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Concentration Effects on the Line Spectra of Bound Holes in Silicon

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The effect of impurity concentration on the line spectra of holes bound to B, Al, and Ga acceptors in silicon has been studied at 21°K. Details of the spectra (i.e., relative positions, line shapes, intensities) differ for the different acceptors. Below an acceptor concentration of about $10^{16}/\text{cm}^3$ the spectra are concentration-independent under the conditions of measurement. Above $10^{16}/\text{cm}^3$ the spectral lines begin to broaden and by $\sim 10^{18}/\text{cm}^3$ the line structure has been almost completely destroyed. A qualititive discussion of the concentration effects is given.

BURSTEIN and co-workers have examined the low-temperature (4°K to 77°K) absorption spectra of the group III and group V elements acting as acceptor or donor impurities in silicon.[1,2] They have found that these spectra are characterized by absorption continua which terminate at low energies with absorption edges. Below these edges in energy, are found series of relatively sharp absorption lines. These spectra have been interpreted as follows: At low temperatures the holes or electrons are "frozen out" at acceptor or donor sites respectively. A sharp absorption line indicates an optical transition from the ground state of the impurity to one of its discrete excited states. The absorption continuum indicates transitions from the ground state to an ionized state lying in either the valence or conduction band respectively. As is to be expected from this interpretation, absorption in the continuum is accompanied by photoconductivity. A correlation exists between the energies at which characteristic features of the absorption spectra appear and the ionization energies of the centers determined from the temperature dependence of the carrier densities (i.e., resistivity and Hall measurements).[3]

The original attempts at a quantitative interpretation of these spectra in terms of the simple hydrogenic model (Coulomb field in a dielectric and a single effective mass) were not completely successful.[1,2] Recently an improved calculation based on an effective mass approximation which involves the most recent information (i.e., cyclotron resonance data) about the valence and conduction band structure has shown greater promise of quantitative success.[4]

The present work describes some studies of the discrete absorption lines of the group III acceptors B, Al, and Ga as a function of the density of impurity centers.[5] The study was undertaken with the thought that it could yield detailed information about the behavior of individual energy states with concentration. This, in turn, could perhaps give a more detailed picture of the phenomena associated with the terms "impurity banding" and "degeneracy."[6–12]

EXPERIMENTAL

Single crystals of silicon with the desired concentration of impurity were grown from quartz crucibles by the usual pulling and doping techniques. The starting material was zone-refined DuPont silicon having an uncompensated hole concentration of approximately $4\times10^{14}/\text{cm}^3$. The absorption spectra subsequently proved the expected result that these holes were derived from boron centers. Sections for the absorption measurements were cut transverse to the direction of crystal growth to obtain maximum homogeneity. These were ground and polished to the desired thickness. Samples were mounted in a metal double Dewar equipped for transmission measurements. Samples less than about 5 mils in thickness provided a problem in mounting because of their fragility and limited thermal conductivity. To circumvent these difficulties the samples were cemented to a polished plate of silicon of high purity about 1 mm thick using a calorimeter adhesive. The sample and mounting plate assembly could then be handled in the same way as the thicker specimens. The chief problem was to adjust the solid content and viscosity of the adhesive to provide a uniform (for thermal contact) and thin (optically nonabsorbing) layer of adhesive between the two pieces of silicon when the adhesive set.

The measurements quoted here were all made at about liquid hydrogen temperature. The results, to the resolution of the measurements, were indistinguishable from a few made at liquid He temperature. Sample temperatures were measured directly by affixing

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[1] Burstein, Bell, Davisson, and Lax, J. Phys. Chem. **57**, 849 (1953).

[2] Burstein, Picus, and Sclar, *Proceedings of the Conference on Photoconductivity, Atlantic City, November 4–6, 1954* (John Wiley and Sons, Inc. New York, 1955).

[3] F. J. Morin *et al*, Phys. Rev. **96**, 833(A) (1954).

[4] W. Kohn, Phys. Rev. **98**, 1856 (1955).

[5] Previous papers described measurements of the absorption line spectrum of In in silicon [reference 2 and R. Newman, Phys. Rev. **99**, 465 (1955)]. However, because of the low solubility of indium in silicon and the proximity of its absorption lines to the lattice bands, it was decided that further work on it would not be very fruitful.

[6] R. O. Carlson, Phys. Rev. **100**, 1075 (1955).

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

[8] G. L. Pearson and J. Bardeen, Phys. Rev. **75**, 865 (1949).

[9] H. Fritzsche and K. Lark-Horovitz, Physica **20**, 834 (1954).

[10] C. S. Hung and J. P. Gliessman, Phys. Rev. **96**, 1226 (1954).

