

## Copper diffusion and photovoltaic mechanisms at Cu–CdS contact

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**Abstract.** Schottky barriers have been formed by vacuum evaporation of Cu on to CdS thin films. The behaviour of these samples has been investigated as a function of time and annealing by standard electrical methods: current–voltage analysis, capacitance–voltage analysis and analysis of the spectral dependence of the photoemission current. The impurity profile deduced from the reverse differential capacitance shows evidence of copper diffusion occurring between 20 and 200 °C. An activation energy of 0.72 eV is found for the temperature dependence of the diffusion coefficient. The Cu–CdS interface has also been investigated by looking at the photovoltaic mechanisms in connection with the different heat treatments. Capacitance measurements performed under junction illumination have been used to obtain the true donor density after copper diffusion.

### 1. Introduction

Cu<sub>2</sub>S–CdS photocells are the result of twenty years of research all over the world (Besson *et al* 1975, Pfisterer *et al* 1976, Rothwarf *et al* 1978). Although technological improvements have been carried out (the achievement of a better stability of characteristics with respect to copper diffusion for instance) it can be said that the energy band model still remains relatively inaccurate. To avoid complexity, our studies are principally concerned with a simple structure: the Cu–CdS Schottky diode which had previously been studied together with Au–CdS. Whereas stable electrical characteristics have been observed over a range of six years for Au–CdS, this was not the case for Cu–CdS. Hence it is interesting to study the evolution and dispersion of the characteristics for this case. In this paper we report on a study of the barrier and photovoltage evolution with time at room temperature and with different annealings. The Cu–CdS interface is investigated by looking at the copper diffusion under different heat treatments and the related photovoltaic mechanisms.

### 2. Experimental methods

Our Cu–CdS structures have been obtained with thin CdS layers created by thermal evaporation (work in the SAT† laboratories); for comparison, some samples were obtained with polished slices of Eagle Picher polycrystals and single crystals grown from the vapour phase at the LCR Thomson CSF. All these substrates, having a resistivity in the

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10–100  $\Omega$  cm range, were treated with diluted hydrogen peroxide. The copper electrode (thickness 0.2  $\mu$ m, typical area 10 mm<sup>2</sup>) was then deposited by thermal evaporation techniques. During copper evaporation the substrate was kept at room temperature. From the electrical measurements performed on these samples, three barrier height values can be deduced:  $\phi_B$  (IV) from the current–voltage characteristic measured in darkness,  $\phi_B$  (CV) from the capacitance–voltage measurements,  $\phi_B$  (ph) from the photoemission current per incident photon of the electrons going from the metal to the semiconductor (Rhoderick 1978). The donor profile derived from the experimental  $C^{-2}$  ( $V$ ) curve is used to observe the copper diffusion in the CdS. Furthermore the open-circuit voltage  $V_{oc}$  was measured under white light illumination of 100 mW cm<sup>-2</sup> from a quartz iodine bulb.

### 3. Copper diffusion

If we consider the formation of a typical Cu–CdS sample at room temperature, we can see that the Cu–CdS contact is ohmic just after the copper is deposited. After two days the Schottky barrier or ‘reference contact’ is set up, with the same barrier height value being given by the three methods,  $\phi_B = 0.55 \pm 0.03$  eV, and with the  $n$  factor of the thermionic emission equation near 1; typically  $n = 1.12$ . The impurity profile in the semiconductor is obtained from the slope of  $C^{-2}$  ( $V$ ) where  $d(C^{-2})/dV = -2/q\epsilon_s N_D(W)$ . Here  $C = \epsilon_s/W$  is the capacitance per unit area,  $V$  the applied voltage in reverse bias and  $W$  the depletion layer width. The average value of the donor density  $N_D$  determined from figure 1 is calculated for different samples to be in the range of  $10^{17}$  to  $1.8 \times 10^{17}$  cm<sup>-3</sup>. The dispersion of the results may come from the polycrystalline character of thin films which introduces an important error in the measurement of the exact area of the junction. For simplicity we use the geometrical projection of this area and we assume that the metal–semiconductor contact is an intimate junction.

