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Electric field broadening of arsenic donor states in strongly compensated n-type Ge:(As, Ga)

Jiro Kato[a], Kohei M. Itoh[a,]*, Eugene E. Haller[b]

[a] *Department of Applied Physics and Physico-Informatics, Keio University, 3-14-1 Hiyoshi, Yokohama 223-8522, Japan*
[b] *UC Berkeley and Lawrence Berkeley National Labs, Berkeley, CA 94720, USA*

Abstract

We discuss on the broadening of ground-state to bound excited-state transitions of shallow donors in strongly compensated n-type Ge in the presence of electric fields and their gradients arising from randomly distributed ionized impurities. Low-temperature ($T = 3.2\,\mathrm{K}$) far-infrared absorption spectra of strongly compensated n-type Ge:(As,Ga) have been obtained for samples having ionized impurity concentration $N_\mathrm{I} = 2.2 \times 10^{13} - 2.6 \times 10^{14}\,\mathrm{cm}^{-3}$. Absorption peaks corresponding to 1s–2p$_\pm$ transition of arsenic impurities are observed, and broadened linearly with the ionized impurity concentration due to interactions between electrons and the quadrupole moments of ionized donors. The slope of the peak line width plotted against N_I changes at $N_\mathrm{I} \approx 8 \times 10^{13}\,\mathrm{cm}^{-3}$ due to the transition of ionized impurity distribution from random ($N_\mathrm{I} < 8 \times 10^{13}\,\mathrm{cm}^{-3}$) to correlated ($N_\mathrm{I} > 8 \times 10^{13}\,\mathrm{cm}^{-3}$). © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

In a recent publication [1], Itoh et al. have reported on the broadening of the 1s–2p-like Ga acceptor absorption peak in heavily compensated Ge samples having ionized impurity concentration $N_\mathrm{I} = 9.0 \times 10^{13} - 6.8 \times 10^{15}\,\mathrm{cm}^{-3}$. Their line widths as a function of N_I have been compared with theories for the hydrogenic donor 1s–2p transitions [2–4]. For the concentration range they investigated, they found very good agreement with the theory based on the correlated distribution of ionized impurities [2] than the theory assuming a random distribution [3,4]. They also have found that the quadrupole interaction is a dominant broadening mechanism.

In this work, we have repeated a similar investigation on donors because the relevant theories [2–4] have been developed assuming hydrogenic donors, not acceptors, in semiconductors. Moreover, we have probed the lower concentration region for which the random distribution of ionized impurities is predicted. As it will be shown below, the ionized impurity distribution is predicted to be random when $N_\mathrm{I} < 1 \times 10^{13}\,\mathrm{cm}^{-3}$ [3,4] and correlated when

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*Corresponding author. Tel.: +81-45-566-1594; fax: +81-45-566-1587.

E-mail address: kitoh@appi.keio.ac.jp (K.M. Itoh).

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$N_\mathrm{I} > 3 \times 10^{14}\,\mathrm{cm}^{-3}$ [2] for our Ge:(As,Ga), i.e., there may be a transition of the ionized impurity distribution as a function of N_I from random to correlated between $N_\mathrm{I} = 10^{13}$ and $10^{14}\,\mathrm{cm}^{-3}$. The present work reports on the experimental observation of such a transition for the first time in doped semiconductors. The experimentally determined critical ionized-impurity concentration for the transition is $N_\mathrm{I} = 8 \times 10^{13}\,\mathrm{cm}^{-3}$ for Ge:(As,Ga) at $T = 3.2\,\mathrm{K}$. It will be also shown that the quadrupole interaction is a dominant broadening mechanism of the 1s–2p$_\pm$ absorption peaks of As in Ge for the concentration range we investigated.

In the past, four major broadening mechanisms of the impurity absorption lines have been treated theoretically:

1. phonon lifetime broadening due to interaction of bound electrons (holes) with phonons [5,6];
2. concentration broadening due to overlap of the extended hydrogenic impurity wave functions [7];
3. strain broadening due to strains arising from the presence of dislocations, precipitates, and impurities [8]; and
4. Stark and quadrupole broadening due to random electric fields arising from ionized impurities [2–4].

