PHYSICAL REVIEW B VOLUME 32, NUMBER 12 15 DECEMBER 1985

Photoconductivity and dark-conductivity studies of $CdS_{1-x}Se_x(Cu)$ sintered layers

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(Received 14 January 1985; revised manuscript received 8 July 1985)

The photoconductivity and dark conductivity of $CdS_{1-x}Se_x(Cu)$ layers sintered at 773 K have been studied in a configuration similar to that under actual use in a solid-state image intensifier. The dark current shows linear dependence on voltage at lower voltages. At higher voltages the current shows non-Ohmic behavior. The photocurrent is found to be space-charge limited at the lowest voltage studied; this behavior is explained by the nonuniform illumination of the sample. Supralinearity and subsequent sublinearity in the photocurrent dependence on light intensity indicate the presence of sensitizing centers near the valence band as well as an exponential trap distribution nearer the conduction band. The thermal quenching of the photocurrent seems to confirm this. The unusual decrease in the dark current with increase in temperature around room temperature (313 K) can be explained on the basis of these centers. The spectral studies indicate the filtering effect of selective absorption because of the particular configuration. Infrared spectral studies indicate the presence of sensitizing centers about 1 eV above the valence band.

I. INTRODUCTION

Although much work has been done on various methods of fabrication and operation of solid-state image intensifiers,[1-3] not many studies on the characteristics of the photoconductive input element seem to be reported. A solid-state image intensifier is a visual-to-visual converter which consists basically of a photoconductive layer and an electroluminescent layer sandwiched together and illuminated through the transparent electrode from the photoconductor side.[4] Although a lot of literature does exist on the photoconducting properties of CdS (Refs. 5—8) and CdSe (Refs. 9—11) and some studies have been carried out on $CdS_{1-x}Se_x$ solid solutions,[12-14] most of these studies are made either on single crystals[5,6,12] or on thin films illuminated perpendicular to the field direction.[7-11] Very little work has been done on the conductivity of thick films, especially when the direction of illumination and field are the same.[15,16]

We had earlier reported a study of the photoconducting properties of $CdS_{1-x}Se_x(Cu)$ in silicon resin binder layers.[17] In the present paper a study of the photoconductivity and dark conductivity of sintered layers formed by using the same $CdS_{1-x}Se_x(Cu)$ powder has been presented.

II. EXPERIMENTAL

$CdS_{1-x}Se_x(Cu)$ powder was obtained from GTE Sylvania, Incorporated.[18(a)] The composition of the powder was 98 wt. % CdS and 2 wt. % CdSe. Approximately 200 ppm of Copper and about 3% by weight of $CdCl_2$ were used in the processing.[18(b)] The powder was deposited using a xylene suspension onto SnO_2-covered conducting glass substrates. The layers were sintered at 773 K for 60 min and cooled rapidly under a strong air flow.

Dark conductivity and photoconductivity measurements were carried out on test samples of thickness 95 μm by making pressure contact with a second conducting glass of area 1 cm^2. The sandwich sample was kept in a temperature-controlled cell[19] and illuminated through one of the transparent electrodes using white light from a tungsten filament lamp (220 V, 200 W).

Current measurements were carried out using a Keithley 610C electrometer. The light intensity was varied by means of neutral density filters and by varying the sample-to-bulb distance.

The spectral sensitivity measurements were made by using different interference filters. Equal photon flux was made incident on the sample for all wavelengths. This value was 10^{12} photons/sec for the visible range (400 to 700 nm), whereas in infrared range it was ten times greater.

The absorption-coefficient (α) values at different wavelengths were calculated from the reflection and transmission spectra of the vacuum-deposited film of sintered $CdS_{1-x}Se_x(Cu)$ powder. These spectra were obtained by means of a Pye Unicam Spectrophotometer (No. SP8-100).

