Low-temperature irradiation-induced defects in germanium: *In situ* analysis

A. Mesli,[1] L. Dobaczewski,[2] K. Bonde Nielsen,[3] Vl. Kolkovsky,[3] M. Christian Petersen,[3] and A. Nylandsted Larsen[3]
[1]*Institut d'Electronique du Solide et des Systèmes, CNRS/ULP, Strasbourg, France*
[2]*Institute of Physics Polish Academy of Science, al. Lotników 32/46, 02-668 Warsaw, Poland*
[3]*Department of Physics and Astronomy, University of Aarhus, DK 8000 Aarhus C, Denmark*
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The electronic properties of defects resulting from electron irradiation of germanium at low temperatures have been investigated. The recent success in preparing n^+p junctions on germanium has opened a new opportunity to address fundamental questions regarding point defects and their related energy levels by allowing an access to the lower half of the band gap. In this work we apply various space-charge capacitance-transient spectroscopy techniques connected on line with the electron-beam facility. In *n*-type germanium we identify a level at about 0.14 eV below the conduction band whose properties resemble in many respects those of a defect assigned previously to the close vacancy-interstitial or Frenkel pair. This pair seems to annihilate over a small barrier at about 70 K, and its stability is particularly sensitive to the irradiation temperature and energy. We also observe two coupled levels at 0.08 and 0.24 eV below the conduction band stable up to 160 K. Recent independent theoretical work has predicted the existence of the single and double donor of the germanium interstitial with energy levels matching exactly these two values. Given these identifications hold, they mark a major difference with silicon where both the Frenkel pair and self-interstitial have never been caught. In *p*-type germanium, two levels were found. The shallower one, located at about 0.14 eV above the valence band, is tentatively assigned to the vacancy. It exhibits a field-driven instability at about 80 K making its analysis quite difficult. The application of a reverse bias, required by the space-charge spectroscopy, leads to a strong drift process sweeping this defect out of the observation area without necessarily provoking its annealing. Unlike silicon, in which the vacancy has four charge states, only one vacancy-related level seems to exist in germanium and this level is very likely a double acceptor. Finally, a very peculiar observation is made on a hole midgap trap, which, in many respects, behaves as the boron interstitial in silicon. This has led us to suggest that it may stem from the gallium interstitial, a natural dopant of our germanium materials, whose presence would be the fingerprint of the Watkins replacement mechanism in germanium.

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I. INTRODUCTION

In the early days of defects in semiconductors, almost fifty years ago, the group-IV materials (Si, Ge, and diamond) were extensively studied. After a short time, however, work on diamond and germanium was ultimately abandoned in favor of silicon, as the former materials came under the shadow of impracticability.[1] Therefore, today the knowledge accumulated on silicon, although it continues to stimulate new surprises,[2] is by far more complete than that of, e.g., germanium. Recently, the higher low-field mobility attainable in germanium has brought this material back to practicability, leading to a renewed attention to the physics of its point defects. However, in sharp contrast to silicon in which the electron paramagnetic resonance (EPR) technique revealed to be crucial in addressing fundamental questions regarding the atomic structure of point defects, in germanium this method turned out to be much less efficient. We are thus left to rely on space-charge spectroscopy techniques provided good rectifying junctions on both *p*- and *n*-type materials are available. However, until very recently, these methods were confined to *n*-type Ge, and the lack of data from the lower half of the band gap became obvious. Some of the authors of the present work succeeded two years ago in preparing good n^+p diodes on highly Ga-doped germanium,[3] opening thereby a real possibility to investigate the whole band gap.

In the present work we focus our attention on point defects created after electron irradiation at cryogenic temperatures, and analyzed on line. Our main objective through this approach is to catch and try to identify the primary defects [interstitials, vacancies, and their possible stabilization as Frenkel pairs (FP)] and study their behavior while applying different stimuli such as temperature, electric field, light—processes in which the charge states play major roles. The dynamics of the secondary defects, which result from manipulating some of these parameters, will be very instructive to our purpose.