We focus in this work on the fourth broadening mechanism. For weak electric fields, the energy ε of the bound state of a hydrogenic impurity with quantum numbers n, m, n_1, and n_2 in the unit of effective Rydberg of the hydrogenic impurity is given by

$$\varepsilon = \left[-\frac{1}{n^2} + \frac{3}{2} n(n_1 - n_2) eEa - [17n^2 - 3(n_1 - n_2)^2 - 9m^2 + 19] \times \frac{E^2 a^2 e^2 n^4}{32} + \cdots \right] \mathrm{Ry}, \tag{1}$$

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

$$n = n_1 + n_2 + |m| + 1. \tag{2}$$

The second term in Eq. (1), which is proportional to E, represents the linear Stark effect, while the third term, which is proportional to E^2, represents the quadratic Stark effect. Apart from Eq. (1), there exists a quadrupole interaction between donor-bound electrons and the quadrupole moments of ions leading to an energy shift proportional to the gradients of the electric field. The line width of the absorption peaks broadened by the electric field is proportional to [3,4]

1. $(N_\mathrm{I}/N_0)^{2/3}$ when the linear Stark effect is dominant,
2. $(N_\mathrm{I}/N_0)^{4/3}$ when the quadratic Stark effect is dominant, and
3. N_I/N_0 when the quadrupole interaction is dominant,

where N_0 is the concentration of the neutral absorption centers. In this study we probe 1s–2p$_\pm$ transition of electrons bound to As donors in Ge. Such a transition corresponds to $n = 2$, $n_1 = 0$, $n_2 = 0$ and $m = \pm 1$ in Eq. (1), i.e., the linear Stark term ($\propto E$) vanishes. Moreover, the quadrupole interaction is expected to be dominant in the limit of small N_I and for the transition having n even integers ($n = 2$, 4, 6, etc.). Therefore, we expect our 1s–2p$_\pm$ transition peaks to be broadened dominantly by the quadrupole effect.

For the quantitative calculation of absorption line widths broadened by the electric field, it is important to assume an appropriate distribution of ionized impurities. Up to now, two kinds of ion distributions have been proposed for compensated semiconductors at low temperatures: random distribution [3,4] and correlated distribution [2]. Fig. 1 depicts examples of the two distributions for Ge:(As,Ga). There are more As donors than Ga acceptors, so all Ga lose their holes at low temperatures and are ionized negatively. The negatively ionized Ga acceptors cannot move, so that their positions are fixed. However, electrons bound to As donors are free to choose As sites to which they bind. In the example shown in Fig. 1, four electrons can hop between eight As sites. The ionized impurity distribution is random [3,4] when these four electrons distribute themselves randomly among eight As sites that are available to

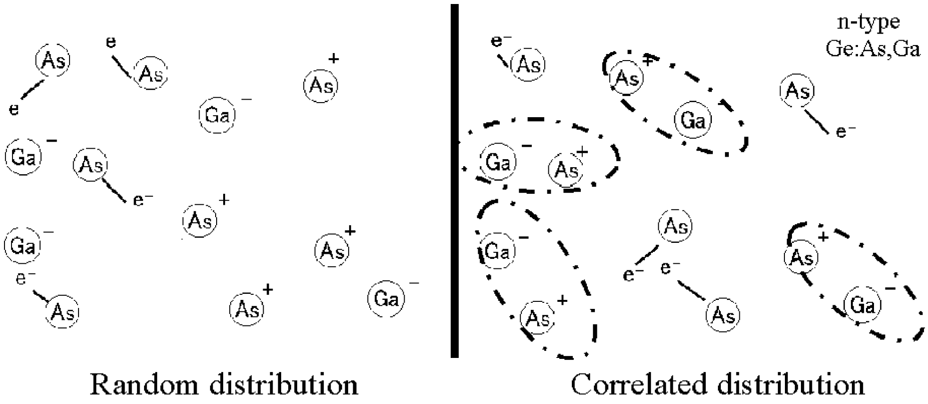

Fig. 1. Two kinds of distributions of ionized impurities in compensated Ge(As,Ga): random distribution (left half) and correlated distribution (right half).

