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Correlated to random transition of ionized impurity distribution in n-type Ge : (As, Ga)

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Abstract

We discuss the broadening of ground-state to bounded 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. © 2001 Published by Elsevier Science B.V.

Keywords: Impurity distribution; Compensated semiconductor; Impurity absorption

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. In this paper, it is demonstrated that the quantitative comparison of the experimental donor $1s–2p_{\pm}$ hydrogenic absorption linewidths and Monte Carlo simulations lead to an unambiguous determination of the ionized impurity distribution as a function of the ionized impurity concentration (N_I) and 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 [1,2]. Electrons distribute themselves among donors in such a way 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 correlated distribution is expected to dominate for the condition [1–3]

$$N_I = 2K\left(\frac{k_B T\kappa}{e^2}\right)^3 \quad (1)$$

with κ is the dielectric constant, K is the compensation ratio. 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 [4].

When the thermal energy becomes larger than the correlation energy, electrons will be randomly distributed among donors, and 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 [5,6]

$$N_I \leqslant 0.7\times 10^{-5} a^{*-3}, \quad (2)$$

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

The experimental determination of the transition temperature allows us to estimate the value of the correlation energy. 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

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little direct evidence for the random distribution of ionized impurities at low temperatures in semiconductors.

For our studies, we cut samples 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 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 measurements. The infrared absorption spectra were recorded with a BOMEM DA-8 Fourier transform spectrometer. The signal-to-noise ratio was improved by coadding 100–720 spectra. A composite silicon bolometer operating at $T = 4.2\,\mathrm{K}$ 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 0.1 μm black polyethylene film was placed in front of the samples to eliminate the above band-gap radiation.

The inset of Fig. 1 shows the absorption spectrum of a sample having $N_D = 3.03 \times 10^{13}\,\mathrm{cm}^{-3}$, $N_A = 1.75 \times 10^{13}\,\mathrm{cm}^{-3}$, i.e., $N_I \approx 2N_A = 3.50 \times 10^{13}\,\mathrm{cm}^{-3}$. The spectrum has been recorded at $T = 4\,\mathrm{K}$ with a resolution of $0.026\,\mathrm{cm}^{-1}$ in the wavenumber range between 70 and $110\,\mathrm{cm}^{-1}$. Three distinct peaks correspond to transitions of bound electrons of As in Ge from the 1s ground state to $2p_0$, $2p_\pm$, and $3p_0$ excited states, respectively. The main frame of Fig. 1 shows, from bottom to top, the enlargement of the 1s to $2p_\pm$ transition peaks; the experimental result (open circles), a Monte Carlo simulation assuming a random distribution of ionized impurities (open squares), and a Monte Carlo simulation assuming a correlated distribution of impurities (open triangles). The solid curves are Lorentzian fits to each set of data.

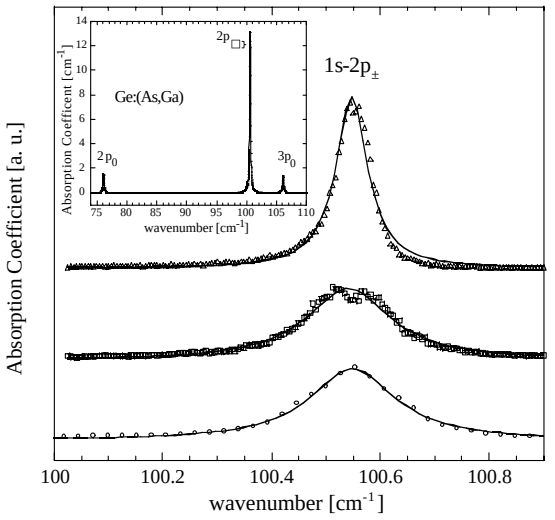

Fig. 1. The main frame shows the enlargement of the $1s–2p_\pm$ ($100\,\mathrm{cm}^{-1}$) absorption peak determined experimentally (○), calculated assuming random (□) and correlated (△) distributions of ionized impurities using the Monte Carlo method. The solid curves are the best fits to the experimental and calculated points assuming Lorentzian distributions. The inset shows As-donor absorption peaks recorded at $T = 4\,\mathrm{K}$ with a sample having $N_I = 3.50 \times 10^{13}\,\mathrm{cm}^{-3}$. The three absorption peaks correspond to the As donor $1s–2p_0$ ($76\,\mathrm{cm}^{-1}$), $1s–2p_\pm$ ($100\,\mathrm{cm}^{-1}$), and $1s–3p_\pm$ ($106\,\mathrm{cm}^{-1}$) transitions.