III. RESULTS AND DISCUSSION

A. Photocurrent and dark-current variation with applied voltage

Figure 1 gives the dark current and photocurrent as a function of applied voltage. The dark current I_D versus V (curve A in Fig. 1) shows an approximately linear dependence on voltage until approximately 100 V. Above this voltage the I_D-versus-V curve becomes nonlinear, suggesting space-charge formation. In contrast, the photocurrent (I_P versus V) dependence is space-charge limited right from the lowest voltage used. Since the space-charge-limited currents are not found in the dark at lower voltages, it seems reasonable to presume that the additional space charge is due to trapping of photogenerated car-

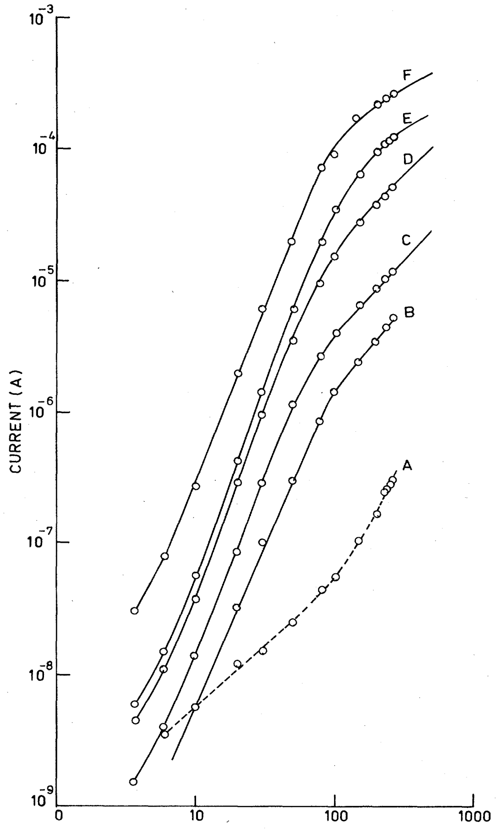

FIG. 1. Variation of dark current and photocurrent with applied voltage. *A*, Dark current $I_D \times 10^2$; *B*, photocurrent at 110 lx; *C*, photocurrent at 158 lx; *D*, photocurrent at 295 lx; *E*, photocurrent at 1090 lx; *F*, photocurrent at 2800 lx. Temperature 40 °C.

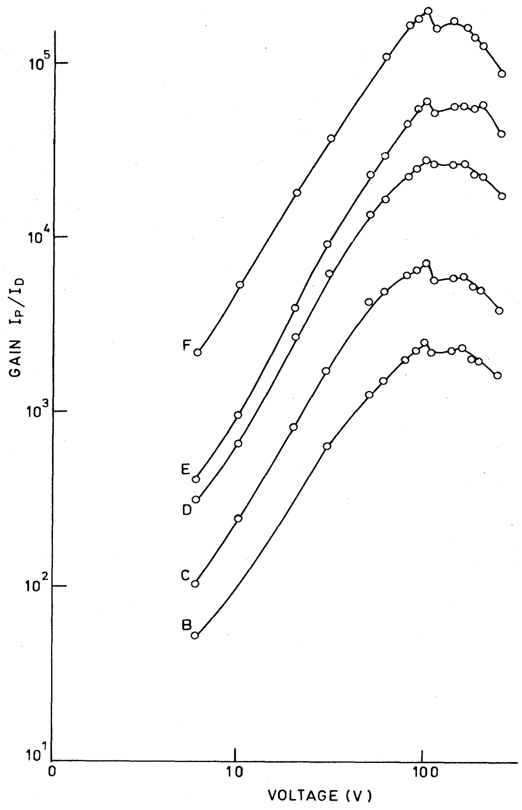

FIG. 2. Variation of I_P/I_D ratio as a function of voltage for different light intensities. *B*, 110 lx; *C*, 158 lx; *D*, 295 lx, *E*, 1090 lx; *F*, 2800 lx.

riers. This could be due to the nonuniform illumination of the thick sample, leading to the rapid trapping of photogenerated holes in the region near the electrode as the thickness of the sample is 95 μm.[20] The resultant current will therefore be space-charge limited initially. As voltage increases and hence transit time of the photogenerated carriers decreases, the effect of the space charge due to these trapped holes becomes less significant than the primary current contributed by the electrons freed directly by excitation, and the current voltage behavior becomes more linear.

At still higher voltages a trend towards saturation is seen in curves *F* and *E*. The possible explanation of this effect will be discussed in Sec. III C.

