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Infrared Absorption, Photoconductivity, and Impurity States in Germanium*

W. KAISER AND H. Y. FAN
Purdue University, Lafayette, Indiana

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Infrared absorption and photoconductivity in p-type germanium with gold and copper impurities have been investigated at different temperatures. Photoconductivity in gold-doped germanium at liquid nitrogen and liquid helium temperatures shows a long wavelength tail beyond the fundamental absorption edge, which falls off sharply at about 6 microns corresponding to 0.21 ev. This value agrees well with the acceptor activation energy determined by electrical measurements. For copper-doped germanium at low temperatures both absorption and photoconductivity show a maximum at about 22 microns corresponding to 0.055 ev. This value also agrees with the acceptor activation energy given by Hall effect measurements. At room temperature more absorption is found in the region 2 to 5 microns as compared to p-type germanium doped with indium and aluminum. This is likely to be due to photoionization from a deeper level 0.25 ev above the valence band.

OPTICAL excitation of electrons or holes from impurity states was fround in silicon from absorption measurements.[1] Later, photoconductivity associated with such processes was reported, with maximum at a wavelength corresponding to several hundredths of an electron-volt for the ionization energy.[2] In the case of germanium it is known from resistivity and Hall effect measurements that the ionization energy for commonly used acceptor and donor impurities is much smaller than in the case of silicon, $\lesssim 0.01$ ev. The threshold of photoionization should be >100 microns, which is difficult to reach. Furthermore, anomalous behavior of Hall coefficient at low temperatures makes the determination of free carrier concentration ambiguous. On account of this complication, low-temperature absorption measurements have not as yet given conclusive evidence of photoexcitation of impurities.[3] This has been found for germanium with two special acceptor impurities: gold and copper.

GOLD-DOPED GERMANIUM

The study of gold-doped germanium at this laboratory was initiated by Lark-Horovitz some time ago.[4] Gold added to high-resistivity germanium gives p-type semiconductors. The activation energy of the acceptor state has been determined from electrical measurements to be ~0.2 ev. Figure 1 gives the curves of absorption coefficient for two temperatures. The specimen has a resistivity $\rho = 1.3$ ohm cm and a hole concentration $n_h \sim 6\times10^{15}$ cm^{-3} at 300°K, and $\rho = 1.5\times10^6$ ohm cm, and $n_h \sim 10^9$ cm^{-3} at 77°K. Thus very few holes are left at the lower temperatures, most of them having settled in the acceptor states. At 300°K the strong absorption beyond 7 microns agrees with other p-type germanium of same hole concentration, whereas at 77°K only lattice absorption (dotted curve) remains. This provides a strong evidence that the long wavelength absorption at 300°K (aside from the lattice bands) is due to the presence of free holes. For shorter wavelengths, 7 to 2 microns, the absorption at 300°K does not show distinctly two peaks as observed in other p-type germanium and is generally higher in magnitude. Furthermore the almost flat absorption at 77°K from 4 to 14 microns is higher than in other high-resistivity germanium. This is very likely true because of the scattering by islands of precipitated gold in the specimen, which are clearly visible on the surface.

Figure 2 gives the spectral response of photoconductivity at liquid nitrogen and liquid helium temperatures. Coming from the short wavelength side there is a sharp drop near 2 microns corresponding to the edge of the fundamental absorption, electron excitation across the energy gap. This is followed by a flat response up to about 6 microns, corresponding to ~0.21 ev, where it again drops sharply. The response beyond 2 microns is evidently associated with photoionization of holes on

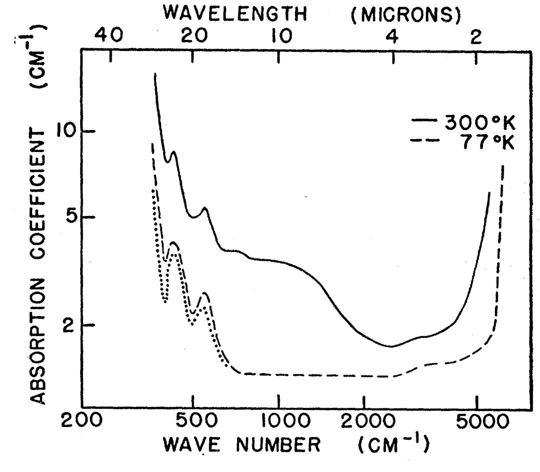

FIG. 1. Absorption coefficient of gold-doped germanium. Dotted line gives lattice absorption.

