Evidence for correlated hole distribution in neutron-transmutation-doped isotopically controlled germanium

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(Received 24 October 1995)

We report on low-temperature infrared-absorption spectroscopy studies of compensated p-type Ge(Ga,As) samples with varying doping compensation ratios. Previous difficulties in preparing appropriate samples are overcome by neutron-transmutation doping of high-purity, isotopically controlled germanium composed exclusively of ^{70}Ge and ^{74}Ge, viz. $^{70}Ge_x\,^{74}Ge_{1-x}$. With this technique, we have produced a series of crystals with compensation ratios between 0.082 and 0.87, while maintaining the net-acceptor concentration [Ga]-[As] constant at 5×10^{14} cm^{-3}. The observed excitation lines of Ga acceptors broaden linearly with the ionized impurity concentration due to the quadrupole interactions between Ga bound holes and the electric-field gradient. Experimental linewidths are quantitatively compared with existing theories of electric-field broadening developed in the context of donor transitions. We find excellent agreement with the theory based on the correlated distribution of ionized impurity centers.

I. INTRODUCTION

Highly compensated semiconductors are important for both technological applications and basic research issues. A semi-insulating GaAs substrate for high-speed, high-frequency electronic applications is an example of the importance of such a material in technology. Highly compensated semiconductors are ideal systems to study the effect of the disordered impurity distribution on the spatial fluctuations of the electron potential energy.

A number of physical properties such as the free-carrier mobility and the widths of optical transition lines observed in impurity absorption spectra or photoluminescence depend upon the spatial fluctuations of the electrostatic potential created by ionized donors and acceptors in the crystal. In this paper we specifically discuss the broadening of ground-state to bound excited-state transitions of shallow acceptors in Ge in the presence of electric fields and their gradients arising from randomly distributed ionized impurities.

The four major broadening mechanisms of the impurity absorption lines have been treated theoretically some time ago: (1) phonon lifetime broadening due to interaction of bound electrons (holes) with phonons;[1,2] (2) concentration broadening due to overlap of the very extended hydrogenic impurity wave functions;[3] (3) strain broadening due to strains resulting from the presence of dislocations, precipitates, and impurities;[4] and (4) Stark and quadrupole broadening due to random electric fields produced by ionized impurities.[5–7]

In the past few decades a number of experiments have provided a good understanding of the first three broadening mechanisms. Navarro, Haller, and Keilmann[8] have used the extremely sharp absorption lines of the stress-insensitive hydrogen-oxygen-related shallow donors D(O,H) in ultrapure Ge to demonstrate the quantitative validity of Barrie and Nishikawa's theory of phonon lifetime broadening.[1,2] Colbow,[9] Newman,[10] and White[11] used Si(B), while Nisida and Horii[12] and Imatake[13] studied Ge(Sb) with a wide range of doping concentrations to measure the concentration broadening of the absorption lines. Most experimental results were in good agreement with the semiempirical theory of concentration broadening proposed by Baltensperger.[3] Artjemenko

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et al.[14] observed a splitting in the gallium absorption lines in Ge due to stress caused by the presence of neutral barium impurities. Jagannath, Grabowski and Ramdas[15] studied all the above-mentioned broadening mechanisms by performing spectroscopic measurements on a wide variety of donors in Si (Si:P, Si:As, Si:Li, and Si:Li-0). Inspection of the extensive number of spectra given by Jagannath, Grabowski, and Ramdas[15] quantitatively confirmed the validity of the theories regarding the three broadening mechanisms.

Experiments have also been performed on the fourth broadening mechanism, Stark and quadrupole broadening.[9,11,15,16] However, only a few aspects of this topic have been understood because of the difficulty in producing appropriate samples. A rather limited range of ionized impurity concentrations were investigated in most of these studies. Although the effect of the phonon lifetime and strain broadenings were negligibly small in the compensated samples used in the previous studies of the electric-field broadening, the interpretation of these results was complicated by the uncontrolled coexistence of concentration broadening.

In the present investigation, we have overcome the difficulties of producing samples of controlled compensation by neutron-transmutation doping (NTD) of high-purity Ge single crystals containing controlled atomic fractions of ^{70}Ge and ^{74}Ge isotopes, i.e., $^{70}\mathrm{Ge}_x\,^{74}\mathrm{Ge}_{1-x}$.[17] This method enables us to control independently the majority N_{MJ} and minority N_{MN} impurity concentrations, i.e., the net-impurity concentration $N_{MJ}-N_{MN}$ and the compensation ratio $K=N_{MN}/N_{MJ}$. Using this method, a series of p-type Ge (Ga,As) samples of constant $N_{\mathrm{Net}}=[\mathrm{Ga}]-[\mathrm{As}]=5\times10^{14}$ cm^{-3}, with K ranging between 0.082 and 0.87, was produced in order to study the electric-field broadening of the excitation lines of Ga acceptors at low temperatures. By maintaining the same N_{Net} for all samples, we can assume that the line broadening due to concentration is the same in all samples. This enables us to isolate the effect of the electric-field broadening without interference from other broadening mechanisms. Further decided advantages of the NTD method are homogeneous distributions of both majority and minority impurities down to the atomic level.[18] This point is as important as the precise control of [Ga] and [As], because the most advanced theories of the electric-field broadening have been developed based on the assumption that the majority and minority dopants are randomly distributed.

