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Gallium interstitial in irradiated germanium: Deep level transient spectroscopy

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Two electronic levels at 0.34 eV above the valence band and 0.32 eV below the conduction band, in gallium doped, *p*-type Ge irradiated with 2 MeV electrons have been studied by deep level transient spectroscopy (DLTS) with both majority- and minority-carrier injections, and Laplace DLTS spectroscopy. It is concluded that these levels, having donor and acceptor characters, respectively, are correlated with interstitial Ga atoms, formed by the Watkins-replacement mechanism via self-interstitials.

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Vacancy- and interstitial-related defects are reasonably well understood in silicon, although surprises still pop out;[1] the situation is, however, more difficult in germanium. The high number of nuclear spins from the different Ge-isotopes in germanium has hindered the microscopic identification of the structure of point defects using electron-paramagnetic resonance. Identification of irradiation-induced defects must, therefore, rely on indirect methods such as capacitance techniques [deep level transient spectroscopy (DLTS) and high-resolution Laplace DLTS] or Hall-effect measurements combined with various types of annealing procedures.[2–8] From such measurements the vacancy and self-interstitial, and their combination into the Frenkel pair have been recently observed and unambiguously identified in electron-irradiated *n*- and *p*-type germaniums.[7] Some controversy still exists in relation to theoretical models and to, for example, perturbed angular correlation spectroscopy experiments.[9] For an exhaustive discussion of these aspects the reader is referred to Ref. 8.

In this Brief Report the attention will be focused on the Ga-interstitial defect and its properties in *p*-type germanium. The existence of an energy level of $\mathrm{Ga_i}$ with an activation energy for hole emission of 0.62 eV, tentatively assigned to a donor level, was reported briefly in Ref. 8. Although the activation energy for hole emission was found to be 0.62 eV, the activation enthalpy for hole emission was concluded to be only 0.33 eV because of a large energy barrier for hole capture of about 0.29 eV. The trap was assumed to be interstitial gallium as a consequence of its similar behavior and electrical properties as the interstitial boron defect in Si.[8] However, no direct evidence of this was presented. The present Brief Report extends this work providing additional information on diffusion and charge-state properties of the isolated interstitial-Ga defect in Ge. The intrinsic point defects (self-interstitials and vacancies) were introduced into the lattice by 2 MeV electron irradiation at cryogenic temperature (around 22 K). When irradiating Ge crystals with electrons germanium atoms are knocked out of their lattice positions forming simple interstitial germanium atoms and lattice vacancies. The use of irradiation at cryogenic temperatures serves to freeze in these primary defects, which is of vital importance for the possibility of tracing the subsequent formation of secondary defects via *in situ* capacitance measurements.

$\mathrm{N^+}\,p$ diodes were prepared from gallium doped, oxygen- and carbon-lean Ge crystals from UMICORE. A n^+-top layer was grown by molecular-beam epitaxy (MBE), and mesa diodes were made by photolitography and chemical etching following the procedure described in Ref. 10. Two sets of samples with gallium concentrations of 4×10^{14} and $1\times10^{15}\ \mathrm{cm^{-3}}$ were used. In order to exclude any possible influence of injection of defects from the n^+ top layer which could influence the present analysis, Schottky diodes were used as well. The gallium concentration was $2\times10^{14}\ \mathrm{cm^{-3}}$ in this case. The Schottky diodes were formed by vacuum evaporation of indium on the polished side of Ge. Capacitance-voltage (CV) measurements were done in the reverse-voltage range from 0 to 9 V. These CV measurements were used to determine the concentration of acceptors in the depletion layer of the diode before and after irradiations with electrons. Electron irradiations were done to different doses while the diodes were held at 22 K; beam-current densities were about $100\ \mathrm{nA/cm^2}$. The irradiated samples were subjected to isochronal thermal annealing in the temperature range of 50–300 K. *In situ* conventional deep level transient spectroscopy and high-resolution Laplace DLTS techniques were used to analyze the resulting deep electronic levels. No deep levels were detected prior to irradiation.

A conventional DLTS spectrum recorded *in situ* during the warming up after a low-temperature irradiation of a n^+p diode at 22 K with 2 MeV electrons is shown in Fig. 1(a). These irradiation conditions resulted in the appearance of two dominant peaks labeled H110 and H650. The first peak, H110, matches the one reported recently in Ref. 8 in *p*-type Ge and stems from the double-acceptor level of the vacancy. The other dominant peak, H650, was assumed to be related to $\mathrm{Ga_i}$ in Ref. 8, and plays the lead role in the present work. The electronic level corresponding to this defect is characterized by an apparent capture cross section of $\sigma_{\mathrm{na}}=4\times10^{-16}\ \mathrm{cm^2}$ and an activation energy for hole emission of $\Delta E_{pe}=0.65\ \mathrm{eV}$.[11] From a combined analysis of emission and capture processes the energy barrier for capture of holes and, respectively, the enthalpy of the ionization of the H650 defect were determined to be as $\Delta E_{p\sigma}=0.31\ \mathrm{eV}$ and ΔH

