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Effect of Impurities on Free-Hole Infrared Absorption in *p*-Type Germanium

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The free-hole absorption in *p*-type germanium (gallium-doped) is studied as a function of concentration over the range from 10^{15} to 10^{20} acceptors/cm^3. The spectra are modified as the carrier and total impurity concentrations are increased. With increasing concentration the structure in the spectrum becomes less pronounced. The effects observed are consistent with changes in the Fermi level and with nonvertical transitions induced by charged impurity centers.

INTRODUCTION

THE room temperature infrared absorption due to free holes in *p*-type germanium is characterized by three absorption peaks located at 0.36, 0.26, and ~0.1 ev.[1-3] As the temperature is lowered, the bands sharpen and become displaced slightly from these positions. Studies of the absorption spectra of injected carriers have helped establish the conclusion that the spectra result from absorption by *free* holes and not from some unknown impurity effect.[2,4,5]

Kahn[6] has shown how the features of the free hole absorption can be explained in terms of vertical transitions ($\Delta k=0$) between the different branches of the valence band. From his interpretation of the data it is possible to obtain a value for the spin-orbit splitting in germanium at $k=0$. This, together with the band parameters obtained from cyclotron resonance data permits a complete description of the valence band near $k=0$.

This paper reports studies of the effects of free-hole concentration and total impurity concentration on the free-hole absorption. The impurity and carrier concentration effects which must be considered in analyzing the data are the following: (1) modification of the band structure due to impurities, (2) position of the Fermi level within the valence band, and (3) nonvertical transitions induced by charged impurity centers.

In this work attention will be directed at the behavior of the absorption corresponding to the excitation of a hole from the heavy-mass band (V_1) to the split-off band (V_3). This is done to avoid the complication of overlapping transitions that occur in some other regions of the spectrum. In a subsequent publication, Kane will present an absolute theory of the absorption due to the various impurity and carrier concentration effects, noted above, which modify the spectrum.[7]

EXPERIMENTAL

Single crystals of gallium-doped germanium were prepared by conventional doping and pulling techniques. Samples were cut transverse to the direction of crystal growth to maximize homogeneity. Hall coefficient measurements at 6×10^3 gauss were made on samples adjacent to the ones used for the optical measurement. The high field approximation was used to calculate carrier densities from the measured Hall coefficients.[8] At the higher impurity concentrations this procedure could be in error by as much as a factor of two since the magnetic field dependence of the Hall coefficient has not been examined under conditions of impurity scattering.

For the optical measurements the samples were cut with parallel faces and were ground to the desired thickness and then polished. The very thin samples (2–100 μ) were prepared in a manner already described,[9] except that the samples were mounted on synthetic sapphire disks. Low-temperature measurements were made with the sample mounted in a double Dewar cryostat. Transmission was measured by the "simple in, sample out" method. A Perkin-Elmer 112 spectrometer with CaF$_2$ and NaCl optics was employed. Absorption coefficients were obtained in the usual way, correcting for reflection loss by assuming a constant reflectivity of 0.35.

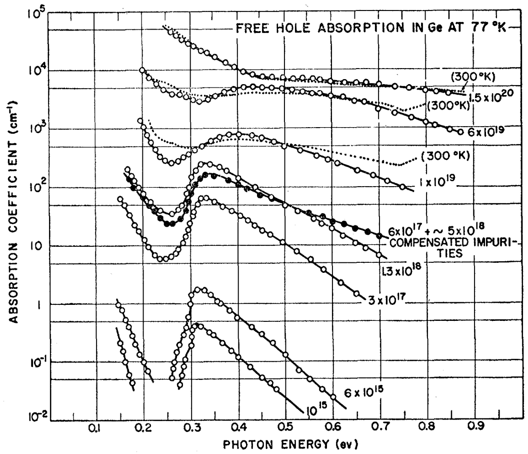

FIG. 1. Absorption spectra at 77°K of *p*-type germanium for a range of carrier and total impurity concentrations. Numbers on each curve gives the hole concentration in carriers/cm^3.

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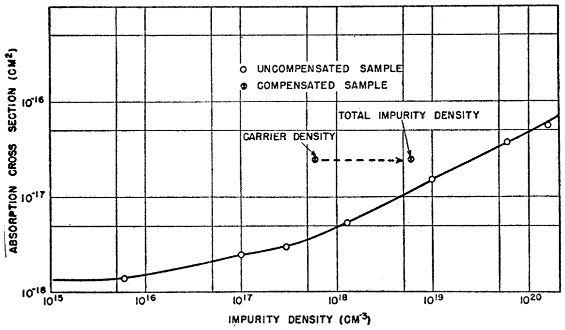

FIG. 2. The 77°K absorption cross section of p-type germanium as a function of impurity concentration at 0.7 ev. Points at two lowest concentrations are extrapolated values.