[11] C. Erginsoy, Phys. Rev. **80**, 1104 (1950); **88**, 893 (1952).

[12] W. Baltensperger, Phil. Mag. **44**, 1355 (1953).

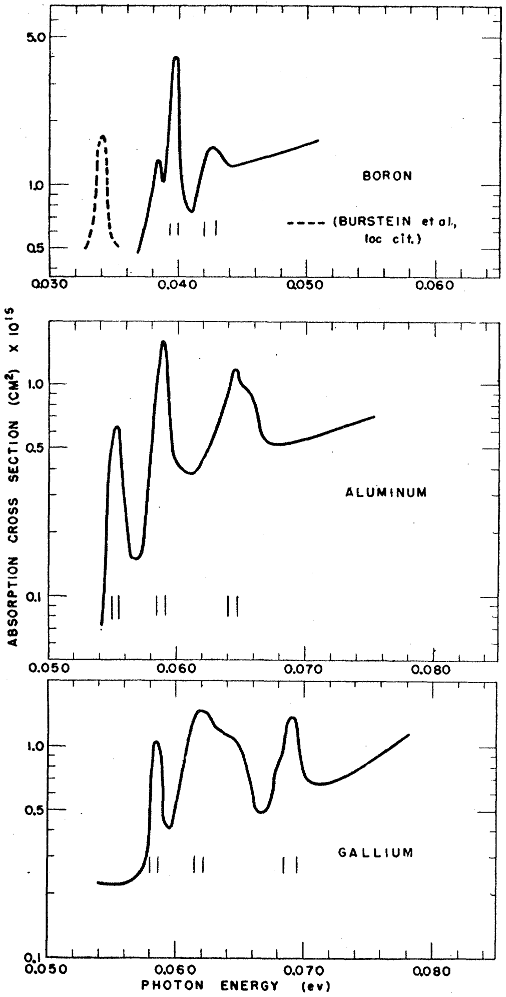

FIG. 1. Absorption line spectra of B, Al, and Ga acceptors in silicon at 21°K. The data were taken from samples having from 10^{15} to 5×10^{15} acceptors/cm^3. The dashed curve represents some data of Burstein *et al.* (reference 2). The spectral resolving power employed at various wavelengths is indicated.

a copper-constantan thermocouple to the sample itself. A Perkin-Elmer spectrometer with CsBr optics and continuous nitrogen flush was used. A rough-ground mirror and a polyethylene filter in the collimator were used to reduce stray light. Over most of the range of the measurements, stray light in the blank beam, as measured with a NaCl plate, amounted to considerably less than 0.5% and was corrected for. Sample thicknesses were adjusted to give transmissions in the range 1% to 20%. The spectral resolution quoted in the figures was determined by observation of the full width at half-power points for several sharp atmospheric absorption bands as a function of slit width. The resolving power of the measurements was limited by the available signal power.

The acceptor densities were obtained from measurements of the room-temperature resistivities of the samples employed. The data of Carlson[6] were used to convert resistivity to carrier (acceptor) density.

RESULTS AND DISCUSSION

A. Low-Concentration Limit

The spectra obtained at the low-concentration limit differ in some details from the spectra already reported.[1,2] Since these details will be important in any subsequent quantitative interpretation of the spectra, a digression from the main material of this report seems in order.

Figure 1 shows the line spectra, expressed as absorption cross sections, for B-, Al-, and Ga-doped silicon at 21°K. The spectra shown appear to be the asymptotic limits at low concentrations. The concentrations used were 1 to 5×10^{15}/cm^3. The spectral resolution is indicated. Our data for boron are, unfortunately, incomplete. Our instrumentation did not permit a satisfactory observation of the B line located at 0.034 ev. For completeness' sake Burstein's data[2] for this line are included and shown as a dashed curve. In Table I, the energies of the observed lines are given.

As is apparent from Fig. 1, certain gross features of the three spectra are the same. For example, all show three major components. However, beyond this there appear to be rather profound differences in the sizes, shapes, and relative positions of corresponding major components in the different spectra. Of particular interest is the fact that the shapes of several of these components appear to be the result of the superposition of two or more incompletely resolved lines.

Using the mass parameters of the degenerate valence band as determined from cyclotron resonance data, Kohn has calculated some of the excited energy levels associated with a hole bound to a Coulombic acceptor center in silicon.[13] He has found a rather complex level scheme. One would like to make a one-to-one correspondence between Kohn's energy levels and the energies of the absorption lines which have been observed. That is, for each acceptor, one would correlate a line of a particular energy with a given excited state. This procedure involves the tacit assumption that the differences, from one acceptor to another, between the energies and intensities of the lines to be associated with the given excited state, are ascribable to the

TABLE I. Photon energies (ev). The symbol ~ indicates shoulder to an adjacent line.

