CdS-Type Photoconductivity in ZnTe Crystals

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An investigation of photoconductivity in single crystals of ZnTe has revealed that the mechanism proposed for photoconductivity phenomena in CdS and CdSe may also be applied to ZnTe. These phenomena include the variation of photocurrent with light intensity and temperature, and the infrared quenching of photoconductivity.

SINGLE crystals of ZnTe were grown from the melt by gradient-freezing with added n-type Al or In impurity.[1] These added impurities compensated a small proportion of residual p-type Cu impurity (1–10 parts per million), to produce high-resistivity crystals (10^{11} ohm cm at room temperature). Absorption spectra[1] and photoconductivity excitation spectra[2] (Fig. 1) indicate a band gap of 2.1 ev. Conductivity measurements as a function of temperature in ZnTe with added Cu impurity indicate an activation energy of 0.11 ev for the Cu acceptors.[3]

Figure 2 shows the variation of photocurrent for ZnTe:Cu:Al and ZnTe:Cu:In as a function of temperature. Both crystals show a very rapid increase in photocurrent with increasing temperature at low temperatures, corresponding to an exponential variation of photocurrent with reciprocal temperature with a slope of 0.12 ev. Such a variation of photocurrent with temperature is expected if the density of photoexcited trapped holes[4] below the steady-state hole Fermi level is greater than the density of trapped holes above the Fermi level.[5] On the basis of a model assuming a uniform distribution of traps to a height E_0 above the valence band, a value of $E_0=0.24$ ev (twice the slope) is obtained. This model also predicts that the photocurrent should vary as the square root of light intensity in the temperature range where the photocurrent varies exponentially with reciprocal temperature.

Figure 3 shows the variation of photocurrent as a function of temperature for ZnTe:Cu:In for two light intensities. The numbers indicated on the curves of Figs. 2 and 3 are calculated values for the distance of the hole steady-state Fermi level above the valence band. The results of Fig. 3 indicate that the breaks in the photocurrent-temperature curve occur at an approximately constant value of hole Fermi level.

The variation of photocurrent with light intensity as a function of temperature for the ZnTe crystals is summarized in Table I. The results are as follows:

TABLE I. Variation of photocurrent with light intensity as a function of temperature.

Temperature range[a]	Range of exponent n ($\Delta i \propto L^n$)	Location of Fermi level for change in n[b]
	ZnTe:Cu:Al	
−177° to −5°C	0.77–0.84	0.44 ev
−59° to 126°C	0.97–1.09	
	ZnTe:Cu:In	
−179° to −115°C	0.66–0.83	0.30 ev
−153° to −85°C	1.54–2.00	0.39 ev
−115° to −29°C	1.03–1.20	0.53 ev
−29° to 27°C	1.41–1.66	0.67 ev
3° to 47°C	0.74–0.79	

[a] More than one value of exponent n is found, over the light intensity range used (900 ft-c to 0.4 ft-c), between −59° and −5° for ZnTe:Cu:Al, and between −153° and −115°, −115° and −85°, and 3° and 27°C for ZnTe:Cu:In.
[b] Distance of the hole Fermi level above the valence band.

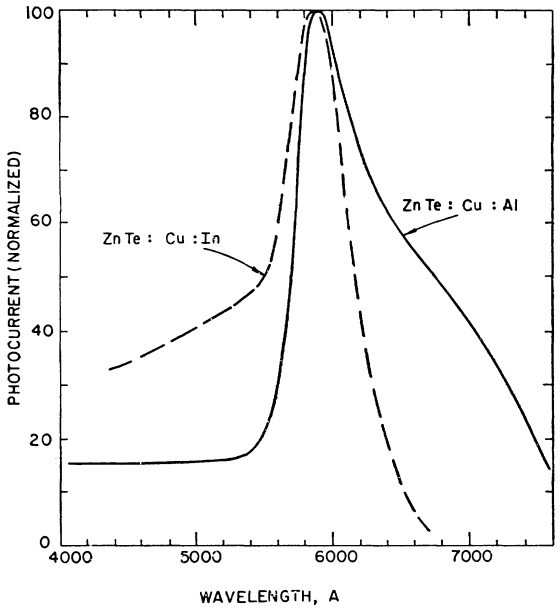

FIG. 1. Photoconductivity excitation spectra for ZnTe:Cu:Al and ZnTe:Cu:In single crystals.

[1] E. L. Lind and R. H. Bube, Bull. Am. Phys. Soc. Ser. II, 1, 110 (1956).
[2] R. H. Bube and E. L. Lind, Bull. Am. Phys. Soc. Ser. II, 1, 110 (1956).
[3] Measurements by M. L. Schultz.
[4] It has not been possible to definitely determine the sign of the majority photoexcited carriers, because of the high resistivity and relatively low photosensitivity of the samples. Rectification tests have generally indicated p-type photocurrents, but it is not impossible that the differences between ZnTe:Cu:Al and ZnTe:Cu:In may arise from p-type photocurrents in one and n-type in the other. In the discussion of the paper, terminology will be phrased to be consistent with p-type photoconductivity.
[5] A. Rose, RCA Rev. 12, 362 (1951).