In this paper, the widths of Ga excitation lines in the set of Ge (Ga,As) samples are quantitatively compared with the theoretically predicted linewidths[5–7] resulting from the Stark and quadrupole broadening mechanisms. Results from a similar work using the far-infrared magneto-optical absorption technique will be published elsewhere.[19] The present work demonstrates that a quantitative understanding of the electric-field broadening mechanism allows the determination of K in highly compensated semiconductors by means of infrared-absorption spectroscopy.

II. THEORY

We shall first consider the energy shift of hydrogenic impurity bound levels in an external electric field. Choosing the neutral impurity center as the origin of the spherical coordinates, the external potential $V(r)$ evaluated at a point $\vec{r}$ near the neutral impurity is given by[20]

$$V(r)=\sum_i \frac{e_i}{\kappa|\vec{R}_i-\vec{r}|}=4\pi\sum_i \frac{e_i}{\kappa R_i}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\frac{1}{(2l+1)}\left(\frac{r}{R_i}\right)^l \times Y^*_{lm}(\theta_i,\phi_i)Y_{lm}(\theta,\phi), \tag{1}$$

where κ is the dielectric constant; e_i is the charge on the ith impurity ion; R_i, θ_i, and ϕ_i denote spherical coordinates of the ith ion; Y_{lm} are the spherical harmonics; and r, θ, and ϕ are the spherical coordinates of $\vec{r}$. As pointed out by Larsen,[5] the multipole expansion of $V(r)$ is equivalent to a Taylor expansion of $V(r)$ about the donor center $(r=0)$. The $l=0$ terms in Eq. (1) correspond to the potential $V(r)$ evaluated at $r=0$. Because $l=0$ terms do not depend on r, these terms simply shift all levels of the neutral impurity up or down, and do not change the energy spacing between the levels, i.e., $l=0$ terms do not cause a shift in hydrogenic transition energies. $l=1$ terms, on the other hand, produce the well-known Stark shift of the hydrogenic transition energies. These terms reduce to a simple potential $-\vec{E}(0)\cdot\vec{r}$ of the uniform electric field $\vec{E}(0)$. For weak electric fields the Stark-shifted energy levels ε of the impurities with quantum numbers n, m, n_1, and n_2 are given by the familiar expression[21]

$$\varepsilon=-\frac{e^2}{2an^2}+\tfrac{3}{2}n(n_1-n_2)eEa-a^3[17n^2-3(n_1-n_2)^2-9m^2+19]\frac{E^2n^4}{16}+\cdots, \tag{2}$$

where n is the principal quantum number, m is the magnetic quantum number, a is the effective Bohr radius, and n_1 and n_2 are integers greater than or equal to zero which obey the condition

$$n=n_1+n_2+|m|+1. \tag{3}$$

In Eq. (2), the second term proportional to E is the linear Stark term, while the third term proportional to E^2 is the quadratic Stark term. Finally, it can be shown that the $l=2$ terms in Eq. (1) are linear in the electric-field gradients, e.g., they are proportional to $(\partial E/\partial z)_{r=0}$. The broadening due to $l=2$ terms is known as a quadrupole broadening.

From the preceding discussion, we find three distinctive mechanisms that lead to electric-field broadening of hydrogenic transition peaks: the linear Stark effect $(\propto E)$, the quadratic Stark effect $(\propto E^2)$, and the quadrupole interaction $(\propto \partial E/\partial z)$. Extensive theoretical studies of donor and acceptor excitation spectra conclude that the increase of linewidths is proportional to (i) $(N_I/N_0)^{2/3}$ when the linear Stark effect dominates,[6] (ii) $(N_I/N_0)^{4/3}$ when the quadratic Stark effect dominates,[6,22] and (iii) N_I/N_0 when the quadrupole interaction dominates.[6,22] N_I and N_0 are the ionized impurity and neutral impurity concentrations, respectively. The quadru-

pole interaction is proposed to be dominant in the limit of small N_I, while the quadratic Stark effect becomes most important in the other limit.[6,22] The effect of the linear Stark terms is much smaller than the other two effects, i.e., it can be neglected to the first order.[6,22] Thus it is of significant interest to see whether linewidths in our samples obey the $\propto(N_I/N_0)^{4/3}$ or $\propto N_I/N_0$ dependence. Neither dependence has yet been observed clearly.

