Sensitisation effects in the photoconductivity of CdS:Y

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Abstract. A relative photosensitivity factor S equal to 1430 is observed due to incorporation of Y in CdS. Dye-treatment enhances this value to 4516. A charge-transfer mechanism may be considered to be responsible for this process. Superlinear photoconductivity and thermal quenching observed in the temperature range 133–366 K are explained in terms of a two-centre model.

Except for recent reports by Bhushan and Diwan 1986, Bhushan and Giriya 1987, 1988a, b, Bhushan and Abraham 1988 and Bhushan and Sharma 1988 and a few others (Fialkovskaya and Khirunenko 1974, Zaitov et al 1982), not much attention has been paid to the photoconductivity of rare-earth-doped II–VI compounds. Further dye sensitisation has been reported in ZnO (Dudkowski et al 1967, Comizzoli 1970, Daltrozzo and Tributsch 1975) but with differing opinions as to the role of the dye. The present communication deals with the sensitisation effect due to Y and dye treatment in the photoconductivity of the system CdS:Y.

Details of sample preparation (except for yttrium oxide in place of lanthanum nitrate), cell geometry and experimental arrangements are described elsewhere (Bhushan and Sharma 1989). All the concentrations reported in this paper are by weight of base (CdS). The spectra reported in this paper are those which result after necessary correction by a method published earlier (Bhushan and Sharma 1988).

The dark current has been found to vary linearly within the voltage range of study (100 V). Figure 1(a) shows the rise and decay curves for different CdS photoconductors. In CdS:NaF the highest photocurrent is found at 8% NaF. Using this value and varying the concentration of Y maximum photocurrent is found at a concentration of 0.157% Y. The role of NaF may be considered to be twofold: it acts as dopant since at its particular concentration the highest photoresponse is found and as a flux because without it rare earths do not become effective dopants. Higher photocurrents in Y-doped samples may be due to release of valence electrons, and lower photocurrents at higher concentrations of Y may be due to concentrations quenching.

The rise and decay curves for different dye treated samples are shown in figure 1(b). The highest photocurrent appears for treatment with 0.8% Rhodamin B. Results of undoped CdS and CdS:NaF are also reported for comparison. Lower photocurrents at higher concentration of Rhodamin may be due to absorption of radiation in the comparatively thicker dye layer. Further, faster decay may be due to the fact that dye-illumination increases the recombination rate by contributing recombination centres (Comizzoli 1970).
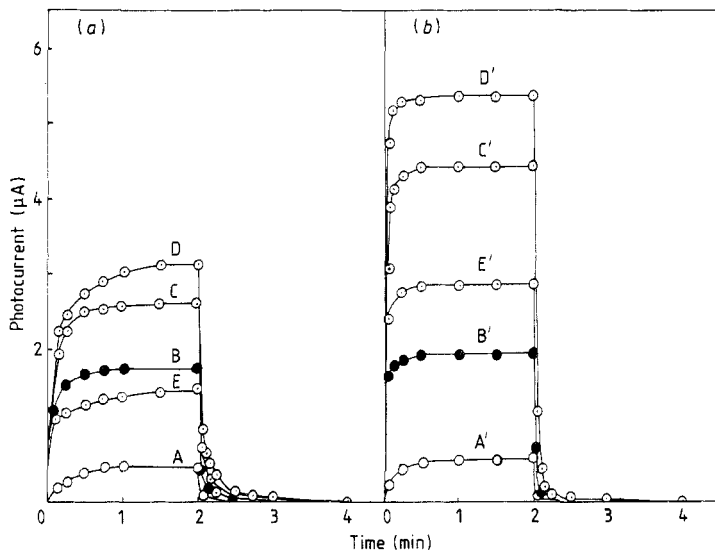
Figure 1. Rise and decay curves of (a) CdS photoconductors: curve A, undoped CdS; curve B, CdS:NaF(8%); curve C, CdS:NaF(8%), Y(0.118%); curve D, CdS:NaF(8%), Y(0.157%); curve E, CdS:NaF(8%), Y(0.236%). (b) The same for dye-treated CdS photoconductors: curve A', undoped CdS(0.8% dye); curve B', CdS:NaF(8%): (0.8% dye); curve C', CdS:NaF(8%), Y(0.157%): (0.6% dye); curve D', CdS:NaF(8%), Y(0.157%): (0.8% dye); curve E', CdS:NaF(8%), Y(0.157%): (1% dye).
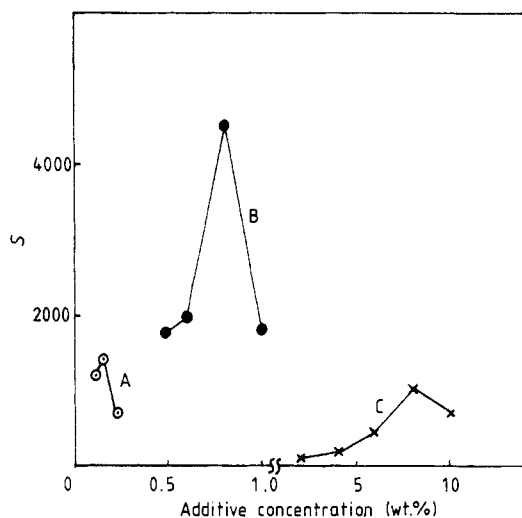
The relative photosensitivity factor S, defined by

