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.

$N_1 = 2K \left( \frac{k_B T \kappa}{e^2} \right)^3$ (1)

with $\kappa$ 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 $N_1$ 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]

$N_1 \leq 0.7 \times 10^{-5} a^*^{-3}$, (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 $N_1$. 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 $T = 4.2$ 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 mm 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 $N_D = 3.0 \times 10^{13}$ cm$^{-3}$, $N_A = 1.75 \times 10^{13}$ cm$^{-3}$, i.e., $N_I \approx 2N_A = 3.50 \times 10^{13}$ cm$^{-3}$. The spectrum has been recorded at $T = 4$ K with a resolution of 0.026 cm$^{-1}$ in the wavenumber range between 70 and 110 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. 2 shows FWHM vs. $N_I$ at $T = 4$ K. The experimental data (filled circles) are compared with the theoretical linewdths 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 cm$^{-1}$ [8], which is negligibly small compared to the linewidths shown. Also $N_D < 1 \times 10^{15}$ 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 $N_I < 7.5 \times 10^{13}$ cm$^{-3}$ is clear evidence for the random distribution of ionized impurities in this low $N_I$ region. When $N_I$ is larger than $7.5 \times 10^{13}$ 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. 2 has been performed for $T = 0 \text{K}$. However, the measurement was performed at finite temperature ($T = 4 \text{K}$) 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 $10 \text{K}$. As expected, the linewidths at $4 \text{K}$ and $10 \text{K}$ for the “completely random” region ($N_I < 7.5 \times 10^{13} \text{cm}^{-3}$) are the same while that of $10 \text{K}$ is broader than $4 \text{K}$ due to the larger degree of thermal randomization of the ionized impurity distribution. The critical ionized impurity concentration ($N_{\text{IC}}$), where the change of slope occurs in Fig. 3, shifts from $7.5 \times 10^{13} \text{cm}^{-3}$ at $T = 4 \text{K}$, to $1.0 \times 10^{14} \text{cm}^{-3}$ at $T = 10 \text{K}$. Eq. (2) predicts $N_{\text{IC}} = 1.0 \times 10^{13} \text{cm}^{-3}$ for Ge at $T = 0 \text{K}$. Considering the fact that $N_{\text{IC}}$ shifts to larger values for $T > 0 \text{K}$, the experimentally observed $N_{\text{IC}} = 7.5 \times 10^{13} \text{cm}^{-3}$ at $T = 4 \text{K}$ should be considered to be in excellent agreement with the prediction of Eq. (2). Fig. 4 shows the temperature dependence of the FWHM ($\Delta$) for a sample having $N_I = 7.8 \times 10^{13} \text{cm}^{-3}$, which is just above the critical concentration $N_{\text{IC}} = 7.5 \times 10^{13} \text{cm}^{-3}$ for $T = 4 \text{K}$. We are interested in whether we observe a random to correlated transition with temperatures increasing from $T = 2 \text{K}$. Fig. 4 shows clearly that the FWHM increases in two steps; the first gradual increase occurs between $T = 5$ and $11 \text{K}$ and the second rapid increase takes place above $T = 14 \text{K}$. The second increase at $T > 14 \text{K}$ 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 $T = 2$–$5 \text{K}$ and $11$–$13 \text{K}$ 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 $\Delta$ for three dimensions is approximately [3]:

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

![Fig. 4. The main frame shows FWHM vs. temperature for a sample having $N_I = 7.80 \times 10^{13} \text{cm}^{-3}$. 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 $N_I = 4.32 \times 10^{13}$ (▲), $7.80 \times 10^{13}$ (■), and $2.26 \times 10^{14} \text{cm}^{-3}$ (▼).](image)
\[ \Delta = e^3 g_0^{1/2} / k T^{3/2}, \]  
(3)

where \( g_0 \) is the density of states at the Fermi level and can be estimated with
\[ g_0 = K N_D \theta_D / e^2. \]  
(4)

\( r_D = (3/4\pi N_D)^{1/2} \) is the distance between donors. Using Eqs. (3) and (4), \( \Delta = 0.31 \) meV has been obtained for the sample having \( N_I = 7.8 \times 10^{13} \text{ cm}^{-3} \) in Fig. 4. To first order, we expect \( T_c \) to be of the same order as \( \Delta \), 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 \( 10^{13} \text{ cm}^{-3} \) has been the key for the successful observation of the random-to-correlated transition of the ionized impurity distribution in semiconductors.

References