RB-47

# PHOTOCONDUCTIVITY SPEED OF RESPONSE FOR HIGH-INTENSITY EXCITATION IN CADMIUM SULFIDE AND SELENIDE

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The rise and decay time of photoconductivity in single crystals, sintered layers, and evaporated layers of cadmium sulfide and cadmium selenide with a wide range of sensitivities, has been measured for excitation at room temperature by a 1900 degree Kincandescent source giving 1740 foot-candles illumination on the sample. The data thus obtained are useful for determining the dependence of the speed of response on the sample's photosensitivity and for estimating a practical upper limit to the speed of response of these photoconductors. The minimum response times found for the samples tested were a rise time of 250 microseconds and a decay time of 300 microseconds for cadmium sulfide, and a rise time of 17 microseconds and a decay time of 8 microseconds for cadmium selenide. Carrier mobilities of between 200 and 1000 $cm^2$/volt sec, trap densities between $10^{13}$ and $10^{15}$ per $cm^3$, recombination center densities of about $10^{15}$ per $cm^3$, recombination cross-sections of about $2 \times 10^{-19}$ $cm^2$ for recombination through centers in the forbidden gap, and recombination cross-sections of about $10^{-20}$ $cm^2$ for free electron-free-hole recombination, are indicated.

## Introduction

When the density of free electrons in an n-type photoconductor is greater than the density of trapped electrons[1], the measured decay time of photocurrent is equal to the lifetime of a free electron, and is related to the gain and to the mobility of the free electrons according to the equation[2]:

$$\text{Gain} = t^* \mu V / L^2 \qquad (1)$$

where the gain is the number of electrons passing through the crystal between the electrodes per unit time for one photon absorbed per unit time, $t^*$ is the measured decay time, $\mu$ is the mobility of a free electron, V is the applied voltage, and L is the distance between electrodes. To obtain the condition where the density of free electrons exceeds the density of trapped electrons for CdS and CdSe, it is usually necessary to use high intensity excitation.

Recombination under these circumstances may follow one of three possible schemes: (a) recombination with bimolecular kinetics may occur through levels in the forbidden gap lying below the hole demarcation level[3] appropriate for such levels, (b) recombination with monomolecular kinetics may occur through levels in the forbidden gap lying above the hole demarcation level, or (c) recombination with bimolecular kinetics may occur between free electrons and free holes when the hole demarcation level lies below the levels in the forbidden gap and the density of free carriers exceeds the density of these levels. Since the hole de-

[1] In this bulletin the expression "trapped electrons" refers to electrons excited by the incident illumination, which are trapped in high-lying levels without taking part in the recombination process until they are thermally raised into the conduction band.

[2] A. Rose, *RCA Rev. 12*, 362 (1951).

[3] R.H. Bube, *Proc. I.R.E. 43*, 1836 (1955).

marcation level lies below the major set of recombination levels in CdS and CdSe (those levels which are responsible for the high photosensitivity[3]) for the light intensities used recombination may follow either of the two latter schemes outlined above.

When the density of free electrons is less than the density of trapped electrons, the measured decay time will be larger than the lifetime of a free electron. If the measured decay time is substituted in Eq. (1) under such circumstances, therefore, the gain calculated from the right side of the equation using the known value of the electron mobility, will be larger than the observed gain. From the value of the free electron density at which the measured decay time becomes equal to the true electron lifetime, as indicated by the applicability of Eq. (1) to all measured quantities, it is possible to estimate the density of trapping centers.

When the density of free electrons is greater than the density of trapped electrons and monomolecular kinetics is found, the capture cross-section of the recombination centers with levels in the forbidden gap is given by:

$$S = (t^* v N')^{-1} \qquad (2)$$

where S is the capture cross-section for electron capture by recombination centers which have already captured a hole, $t^*$ is the measured decay time, v is the thermal velocity of an electron, and N' is the density of empty recombination centers. Since the occupancy of these centers lying above the corresponding hole demarcation level is determined by the ratio of the capture cross-section for electrons to that for holes, and since these levels have a much larger cross-section for holes than for electrons[3], the density of empty recombination centers will be (for practical purposes) equal to the density of recombination centers. It is possible to estimate the density of recombination centers (assuming that this density is greater than that for trapping centers) from the value of the free electron density at which the recombination kinetics change from monomolecular to bimolecular.

