Vacancies and Self-Interstitials in Germanium Observed by Perturbed Angular Correlation Spectroscopy

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Trapping of two different point defects produced by electron irradiation at ^{111}In probes is studied as a function of the Fermi level in germanium by perturbed angular correlation spectroscopy. The defects are identified as monovacancies and self-interstitials, respectively. An acceptor state for the vacancy at $E_V + 0.20$ eV and, tentatively, a donor state for the interstitial close to the conduction band ($E_C - 0.040$ eV) is deduced from the trapping behavior. Long range migration of the neutral vacancy and the positive interstitial takes place at 200 and 220 K, respectively. [S0031-9007(98)05515-X]

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The elementary point defects in germanium have attracted intensive research for a long time and numerous results have been obtained, mostly by electrical methods [1] and capacitance techniques [2]. However, contrary to the case of silicon [3], no microscopic identification of either the vacancy or the self-interstitial has yet been accomplished. This is due mainly to the fact that methods suited to give microscopic information such as electron paramagnetic resonance (EPR) have, for various reasons, only limited success when applied to germanium. Thus, a definite assignment of the collected data to the basic defects and their properties is still missing and interpretation of the results has remained speculative.

In this Letter, we present experiments providing microscopic information on the monovacancy and, to a high degree of certainty, also on the self-interstitial in Ge. This is accomplished by the perturbed angular correlation spectroscopy (PAC) method, which we perform in the following way: The Ge samples are doped with ^{111}In probes followed by defect introduction via electron irradiation at 77 K. In a subsequent annealing process, the defects are mobilized and may be trapped at the probes if an attractive interaction exists. In such a case, an electric field gradient is induced at the probe nucleus leading to a nuclear quadrupole interaction measured on the $5/2^+$ state of the ^{111}Cd daughter nucleus by means of a perturbed γ-γ angular correlation experiment [4,5]. Preliminary results were presented in [6].

Of particular importance is the low ^{111}In concentration $\leq 5 \times 10^{13}$ cm^{-3}, which allows setting the Fermi level by the predoping of the samples. This is achieved by using a recoil implantation technique resulting in an almost constant depth profile of the ^{111}In atoms up to 4 μm [5]. The samples were cut from commercial Czochralski-type material of 300 μm thickness partly labeled as electronic grade. p-type (Ga) and n-type (Sb) material in a wide range of acceptor/donor concentrations was used. Following recoil implantation, the samples were annealed in an Ar atmosphere at 600 °C for 10 min to remove the implantation damage. A subsequent PAC spectrum measured at room temperature showed a completely flat spectrum proving that all of the probe atoms are in a defect-free environment, which for the single acceptor In in Ge is the substitutional site [Fig. 1(a)]. After annealing, the samples were irradiated with 1.2 MeV electrons at 77 K to a fluence of $5(1) \times 10^{16}$ cm^{-2} producing almost exclusively single Frenkel pairs. Subsequently, PAC spectra were measured at room temperature.