B. I_P/I_D ratio

For use in a solid-state image intensifier (SSII) a photoconductive layer should have a good I_P/I_D ratio in the configuration described earlier. Figure 2 gives the variation of I_P/I_D with applied voltage for different light intensities. The average value is approximately 10^4. The ratio increases rapidly with applied voltage until approximately 100 V. At 100 V a peak is obtained, due to the increasing slope in the I_D-versus-V curve and the decreasing slope in the I_P-versus-V curve.

C. Variation of I_P with light intensity L

The variation of photocurrent with the input light intensity is shown in Fig. 3 on a log-log scale. These are straight-line curves having different slopes for lower and higher light intensities and can be represented by $I_P \propto L^{\gamma}$. The value of γ is 2.3 at lower intensities, suggesting a supralinear dependence of I_P on light intensity. Above an incident intensity of around 300 lx the nature of the variation changes to sublinear, with slopes varying between 0.6 and 0.8.

The supralinearity and subsequent sublinearity may be understood in terms of charge-trapping and recombination processes. We assume that, among the various imperfections present, there are two kinds of dominant states (class I and class II) in the forbidden gap. Class I consists of states which have roughly similar cross section for both electrons and holes. Class-II states are close to the valence band and have a higher capture cross section for holes than for electrons.[21]

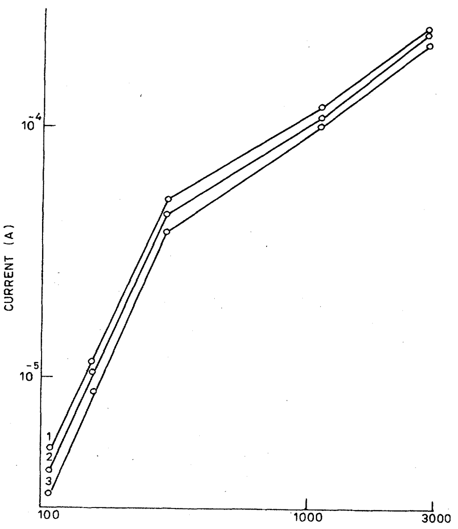

FIG. 3. Photocurrent versus light intensity at different voltages: 1, 260 V; 2, 230 V; 3, 200 V.

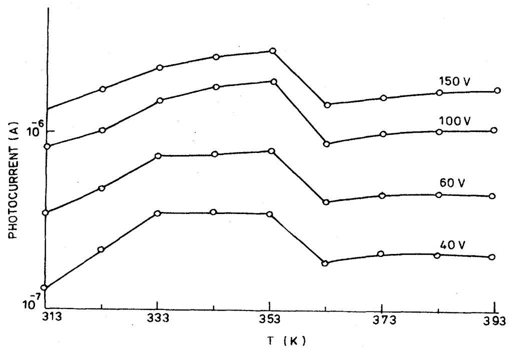

FIG. 4. Photocurrent versus temperature at various voltages.

As usual we denote states lying between the electron and hole demarcation levels as recombination centers and those located between the filled or empty band and the position of the demarcation levels as traps. The intuitive expectation that more recombination centers would mean shorter lifetimes applies to class-I centers. However, because of the ratio of the electron-to-hole cross sections of the class-II centers, they act to increase the lifetime of electrons, which in effect sensitizes the sample when they act as recombination centers.[21]

At some very low level of illumination and high temperature, the steady-state Fermi level may be such that class-II states act as hole traps. Now when the light intensity is increased the Fermi levels would split further apart and cause some of these states to act as recombination centers and hence sensitize the sample. This continuous increase of lifetime with light intensity gives rise to the supralinearity in the I_P-versus-L curve. According to the model[21] after full conversion, the photocurrent would again vary linearly with light intensity. However, we find a sublinear dependence in the sintered $\mathrm{CdS}_{1-x}\mathrm{Se}_x(\mathrm{Cu})$ samples. This suggests that the class-I centers consist of a continuous distribution of electron-trapping levels, roughly exponential in nature, lying between the conduction level and the electron Fermi level. This type of dependence was also found in the $\mathrm{CdS}_{1-x}\mathrm{Se}_x(\mathrm{Cu})$ powder as used in a binder-type layer.[17]. The effect of Fermi-level splitting would be to convert more of the class-I centers to recombination levels, decreasing the electron lifetime and giving rise to the observed sublinearity in Fig. 3.

