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Observation of the random-to-correlated transition of the ionized-impurity distribution in compensated semiconductors

Jiro Kato,[1] Kohei M. Itoh,[1] and Eugene E. Haller[2]
[1]*Department of Applied Physics and Physico-Informatics, Keio University, Yokohama 223-8522, Japan*
[2]*UC Berkeley and Lawrence Berkeley National Labs, Berkeley, California 94720*
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We discuss the broadening of ground state to bound excited-state transitions of shallow donors in strongly compensated *n*-type Ge:(As, Ga) in the presence of electric fields and their gradients, arising from randomly distributed ionized impurities. Quantitative comparison of the experimentally obtained linewidths with Monte Carlo simulation results makes possible a unique determination of the ionized-impurity distribution in the samples. We present clear evidence for the random-to-correlated transition of the ionized-impurity distribution as a function of the ionized-impurity concentration and of temperature.

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Many-body Coulombic interactions between randomly distributed positive and negative charges play important roles in a wide variety of physical systems. Such interactions become important especially, when the charges are mobile and redistribute themselves in order to minimize the total Coulombic energy of the system. We have shown, recently that compensated semiconductors, e.g., germanium doped simultaneously by hydrogenic donors and acceptors, serve as ideal systems for the investigation of many-body Coulombic interactions between mobile ions.[1] Let us consider a *n*-type semiconductor with the concentration of hydrogenic donors (N_D), being twice of that of hydrogenic acceptors (N_A); $N_D=2N_A$. At sufficiently low temperatures one half of N_D is positively charged ($\frac{1}{2}N_D=N_D^+$) because their bound electrons are taken away by acceptors. These become negatively charged after accepting electrons ($N_A=N_A^-$). The remaining half of N_D binds electrons, so that their charge state is neutral ($\frac{1}{2}N_D=N_D^0$). This system is interesting because the ionized donors (D^+) can modify their distribution with respect to the fixed position of ionized acceptors (A^-) via the transfer of electrons between neutral (D^0) and ionized (D^+) donors. Therefore, the distribution of the ionized donors can be either random or correlated depending on the ionized-impurity concentration and on the temperature. Probing the many-body Coulombic interactions in such systems can be performed simply by measuring the electric-field broadening of neutral donor absorption lines by far-infrared spectroscopy. As it will be demonstrated in this paper, the quantitative comparison of the donor $1s$-$2p_{\pm}$ hydrogenic absorption linewidths between experiment and Monte Carlo simulation leads to an unambiguous determination of the ionized-impurity distribution as a function of the ionized-impurity concentrations ($N_I=N_D^+ + N_A^- = 2N_A$) and of the temperature (T).

It has been expected theoretically that the ionized-impurity distribution is correlated, when the available thermal energy is sufficiently smaller than the correlation energy.[2] Electrons distribute themselves among donors in such a way so as to reduce the total Coulombic energy, i.e., an energy gap known as ''Coulomb gap'' appears at the Fermi level in the density of the states of the donor band.[3] The correlation energy is of the same order of magnitude as the Coulomb energy between impurities, $e^2N_D^{1/3}/\kappa$, where κ is the dielectric constant. With $N_I=2KN_D$ where $K=N_A/N_D$ is the compensation ratio defined for *n*-type semiconductors, the correlated distribution is expected for the condition:[2,3]

$$N_I \gg 2K\left(\frac{k_BT\kappa}{e^2}\right)^3. \tag{1}$$

The correlated distribution of the ionized impurities has been confirmed for the condition given by Eq. (1) in *p*-type Ge in our previous study.[1]

When the thermal energy becomes larger than the correlation energy, i.e., the left-hand side of Eq. (1) is much smaller than the right-hand side, electrons are randomly distributed among donors, so that the ionized-impurity distribution is completely random. The random distribution is preferred for lower N_I since, the larger distance between ions leads to weaker correlation. Larsen's classic theory for the calculation of the linewidth assuming the random distribution is valid for the range,[4,5]

$$N_I \ll 0.7\times 10^{-5}a^{*-3}, \tag{2}$$

where a^* is the effective Bohr radius of donor impurities.

