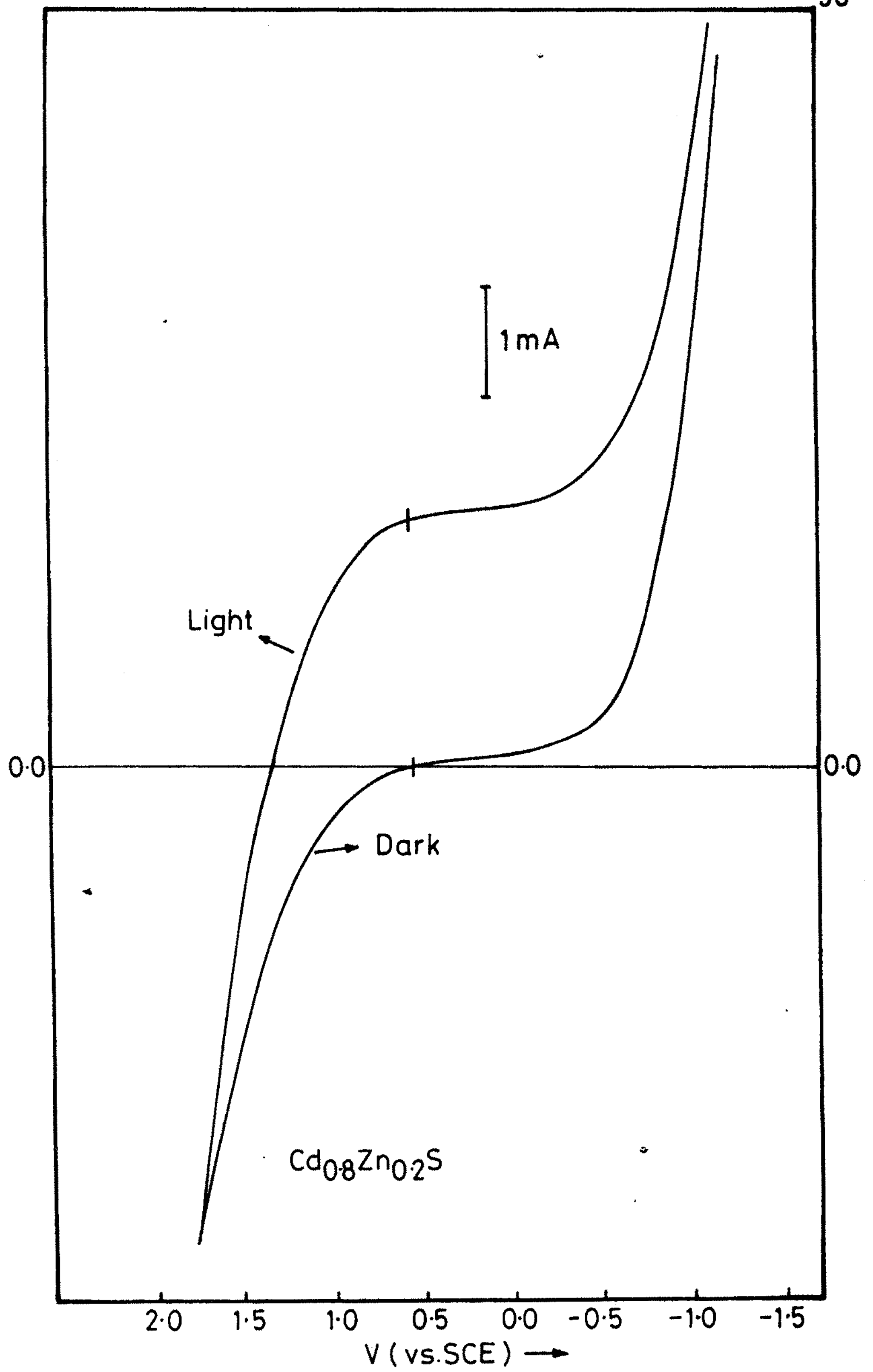

Fig. 5·2 (d) Current-voltage characteristics in dark and under illumination for $Cd_{0.8}Zn_{0.2}S$ film.

