EFFECTS OF CdCl2 ON THE GROWTH OF CdTe ON CdS FILMS FOR SOLAR CELLS BY ISOTHERMAL CLOSE-SPACED VAPOR TRANSPORT

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ABSTRACT

CdS/CdTe solar cells were made by depositing CdTe films by an isothermal close-spaced vapor transport method on sintered CdS/glass substrates. The influence of amounts of CdCl2 ranging from 0 wt% to 8 wt% in the CdTe source on the solar cells performance was studied. Increasing the CdCl2 content enhances the CdTe grainsize but degrades the spectral response and increases the reverse saturation current. An optimal CdCl2 concentration of 1 wt% was found for a growth temperature of 620 C.

1. INTRODUCTION

CdS(n)/CdTe(p) thin film solar cells with an efficiency higher than 10% have been prepared by several fabrication methods. These methods include close-spaced vapor transport [1] and sintering [2]. The last one, usually prepared by screen printing, has been specially attractive owing to the simplicity of the equipment and the small material waste. This method implies coating the substrate with a slurry prepared with the semiconductor powder, an adequate binder and a sintering aid.

The Matsushita group has reported the commercial production of CdS/CdTe thin film solar cells made with this method [3]. Roh and Im recently reported an ample investigation about the influence of CdCl2 as a sintering aid for the deposition of CdTe on CdS [4]. They concluded that for less than 2 wt% of CdCl2 the material developed abnormal grain growth and large porosity, and that the presence of a large amount, greater than 5 wt%, of CdCl2 enhances the sintering significantly via a liquid phase mechanism.

Nakayama et al. [5] have studied the junction cross-sections of the CdS/CdTe sintered cells. They found that the CdS film is very dense whereas the CdTe film is dense only near the heterojunction.

We reported preliminary results that indicate that growing of CdTe films on CdS substrates could occur through a vapor phase mechanism during the sintering stage of CdS/CdTe solar cells [6].

In the present work we report results related with the influence on the solar cells performance of the CdCl2 content in the source material, for CdTe deposition by the isothermal close-spaced vapor transport (ICSVT) method [7].

2. EXPERIMENTAL PROCEDURE

The CdS material used in our work was obtained by precipitation with H2S in a CdSO4 solution. This solution was prepared by the action of H2SO4 on 99.999% pure cadmiun metal using platinum wire as a catalyst. The precipitate was washed, dried, calcined at 700C for two hours in nitrogen and crushed in an agate mortar until a powder with an average particle size of 0.5 μm was achieved. This powder was used to make a slurry by mixing with 10 wt% of CdCl2 and an adequate amount of ethylene glycol. A soda glass substrate was coated with this slurry using a brush and an adhesive tape mask. After drying in air at 100C the coated substrate was placed in a quartz container with a 1 mm diameter hole and the CdS was sintered at 640C for one hour in a nitrogen atmosphere.

In order to prepare the cells the CdTe layers were deposited on the CdS sintered layer using the following procedure:

Soda glass substrates were painted with slurries made by grinding together into an agata mortar cadmiun powder (Johnson-Matthey -100+200 mesh, 99.999% pure), tellurium (99.999% pure), various amounts of CdCl2 (99.8% pure), and an adequate amount of ethylene glycol.

After drying in air at 100C, these (Cd+Te) films were used as the sources and the CdS sintered layers as the substrates in the ICSVT method. The deposition was done at 620C for one hour in nitrogen atmosphere.

Contacts to CdS were made with indium solder and to CdTe with graphite paint mixed with 100 ppm of CuCl. The contacts were annealed at 350C for 10 minutes in nitrogen atmosphere.

The cells response was measured in the dark, under an illumination of 10 mW/cm2 from a halogen lamp with an IR-absorbing

filter, and under direct sunlight (76 mW/cm2, 41 S latitude, 700 meters above sea level, June, clear sky at noon). The spectral response was measured with a Bausch&Lomb monochromator and a halogen lamp. Data acquisition was performed with an HP-86B microcomputer and Keithley 195A multimeters.

Grainsize was measured with a Reichert metallographic microscope by the line intersection method.

3. RESULTS AND DISCUSSION

The CdTe film deposited from a source without CdCl2 has the smallest grainsize, it is highly porous, and the CdS substrate keeps its light yellow color. With increasing contents of CdCl2 in the source, the CdTe films have larger grainsize and the porosity almost disappears, but the CdS turns orange colored. The figure 1 shows the dependence of CdTe grainsize with CdCl2 source content.

The color variation of the CdS films appears evident in the dependence of the spectral response of the cells. Figure 2 shows the normalized quantum efficiency versus light wavelength. The short wavelength edge shifts from the CdS intrinsic absorption edge (515 nm), for the CdTe film deposited from a source without CdCl2, to 620 nm for an 8wt% of CdCl2 content in the source.

Analogous behaviour was found by Im et al [4] when they changed the CdCl2 content in their screen printed CdTe layers; they assumed that the short wavelength response degradation is originated by a deeper junction.

