correlation can be made between the principal trap depths in cadmium sulfide crystals without added impurity and the peaks of the low-temperature spectrum of the photostimulation of photoconduction for CdS:Ag crystals reported by Lambe.[9] Although Lambe ascribed these peaks to absorption by the silver, the present data indicate that they may be fundamental to cadmium sulfide itself.

A transition in $n$ with increasing light intensity from a value near unity to a value near one-half was shown, for many cadmium sulfide crystals, to occur, not when the density of free electrons exceeds the density of trapped electrons, but when the Fermi level is about to rise into the main group of characteristic traps.

Further research on surface-excited and volume-excited photoconduction might well be directed toward (1) measurements of electron mobility as a function of excitation wavelength for a crystal with a large sensitivity ratio to determine whether the mobility for surface excitation is the same as that for volume excitation, (2) measurements of photoconduction phenomena for cadmium sulfide crystals in controlled atmospheres of other gases, and (3) measurements on cadmium selenide crystals which show a large transition from an $n$ greater than unity to an $n$ less than unity.[16,17]

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[17] R. H. Bube, paper in *Proceedings of the Conference on Photoconductivity, Atlantic City, 1954* (John Wiley and Sons, Inc., New York, to be published).

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# Radiation Resulting from Recombination of Holes and Electrons in Silicon

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Radiation produced by the recombination of excess electrons and holes in silicon has been examined both at room temperature and at 77°K. The radiation obtained at room temperature is shown to be an intrinsic property of silicon. It is probably due to indirect transitions of electrons from the conduction band minima to the valence band with phonon cooperation. Additional radiation is found at 77°K which is structure-sensitive. This radiation is shown to be produced by the recombination of excess carriers with un-ionized donor and acceptor impurities. Differences between the photon energies associated with the maximum photon emission of intrinsic and extrinsic radiation are in semiquantitative accord with accepted values of ionization energies of the donor and acceptor impurities introduced in the crystal-growing process.

THE existence of radiation due to the recombination of holes and electrons in silicon at room temperature has been reported by Haynes and Briggs.[1] It was found that a maximum intensity occurred at about 1.1 microns. The experiments to be described not only show that this radiation is an intrinsic property of silicon but also demonstrate that other radiation occurs which is structure-sensitive.

Recombination radiation was produced by applying current pulses to grown silicon *p-n* junctions with current flow from *p*- to *n*-type. Under these conditions large concentrations of minority carriers are produced in the immediate vicinity of the junction. The radiation resulting from the recombination of these carriers was analyzed with a Perkin-Elmer spectrometer and detected by a lead sulfide cell. The spectral distribution was corrected for the over-all spectrometer and detector response by comparing the observed intensities with those obtained from a tungsten lamp of known color temperature used as a radiation source.

The samples used have dimensions of 1.5×1.0 cm. They were cut with the junction parallel to the long dimension and range in thickness from 0.15 to 0.010 cm. The large surfaces were ground flat and optically polished.

The results obtained by using a silicon sample containing boron and arsenic as added impurities are shown in Fig. 1. Here we have plotted the relative number of emitted photons per unit energy interval per unit time as a function of the photon energy in electron volts for three conditions: (1) Using a *p-n* junction specimen 0.01 cm thick at room temperature (dashed curve), (2) using a sample 0.12 cm thick at room temperature (dotted trace), and (3) with either sample at liquid nitrogen temperature (solid curve). The data points for the dashed curve have been included to show the degree of delineation and all three curves have been normalized. It may be observed that both the dashed and dotted curves have a maximum at 1.088 ev and coincide for energies less than 1.10 ev. This implies that the radiation spectrum of photons having energies less than 1.10 ev is little altered in the process of emerging from the silicon sample 0.12 cm thick. Calculation[2] using optical absorption data[3] indicates that the radiation

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[1] J. R. Haynes and H. B. Briggs, Phys. Rev. **86**, 647 (1952).

[2] It is assumed that the alteration of the spectrum in escape from the silicon is a function only of the product of absorption constant and sample thickness.

[3] H. B. Briggs, Phys. Rev. **77**, 727 (1950); Fan, Shepherd, and Spitzer, in *Proceedings of the Photoconductivity Conference, Atlantic City*, 1954 (to be published); Dash, Newman, and Taft, Phys. Rev. **98**, 1192 (1955); G. G. Macfarlane and V. Roberts, Phys. Rev. **98**, 1865 (1955).

from the 0.010-cm thick sample (dashed line) is as little altered for photon energies less than 1.18 ev.[4]

The effect of cooling the samples to 77°K is also shown in Fig. 1 (solid trace). Three maxima are seen to occur: a very sharp peak[5] at 1.100 ev and two smaller maxima at 1.072 and 1.038 ev. This trace is obtained with either sample, as expected, since the absorption constant is reduced from the room temperature values by two orders of magnitude and the radiation distribution is consequently unaltered in escaping from the samples.