When the density of free electrons is greater than the density of trapped electrons and bimolecular kinetics is found, the capture cross-section for free-electron-free-hole recombination will be given by:

$$S' = (t^* v n_0)^{-1} \qquad (3)$$

where S' is the recombination cross-section for free electrons and free holes, and $n_0$ is the density of free electrons at the beginning of the decay.

## Experimental

Measurements were made on single crystals of "pure" CdS, "pure" CdSe, CdS:Cl:Cu, and CdSe:I:Cu[4,5]; on sintered layers of CdS:Cl:Cu and CdSe:Cl:Cu[6]; and on evaporated layers of CdSe:Cl:Cu[7]. Ohmic contacts to the crystals were provided with melted indium electrodes[8]; contacts to the sintered and evaporated layers were made with silver paste. Samples were selected to show a wide range of photosensitivities.

The excitation source was a GE(6v, 9 amp) oscillograph lamp with a 1mm tungsten ribbon filament which was focused with unity magnification on a rotating wheel light chopper, and which gave an illumination of 1740 foot-candles on the sample when operated at the indicated rating. Two rotating wheels were used: wheel 1 was a lucite wheel, 4 inches in radius, completely opaque except for one clear 3 degree sector, 5 mm wide at the circumference of the wheel; wheel 2 was a lucite wheel, 4 inches in radius, completely clear except for one opaque 3 degree sector. The photocurrents were displayed on a model 512 Tektronix oscilloscope.

Fig. 1 illustrates the way in which the measurements were made. Fig. 1a shows the variation of light on the sample with time for wheel 1; Fig. 1b shows the corresponding variation of current through the sample with time.

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[4]. Prepared by S.M. Thomsen and C.J. Busanovich.

[5]. R.H. Bube and S.M. Thomsen, *J. Chem. Phys.* 23, 15 (1955)

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

[7]. Prepared by S. Ochs and S.M. Thomsen.

[8]. R.W. Smith, *Phys. Rev.* 97, 1525 (1955).

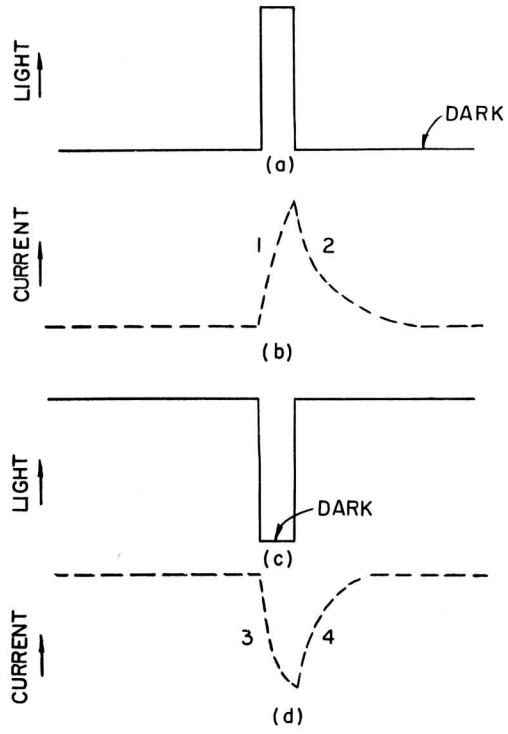


*Fig. 1 - Schematic representation of the chopped-light pattern and the corresponding variation of current, used to determine the speed of response.*

The sample is subjected to a period of darkness long compared to the rise or decay times to be measured; this period varies between 12 and 500 milliseconds, depending on the speed at which the wheel is rotated. After this comparatively long period of darkness, the sample receives a short pulse of light. Two quantities are measured: (a) the rise time after a comparatively long period of darkness (curve 1), and (b) the decay time after a short pulse of light (curve 2). The rise time is determined by varying the speed at which the wheel is rotated until the photocurrent rises one-half of the way from the dark current to the steady current which would be obtained from continuous illumination, during the length of the light pulse. The pulse-decay-time is taken as the time required for the photocurrent to decrease one-half the way from the value of the photocurrent after a 100-microsecond light pulse to the dark current value.

Fig. 1c shows the variation of light on the sample with time for wheel 2; the corresponding variation of current with time is given in Fig. 1d. The sample is under continuous illumination for a time long compared to the rise and decay times to be measured; the illumination is interrupted for a short time. Again two quantities are measured: (a) the decay time after a comparatively long period of illumination (curve 3), and (b) the rise time after only a short period of darkness (curve 4). The decay time is determined by varying the speed at which the wheel is rotated until the photocurrent decays to one-half its value for continuous illumination, during the length of the dark period. The pulse-rise-time is taken as the time required for the photocurrent to increase one-half the way from the value of the photocurrent after a 100-microsecond period of darkness to the equilibrium value for continuous illumination.