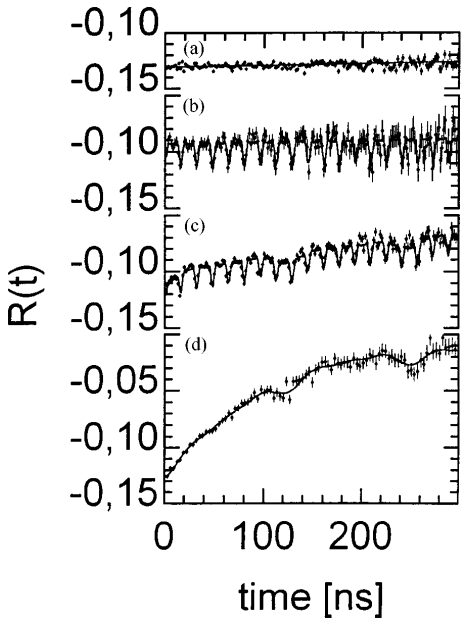

FIG. 1. PAC spectra of variously doped Ge samples recoil implanted with ^{111}In and annealed at 600 °C, measured at room temperature. (a) n(Sb)-type, 5×10^{17} cm^{-3}; (b)–(d) after additional electron irradiation at 77 K; (b) n(Sb)-type, 1×10^{14} cm^{-3}; (c) p(Ga)-type, 6×10^{15} cm^{-3}; (d) p(Ga)-type, 6×10^{17} cm^{-3}. Spectrum (b) shows the defect ν_{Q2} (415 MHz), (c) shows both ν_{Q2} and ν_{Q1} (415 and 52 MHz), (d) shows ν_{Q1} only. The overall slope of the spectra getting steeper from (b) to (d) reflects the electronic state of the substitutional ^{111}In/^{111}Cd probe and not a residual damage from implantation or electron irradiation [7]. All carrier concentrations given here are nominal values $|N_A - N_D|$ given by the suppliers.

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The central result from these experiments is that, depending on the predoping of the starting material, either one or two different quadrupole interaction frequencies appear in the PAC spectra, $\nu_{Q1} = 52(1)$ MHz and $\nu_{Q2} = 415(1)$ MHz, both with axial symmetry described by the asymmetry parameter $\eta = 0$ [Figs. 1(b)–1(d)]. These frequencies were obtained by fitting the spectra to the function

$$R(t) = A_2 \sum_{i=0}^{2} f_i G_2^i(t), \qquad (1)$$

with $G_2(t)$ being the PAC perturbation function $G_2(t) = S_0 + \sum_{n=1}^{3} S_n \cos(\omega_n t)$. The frequencies ν_Q are related to the ω_n by $\omega_n = (n3\pi/10)\nu_Q$ when the interaction is axially symmetric [5,6]. Three different fractions of probes f_i are incorporated in the fit, f_1 and f_2 describing the presence of defects leading to ν_{Q1} and ν_{Q2}, and a fraction f_0 ($f_0 = 1 - f_1 - f_2$) due to probes in undisturbed or weakly disturbed surroundings.

The defects described by ν_{Q1} and ν_{Q2} were first reported in [8–10]. It was also shown that both components are oriented along the $\langle 111 \rangle$ crystallographic direction [10]. Only speculative interpretations could be given at that time. It was shown, however, that the formation of both defects after 77 K electron irradiation takes place between 200 and 300 K and that the thermal stability extends up to a region of 400 to 600 K [5].

As a key to the defects' assignment, we make use of a recent identification of the defect ν_{Q1} by means of the neutrino recoil method [5]. In this technique, the PAC probe ^{111}In serves as the primary knockon atom due to a recoil energy of 29 eV from a neutrino produced in the β decay of the probe's radioactive precursor ^{111}Sn. This leads to the production of Frenkel pairs with the probe atom residing as the nearest neighbor to a vacancy, resulting in an interaction frequency of 52 MHz, which we identify with the defect occurring in the present experiment: a ^{111}In-V pair. The component ν_{Q2}, however, cannot be produced in this way. It will be shown in what follows that ν_{Q2} corresponds to a self-interstitial trapped at the substitutional ^{111}In probe.

Figure 2 shows the formation of f_1 and f_2 as a function of the samples' carrier concentration (n or p, respectively). This carrier concentration was determined from Hall effect measurements at $T \approx 200$ K on the electron irradiated samples. This temperature was chosen since it resulted that trapping of the defects leading to f_1 and f_2 takes place around this temperature, see below and Ref. [11]. It is clearly seen that the occurrence of f_1 and f_2 depends on this carrier concentration. f_1 is present only in p-type Ge for $p > 10^{15}$ cm^{-3} with a fraction of about 5% to 8% but is absent in n-type Ge. We interpret this dependence in terms of a Fermi level dependent trapping process. Since the ^{111}In probes (and also the Ga dopants) as shallow acceptors are negatively charged, negative vacancies are excluded from trapping (or have a very small probability) due to long range Coulomb repulsion. But positive vacancies