The room temperature radiation and that having a maximum at 1.10 ev at 77°K are an intrinsic property of silicon, since the photon distributions have been found to be independent of the nature of the added impurities and are consistent with the optical absorption constants and the principle of detailed balancing as used by van Roosbroeck and Shockley.[6] Because this radiation occurs at the first absorption edge, it should be due to indirect transitions of electrons from the (1,0,0) minimum to the top of the valence band involving phonon cooperation (indirect intrinsic radiation). No radiation due to direct transitions (direct intrinsic radiation) was found and none is expected from the absorption data. In this respect the radiation from silicon differs from that from germanium.[7]

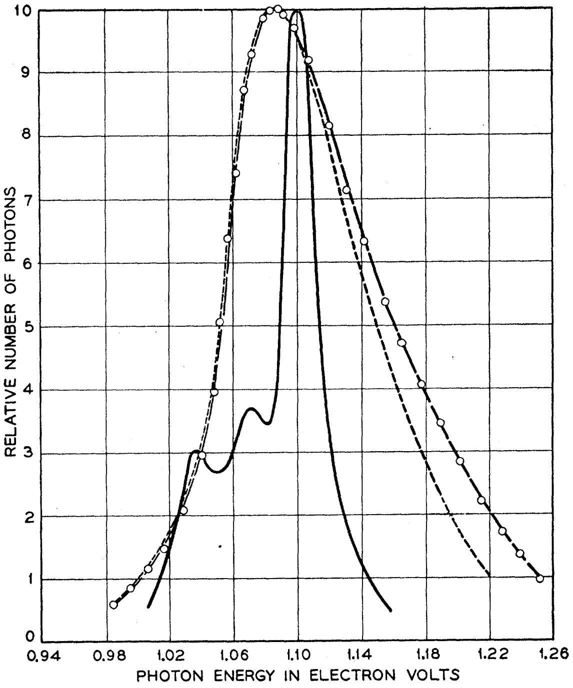

FIG. 1. Relative number of emitted quanta per unit energy interval per unit time as a function of photon energy. The samples used were cut from a single crystal of silicon containing arsenic and boron (conductivity: $n=18$ ohm$^{-1}$ cm$^{-1}$, $p=5$ ohm$^{-1}$ cm$^{-1}$). The data points were obtained at room temperature with a sample 0.010 cm thick. The dotted curve was obtained at room temperature with a sample 0.12 cm thick. The solid trace is characteristic of either sample at 77°K.

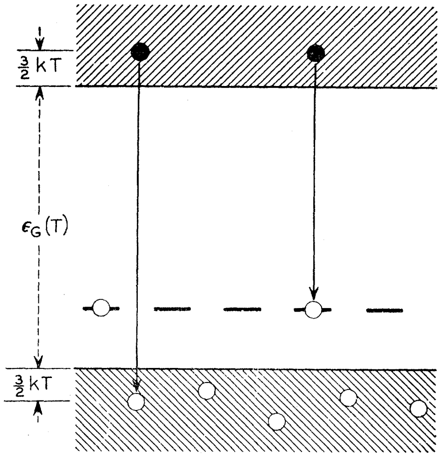

FIG. 2. Energy level diagram.

The additional maxima obtained at 1.072 and 1.038 ev are characteristic of the added impurities and are, therefore due to extrinsic radiation.

The processes involved in the production of intrinsic and extrinsic radiation can be visualized with the aid of the energy level diagram shown in Fig. 2, which is drawn for a $p$-type region. The holes, which are indicated by open circles, are shown at an average thermal energy of $\frac{3}{2}kT$ below the top of the valence band. The acceptors, represented by dashes, are shown partially ionized. With this condition, injected electrons (solid circles at an average energy of $\frac{3}{2}kT$ above the conduction band) may recombine either with a hole in the valence band or with one on an acceptor. For the first alternative (intrinsic radiation), the emitted photon will have an energy $h\nu_1=E_g(T)+3kT-\hbar\omega$, where $\hbar\omega$ is the phonon energy required for conservation of crystal momentum. The sign of $\hbar\omega$ is negative since the transition is usually accompanied by phonon emission, there being a negligible number of phonons of the required energy available for absorption, even at room temperature. For the second alternative (extrinsic radiation), phonon cooperation will also be required, at least where acceptors of low ionization energy are concerned, so that the emitted photon will have an energy $h\nu_2=E_g(T)-E_i+\frac{3}{2}kT-\hbar\omega$, where $E_i$ is the ionization energy of the acceptor.

From the photon energy associated with the intrinsic radiation maximum at 77°K and 295°K and on the assumption that $E_g(T)=E_g(0)-\beta t$, where $\beta$ is the temperature coefficient of the energy gap,[8] we calcu-

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[4] No correction has been made for the effect of finite spectrometer slit width. The correction to the width at half-intensity of this relatively broad curve due to this cause is, however $<1\%$.

[5] This maximum is appreciably narrower than measured values indicate, since the effective slit width of the spectrometer (0.014 ev) has increased the measured width at half-intensity by $\sim 20\%$.

[6] W. van Roosbroeck and W. Shockley, Phys. Rev. **94**, 1558 (1954).

[7] J. R. Haynes, Phys. Rev. **98**, 1866 (1955).

[8] If the energy gap varies quadratically in this range as indicated in reference 12, the results will be little effected.