Additionally, we measured the absorption spectrum for the CdS layer from the cell made with 8 wt% of CdCl2 after etching away the CdTe film with a solution of three parts of Cr2K2O7 saturated water solution and one part of SO4H2, diluted 1:10 in distilled water. Figure 3 shows how the content of CdCl2 in the CdTe source

shifts the absorption edge of the CdS window toward longer wavelengths. The edge is around 650 nm which is about the value obtained for the short wavelength edge of the spectral response of the same cell shown in figure 2.

The open circuit voltage and the short circuit current show a maximum for the cells made with sources containing 1wt% of CdCl2 under halogen lamp (figures 4a and 4b) and direct sunlight illumination (figures 5a and 5b). The two points for each source composition belong to two cells processed together.

The filling factor has a maximum for the cells made with sources containing 2wt% of CdCl2 (figure 4c). The highest efficiency is obtained for the 1wt% CdCl2 cell (figure 4d).

The reverse saturation current Isincreases more than one order of magnitude, as it is shown in figure 6a. A smaller barrier in the junction could be responsible for this behaviour.

The diode factor n, shown in figure 6b, shows a maximum for the 2wt% CdCl2 cell and decreases for higher CdCl2 content. The values between 1.4 and 1.8 are compatible with interface recombination currents as transport mechanism in the junction.

Figure 7 shows the voltage-current (V-I) characteristics of the 1wt% CdCl2 cell. The efficiency is 7.8% under halogen lamp light, for an active area of .12 cm2, and the open circuit voltage, short circuit current and filling factor are .648 V, 2.2 mA/cm2, and 54% respectively.

Dark forward V-I characteristics of the same cell is shown in figure 8. The forward characteristics could be expressed by the equation

$$I = Is * \exp(qV/nkT) \qquad \{1\}$$

The values of the diode quality factor n and reverse

saturation current Is were 1.68 and 2.1*10E-9 respectively for the cell in the dark.

The series resistance originates in the CdS sheet resistance, the CdTe resistance and the CdTe/graphite contact resistance. The measured CdS/In contact resistance is negligible.

According to cell geometry, the CdS contribution to the distributed series resistance is given by [8]

$$Rs(CdS) = (1/12)(b/a)R\ (CdS) \qquad \{2\}$$

where a is the contact length, b is the separation between contacts, and R is the CdS sheet resistance.

The CdS film for the 1wt% CdCl2 cell has R = 1500 ohms, a = .3 cm, and b = .4 cm. Then there is 167 ohms of series resistance originated in the CdS distributed resistance. There are .1 cm strips of free CdS film between the active area and the indium contact strips that add approximately 188 ohms to the series resistance, giving nearly 355 ohms of series resistance originated in the CdS film.

The total series resistance of the cell, measured from the deviation of the V-I characteristics from the exponential behaviour [9], is 1850 ohms, then there is nearly 1500 ohms of series resistance originated in the CdTe film and in the CdTe/graphite contact.

The influence of the shunt resistance in the cell behaviour is negligible.

4. CONCLUSIONS

The influence of CdCl2 added in the Cd plus Te source, for growing CdTe films by the ICSVT method on CdS films was studied.

Increasing the CdCl2 content enhances CdTe grainsize, but

degrades the short wavelength spectral response and increases the reverse saturation current. There would be two competing effects

degrades the short wavelength spectral response and increases the reverse saturation current. There would be two competing effects related to the CdCl2 increment: larger grainsize increases the efficiency by diminishing grain boundary recombination, but photon loss in the window and higher saturation currents decrease the efficiency. The optimun value of CdCl2 addition would be around 1 wt%.

The series resistance originated principally in the CdTe film or in the CdTe/graphite contact greatly limits efficiency for high intensity illumination.

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FIGURE CAPTIONS

Figure 1. Grainsize of the CdTe films as a function of amounts of CdCl2 added to the (Cd+Te) sources.

Figure 2. Spectral quantum efficiency for solar cells made with CdTe sources containing various amounts of CdCl2. a) 0 wt% b) 0.5 wt% c) 1 wt% d) 2 wt% e) 4 wt% f) 8 wt%.

Figure 3. Absorption spectrum of the CdS layer after etching away the CdTe film from a solar cell made with a (Cd+Te) source containing 8 wt% of CdCl2.

Figure 4. Cell parameters of the CdS/CdTe solar cells under an illumination of 10 mW/cm2 from a halogen lamp as a function of amounts of CdCl2 added to the (Cd+Te) source.

Figure 5. Cell parameters of the CdS/CdTe solar cells under direct sunlight illumination as a function of amounts of CdCl2 added to the (Cd+Te) source.

Figure 6. Reverse saturation current (a) and diode factor (b) of the CdS/CdTe solar cells in the dark as a function of amounts of CdCl2 added to the (Cd+Te) source.