them. On the other hand, the ionized impurity distribution is correlated [2] when electrons choose specific sites to lower the total Coulombic energy of the system. As atoms that are close to negatively charged Ga ions may prefer to remain positive in order to lower the Coulombic energy. The average electric field arising from the random distribution is larger than that from correlated distribution, i.e., the absorption line widths become broader for the random distribution than for the correlated distribution. Whether the distribution becomes random or correlated depends on the concentrations of ionized impurities and temperature. The random distribution is preferred for the lower N_I since the larger distance between ions leads to weaker correlation. According to the estimation due to Larsen, the random distribution is dominant when

$$N_I \leqslant 0.7 \times 10^{-5} a^{-3}, \tag{3}$$

where a is the Bohr radius of absorption centers. Inserting $a = 87.6\,\text{Å}$ for As in Ge, we expect the random distribution to be dominant when $N_I < 1 \times 10^{13}\,\text{cm}^{-3}$. The correlation energy, on the other hand, is of the same order of magnitude as the Coulomb interaction energy between impurities, i.e., $e^2 N_D^{1/3}/\kappa$, where κ is the dielectric constant and N_D is the donor concentration in an n-type semiconductor. The correlated distribution of ionized impurities is expected when the correlation energy is larger than the thermal energy, i.e., $e^2 N_D^{1/3}/\kappa > k_B T$. Assuming $N_I = 2KN_D$ where K is the compensation ratio defined by the minority impurity concentration divided by the majority impurity concentration, the correlated distribution becomes dominant when [3,4]

$$N_I \geqslant 2K \left(\frac{k_B T \kappa}{e^2} \right)^3. \tag{4}$$

Eq. (4) becomes $N_I > 3 \times 10^{14}\,\text{cm}^{-3}$ for our measurements performed at $T = 3.2\,\text{K}$. The purpose of this study is to obtain evidences for both kinds

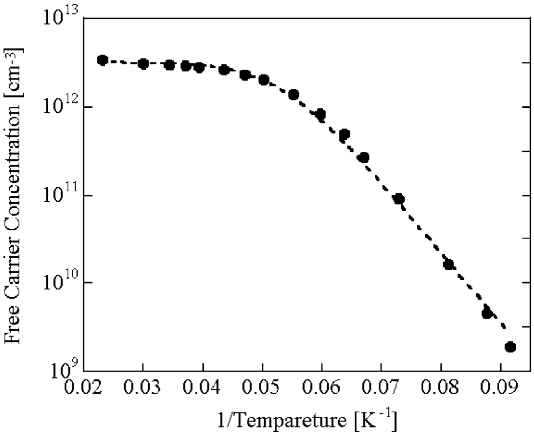

Fig. 2. Experimentally determined free carrier concentration (filled circles) vs. inverse temperature. The dotted curve is the best fit to the experimental data using Eq. (5) with [As] = $2.19 \times 10^{13}\,\text{cm}^{-3}$ and [Ga] = $1.85 \times 10^{13}\,\text{cm}^{-3}$.

of ion distributions via precise absorption measurements using a series of Ge:(As,Ga) samples having appropriate concentrations of N_{I}.

Samples are cut from a Cz-grown n-type Ge:(As,Ga) single-crystal ingot. The concentrations of As and Ga vary as a function of the position of the ingot along the growth direction due to impurity segregation during the growth. We have obtained a series of samples as a position of the ingot and determined the concentrations of As and Ga using variable-temperature Hall effect. Fig. 2 shows the free carrier concentration n vs. $1/T$ for one of the samples as an example. The data have been fitted very well by the standard semiconductor statistics (dashed curve in Fig. 2) using the relation

$$n = \frac{2([\mathrm{As}]-[\mathrm{Ga}])}{1+\frac{\beta[\mathrm{Ga}]}{N_{\mathrm{C}}}\exp\left(\frac{E_{\mathrm{D}}}{k_{\mathrm{B}}T}\right)+\sqrt{\left\{1+\frac{\beta[\mathrm{Ga}]}{N_{\mathrm{C}}}\exp\left(\frac{E_{\mathrm{D}}}{k_{\mathrm{B}}T}\right)\right\}^2+\frac{4\beta([\mathrm{As}]-[\mathrm{Ga}])}{N_{\mathrm{C}}}\exp\left(\frac{E_{\mathrm{D}}}{k_{\mathrm{B}}T}\right)}}, \quad (5)$$