Another point of interest is the quantitative comparison of our experimentally measured linewidths to theoretically predicted ones. For many years the electric-field line-broadening mechanisms has been theoretically investigated by assuming a random distribution of ionized impurity centers.[5,6,9,11,23] The most in-depth and complete studies were performed by Larsen.[5,6] After an extensive derivation of the relevant mathematical expressions, Larsen used the Monte Carlo technique to calculate the shape of the $1s$-$2p$ and $1s$-$3p$ transition lines due to donors associated with a simple spherical conduction band. However, it has been pointed out that the ionized impurity distribution at low temperatures may be correlated rather than random.[24,25] This correlated distribution occurs through redistribution of electrons (holes) among *randomly distributed donors (acceptors)* in such a way that the ionized impurity distributions are frozen in the state of minimum energy.[26] Kal'fa and Kogan found that this correlated distribution reduced the average strength of the electric fields in samples so that this effect should be taken into account in the theory of electric-field broadening of absorption lines.[22] Later the same group[7] incorporated the correlation effect in the theory of Larsen,[5,6] and calculated numerically the $1s$-$2p$ linewidth of donors associated with a simple spherical conduction band. According to Kogan and Lien[7] the correlation energy is of the same order of magnitude as the Coulomb interaction energy between majority impurities: $\sim e^2 {N_{MJ}}^{1/3}/\kappa$. Therefore, one would expect to see a strong effect of the correlation if the impurity excitation line is measured at temperatures $k_BT \ll e^2 {N_{MJ}}^{1/3}/\kappa$. On the other hand, one would expect Larsen's random distribution based prediction when $k_BT \gg e^2 N_{MJ}^{1/3}/\kappa$. Thus the transition temperature T_t separating the two temperature regimes is given by

$$T_t = e^2 N_{MJ}^{1/3}/k_B\kappa. \tag{4}$$

The observation of this transition was claimed by Golka *et al.*[27] and Baranovskii *et al.*[28,29] in n-type GaAs. However, whether the transition they observed was due to the correlation effect or not requires discussion. We shall come back to this point later in this paper.

No quantitative calculation has been reported so far regarding the impurity absorption linewidth arising from acceptors in semiconductors. Thus, in this work, we measure the absorption linewidths of hole transitions from the $1\Gamma_8^+$ ground states to the $2\Gamma_8^-$ bound excited states in Ga acceptors, and compare them quantitatively to the theoretically predicted linewidths of the $1s$-$2p$ transitions in shallow donors. We shall discuss below why this comparison is appropriate.

Two distinct peaks corresponding to C- and D-hole transitions in neutral Ga acceptors (labeled as in Jones and Fisher[30]) were observed in our absorption measurements

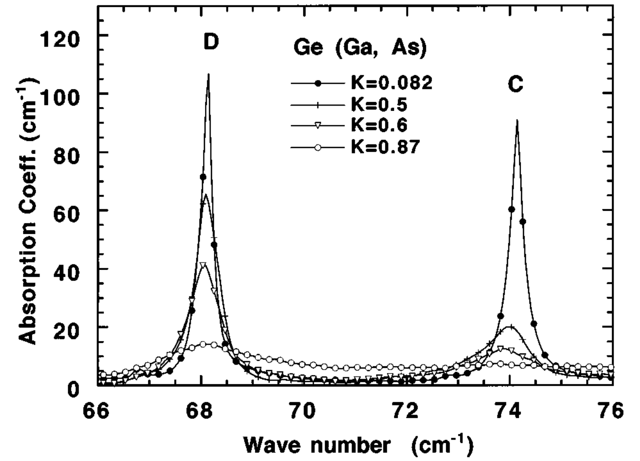

FIG. 1. Excitation spectra of Ge(Ge,As) samples of different compensation ratios (K) recorded with a resolution of 0.2 cm^{-1} at a temperature $T = 4.6$ K.

(Fig. 1). In the effective-mass approximation, the ground state of a group-III impurity in Ge has a symmetry $1\Gamma_8^+$ of the cubic group O_h. The D transition corresponds to the $1\Gamma_8^+$ ground-state to $2\Gamma_8^-$ excited-state hole transition, while the C transition is the excitation of holes from $1\Gamma_8^+$ to the accidentally degenerate $1\Gamma_7^-$ and $3\Gamma_8^-$ states. The classification of the familiar hydrogenic spectroscopic notation of $s,p,d,\ldots$ are given as[31]

$$s \rightarrow \Gamma_8^+ \tag{5}$$

$$p \rightarrow \Gamma_7^- + \Gamma_6^- + 2\times\Gamma_8^- . \tag{6}$$

Thus the symmetry of the s-like ground state of the spin $\frac{3}{2}$ hole in the tetrahedral site is Γ_8^+, while the p-like excited state splits into four states of various symmetries. It is not appropriate to conclude immediately from Eqs. (5) and (6) that the Γ_8^+ ground state has only an s-like envelope function, and that the $2\Gamma_8^-$ excited state is composed of only p-like functions. One should be aware that any even or odd spherical symmetry can give the Γ_8^+ or Γ_8^- cubic symmetry, respectively. This can be demonstrated by using the f-like state as an example:

$$f \rightarrow 2\times\Gamma_8^- + 2\times\Gamma_7^- + 2\times\Gamma_6^- . \tag{7}$$