It is, therefore, of great interest to observe the correlated to random transition of the ionized-impurity distribution as a function of the ionized-impurity concentration and temperature. The experimental determination of the transition temperature allows us to estimate the value of the correlation energy. Similarly, the correlation energy (or equivalently the width of the Coulomb gap) becomes larger with increasing ionized-impurity concentration N_I. While, there have been many experiments to confirm the existence of the Coulomb gap, there has been very little direct evidence for the random distribution of ionized impurities at low temperatures in semiconductors. The present paper, describes the observation of the random-to-correlated distribution transition of ionized impurities as a function of N_I and T.

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 along the ingot growth direction due to impurity segregation during the growth. We have obtained a series of samples from various positions of the ingot and determined the concentrations N_D and N_A of As and Ga, respectively, using variable-temperature Hall-effect measure-

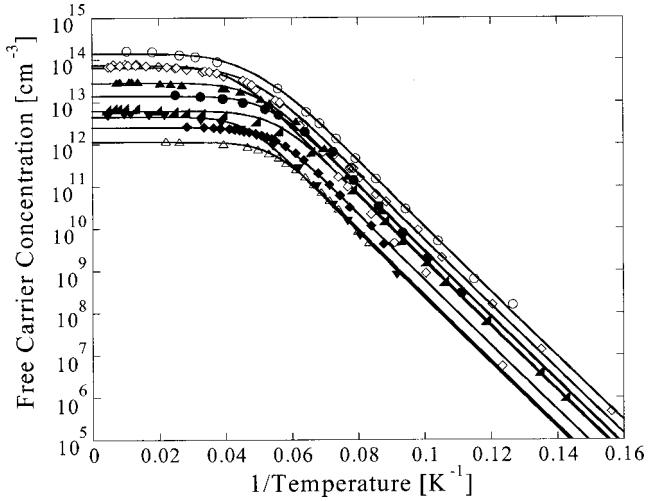

FIG. 1. Experimentally determined free-carrier concentration vs inverse absolute temperature. The curves are the best fits to the experimental data using Eq. (3).

ments. Figure 1 shows the free-carrier concentration n vs $1/T$ for nine selected samples measured in the van der Paw configuration. To minimize the in-plane impurity concentration inhomogeneity within each sample, distances between electric contacts are chosen to be less than 4 mm. The data have been fitted very well using standard semiconductor statistics (solid curves in Fig. 1) with the relation:

$$\frac{n(n+N_A)}{(N_D-N_A-n)}=\frac{1}{\beta}N_C\exp(-E_D/k_BT), \tag{3}$$

where $\beta=2$ is the degeneracy factor for donors, N_C is the effective density of states in the conduction band, and E_D is the ionization energy of the donors. After we obtain N_D and N_A for each sample, we determine the ionized-impurity concentration N_I as a function of temperature

$$N_I=n(T)+2N_A. \tag{4}$$

$N_I\approx 2N_A$ in the low-temperature carrier freeze-out region since $n(T)\ll 2N_A$. The error in the values of N_D and N_A determined by this method is expected to be less than 10%. Typical values of the compensation ratio ($K=N_A/N_D$) is $\sim$0.6 for all of the samples and their exact values along with N_D and N_A are tabulated in our recent publication.[6] The infrared absorption spectra were recorded with BOMEM DA-8 Fourier-transform spectrometer. The signal-to-noise ratio was improved by coadding 100 to 720 spectra. A composite silicon bolometer operating at $T=4.2$ K was used as a detector. The samples were cooled in the Oxford Optistat cryostat and the sample temperature was monitored with a calibrated thermometer installed at the sample mount. A black-polyethylene film (34-μm thick) was used in front of samples to eliminate above band-gap radiation.

