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Dependence of the Hole Ionization Energy of Imperfections in Cadmium Sulfide on the Impurity Concentration

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The variation of the hole ionization energy of imperfections in cadmium sulfide as a function of the impurity concentration has been measured using photoconductivity in a series of CdS:Ga:Cu powders. The Cu concentration varies from 4×10^{17} to 2×10^{20} cm^{-3}, and each sample was prepared with a Cu-concentration to Ga-concentration ratio of 1.05. The hole ionization energy of the sensitizing centers, as determined from the thermal quenching of photoconductivity, decreases from about 1.0 ev for low Cu concentrations to about 0.3 ev for 2×10^{20} Cu cm^{-3}. The results are analogous to other recent findings of small hole ionization energies in CdS and CdSe crystals.

INTRODUCTION

A DECREASE in impurity ionization energy for high impurity concentrations in semiconductors has been well known since the experiments of Pearson and Bardeen[1] with boron impurity in silicon. Similar experiments have not been carried out to date, however, for impurity ionization energies in insulators; of particular interest are those impurities with very large ionization energies, such as the acceptors in sulfides. The present paper uses the phenomenon of thermal quenching of photoconductivity in CdS:Ga:Cu powders to follow the hole ionization energy of sensitizing centers as a function of impurity proportion. It is found that for high impurity concentrations in the range of 10^{18} to 10^{20} cm^{-3}, a large decrease in hole ionization energy does occur.

Previous investigations[2] have indicated that the photosensitivity of CdS photoconductors is associated with the capture of photoexcited holes by centers with a small cross section for subsequent capture of photoexcited electrons. These particular centers may be called sensitizing centers; they are characterized by a single or double negative charge relative to the crystal, and may be associated with either crystal defects such as cation vacancies or with impurities such as copper. Such centers give rise to high photosensitivity only when they are affecting the recombination kinetics of photoconductivity; at temperatures or light levels at which these centers act only as hole-trapping centers, the photosensitivity decreases to a low value determined by other high-probability recombination centers. It can be shown[2] that the beginning of a decrease in sensitivity with decreasing light intensity at constant temperature, or with increasing temperature at constant light intensity, occurs when the hole demarcation level associated with these centers is located at these levels, i.e., when the probability for thermal escape of a hole out of these centers into the valence band is equal to the probability of recombination of a free electron with a hole captured at the centers. Identification of the location of the hole demarcation level for the onset of desensitization, therefore, provides a determination of the hole ionization energy for the sensitizing centers. Since electron currents are being measured, it proves most convenient to calculate the location of the steady-state electron Fermi level for the onset of desensitization from

$$E_{fn}=kT\ln[N_c/n]. \tag{1}$$

Here E_{fn} is the energy difference between the bottom of the conduction band and the steady-state Fermi level, T is the temperature for the onset of desensitization, N_c is the effective density of states in the conduction band, and n is the free electron density at the onset of desensitization. Once the value of E_{fn} is known, the location of the hole demarcation level can be calculated from it[2]:

$$E_{dp}=E_{fn}+kT\ln[S_p/S_n]. \tag{2}$$

Here E_{dp} is the energy difference between the hole demarcation level and the top of the valence band, S_p is the capture cross section of a sensitizing center for a hole when occupied by an electron, and S_n is the capture cross section of a sensitizing center for an electron when a hole has been previously captured. Past research[2] has indicated $S_p/S_n=10^6$ as the value to be taken for sensitizing centers in CdS. This value has been assumed to be constant throughout the series of measurements discussed in this paper; a decrease in S_p/S_n with increasing impurity concentration would only accentuate the decrease in hole ionization energy with impurity concentration, whereas an increase in S_p/S_n of sufficient magnitude to make an appreciable difference is unlikely.

