Infrared Photoconductivity due to Neutral Impurities in Germanium

E. BURSTEIN, J. W. DAVISSON, E. E. BELL,* W. J. TURNER,† AND H. G. LIPSON
Crystal Branch, Metallurgy Division, U. S. Naval Research Laboratory, Washington, D. C.
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Impurity photoconductivity studies have been carried out at liquid helium temperature over the range of 1 to 38 microns for *n*- and *p*-type germanium containing various donor and acceptor impurities. As expected from the thermal ionization energy data, the impurity photoconductive response of germanium containing group III or group V impurity elements extends beyond 38 microns, the limit of measurement; the response of zinc-doped germanium also extends beyond 38 microns, indicating an upper limit of 0.033 ev for zinc acceptor centers; the photoconductive response of copper-doped germanium extends only to 29 microns, indicating an optical ionization energy for copper impurity centers of 0.043 ev. An electrical "breakdown" is observed at liquid helium temperature in germanium containing small concentrations of group III or group V impurity elements which makes it necessary to use relatively low applied fields in the photoconductivity measurements.

INTRODUCTION

GERMANIUM exhibits optical absorption extending to the near infrared which is due to electronic transitions from the filled band to the conduction band.[1] This intrinsic absorption is accompanied by photoconductivity whose long wavelength limit coincides with the intrinsic absorption edge at 1.85 microns.[2] Germanium also exhibits absorption beyond the intrinsic absorption edge due to lattice vibrations which appears as bands in the region from 12 to 32 microns.[3,4] Free charge carriers arising from intrinsic and impurity ionization processes also contribute to the absorption beyond the intrinsic absorption edge.[5,6]

At sufficiently low temperatures neutral impurities may also be expected to contribute to the infrared absorption in germanium. Optical absorption by neutral impurities involving the photoionization of bound charge carriers has previously been demonstrated in *n*- and *p*-type silicon at liquid nitrogen temperature.[1,7] At liquid helium temperature this absorption is accompanied by photoconductivity which may extend to 38 microns in the infrared.[8,9] More recent infrared studies at low temperature have revealed further the existence of excited states of the impurity centers in silicon and have enabled us to obtain rather precise information about the ionization energies of impurity centers in silicon.[10]

Photoconductivity studies have now been carried out at liquid helium temperature for *n*- and *p*-type germanium containing various donor and acceptor impurities. These studies demonstrate the existence of optical absorption and photoconductivity due to neutral donor and acceptor impurities in germanium and enable us to obtain information about the ionization energies of known or unknown impurities which are present.[11] The present studies do not extend beyond 38 microns so that such information is limited to impurities having ionization energies greater than 0.033 ev.

EXPERIMENTAL

Photoconductivity measurements were carried out over a range of wavelengths from 1 to 38 microns using a model 12-C Perkin-Elmer monochromator equipped with interchangeable NaCl, KBr, and KRS-5 prisms. Care was taken to eliminate or minimize scattered light errors by using appropriate reflection and transmission filters. A simple arrangement of two concentric glass Dewars was used to maintain the specimen at liquid helium temperature. Monochromatic radiation chopped at 1080 cps entered through a KRS-5 window at the top of the inner Dewar. A dc voltage was applied across the specimen in series with a one megohm load resistance, and the ac signal across the series load resistance was amplified by a tuned amplifier, rectified synchronously and recorded by means of a Brown Electronik recorder.

Photoconductivity studies were carried out at liquid helium temperature for germanium specimens doped with antimony, copper, indium, and zinc, respectively. The resistivity of the specimens at liquid helium temperature ranged from 10^6 to 10^8 ohm-cm. Fairly complete data have thus far been obtained for germanium specimens doped with copper, indium, and zinc. The specimens doped with antimony were found to be photoconductive out to 38 microns but were noisy and unstable so that it was not possible to obtain

* Present address: Ohio State University, Columbus, Ohio.
† Present address: National Bureau of Standards, Washington, D. C.
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[10] Burstein, Bell, Davisson, and Lax, "Symposium on Impurity Phenomena, June, 1953" [J. Phys. Chem. (to be published)].
[11] Photoconductivity due to neutral impurities in germanium is also being investigated by Dr. G. Morton and his co-workers at RCA. We wish to acknowledge the valuable exchange of information between the two groups on these problems.