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[1] H. Y. Fan and M. Becker, Phys. Rev. **78**, 178 (1950).

[2] Burstein, Oberly, and Davisson, Phys. Rev. **89**, 331 (1953).

[3] Kaiser, Collins, and Fan, Phys. Rev. **91**, 1380 (1953).

[4] Single crystals with gold additions were first made by W. L. Taylor (1950) and later by L. M. Roth; Benko, Fan, and Lark-Horovitz, Purdue Semiconductor Research Progress Report, June, 1952 (unpublished); M. Nisenoff, Master's thesis, Purdue University, 1952 (unpublished); R. Dreyfus, Master's thesis, Purdue University, 1953 (unpublished); see also W. C. Dunlap, Jr., Phys. Rev. **91**, 1282 (1953).

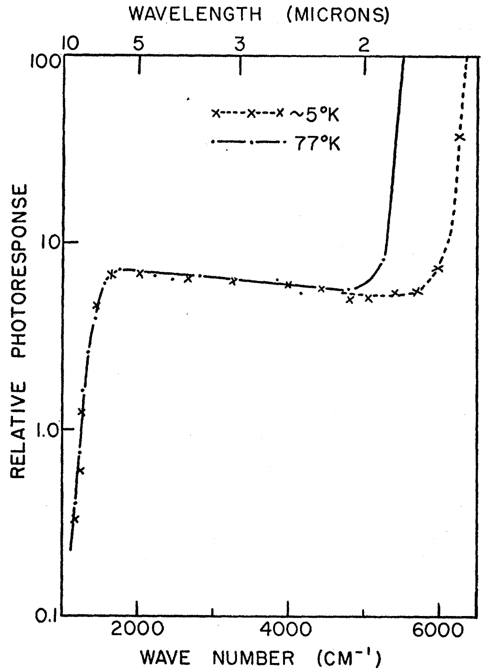

FIG. 2. Photoconductive response (increment of conductance for constant incident energy) of gold-doped germanium at 77°K and ~5°K. The values are given on arbitrary scales which are not the same for the two temperatures.

acceptor states, the threshold 0.21 ev agreeing closely with the activation energy determined electrically. The absorption due to this process did not however show up in the absorption curve at 77°K. According to the theory of photoionization of atoms,[5] the absorption coefficient is given approximately by

$$\mu_i \propto (1/\nu)^{\alpha}, \tag{1}$$

where α depends on the wave function of the bound state and has somewhat different values for frequencies near the threshold ν_0 and frequencies much smaller than ν_0. For simple wave functions 1*s*, 2*s*, and 2*p* the value of α is close to 3 or 4. In terms of the ionization energy E the maximum absorption coefficient at ν_0 is

$$\mu_i = C\frac{N}{K(E/E_H)} \times 10^{-17}\,\mathrm{cm}^{-1}, \tag{2}$$

where E_H is the ionization energy of a hydrogen atom, N is the concentration of atoms, and K is the dielectric constant of the medium. The value of C is of the order of unity depending on the wave function of the bound state, e.g., $C=0.63$ for 1*s*, 0.37 for 2*s*, and 0.34 for 2*p*. Resistivity and Hall effect measurements give $N=6\times10^{15}$ cm^{-3} for the sample used. Taking $K=16$ and $C=0.63$ we get $\mu_i=0.64$ cm^{-1}. With this small magnitude expected, it is not surprising that the absorption did not show up, especially in view of the scattering by precipitated gold.