Usual measurements of photoconductivity in single crystals of CdS have been made with fairly low impurity concentrations, i.e., below about 10^{18} cm^{-3}, and the variations of hole ionization energy with impurity concentration described in this paper have not been observed. There have been a number of incidental observations on CdS photoconducting powders, however, which have indicated a change in the hole ionization energy with impurity concentration. Such

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[1] G. L. Pearson and J. Bardeen, Phys. Rev. **75**, 865 (1949).
[2] R. H. Bube, J. Phys. Chem. Solids **1**, 234 (1957).

observations[3–5] have been concerned primarily with the variation of photocurrent as a function of light intensity at various temperatures for different impurity concentrations. Photocurrents varying as a power of light intensity less than or equal to unity were found for low impurity concentrations at both room temperature and liquid nitrogen temperature. When the copper concentration was in the range of about 10^{19} cm^{-3} or higher, however, it was found that the photocurrent varied as a power of light intensity greater than unity at room temperature while still varying as a power of light intensity less than or equal to unity at liquid nitrogen temperature. Thus, these observations indicated that desensitization could occur at room temperature in the materials with high Cu concentrations, whereas for low Cu concentrations desensitization did not occur at room temperature. There have, in addition, been several recent observations of low hole ionization energies in certain specially treated single crystals of CdS and CdSe.[6] In these cases the treatment involved seems likely to lead to situations where at least local concentrations of impurities much higher than normal are encountered. The investigation described in this paper is a detailed study of this phenomenon.

EXPERIMENTAL

A series of CdS:Ga:Cu photoconducting powders were prepared with a [Cu]/[Ga] ratio of 1.05, where the square brackets indicate concentration in moles per mole of CdS. This ratio was shown experimentally to give optimum light-to-dark current ratio for a given [Cu], in agreement with the work of van Santen.[7] Keeping this ratio fixed, the [Cu] was varied from 2×10^{-5} to 10^{-2}; this corresponds to a variation from 4×10^{17} to 2×10^{20} Cu atoms cm^{-3}.

TABLE I. Photoconductivity characteristics of of CdS:Ga:Cu powders.

				$\Delta i \propto V^b$ (for a light intensity of 13 ft-c) b		$\Delta i \propto L^n$ (for an applied voltage of 300 volts) n	
Sample No.	[Cu] moles per mole of CdS	[Ga] moles per mole of CdS	$i_d \propto V^a$ a	High V	Low V	High L	Low L
1	2×10^{-5}	1.9×10^{-5}	4.3	1.6		0.5	
2	4×10^{-5}	3.8×10^{-5}	4.3	1.7	1.4	0.5	
3	10^{-4}	9.5×10^{-5}	4.3	2.1	1.4	0.7	
4	2×10^{-4}	1.9×10^{-4}		2.4	1.5	0.7	1.0
5	4×10^{-4}	3.8×10^{-4}		3.0	1.6	0.7	1.7
7	2×10^{-3}	1.9×10^{-3}		2.7	1.7	1.8	1.0
8	4×10^{-3}	3.8×10^{-3}		1.9		1.0	
9	10^{-2}	9.5×10^{-3}		2.1		1.0	
A[a]						0.5	
B	2×10^{-2}			1.6		0.8	

[a] Sample without added Cu or Ga, fired like other members of the series. Spectrographic analysis by H. Whittaker indicated about 30 ppm Cu present in this starting material.

TABLE II. Cu concentrations after firing and cyanide washing.[a]

Sample No.	% Cu added	% Cu present after firing	% Cu present after cyanide wash
7	0.088	0.090	
8	0.176	0.173	
8*W*			0.165
9	0.440	0.410	
9*W*			0.398
B	0.880	0.787	
BW			0.203

[a] Analysis for Cu concentrations by R. J. Paff and M. C. Gardels.

Standard solutions of Ga and Cu were prepared by dissolving the pure metals in nitric acid. Appropriate volumes of the standard solutions were pipetted into an aqueous slurry of 5 grams of CdS (RCA 33C-291A); this activated slurry was then dried for 15 hours at 110°C, ground and intimately mixed in an agate mortar, and a portion of the mixed sample fired for 1 hour in an atmosphere of H_2S at 850°C and rapidly cooled. Test cells of the fired material were prepared without further grinding or sieving, by mixing the powder with 1% ethyl cellulose in amyl alcohol as a binder and applying to a 0.5×5.0 mm gap between two conducting portions of a glass slide. The various concentrations used are summarized in Table I, together with certain photoconductivity characteristics.