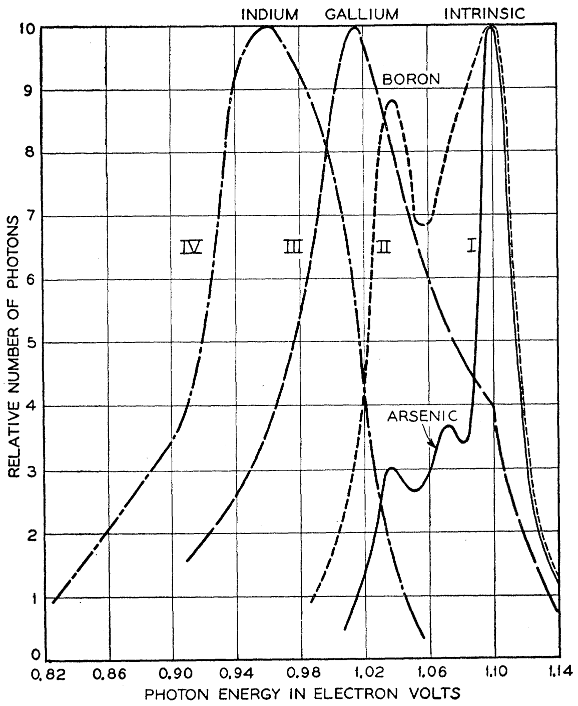

FIG. 3. Effect of added donor or acceptor impurities on recombination radiation. The maxima are labeled with the name of the element believed responsible. See text for details.

late that $\beta=3.3\times10^{-4}$ ev deg$^{-1}$ and $E_g(0)=1.105+\hbar\omega$. If the (1,0,0) minimum lies $\sim\frac{3}{4}$ of the distance from the center to the edge of the Brillouin zone as indicated by Kohn[9] $\hbar\omega\sim0.06$ ev[10] so that $E_g(0)\simeq1.165$ ev and $E_g(295°\text{K})\simeq1.07$ ev. These values are in good agreement with those found by Morin and Maita[11] as determined from measurements of Hall constant and conductivity. They are in even better agreement with the values determined by Macfarlane and Roberts[12] from optical absorption data.

The extent to which the extrinsic radiation may be altered by changing the density and nature of the added impurities is shown in Fig. 3. The solid trace (curve I) is a reproduction of the solid trace of Fig. 1. The dotted trace (curve II) is the result obtained by increasing the concentration of added boron by ~50-fold while keeping the arsenic content substantially constant. The large relative increase in the radiation having a maximum at 1.039 ev indicates that it is due to the recombination of electrons with holes on un-ionized boron atoms. The origin of the radiation having a maximum at 1.072 ev is uncertain at present, but it is thought to be due to the recombination of injected holes with electrons on un-ionized arsenic atoms. The effect of substituting gallium for boron is shown by the dashed trace (curve III). A trace of intrinsic radiation may be observed at 1.10 ev. The maximum, however, occurs at 1.015 ev and is shifted to lower energy as expected for an increased ionization energy. A still further shift in the position of the maximum to 0.960 ev is observed when the acceptor impurity is changed to indium (curve IV) which is again qualitatively in accord with a further increase in ionization energy.

According to our analysis, $E_i=h\nu_1-h\nu_2-\frac{3}{2}kT$. The values of $E_i$ obtained by substituting the photon energies associated with the maxima in this equation are shown in Table I together with the ionization energies as determined thermally by Morin *et al.*[13] as well as those obtained by Burstein *et al.*[14] from optical absorption and photoconductivity. The values of $E_i$ which we obtain for boron, gallium, and indium are within present experimental error of those determined in other ways.

TABLE I Ionization energies (ev).

| Element | $E_i$ (our result) | $E_i$ (thermal) | $E_i$ (optical) |
|---|---|---|---|
| B | 0.051 | 0.045 | 0.046 |
| Ga | 0.075 | 0.065 | 0.071 |
| In | 0.13 | 0.16 | 0.16 |
| As | 0.018 | 0.049 | 0.056 |

The peak at 1.072 ev gives a value of $E_i=0.18$ ev. If this maximum is due to recombination through arsenic donors, it is difficult to understand the considerable discrepancy, shown in Table I, which exists between this value and the ionization energy of arsenic as measured in other ways. It is hoped that the solution to this problem will be found as the investigation continues.

We would like to thank J. A. Burton for helpful suggestions and M. Lax for theoretical interpretation.

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[9] W. Kohn, Phys. Rev. **98**, 1561 (1955).

[10] We are indebted to R. H. Parmenter for a discussion on this point.

[11] F. J. Morin and J. P. Maita, Phys. Rev. **96**, 28 (1954).

[12] G. G. Macfarlane and V. Roberts, Phys. Rev. **98**, 1865 (1955).

[13] Morin, Maita, Shulman, and Hannay, Phys. Rev. **96**, 833 (1954).

[14] Burstein, Bell, Davisson, and Lax, J. Phys. Chem. **57**, 849 (1953); Burstein, Picus, and Henvis, in *Proceedings of the Photoconductivity Conference, Atlantic City*, 1954 (to be published).