## Discussion of Results

*Speed of Response after Long Period of Excitation or Darkness*

Data are summarized in Table I and Fig. 2. The headings of the various columns of Table I need a few additional comments. The computed

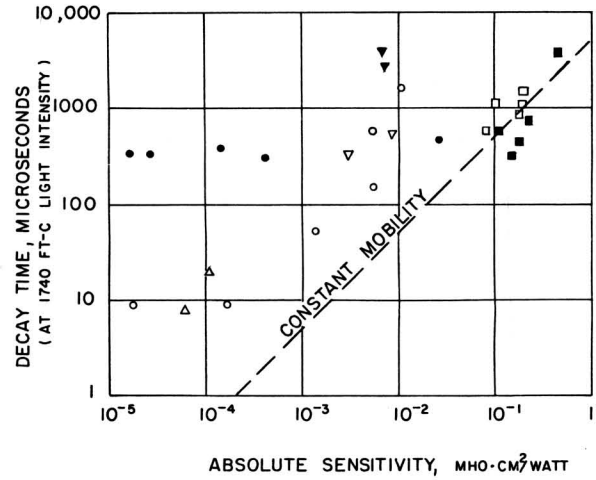


*Fig. 2 - Summary of the data of Table I. Decay time as a function of the sensitivity, for illumination by 1740 foot-candles, for various samples of (1) ● "pure" CdS crystals, (2) ■ CdS:Cl:Cu crystals, (3) ▼ sintered layers of CdS:Cl:Cu, (4) ○ "pure" crystals, (5) □ CdSe:I:Cu crystals, (6) ▽ sintered layers of CdSe:Cl:Cu, and (7) evaporated layers of CdSe:Cl:Cu.*

**Table I**

Speed of Response and Sensitivity Data
(Illumination = 1740 foot-candles)

| No. | Type | Length between Electrodes, mm | Sensitivity, mho $cm^2$/watt | Rise Time, microsec. | Decay Time, microsec. | Gain at 2V | Theor. $t^*\mu$ / Decay Time |
|---|---|---|---|---|---|---|---|
| 1 | "Pure" CdS | 1.0 | $1.5 \times 10^{-5}$ | 392 | 317 | 0.0075 | 0.12 |
| 2 | " | 0.5 | $2.7 \times 10^{-5}$ | 250 | 317 | 0.054 | 0.21 |
| 3 | " | 0.5 | $1.3 \times 10^{-4}$ | 467 | 383 | 0.23 | 0.76 |
| 4 | " | 0.6 | $4.1 \times 10^{-4}$ | 417 | 300 | 0.56 | 3.3 |
| 5 | " | 0.7 | $2.7 \times 10^{-2}$ | 665 | 492 | 26 | 130 |
| 6 | CdS:Cl:Cu | 0.8 | $1.1 \times 10^{-1}$ | 475 | 575 | 86 | 480 |
| 7 | " | 0.6 | $1.3 \times 10^{-1}$ | 485 | 315 | 176 | 1000 |
| 8 | " | 0.8 | $1.7 \times 10^{-1}$ | 392 | 450 | 133 | 945 |
| 9 | " | 0.6 | $2.2 \times 10^{-1}$ | 685 | 735 | 294 | 720 |
| 10 | " | 0.6 | $4.3 \times 10^{-1}$ | 1750 | 3830 | 580 | 273 |
| 11 | Sintered CdS:Cl:Cu | 0.7 | $6.5 \times 10^{-3}$ | 565 | 3830 | 6.7 | 4.3 |
| 12 | " | 0.75 | $7.3 \times 10^{-3}$ | 375 | 2670 | 6.3 | 6.6 |
| 13 | "Pure" CdSe | 0.8 | $1.9 \times 10^{-5}$ | [17] | [9] | 0.01 | [3.7] |
| 14 | " | 0.7 | $1.8 \times 10^{-4}$ | [20] | [9] | 0.13 | [35] |
| 15 | " | 0.6 | $1.3 \times 10^{-3}$ | 216 | [52] | 1.2 | [42] |
| 16 | " | 0.5 | $5.5 \times 10^{-3}$ | 530 | 137 | 6.7 | 45 |
| 17 | " | 0.9 | $5.7 \times 10^{-3}$ | 580 | 580 | 2.4 | 17 |
| 18 | " | 0.6 | $1.1 \times 10^{-2}$ | 890 | 1500 | 10 | 12 |
| 19 | CdSe:I:Cu | 0.5 | $8.0 \times 10^{-2}$ | 350 | 600 | 110 | 230 |
| 20 | " | 0.7 | $1.0 \times 10^{-1}$ | 610 | 1120 | 75 | 163 |
| 21 | " | 0.3 | $1.7 \times 10^{-1}$ | 425 | 915 | 688 | 330 |
| 22 | " | 0.7 | $1.8 \times 10^{-1}$ | 570 | 1040 | 128 | 300 |
| 23 | " | 1.2 | $1.9 \times 10^{-1}$ | 570 | 1270 | 46 | 260 |
| 24 | Sintered CdSe:Cl:Cu | 1.0 | $3.0 \times 10^{-3}$ | 290 | 325 | 1.0 | 16 |
| 25 | " | 0.7 | $8.7 \times 10^{-3}$ | 250 | 520 | 5.9 | 28 |
| 26 | Evaporated CdSe:Cl:Cu | 0.6 | $6.3 \times 10^{-5}$ | [84] | [8] | 0.06 | [14] |
| 27 | " | 0.5 | $1.1 \times 10^{-4}$ | 217 | [20] | 0.16 | [10] |

