

## Optical Properties of Heavily Doped Compensated Germanium

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Measurements of the optical properties of a compensated heavily doped sample of germanium are reported. Although the sample contained about  $10^{20}$  gallium atoms/cc and  $10^{20}$  arsenic atoms/cc, the compensation was such that the absorption coefficient could be measured from a minimum value of  $7 \text{ cm}^{-1}$  to a maximum at about  $10^4 \text{ cm}^{-1}$ . The major observation was that of an exponential tail beginning at about 0.78 eV which was not strongly dependent on the carrier concentration for densities between  $2 \times 10^{17}/\text{cm}^3$  and  $10^{19}/\text{cm}^3$ .

THERE have been numerous attempts, both theoretical and experimental, to determine the influence of a large density of impurities on the band structure of a semiconductor. Unfortunately, the problem is quite complex, and the extent to which various investigators disagree suggests that a satisfactory solution is still a long way off. In this paper, we present some results of optical experiments on highly compensated, heavily doped germanium. These results indicate a larger change of absorption edge with doping than has previously been reported.

### I. INTRODUCTION

The interest in the band structure of impure semiconductors has centered principally on two aspects: (1) the dependence of energy gap on impurities and (2) the shape of density-of-states vs energy curves.

Pankove<sup>1,2</sup> first reported evidence of a large decrease ( $>0.1 \text{ eV}$ ) in the energy gap of degenerate Ge doped to greater than  $10^{19}$  impurities/ $\text{cm}^3$ . He attributed the decrease to a "tailing" of the density of states, as predicted by Parmenter's theory<sup>3</sup> for the band structure of alloys. Cardona and Sommers<sup>4</sup> measured the dependence on doping of the 2.1-eV reflectivity peak in Ge and estimated that the energy-gap decrease was probably no more than 0.03 eV for impurity densities up to  $10^{20}/\text{cm}^3$ . Sommers<sup>5</sup> later concluded that most of the available data on tunnel diodes and on bulk degenerate Ge could be explained without requiring the band gap to decrease by more than 0.03 eV for  $4 \times 10^{19}$  impurities/ $\text{cm}^3$ .

Recently, more extensive optical absorption measurements have been reported by Haas<sup>6</sup> and by Pankove and Aigrain.<sup>7</sup> Haas measured a number of samples of degenerate *n*-type Ge which included some that were slightly compensated  $(N_D - N_A)/(N_D + N_A) \approx \frac{1}{2}$ . He concluded that the indirect absorption edge was decreased by an amount proportional to  $(N_D + N_A)^{\frac{1}{2}}$  and

equal to 0.07 eV for  $N_A + N_D = 4.7 \times 10^{19}/\text{cm}^3$ . Haas also proposed that for degenerate Ge most of the indirect absorption took place by means of electron-electron scattering rather than lattice scattering or impurity scattering. (Price<sup>8</sup> has pointed out that indirect absorption by electron-electron scattering is not an allowed process.) Pankove and Aigrain also measured degenerate Ge (uncompensated) in about the same range of impurities and found a decrease of indirect energy gap equal to 0.093 eV for  $4 \times 10^{19}$  donors/ $\text{cm}^3$ .

There are two aspects common to the work of Haas and of Pankove and Aigrain which should be emphasized here. First, for heavily doped Ge which was uncompensated or only slightly compensated there was a very large free carrier absorption which prevented the direct measurement of small values of absorption coefficient at the absorption edge. Both authors extrapolated the free carrier absorption from long wavelengths according to a  $\lambda^2$  law, and then subtracted it from the total absorption to obtain the band-gap absorption for small absorption coefficient. As they have pointed out, the  $\lambda^2$  law was not necessarily valid for the short-wavelength region of the extrapolation. Because the difference between the extrapolated free carrier absorption and the measured absorption was orders of magnitude smaller than either at some wavelengths the absorption edges derived are uncertain at low absorption coefficients. A second point to be noted is that in both studies the authors fitted their absorption data to the theoretical energy dependence for indirect absorption with parabolic bands. One of the results common to several theoretical treatments of the problem<sup>9-12</sup> is the likelihood that for large impurity densities, the net perturbation of the electron energy states will be strongly momentum dependent, thus producing a "tailing" or nonparabolicity of the bands.