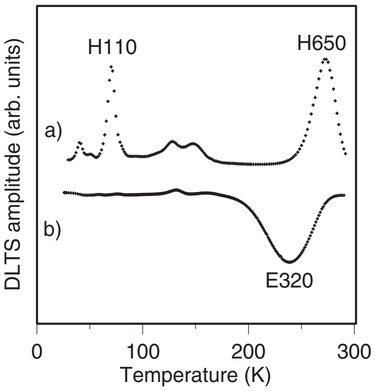

FIG. 1. DLTS spectra of n^+ p-mesa diodes after 2 MeV electron irradiation to a dose of 4×10^{10} cm^{-2}. Spectrum (b) was recorded upon application of forward-bias pulses to the mesa diode. The DLTS settings were: (a) $e_n=20$ s^{-1}, $V_R=-8$ V, $V_p=-2$ V, and (b) $e_n=20$ s^{-1}, $V_R=-3$ V, $V_p=+2$ V. The duration of the filling pulse was 50 ms in both cases.

$=0.34$ eV, respectively. There is no indication of any electric-field dependence of the position of H650 in the Laplace DLTS spectrum for both doping levels used in the present investigation. These observations are consistent with those of Ref. 8. In addition to the two dominant peaks of Fig. 1(a), some minor features are detected in the DLTS spectrum as well; they will not be further discussed in this Brief Report.

Figure 1(b) shows a conventional DLTS spectrum recorded with the application of "injection" pulses using forward-bias pulsing. Under this condition, both majority and minority carriers are injected and, respectively, traps in the upper half of the band gap can be filled with electrons. In this case, besides the previously seen minor hole trap at about 130 K, another dominant electron trap E320 is observed. The electronic level corresponding to this defect is characterized by an apparent capture cross section of 3×10^{-21} s^{-1} K^{-2} estimated from the pre-exponential factor of the Arrhenius plot and an activation energy for electron emission of $\Delta E_{pe}=0.32$ eV. No trace of H650 is observed in Fig. 1(b) when, as mentioned above, both majority and minority carriers are injected into the depletion layer. This can be understood if capture of minority carriers (electrons) is the most preferable process for the defect. The absolute concentrations of H650 and E320 seen in Figs. 1(a) and 1(b) are found to be identical. Similar experiments have been performed by Markevich *et al.*[6] confirming the presence of different charge states of the VO and E centers in the band gap of Ge. In addition, as seen in Fig. 2, the behavior of the H650 and E320 lines upon 15 min isochronal annealing are also identical. When the bias is off, these defects anneal out within some minutes at room temperature as was also observed in Ref. 8. This observation is consistent with the absence of this peak in DLTS measurements of p-type Ge irradiated at room temperature.[10,12,13]

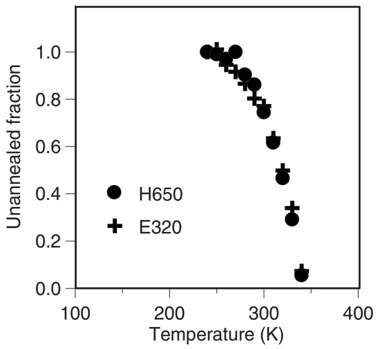

FIG. 2. Relative concentrations of the H650 and E320 traps as a function of 1 min isochronal annealings without bias.

In order to exclude the possibility that defects injected from the n^+-top layer could act as a precursor for the H650 line we compared Laplace DLTS signals observed in mesa and Schottky diodes; Fig. 3(a) shows a Laplace DLTS spectrum of a mesa diode measured at 275 K corresponding to the temperature of the maximum of the H650 peak observed in Fig. 1(a). The main feature of this spectrum is one dominant sharp line in agreement with a monoexponential emission process expected from a well-defined single energy level. A slightly broadened Laplace DLTS peak is observed in the p-type Ge Schottky diode shown in Fig. 3(b) with otherwise identical electrical properties as those mentioned above for the n^+ p diode. This clearly demonstrates that the H650 peak is not related to defects which could have been injected from the n^+-top layer during the MBE growth or the irradiation. The broadening of the peak can be ascribed to the high value of the reverse-bias leakage current (some milliampere at room temperature) observed in the Schottky diode resulting in a high noise level which Dobaczewski *et al.*[14] have shown can lead to a broadening of Laplace DLTS peaks. Thus, this broadening observed in the Laplace DLTS spectrum is linked with the limitations of the numerical software rather than with a physical phenomenon.