The behavior of shallow acceptor wave functions is better understood by expanding the envelope radial functions of Ga acceptors in the basis of hydrogenlike functions using appropriate hole masses. This follows from the calculations of Buczko and Bassani,[32] who show that, although the Γ_8^+ ground state is composed of a number of hydrogenlike wave functions, the s-like state is by far the dominant component. Similary, we find the p-like components to be dominant in the envelope functions of the first odd-parity excited states. The calculated mean radii $\langle r\rangle$ for Ga acceptor states are

$$1\Gamma_8^+, \quad \langle r\rangle = 1.50a_0,$$

$$1\Gamma_8^-, \quad \langle r\rangle = 5.08a_{hh},$$

$$2\Gamma_8^-, \quad \langle r\rangle = 4.73a_0,$$

$$1\Gamma_7^-, \quad \langle r\rangle = 6.93a_0,$$

$$3\Gamma_8^-, \quad \langle r\rangle = 11.1a_{hh}.$$

a_0 is the Bohr radius calculated from the average of the heavy- and light-hole masses, and a_{hh} is the Bohr radius calculated from the heavy-hole mass alone. Comparing these results with the $\langle r\rangle$ given by the hydrogenlike wave functions

$$1s, \quad \langle r\rangle = 1.5a,$$

$$2p, \quad \langle r\rangle = 5a,$$

$$3p, \quad \langle r\rangle = 12.5a,$$

where a is the Bohr radius of the hydrogenlike atom, we find that the spatial extent of the $1\Gamma_8^+$ and $2\Gamma_8^-$ states are very close to those of the $1s$ and $2p$ hydrogenlike states (with the average Bohr radius a_0), respectively. On the other hand, the $1\Gamma_8^-$ and $3\Gamma_8^-$ states are similar to $2p$ and $3p$ hydrogenlike states (with the heavy-hole Bohr radius a_{hh}), respectively. It is also important to point out that the energy of the $2\Gamma_8^-$ state is one-fourth that of the ground state, as for an $n=2$ hydrogenlike state. Similarly, the energy of the $1\Gamma_8^-$ and $3\Gamma_8^-$ states are one-fourth and one-ninth of the heavy-hole ground state, respectively, consistent with conclusions drawn from the calculated mean radii.

From such theoretical considerations we expect the acceptor D transitions to be very similar to the $1s$-$2p$ donor transition.[33] The C transition, on the other hand, is a more complicated $1s$ to $2p$-$3p$ degenerate state transition. Thus a comparison of linewidths between the theories for the $1s$-$2p$ donor transition and our experimentally measured acceptor D transitions should provide an excellent opportunity to compare quantitatively the random theory of Larsen[6] with the correlated theory of Kogan and Lien.[7]

III. EXPERIMENT

Our sample preparation method has been described in detail in Ref. 17. Briefly, high-purity single crystals consisting of controlled mixtures of ^{70}Ge and ^{74}Ge were first grown using our modified vertical Bridgman method.[34] The electrically active residual impurity concentration in the Ge crystals before NTD is typically $\sim 10^{12}$ cm^{-3}. Wafers were cut from each ingot and irradiated with thermal neutrons at the University of Missouri Research Reactor facility. After the irradiation, a certain fraction of ^{74}Ge isotopes contained in the sample become As donors due to the $^{75}\mathrm{Ge}\rightarrow{}^{75}\mathrm{As}$ β^- decay reaction, while some of the ^{70}Ge isotopes convert to Ga acceptors due to the $^{71}\mathrm{Ge}\rightarrow{}^{71}\mathrm{Ga}$ electron-capture reaction. Unavoidable fast neutron radiation damage was removed by thermal annealing at 650 °C for 10 s in a N_2 atmosphere. Our doping method is very well calibrated.[17] We can control precisely the compensation ratio $\{K=[\mathrm{As}]/[\mathrm{Ga}]$ for p-type Ge(Ga,As)$\}$ by adjusting the composition ratio of ^{70}Ge and ^{74}Ge isotopes in the starting Ge crystals. The net-impurity concentration [Ga]-[As] is controlled independently by adjusting the thermal neutron fluence. Table I shows the Ga and As concentrations in each sample predicted from the combination of the of the isotopic composition and the thermal neutron irradiation time. As described in Ref. 17, Hall measurements were performed as a function of temperature for all samples in order to confirm the values of [Ga] and [As] predicted by the isotopic composition and the neutron fluence. The predicted values of [Ga] and [As] are in good agreement (within an error of 5%) with the [Ga] and [As] measured by the Hall effect. Also shown in Table I is the low-temperature ionized impurity concentration $N_I = 2N_{MN} = 2[\mathrm{As}]$.

TABLE I. Ga, As, and ionized impurity concentrations in the neutron transmutation-doped $^{70}\mathrm{Ge}_x$ $^{74}\mathrm{Ge}_{1-x}$ samples.

K	[Ga] (cm^{-3})	[As] (cm^{-3})	N_I (cm^{-3})
0.082	5.5×10^{14}	4.5×10^{13}	9.0×10^{13}
0.4	8.3×10^{14}	3.3×10^{14}	6.6×10^{14}
0.5	1.0×10^{15}	5.0×10^{14}	1.0×10^{15}
0.6	1.3×10^{15}	7.5×10^{14}	1.5×10^{15}
0.76	2.1×10^{15}	1.6×10^{15}	3.2×10^{15}
0.87	3.9×10^{15}	3.4×10^{15}	6.8×10^{15}

The infrared-absorption spectra were recorded with a BOMEM DA-3 Fourier transform spectrometer. Unapodized resolutions between 0.2 and 0.5 cm^{-1} were employed, and the signal-to-noise ratio was improved by coadding 100 spectra. A 4.2 K composite silicon bolometer with a cooled 370-cm^{-1} long pass filter was used as the detector. The samples were cooled in a Janis 10DT Supervaritemp cryostat with polypropylene windows for optical access, and the sample temperature was monitored with a calibrated thermometer installed at the sample mount. A black polyethylene film was used to eliminate band-gap radiation from illuminating the samples.