The evolution of the interface during copper diffusion is studied by capacitance measurements, at room temperature. This nondestructive method allows us to follow the evolution of the electrical and photoelectrical characteristics of the junction after different annealings. The copper atoms diffuse in the bulk CdS after heating and copper in CdS is an acceptor (Bube 1960). If we assume a substitution mechanism under which each diffused atom produces an ionised centre, the space charge density in the semiconductor is:

$$\rho(x) = q [N_D - N_A(x, t)] \quad (1)$$

where  $N_A(x, t)$  is the distribution of diffused atoms derived from the resolution of Fick’s equation. Because of the thickness of the copper electrode, 0.2  $\mu$ m, two solutions may be considered: a constant reservoir and a limited source.

In the case of a semi-infinite sample with a constant reservoir of density  $N_0$  at the interface, the distribution  $N_A(x, t)$  is given by equation (2) where  $L = 2\sqrt{Dt}$ ,  $D$  being the diffusion coefficient:

$$N_A(x, t) = N_0 \operatorname{erfc} \left( \frac{x}{L} \right) \quad (2)$$

Substituting the acceptor profile in Poisson’s equation we obtain:

$$V_{bi} - V = \frac{q}{2\epsilon_s} (N_D - N_0) W^2 + \frac{qN_0}{2\epsilon_s} \left[ \frac{WL}{\sqrt{\pi}} \exp \left( -\frac{W^2}{L^2} \right) + \left( W^2 - \frac{L^2}{2} \right) \operatorname{erf} \left( \frac{W}{L} \right) \right] \quad (3)$$

where  $V_{bi}$  is the built-in potential.

In the case of a limited source, the resulting acceptor distribution is gaussian:

$$N_A(x, t) = N_0 \exp(-x^2/L^2) \quad (4)$$

The depletion layer width is determined by:

$$V_{bi} - V = \frac{q}{2\epsilon_s} N_D W^2 - \frac{q}{2\epsilon_s} N_0 L^2 [1 - \exp(-W^2/L^2)] \quad (5)$$

The two models, gaussian and erfc have been used and the unknown parameters  $V_{bi}$ ,  $N_D$ ,  $N_0$  and  $L$  are obtained by least squares fitting, of the measured values  $V$  and  $C = \epsilon_s/W$ . In this method we assume a constant donor density in the semiconductor, hence a linear relation between  $C^{-2}$  and  $V$  before copper diffusion as shown in figure 1.

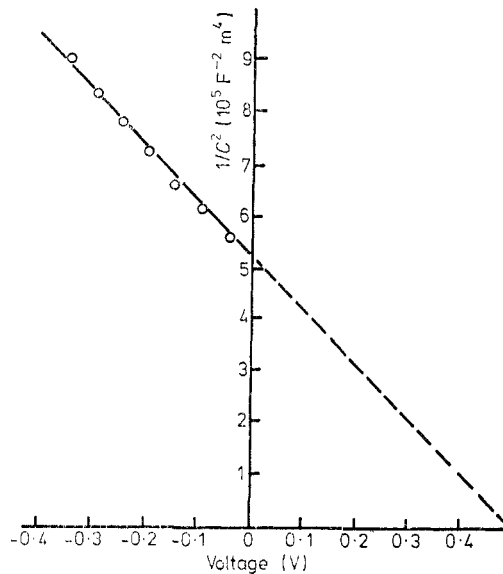
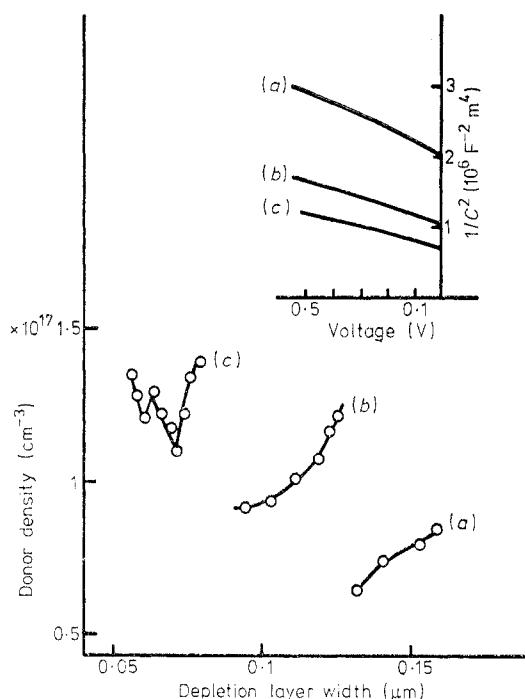


Figure 1.  $C^{-2}(V)$  curve of the Cu-CdS contact before diffusion.  $N_D$  range  $10^{17}$ – $1.8 \times 10^{17} \text{ cm}^{-3}$ .