where [As] and [Ga] are the concentrations of As donors and Ga acceptors, respectively, E_{D} is the binding energy of As donors, N_{C} is the effective density of the states, and $\beta = \frac{1}{2}$ is the degeneracy factor for a shallow donor. [As] and [Ga] that have been determined for each sample by the fitting are tabulated in Table 1 along with the ionized impurity concentration in the low-temperature carrier freeze-out region $N_{\mathrm{I}} = 2N_{\mathrm{A}}$ and the compensation ratio $K = N_{\mathrm{A}}/N_{\mathrm{D}}$. The error in the values of N_{D} and N_{A} determined by this method is less than 10% [9]. The infrared absorption spectra were recorded with a BOMEM DA-8 Fourier transform spectrometer. The signal-to-noise ratio was improved by simultaneously adding 100–720 spectra. A composite silicon bolometer operating at $T = 4.2\,\mathrm{K}$ was used as a detector. The samples were cooled in an OXFORD OPTISTAT cryostat and the sample temperature was monitored with a calibrated thermometer installed at the sample mount. A black polyethylene film was used to eliminate above band-gap radiations.

Fig. 3 shows the absorption spectrum (filled circles) of a sample having $N_{\mathrm{I}} = 1.84 \times 10^{14}\,\mathrm{cm}^{-3}$. It has been recorded at $T = 3.2\,\mathrm{K}$ with a resolution of $0.05\,\mathrm{cm}^{-1}$ in the wave number range between 95 and $110\,\mathrm{cm}^{-1}$. The peak corresponds to the 1s–2p$_{\pm}$ absorption of As in Ge. The full widths at half maximum (FWHM) of 1s–2p$_{\pm}$ transition are determined by the standard Lorentzian fitting (a solid curve in Fig. 3). Exactly like the example shown in Fig. 3, the absorption peaks of all samples are very nicely fitted by the Lorentzian function. The fact that the line shape is symmetrical around the center of the peak implies that the quadratic Stark effect does not play an important role. As can be seen in Eq. (1), the sign of the quadratic term (third term) is always negative, i.e., the absorption peaks are shifted only to lower energy and become asymmetric when the quadratic Stark effect is dominant. Therefore, the quadrupole interaction must be the dominant broadening mechanism for the series of samples investigated in this work.

Fig. 4 shows our main results: FWHM vs. N_{I}. The experimental data (filled circles) are compared with the theoretical line widths assuming random (dashed line) and correlated (solid line) distribution of ionized impurities. Larsen has shown that the line width for the random distribution is given by $5.4 \times 10^{-4}\,\mathrm{Ry}$ for $N_{\mathrm{I}}a^3 = 0.5 \times 10^{-5}$. This relation provides FWHM = $0.072\,\mathrm{cm}^{-1}$ for $N_{\mathrm{I}} = 7.46 \times 10^{12}\,\mathrm{cm}^{-1}$ for our Ge:(As,Ga) using Ry = $133.4\,\mathrm{cm}^{-1}$ and $a = 87.6\,\text{Å}$. Therefore, we simply draw a straight line (the dashed line labeled “Random theory” in Fig. 4), which goes through the origin and the point (FWHM = $0.072\,\mathrm{cm}^{-1}$, $N_{\mathrm{I}} = 7.46 \times 10^{12}\,\mathrm{cm}^{-3}$), since FWHM is proportional to N_{I} when quadrupole interaction is the dominant broadening mechanism. Kogan and Van Lien, on the other hand, have calculated the line width assuming the correlated distribution and found FWHM = 3.0×10^{-4}, 7.4×10^{-4}, and $24 \times 10^{-4}\,\mathrm{Ry}$ for $N_{\mathrm{I}}a^3 = 1 \times 10^{-5}$, 3×10^{-5}, and