Three samples with the highest Cu concentrations were washed by boiling for one-half hour in a solution of 5% NaOH–10% NaCN to remove unincorporated copper. The powder was washed with water by decantation after the CN treatment until washings were neutral to *p*H paper, and then dried for 15 hr at 105°C. The results of the washings are given in Table II, indicating that, except for the special sample with only Cu and no Ga, essentially all the added Cu was incorporated in the final sample.

Measurements of the photoconductivity properties of the cells were made in an atmosphere of He gas, between the temperatures of liquid nitrogen and 100°C. Spectral response curves were obtained with a Bausch & Lomb grating monochromator; other curves were obtained by excitation from an incandescent source, using neutral wire-mesh filters to vary the light intensity.

RESULTS

General

A summary of the over-all effects of increasing impurity concentration on dark conductivity and photosensitivity is given in Fig. 1. Beyond a critical impurity concentration at room temperature, the photosensitivity decreases rapidly; the decrease sets in at a lower impurity concentration the lower the light

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[3] S. M. Thomsen and R. H. Bube, Rev. Sci. Instr. **26**, 664 (1955).

[4] W. Veith, Z. angew. Physik **7**, 1 (1955).

[5] Tolstoi, Kolomiets, Golikova, and Tsenter, J. Exptl. Theoret. Phys. (U.S.S.R.) **30**, 575 (1956) [translation: Soviet Phys. JETP **3**, 465 (1956).

[6] R. H. Bube, J. Chem. Phys. **30**, 266 (1959).

[7] W. van Santen, paper in the Proceedings of the Brussels Conference, 1958 (unpublished).

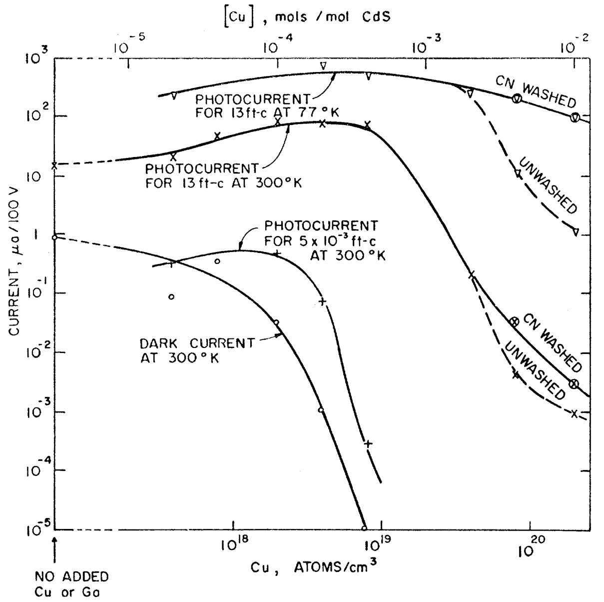

FIG. 1. Variation of dark current, and photocurrents at several light intensities and temperatures, as a function of Cu concentration.

intensity used. At liquid nitrogen temperature, however, there is little variation in photosensitivity over the whole impurity concentration used. Here it must be noted that the CN wash did increase the low-temperature photosensitivity of the high concentration samples,

TABLE III. Types of variation with similar functional dependence.

	Quantity A	as a function of Quantity B	Secondary variable	Fixed parameter
		Type I		
(Fig. 1)	Δi	[Cu]	L	T
(Fig. 4)	Δi	T	[Cu]	L
	Δi	T	L	[Cu]
		Type II		
(Fig. 3)	Δi	L	[Cu]	T
	Δi	L	T	[Cu]
	Δi	[Cu]	T	L

even though analysis shows that the CN wash removed only 3% or 4% of the total added Cu; we shall discuss this point again further on. Because of the nature of the phenomena involved, the experimental curves of Figs. 1, 3, and 4 are very similar to other curves commonly measured at fixed impurity concentration.[2] These interesting correspondences are summarized in Table III.