Consider first diffusion at ambient temperature. The insert in figure 2 shows the evolution of  $C^{-2}(V)$  with time of a typical sample held at room temperature during four months. From these curves we deduce donor profiles as a function of  $W$  as shown in this figure. Initially the impurity profile is abrupt, but after several months it becomes non-uniform. This would be due to the diffusion of Cu acceptors in the bulk CdS. The characteristic length  $L$ , as determined by the generalised least-squares optimisation technique, is also given on the corresponding profiles. The resulting values of the diffusion coefficient at ambient temperature are in the range of  $7 \times 10^{-18}$  to  $3.6 \times 10^{-17} \text{ cm}^2 \text{ s}^{-1}$ . These results are about 100 times larger than the values given by Partain and Birchenall (1975), which were obtained on thin films used in the production of solar cells. These results were deduced from an extrapolation of measurements made in the  $146^\circ\text{C}$  to  $400^\circ\text{C}$  range assuming Sullivan's law (1969). Their study was concerned with Cu acceptor diffusion parallel to the  $c$  axis in CdS single crystals. These discrepancies can



**Figure 2.** Evolution of the donor profile for a typical Cu-CdS thin film sample held at 20°C. The insert shows the corresponding  $C^{-2}(V)$  curves.

(a)  $t=120$  days      (b)  $t=30$  days      (c)  $t=2$  days  
 $L=0.20\ \mu\text{m}$        $L=0.15\ \mu\text{m}$        $L=0.02\ \mu\text{m}$

be due to the presence in our samples of grain boundaries which are known to enhance diffusion.

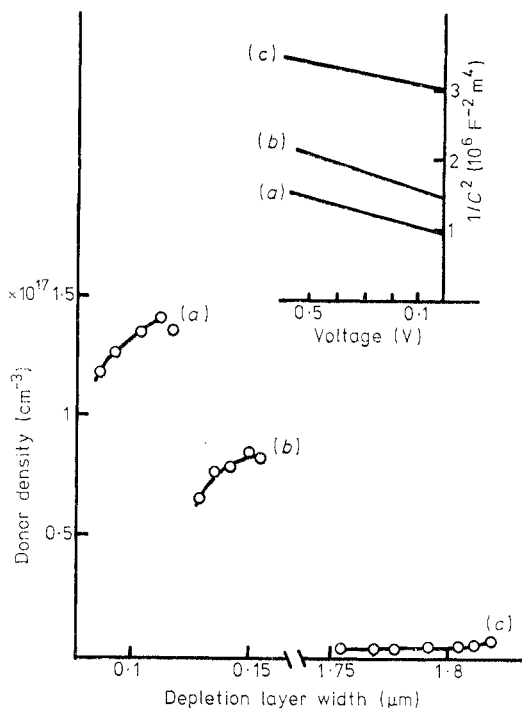
To determine the variation of the diffusion coefficient with temperature, the junctions were annealed in vacuum for one hour just after copper evaporation using the same type of thin-film samples with an average donor density of  $1.5 \times 10^{17}\ \text{cm}^{-3}$ .

The corresponding profiles are shown in figure 3. The average value found for  $N_0$ ,  $3 \times 10^{17}\ \text{cm}^{-3}$ , agrees well with the maximum solubility of copper in cadmium sulphide, 0.02% (Dreeben 1964). Figure 4 shows the variation of the diffusion coefficient with temperature. Our results can be compared to those obtained by Sullivan (1969), Clarke (1969) and Woodbury (1965) on CdS single crystals.

The gaussian and erfc profiles do not show any significant difference for the dispersion in the values of  $D$  so we use an average slope. The activation energy deduced from:

$$D = D_0 \exp(-\Delta E/kT) \quad (6)$$

is  $\Delta E = 0.72 \pm 0.1\ \text{eV}$  with  $D_0 = 8 \cdot 10^{-5}\ \text{cm}^2\ \text{s}^{-1}$ . This value is lower than that reported by Sullivan (1969) of 0.96 eV and that by Woodbury (1965) of 1.2 eV, but in agreement with that determined by Clarke (1959) of 0.77 eV, on single crystals for temperatures higher than 400°C. Clarke and Woodbury used the radiotracer technique which determines the total impurity density, in contrast to the capacitance measurements which are sensitive only to electrically active impurity centres.