Table 1
Concentrations of As ([As]), Ga ([Ga]), and ionized impurities (N_I), and compensation ratio K of each sample

[As] (cm^{-3})	[Ga] (cm^{-3})	N_I (cm^{-3})	N_0 (cm^{-3})	K
2.19×10^{13}	1.85×10^{13}	3.71×10^{13}	3.38×10^{12}	0.846
1.60×10^{13}	1.35×10^{13}	2.69×10^{13}	2.51×10^{12}	0.843
1.52×10^{13}	1.41×10^{13}	2.81×10^{13}	1.13×10^{12}	0.926
2.86×10^{13}	2.06×10^{13}	4.13×10^{13}	7.93×10^{12}	0.722
2.99×10^{13}	1.59×10^{13}	3.17×10^{13}	1.40×10^{13}	0.531
1.70×10^{13}	1.09×10^{13}	2.18×10^{13}	6.12×10^{13}	0.640
5.95×10^{13}	3.10×10^{13}	6.20×10^{13}	2.85×10^{13}	0.521
4.22×10^{13}	2.99×10^{13}	5.98×10^{13}	1.22×10^{13}	0.701
4.29×10^{13}	2.06×10^{13}	4.12×10^{13}	2.22×10^{13}	0.481
9.00×10^{13}	4.06×10^{13}	8.12×10^{13}	4.94×10^{13}	0.451
7.89×10^{13}	6.01×10^{13}	1.20×10^{14}	1.88×10^{13}	0.762
1.23×10^{14}	4.98×10^{13}	9.95×10^{13}	7.29×10^{13}	0.406
5.92×10^{13}	3.22×10^{13}	6.44×10^{13}	2.69×10^{13}	0.545
1.52×10^{12}	1.42×10^{11}	2.84×10^{11}	1.38×10^{12}	0.93
2.16×10^{13}	1.05×10^{14}	2.09×10^{14}	1.12×10^{14}	0.483
1.38×10^{14}	9.96×10^{13}	1.99×10^{14}	3.84×10^{13}	0.722
1.21×10^{14}	8.01×10^{13}	1.60×10^{14}	4.12×10^{13}	0.660
1.18×10^{14}	1.16×10^{14}	2.31×10^{14}	2.60×10^{12}	0.978
1.87×10^{14}	1.16×10^{14}	2.32×10^{14}	7.07×10^{13}	0.621
1.52×10^{14}	9.19×10^{13}	1.84×10^{14}	6.04×10^{13}	0.603
6.83×10^{13}	6.38×10^{13}	1.28×10^{14}	4.49×10^{12}	0.934
2.88×10^{14}	1.10×10^{14}	2.20×10^{14}	1.78×10^{14}	0.382
2.00×10^{14}	1.32×10^{14}	2.64×10^{14}	6.79×10^{13}	0.660

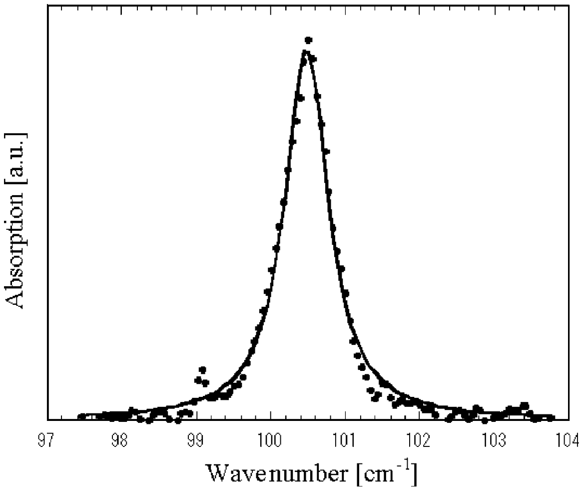

Fig. 3. An experimentally obtained 1s–2p$_{\pm}$ absorption spectrum (filled circles) of As in Ge with $N_I = 1.84 \times 10^{14}\,\text{cm}^{-3}$ taken at $T = 3.2\,\text{K}$. A solid curve is the best fit using the Lorentzian distribution.