Note: Extrapolated values are enclosed in brackets.

value of the gain is obtained from a measured value of photocurrent per unit incident energy in units of microamps/watt. For light of 5000Å wavelength, a gain of unity corresponds to $4 \times 10^5$ microamps/watt. Correction for the fact that the maximum photosensitivity does not lie at 5000Å gives, for a gain of unity, $4.1 \times 10^5$ microamps/watt for CdS with sensitivity peak at 5150Å, and $5.8 \times 10^5$ microamps/watt for CdSe with sensitivity peak at 7300Å. Measurements with an optical pyrometer gave a temperature of 1900 degrees K for the radiation temperature of the source; the energy output of the source as a function of wavelength was assumed to be that of a 1900degree Kblack body, giving an output at 7300Å about fourteen times that at 5150Å. Correction for this difference in output was applied in the calculation of the gain. The

use of these corrections as outlined here assumes that the major contribution to the photosensitivity comes from light in a narrow band around 5150Å for CdS and around 7300Å for CdSe; this assumption is generally justified for most samples of these photoconductors.

The sensitivity is a value which expresses the inherent sensitivity of the material for illumination by 1740 foot-candles, independent of applied voltage or geometry. It is obtained by multiplying the mhos per watt by the square of the distance between electrodes.

The theoretical value of $t^*\mu$ is obtained from the measured gain and Eq. (1). If the density of free electrons is less than the density of trapped electrons, the ratio of the theoretical value of $t^*\mu$ to the measured decay time will give a number which is smaller than the true value of the electron mobility.

Inspection of the data of Table I and Fig. 2 shows that the smallest rise and decay times observed for CdS were 250 and 300 microseconds respectively, and for CdSe, 17 and 8 microseconds respectively. The speed of response of CdS is relatively independent of sample sensitivity for all except the most sensitive crystals; whereas the speed of response of CdSe increases with decreasing sample sensitivity over a wide range.

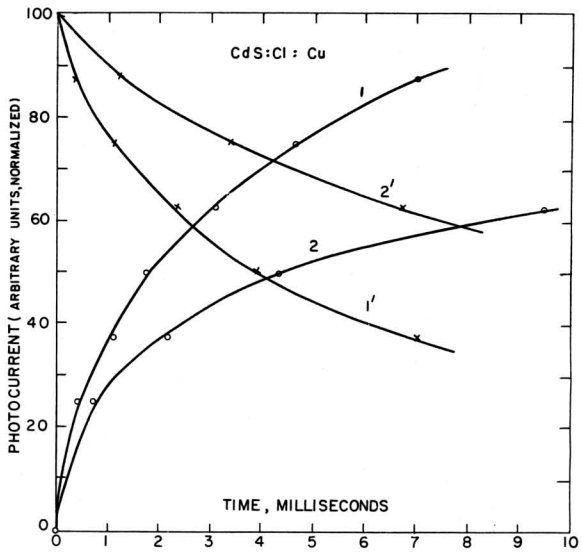


*Fig. 3 - Rise and decay curves for CdS:Cl:Cu crystal (No. 10) for 1740 foot-candles illumination (curves 1 and 1') and 240 foot-candles illumination (curves 2 and 2').*

Fig. 3 and 4 give typical rise and decay curves for sensitive CdS:Cl:Cu and CdSe:I:Cu crystals.