IV. RESULTS

Figure 1 shows four selected absorption spectra recorded at $T=4.6$ K in the wave-number range 66–76 cm^{-1} for samples of different compensations but equal net-acceptor concentrations. Each spectrum shows the two distinct peaks corresponding to C- and D-hole transitions of neutral Ga acceptors according to the notation of Jones and Fisher.[30]

As we have mentioned previously, the widths of the D transitions should be compared to the widths of donor $1s$-$2p$ electron transitions. Because we are interested in comparing our experimental results to theoretically predicted $1s$-$2p$ absorption linewidths for donors, we are going to concentrate on the linewidths of D transitions for the rest of this paper. The discussion regarding the C-transition linewidths will be excluded completely since, as was explained in Sec. II, the accidentally degenerate excited states ($1\Gamma_7^-$ and $3\Gamma_8^-$) of the C transition broaden in a complicated manner under the external electric field due to interactions between $1\Gamma_7^-$ and $3\Gamma_8^-$ states.

The D lines broaden strikingly with increasing compensation, as can be clearly seen in Fig. 1. The area under the D-transition peaks in all samples remains approximately constant, reflecting the same concentration of neutral Ga ab-

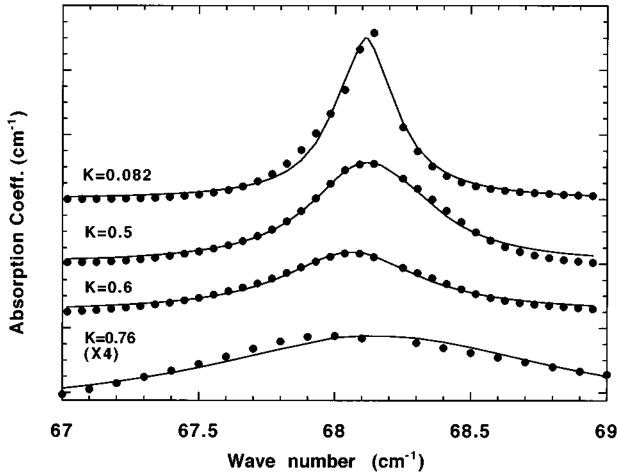

FIG. 2. Lorentzian fits to the D lines in order to deduce the full width at half maximum (FWHM).

sorbing centers ($[Ga^0] \sim 5 \times 10^{14}$ cm^{-3}). The full width at half maximum (FWHM) of each D line, determined by the standard Lorentzian fitting procedures, is as follows:

$$\alpha(k) = A \frac{\mathrm{FWHM}/2}{(k-k_0)^2 + (\mathrm{FWHM}/2)^2}, \tag{8}$$

where $\alpha(k)$ is the absorption coefficient, k is the wave number, and A and k_0 are the amplitude and the position of the peak, respectively. The fitting results are shown in Fig. 2 for the D transitions of four samples. Good fits are obtained up to $K \sim 0.76$. However, Eq. (8) does not represent the shape of a peak very well when the samples have a compensation K larger than 0.76. Therefore, the FWHM's of all $K > 0.76$ samples are determined by directly measuring the width at the half maximum rather than by the Lorentzian fit.

Figure 3 shows the main experimental result, viz. the FWHM as a function of the ionized impurity concentration at $T = 4.6$ K. The linewidth of the D transitions is temperature independent below 15 K, so that the thermal ionization of the neutral Ga centers is negligibly small. Thus the widths shown in Fig. 3 represent the FWHM of the D-transition characteristic for the total ionized impurity concentration of the particular sample. The linewidth of the D transition as a function of the ionized impurity concentration is linear within our experimental error. The best linear fit to the experimental points is represented by the dashed line. Figures 4(a) and 4(b) show the temperature dependence of the D-transition linewidths for $K = 0.082$ and 0.5, respectively. The linewidths are constant in both samples for $T < 15$ K.

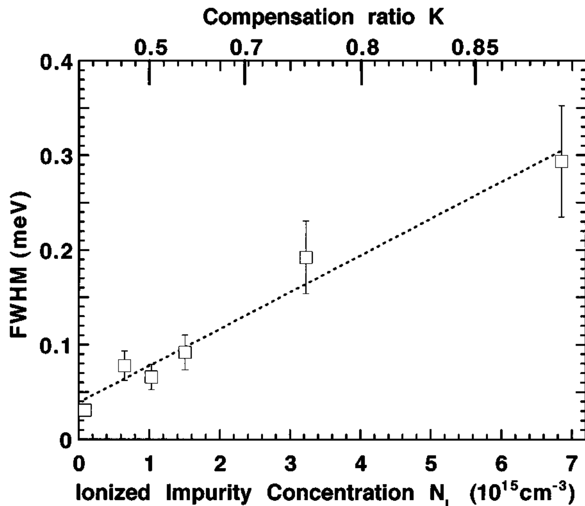

FIG. 3. Experimentally measured FWHM of the D (Ga) peaks in p-type Ge(Ga,As) as a function of the ionized impurity concentration (N_I).