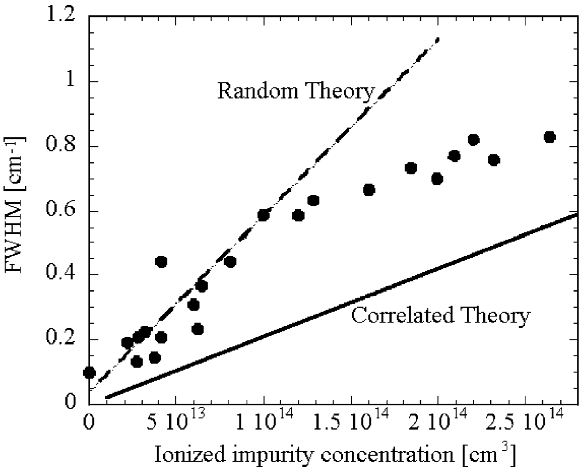

Fig. 4. Experimentally determined FWHM (filled circles) vs. N_I. The dashed line is the prediction based on the random distribution of ions while the solid line is the prediction based on the correlated distribution of ionized impurities.

1×10^{-4}, respectively [2]. The theoretical curve based on the correlated distribution shown in Fig. 4 (the solid line labeled "correlated theory") has been drawn based on this relation.

The comparison between the experimental results and theoretical estimations leads us to very interesting conclusions. An excellent agreement between experimentally determined FWHM and the random theory for $N_\mathrm{I} < 8 \times 10^{13}\,\mathrm{cm}^{-3}$ is a clear evidence for the random distribution of ionized impurities in this low N_I region. When N_I is larger than $8 \times 10^{13}\,\mathrm{cm}^{-3}$, experimental data points are between estimations of random theory and correlated theory. However, the slope of experimental data for $N_\mathrm{I} > 8 \times 10^{13}\,\mathrm{cm}^{-3}$ agrees very well with that of correlated theory. For $N_\mathrm{I} > 8 \times 10^{13}\,\mathrm{cm}^{-3}$, we believe there are two important effects that are responsible for the extra broadening of experimentally determined peaks with respect to the prediction of the correlated theory: the effect of donor wave function overlaps (concentration broadening) and the effect of finite temperature ($T = 3.2\,\mathrm{K}$). As the concentrations of As and Ga (i.e., N_I) are increased, the overlaps between wave functions of adjacent impurities become larger. This has an effect of increasing FWHM without changing the slope of the prediction based on the correlated theory. Such an effect was demonstrated clearly in Ref. [1]. The thermal energy arising from non-zero temperature is also an important factor. The line width calculation based on the correlated distribution was carried out assuming $T = 0$. However, the ionized impurity distribution in our Ge:(As,Ga) samples at $T = 3.2\,\mathrm{K}$ may not be as strongly correlated as was predicted for $T = 0$ due to a certain degree of randomization induced by the available thermal energy. In this case we expect the line width to be somewhere between the predictions of the random theory and correlated theory. In either scenario, it is clear that the line widths for $N_\mathrm{I} > 8 \times 10^{13}\,\mathrm{cm}^{-3}$ are significantly smaller than the prediction of the random theory, and there exists an effect of correlated distribution of impurities. Therefore, the impurity distribution changes from completely random to correlated at $N_\mathrm{I} \approx 8 \times 10^{13}\,\mathrm{cm}^{-3}$, i.e., we have observed experimentally the random to correlated ionized impurity distribution transition as a function of N_I for the first time.

In summary, we have performed a systematic investigation of the impurity absorption line widths with n-type Ge:(As,Ga). The broadening of the 1s–$2\mathrm{p}_\pm$ peaks has been determined and compared quantitatively to predictions of theories based on random and correlated distributions of ionized impurities. The slope of the peak line widths plotted against N_I changes at $N_\mathrm{I} \approx 8 \times 10^{13}\,\mathrm{cm}^{-3}$ due to the transition of ionized impurity distribution from random ($N_\mathrm{I} < 8 \times 10^{13}\,\mathrm{cm}^{-3}$) to correlated ($N_\mathrm{I} > 8 \times 10^{13}\,\mathrm{cm}^{-3}$).

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