$$S = \Delta\sigma/\sigma_d = (R_d - R_i)/R_i$$

where R_d and R_i represent dark resistance and resistance under illumination, depends on the concentrations of NaF, Y and dye and the corresponding results are shown in figure 2. In CdS:NaF S reaches a maximum at 8% NaF, having a value of 1045. In CdS:NaF (8%), Y (0.157%) the highest value of S is found to be 1430. Dye treatment of this sample gives a maximum value of S equal to 4516.

Figure 3 shows excitation spectra of undoped CdS, CdS:NaF, CdS:NaF:Y and dye-treated CdS:NaF, Y photoconductors. The lower wavelengths peak (510–530 nm) may be attributed to the host lattice. The effect of dye-treatment or the incorporation of impurities (not very pronounced) results in some longer wavelength peaks along with enhancements of the shorter wavelength peak. Thus the role of dye treatment is understood in terms of creating photoelectrons helping in photosensitisation. Since peaks observed in dye treated CdS:NaF, Y appear with pronounced intensity it may be proposed that charge transfer takes place from excited dye molecules thus favouring the charge transfer mechanism (Daltrozzo and Tributsch 1975).

The behaviour of photocurrent as a function of light intensity in the temperature range 133–366 K is shown in figure 4. At lower temperatures two straight lines represent the behaviour and at higher temperatures one straight line is sufficient. The lower intensity part starts with superlinear behaviour which continues up to 281 K. The higher intensity part starts with a lower slope and shows superlinearity when the slope of the earlier part is reduced. Finally, both are combined in one straight line and the slope is lowered. This last behaviour is seen in terms of a quenching effect at higher temperatures

Figure 2. Dependence of relative photosensitivity factor *S* on the additives concentration. Curve A, CdS:NaF(8%), Y; curve B, CdS:NaF(8%), Y(0.157%): dye; curve C, CdS:NaF.
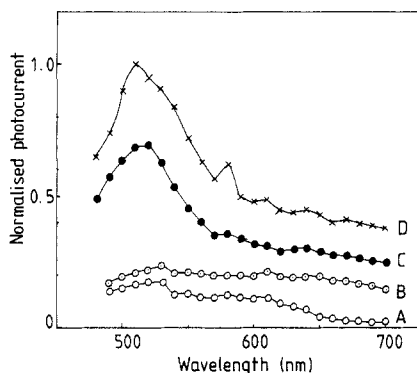
Figure 3. Excitation spectra of different CdS photoconductors (normalised with respect to the maximum of the most sensitive sample). Curve A, undoped CdS; curve B, CdS:NaF(8%); curve C, CdS:NaF(8%), Y(0.157%); curve D, Dye-treated (0.8%) CdS:NaF(8%), Y(0.157%).

as shown in figure 5. This figure shows the behaviour of photocurrent with temperature at different intensity of excitations. Considering a two-centre model it may be assumed that the material exists initially with certain recombination centre with a relatively large capture coefficient for electrons and holes. The imperfection centres added to this material have a considerably different set of capture coefficients. The intensity of excitation and temperature control the position of the hole demarcation level of sensitising centres. When the hole demarcation level is lowered through the level of sensitising centres by increasing light intensity at fixed temperature, the photosensitivity increases as the electron lifetime increases and results in superlinear photoconductivity. Similarly when the hole demarcation level is raised through the level of sensitising centres by increasing the temperature at fixed excitation intensity, the photosensitivity decreases due to a decrease in electron lifetime and results in thermal quenching.

Let us apply hole trapping theory to the present case (Smith 1978). If a number of trapping centres exist at different energies, the resulting decay curve of the photocurrent I_p can be considered as a sum of exponential terms given by (Bube 1960)

$$I_p = \sum_{i=1}^{n} A_i \exp(-t/\tau_i) \tag{1}$$

where A_i is a constant and τ_i is the time constant associated with the ith exponential term. The mean time τ that a hole spends in a trap at a temperature T is given by (McKeever 1985)