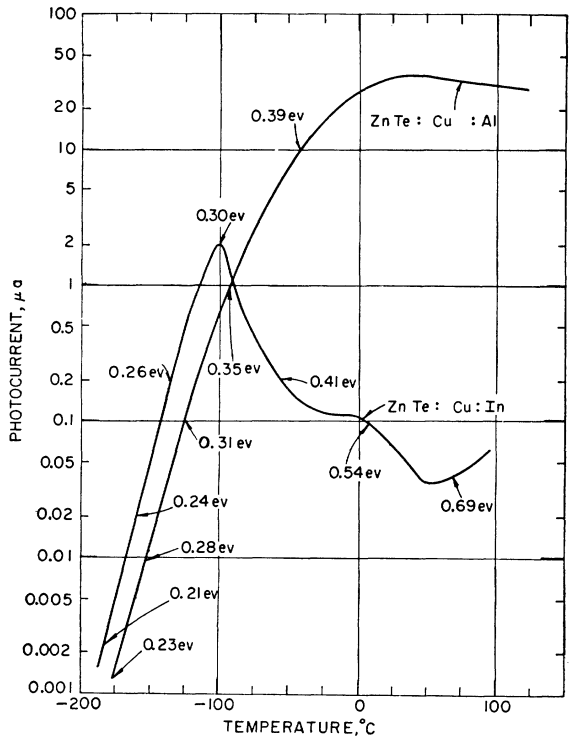

FIG. 2. Photocurrent for ZnTe:Cu:Al and ZnTe:Cu:In as a function of temperature for illumination by 900 ft-c; 100 volts applied.

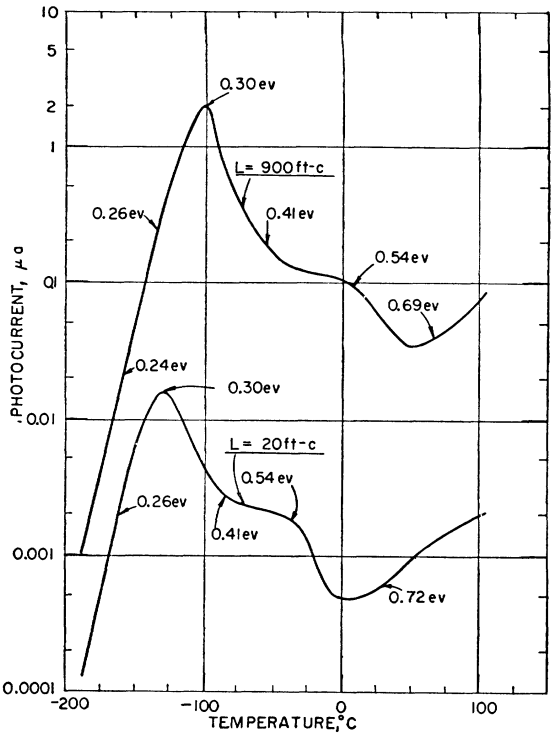

FIG. 3. Photocurrent for ZnTe:Cu:In as a function of temperature for illumination by 900 ft-c and by 20 ft-c; 100 volts applied.

(1) In the temperature range of exponential increase of photocurrent with reciprocal temperature, the lowest values of the exponent n (photocurrent proportional to nth power of light intensity) are found; these values are always higher than the value of one-half expected from the model, but are definitely less than unity. (2) In the temperature range of approximately constant photocurrent, n assumes values near unity. (3) In the temperature range of quenching of photocurrent, n becomes greater than unity. There are two distinct ranges of temperature quenching for the ZnTe:Cu:In crystal. These results therefore reproduce the correlation between temperature quenching of photoconductivity and values of $n>1$, established for CdS and CdSe.[6–8]

At room temperature, infrared quenching in the range between 1.0 and 1.8 microns is observed for ZnTe:Cu:Al, which has not yet shown temperature quenching, but is not found for ZnTe:Cu:In, which has passed through temperature quenching at a lower temperature. These results are also analogous to those found for infrared quenching in CdS and CdSe.

Applying the analysis of photoconductivity discussed in a previous publication[8] to the temperature-shift of the major break point for temperature quenching for ZnTe:Cu:In with variation of light intensity gives an activation energy of 0.34 ev and a capture cross section ratio of 10 for the "sensitizing," small capture cross-section centers.[9] These values may be compared with those of CdSe which are 0.64 ev and a ratio of 8×10^5. The smaller activation energy for ZnTe agrees well with the lower break-point for temperature quenching (near -100°C) compared to CdSe (near 0°C). (In ZnTe:Cu:Al, the "sensitizing" centers must have a larger activation energy even than those in CdSe.) All other pertinent quantities being comparable, the fact that the cross section ratio in ZnTe:Cu:In is about 10^{-5} that in CdSe is compatible with the fact that the maximum sensitivity of ZnTe:Cu:In observed is only about 10^{-4} to 10^{-5} that of sensitive CdSe crystals.

[6] A. Rose, Phys. Rev. **97**, 322 (1955).
[7] R. H. Bube, Proc. Inst. Radio Engrs. **43**, 1836 (1955).
[8] R. H. Bube, J. Phys. Chem. Solids (to be published).

[9] If p-type photoconductivity is assumed, this means that the "sensitizing centers" in ZnTe lie 0.34 ev from the conduction band and have a capture cross section for electrons ten times greater than their capture cross section for holes. If n-type photoconductivity is assumed, the levels lie 0.34 ev above the valence band and have a hole cross section ten times their electron cross section. Photoconductivity in CdSe is n type.