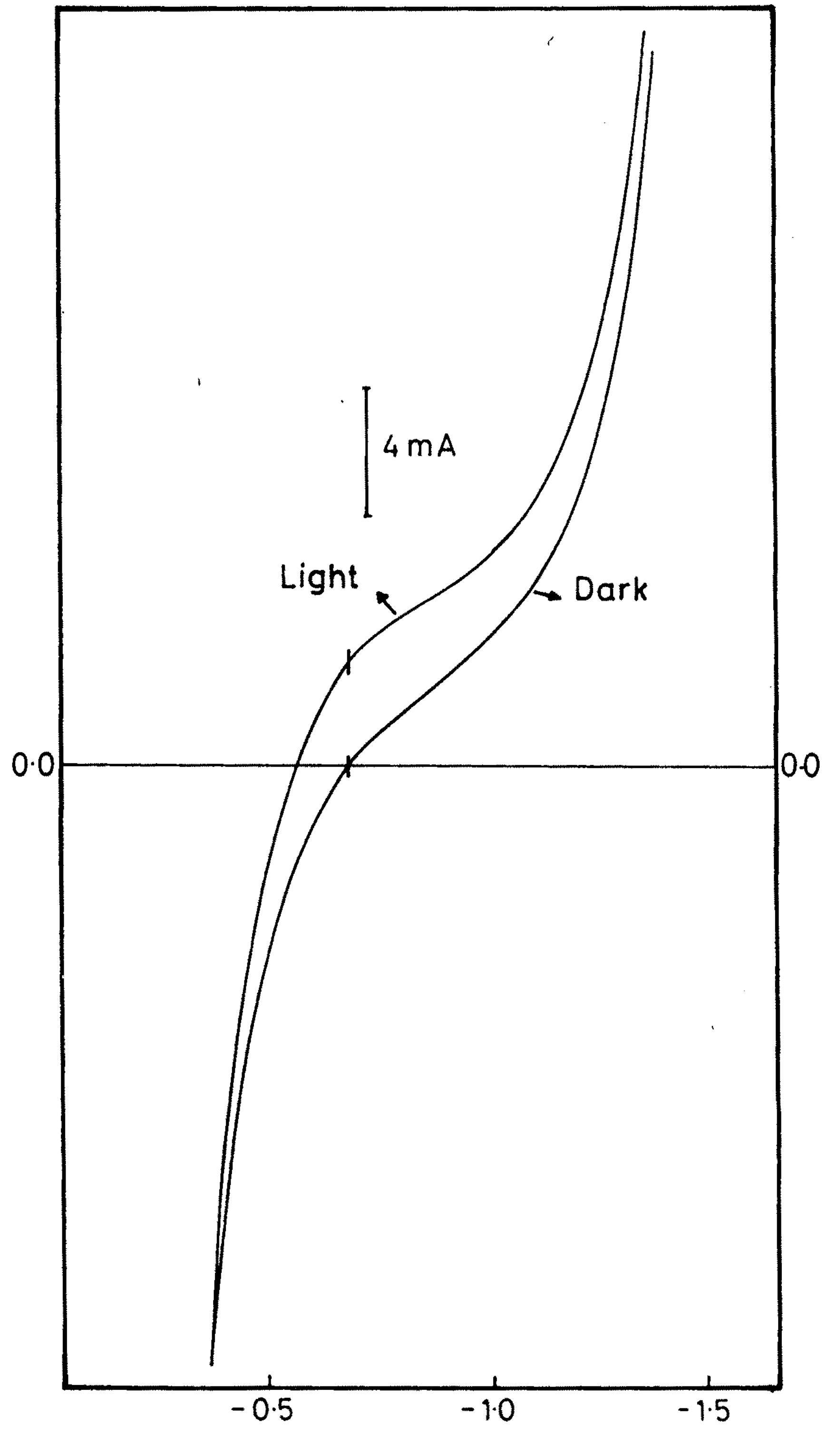

Fig. 5·2 (e) Current-voltage characteristics in dark and under illumination for Cd-Bi-S film.

information which is useful in identifying the recombinatioin centres and consequently in diagnosing the problems that lead to the efficiency losses (8,9).

Fig. 5.3 shows the spectral response of the ECPV cell formed with Cd-Zn-S as photoanode. The variation of short circuit current (I_{sc}) with wavelength (λ) shows a peak at 460 nm which represents the band gap energy equal to 2.7 eV, whereas (E_g = 2.6 eV) was obtained by optical absorption method.

Lower photocurrent on the shorter wave length side may be due to the absorption of light in the electrolyte and large amount of surface recombination of the photogenerated minority carriers; similarly lower photocurrent at the larger wavelength side in attributed to the lower absorption of light at the photoanode used.

The spectral response of the ECPV cell formed with photoanode Cd-Bi-S film was studied by variation of short circuit current (I_{sc}) with wave length (λ). The fig. 5.4 represents the relative spectral response with a peak at 540 nm. (E_g = 2.3 eV) while it is found at cut off at 650 nm. (E_g = 1.9 eV) by optical absorption method was reported (10).

Such shifting of peaks towards high energy side for ECPV cell formed with photoanode CdS was reported (11). The lower photocurrent on shorter wavelength side may be due to the absorption of light in electrolyte and large amount of surface recombination of photogenerated minority carriers. Similarly, lower photocurrent at the longer wavelength side is attributed to the lower absorption of light at the photoanode used.