The photoresponse per unit incident energy should be

$$\Delta\sigma \propto \frac{\mu_i}{\mu}\frac{W}{h\nu}, \tag{3}$$

where μ is the total absorption coefficient and W is the power absorbed in the sample. W can be estimated from the absorption coefficient and the thickness of the sample. For the sample used μ and W are practically constant over the range 2 to 14 microns at 77°K. Therefore we should expect $\Delta\sigma \propto \mu_i/\nu$ giving a fairly large frequency dependence. The measured photoresponse is, however, practically flat. This might be caused by a tail in the photoconductivity due to fundamental absortion which decreases with increasing wavelength.

Figures 1 and 2 show that the edge of the fundamental absorption and its associated photoconductivity shifts to shorter wavelengths with decreasing temperature. This has been interpreted as variation of energy gap with temperature.[6] The threshold of photoconductivity, on the other hand, shows no shift at liquid helium from that at 77°K. This indicates that the acceptor energy level remains fixed relative to the valence band while the energy gap is changed.[7]

COPPER-DOPED GERMANIUM

It is known that copper diffuses readily into germanium at elevated temperatures and that it acts as acceptors. A sample of *n*-type germanium 26-ohm cm with a layer of copper deposited on its surfaces was heated to 900°C and rapidly quenched to room temperature. It became *p* type with resistivity 0.2-ohm cm. Table I gives the results obtained from Hall effect measurements.[8] An identical sample of *n*-type germanium was heat-treated in the same way but without surface deposit of copper. The sample became *p* type of 1.5-ohm cm at room temperature. The results of Hall effect measurement are also given in Table I. The concentration of introduced acceptors is about ten times smaller than in the sample with added copper. Thus in the first sample at least most of the acceptors are due to copper. The acceptor activation energy is the same for the two samples. Furthermore, absorption

TABLE I. Data for quenched germanium from electrical measurements.

Sample	Resistivity ohm cm 300°K	77°K	~5°K	Hole concentration 10^{15} cm^{-3} 300°K	77°K	Acceptor activation-energy ev
Quenched only	1.5	0.43	$\sim10^6$	2.3	1.0	0.050
Copper added	0.2	0.19	$\sim10^7$	20	3.3	0.051

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[5] H. Hall, Revs. Modern Phys. **8**, 358 (1936).

[6] H. Y. Fan, Phys. Rev. **82**, 900 (1951).

[7] Attention was drawn to this interesting point by K. Lark-Horovitz.

[8] We are indebted to D. L. Waldorf for making these measurements.

and photoconductivity measurements also give similar results for the two samples. It has been reported recently[9] that quenching from 900°C introduces into germanium only $\sim 10^{14}$ cm^{-3} acceptors if special care is taken to remove any trace of copper from the surfaces before heat treatment. Thus it seems that the sample quenched without copper addition had nevertheless enough copper to determine its observed behavior.

The absorption curves for three temperatures are shown in Figs. 3(a) and 3(b) for the two samples. Consider first the long-wavelength region, beyond 5 microns. The room temperature curves have the same shape and agree reasonably well in magnitude with results on other *p*-type samples. The absorption is thus due to free holes. The low-temperature curves on the other hand are quite different from those of other samples and drop sharply at the long-wavelength end. The liquid helium curve of Fig. 3(a) is replotted in Fig. 4 (curve *A* beyond 5 microns) after subtracting the lattice bands. It shows a maximum around 22 microns corresponding to 0.055 ev. The close agreement between this value and the acceptor activation energy determined by Hall effect measurement indicates that the absorption is due to photoionization of neutral acceptors. The data in Table I show that practically all acceptors became neutral at helium temperature. Thus this curve in Fig. 4 gives the cross section for photoionization of an acceptor. The liquid helium curve of Fig. 3(b) gives values about 30 percent lower. These results are less reliable as the proportion of lattice absorption which has to be subtracted from the measured curve is much higher in this case. Also, there may be in this sample a significant proportion of acceptors other than copper. The difference between the liquid helium curves and the corresponding liquid nitrogen curves can be explained by the fact that at the higher temperature the absorption of free holes was not negligible and not all the acceptors were neutral.