A recent survey by Emtsev[4] allows the highlighting of some important and helpful guide lines. In germanium a common analogy with the known defects in silicon has been adopted. There are, however, many examples in which striking differences between these two simple materials have been exposed. The first one concerns the self-interstitial and its parent defect, the Frenkel pair. There is little doubt today that the silicon self-interstitial has never been experimentally observed, but a consensus in its involvement in various reactions, via the so-called Watkins replacement mechanism,[5] is well accepted, although the situation is still not clear when we compare *n*- and *p*-type silicon.[6] As a corollary, the Frenkel pair could not be caught in any ultimate condition. However, it seems that the Frenkel pair in *n*-type germanium could be frozen into the lattice and thus observed.[4] From annealing studies a double acceptor state has been attributed to the Frenkel pair somewhere between 35 and 70 meV be-

low the conduction band. The uncertainty originates mainly from the mean distance between the vacancy and the interstitial, which is determined by the energy deposited by the irradiating particle. As a consequence, the annihilation process of the correlated components is mainly linked to the irradiation energy, the highest stability being found at around 65 K: A significant shift of the annealing stage toward lower temperature (≈55 K) was observed after γ irradiation from ^{60}Co, where the defect is mainly created by the Compton electrons with a relative low average energy of ≈600 keV, giving rise to a shorter distance between the two components. As to the impact of the irradiation energy in the creation and stabilization of the Frenkel pair in germanium, various works cited in Emtsev's survey[4] would deserve citation. But so far one of the most complete and instructive ones was done by Callcott and MacKay,[7] who investigated the range 0.7 to 4.5 MeV in which they observed the fingerprint of the close vacancy-interstitial or Frenkel pair, although the threshold energy for atomic displacement of about 0.5 MeV is below this range. Callcott and MacKay found that the Frenkel pairs account for 95% of the loss of conductivity produced by irradiation at 0.7 MeV, whereas this fraction drops to 50% when the irradiation is performed at 4.5 MeV. It should be noted that the conductivity is sensitive to about 1% of carrier removal. Since this earlier work, the techniques improved considerably, and with the space-charge spectroscopy based methods used in the present work, we can easily detect a change in carrier trapping of 0.01% of the total carrier concentration. The Frenkel pair can thus be observed even for irradiating energies much higher than the threshold. In probing the conductivity as a function of temperature, a sharp transition was found at about 65 K following electron irradiations in the range 1 to 4.5 MeV. This sharp transition, representing the recovery of free electrons, initially trapped by Frenkel pairs, is clearly in favor of a very narrow distribution of separation distances of close vacancy-interstitial pairs. Two to three atomic distances have been speculated,[4] above which the pair dissociate and below which it annihilates. We will show below that a single level, also unstable at about 65 K, is detected and tentatively assigned to this primary defect. A final point worth mentioning is the following: The situation in germanium is markedly different from compound semiconductors such GaAs and ZnSe where the Frenkel pair can be stabilized at much higher temperatures with a much broader distribution of separation distances. In an interesting review given by Watkins,[6] we can learn, for instance, that well-resolved EPR spectra of several distinguishable Frenkel pairs have been observed in electron-irradiated ZnSe. They anneal in a series of discrete steps, the closest first and the more distant ones at progressively higher temperatures. This is so far not observed in germanium.

The possibility of forming the Frenkel pair in germanium implies the possibility of being able to observe each constituent (self-interstitial and vacancy) separately, which would, at least for the self-interstitial, be markedly different from silicon. According to the present knowledge,[4] the mobility of the self-interstitial (hereafter noted independently Ge_i or I) seems to increase in the sequence of $I^0 \rightarrow I^+ \rightarrow I^{++}$. This implies that the species is electrically active, introducing two coupled states $I^{0/+}$ and $I^{+/++}$ into the band gap, although not firmly quantified. The Ge_i-related levels might be expected not far from those of the Frenkel pair as a Ge_i should only be slightly affected by the presence of a vacancy. The vacancy is relatively easy to detect at least in n-type material, where it is ultimately trapped by the group V dopants (P, As, Sb) to form the well-known E center.[3,8,9] However, the number of coupled states associated to the vacancy and their position in the band gap were difficult to determine. We show in this work that this is due to the tendency of the vacancy to drift even at very low temperatures.

When addressing the thermal stability of the primary defects, we discovered that an early conclusion by Watkins,[10] stating that in silicon the same defects are produced whether it is a room-temperature irradiation or a low-temperature irradiation followed by annealing, as should logically be expected, does not hold in germanium. We believe that this difference is mainly due to the existence of the Frenkel pair and self-interstitial, and also to their relative charge state distribution in the band gap, which is totally different from silicon.