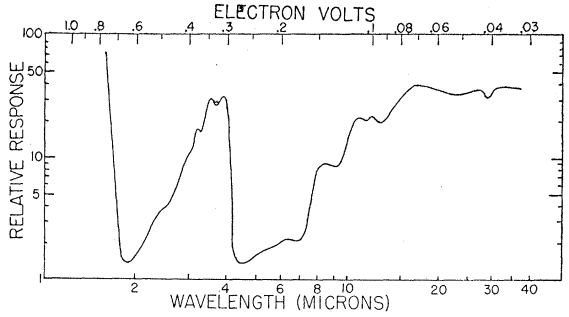

FIG. 1. Spectral response of a GE indium-doped germanium specimen containing 4×10^{15} charge carriers/cm^3 at room temperature.

quantitative data. Spectral response (relative photoconductive response/flux density of incident radiation plotted against wavelength) curves are given in Figs. 1, 2, and 3 for (a) a General Electric (GE) indium-doped specimen, No. 132, containing 4×10^{15} charge carriers/cm^3 at room temperature; (b) a GE zinc-doped specimen, No. 152, containing 2×10^{16} charge carriers/cm^3 at room temperature; and (c) a Bell Telephone Laboratories (BTL) copper-doped specimen, No. 153, containing 1×10^{15} charge carriers/cm^3 at room temperature. Preliminary time-constant measurements were carried out for the zinc-doped specimen No. 152. The results indicate a time constant for the impurity photoconductive response which is less than 10^{-5} sec.

DISCUSSION

Optical absorption by neutral impurities may involve transitions from the ground state of the impurity center to higher energy states, corresponding to optical excitation of the bound charge carriers, as well as transitions from the ground state to the conduction band, corresponding to photoionization of bound charge carriers (Fig. 4). At sufficiently low temperatures, where the density of free charge carriers is small, the photoionization absorption by neutral impurities may be expected to be accompanied by photoconductivity having a long wavelength limit which coincides with the photoionization limit. The position of the long wavelength photoionization limit for the various impurities in germanium may be estimated from thermal ionization data, since the optical ionization energy may reasonably be expected to be equal to the thermal ionization energy in homopolar materials (Table I). Thus, the long wavelength photoconductive response limit should occur at 120 microns for specimens containing group III or group V impurity elements, corresponding to a thermal ionization energy of 0.01 ev; at 40 microns for zinc-doped specimens, corresponding to a thermal ionization energy of 0.031 ev; and at 31 microns for copper-doped specimens, corresponding to a thermal ionization energy of 0.040 ev. Optical excitation of the neutral impurities would be expected to appear as relatively narrow bands at wavelengths just beyond the photoionization absorption limit. It is not probable that the optical excitation of neutral impurities will be accompanied by any appreciable photoconductivity at liquid helium temperature except, possibly, in the case of transitions to states very close to the conduction band, since the probability that the excited bound charge carriers will be thermally ionized before returning to the ground state may be expected to be relatively small.

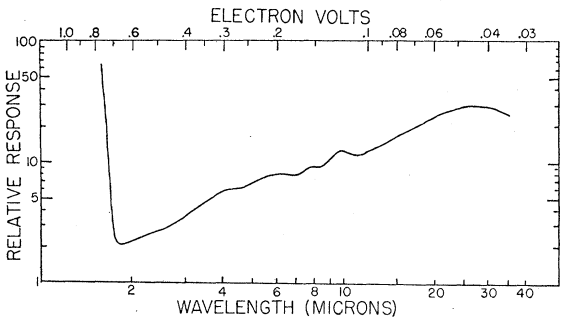

FIG. 2. Spectral response of a GE zinc-doped germanium specimen containing 2×10^{16} charge carriers/cm^3 at room temperature.

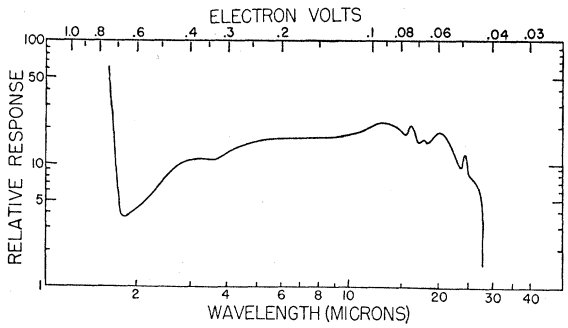

FIG. 3. Spectral response of a BTL copper-doped germanium specimen containing 1×10^{15} charge carriers/cm^3 at room temperature.