The inset of Fig. 2 shows the absorption spectrum of a sample having $N_D=3.03\times10^{13}$ cm^{-3}, $N_A=1.75\times10^{13}$ cm^{-3}, i.e., $N_I\approx 2N_A=3.50\times10^{13}$ cm^{-3}. It has been recorded at $T=4$ K with a resolution of 0.026 cm^{-1} in the wave-number range between 70 and 110 cm^{-1}. Three distinct peaks correspond to excitations of bound electrons of As in Ge from ground state to $2p_0$, $2p_\pm$, and $3p_\pm$ excited states, respectively. The main frame of Fig. 2, shows from bottom to top the enlargement of the $1s$ to $2p_\pm$ transition peaks; the experimental result (open circles), Monte Carlo simulation assuming random distribution of ionized impurities (open squares), and Monte Carlo simulation assuming correlated distribution of impurities (open triangles). The solid curves are Lorentzian fits to each set of data. In this paper we focus on the $1s$-$2p_\pm$ transition only because its linewidth is broaden solely by the quadrupole interaction among a number of electric-field broadening mechanisms such as linear- and second-order Stark effects and quadrupole interactions.

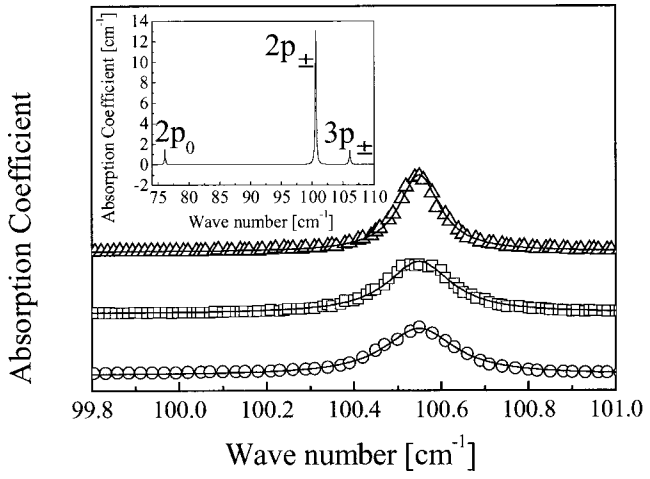

FIG. 2. An inset shows As donor absorption peaks recorded at $T=4$ K with a sample having $N_I=3.50\times10^{13}$ cm^{-3}. The three absorption peaks correspond to the $1s$-$2p_0$(76 cm^{-1}), $1s$-$2p_\pm$(100 cm^{-1}), and $1s$-$3p_\pm$(106 cm^{-1}) transitions. The main frame shows the enlargement of the $1s$-$2p_\pm$(100 cm^{-1}) absorption peak determined experimentally (○), calculated assuming random (□) and correlated (△) distributions of ionized impurities using the Monte Carlo method. Solid curves are the best fits to the experimental and calculated points assuming Lorentzian distributions.

The Monte Carlo linewidth simulation in the present paper has been performed using a method similar to the one developed by Larsen [Eq. (25) of Ref. 5] for the electric-field broadening of the $1s$-$2p$ peaks in GaAs. In order to better simulate our Ge system, we introduce the effect of an anisotropy of a $2p_\pm$ wave function since, the strong anisotropy in conduction band of Ge has a large contribution to the broadening. We calculated the anisotropic wave function according to the method developed by Faulkner.[7] The energy shift Δ of $1s$-$2p_\pm$ peak for Ge is described by

$$\Delta=N_I a^{*3}\mathrm{Ry}^*\left(-6.0319\frac{\partial E_z}{\partial z}\pm 10.5886\sqrt{T_A^2+T_B^2}\right), \tag{5}$$

where values of $\partial E_z/\partial z$, T_A, and T_B are given in the unit of eN_I/ε_0, i.e., Δ has the same unit as Ry*. $\partial E_z/\partial z$, T_A, and T_B are described by