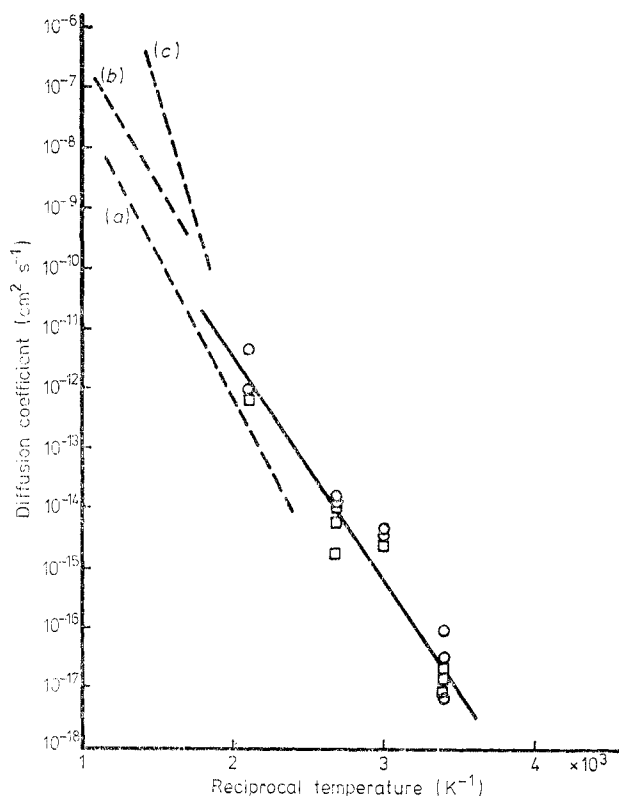
**Figure 3.** Evolution of the donor profile after 1 h annealing at (a) 60 °C, (b) 100 °C or (c) 200 °C. The insert shows the corresponding  $C^{-2}(V)$  curves. (a)  $L=0.08\ \mu\text{m}$ , (b)  $L=0.15\ \mu\text{m}$ , (c)  $L=1.2\ \mu\text{m}$ .

Thus a comparison of our results with those of Sullivan is more valid, since the results which he gives were also obtained by capacitive measurements. When extrapolating Sullivan's results we find that our values for  $D$  measured on thin films are higher by about a factor of 10 at 200 °C and 100 at 20 °C. The process of grainboundary diffusion is superposed on that of bulk diffusion in the crystallites parallel to the  $c$  axis, which could explain the discrepancy which we observe. Bearing in mind the polycrystalline structure and grain size, this discrepancy may seem small but can be explained by the fact that electrically efficient copper atoms diffusing in the grain boundaries make up a small proportion of the total copper density. Sullivan (1969) and Zmija and Demianiuk (1971) attributed bulk diffusion to a substitutional mechanism under which diffusing copper atoms occupy consecutively vacant cadmium sites of the lattice. Using the optical absorption technique, Szeto and Somorjai (1966) found values in good agreement with Clarke's result but an activation energy of 0.58 eV.

#### 4. Photovoltaic mechanisms

##### 4.1. Contact evolution

The behaviour of the Cu-CdS contact has been investigated as a function of time for samples kept at ambient temperature and as a function of annealing temperature for heat treated samples.



**Figure 4.** Temperature dependence of the diffusion coefficient of copper atoms in CdS thin films. Solid line: ○ erfc model, □ gaussian model. Dashed lines: comparison with Sullivan (a), Clarke, (b) and Woodbury (c) results.