The samples used at the low-concentration limit are nonuniform because of the long optical path required. For the sample termed $10^{15}/\text{cm}^3$ in Fig. 1 the variation in carrier density was approximately a factor of 3 from one end to the other with $10^{15}/\text{cm}^3$ as a rough average. For the sample with a concentration of $1.5\times10^{20}/\text{cm}^3$ the values of absorption constant shown in Fig. 1 may be low by a factor less than 2. This resulted from our inability to make a very precise determination of sample thickness in the 1 to 2 micron range.

RESULTS AND DISCUSSION

Figure 1 shows the hole absorption spectra from 0.1 to 0.8 ev at 77°K for a series of samples whose impurity concentration ranged from $\sim10^{15}$ to 10^{20} per cm^3. For several of the more highly doped samples, room temperature data are also given as dotted curves. For the remainder of the samples the room temperature data were identical with those already reported.[2,3,10] Since the effects under study were most pronounced at 77°K, the discussion will refer exclusively to data taken at this temperature.

As indicated above the carrier concentration and impurity effects arise in three ways. Of these the Fermi level effect and the enhancement of indirect transitions by charged impurity centers are probably the most important.[7]

The effect of changes in Fermi level position within the valence band result in changes in the position of the absorption peak. For example, the peak of the $V_1\rightarrow V_3$ transition should shift to higher photon energy as the Fermi level goes deeper into the valence band. However, at points sufficiently removed to the high-energy side of the absorption peak, the direct transition process would require the same slope and the same temperature dependence for the absorption coefficient *vs* photon energy curves for all concentrations. This clearly is not the case. Not only are the slopes at high energies different, but for the higher carrier concentration values they are almost temperature independent. Consideration of these facts suggested the second important mechanism, namely the enhancement of indirect transitions by charged impurity centers. The basic idea is that scattering of a carrier by a charged center produces a mixing of the k states which describe the motion of the carrier. This results in a relaxation of the selection rule $\Delta k=0$. The effect on the spectrum is to tend to "wash out" the structure. For example, the slope on the high-energy side of the absorption due to the $V_1\rightarrow V_3$ transition is almost an exponential in photon energy for the direct transition process, reflecting the hole distribution function. On the other hand, the absorption curve determined by the indirect process would principally reflect the matrix element for the indirect transition which is a less rapidly varying function of photon energy.

As a specific test of the effect of charged impurities, the absorption spectra at 77°K was measured for two samples with almost the same carrier density but for which the total density of charged impurities was different. The results are indicated by the curves in Fig. 2 labeled 1.3×10^{18} carriers/cm^3 and 6×10^{17} carriers/cm^3+5×10^{18} compensated impurities/cm^3 (Ga and As). The high energy slope of the absorption region corresponding to the $V_1\rightarrow V_3$ transition is less for the sample having a higher charged impurity content than for the sample having the higher carrier concentration. Also the slopes are the same for the curves labeled 1×10^{19} carriers/cm^3 and for that of the compensated sample which had almost the same total impurity content but a smaller carrier density. These observations are in accord with the indirect transition idea. The difference between these latter two curves (e.g., position of the absorption peak) then reflects the change in the position of the Fermi level.[11]

In Fig. 2 is shown a plot of absorption cross section as a function of impurity concentration for 0.7 ev. It is to be noted that for the compensated sample, the total impurity density rather than the carrier density seems the more appropriate choice of abscissa value in order to fit the point to the data for the other samples.

SUMMARY

In summary, the interpretation of the impurity effects on the free-hole absorption in germanium has shown the importance of two effects: the Fermi level effect and the impurity induced indirect transition effect. The accuracy of the theoretical calculation of these effects is sufficient to show that band structure modification does not contribute significantly to the observed results.[7]

ACKNOWLEDGMENTS

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[10] R. Newman and W. W. Tyler, Bull. Am. Phys. Soc. Ser. II, **1**, 49 (1956), contains a preliminary account of this work.

[11] Kane's theory of the indirect transitions predicts a slow variation in the absorption transition probability with free carrier concentration, due to a screening of the impurity centers by the carriers. For the purpose of this discussion the slow variation may be neglected.