$$\frac{\partial E_z}{\partial z}=-\sum_i\frac{e_i}{\varepsilon_0 R_i^5}(3Z_i^2-R_i^2). \tag{6}$$

$$T_A = \sum_i \frac{e_i}{\varepsilon_0 R_i^5}(X_i^2 - Y_i^2), \tag{7}$$

$$T_B = 2\sum_i \frac{e_i}{\varepsilon_0 R_i^5}(X_i Y_i). \tag{8}$$

An origin of the (X,Y,Z) coordinate is determined by the position of an absorption center. ε_0 is the static dielectric constant, e_i is the charge of the ith ion, and $R_i(X_i, Y_i, Z_i)$ is the distances between the ith ionized impurity and the absorption center. The direction of Z axis corresponds to that of longitudinal direction of an ellipsoidal conduction band and E_z is the Z component of the electric field. Equation (5) expresses the contribution from only the quadrupole interaction since the quadratic Stark effect is negligibly small in our set of samples. In order to find Δ at one neutral impurity center, 50 donors and 30 acceptors are randomly distributed in the unit cell of the Monte Carlo calculation. 30 donors and 30 acceptors are ionized, while 20 donors remain electrically neutral. The compensation ratio 0.6 (=30/50) reflects our experiment very well. The energy shift Δ for a particular configuration of donors and acceptors is calculated based on Eq. (5). We repeat this procedure for 30 000 times in order to obtain the statistical distribution of Δ, i.e., the linewidth for random distribution of ionized impurities. For the case of the correlated distribution of ionized impurities, a psuedoground state of the total Coulombic energy in the unit cell is obtained by changing the distribution of ionized and neutral impurities. A pair of one neutral donor and one ionized donor is selected randomly and the change in the total Coulombic energy of the whole cell is calculated as a result of the electron exchange within the selected pair. We accept the new distribution of the ionized and neutral impurities, if the energy is reduced due to the electron exchange within the pair, and reject the new distribution if the energy is increased. This trial is repeated for 3000 times in order to obtain the pseudoground state of the correlated distribution of impurities. The linewidth is then, calculated by repeating the Δ calculation for 30 000 different impurity configurations.

Figure 3 shows full width at half maximum (FWHM) vs N_I at $T=4$ K. The experimental data (filled circles) are compared with the theoretical linewidths assuming random (dashed line) and correlated (solid line) distributions of ionized impurities. The intrinsic linewidth due to phonon lifetime broadening[8] for Ge has been found experimentally to be 0.066 cm^{-1},[9] i.e., it is negligibly small compared to the linewidths shown in Fig. 3. Also $N_D < 1\times10^{15}$ cm^{-3} for all of the samples employed, i.e., the broadening due to overlap of donor wave functions (concentration broadening) is negligible with respect to the amount of electric-field broadening.[10] Therefore, it is appropriate to compare the experimentally found FWHM directly to the calculation based on the effect of the electric-field broadening only. The comparison between the experimental results and theoretical estimations leads us to very interesting conclusions. Excellent agreement between experimentally determined FWHM and the random theory for $N_I < 7.5\times10^{13}$ cm^{-3}, is clear evidence for the random distribution of ionized impurities in this low N_I region. When N_I is larger than 7.5×10^{13} cm^{-3}, the experimental data lie between the estimates of random theory and correlated theory. This implies that the ionized-impurity distribution is somewhere between ''completely random'' and ''completely correlated.'' The Monte Carlo simulation for the correlated distribution shown in Fig. 3 has been performed for $T=0$ K. However, the measurement was performed at the finite temperature ($T=4$ K) at which a certain degree of randomization of ionized impurities occurs due to the finite-thermal energy.[11] In this case, we expect the linewidth to be between the prediction of ''completely random'' and ''completely correlated'' assumptions. Figure 4 shows the comparison of the linewidths between $T=4$ and 10 K. As expected, the linewidths at 4 and 10 K for the ''completely random'' region ($N_I < 7.5\times10^{13}$ cm^{-3}) are the same while that of 10 K is broader than 4 K due to the larger degree of thermal randomization of the ionized-impurity distribution. The critical ionized-impurity concentration (N_{IC}), where the change of slope occurs in Fig. 4, shifts from 7.5×10^{13} cm^{-3} at $T=4$ K to 1.0×10^{14} cm^{-3} at $T=10$ K. Lee *et al.* have shown for Si:B that the Coulomb gap smears out with increasing temperature due to increasing population of above gap states.[12] Our observation of the increasing N_{IC} and FWHM above N_{IC} with T is consistent with what has been shown for Si:B. Figure 5