### II. CRYSTAL

The crystal used in this study was grown in the  $\langle 111 \rangle$  direction by the normal Czochralski pulling tech-

<sup>1</sup> J. I. Pankove, Phys. Rev. Letters 4, 20 (1960).

<sup>2</sup> J. I. Pankove, Phys. Rev. Letters 4, 454 (1961).

<sup>3</sup> R. H. Parmenter, Phys. Rev. 97, 587 (1955).

<sup>4</sup> M. Cardona and H. S. Sommers, Jr., Phys. Rev. 122, 1382 (1961).

<sup>5</sup> H. S. Sommers, Jr., Phys. Rev. 124, 1101 (1961).

<sup>6</sup> C. Haas, Phys. Rev. 125, 1965 (1962).

<sup>7</sup> J. I. Pankove and P. Aigrain, Phys. Rev. 126, 956 (1962).

<sup>8</sup> P. J. Price (private communication).

<sup>9</sup> M. Lax and J. C. Phillips, Phys. Rev. 110, 41 (1958).

<sup>10</sup> H. Frisch and S. Lloyd, Phys. Rev. 120, 1175 (1960).

<sup>11</sup> J. R. Klauder, Ann. Phys. (New York) 14, 43 (1961).

<sup>12</sup> P. A. Wolff, Phys. Rev. 126, 405 (1962).

nique. Because of the difference of the segregation coefficients ( $k$ ) of arsenic and gallium in germanium and their unknown interdependence it was necessary to grow several crystals from melts containing different relative concentrations of impurities before the required degree of compensation was achieved. The crystal showed some radial impurity segregation and had a  $p$ -type core about 2 mm in diameter; the remainder of the crystal was  $n$ -type. This structure was consistent with effects observed in crystals doped with As and Ga separately. X-ray fluorescence analysis for gallium and wet chemical analysis for arsenic indicated concentrations of  $(1.13 \pm 0.2) \times 10^{20}/\text{cm}^3$  and  $(0.97 \pm 0.04) \times 10^{20}/\text{cm}^3$ , respectively, for the  $n$ -type region.

Under normal growth conditions, it has not been possible to achieve this concentration of arsenic in solution when it is the only impurity. The gallium seems to enhance the solubility of the arsenic to the high level of about 0.2% observed in this crystal. Examination of the etched crystal under a microscope showed no evidence of germanium arsenide occlusions such as were observed by Spitzer, Trumbore, and Logan<sup>13</sup> with high arsenic doping levels.

The lattice parameter of the crystal was measured, using x rays, by N. R. Stemple and was determined to be equal to that for pure Ge to an accuracy of 0.02%.

Electrical measurements were made by J. F. Woods on a bridge-type sample cut from the  $n$ -type bulk of the crystal. For a homogeneous crystal, the results would indicate a carrier concentration  $n$  equal to  $(1.25 \pm 0.2) \times 10^{19}/\text{cm}^3$  and a mobility of about  $180 \pm 40 \text{ cm}^2/\text{V sec}$ .<sup>6</sup> This mobility is lower than one would expect for Ge doped with As alone to  $1.25 \times 10^{19}/\text{cm}^3$  ( $370 \text{ cm}^2/\text{V sec}$ ).<sup>14</sup> On the other hand, it is higher than has been observed for Ge doped with As to  $8 \times 10^{19}/\text{cm}^3$  ( $\sim 150 \text{ cm}^2/\text{V sec}$ ).<sup>13</sup>

### III. OPTICAL MEASUREMENTS

Absorption measurements were made with a Perkin-Elmer 12-G fore prism-grating monochromator and with a Perkin-Elmer 98 monochromator using quartz and NaCl prisms. The poorest resolution corresponded to 0.01 eV, but usually it was better than 0.005 eV. The absorption coefficient,  $\alpha$ , was calculated using the expression  $I/I_0 = (1-R)^2 \exp(-\alpha x)$ , where  $I/I_0$  was the ratio of transmitted to incident radiation,  $x$  the transmission path, and  $R$  the reflection coefficient taken to be 0.36. Accordingly, sample thicknesses of 3 mm, 930  $\mu$ , 280  $\mu$ , 240  $\mu$ , 106  $\mu$ , 33  $\mu$ , 22.4  $\mu$ , and 12  $\mu$  were measured so that  $\alpha x$  varied between 1.8 and 10 in the extreme cases. Thermocouples, a PbS detector and a cooled PbSe detector were used and gave consistent results.