As mentioned above under zero-junction-bias conditions a large enhancement in the H650 defect-annealing rate is observed compared to that under reverse bias. In this case the Fermi level is between the H650-defect level and the valence-band edge, and the trap is believed to be occupied by a hole while it is unoccupied in the case of a reverse-biased diode. As seen in Fig. 4 the variation in annealing kinetics

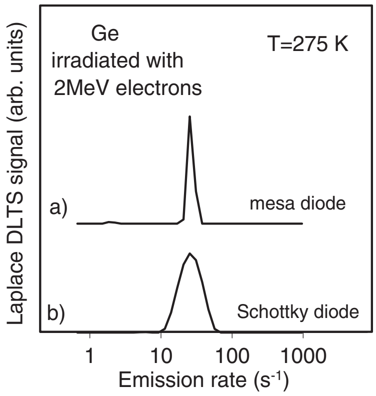

FIG. 3. Laplace DLTS spectra recorded at 275 K in 2 MeV electron-irradiated p-type Ge mesa diodes (a) and diodes with Schottky contacts (b). Measurements settings were $V_R=-8$ V, $V_p=-2$ V, and pulse duration 50 ms.

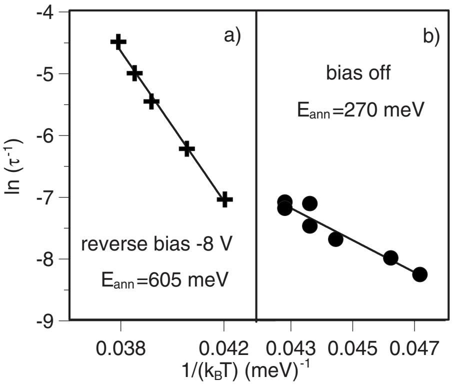

FIG. 4. Annealing kinetics for the loss of the H650 line under zero (b) and reverse bias (a) in *p*-type Ge irradiated with 2 MeV electrons.

for the different charge states results from different annealing-activation energies. Moreover, the pre-exponential factors also significantly differ in these two cases: the pre-exponential factor which is mainly governed by the attempt frequency of the interstitial gallium atom during its passage over a classical potential barrier is found to be about $\sim 10^8$ and $\sim 10^2$ s^{-1} in the case of a reverse-biased and unbiased diode, respectively. The first value is in agreement with what should be expected for a long-range diffusion.[15] The much smaller pre-exponential factor found in the latter case, and also found in Ref. 8, clearly indicates that the process of the capture of a hole plays the major limiting factor. The energy barrier of 0.27 eV can then be interpreted as the barrier which a hole must overcome in order to be captured by the defect. Furthermore, in support of this idea the value of 0.27 eV is very close to the measured capture cross-section barrier (0.31 eV in the present work and 0.29 eV reported in Ref. 8).

The H650 and E320 peaks have similar concentrations and anneal almost identically. Thus, it is very likely that they represent two different charge states of the same defect. Of course, one should keep in mind that, being a midgap level in the Ge band gap, the defect could simultaneously interact with the valence and conduction bands. This could lead to the observation of the same defect as the H650 line in the conventional DLTS spectrum and as the E320 line when injecting both electrons and holes into the depletion layer of the diode. Such a behavior was observed for gold impurities in *n*-type silicon where a single acceptor level $(-/0)$ was detected in both the DTLS and MCTS (minority-carrier transient spectroscopy) experiments.[16] However, this possibility can be safely ruled out by the very small apparent capture cross section observed for the E320 trap which clearly indicates that the defect is, at least, neutral before capturing an electron which is not compatible with the donor character of the H650 level reported in Ref. 8.

The H650 and E320 peaks are not observed in *n*-type Ge,[4,8] clearly suggesting that Ga is involved in their formation. This is also supported by the fact that an increase in the Ga concentration leads to a corresponding increase in the intensity of both of these lines. Thus, it can be concluded that Ga is involved in the defect and with only one Ga atom per defect.

An essential feature of the low-temperature irradiation and *in situ* measurements is the possibility of tracing the formation of secondary defects at increasing temperatures from the primary defects created during irradiation. However, due to the high activation energy of H650 together with the huge relaxation process observed for this defect during the emission process one cannot unambiguously determine its formation temperature with the present capacitance techniques. On the other hand, following the irradiation with 2 MeV electrons at cryogenic temperatures the diode capacitance increases significantly for the whole range of applied bias. This is correlated with the introduction of a large concentration of negative charge into the depletion region of the $n^+ p$ diode which adds up with the negatively charged dopant (Ga^-). As shown in Fig. 2(a) two dominant peaks are observed in the conventional DLTS spectrum in the electron-irradiated *p*-type Ge. The H110 line is related to the double-acceptor level of the monovacancy[8] while H650 arises from the deep donor trap discussed above. It can then be expected that the observed increase in the diode capacitance as a result of irradiation is connected to the appearance of monovacancies and/or other acceptors in the depletion layer of the $n^+ p$ diode. Indeed, only the presence of an equal number of doubly negatively charged monovacancies[8,9] and singly positively charged self-interstitials[8,9] which are believed to be dominant defects after electron irradiation, and no positively charged Ga_i can lead to the observed changes in the CV measurements at cryogenic temperature. Otherwise, either a constant value of the capacitance or a decrease is expected. Also supporting this interpretation is the observed decrease in the capacitance to its initial value after an annealing for some minutes at around 200 K, which happens before it becomes possible to observe the H650 line in the conventional DLTS spectrum. This observation is in contrast to the case of silicon in which Ga, B, and Al interstitial defects are believed to be formed just after implantation at cryogenic temperature.