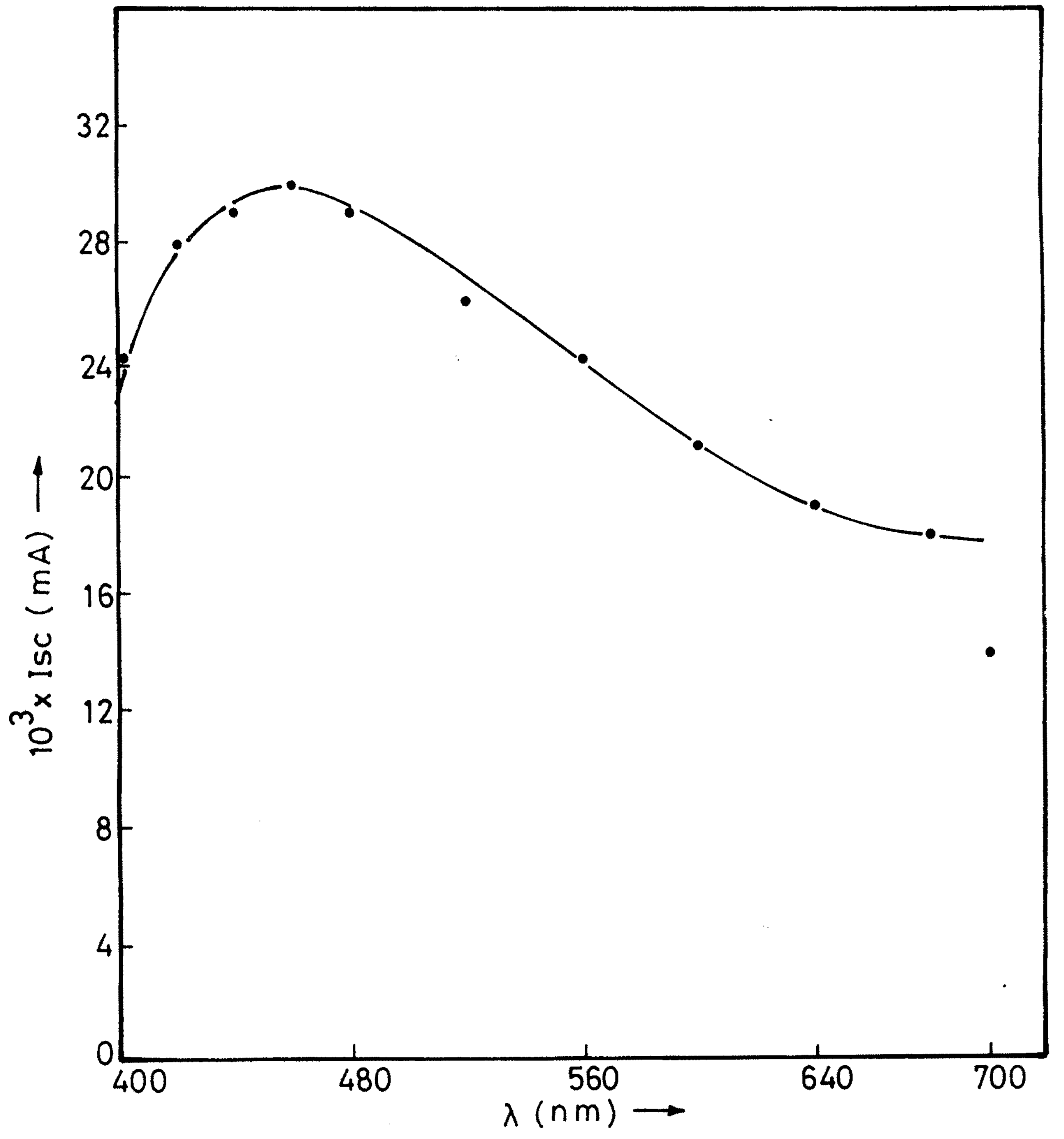

Fig. 5·3 Variation of I_{sc} with wavelength (λ) for ECPV cell formed with $Cd_{0.8}Zn_{0.2}S$ film as a photoelectrode