The barrier height, open-circuit voltage, and  $n$  factor as function of time are displayed in figure 5 for a thin film sample. The barrier corresponding to the reference Cu–CdS contact without heat treatment was reached after two days. Afterwards, for a period of several months, the current decreased slowly with time causing the apparent barrier height to increase. These variations are in agreement with Butendeich and Ruppel's investigations (1978).  $\phi_B(CV)$  increases more drastically than  $\phi_B(IV)$ . This is related to the charge variation in the depletion region caused by diffused copper acceptor centres. Open-circuit voltage increases from 1 to 170 mV and the barrier height  $\phi_B(IV)$  from 0.52 to 0.75 V after one year. The single crystal barrier height and the open-circuit voltage increase more slowly. Polycrystal characteristics are intermediate between those of single crystals and thin films. Diffusion may account for this result, since it is slow for single crystals and faster for polycrystals and thin films. In thin films, grain boundaries and intergranular cracks enhance diffusion. Obviously there is a close correlation between the barrier height, the open-circuit voltage and the diffusion of copper acceptor centres. Copper diffusing into the CdS compensates donors in the CdS, and thus the depletion layer width increases. If the donors are over-compensated by the acceptors, resulting in a barrier which initially increases with distance from the metal, in the manner described by Basterfield *et al* (1975), the effective barrier height increases and this would also give rise to an increase in  $n$ .

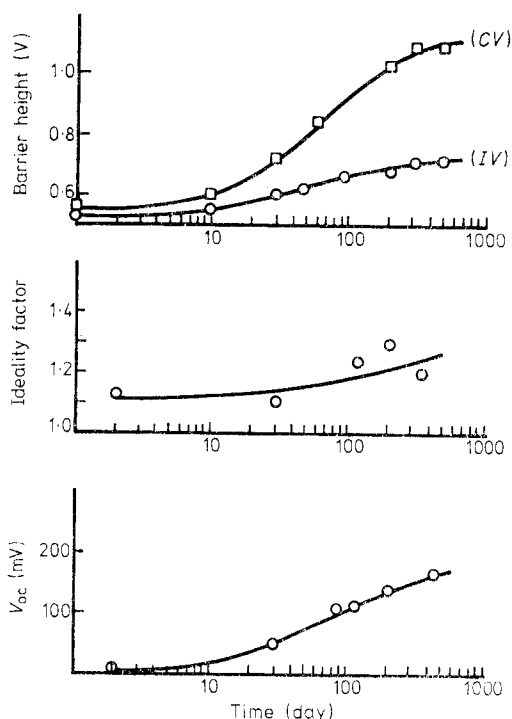


Figure 5. Time dependence of barrier height, ideality factor and open-circuit voltage for thin film Cu-CdS held at 20°C.

The changes in properties as a result of different heat treatments consisting of annealing for one hour at 60°C, 100°C and 200°C are displayed on figure 6. Increasing annealing temperature causes an increase of the barrier height  $\phi_B(IV)$  from 0.52 V to 0.91 V. The increase of  $\phi_B(CV)$  is much larger and consequently the open-circuit voltage goes from 1 to 300 mV. The ideality factor becomes greater as well; after a heat treatment of 200°C thermionic emission is no longer the dominant transport mechanism. On the high current range we find  $n=1.45$  and in the low current range  $n$  reaches a value of 2.2 implying recombination processes.

The copper electrode thickness was at least 2000 Å in order to investigate copper diffusion after heat treatments. This high value accounts for the weak values measured for the open-circuit voltage  $V_{oc}$  and the short-circuit current  $I_{cc}$ .

Nevertheless, experiments have shown an increase in the magnitude of  $V_{oc}$  and  $I_{cc}$  with time during illumination. After five hours of illumination,  $V_{oc}$  was enhanced by about a factor of 2 and  $I_{cc}$  by a factor of 10. Figure 7 shows the variation of  $V_{oc}$  with  $I_{cc}$  for a thin film CdS sample during illumination for five hours.  $V_{oc}$  is found to be proportional to  $\ln(I_{cc})$ . Therefore the diode saturation current  $I_s$ , and hence the barrier height, remains constant as  $V_{oc}$  increases, as deduced from the following relation, valid for conditions of high illumination:

$$V_{oc} \simeq (kT/q) \ln(I_{cc}/I_s). \quad (7)$$

The increase of  $V_{oc}$  and  $I_{cc}$  with time can be related to the displacement of the dependence of  $C^{-2}$  on  $V$  during illumination as discussed below. A slow trapping mechanism, involving deep hole traps located near the interface, may be responsible for this variation.