The existence of the class-II trapping sites can also explain the slight saturation effect observed in the I_P-versus-voltage curves at higher intensities. We consider that at a particular light intensity and voltage the position of the Fermi levels are such that they have just converted all the class-II states into recombination levels. The effect of the additional electrons injected into the material by the additional voltage will be to raise the Fermi level upwards towards the conduction band. This would cause some of the class-II centers to act as hole traps again, leading to desensitization and the decrease in electron lifetime with increasing voltage. This could account for the saturation-type sublinear nature of curves F and E in Fig. 1.

D. Temperature dependence of photocurrent

The nature of the dependence of the photocurrent on temperature brings out the opposing effects of the class-I and class-II centers on the lifetime of the carriers.

At first a fairly steep increase is obtained in the photocurrent as temperature is increased (Fig. 4). This indicates that the Fermi level is moving in the midst of an exponential trap distribution.[22] As temperature increases there is a marked decrease in the current with rising temperature. However, this is found over a short range of temperature after which the current again increases with temperature though at a less rapid rate. The decrease in current with rising temperature can be explained on the basis of the desensitization effect of the class-II centers.[21] The hole demarcation level will move upwards due to the shift of the Fermi level with increase in temperature. This will lead to the conversion of some of the recombination centers to hole traps and consequent desensitization. It seems that this begins to happen predominately in this material around 343 to 353 K (seen more clearly in Fig. 5,

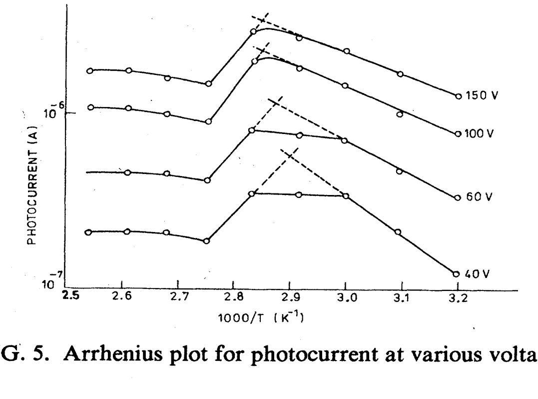

FIG. 5. Arrhenius plot for photocurrent at various voltages.

the Arrhenius plot for Fig. 4). After about 363 K a slight increase in I_P with temperature is observed, which may be attributed to the combined effects of the properties of class-I and class-II traps on the photocurrent dependence on temperature.

E. Temperature dependence of dark current

The dark current is shown as a function of temperature for different voltages in Fig. 6. We see that the dark current shows a decrease with increasing temperature up to 333 K. At first this was attributed to experimental error or to evaporation of moisture held in the sample at room temperature (313 K) upon heating the sample, causing a fall in conductivity. However several repetitions of the experiment gave the same feature. The trend and values remained constant whether the readings were taken while heating or cooling the sample and with varying applied voltage. This unusual dependence of the dark conductivity on temperature may be explained on the basis of the class-II type of imperfection centers.

In the dark the sintered $CdS_{1-x}Se_x(Cu)$ material can be considered as essentially a semiconductor. In the absence of illumination there will be only one Fermi level for both holes and electrons. Thus there will be only one common demarcation level.[23] Since $CdS_{1-x}Se_x(Cu)$ is a n-type material, the Fermi level will be closer to the conduction band. The demarcation level can to a first approximation be considered as a mirror image of the Fermi level reflected about the middle of the forbidden gap.[23] Thus the demarcation level could conceivably be located somewhere in the region of the class-II imperfection levels. Now as we increase the temperature in the dark, the Fermi level will come closer to the center of the forbidden gap and simultaneously the demarcation level will rise upwards, away from the valence band. The correction factor to this simple approximation is $k_B T \ln S_n / S_p$,[24] where k_B is the Boltzmann constant, T is the temperature, S_n is the capture cross section for holes, and S_p is the capture cross section for electrons; thus for traps where $S_p \gg S_n$, the demarcation level will be furthered by this correction factor from the valence band than the Fermi level is from the conduction band.[24] During this upwards movement the demarcation level may cross the class-II imperfection levels—changing them from recombination centers to hole traps, and thus effectively desensitizing the sample.