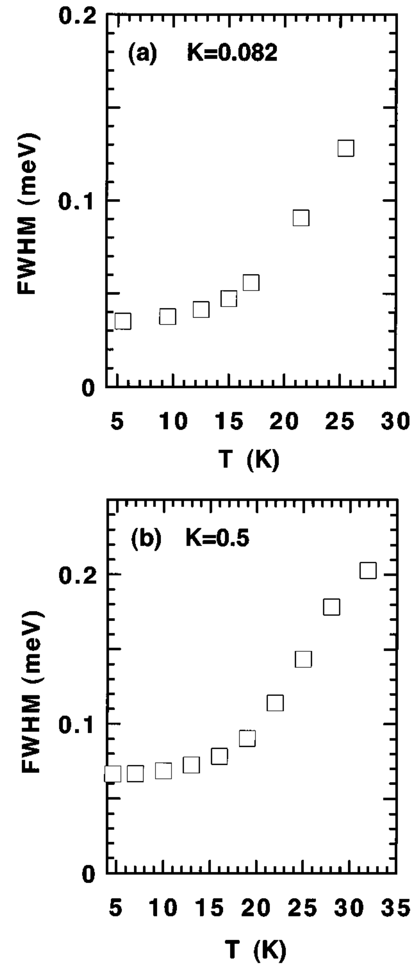

FIG. 4. Temperature dependence of the D-transition linewidths in the (a) $K = 0.082$ and (b) $K = 0.5$ samples.

V. DISCUSSION

A. Ionized impurity concentration dependence of the absorption linewidths

The unambiguous linear dependence of the FWHM on N_I/N_0 shown in Fig. 3 has been clearly observed here for the first time, to our knowledge. This linear dependence, as discussed in Sec. II, has been predicted for lightly doped semiconductors in which the quadrupole interaction is dominant.

The linear fit in Fig. 3 has a nonzero value 39 μeV for $N_I = 0$. This small residual broadening arises from a broadening mechanism other than the quadrupole interaction. In this set of samples, we can assume that the line broadening due to the concentration in each sample is the same, since we

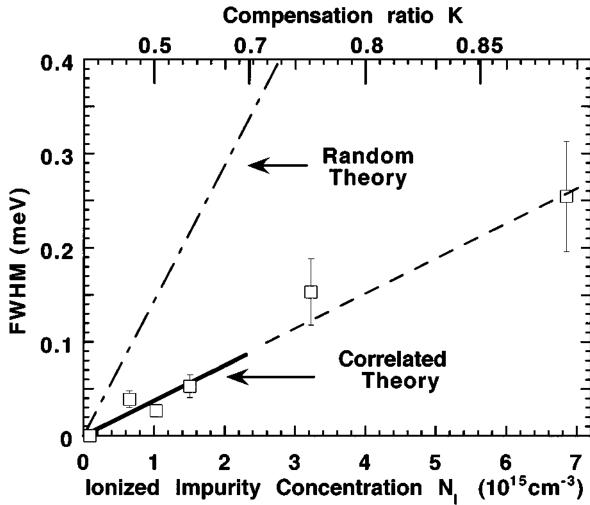

FIG. 5. FWHM vs N_I. A comparison of experimental results with the predictions of "random" ionized impurity theory and "correlated" distribution theory (see text for details).

have a constant $N_{\rm Net}=$ [Ga]-[As]$=5\times10^{14}$ cm^{-3} for all samples. Also, all samples were grown under the same condition, i.e., the broadening due to strain arising from the grown-in lattice defects must be very similar. Thus we are justified in deducing the linewidths due purely to quadrupole broadening by simply subtracting 39 μeV from all experimentally measured points in Fig. 3. These experimentally determined electric-field-broadened linewidths are compared to theories for hydrogenic donor $1s$-$2p$ transitions in Fig. 5. This figure shows the comparison between our experimentally determined electric-field-broadened D linewidths (indicated by open squares) and theoretical linewidths of hydrogenic donor $1s$-$2p$ transitions representing the random ionized impurity distribution theory of Larsen[6] and the correlated distribution theory of Kogan and Lien[7] in the range $0\leq N_I\leq 7\times10^{15}$ cm^{-3}. First, it is important to explain how these two theoretical curves for our Ge(Ga,As) samples were determined: (1) The random theory predicts that the linewidth is determined solely by the concentration of ionized impurity centers. Larsen's Monte Carlo result for $N_I a^3=5\times10^{-6}$ (Fig. 2 in Ref. 6) shows a FWHM of 10.8×10^{-4} Ry*, where Ry* is the effective Rydberg energy. Taking Ry*$=11$ meV for Ga in Ge, we find one point, FWHM$=12$ μeV at $N_I=8\times10^{13}$ cm^{-3} in Fig. 5. Based on the predicted linewidths dependence $\propto N_I/N_0$ (that has been experimentally confirmed in Fig. 3), we simply draw a straight line (the broken line labeled "Random Theory") which goes through both the origin and the one point at $N_I=8\times10^{13}$ cm^{-3} given by Larsen's calculation. (2) The linewidth predicted by the correlated theory depends solely on the ionized impurity concentration only when the compensation ratio K is smaller than 0.7.[7] When $K>0.9$, Kogan and Lien predicted that potential fluctuations due to ionized impurities become much larger than the correlation energy, and the effect of the correlation disappears. As a consequence, the width of the peaks becomes comparable to the prediction of the random theory when $K>0.9$. The compensation range $0.7<K<0.9$ can be characterized as a "correlated" to "fluctuating potential" transition region. Kogan and Lien[7] performed a numerical calculation of the linewidth as a function of the majority impurity concentration N_{MJ} for two different compensations: $K=0.5$ and 0.9. They assumed the quadrupole interaction to be dominant, i.e., the linewidths due to the given compensation scales linearly with N_{MJ} (see Table I of Ref. 7). Because the linewidths according to Kogan and Lien are proportional to N_I/N_0 only when $K<0.7$, we calculate one point at $K=0.5$ (i.e., $N_I=1\times10^{15}$ cm^{-3}) for our Ge using the correlated distribution theory, and draw a line between $0<K<0.7$ that goes through the origin and the calculated point at $K=0.5$ (the solid line labeled "Correlated Theory"). Unfortunately we cannot determine the prediction of the correlated theory anywhere above $K=0.7$ at this point except for the $K=0.9$ point given by Kogan and Lien. Because of the disorder effect arising from the strongly fluctuating potential, the linewidths are predicted to increase more rapidly than the $\propto N_I/N_0$ dependence when $K>0.7$. However, contrary to this prediction, our experimental results continue to be linear in N_I/N_0 for all K up to $K=0.87$. Thus, for the purpose of the comparison with our experimental results, we simply extend the $\propto N_I/N_0$ linear dependence of the correlated theory into the $K>0.7$ region indicated by a dashed line in Fig. 5.