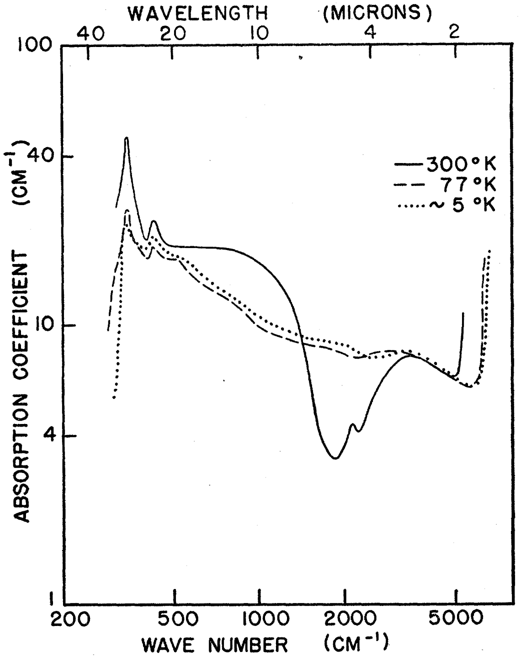

FIG. 3. (a) Absorption coefficient at different temperatures for germanium quenched with added copper.

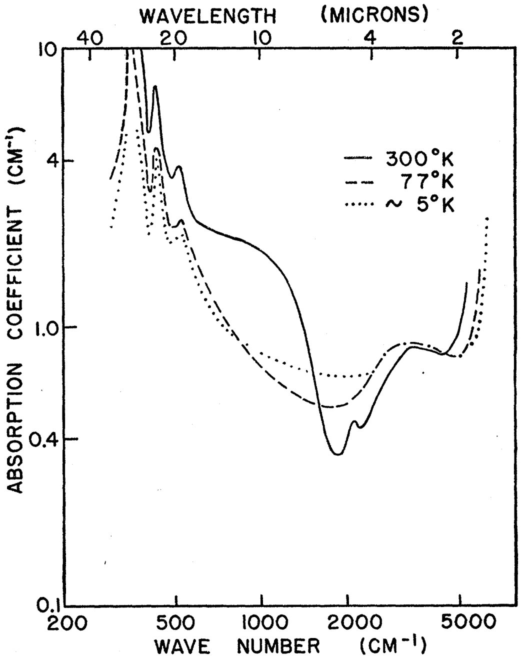

FIG. 3. (b) Absorption coefficient of germanium quenched without adding copper.

Consider now the short-wavelength region, 2 to 5 microns. At room temperature the absorption in this region relative to the long-wavelength absorption is higher than in "ordinary" *p*-type samples, doped, for example, with indium or aluminum.[3,10] Curve *B*, Fig. 4, gives the "excess" absorption coefficient divided by the acceptor concentration. Both samples give the same curve indicating that the excess absorption is proportional to the number of acceptors. For ordinary *p*-type germanium the absorption in this region becomes a sharp band at low temperatures.[3] However, the low temperature curves in Fig. 3(a) and 3(b) do not show a sharp band. On the other hand the curves in Fig. 3(b), especially the liquid nitrogen curve, do show a rise at about 5 microns. The following hypothesis is proposed to explain these behaviors. The absorption is assumed to consist of two parts. One component is the same as observed in other *p*-type germanium, but it becomes very small at low temperatures instead of merely sharpening up as in other samples. One difference between these and other samples is that the hole

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[9] R. A. Logan, Phys. Rev. **91**, 757 (1953).

[10] This has been observed independently by D. H. Rank and D. C. Cronemeyer, Phys. Rev. **90**, 202 (1953).