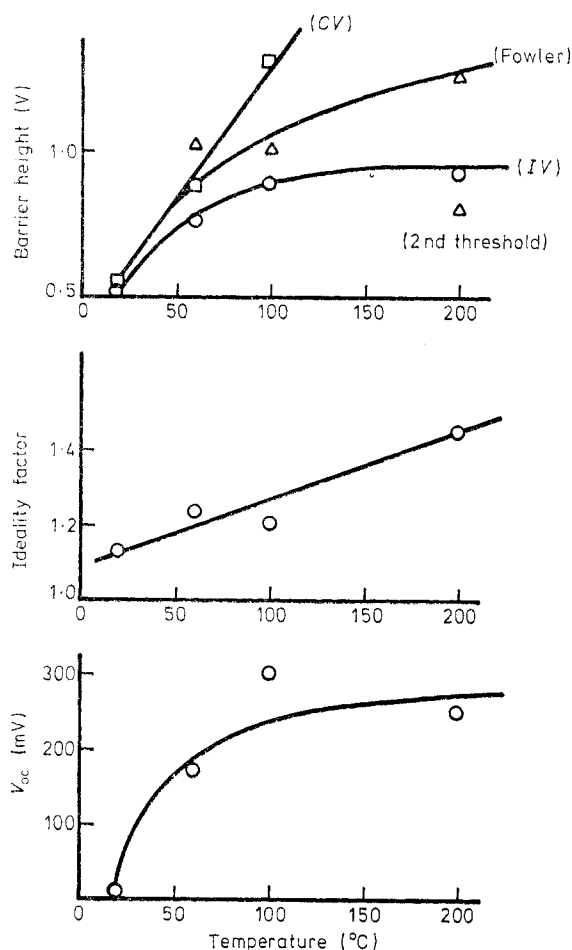
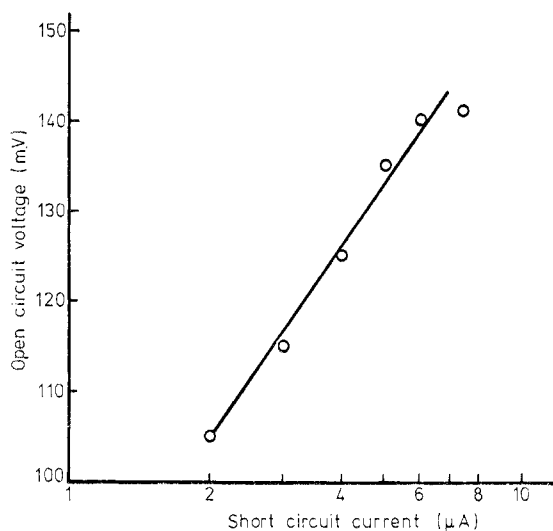


Figure 6. Variation of barrier height, ideality factor and open-circuit voltage with annealing temperature for Cu-CdS thin film diodes.