<sup>13</sup> W. G. Spitzer, F. A. Trumbore, and R. A. Logan, J. Appl. Phys. **82**, 1822 (1961).

<sup>14</sup> J. F. Woods (private communication).

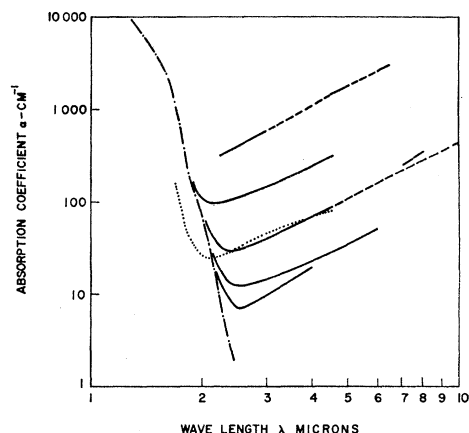


Fig. 1. Optical absorption. The solid lines represent absorption for different regions in which the free carrier absorption dominates. The dashed lines are interpolations for wavelengths not measured. The dash-dot line represents the absorption edge. Only the lowest part has been constructed from the extrapolation of the free carrier absorption. The dotted line is the absorption at 77°K.

Because the samples were not homogeneous it was necessary to mount the sample holder on a micrometer drive. To find regions of minimum free carrier absorption (maximum compensation), the monochromator was stopped down as much as possible both in width and height of aperture. The prism monochromator was used to study the most highly compensated regions because its lower dispersion allowed narrower slits to be used. The smallest image on the sample was 100  $\mu$  by 200  $\mu$  in size. In a given run the most compensated region would be found by looking for maximum transmission at long wavelengths ( $> 2.5 \mu$ ).

Figure 1 shows a composite curve of the absorption data for the several sample thicknesses and for several regions of the crystal. Although the free carrier absorption varied by a factor of 50 depending on compensation, the absorption edge did not vary appreciably from region to region. When the free carrier absorption in the less compensated regions, which roughly followed a  $\lambda^2$  law, was extrapolated to short wavelengths and subtracted from the total absorption, the resulting curve coincided very closely with that for the more highly compensated regions. The free carrier absorption was also subtracted from the curves for the two most highly compensated regions and the resulting curve is shown as an extension of the edge. The magnitude of the free carrier absorption subtracted was never more than about two thirds of the total absorption. It should also be noted that the minimum absorption occurred at 2.5  $\mu$  and that the extrapolated data has not been extended to quite that wavelength.

The least compensated regions were typical of the part of the crystal on which conductivity and Hall measurements were made. As these regions had a carrier density of  $1.25 \times 10^{19}/\text{cm}^3$  and the most highly compensated regions exhibited 1/50 as much free carrier

absorption one can infer that the most compensated region observed had a carrier concentration of about  $2.2 \times 10^{17}/\text{cm}^3$ . Thus  $(N_D - N_A)/(N_D + N_A)$  was approximately equal to 1/1000.

Although the curves for the various compensations fell reasonably well upon each other on the edge, the least highly compensated regions did show a slight shift to higher energies (less than 0.01 eV), which could be interpreted as a Burstein shift.<sup>15</sup> It should also be noted that the most highly compensated regions were not measured in thin samples so that no measurements for values of absorption coefficient greater than 100 exist for these regions. It is possible that at shorter wavelengths the absorption in these regions departs from that of the curve shown, but on the basis of measurements at high absorption coefficients in regions where the free carrier concentration differed by a factor of 10, this seems unlikely.