B	Al	Ga
0.034[a]	0.0555	0.0585
0.0382	0.0590	0.0620
0.0398	0.0645	~0.0640
0.0428	~0.648	~0.0680
		0.0690

[a] Reference 2.

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[13] W. Kohn (to be published).

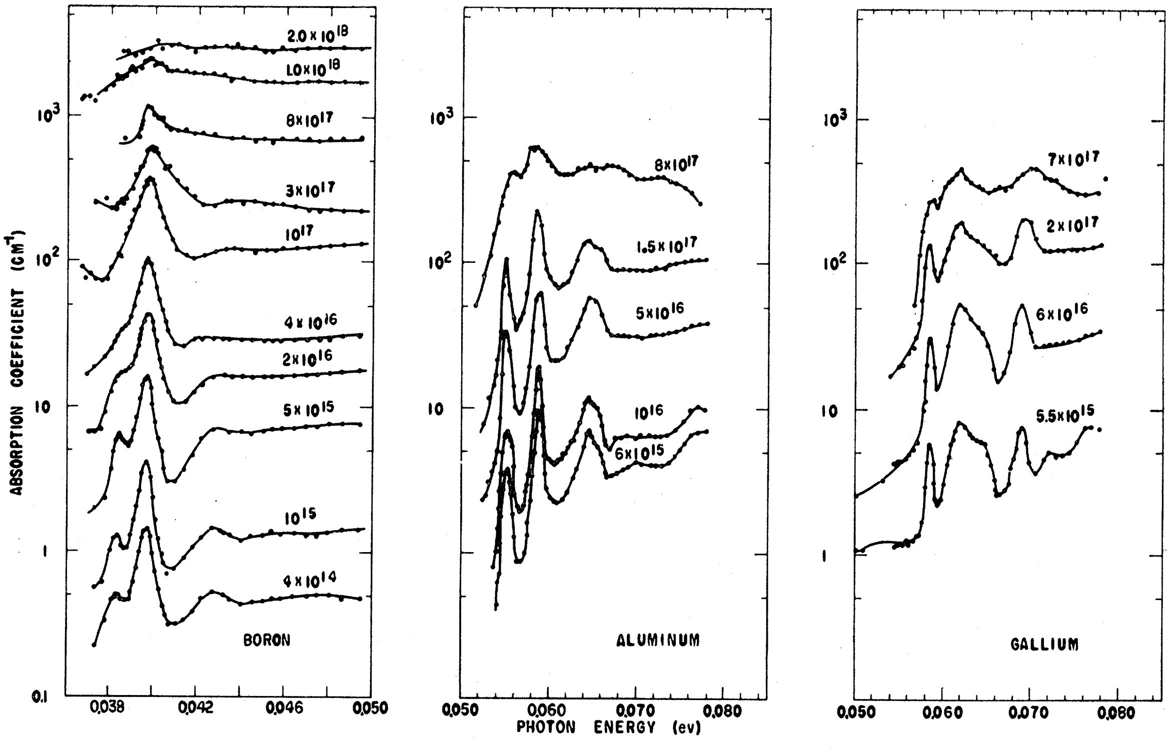

FIG. 2. Concentration dependence of the absorption line spectra of B, Al, and Ga acceptors in silicon at 21°K. The acceptor concentrations are indicated.

properties of the ground state alone. The ground-state wave function for each impurity is presumably different as evidenced, for example, by the different ionization energies. It is surprising, however, that impurities with as closely similar properties as Ga and Al (i.e., ionization energies differing by about 10%) should show widely differing size, shape and relative positions for the absorption lines. These differences make a reduction of the different sets of data to a single term scheme a somewhat problematic operation at present.

B. Concentration Effects

In Fig. 2 are shown the spectra of B-, Al-, and Ga-doped silicon at 21°K as a function of concentration. The concentrations are noted on the figure. The spectral resolving power is the same as is indicated in Fig. 1.

From a study of the data, one can make certain qualitative generalizations. For example, at concentrations less than about $10^{16}/\mathrm{cm}^3$ the spectral line shapes, at least to the noted resolution, are independent of concentration. The absorption coefficient at any particular energy is linearly dependent on concentration up to about $10^{16}/\mathrm{cm}^3$.

Above about $10^{16}/\mathrm{cm}^3$ the lines begin to broaden although the positions of the peaks remained essentially fixed in energy. The individual lines are not well resolved from one another even at the lowest concentrations. For this reason it is difficult to make any completely unambiguous and quantitative statement as to the details of the broadening. However, it would appear that in the broadening process a line at a higher energy will begin to broaden sooner than a line at a lower energy.