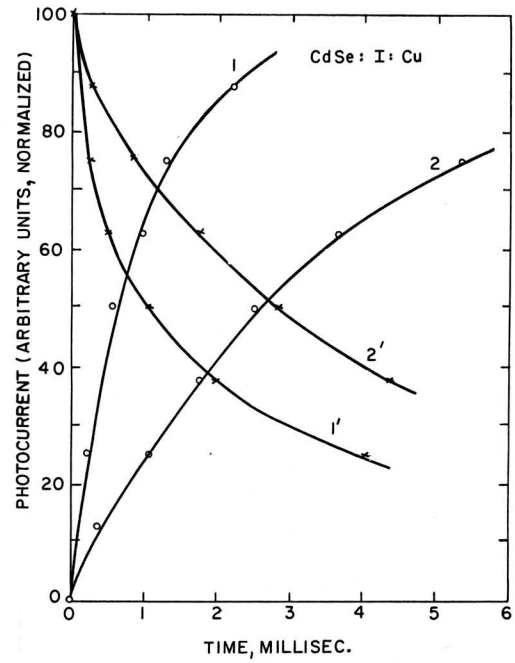


*Fig. 4 - Rise and decay curves for CdSe:I:Cu (No. 23) for 1740 foot-candles illumination (curves 1 and 1') and 240 foot-candles illumination (curves 2 and 2').*

*Speed of Response as a Function of Light Intensity*

The photocurrents, rise times, and decay times for a light intensity of 1740 foot-candles illumination were compared to those for 240 foot-candles illumination. The results can be summarized in three categories: (a) for all the samples except the sensitive CdS:Cl:Cu and CdSe:I:Cu single crystals, the photocurrent varies with a power of the light intensity near to unity, and the small value of the ratio of theoretical $t^*\mu$ to measured decay time indicates that the decay process is dominated by trapping; (b) for samples 6 through 9 of the CdS:Cl:Cu single crystals, the photocurrent varies with a power of the light intensity near to unity, and the large value of the ratio of theoretical $t^*\mu$ to measured decay time, agreeing approximately with the known electron mobility, indicates that the measurements are in the region of monomolecular recombination between free electrons and recombination cen-

ters; and (c) for sample 10 of CdS:Cl:Cu and samples 19 through 23 of CdSe:I:Cu single crystals, the photocurrent varies as the square root of the light intensity and the decay time varies as the inverse square root of the light intensity; the large value of the ratio of $t^*\mu$ to the measured decay time indicates that these measurements are in the region of bimolecular recombination between free electrons and free holes.

A mobility of 270 $cm^2$/volt sec is calculated from the experimental data for CdS:Cl:Cu sample 10, with values between 480 and 1000 $cm^2$/volt sec for the other sensitive CdS:Cl:Cu crystals tested. A mobility between 160 and 330 $cm^2$/volt sec is indicated for the sensitive CdSe:I:Cu crystals. The values of mobility found for the CdS:Cl:Cu crystals are in particular somewhat larger than the values which average at about 200 $cm^2$/volt sec, reported in the literature.[9] The discrepancy may be caused to some extent by the additional sensitivity of these CdS:Cl:Cu crystals in the red portion of the spectrum because of the Cu impurity, which has been neglected in assuming that the photosensitivity in CdS is caused by light in a narrow band around 5150Å. Similarly some of the theoretical values of $t^*\mu$ for insensitive crystals may be too small because such crystals have a response below the absorption edge only, without a maximum at the edge.[9]

Fig. 5 is a replot of Fig. 1 with decay time at 1740 foot-candles illumination plotted against the density of conduction electrons (assuming a mobility of 500 $cm^2$/volt sec for the calculation) for the various crystals and layers of Table I. The data may analyzed as follows:

(1) The density of traps in CdS is about $10^{14}/cm^3$ and the density of recombination centers in sensitive CdS crystals is about $10^{15}/cm^3$. When the density of electrons is less than $10^{14}/cm^3$ the decay time is dominated by trapping, and for the level of excitation used, is maintained approximately constant at about 300 microseconds, indicating that the density of traps is approximately independent of the sample's sensitivity. When the density of free electrons is between about $10^{14}$ and $10^{15}/cm^3$, recombination is dominated by free electrons recombining with holes at recombination centers. When the density of free electrons exceeds $10^{15}/cm^3$, bimolecular recombination between free electrons and free holes dominates. A value for the capture cross-section of a recombination center, S, may be calculated from Eq. (2) from the data for samples 6 through 9 to give a value of $2 \times 10^{-19}$ $cm^2$. A value for the recombination cross-section for free electrons and free holes, S', may be calculated from Eq. (3) for sample 10 to give $10^{-20}$ $cm^2$.