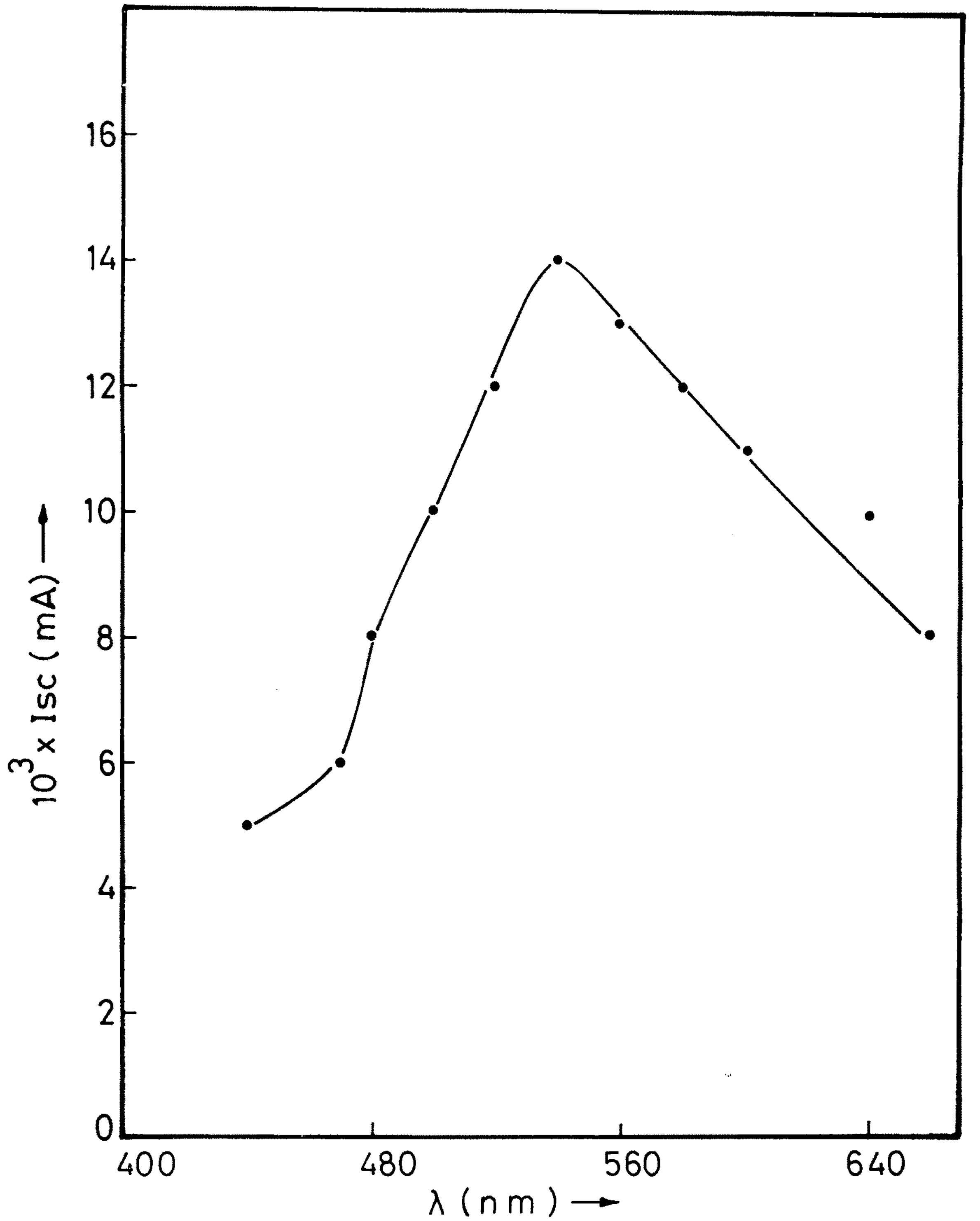

Fig. 5·4 Variation of I_{sc} with wavelength (λ) for ECPV cell formed with Cd-Bi-S film as a photoelectrode.

5.3.4 Photo Response :

The variations of short circuit current (I_{sc}) and open circuit voltage (V_{oc}) with light intensity is shown in fig. 5.5 (a-e) with photo-anode CdS, ZnS, Bi_2S_3, Cd-Zn-S and Cd-Bi-S films. In photoresponse study, open circuit voltage (V_{oc}) varies exponentially whereas short circuit current (I_{sc}) varies linearly with light intensity. The open circuit voltage (V_{oc}) follows the relation (12)

$$V_{oc} = \frac{nKT}{q} \text{ Log } \frac{CF_L}{I_o} \qquad \ldots (5.3)$$

where C is a constant and other parameters have their usual meanings. The short circuit current shows a linear variation with light intensity is given by the relation

$$I_{sc} = CF_L \qquad \ldots (5.4)$$

This is in good agreement with theory. SCE potential for electrolyte polysulfide was 0.530 volts. Table 5.1 shows the ECPV cell parameters for CdS, ZnS, Bi_2S_3, Cd-Zn-S and Cd-Bi-S films.