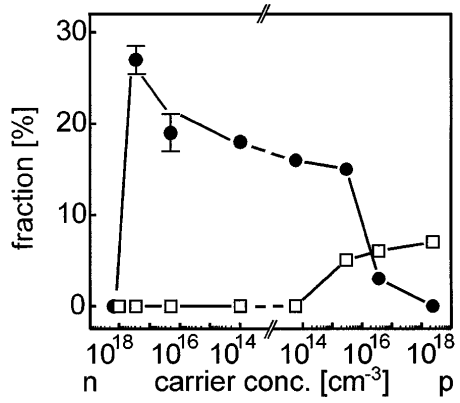

FIG. 2. Fractions f_1 (squares) and f_2 (circles) of ^{111}In probes decorated with defects ν_{Q1} (52 MHz) and ν_{Q2} (415) MHz versus carrier concentration in n(Sb)- and p(Ga)-type Ge after electron irradiation. The carrier concentration was determined from Hall effect measurements at about 200 K including the (small) effect from electron irradiation, see text. Electron irradiations were performed at 77 K to a fluence of $5(1) \times 10^{16}$ cm^{-2}. PAC was measured at room temperature.

are also excluded: A hypothetical V^+ would be Coulomb attracted by the Ga$^-$ dopants and the In$^-$ probes alike. Since the Ga concentration extends to values $>10^{18}$ cm^{-3}, these trapping centers outnumber the available V defects by several orders of magnitude and formation of Ga$^-$-V^+ pairs would reduce and ultimately cancel the ^{111}In-V pair formation (f_1) in conflict with the observation. The available V defects can be estimated from Ref. [12]. Here, it is shown that the low temperature defect introduction rate surviving annealing up to about 200 K is 0.1 cm^{-1}. Taking this value, a defect concentration of 5×10^{15} cm^{-3} is available for trapping in our experiment. Thus, one can infer that the observed ^{111}In-V pairing must be driven by elastic interaction between the oversized ^{111}In$^-$ and a neutral V^0 to form In$^-$-V^0 pairs, whereas the Ga$^-$ dopants fit into the Ge lattice producing a much smaller interaction to V^0.

The fact that, for $p < 10^{15}$ cm^{-3}, no formation of f_1 is apparent can then be explained by a change of the charge state $V^0 \rightarrow V^-$, which quenches the attractive interaction. Based on this model that ^{111}In-V pair formation is possible only when V is neutral, we can determine the V acceptor level $E_{\mathrm{Vac}}(-/0)$ from Fermi-Dirac statistics. The concentration of ionized vacancies $[N_{\mathrm{Vac}}]^-$ is related to the total vacancy concentration $[N_{\mathrm{Vac}}]$ by

$$\frac{[N_{\mathrm{Vac}}]^-}{[N_{\mathrm{Vac}}]} = \left[1 + g_{\mathrm{Vac}} \exp\left(\frac{E_{\mathrm{Vac}}(-/0) - E_F}{kT}\right)\right]^{-1}, \qquad (2)$$

where g_{Vac} is a degeneracy factor, which we take as 1. Figure 2 shows that the transition from a defect-free surrounding of the ^{111}In probe to pair formation In$^-$-V^0 takes place between $p = 5.6 \times 10^{13}$ and 2.9×10^{15} cm^{-3}. In the first case, we have $[N_{\mathrm{Vac}}]^-/[N_{\mathrm{Vac}}] \approx 1$ ($f_1 = 0$), and it follows from Eq. (2) that the Fermi level E_{F1}

must be well above $E_{Vac}(-/0)$. In the latter case, f_1 has practically reached maximum, implying that $[N_{Vac}]^-/[N_{Vac}] \approx 0$. In this case, E_{F2} must be below $E_{Vac}(-/0)$ and we get an energy window for $E_{Vac}(-/0)$: $E_{F2} < E_{Vac}(-/0) < E_{F1}$. E_{F1} and E_{F2} were evaluated from the respective carrier concentration at $T = 200$ K (Fig. 2), the temperature where the pair formation occurs (see below and Ref. [11]). Thus, we obtain $E_V + 0.16$ eV $< E_{Vac}(-/0) < E_V + 0.24$ eV, which we write as $E_{Vac}(-/0) = E_V + 0.20(4)$ eV.