The most important feature we see in Fig. 5 is the good agreement between our experimentally measured electric-field-broadened linewidths and the correlated theory of Kogan and Lien in the $K<0.7$ region. In fact, even the linear extension of the correlated theory into the $K>0.7$ region (the dashed line) agrees well with our experiment, in spite of the deviation from proportionality predicted by Kogan and Lien for $K>0.7$. These observations lead us to the following two conclusions:

(i) The ionized impurity distribution at low temperature is correlated based on the excellent agreement between our experimental data and the correlated theory of Kogan and Lien. Larsen's theory, which neglects the correlation effect, clearly overestimates the width by 4–5 times.

(ii) The correlation energy determines the distribution of the ionized impurities up to $K<0.87$, even though Kogan and Lien predicted that the potential fluctuation energy becomes dominant for $K>0.7$. Therefore our results appear to suggest that the relative amount of the correlation energy with respect to the fluctuation potential energy is larger than what was estimated by Kogan and Lien. This point is also supported by our interpretation of the temperature dependence of the linewidths, as we will show in Sec. V B.

B. Temperature dependence of the absorption linewidths

Here we discuss our interpretation of the temperature dependence of the linewidths shown in Fig. 4. The experimental confirmation of the correlated ionized impurity distribution motivated us to search for the correlated-to-random (CR) ionized impurity distribution transition at elevated temperatures. Using Eq. (4), we find T_t for the CR transition in the $K=0.082$ and 0.5 samples shown in Fig. 4 to be 8.5 and 10.4 K, respectively. However, it can be seen in Fig. 4 that the width of D peaks in both samples remains temperature independent up to $T=15$ K, and rapidly increases at temperatures larger than 15 K. This increase probably occurs due to the thermal ionization of neutral Ga impurities rather than due to the CR transition. In order to confirm this, we first

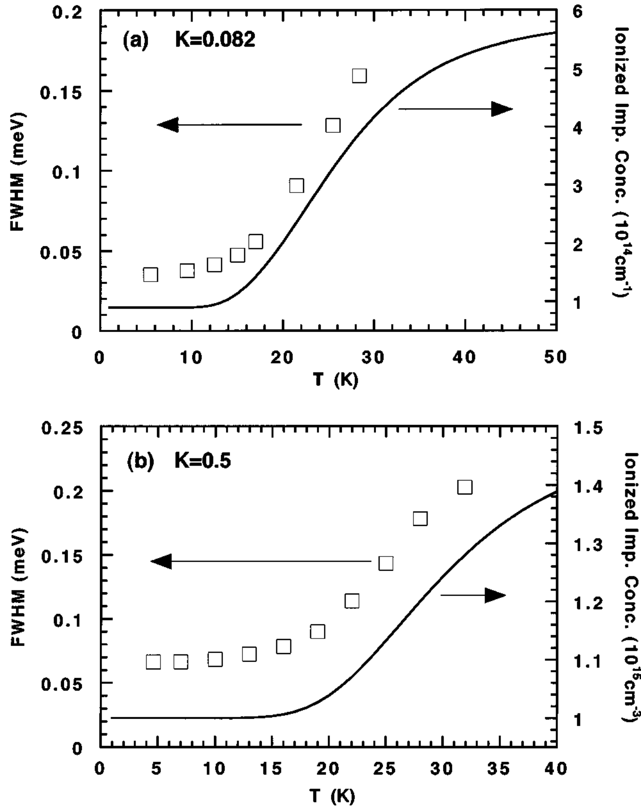

FIG. 6. Temperature dependence of the D-transition linewidths in the samples with (a) $K=0.082$ and (b) $K=0.5$. The solid curves are the calculated ionized impurity concentration in each sample.