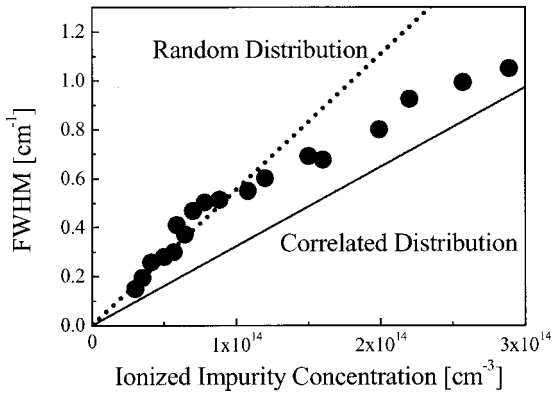

FIG. 3. Experimentally determined FWHM (filled circles) vs N_I at $T=4$ K. The dashed line is the prediction based on a random distribution of ions while the solid line is the prediction based on a correlated distribution of ionized impurities at zero temperature.

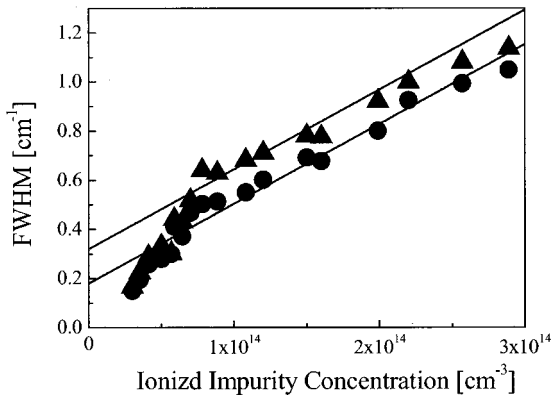

FIG. 4. Experimentally determined FWHM vs N_I at $T=4$ (●) and 10 K (▲).

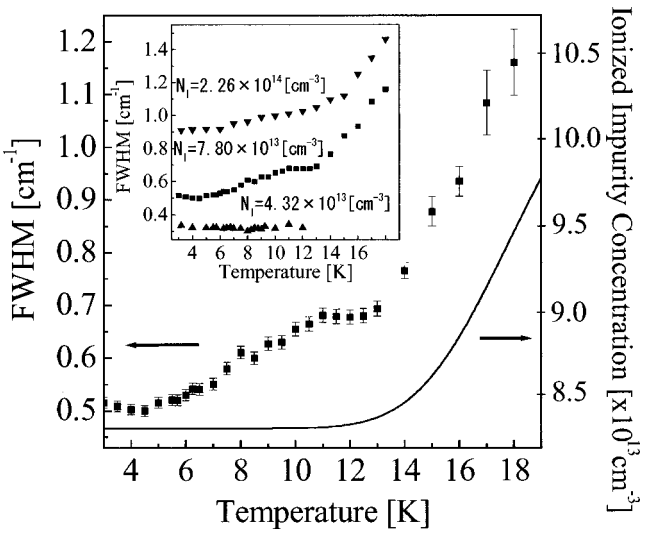

FIG. 5. The main frame shows FWHM vs temperature for a sample having $N_I = 7.80\times10^{13}$ cm^{-3}. The solid curve is the ionized-impurity concentration calculated with Eqs. (3) and (4). The inset compares FWHM vs temperature of three samples having $N_I = 4.32\times10^{13}$ (▲), 7.80×10^{13} (■), and 2.26×10^{14} cm^{-3} (▼).