Since the samples in which this kind of class-II level (sensitizing centers) predominates are expected to be highly photosensitive, this might also explain why Okimura and Sakai.[11] (who have reported a similar type of dark-conductivity dependence on temperature) only observed it in highly photosensitive films.

Above 333 K the dark current starts increasing with temperature. By plotting the I_D-versus-$1/T$ curve, the thermal activation energy is found to be approximately 0.778 eV. This indicates that the dark Fermi level may be about 0.78 eV from the bottom of the conduction band.[15] The correction factor at 338 K would be about 0.33 eV for a hole-to-electron capture cross-section ratio of 10^5.[14] Thus the demarcation level is at about 1.1 eV above the valence band edge in the dark at 338 K and would be somewhat closer to the valence band at lower temperatures. This indicates that the class-II centers in this sample are approximately 1 eV above the valence band. This is in agreement with the quoted value in literature for either the Cu impurity level or the cadmium vacancy in CdS or CdSSe solid solutions, as long as the proportion of CdSe to CdS is less than 30—40 wt. %.[12]

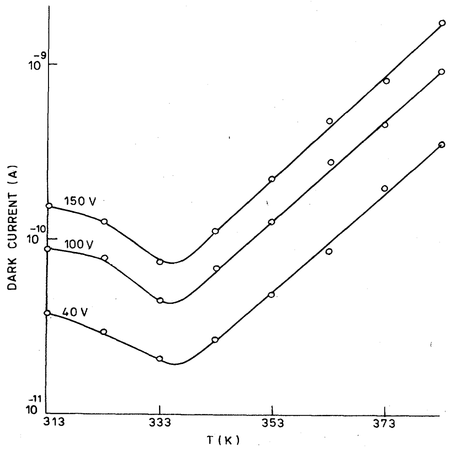

FIG. 6. Dark current versus temperature.

F. Spectral studies

Figure 7 shows the dependence of the photocurrent on the wavelength, for (400—700)-nm light for a fixed incident photon flux. The current rises with wavelength un-

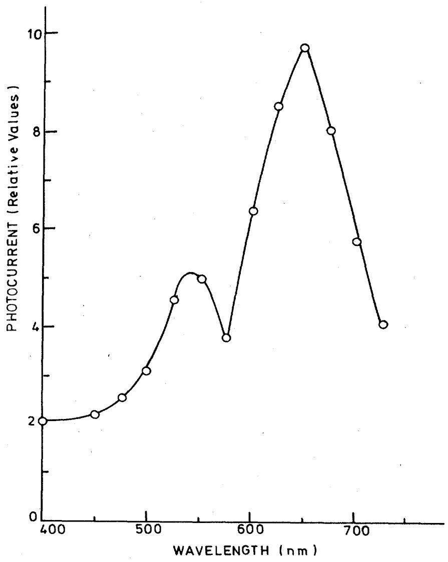

FIG. 7. Spectral response of photocurrent (between 400 and 700 nm).

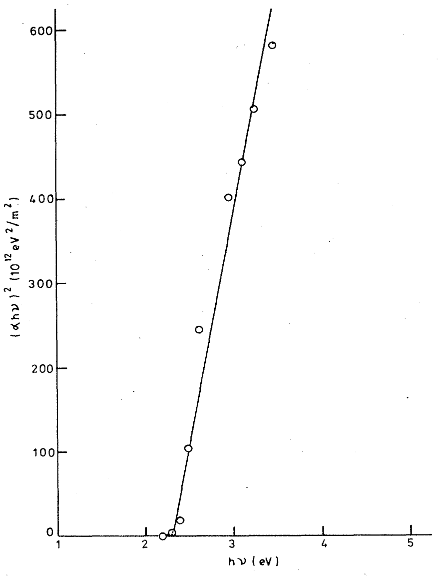

FIG. 8. Plot of $(\alpha h\nu)^2$ vs $h\nu$.