calculate the free-hole concentration $p(T)$ in these samples by solving the free-carrier statistics equation[35]

$$\frac{p(p+N_{MN})}{(N_{MJ}-N_{MN}-p)}=\frac{1}{\beta}N_g\exp(-R_y^*/k_BT) \tag{9}$$

where β is the degeneracy factor 4 for acceptors, $N_g=1.2\times10^{15}\ \mathrm{T}^{3/2}\ \mathrm{cm}^{-3}$ is the effective density of states in the valance band, and R_y^* is the ionization energy of the majority (Ga) impurities. We then determine the ionized impurity concentration N_I as a function of temperature,

$$N_I(T)=p(T)+2N_{MN}. \tag{10}$$

The results for $K=0.082$ and 0.5 samples are shown in Figs. 6(a) and 6(b), respectively, together with the linewidths of D transitions as a function of temperatures. We find that the temperature dependence of the D-transition linewidths is proportional to N_I in both samples. Therefore, the widths' increase above $T=15$ K is due to the thermal ionization of Ga neutral impurities rather than due to the CR transition.

The important point here is that we did not observe any signs of the CR transition at T_t as predicted by Kogan and Lien [Eq. (4)]. One possibility that explains this result is that Kogan and Lien underestimated the correlation energy. The actual T_t is higher than the one predicted by Eq. (4), so that the CR transition is hidden in the background broadening due to thermal ionization of Ga acceptors above $T=15$ K. This possibility is consistent with our observation of the linewidths being proportional to N_I/N_0 all the way up to $K=0.87$. The correlation energy, supposedly comparable with the potential fluctuation energy for $K>0.7$ according Kogan and Lien, was actually much larger, and dominant all the way up to $K=0.87$ in our experiment.

Baranovskii *et al.*[28,29] reported on the observation of the CR transition in n-type GaAs. They measured the temperature dependence of the $1s$-$2p$ transition linewidth by performing photothermal ionization spectroscopy[4] (PTIS) as a function of magnetic field. However, because they did not know the concentration of the majority and minority impurities in their samples, they could not estimate the ionized concentration as a function of temperature. Without comparing the widths and ionized impurity concentrations as a function of temperature, it is not possible to determine whether the sudden increase of the PTIS peak widths in the experiment of Baranovskii *et al.* was due to the CR transition or the ionization of dopants.

C. Determination of the compensation ratio using absorption measurements

Finally we discuss the possibility of determining the compensation ratio K using absorption spectroscopy. Baranovskii *et al.*[28,29] proposed that the comparison of the linewidth before and after the CR transition allows the determination of K. This method obviously does not work for us since we do not observe the CR transition. From our point of view, K can be determined in a much simpler manner using the following steps.

(1) Measure N_{Net} using Hall-effect or capacitance-voltage measurements.

(2) Record one low-temperature absorption spectrum to find the chemical identity of the impurity (from the position of peaks) and the linewidth of the $1s$-$2p$-like transition.

(3) Find the slope of Kogan and Lien's theory that is consistent with the experimentally measured linewidth and the relation $N_{\mathrm{Net}}=N_{MJ}-N_{MN}=N_{MJ}-0.5N_I$.

Our experimental results show that the FWHM is proportional to N_I up to $K=0.87$; i.e., it should be possible to determine the compensation ratios as high as 0.87 using this method. At this point, our K determination method can be used reliably for samples with small compensations ($K<0.6$). The value of K determined by this method in $K>0.6$ samples has an uncertainty as large as 20% due to the large error bars on the linewidth measurement in highly compensated samples.

VI. SUMMARY AND CONCLUSIONS

We have quantitatively shown that the absorption linewidth calculation based on a correlated electron distribution in n-type semiconductors is the appropriate model for the quadrupole-dominated electric-field broadening of D transitions in shallow acceptors. The width was found to be proportional to the ionized impurity concentrations, suggesting that the quadrupole interaction is the dominant electric-field-broadening mechanism. No sign of the correlated-to-random impurity distribution transition was observed around temperatures predicted by the theory. We therefore suggest that the actual correlation energy was larger than what was estimated by the theory. This point is consistent with our observation of the linewidth proportional to the ionized impurity

concentrations all the way up to $K=0.87$, which is far beyond the range predicted by the theory.

We have also demonstrated that the quantitative understanding of the electric-field-broadening mechanism will allow us to determine the compensation ratio in any samples using infrared-absorption spectroscopy. It would be of great interest to repeat the same study using n-type samples of the similar net-impurity concentration or to develop a rigorous theory of the electric-field broadening of acceptor absorption lines.

ACKNOWLEDGMENTS

This work was supported in part by the Lawrence Berkeley Laboratory Director's Research and Development program U.S. DOE Contract No. DE-AC03-76SF00098, and in part by U.S. NSF Grant No. DMR94 17763. The work at Purdue received support from the U.S. NSF Grant No. DMR93 03186. One of us (K.M.I.) was supported by the U.S. NSF Center for Particle Astrophysics at UC Berkeley, Grant No. ADT-8809616. The work at Keio was supported by The Mazda Foundation's Research Grant.

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