Figure 7. I-V characteristic of the CdS/CdTe solar cell made with a (Cd+Te) source which contained 1 wt% of CdCl2 under an illumination of 10 mW/cm2 from a halogen lamp. Voc= 648 mV, Isc= 266 μA, FF= 54%, area= 0.12 cm2, efficiency= 7.8%.

Figure 8. Dark forward I-V characteristic of the CdS/CdTe solar cell made with a (Cd+Te) source which contained 1 wt% of CdCl2.

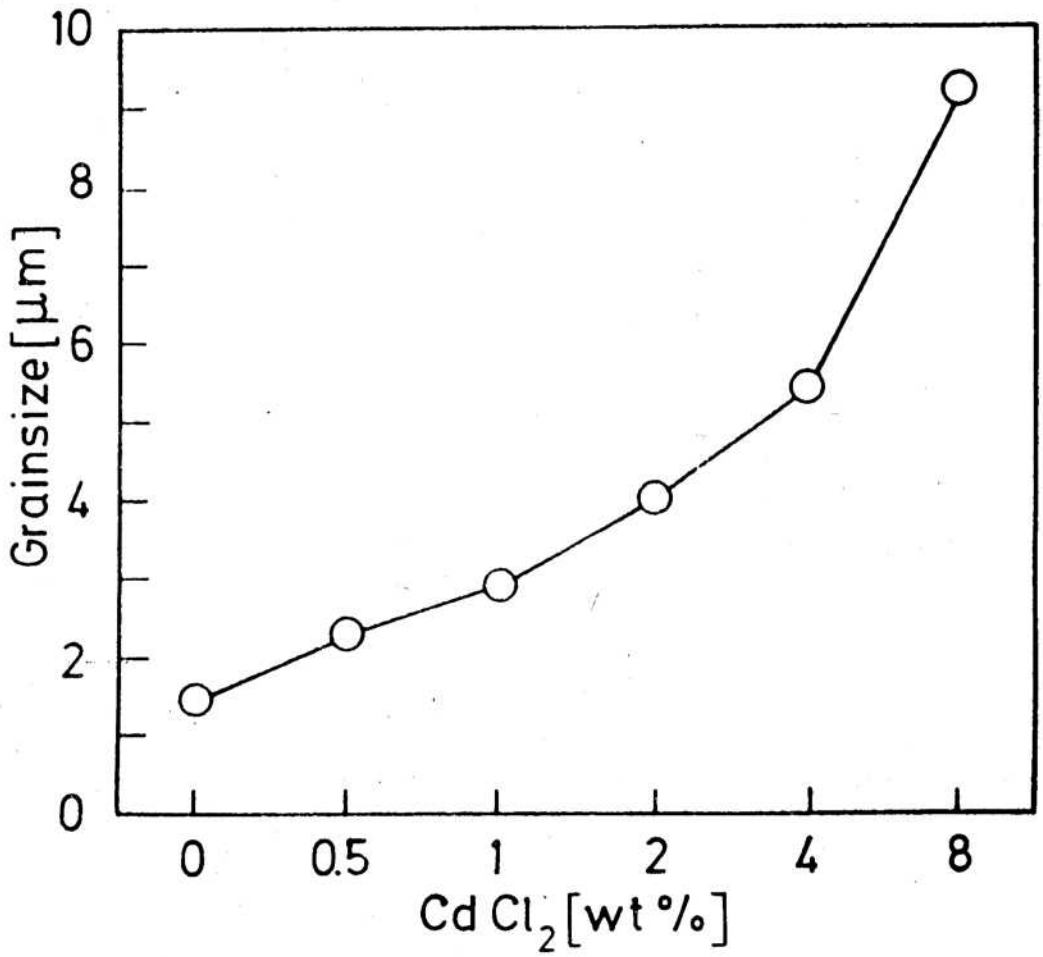

fig 1

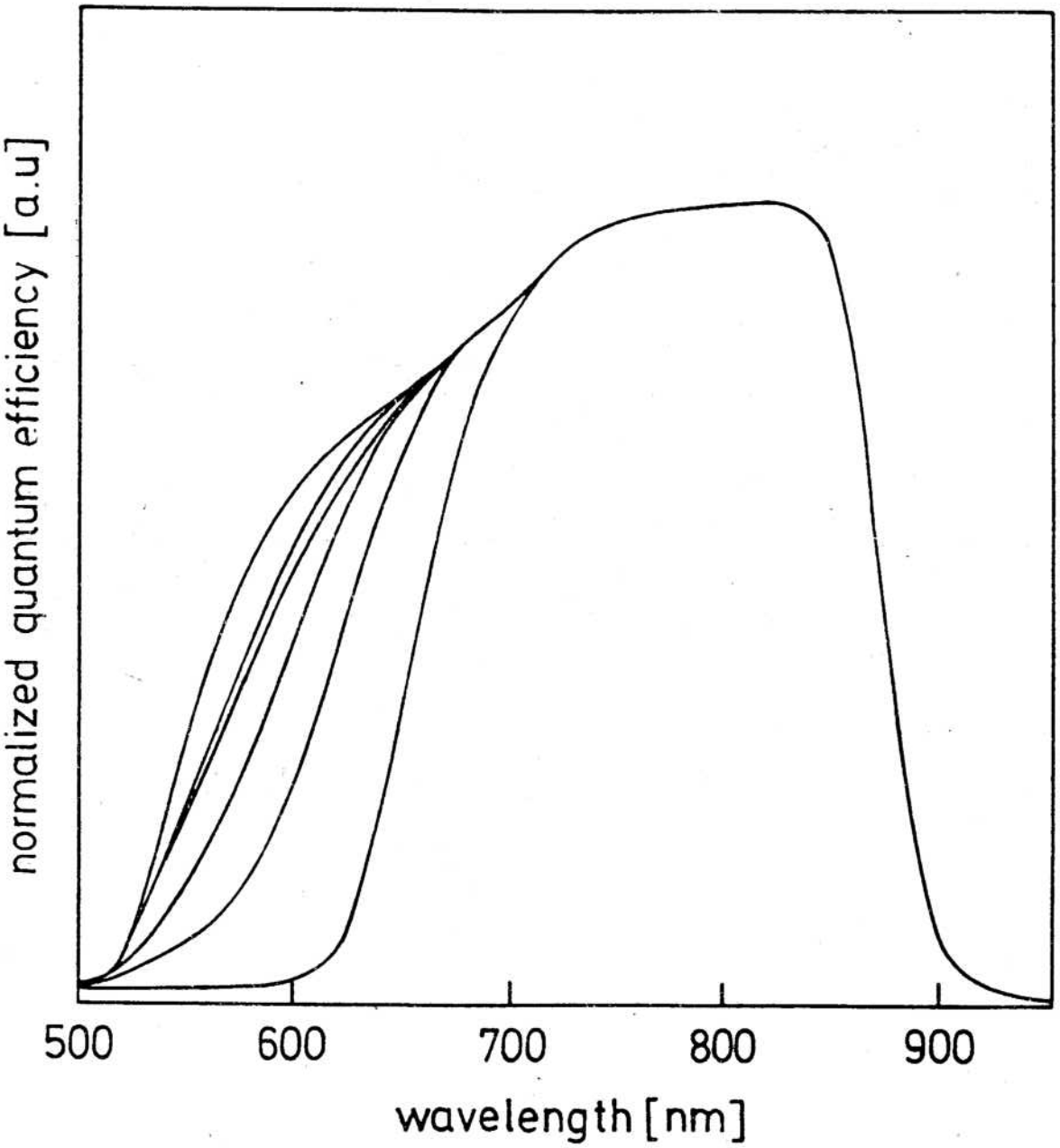
normalized quantum efficiency [a.u]
500
600
700
800
900
wavelength [nm]