Thus, the defect related to the H650 and E320 lines in the DLTS spectrum is a Ga-type defect with only one Ga atom per defect and which is not formed as a primary defect in the collision cascade. The Coulombic repulsion between negatively charged monovacancies[8,9] and negatively charged substitutional Ga atoms makes it very unlikely for them to pair up. On the other hand, the self-interstitials are known to be positively charged over the whole range of Fermi-level positions in *p*-type Ge.[8,9,17] Due to their long-range motion, the self-interstitial atoms in the Ge lattice,[8,9,16] which are produced in the primary damage event, can be trapped by substitutional gallium. Subsequently Ga is ejected into an interstitial site forming Ga_i which would then be responsible for the H650 and E320 lines. This mechanism would then be very similar to the one observed for the interstitial defects (Ga, B, and Al) (Refs. 15 and 18–21) in *p*-type silicon.

Moreover, in the present case where the concentration of H650 is about 1.5 times higher than that of single monovacancy (H110) and taking into account an equal number of vacancy- and interstitial-related defects, it seems unrealistic that the H650 and/or E320 defect can consist of more than one self-interstitial atom. Therefore, taking into account all these arguments we conclude that H650 and E320 belong to two different charge states of the Ga_i defect.

Finally, we would like to address the question as to whether this defect forms an Anderson-negative-U system.[22] For a "normal" defect an additional carrier is bound more weakly than the first carrier due to Coulomb repulsion. However, for the negative-U system this sequence does not hold. For example, as known from previous studies in n-type Si, interstitial boron forms an Anderson-negative-U system where the acceptor level $(-/0)$ at $E_C-0.45$ eV is below the single donor state $(0/+)$ at $E_C-0.13$ eV in the forbidden gap.[18,19] This implies that the neutral charge state of $\mathrm{B_i}$ is unstable in silicon and only the acceptor level corresponding to $\mathrm{B_i^{(-/0)}}$ can be observed in DLTS studies. The negative-U phenomenon has not been observed for the interstitial aluminum defect[20] in silicon whereas isolated interstitial gallium has been concluded not to introduce any electrically active levels into silicon band gap.[21] As shown above, H650 and E320 are believed to belong to different charge states (very likely to a single donor state and a single acceptor state) of the interstitial Ga defect. In this case the acceptor level is closer to the conduction band compared with the donor level and, consequently, there is no Anderson-negative-U ordering of the energy levels. This is also consistent with the observation that concentrations of the $\mathrm{Ga_i}$ $(+/0)$ and V $(--/-)$ defects evaluated from the height of the DLTS peaks differ approximately by a factor 1.5 depending on the reverse bias applied and the doping level. This ratio is smaller than that of 2 which is expected from the sequences of levels creating the negative-U system. On the other hand, the deviation from unity, characteristic for the positive-U sequences of levels, can be explained within the proposed model taking into account the electric-field effects inside the depletion layer. Under the presence of the electric field, doubly negatively charged vacancies are being to sweep away from the depletion region. Moreover, in this case one can assume that such effects should be less pronounced for single charged $\mathrm{Ga_i}$. All of this can lead to a quite large underestimation of the vacancy concentration evaluated from the intensity of the DLTS peak and, thus, distorts the present analysis. Supporting this idea is the observation that in the samples with the higher content of Ga where the electric field is expected to be also higher inside the depletion layer the difference in the intensities of the H650 and H110 lines becomes even more pronounced.[8] However, considering the very small apparent capture cross section found for the E320 level it cannot be excluded that this level has a double-acceptor character in which case there must be a single acceptor level closer to the conduction band; these two levels would then form a negative-U system.

In this Brief Report we have continued our previous work and presented an exhaustive analysis of the annealing and charge state properties of one of the dominant defects in Ga-doped germanium irradiated with 2 MeV electrons. We have demonstrated that in addition to the electrical level at 0.34 eV above the valence band this defect introduces another level at 0.32 eV below the conduction band. These levels were found to belong to interstitial gallium and behave as single donor and single acceptor states, respectively. No Anderson-negative-U system for this sequence of levels has been observed.

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