In Fig. 3 an attempt has been made to give a more quantitative statement to these concentration effects. Figure 3 gives the ratio of the estimated width (full width at half-power) at the acceptor concentration of interest to the same quantity at the low-concentration limit plotted as a function of acceptor concentration. Because of the aforementioned difficulties, the analysis presented in Fig. 3 must be made with reservations. In particular the decomposition of the absorption curves into component lines, each of a definable width, is to a degree arbitrary in some cases.

In any theory of the interaction of impurity states, the parameter of greatest importance will be the ratio of some mean distance between impurities to the equivalent Bohr radius of the impurity state in question.[11,12] When this ratio is large compared to unity, the interaction will be small but will increase as the ratio decreases. For a given mean impurity distance (i.e., concentration), the amount of interaction for the different impurity levels will be determined by their Bohr radii. It is proposed that the analysis of Fig. 3 be understood in this way. Namely, if the broadening of a line is ascribed entirely to the interaction broadening

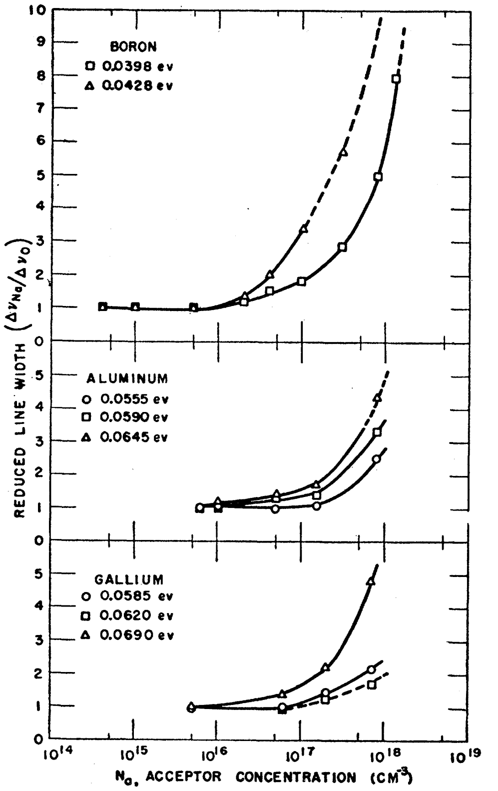

FIG. 3. Reduced line width (see text) of the various absorption lines of B, Al, and Ga acceptors in silicon at 21°K as a function of acceptor concentration. The dashed sections of the curves represent the least reliable estimates.

of the appropriate excited state, then at a given concentration a line of higher energy will be broadened to a greater extent than a line of lower energy.

It is of interest that at any given concentration the broadening effects seem largest for the case of boron. If the broadening is in the excited states and these are identical for different impurities, this observation is difficult to understand.

It would not be expected that there should be any *direct* correlation of the effects observed here and those electrical effects which have been grouped under the term "impurity banding."[6–10] Presumably in the present case we are observing effects which principally reflect modifications in the excited states whereas, to a first approximation, the electrical measurements reflect modifications in the ground state. This presumption is perhaps borne out by the fact that in the optical meaurements appreciable concentration effects are shown at concentrations of the order of 10^{17}/cm^3. On the other hand, in the electrical measurements, at these concentrations, no important concentration effect is shown. For example, the temperature dependence of the Hall coefficient at 10^{17}/cm^3 is essentially the same as that for much lower concentrations. That is, it can be described by a unique ionization energy. Impurity band and degeneration effects are unobservable down to 20°K at concentrations less than $\sim 5\times 10^{17}$/cm^3.[6,7]

In the foregoing discussion it has been tacitly assumed that the impurities are distributed homogeneously. Some recent measurements of the electron spin resonance of bound electrons in silicon at impurity concentrations of the order of 10^{17}/cm^3 and above have been interpreted as indicating a clustering of impurities.[14] Presumably then, in any quantitative discussion of the concentration broadening such inhomogeneities would have to be taken into account. It is perhaps possible that the difference in concentration effects between boron and the others was due to some specific inhomogeneity effect.

SUMMARY

Differences in the form of the line spectra of holes bound to B, Al, and Ga impurities are found. These differences indicate that a rather refined theoretical approach, in which the specific electronic properties of the impurity centers are included, will be required to fully understand the data. Below about 10^{16}/cm^3 the form of the spectra are observed to be independent of concentration. Above 10^{16}/cm^3 the spectral lines begin to broaden and by about 10^{18}/cm^3 the line structure is almost completely destroyed.

ACKNOWLEDGMENTS

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[14] Feher, Fletcher, and Gere, Phys. Rev. **100**, 1784 (1955).