fig 2

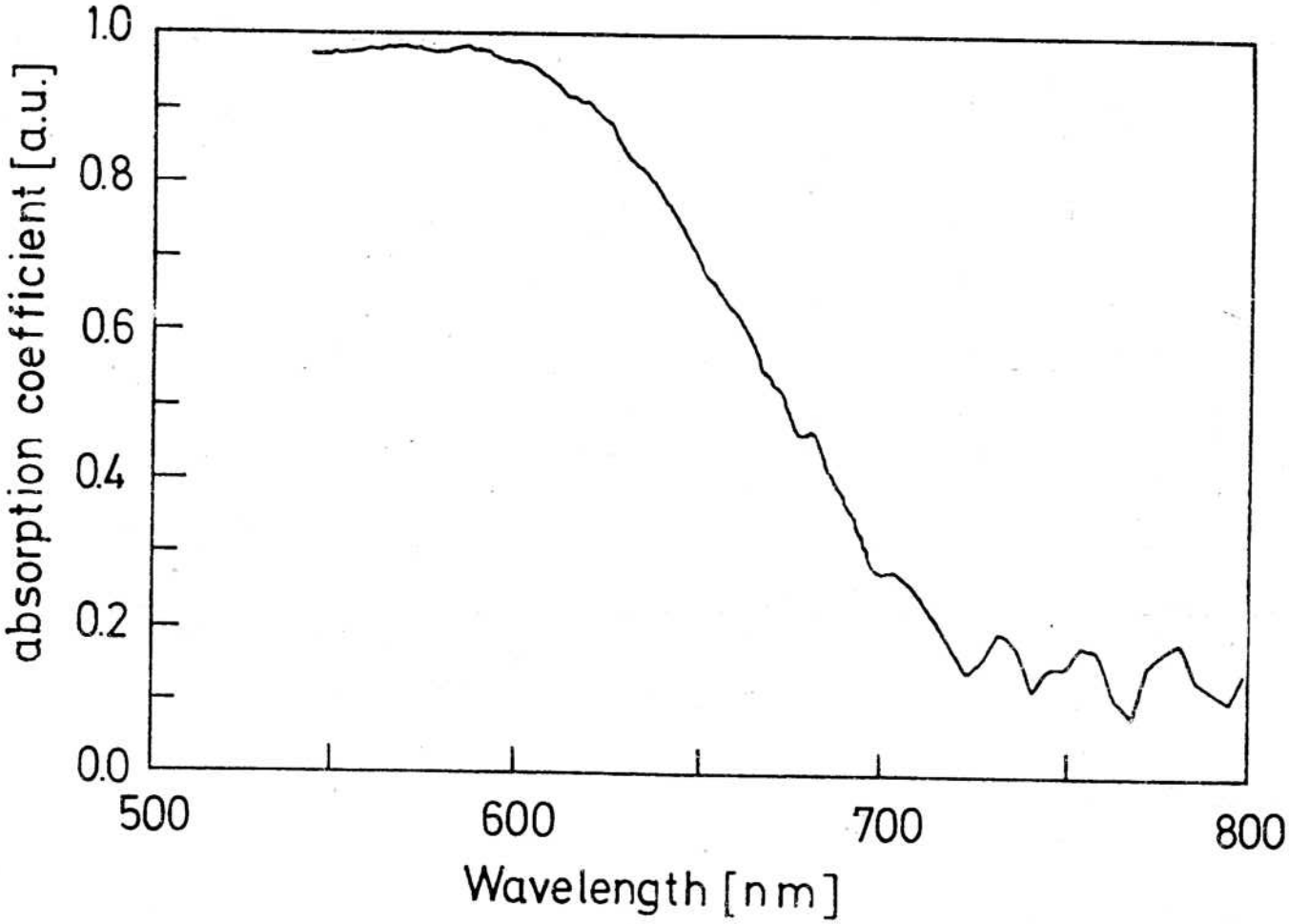
absorption coefficient [a.u.]
1.0
0.8
0.6
0.4
0.2
0.0
500
600
700
800
Wavelength [nm]

fig 3

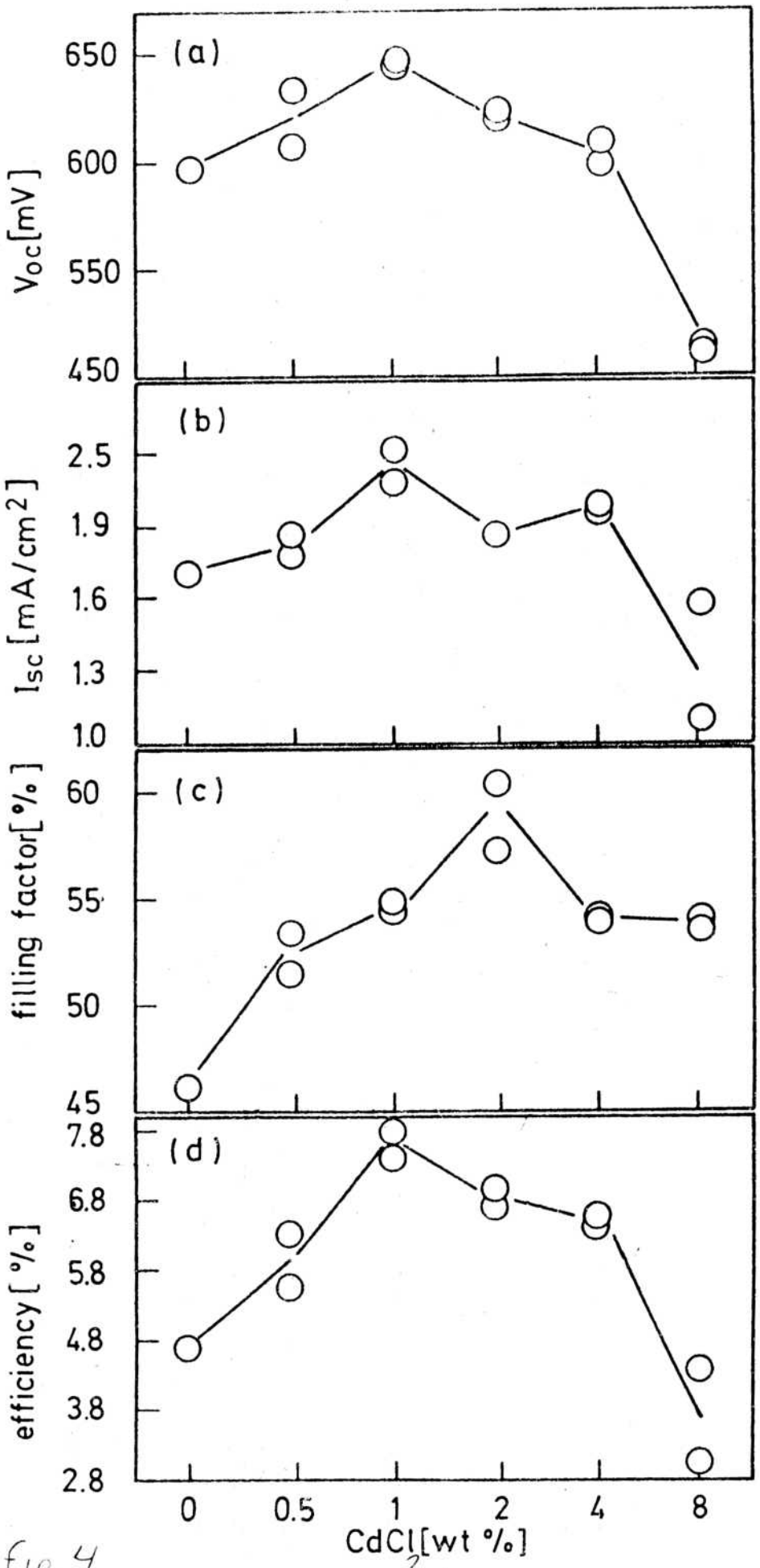
(a)
650
600
550
450
V_{oc}[mV]
(b)
2.5
1.9
1.6
1.3
1.0
I_{sc} [mA/cm^2]
(c)
60
55
50
45
filling factor[%]
(d)
7.8
6.8
5.8
4.8
3.8
2.8
efficiency [%]
0
0.5
1
2
4
8
$CdCl_2$[wt %]