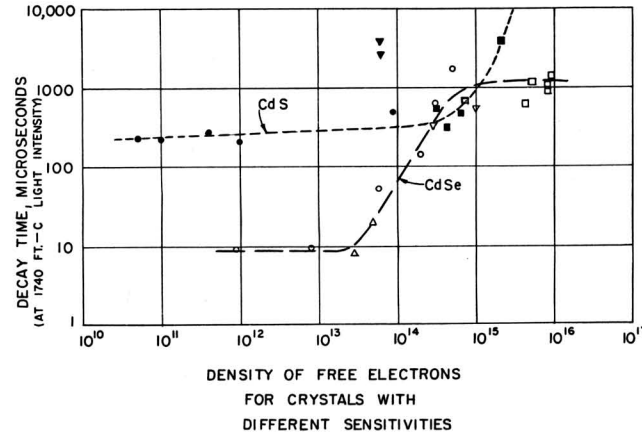


*Fig. 5 - Decay time as a function of the density of conduction electrons, for illumination by 1740 foot-candles, for various samples of (1) ● "pure" CdS Crystals, (2) ■ CdS:Cl:Cu crystals, (3) ▼ sintered layers of CdS:Cl:Cu, (4) ○ "pure" CdSe crystals, (5) □ CdSe:I:Cu, crystals, (6) ▽ sintered layers of CdSe:Cl:Cu, and (7) △ evaporated layers of CdSe:Cl:Cu.*

(2) The density of traps in insensitive CdSe is about $2 \times 10^{13}/cm^3$, but this density increases to about $10^{15}/cm^3$ as the sample's sensitivity increases. The density of recombination centers must be about the same order of magnitude, for bimolecular recombination between free electrons and free holes dominates when the density of free electrons exceeds $10^{15}/cm^3$. An average value for the recombination cross-section for free electrons and free holes, S', may be calculated from Eq. (3) for samples 19 through 23 to give $9 \times 10^{-21}$ $cm^2$, essentially the same as for CdS.

It must be emphasized that the dependence of decay time on the density of free electrons shown in Fig. 5 is found only when the density of electrons is varied by choosing different crystals with different sensitivities, all mea-

[9] R.H. Bube, *Phys. Rev.*, March 1 (1956).

surements being made at the same light intensity. Variation of the density of electrons by varying the light intensity for a given crystal will clearly give a quite different dependence of decay time on free electron density.

As a demonstration that the speed of response can be increased beyond that reported above, by increasing the light intensity further, a sensitive CdSe:I:Cu crystal (No. 21) was illuminated by a secondary source of light to give a photocurrent of 4 milliamperes. The rise and decay times of photocurrent above this reference value due to the 1740 foot-candle source (which gave an additional 2.4 milliamperes photocurrent) were then measured to be 200 and 390 microseconds respectively. Thus under these conditions, the speed of response is more than twice as great as for the 1740 foot-candles illumination alone, and the response sensitivity to that illumination is also slightly less than half that to the 1740 foot-candles illumination alone.

*Speed of Response after Short Pulses of Excitation or Darkness*

Measurements of the pulse-rise-time and pulse-decay-time (see Fig. 1d, curve 4; Fig. 1b, curve 2, respectively) were compared with the rise and decay times after many milliseconds of darkness or light. Decay times were in general only slightly affected by the length of the preceding light period; decay times after the 100 microsecond light pulse were slightly smaller, the largest effect of this type observed for any sample being a factor of four. The rise times of "pure" CdS crystals were affected only slightly by the length of the preceding period of darkness, but the rise times of activated CdS:Cl:Cu photoconductors were from three to nine times smaller after the 100-microsecond period of darkness than after a long period of darkness. Rise times for activated CdSe photoconductors were two to eight times smaller, and rise times for "pure" CdSe crystals were fifteen to thirty times smaller. The increase in the rise time of photocurrent with increasing length of the preceding dark period has previously been reported[3,10] and ascribed to the time needed for redistribution of filled and empty levels in the forbidden gap as the hole demarcation level moves down below the recombination centers previously discussed in this bulletin, the net result being an increase in the photosensitivity.

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

R. H. Bube