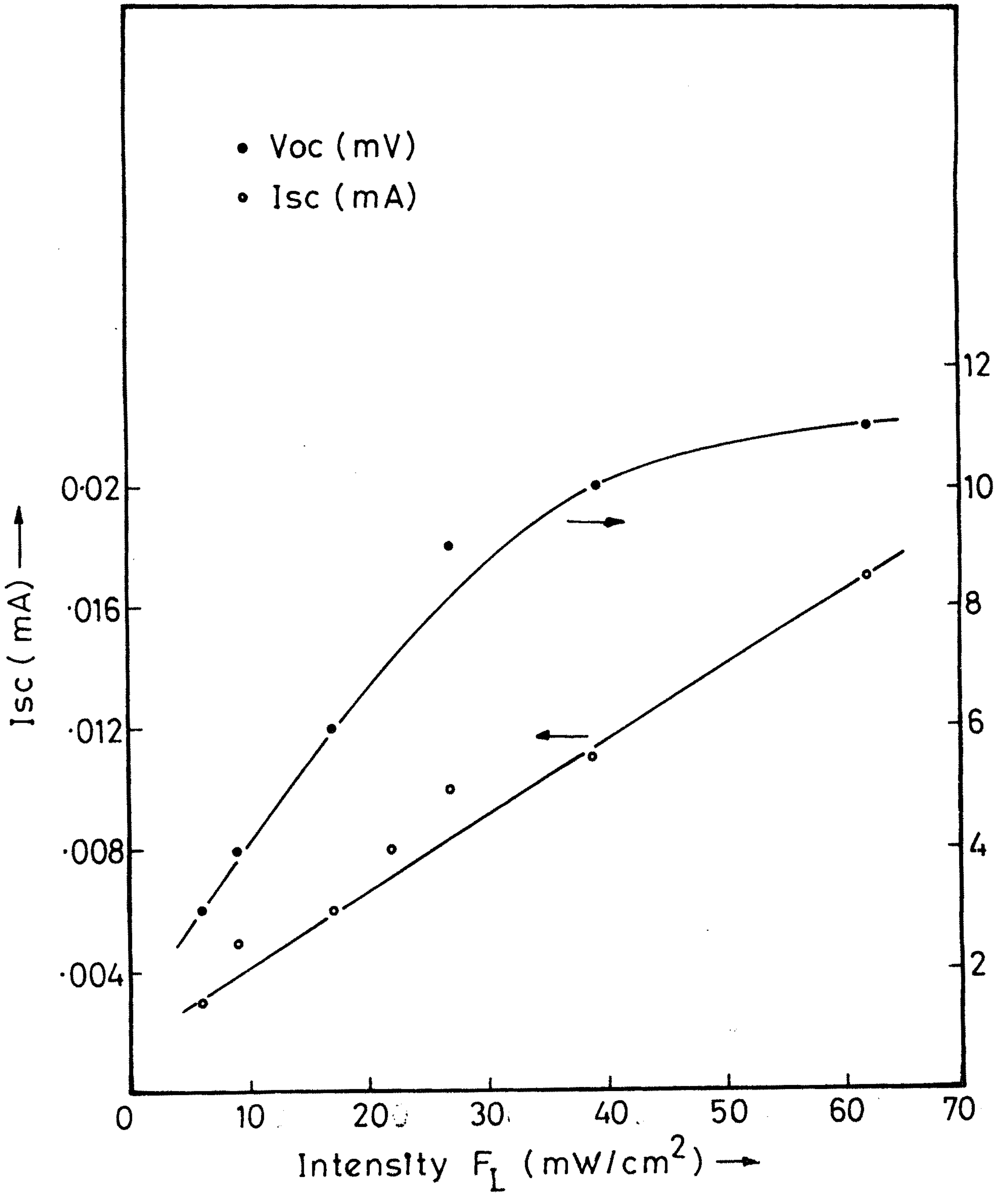

Fig. 5·5 (a) Photoresponse of the ECPV cell formed with CdS.