This survey cannot be complete without mentioning a more recent work by Haesslein *et al.*[11] based on the perturbed angular correlation (PAC) technique, which for the present purpose is considered to be the only alternative to EPR in probing the structure of the atomic environment of a point defect in germanium. This is clearly an advantage over electrical techniques, which are based on the sole carrier exchanges with defect related levels introduced in the band gap and which make them unable, in principle, to identify the defect. The PAC technique requires, however, the presence of a radioactive probe atom, ^{111}In, in the present circumstances, located in the substitutional lattice site next to the point defect of interest. Therefore, strictly speaking the structural information concerns rather secondary defects, i.e., a vacancy or self-interstitial bound to the probe atom. Haesslein *et al.*[11] carried out a detailed study on electron irradiated n- and p-type Ge, the irradiation being performed at liquid nitrogen followed by recording the PAC spectra at room temperature. By crossing PAC results with simple electrical consideration, Haesslein *et al.*[11] could provide some important information on the main primary defects, the vacancy and self-interstitial. In brief, these authors propose that the vacancy carries the charge sequence $V^{-/0}$ located at 0.20 ± 0.04 eV above the valence band and suggest for the self-interstitial the configuration $I^{0/+}$ located at 0.04 ± 0.02 eV below the conduction band. Finally, for both primary species a long-range migration process has been inferred at about 200 K. Although the general trends are quite in line with our findings, looking into the details has led to some important differences and open questions, which will be discussed in more detail in the section devoted to a comparison of our findings with the literature.

II. CONDITIONS FOR RELIABLE SPACE-CHARGE ANALYSIS: KEY FEATURES RELATED TO DEFECT INSTABILITIES

Before describing the experimental results and their implications, it is of particular importance to emphasize a few

key aspects related to a reliable use of space-charge spectroscopy such as deep level transient spectroscopy (DLTS) and Laplace DLTS,[12] which are our main concern in this work. These techniques are mainly based on the recording of the capacitance of a junction or a Schottky barrier in the presence of traps while scanning the temperature.[13,14] The most critical condition, sustaining defect studies when based on capacitance measurements, is the conservation of the defect concentration, required in the observation area. This area is better known as the space-charge region (hereafter called SCR) whose extent is fixed by the pulse sequence (forward and reverse bias).[13,14] Under the condition of conservation, the space-charge spectroscopy technique relies on the following two main equations:

$$\frac{dn_t}{dt} = -n_t[e_n + e_p + c_n n + c_p p] + N_t[e_p + c_n n], \tag{1}$$

$$N_t = n_t(t) + p_t(t). \tag{2}$$

In the rate Eq. (1) the e's stand for emission rates and the c's for capture rate for electrons (n) and holes (p).[13,14] n_t represents the trapped electrons and N_t is the total concentration of the defect within the observation area. In most cases, where the levels act as simple traps for either one of the carriers, Eq. (1) simplifies considerably when one of the carriers can be neglected. For instance, for electron traps e_p and $c_p p$ can be dropped, and vice versa. Moreover, as the technique is based on space-charge effects, the emission and capture rate are separated in time, simplifying further the rate equation above, provided the so-called transition region does not play a significant role.[15] But the most critical point is the boundary condition expressed by Eq. (2), which clearly states that N_t is time independent, and thus conserved, although n_t and p_t ($=N_t - n_t$) are not. This means that the defect must be stable and its total concentration conserved in the SCR, which is expressed by the condition

$$\frac{dN_t}{dt} = 0, \tag{3}$$

allowing a reversible DLTS scan. In other words, the scan can be recorded either in the heating or cooling mode without affecting the defect parameters.[13] Condition (3) must hold during the whole temperature scan, usually in the range of 20 to 300 K. In this interval we basically assume that the defect concentration is not affected in any way. However, there are two instances in which Eq. (3) may not be fulfilled, and this paper is concerned with both of them. (i) The defect may annihilate locally during its observation; (ii) although physically stable, the defect may become mobile within the investigated temperature range. To this thermally stimulated migration, we may need to add a drift process due to the fact that in space-charge spectroscopy the application of an electric filed is required. The drift has been found to play a major role in many circumstances.[16,17] A mobility of the analyzed defect has two main consequences for the experimental signal: violation of the conservation law and mobility-induced capacitance change.