A curve for a low temperature (77°K) measurement is also shown and, as might be expected, is shifted to shorter wavelengths. The shift, for constant  $\alpha$ , is approximately equal to the gap change in pure germanium between 300 and 77°K, suggesting that  $\alpha$  is roughly independent of temperature for the sample. A slight hump may be seen in the free carrier absorption at 77°K at about  $3 \mu$ , which indicates that the highly compensated region was at least partly *p* type.<sup>16</sup>

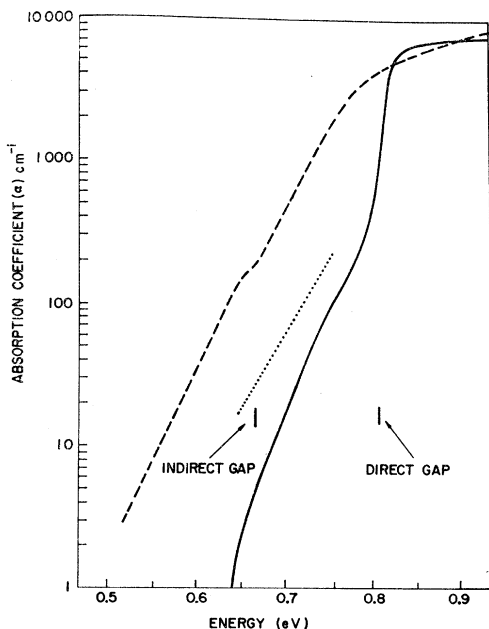


FIG. 2. The absorption edge. The solid line is the absorption edge for pure germanium (Dash and Newman). The dashed line is for the heavily doped sample. The dotted line is the edge at 77°K. The lines designating the direct and indirect gaps refer to pure germanium.

<sup>15</sup> E. Burstein, Phys. Rev. **93**, 632 (1954).

<sup>16</sup> W. Kaiser, R. J. Collins, and H. Y. Fan, Phys. Rev. **91**, 1380 (1953).

The absorption varied approximately as  $(1/\lambda)^{15.5}$ , and as this would appear to have little physical significance the data are presented in Fig. 2 in a semilog plot. The edge appears to follow an exponential law [ $\alpha$  proportional to  $\exp(\beta h\nu)$ ], except for a slight jog at about 0.65 eV, and a leveling off at high energy. A plot of  $(\alpha)^{1/2}$  vs  $h\nu$  did not yield a straight line in any region. The jog very likely represents a Burstein shift, since the larger absorption coefficients were measured for relatively less compensated regions of the crystal. For contrast the absorption curve for pure germanium<sup>17</sup> is also shown. At high energy the pure and heavily doped samples had approximately the same absorption coefficient. At low  $\alpha$  ( $\alpha < 100 \text{ cm}^{-1}$ ) the absorption curve for the impure sample is displaced by at least 0.15 eV from the absorption curve for the pure sample. The low-temperature curve shown was arrived at by subtracting the free carrier absorption. It has almost the same slope as the room-temperature curve.

Reflectivity measurements were made using a Bausch & Lomb Model 33-86-45 grating monochromator with a resolution of 0.005 eV. The measurements were made at about 45° incidence and light was reflected off the sample twice. The data at 298 and 77°K are shown in Fig. 3. The two reflectivity peaks for the  $L_3 \rightarrow L_1$  transitions are clearly resolved at 77°K and occur at 2.175 and 2.34 eV, respectively. The shift from the pure germanium values of the peaks is very close to the maximum shift observed by Cardona and Sommers.<sup>4</sup>

Measurements of the reflectivity between  $3 \mu$  and  $17 \mu$  wavelengths and of the Hall effect indicate that the mass of the electrons is  $0.16(\pm 0.02)m_0$  as in pure germanium and as in the degenerate samples studied by Spitzer *et al.*<sup>13</sup>

#### IV. DISCUSSION

A possible explanation of the data is that there is a tail on the direct absorption edge that masks the indirect absorption. The tail could have resulted from tails in the density of states of the type predicted by Parmenter for both the conduction band and valence band. It has been argued<sup>4</sup> on the bases of the relative *s* and *p* character of the conduction and valence bands and on the difference in effective masses (Parmenter predicted that the shift should be inversely proportional to the effective mass) that the larger effect might be expected in the conduction band. However the effects of the two bands cannot be separated, so that even if simple assumptions about the transition probabilities are made, the densities may not be deduced.