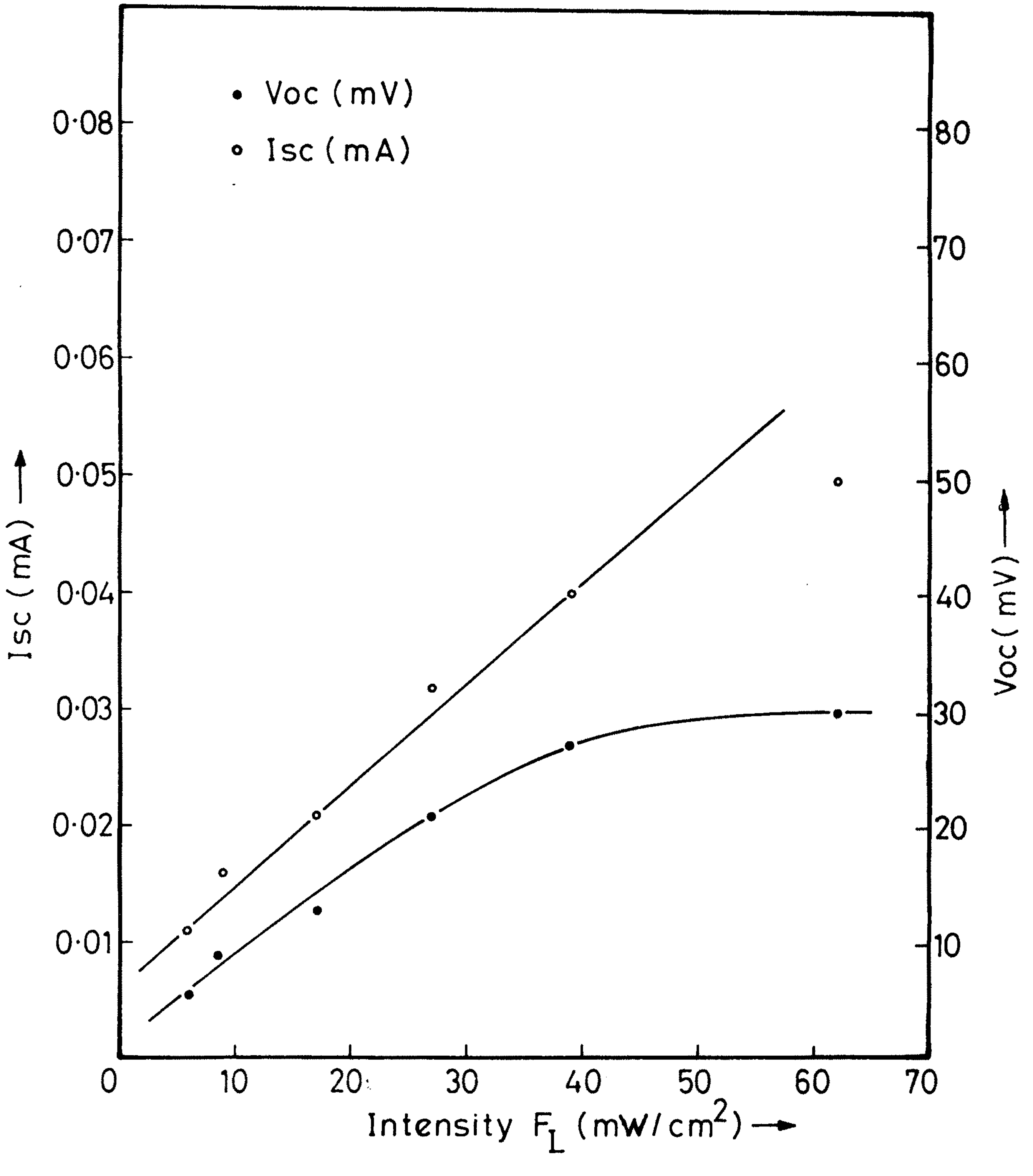

Fig.5·5(b) **Photoresponse of the ECPV cell formed with ZnS.**

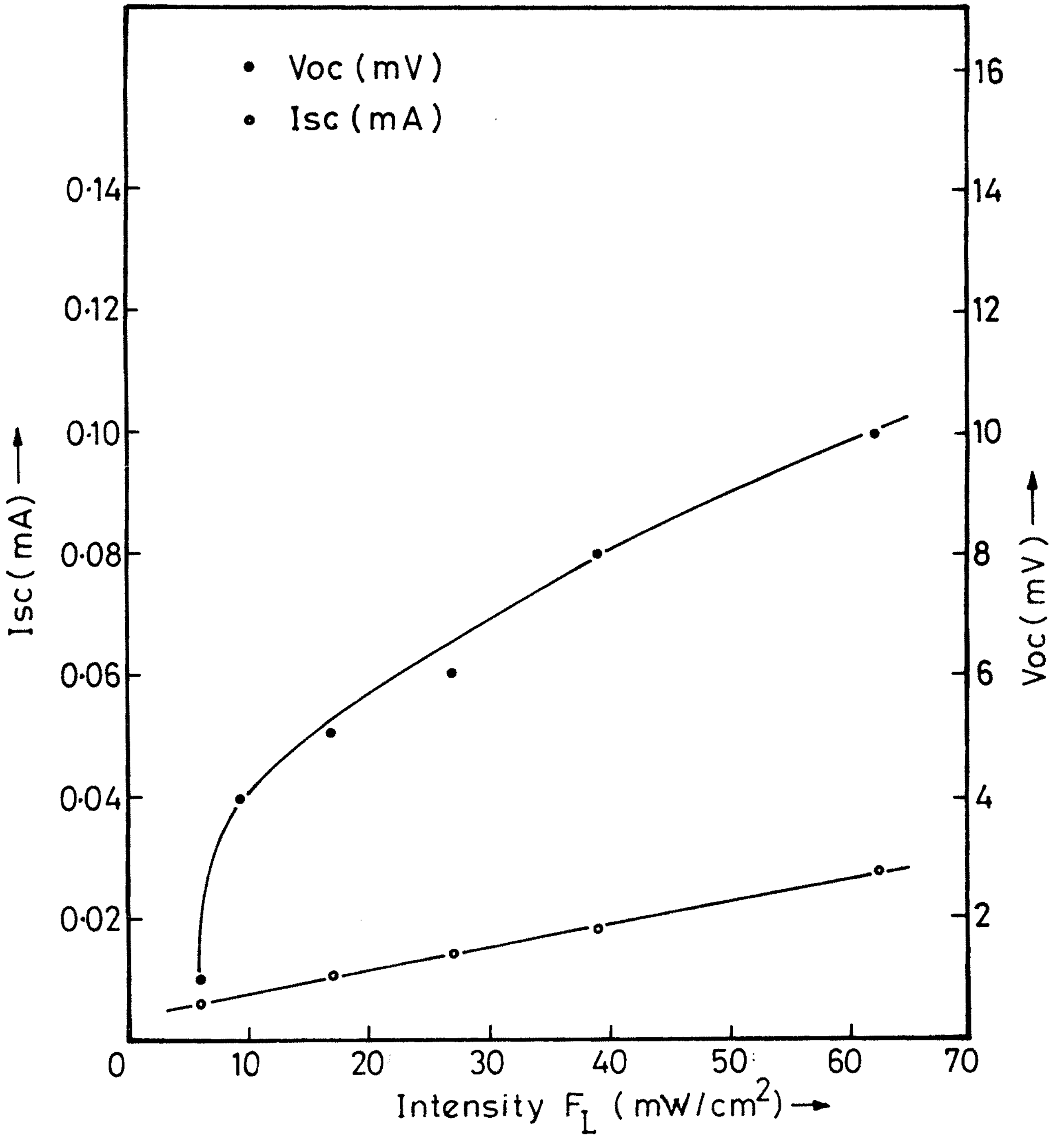