The first case concerns defects that do not need to diffuse or drift to violate condition (3) but simply annihilate within the temperature range necessary for their investigation. The close Frenkel pairs, highly unstable because expected to be governed by a very low barrier of annihilation, belong to this category. For those close vacancy-interstitial pairs the annihilation process is not necessarily controlled by a macroscopic diffusion process. One or two atomic jumps may suffice to trigger the annihilation. If the Frenkel pair gives rise to a level in the band gap, as it is suggested in this paper, its DLTS-related signal may have some peculiarities not observed for stable defects. In particular the signal cannot be recycled, breaking down the reversibility of the DLTS scan mentioned above, and the level may disappear either during or after the temperature scan has been completed. To the best of our knowledge only one similar observation has been reported in the literature.[18] This was the case of hydrogen in silicon where a partial "leak" of the signal had to be considered to account for the observations. In the present work defects are created by irradiation at low temperature. Thus, the temperature scan can only be performed in one direction: toward room temperature. If the temperature of annihilation is close to the temperature at which the DLTS peak is expected to appear, a large uncertainty in both the position of the peak and its amplitude is expected. As the time constant of the capacitance transient is composed of the carrier emission and the annihilation component, if the latter is significant the signal becomes unstable. The shape of the DLTS peak would be distorted with the high-temperature side being more abrupt than that of the low temperature, making the localization of the peak and its intensity uncertain. The Arrhenius plots of the emission rate versus reciprocal temperature, based on a well-defined DLTS peak and a reversible scan, necessary to produce several peaks with different experimental rate windows, will no longer be possible to construct. We will show that a means of partially circumventing this difficulty is to use the Laplace DLTS capabilities. The simplest approach to this issue would be to consider a first-order annihilation process transforming Eq. (3) into

$$\frac{dN_t}{dt} = -\frac{N_t}{\tau_{ann}}. \tag{4}$$

The situation may become very complicated if the annihilation process is charge state dependent. A simple look at Eqs. (1) and (4) shows indeed that the capture process would no longer be a first-order reaction, whereas the emission process may still be of first order but its time constant is the sum $1/\tau_{ann} + 1/\tau_e$ (where $1/\tau_e = e_n$). For the sake of simplicity, we shall, however, assume that the charge state does not affect significantly the stability of the defect. In other words we consider that the filling pulse (responsible for the capture process) is too short to affect the kinetics. Under these conditions, although the extraction of the capacitance signal is an easy matter, the time origin is the key issue. When DLTS is applied to conventional stable defects, the signal is recycled after each pulse as the capture-emission process is perfectly reversible, and to obtain a good signal to noise ratio, the signal is averaged over several periods, provided that the heating rate is low enough.[14] This approach allows

us to take the origin of the time after each pulse. In the present experiments, where *in-situ* annihilation takes place, the signal can no longer be recycled. The initial condition and the real time constant $1/\tau_{ann}+1/\tau_e$ are specific to each pulse and thus to each temperature. To circumvent this difficulty we choose the time origin as being at the onset of the temperature scan, following the irradiation process. The initial condition is fixed by relation (4), making N_t temperature dependent unlike the case of perfectly stable defects. Knowing the heating rate, Eqs. (1) and (4) allow writing the trapped electron concentration as

$$n_t(t) = N_{to} \exp\left(-\frac{(T-T_i)/\alpha_{\text{rate}}}{\tau_{ann}}\right)\exp\left(-\frac{t}{\tau_e}\right), \tag{5}$$

where N_{t0} is the initial concentration of defects before they start to annihilate, that is just after irradiation, T_i is the initial temperature, here the temperature of irradiation (=20 K), T the position in the temperature scale, and α_{rate} the constant heating rate (in K/s). The Laplace DLTS scan can be recorded at regular temperature steps ΔT and time intervals Δt allowing a constant heating rate $\alpha_{\text{rate}}=\Delta T/\Delta t$, where $T-T_i$ is a multiple of ΔT. In the simplified expression (5), time t now has the classical meaning applicable to stable defects and analyzed by conventional DLTS procedures. This relation stresses the important fact that after each data point a fraction of the signal is irreversibly lost until it vanishes completely. In such a situation, averaging, required for an increase in the signal to noise ratio, becomes more misleading than helpful.