Fig. 2 shows FWHM vs. N_I at $T = 4\,\mathrm{K}$. The experimental data (filled circles) are compared with the theoretical linewidths assuming random (dashed line) and correlated (solid line) distributions of the ionized impurities. The intrinsic linewidth due to phonon lifetime broadening [7] for Ge has been found, experimentally, to be $0.066\,\mathrm{cm}^{-1}$ [8], which is negligibly small compared to the linewidths shown. Also $N_D < 1 \times 10^{15}\,\mathrm{cm}^{-3}$ for all of the samples employed, i.e., the broadening due to overlap of donor wavefunctions (concentration broadening) is negligible compared to the amount of electric-field broadening [9]. Therefore, it is appropriate to compare the experimentally found FWHM directly with the calculated widths assuming only an effect of the electric-field broadening. The comparison between the experimental results and theoretical estimates leads us to very interesting conclusions. Excellent agreement between the experimentally determined FWHM and the random theory for $N_I < 7.5 \times 10^{13}\,\mathrm{cm}^{-3}$ is clear evidence for the random distribution of ionized impurities in this low N_I region. When N_I is larger than $7.5 \times 10^{13}\,\mathrm{cm}^{-3}$, the experimental

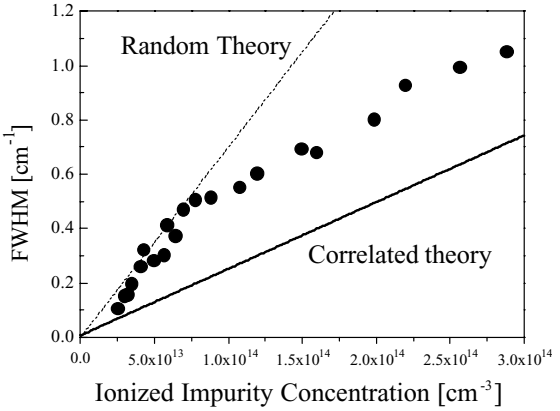

Fig. 2. Experimentally determined FWHM (filled circles) vs. N_I at $T = 4\,\mathrm{K}$. The dashed line is the prediction based on a random distribution of ions, while the solid line is the prediction based on a correlated distribution of ionized impurities at zero temperature.

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. 2 has been performed for $T = 0\,\mathrm{K}$. However, the measurement was performed at finite temperature ($T = 4\,\mathrm{K}$) at which a certain degree of randomization of ionized impurities occurs due to the finite thermal energy. In this case, we expect the linewidth to have a value between the prediction of "completely random" and "completely correlated" distribution. Fig. 3 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 ($N_I < 7.5 \times 10^{13}\,\mathrm{cm}^{-3}$) 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. 3, shifts from $7.5 \times 10^{13}\,\mathrm{cm}^{-3}$ at $T = 4\,\mathrm{K}$, to $1.0 \times 10^{14}\,\mathrm{cm}^{-3}$ at $T = 10\,\mathrm{K}$. Eq. (2) predicts $N_{IC} = 1 \times 10^{13}\,\mathrm{cm}^{-3}$ for Ge at $T = 0\,\mathrm{K}$. Considering the fact that N_{IC} shifts to larger values for $T > 0\,\mathrm{K}$, the experimentally observed $N_{IC} = 7.5 \times 10^{13}\,\mathrm{cm}^{-3}$ at $T = 4\,\mathrm{K}$ should be considered to be in excellent agreement with the prediction of Eq. (2). Fig. 4 shows the temperature dependence of the FWHM (■) for a sample having $N_I = 7.8 \times 10^{13}\,\mathrm{cm}^{-3}$, which is just above the critical concentration $N_{IC} = 7.5 \times 10^{13}\,\mathrm{cm}^{-3}$ for $T = 4\,\mathrm{K}$. We are interested in whether we observe a random to correlated transition with temperatures increasing from $T = 2\,\mathrm{K}$. Fig. 4 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 $T = 14\,\mathrm{K}$. The second increase at $T > 14\,\mathrm{K}$ is due to thermal ionization of donors as it matches with the increment of N_I (solid curve). 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 $T = 2-5\,\mathrm{K}$ and $11-13\,\mathrm{K}$ 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];