Fig. 5·5 (c) Photoresponse of the ECPV cell formed with Bi_2S_3.

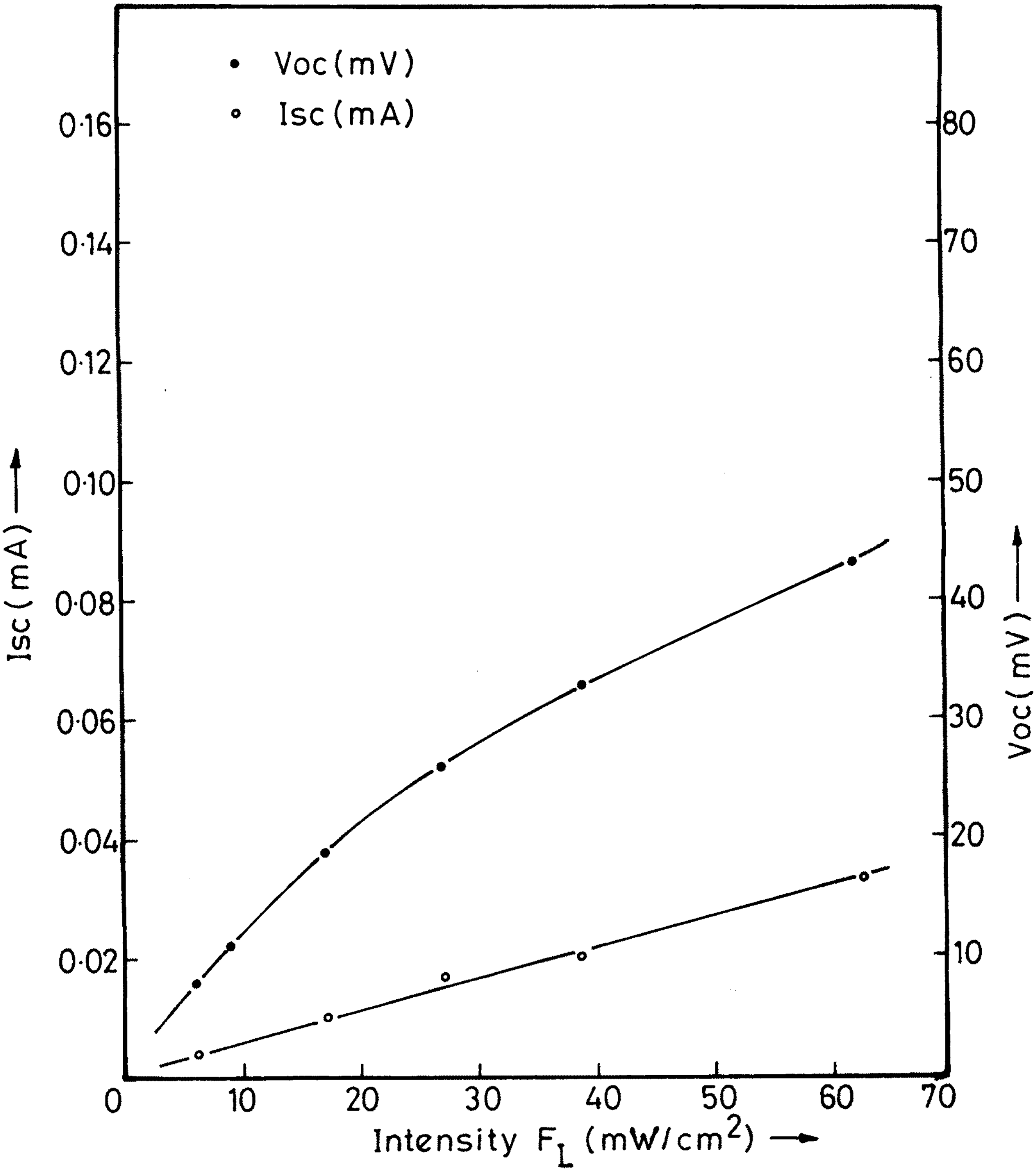

Fig. 5·5 (d) Photoresponse of the ECPV cell formed with $Cd_{0.8}Zn_{0.2}S$.