In contrast to the assignment of ν_{Q1}, a direct assignment of ν_{Q2} is not possible. As mentioned before, it cannot be observed in a neutrino recoil experiment. To check whether it is similar to ν_{Q1} caused by trapping of an intrinsic defect, we varied the electron irradiation fluence within a wide range (1×10^{15}–3×10^{17} cm^{-2}) and also studied the defect structure from the probes' implantation process itself (as implanted) [7]. f_2 (and f_1) approximately scales with electron fluence in the entire range and is also present in the "as implanted" state. An additional experiment using a special high-purity Ge crystal also shows the formation of ν_{Q2} [7]. From all of these experiments, an unintentional trapping of impurities can be safely excluded which is strongly supported by the experiments of Ref. [10], where large ^{111}In concentrations ($>10^{18}$ cm^{-3}), extremely large doping concentrations, and correspondingly large defect concentrations induced by heavy ion irradiation were employed. Thus, we conclude that ν_{Q2}, similar to ν_{Q1}, is caused by an intrinsic defect which, by exclusion of other possibilities, then must be the self-interstitial Ge_I (written as I in the following).

Inspection of Fig. 2 places limits on its possible charge states. Trapping takes place with a large fraction f_2 about 20% in a wide range from n- to p-doped material but ceases for both high n and high p doping. Either a neutral or a positive I might, in principle, lead to pairing with In^-. A positive I seems more reasonable since it is well known that, in the absence of Coulomb attraction, an oversized ion such as ^{111}In is prone to trap vacancies (as could be shown above), whereas undersized ions attract interstitials [13]. Thus, in our case, Coulomb attraction (i.e., In^--I^+) is strongly indicated. Termination of the pairing in p-Ge for $p > 10^{16}$ cm^{-3} can then be interpreted by the influence of the competing Ga^- trapping centers (which was excluded for the vacancy, see above). Loss of the pairing interaction on the n-type side for $n > 2.8 \times 10^{17}$ cm^{-3} is best interpreted in terms of a charge change $I^+ \rightarrow I^0$. To give an estimate for this level $E_I(0/+)$, we argue as outlined for the vacancy level above, this time, however, using the occupation probability for a donor: For $n = 1.2 \times 10^{18}$ cm^{-3} (no pair formation) E_F must be above $E_I(0/+)$, for $n = 2.8 \times 10^{17}$ cm^{-3} (pair formation) E_F is situated below $E_I(0/+)$. The corresponding Fermi levels were again taken from Hall effect measurements, this time taken at 220 K (see below). This leads to an energy window for the donor level $E_I(0/+)$: $E_c - 0.060$ eV $< E_I(0/+) < E_c - 0.020$ eV, which we write as $E_I(0/+) = E_c - 0.040(20)$ eV. We favor this ionic pairing model but consider it tentative. It is interesting in this context that experiments with H-doped Ge show formation of an In-H complex [10,14] with structural and kinetic properties very close but clearly distinguished from the defect ν_{Q2}. The In-H pair is formed by ionic interaction leading to H trapped interstitially at the substitutional In acceptor. This analogy might additionally support our interpretation of the formation and structure of the In-I complex. Figure 3 shows the electrical levels for V and I as deduced from our measurements.

Besides the electrical properties, structural and kinetic information of the defects can be drawn from the PAC spectra. The orientation of the electric field gradient in $\langle 111 \rangle$ crystallographic directions for ν_{Q1} and ν_{Q2} [10] is compatible with the fact that both the vacancy and the interstitial are trapped in the nearest neighbor position of the In probe. To obtain a more detailed picture of the kinetic properties of V and I than previously reported [5], we have performed more precise isochronal annealing sequences (10 min) following electron irradiation at 77 K as described above. Figure 4 shows f_1 and f_2 as a function of the annealing temperature in p-Ge, where both defects appear simultaneously. Trapping of the defects occurs in two stages, at 200(5) for V^0 [15] and at 220(5) for the (posi-tive) interstitial. The pair stability extends to 400(5) K for ^{111}In$^-$-V^0 and to 380(5) K for ^{111}In$^-$-I^+. Thus, we can conclude that long range migration of neutral vacancies and positive interstitials takes place in a closely neighboring temperature range separated by only 20 K. The result that the interstitials do not migrate earlier than 200 K is also in agreement with our neutrino recoil experiment [5]: In that case, recombination of the recoil induced V-I pairs takes place between 200 and 273 K. Since the V after recoil is in the 52 MHz configuration (bound to the ^{111}In probe up to 400 K), it must be the nearby I (in this case, invisible to the PAC probe) that migrates to the vacancy. This completely independent result that the I in p-Ge migrates at $T > 200$ K additionally confirms our interstitial assignment as outlined above.