shows the temperature dependence of the FWHM (■) for a sample having $N_I = 7.8\times10^{13}$ cm^{-3}, which is just above the critical concentration $N_{IC} = 7.5\times10^{13}$ cm^{-3} for $T = 4$ K. We are interested in whether we observe random to correlated transition with increasing temperatures from $T = 2$ K. Figure 5 shows clearly that the FWHM increases in two steps, the first gradual increase occurs between $T = 5$ and 11 K and the second rapid increase takes place above $T = 14$ K. The second increase at $T > 14$ K, is due to thermal ionization of donors as it matches with the increment of N_I (solid curve) calculated using Eqs. (3) and (4). The first gradual increase is due to the transition of the ionized-impurity distribution from correlated to random, and the two plateaus in FWHM at $T = 2-5$ and $T = 11-13$ K represent characteristic FWHM for the two distributions. In order to support, our claim that we have observed the transition, we shall estimate the critical temperature (T_c) for the transition using the theory of Efros and Shklovskii and compare the result directly with our experimental observation. The energy of the Coulomb gap Δ for three dimensions is approximately[3]

$$\Delta = e^3 g_0^{1/2}/\kappa^{3/2}, \tag{9}$$

where g_0 is the density of states at the Fermi level of the order

$$g_0 = K N_D \kappa r_D / e^2. \tag{10}$$

$r_D = (3/4\pi N_D)^{1/3}$ is the distance between donors. Using Eqs. (9) and (10), $\Delta = 0.31$ meV has been obtained for the sample having $N_I = 7.8\times10^{13}$ cm^{-3} in Fig. 5. To first order, we expect T_c to be of the same order as Δ, i.e., $T_c \approx 3.6$ K is what, we estimate based on theory. The experimentally found gradual increase starts around 4 K, in very good agreement with the theoretically estimated $T_c \approx 3.6$ K. The inset in Fig. 5, shows the temperature dependence of the FWHM for samples well below N_{IC} and well above N_{IC}. The width of the bottom curve ($N_I = 4.3\times10^{13}$ cm^{-3}) remains unchanged because its width is determined solely by the random distribution all the way up to 12 K. Above 12 K, the ionization of donors takes place and the peak disappears very quickly, i.e., it was not possible to determine the widths in this high-temperature region. The FWHM of the bottom curve ($N_I = 4.3\times10^{13}$ cm^{-3}) for the temperature range 2–12 K agrees very well with the theoretical prediction of the random theory (the dashed line in Fig. 3). The FWHM of the top curve in the inset ($N_I = 2.26\times10^{14}$ cm^{-3}) for the temperature range shown is determined dominantly by the correlated distribution, because the donor concentration is high enough for the neighboring ionized impurities to interact with one another. The FWHM increases with the increasing temperature because the partial randomization of the correlated distribution proceeds as was shown in Fig. 4.

Observation of the random-to-correlated transition of ionized-impurity distributions as a function of temperature has been claimed before by Baranovskii and co-workers for GaAs.[13,14] However, our analysis of their data, shows that they observe increase of FWHM, due to ionization of donors and not the transition. As one can see in the inset of Fig. 5, it takes extreme fine tuning of N_D and N_A in order to observe a clear signature of the transition with two distinct plateaus below the temperatures where ionization takes place. The precise control of both donors and acceptors at the level of 10^{13} cm^{-3} has been the key for the successful observation of random-to-correlated transition of the ionized-impurity distribution in semiconductors.

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[11] It is also possible that the partial randomization of the ionized impurities was induced partly by the far-infrared radiation used for the measurement. In order to minimize such effects, we have limited ourselves to employ as small intensity of the far-infrared radiation as possible. The fact that the FWHM increases with the temperature (Fig. 5) suggests that the effect of temperature is more significant than the effect of the infrared radiation.
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