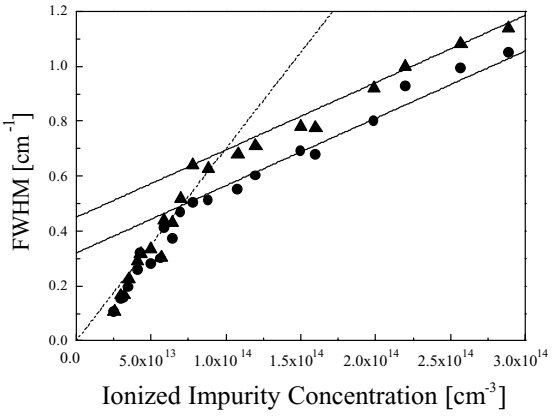

Fig. 3. Experimentally determined FWHM vs. N_I at $T = 4$ (●) and 10 K (▲).

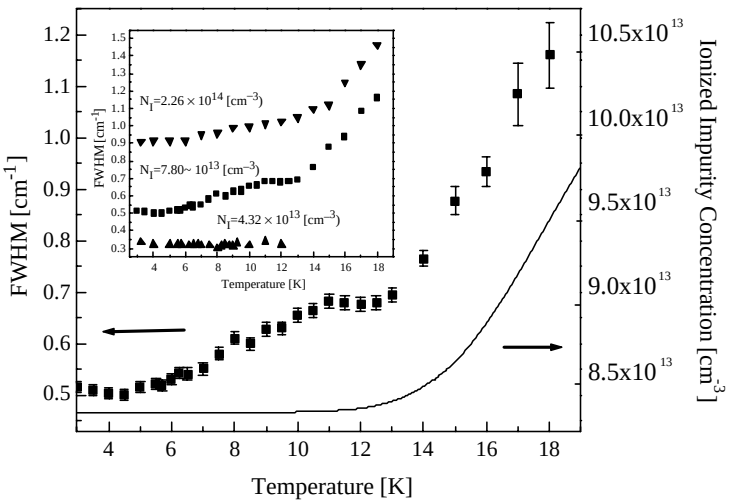

Fig. 4. The main frame shows FWHM vs. temperature for a sample having $N_I = 7.80 \times 10^{13}\,\mathrm{cm}^{-3}$. The solid curve is the ionized impurity concentration calculated with Eqs. (3) and (4). The inset shows the FWHM vs. temperature of three samples having $N_I = 4.32 \times 10^{13}$ (▲),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

$$\Delta = e^3 g_0^{1/2}/\kappa^{3/2}, \quad (3)$$

where g_0 is the density of states at the Fermi level and can be estimated with

$$g_0 = KN_D\kappa r_D/e^2. \quad (4)$$

$r_D = (3/4\pi N_D)^{1/3}$ is the distance between donors. Using Eqs. (3) and (4), $\Delta = 0.31$ meV has been obtained for the sample having $N_I = 7.8 \times 10^{13}\,cm^{-3}$ in Fig. 4. 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. 4 shows the temperature dependence of the FWHM for samples well below N_{IC} and well above N_{IC}. The width of the bottom curve ($N_I = 4.3 \times 10^{13}$) 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 ($N_I = 4.3 \times 10^{13}$) for the temperature range 2–12 K agrees very well with the theoretical prediction of the random theory (the dashed line in Fig. 2). The FWHM of the top curve in the inset ($N_I = 2.26 \times 10^{14}$) 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. 3.

Observation of the random-to-correlated transition of ionized impurity distributions as a function of temperature has been claimed before by Baranovskii et al. for GaAs [10–13]. However, analysis of their data shows that they observe an increase of FWHM due to ionization of donors and not due to the transition. As one can see in the inset of Fig. 4, 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 the random-to-correlated transition of the ionized impurity distribution in semiconductors.

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