Fig. 4

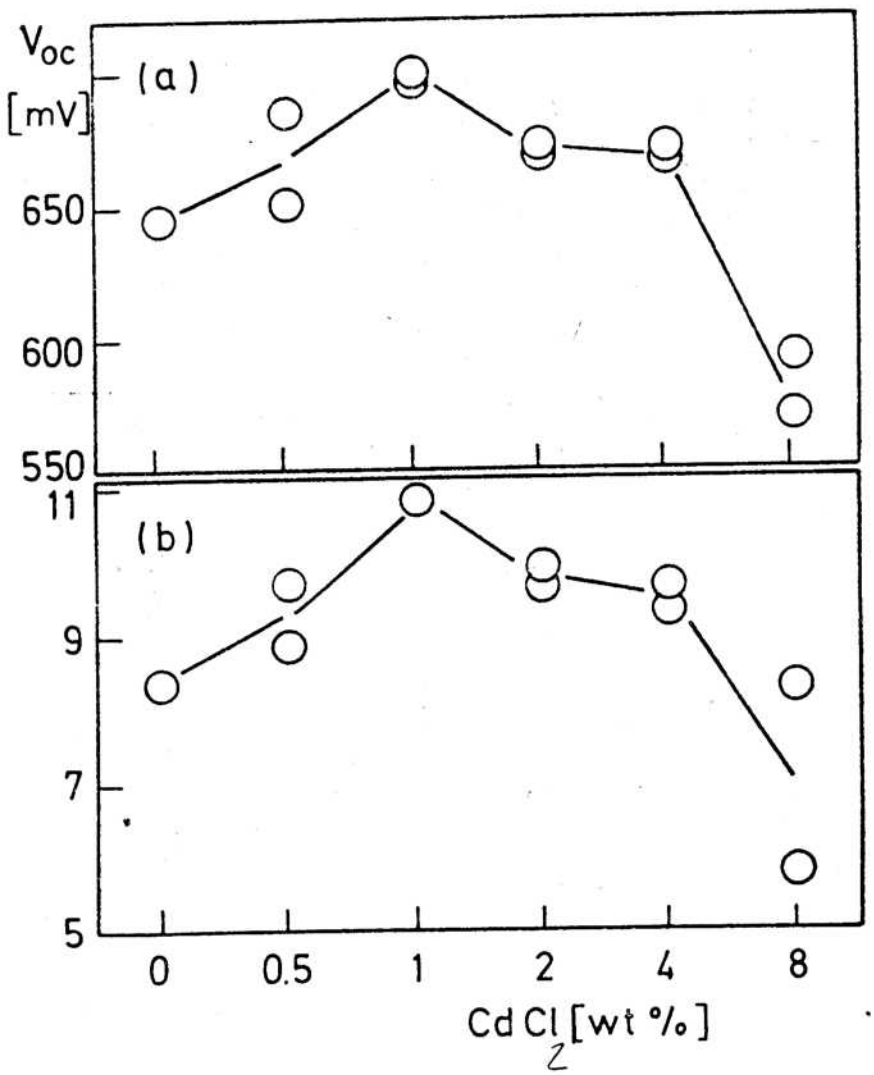

fig. 5