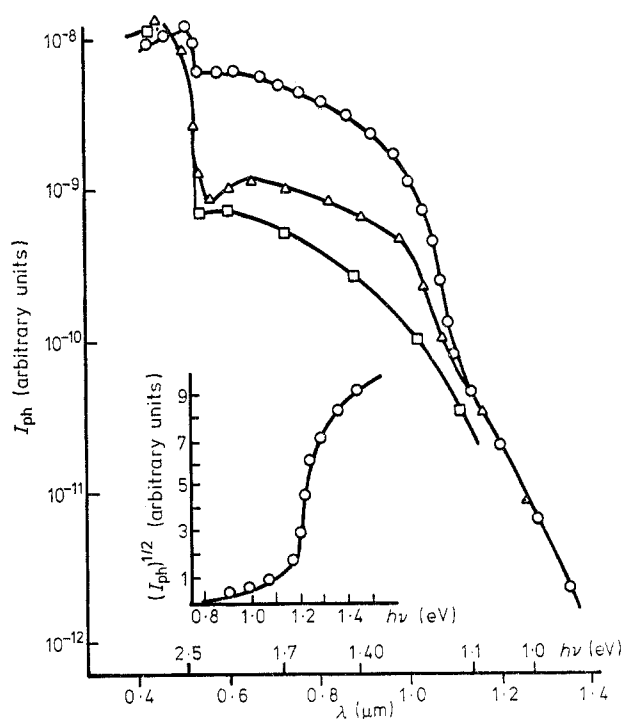
#### 4. 2. Photoresponse

The shape of the photoemission plot was independently established for the crystalline structure and generally two energy thresholds were observed for the Cu-CdS diodes. The barrier height  $\phi_B(\text{ph})$ , which is equal to  $\phi_B(\text{IV})$  (taking into account experimental errors) is associated with the first threshold. The second threshold (from which the contribution of the first is subtracted) was found to be between 1.1 and 1.2 eV. After annealing of the diode, the photoresponse increased towards the red region of the spectrum, and the shape of the photoemission curve as a function of energy became more abrupt as is shown in figure 8. Additionally the second threshold appeared at the absorption edge of  $\text{Cu}_2\text{S}$  at about 1.24 eV (Guastavino *et al* 1978). Furthermore, a similarity between the photoemission currents of an annealed Cu-CdS diode and of a  $\text{Cu}_2\text{S}$ -CdS solar cell has been noted (Renard 1977). Although a copper-sulphur compound was probably formed, the possible and simultaneous existence of copper deep traps in the CdS band gap and in the depletion zone must also be considered. Our capacitance measurements under





**Figure 7.** Variation of the open-circuit voltage in function of the short-circuit current during white light illumination for a typical Cu-CdS thin film sample after 1 year storage at 20°C. Measurements made at intervals between  $t=0$  and  $t=5$  h.

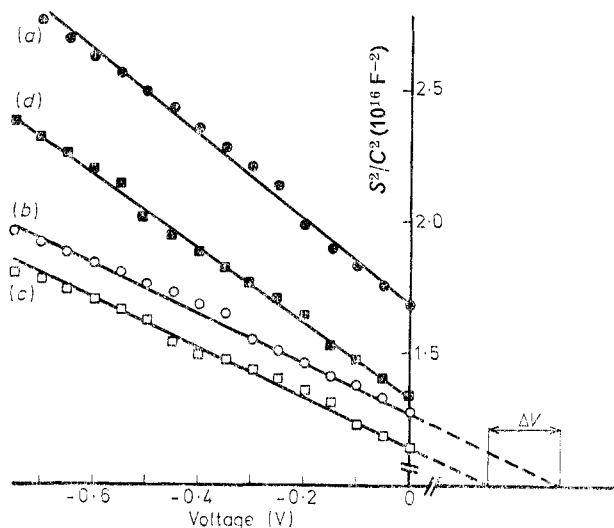


**Figure 8.** Spectral response of a Cu-CdS thin film diode:  $\square$  before annealing;  $\triangle$  after 1 h annealing at 100°C;  $\circ$  after 1 h annealing at 200°C. The insert shows the photo-emission plot after 1 h annealing at 200°C.

illumination show that these traps are the cause of internal transitions which increase the photoresponse towards the red region of the spectrum.

#### 4.3. Capacitance measurements under illumination

Figure 9 shows the  $C^{-2}(V)$  curves under white light illumination for a Cu-CdS thin film sample after one year storage at 20 °C. When the diodes are illuminated, with white light or intrinsic radiation, an increase of the capacitance is observed related to the narrowing of the depletion layer in the CdS by the trapped holes (Lindquist and Bube 1972). The variation of the  $C^{-2}(V)$  curve is characterised by a modification of the slope for all



**Figure 9.** Evolution of the  $C^{-2}(V)$  curves under white light illumination for a Cu-CdS thin film sample after 1 year storage at 20 °C. (a) equilibrium in the dark; (b) immediately after establishing white light illumination; (c) after 3 h 30 min of illumination; (d) in darkness just after 3 h 30 min illumination.  $S$ =sample area.

samples, and a slow parallel displacement for the diodes kept at ambient temperature.

The former may arise from copper acceptor centres, neutralised by illumination. From the slope of curve (b) we deduce the true donor density  $N_D$ , which corresponds exactly to the value obtained in the dark before copper diffusion. The difference between the slopes of the curves (a) and (b) allowed us to determine the density of the copper acceptor centres in the vicinity of the edge of the depletion layer (0.1 to 0.15  $\mu\text{m}$ ). We found  $N_A = 7.7 \times 10^{16} \text{ cm}^{-3}$ . The same value was obtained after a heat treatment at 100 °C or after storage for one year at 25 °C. This density is in good agreement with that deduced from the diffusion profiles given by equations (2) and (4). Consequently we conclude that copper acceptor centres are responsible for the rapid change under illumination between curves (a) and (b).