Spectral Response

Spectral response curves of representative samples are given in Fig. 2 as measured at room temperature. Sample A, with no added impurities, and Sample B, with only a high Cu concentration, both show photosensitivity maximum at the band edge and no strong long-wavelength response characteristic of compensated acceptor centers. All samples containing both Cu and

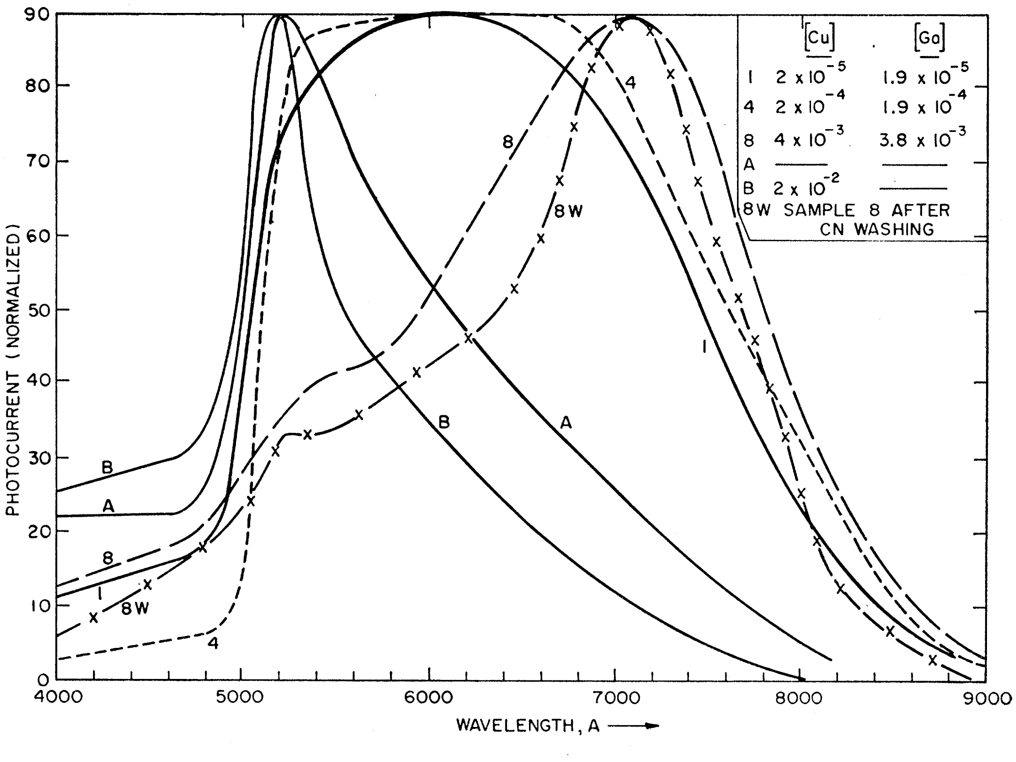

FIG. 2. Spectral response of photoconductivity in selected members of the CdS:Ga:Cu series.

Ga, however, show long-wavelength response out to 9000 A (1.4 ev); when this energy is subtracted from the band gap of CdS (2.4 ev), we obtain the usual level location 1.0 ev above the top of the valence band for sensitizing centers in CdS.[2] In samples with high Cu concentration, the photosensitivity maximum shifts to the infrared; CN-washing does not appreciably alter the spectral response.

Photocurrent *vs* Light Intensity

The variation of photocurrent with light intensity at room temperature for the series is shown in Fig. 3. Breakpoints obtained for Samples 4 and 5 can be used to calculated E_{dp} according to Eqs. (1) and (2). It can be noted that the effect of CN-washing on Sample 8, for example, is not only to increase the photosensitivity, but also to change the behavior of the sample as a whole as if the actual concentration of Cu were nearer to that of Sample 7 (while retaining the same [Cu]/[Ga] ratio). This apparent reduction in Cu as the result of CN-washing is largest in Sample 9, apparent in Sample 8, and negligible for samples with lower impurity concentrations.

Photocurrent *vs* Temperature

The variation of photocurrent with temperature at fixed light intensity for the series is shown in Fig. 4. From estimates of the breakpoint for the onset of desensitization in these curves, values of E_{dp} for Samples 7, 8, 9, 8*W*, and 9*W* can be calculated.