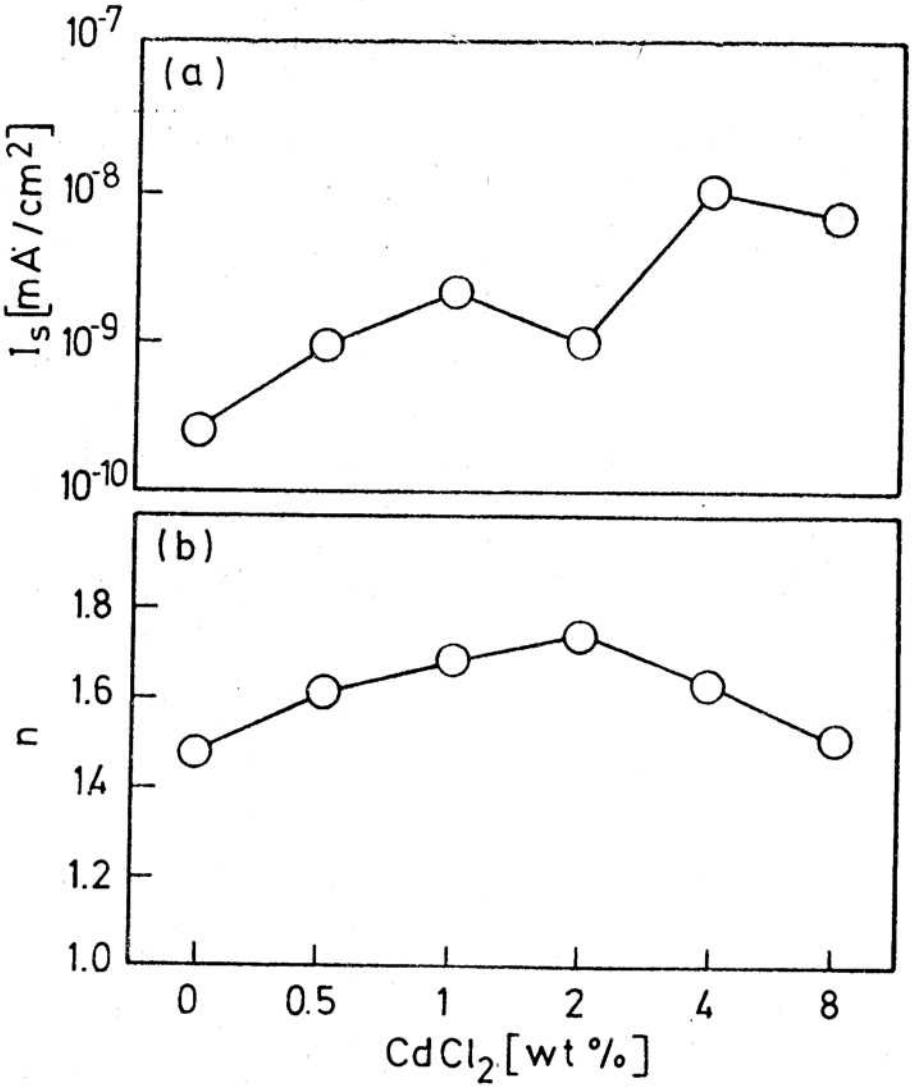

fig 6

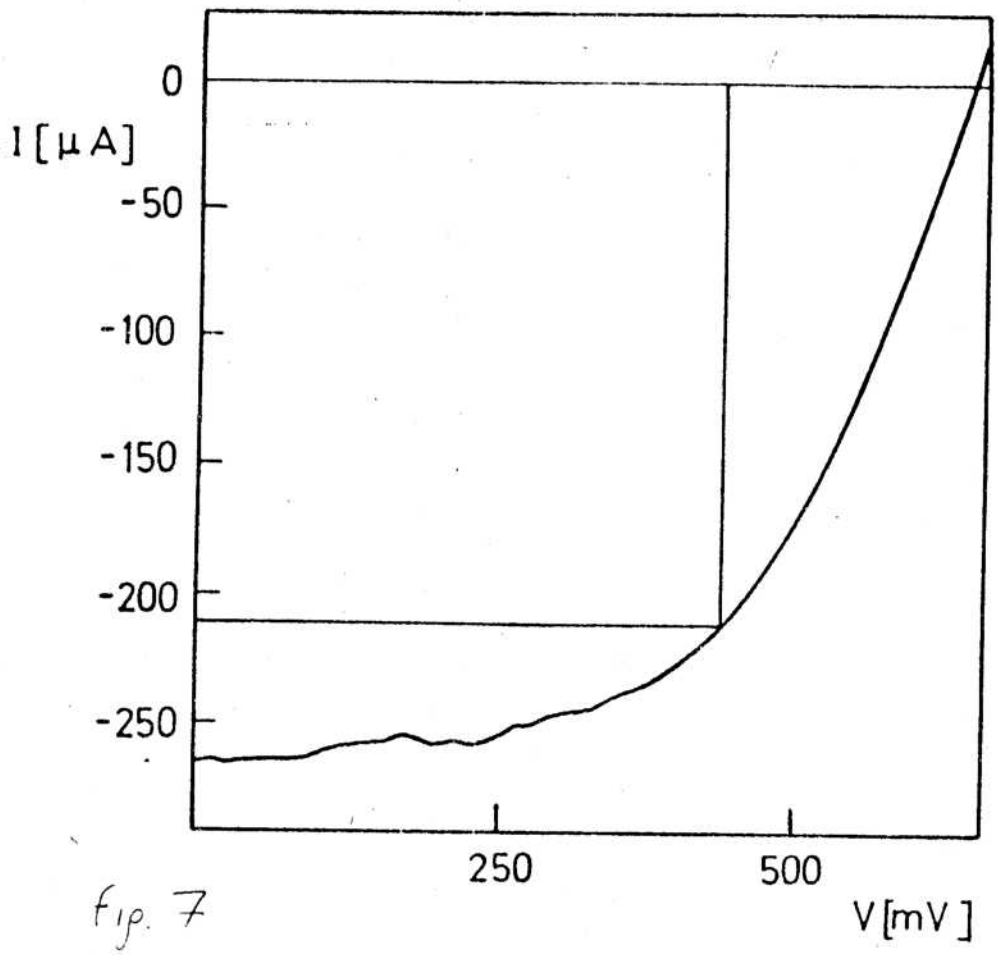