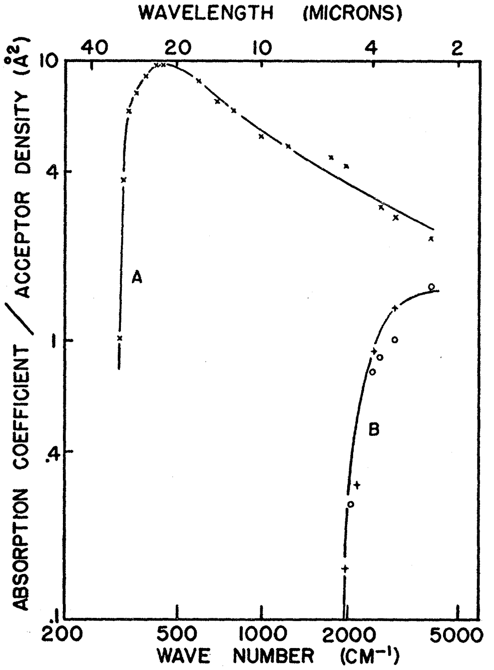

FIG. 4. Absorption coefficient per acceptor concentration. The crosses are points obtained from data in Fig. 3 (a), and the circles are points obtained from data in Fig. 3 (b). Curve *B* gives excess absorption over absorption in indium-doped germanium, at room temperature. Curve *A* gives absorption at liquid helium temperature after subtracting the lattice bands and curve *B*.

concentration here definitely becomes very small at low temperatures. The other component is given then by curve *B*, Fig. 4, at room temperature and is assumed to be independent of temperature. It might be photoionization of a deeper level associated with copper, about 0.25 ev from the valence band. On this basis we get for both samples a smooth curve of absorption due to photoionization of acceptors by subtracting curve *B*, Fig. 4, from the measured absorption curve at helium temperature. The part of curve *A*, Fig. 4, for wavelength <5 microns is obtained in this way for the sample with added copper.

The decrease of absorption from the maximum toward shorter wavelength, as shown by curve *A* in Fig. 4, seems to be also not as fast as might be expected. However, the maximum absorption gives $C=1.2$ according to (2), which is a reasonable value.

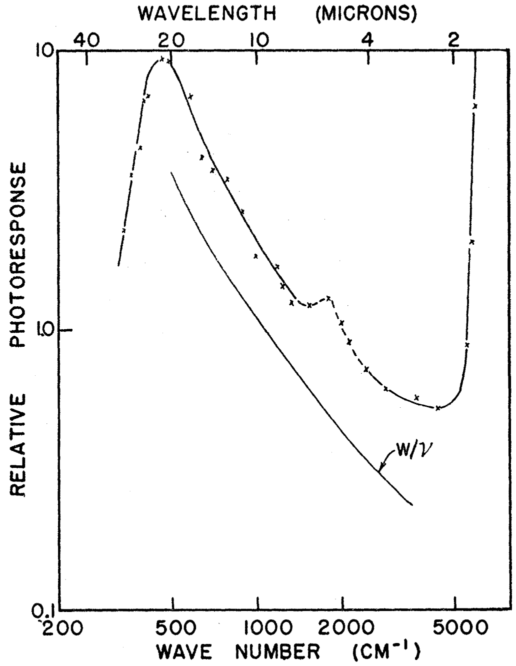

FIG. 5. Photoconductive response of copper-doped germanium at ~5°K. The curve W/ν is calculated by using the absorption curve to estimate W.

Figure 5 gives the observed photoconductive response for the sample with added copper. It shows a maximum at the same wavelength as the absorption curve. There seems to be a small peak at about 5.5 microns, the existence of which is not very certain with the experimental accuracy involved. This is more so as measurements on the other sample gave a curve similar in shape but with no indication of a peak at this wavelength. If all the absorption contributes to photoconductivity then (3) reduces to $\Delta\sigma \propto W/\nu$. The curve of W/ν (Fig. 5), with W calculated according to the absorption curve, does have the same shape as the photoconductive response.