As expected from the ionization energy data, the photoconductive response of germanium containing group III and group V impurity elements extends out to 38 microns, the present limit of measurement. The photoconductive response of the GE indium-doped germanium does, however, exhibit some rather unusual structure beyond the intrinsic absorption edge. The photoconductive response curve of this specimen (Fig. 1) increases with wavelength to a peak at 4 microns but falls abruptly just beyond 4 microns. It also exhibits structure in the region between 8 and 15 microns. The dip in photoconductive response at 29 microns is due to the competitive absorption by the 29-micron lattice-vibration band. Similar results have also been obtained for a BTL indium-doped germanium specimen. The peak at 4 microns appears to be due to the photo-

ionization of an acceptor level with an ionization energy of 0.3 ev.

The photoconductive response of zinc-doped germanium also extends to 38 microns (Fig. 2). There is some evidence of structure in the region from 3 to 12 microns. The absence of a long wavelength limit to the photoconductive response over the range of measurements indicates an upper limit to the optical ionization energy of 0.033 ev for the zinc acceptor centers for which Dunlap[12] has obtained a value of 0.031 ev from electrical measurements. The photoconductive response of copper-doped germanium, on the other hand, extends only to 29 microns (Fig. 3). This long wavelength limit indicates an optical ionization energy for the copper acceptor centers of 0.043 ev which is in good agreement with the value of 0.040 ev which Morin and Maita[13] have obtained from electrical studies. The bump in the curve in the region of 2 to 4 microns may possibly be associated with the 0.3-ev acceptor levels which Burton and his co-workers have shown to be present in copper-doped germanium.[14] The dips in the photoconductive response curve in the region from 15 to 30 microns, on the other hand, are due to the competitive absorption by lattice vibrations (Fig. 5).

TABLE I. Ionization energies of impurities in germanium.

Impurity	E(ev)	λ(microns)
Group III	0.01[a]	120
Group V	0.01[a]	120
Zn	0.031[b]	40
Cu	0.040[c]	31

[a] G. L. Pearson and W. Shockley, Phys. Rev. 71, 142 (1947).
[b] See reference 12.
[c] See reference 13.

During the course of the photoconductivity studies at liquid helium temperature, an interesting electrical "breakdown" effect was observed in germanium containing low concentrations of group III or group V impurity elements. Efforts to detect photoconductivity due to neutral impurities in such specimens were initially unsuccessful. An appreciable impurity photoconductivity was however readily observed in zinc-doped specimens containing 10^{16} charge carriers/cm^3 at room temperature. It was further noted that in the absence of background radiation the "dark" resistivity of the specimens containing low concentrations of group III or group V impurity elements, as measured by an ohmmeter, appeared to be several orders of magnitude smaller than the values which would reasonably be expected from the concentrations and ionization energies of the impurities. Anomalously low "dark" resistivities have previously been observed in n- and p-type silicon specimens where they were attributed to

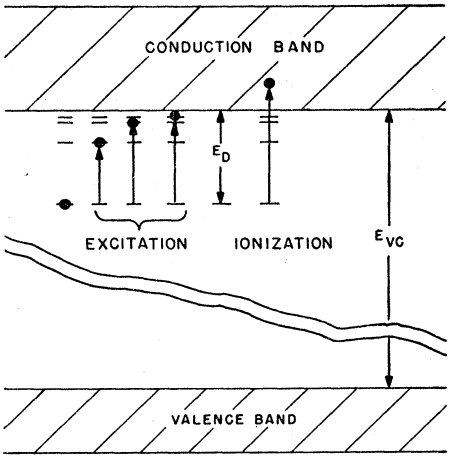

FIG. 4. Energy level diagram showing optical excitation and photoionization of bound charge carriers.