$$\tau = B \exp(E/k_B T) \tag{2}$$

where B is a constant, E is the trap depth, k_B is Boltzmann's constant and T is the absolute temperature. Thus E can be determined by knowing τ as a function of T. For
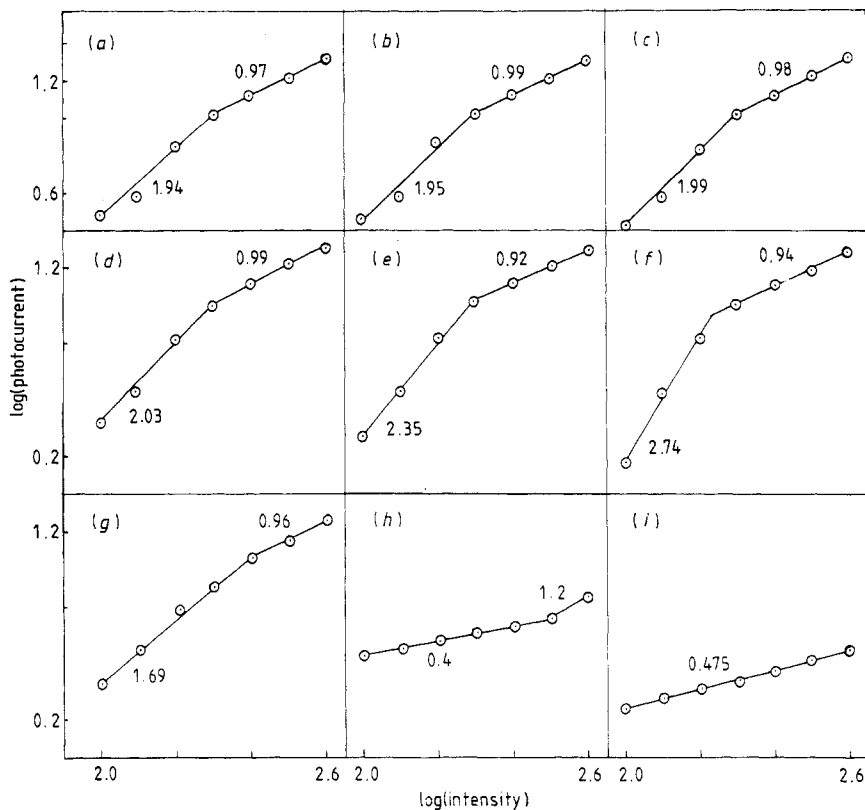
Figure 4. Dependence of photocurrent on excitation intensity at different temperatures for a dye-treated CdS:NaF(8%), Y(0.157%) photoconductor. (a) 133 K, (b) 164 K, (c) 175 K, (d) 201 K, (e) 253 K, (f) 273 K, (g) 281 K, (h) 303 K, (i) 366 K.
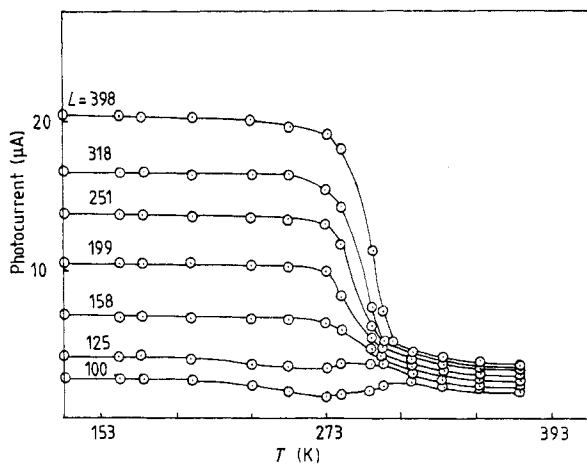
Figure 5. Dependence of photocurrent on temperature at different excitation intensities L for a dye treated CdS:NaF(8%), Y(0.157%) photoconductor.
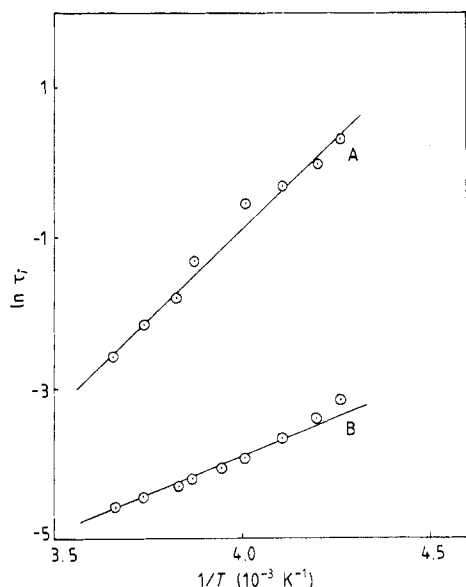
Figure 6. Plot of ln τ_i against reciprocal temperature. Curve A, ln τ_1; curve B, ln τ_2.

a photoconductor having more than one trapping level, the trap depths can be obtained by fitting a function given by equation (1) to the experimental data. By repeating this procedure at a number of temperatures and plotting ln τ_i versus $1/T$, E_i can be evaluated.

In the present case it has been found that two exponentials represent the observed decay curve. From these exponentials τ has been determined at a number of temperatures and is plotted in figure 6. The trap depths calculated for dye treated CdS:NaF, Y are 0.44 eV and 0.18 eV. According to Larach (1965) major hole traps in CdS crystals lie in the range 0.2–1 eV.

Acknowledgments

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