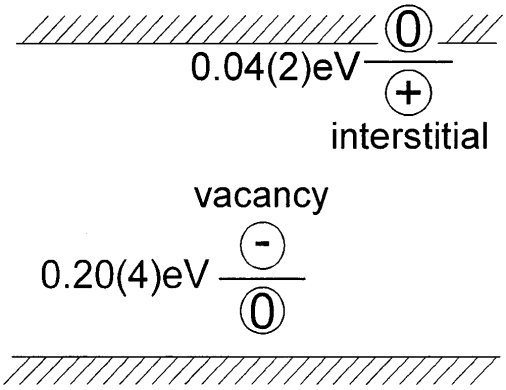

FIG. 3. Electrical levels for the vacancy and self-interstitial in Ge as determined from PAC, the interstitial level is tentative.

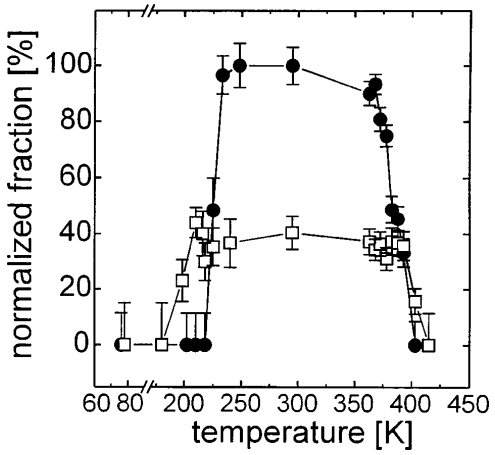

FIG. 4. Normalized fractions f_1 (squares) and f_2 (circles) measured by PAC (at 77 K) as a function of annealing temperature after electron irradiation (at 77 K; fluence as in Fig. 2) in p(Ga)-type Ge samples (6×10^{15} and 5×10^{16} cm^{-3} nominal carrier concentration). Normalization was done to the fractions measured with the lower doped sample, some additional data points for f_1 were measured at the onset of trapping with the higher doped sample.

Some conclusions based on earlier, more indirect measurements shall be mentioned here: An acceptor state for the vacancy in the lower half of the band gap is frequently suggested; a synopsis based on electrical measurements [1] gives an energy estimate $< E_V + 0.3$ eV. An acceptor state for the vacancy was also deduced from self-diffusion experiments [16]. Annealing experiments following irradiation are abundant and an annealing stage at about 200 K was repeatedly found. Discussions of the relevant experimental results in terms of defect models are given in [1,2,17,18], the possible role of self-interstitials is also examined. A recent work using x-ray scattering also reports major annealing somewhat below 200 K [12], which should be compatible with the 200 K region if one takes the very high irradiation fluence used in [12] into account.

In summary, we have produced and microscopically studied the ^{111}In-V pair and by exclusion of alternatives to a high degree of certainty also the ^{111}In-I pair by PAC. From analysis of the pair formation process, a deep acceptor level at $E_C + 0.20$ eV for V is deduced. For I, a donor level close to the conduction band ($E_C - 0.040$ eV) is suggested. The PAC technique applied in this study is able to disentangle an annealing stage at about 200 K, which has been repeatedly reported in the literature: We show that both vacancies and self-interstitials undergo long range migration in this temperature range separated by 20 K.

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