Secondly, the slow parallel displacement of the curve under illumination, showing a constant donor density at the edge of the depletion layer, may be associated with the neutralisation of acceptor-like levels  $N_A^*$  at the interface or within the zero-bias depletion layer. According to the rectangular profile shown in figure 10, similar to that discussed

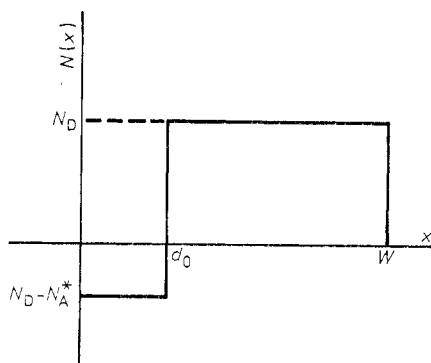


Figure 10. Rectangular profile associated with acceptor-like levels. Solid curve: dark profile. Dashed curve: profile under illumination after neutralisation.

by Lubberts *et al* (1974) for Au-Cu diffused-CdS diodes,  $C^{-2}(V)$  is given by the following relation:

$$\frac{1}{C^2} = \frac{2}{q\epsilon_s N_D} \left[ (V_{bi} - V) + \frac{qN_A^* d_0^2}{2\epsilon_s} \right]. \quad (8)$$

From the difference  $\Delta V_{int} = 0.15$  V between intercepts of the curves (a) and (b) on the voltage axis we can determine  $N_A^* d_0^2$ . If the levels are distributed in a slab of thickness 100 Å near the interface, we obtain  $N_A^* = 1.5 \times 10^{18} \text{ cm}^{-3}$ ; this value can be compared with the density of levels caused by native defects,  $10^{18} \text{ cm}^{-3}$ , and involved in the model of Stirn *et al* (1973) on the CdS photoconductor metal contact. The capacitance variation under illumination was also observed on  $\text{Cu}_2\text{S}$ -CdS thin film photocells by Bernard and Vormus (1977) and by Rothwarf *et al* (1978).

It is interesting to note here that the variation of the slope under illumination attributed to copper diffusion was not observed on diodes for which the CdS substrate was held at 100 K during evaporation in order to prevent diffusion of the copper. Under the evaporation conditions of 100 K and  $10^{-6}$  Torr the CdS substrate is covered with the residual air and water vapour of the vacuum chamber resulting in the formation of an interfacial layer with a large density of interface states at the contact. On these samples, the barrier height is constant and equal to 0.90 V for all crystalline forms, for gold and copper electrodes, and this value corresponds to the position of the oxygen chemisorbed level on the CdS surface (Palz and Ravelet 1970).

In this case, the corresponding curves (a) and (b) were parallel and we can conclude that the variation of the capacitance under illumination is entirely caused by the trapped charge on localised levels at the interface: for single crystal diodes,  $N_A^*$  is about  $8 \times 10^{18} \text{ cm}^{-3}$  as deduced from equation (8) with  $d_0 = 100$  Å. The main result of this low temperature process is to produce high photovoltages with the same copper electrode thickness, typically 300 mV, which corresponds to the values obtained on the heat treated samples.

## 5. Conclusions

Measurements have been carried out on the rate of diffusion of copper in CdS thin films in the 20 °C to 200 °C range using a capacitance method. Electrical and photoelectrical characteristics have been investigated in connection with copper diffusion. The activa-

tion energy found for the diffusion coefficient is  $0.72 \pm 0.1$  eV. This nondestructive method is interesting to investigate the lifetime of the photocells. Our results on undoped CdS thin films imply a short lifetime but it would be interesting to use this method to study the lifetime parameters of the photocells manufactured on doped CdS thin films.

Examination of the photoresponse per incident photon after heat treatments shows evidence for the formation of a copper sulphide phase at the Cu–CdS contact. Simultaneously the diffused copper atoms induce deep lying acceptor centres in the CdS bulk. We have shown that the increase of the width of the depletion layer caused by copper diffusion is suppressed by illumination, the effect of which is to neutralise the copper acceptor centres. The true value of the donor density is deduced from the curve of  $C^{-2}(V)$  measured under conditions of illumination for the diffused samples.

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