The major effect observed was the tail. However there does appear to be a shift in the direct absorption if the break in the absorption curve at about 0.775 eV is taken to be the point at which the absorption takes

<sup>17</sup> W. C. Dash and R. Newman, Phys. Rev. **99**, 1151 (1955).

place between approximately parabolic regions in the density of states. This energy is rather ill defined.

The effects on the reflectivity peaks seem far less drastic than those on the absorption edge. This is probably because the major effect seems to be a tailing of the distribution of states and such a tailing might be expected to show up as a broadening of the peaks. The peak should still correspond roughly to a maximum in the derivative of the absorption coefficient. However it is no longer clear where the maximum derivative should occur when the bands have tails. Therefore care must be taken in making quantitative inferences about the bands in impure germanium from the reflectivity data.

It has been suggested<sup>18</sup> that the smearing of the edge might be explained on the basis of a small but finite probability of a clustering of like ions. Such clusters would raise or lower the potential locally leaving the band gap unchanged. Then optical transitions might be made by a tunneling-like process from one region to another. This would seem to be a difficult approach to treat and may be equivalent to the perturbational approaches. Furthermore, clustering of many like ions is energetically unlikely.

In fact the opposite effect, pairing of unlike ions, seems far more likely. An estimate may be made of the percentage of ions paired as closest neighbors using the theory Reiss, Fuller, and Morin<sup>19</sup> applied successfully to ion pairing for boron and lithium in silicon. This theory predicts that if the crystal were annealed and quenched from 1200, 1100, 1000, and 800°K, then 22, 27.5, 36, and 52%, respectively, of the ions would be paired. The distances that atoms would have to diffuse to effect the pairing are small (approximately  $10^{-7}$  cm) so that equilibrium might be established at fairly low temperatures. One might reasonably expect then that of the order of  $\frac{1}{3}$  of the atoms are paired as nearest neighbors. Such paired atoms will act as dipoles and their scattering will be greatly reduced as compared to two monopoles. This may explain why the mobility measured was higher than that expected for the impurity concentration present. One dipole should

<sup>18</sup> T. N. Morgan and P. J. Price (private communications).

<sup>19</sup> H. Reiss, C. S. Fuller, and F. J. Morin, *Bell System Tech. J.* **35**, 535 (1956).

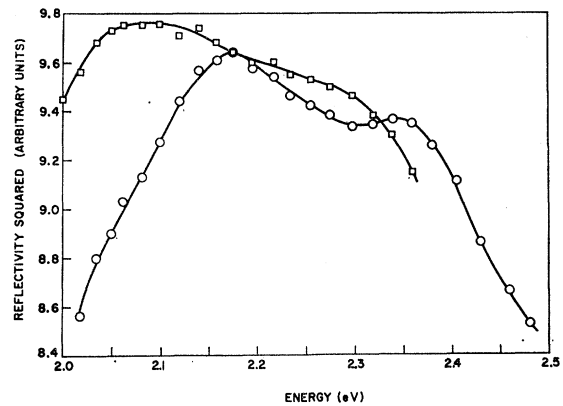


FIG. 3. The reflectivity of the heavily doped sample. Data are shown for room temperature (□) and 77°K (○).

cause a smaller perturbation to the absorption edge than two monopoles. If to a first approximation it can be assumed that the paired ions do not perturb the band structure, the edge should depend on the number of unpaired ions only. Thus the edge shape should depend on the temperature at which the pair distribution was brought to equilibrium. We have not yet made measurements to see whether the absorption edge may be changed by annealing and quenching from different temperatures.

In conclusion it may be stated that this absorption data is good evidence for a tailing effect in heavily doped germanium. Also the gap, insofar as band-to-band transitions such as optical transitions or tunneling are concerned, is effectively reduced by at least 0.15 eV from that of pure germanium.

#### ACKNOWLEDGMENTS

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