Fig. 7

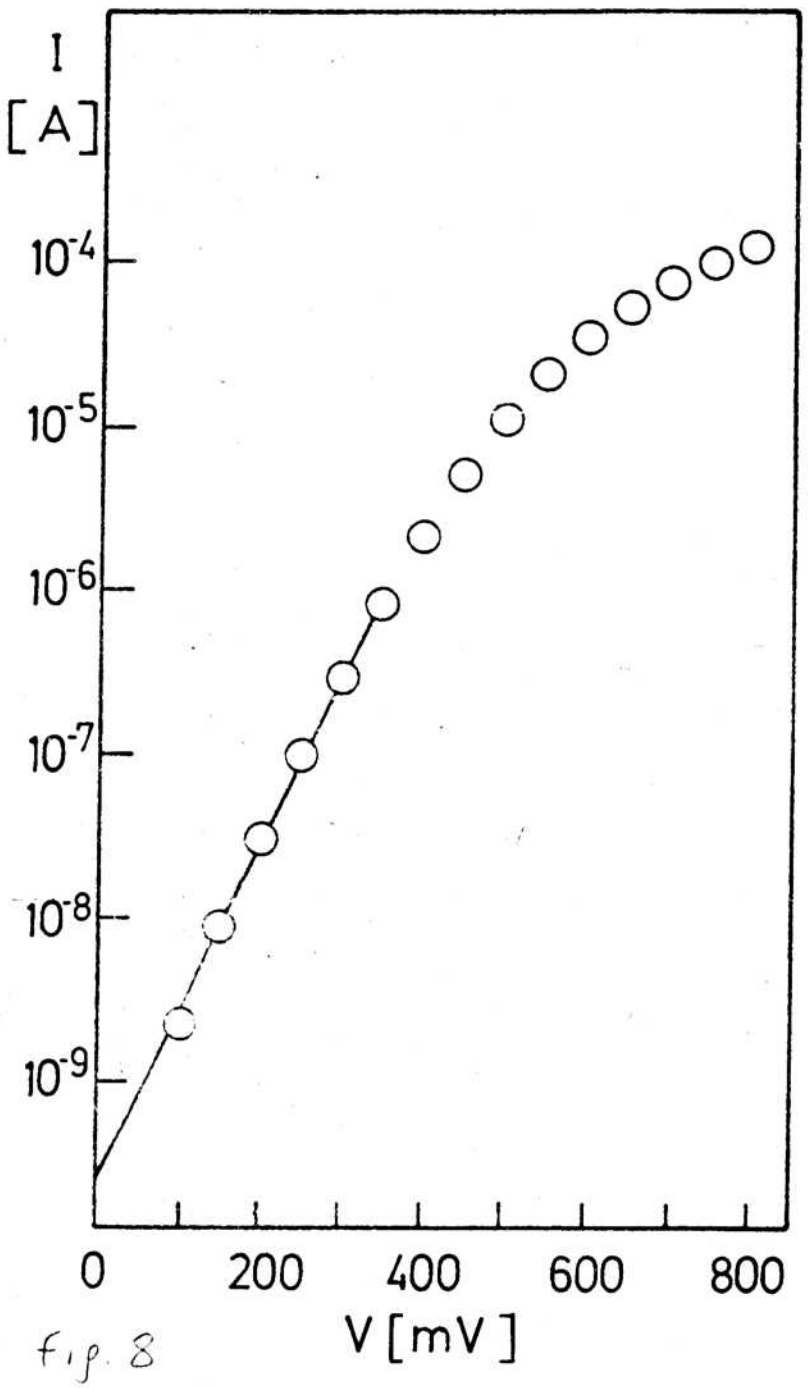

fig. 8