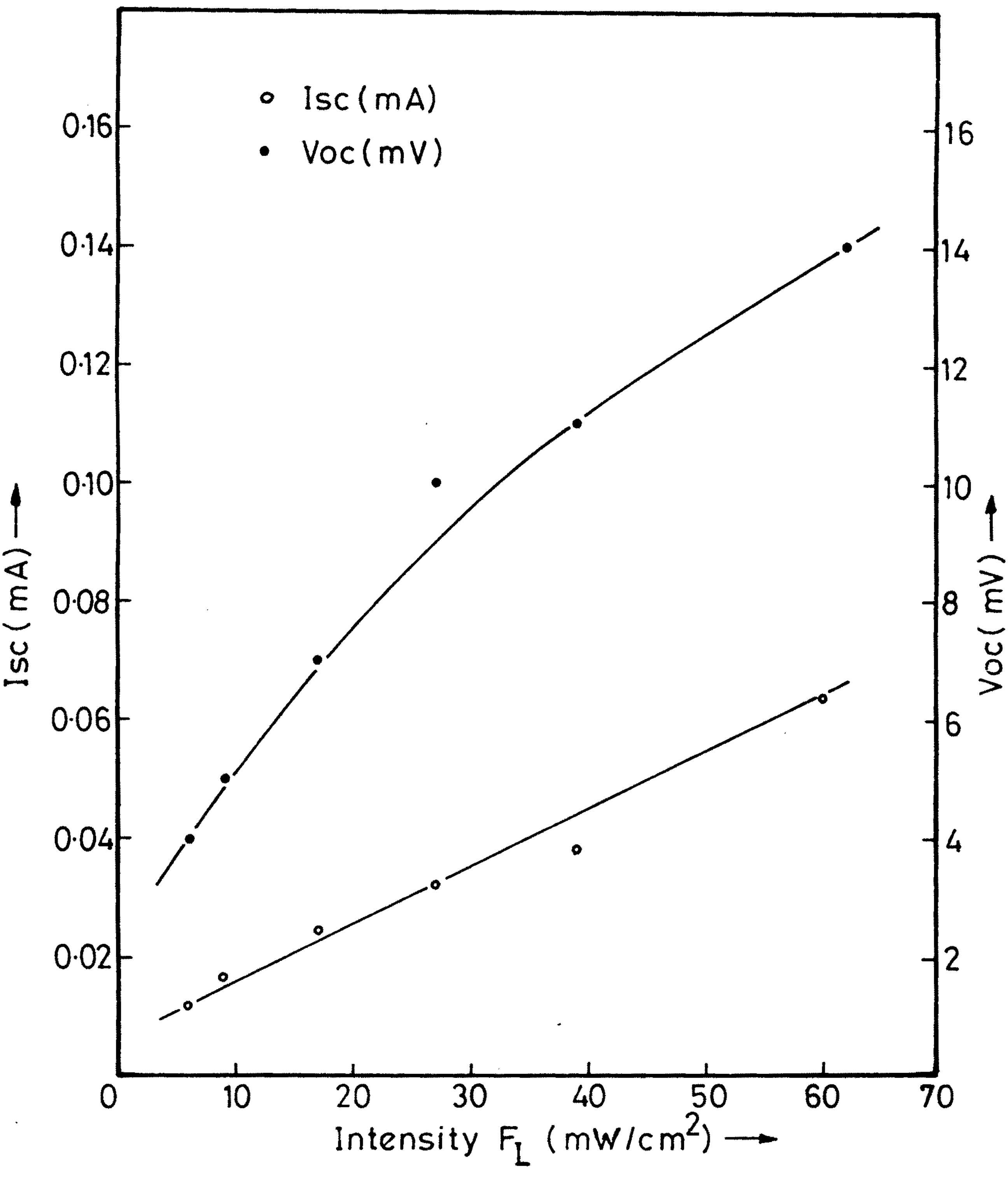

Fig. 5·5 (e) Photoresponse of the ECPV Cell formed with Cd-Bi-S.

TABLE : 5.1

ECPV Cell with Semiconductor Photoanode	Band gap (eV)	I_{sc} (mA)/cm^2	V_{oc} (Volts)	I_m (mA)/cm^2	V_m (Volts)	R_sx10^3 (ohms)	R_{sh}x10^3 (ohms)	Fill Factor FF%	Efficiency of cell n %
CdS	2.4	1.35	0.050	1.00	0.033	28	2266	49.2	0.033
ZnS	3.125	0.882	0.290	0.529	0.133	403	3051	27.5	0.0703
Bi_2S_3	1.8	1.555	0.112	1.333	0.085	160	1126	65.0	0.113
$Cd_{0.8}$-$Zn_{0.2}$-S	2.6	2.470	0.256	2.117	0.114	181	4273	38.10	0.241
$Cd_{0.4}$-$Bi_{0.6}$-S	1.9	3.764	0.109	1.882	0.046	24.4	304	20.92	0.086

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