the presence of impurity centers with very low or zero ionization energies.[3] However, a study of the current-voltage characteristics of the germanium specimens containing group III or group V impurity elements revealed the existence of a reversible electrical "breakdown" effect which set in at applied electrical fields of the order of 10 volts/cm.[15] These fields were considerably lower than those normally employed in the photoconductivity studies, and also lower than the fields applied to the samples in the ohmmeter measurements. An appreciable impurity photoconductivity was readily observed when the applied fields were kept below the critical breakdown value. The electrical breakdown effect, which is also observed when microsecond pulses are used, manifests itself as a sharp increase in conductivity of several orders of magnitude over a small range of applied field and is accompanied by a sharp increase in current noise.[16] Exposure of the specimen to room-temperature background radiation increases the conductivity of the specimens by one or two orders of magnitude in the pre-breakdown region, but does not effect

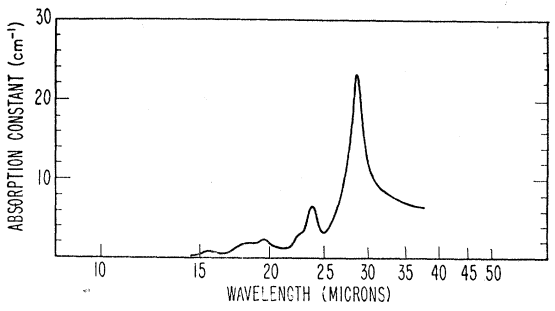

FIG. 5. Contribution to the infrared absorption spectrum of germainium due to lattice vibrations.

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the conductivity at higher fields. No electrical breakdown effects were observed up to several hundred volts in the zinc-doped specimens, which condition accounts for the fact that an impurity photoconductivity was readily observed in these specimens when higher electric fields were employed. Electrical breakdown effects were also absent in n- and p-type polycrystalline silicon for fields up to 1000 volts/cm.

The electrical breakdown effect in germanium at liquid helium temperature is at present attributed to charge-carrier multiplication involving the impact ionization of neutral impurities by charge carriers which gain the necessary energy from the applied field.[17,18] The relatively low applied field required for breakdown is apparently due to the low ionization energy of the impurity centers and to the high mobility of the charge carriers at low temperatures in germanium containing low concentrations of group III or group V impurity elements. The fact that charge carriers which receive their energy from the applied electrical field can produce an appreciable impact ionization of neutral impurities, suggests that charge carriers produced by photoionization may also produce secondaries by impact ionization before losing their initial kinetic energy by other processes. The quantum efficiency for the photoionization process may therefore be greater than one for photons whose energies are greater than the ionization energies of the impurity centers.

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ACKNOWLEDGMENTS

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Note added in proof.—We have more recently carried out optical absorption measurements at low temperature on indium-doped germanium. We find, in agreement with the results of Kaiser, Collins, and Fan [Phys. Rev. **91**, 1380 (1953)] that at liquid helium temperature indium-doped germanium exhibits a band at 3.6 microns. This band is very similar to the 3.6-microns band observed at liquid nitrogen temperature which is attributed to optical transitions of free holes between two of the branches of the degenerate valence band. The 3.6-microns band at liquid helium temperature is apparently responsible for the photoconductivity peak at 4 microns and is accordingly now attributed to optical transitions of holes from bound indium acceptor levels to levels within one of the branches of the valence band. The similarity of the band at liquid nitrogen temperature (where the holes are free) to the band at liquid helium temperature (where the holes are bound) is apparently due to the very small ionization energy of the indium acceptor centers and to the similarity in character of free holes at the top of the valence band to bound holes at the acceptor levels.

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Magnetic Resonance in Ferrimagnetics

ROALD K. WANGSNESS
United States Naval Ordnance Laboratory, White Oak, Maryland
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It is shown that the general expression for the magnetic resonance frequency of the two-sublattice model of a ferrimagnetic crystal has essentially the same form as that originally obtained for the ferromagnetic case provided that the product of the molecular field coefficient and the net magnetization is large compared to the applied and anisotropy fields. The special cases of vanishing magnetization and angular momentum are considered separately, and the relation of these results to the theory of antiferromagnetic resonance is discussed.

INTRODUCTION

SEVERAL magnetic resonance experiments have been made with ferrimagnetic[1] materials in order to test the standard theory of ferromagnetic resonance.[2] In general, the agreement between the measured and predicted dependence of the resonance frequency upon the angles made by the static field with the principal crystallographic axes was very good, so good, in fact, that the theoretical expressions for the frequency were then used to deduce values of the anisotropy constants for the materials.[3] There seems to have been no theoretical justification for the detailed use of these formulas

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