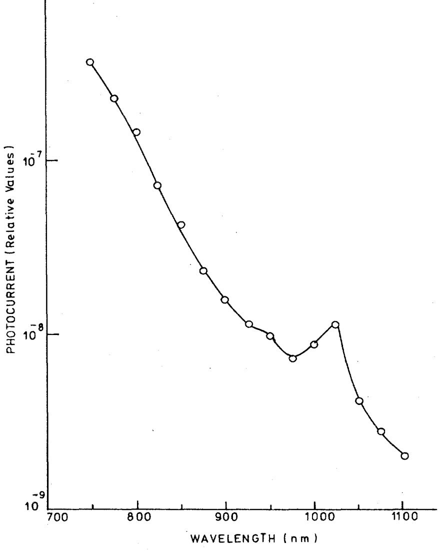

FIG. 9. IR spectral response of photocurrent.

til 650 nm, after which it drops abruptly. A peak is obtained between 525 and 550 nm.

The band gap for CdS is about 2.4 eV and for CdSe 1.7 eV. The variation of the band gap with composition has been described by Bube.[12] For 98 wt. % CdS and 2 wt. % CdSe the band gap is given as 2.26 eV at 300 K. The value of the band gap was also determined experimentally. Figure 8 shows the plot of $(\alpha h\nu)^2$ versus $h\nu$.[25,7] (α is the absorption coefficient and ν the frequency of light used.) The X-axis intercept of the straight line obtained gives the value of the band gap of the $CdS_{1-x}Se_x$(Cu). It can be seen that the value obtained (2.29 eV) is close to the theoretically predicted value. Thus the first peak obtained in Fig. 7 corresponds to the band-gap photoconductivity of $CdS_{1-x}Se_x$(Cu).

The broadening of the peak ad the relatively high response in the red region and low response at lower wavelength can be explained by considering that measurements were carried out on a thick (95 μm) layer of $CdS_{1-x}Se_x$(Cu) with electrodes on opposite surfaces and illuminated through the electrode surface. The blue light is absorbed primarily near the interface, the relatively lower surface lifetime resulting in a lower photoconductivity. This is due to the additional trapping sites available at the region nearer to the interface, which reduce the free lifetime of the charge carrier. The lower energy light (which is not absorbed close to the interface) will tend to penetrate deeper into the sample and produce volume photoexcitation. Thus this filtering effect of layers nearer to the illuminated surface causes the spectral response to be shifted towards the low-energy side.

At the energies lower than the band gap the photosensitivity can be associated with the imperfection centers in the layer. In this higher wavelength region, both excitation and quenching may take place and the magnitude of the photocurrent we measure would be the resultant value from both processes.

The photocurrent decreases rapidly with wavelength, as seen in Fig. 9. However, at approximately 1025 nm a peak is seen in the photoexcitation spectra. This may be considered to correspond to the dip usually found in IR quenching in photosensitive CdS samples, between the narrow IR quenching peak at 0.9 eV and the higher energy broader band.[24]

The excitation peak is seen at about 1.21 eV. If we consider this to be the necessary energy required to just excite charge carriers from imperfection centers to the conduction band and take the band gap of the material as 2.29 eV, the location of the imperfection centers appears to be 1.08 eV from the valence band, which is in fairly good agreement with the earlier estimate of the position of the class-II centers.

IV. CONCLUSIONS

When $CdS_{1-x}Se_x$(Cu) layers are sintered, their photoconductivity properties are governed primarily by the kinetics of the class-II imperfection centers.

The presence of these centers gives rise to supralinearity in the I_P-versus-V characteristics, thermal quenching of photoconductivity, and current saturation with voltage. The sensitizing centers seem to be situated approximately 1 eV from the valence band. The anomalous decrease of the dark current with increase in temperature can also be explained on the basis of this.

ACKNOWLEDGMENTS

Two of the authors (N.S. and A.K.T.) acknowledge the financial assistance given by the Department of Science and Technology (India). The authors would also like to thank Dr. A. K. Raturi for his help in obtaining the transmission and reflection spectra.

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