DISCUSSION

The calculation of E_{dp}, i.e., the hole ionization energy for the imperfection centers involved, from the data of Figs. 3 and 4, is summarized in Table IV. Several assumptions are involved, none of which greatly affect the ultimate results. An electron mobility and an effective cell thickness must be assumed in order to calculate the location of E_{fn} from the temperature and photocurrent; it was assumed that the electron mobility was 100 cm^2/volt sec, and that the effective thickness lay in the range of 1 to 100 microns. Values are calculated for the two extremes of this thickness range, and the values for a thickness of 1 micron are plotted as a function of Cu concentration in Fig. 5. The choice of effective thickness makes only a small difference in the values of E_{dp}, especially at high values of Cu concentration.

TABLE IV. Calculated locations of hole demarcation level for onset of desensitization.

Sample No.	T, °K	Δi, μa	E_{dp}, ev $d \approx 100\mu$	E_{dp}, ev $d \approx 1\mu$
		From Δi *vs* L		
4	298	12	0.87	0.75
5	298	66	0.82	0.70
		From Δi *vs* T		
7	240	240	0.63	0.54
8	167	12	0.48	0.42
8*W*	205	190	0.55	0.46
9	110	1.8	0.30	0.29
9*W*	176	100	0.48	0.41

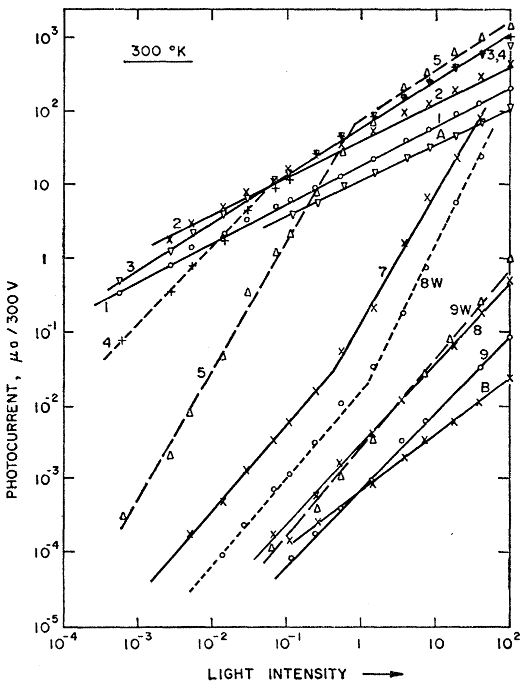

FIG. 3. Photocurrent as a function of light intensity at room temperature for the members of the CdS:Ga:Cu series defined in Table I.

In Fig. 5 the values calculated for the CN-washed samples are plotted at the same Cu concentrations as

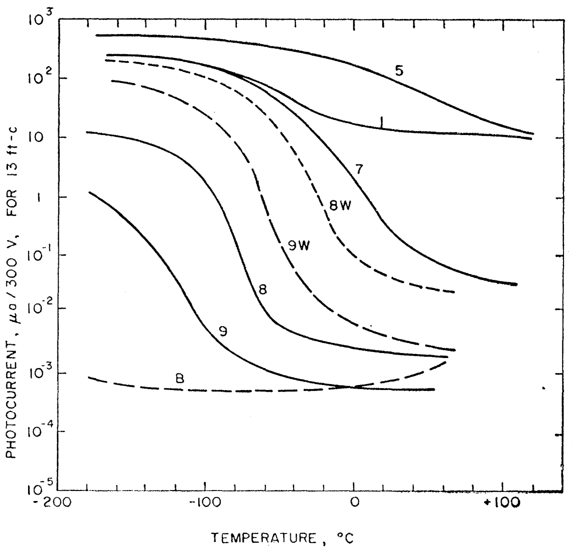

FIG. 4. Photocurrent as a function of temperature at fixed light intensity for the members of the CdS:Ga:Cu series defined in Table I.

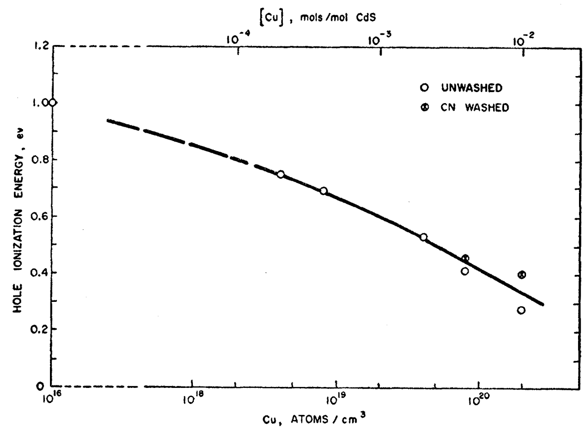

FIG. 5. Hole ionization energy calculated from the data of Figs. 3 and 4 as a function of the Cu concentration, assuming a cell thickness of 1 micron as far as optical absorption is concerned.

the unwashed samples. The following line of reasoning, however, seems valid: (1) the light in the high concentration samples particularly is being absorbed in a portion of the crystallites very near the surface; (2) although CN-washing should not affect incorporated Cu, yet it might well have an effect on the surface layers; (3) if the 3% or 4% of the total Cu which is removed by CN-washing were to come mainly from these surface layers, the actual Cu concentrations in the regions of light absorption would be sufficiently decreased by the CN-washing so that the points for the washed samples in Fig. 5 should actually fall on the same curve as that fitting the points for the unwashed samples.

There are two ways for the hole ionization energy of the imperfection centers to decrease: (1) the imperfection level can effectively move down closer to the top of the valence band, or (2) the top of the valence band can move up closer to the imperfection level. The fact that the long-wavelength cutoff of the spectral response does not change with increasing impurity concentration, as shown in Fig. 2, indicates that the level lying 1.4 ev below the bottom of the conduction band remains present in all the samples.

In considering the second possibility, i.e., that in some manner the top of the valence band moves up toward the imperfection level, it is proper to call attention to the work of Stern and Talley[8] and Stern and Dixon.[9] These authors have shown on a simple hydrogenic impurity model that for high concentrations of compensating impurities, an effective decrease in the width of the band gap can be expected. Since the acceptors in sulfides are by no means hydrogenic impurities, any quantitative comparison would be unjustified. Such a mechanism would require also that the sensitizing imperfection centers be of a different nature than the Cu centers which would raise the top of the valence band by impurity band formation.

The sample with high concentration of Cu and no Ga does not show high conductivity such as might be expected if the hole ionization energy for Cu centers were reduced from 1.0 ev to 0.3 ev as the result of the high concentration of Cu. The decrease of the hole ionization energy seems to occur only when compensated Cu centers are present.

It has been well established that the energy level structure of the Cu center in sulfides is not just a simple level lying 1.0 ev above the top of the valence band, but that there are also lower levels lying in a range about 0.3 ev above the top of the valence band. These lower levels have been detected through optical quenching of photoconductivity,[10] as well as by excitation of infrared luminescence emission and observation of the emission itself.[11] Interaction between centers at high concentration might well cause these lower levels to effectively raise the top of the valence band and produce the observed decrease in hole ionization energy.

If the valence band is considered by some mechanism to be moving upward to decrease the band gap and hence the hole ionization energy, in samples with high impurity concentrations, it would be expected that the band gap would be decreased by the same energy as the hole ionization energy, or by about 0.7 ev (assuming negligible shift of conduction band edge). This would mean that the band gap would be decreased to 1.7 ev, corresponding to a wavelength of 7300 A; the spectral response curves of Fig. 2 show that the photosensitivity maximum, usually associated with the absorption edge, has indeed shifted to about 7100 A.

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[8] F. Stern and R. M. Talley, Phys. Rev. **100**, 1638 (1955).

[9] F. Stern and J. R. Dixon, J. Appl. Phys. **30**, 268 (1959).

[10] R. H. Bube, Phys. Rev. **99**, 1105 (1955).

[11] P. F. Browne, J. Electronics **2**, 154 (1956); see also R. H. Bube, *Photoconductivity of Solids* [John Wiley & Sons, Inc., New York (to be published)], Chap. 11.