The second case deserving special attention holds for defects which are highly mobile at a macroscopic scale below 300 K. These defects are better known as fast diffusers, among which copper is the most illustrative example, studied at length by one of us.[16,17] If these defects carry a charge, which is mostly the case, then the drift dominates. It has been shown that even without experiencing any electronic transition to the conduction band, a simple drift within the SCR gives rise to a "drift-induced transient capacitance," which can wrongly be interpreted as a DLTS signal.[16,17] This mechanism has been exploited to extract the diffusivities of highly mobile species at very low temperatures.[16,19] We will show below that a shallow trap, tentatively assigned to the vacancy, undergoes a drift process while exchanging holes with the valence band. To understand the main consequences of the drift during a DLTS scan, the following relationship is worth mentioning:

$$\frac{\Delta C}{C}(\bar{x}) = -\frac{n_t(\bar{x})}{N_{D,A}W^2(V_r)}\bar{x}\Delta x. \tag{6}$$

In this relation, which originates from the solution of the Poisson equation,[13,14] $\bar{x}$ denotes the mean position of the defects distribution in the SCR $[W_r(V_f)<\bar{x}<W_r(V_r)]$ and $(n_t\bar{x})$ the trapped electrons in the interval Δx at $\bar{x}$, whereas $N_{D,A}$ is the doping concentration that is assumed to be fully ionized at the working temperature. The mean position of the defect distribution is obtained as a ratio of the first (M_1) and the zero (M_0) moments $(\bar{x}=M_1/M_0)$ of the defects distribution, where M_0 and M_1 are given, respectively, by

$$M_0 = \int_{W_f}^{W_r} n_t(x)dx \quad \text{and} \quad M_1 = \int_{W_f}^{W_r} xn_t(x)dx. \tag{7}$$

Equation (6) shows clearly that the capacitance is very insensitive to charges trapped near the junction $(\bar{x}\approx 0)$. But the most striking feature is the fact that a drift of the defect within the SCR in either direction results in a change of the capacitance as such a motion produces a net change in the first moment of the defect distribution.[13,14] This is particularly striking in the case where the total charge in the SCR is conserved, which corresponds to a constant zero moment M_0,[14] in agreement with condition (4). Clearly, the sensitivity of the transient capacitance to detect a change in the charge distribution would depend on the direction of the drift: toward the junction drift would lead to a less capacitance change than toward the outer edge of the SCR. As mentioned above, this effect revealed to be very important in the case of Cu^+ in *p*-type silicon.[16] In the present work, the defect under concern is negatively charged, and thus the drift contribution to the capacitance change would be negligible in *p*-type germanium but large in *n*-type germanium. The major consequence of the drift is that the boundaries of the SCR, W_f and W_r, are not impermeable and the total charge cannot be conserved indefinitely. The electric field, which is maximum at the junction and vanishing at the outer edge of the SCR, leads to a leak of the defect, violating again condition (4), breaking thus the invariance of the zero moment M_0. The consequence is a progressive and irreversible loss of the defect, although here the loss is not due to a physical disappearance of the mobile species but simply to its escape from the observation region. The situation becomes more complicated if the mobile defect pairs off with other existing species: in the present case negatively charged vacancies react with donors of the group *V* dopant in *n*-type germanium in the same manner as does Cu^+ with acceptors in *p*-type silicon.[16] Pairing is thus a very efficient channel for irreversible loss depending upon the binding energy with the dopant. Contrary to the weak pairing of Cu_i^+ with acceptor, the pairing of the vacancy with Sb is much stronger, requiring temperatures well above 300 K to dissociate. This is a major difference between the negatively charged vacancy $(V^=)$ in *n*-type germanium and positively charged copper (Cu^+) in *p*-type silicon. The process is reversible in the latter case but clearly irreversible in the former.

To summarize, we should expect complex transients resulting from the primary defects in germanium. Such transients could be a complex mixture of three processes: (i) the emission-capture process; (ii) the net change in the first moment of the mobile species distribution (related to its drift), and (iii) a loss of charges if the net flux of mobile species entering the SCR does not balance with the net flux of those leaving the SCR. We shall show below that a non-negligible fraction of charged vacancies is lost simply by pairing with the group-*V* dopants, resulting in a deactivation of the latter, affecting in turn the capacitance given by Eq. (6). This mechanism belongs to case (iii) in which the zero moment is no longer constant. Finally, the case of annihilation (iv), discussed above, also results in a dramatic change in the shape of the signal and its stability. If all these contributions were

equally important it would be a difficult task to derive reliable information. No matter which one of the aspects depicted above plays the main role, the major impact will be seen on a distortion of the shape of the related DLTS peaks and we must be prepared to be satisfied with qualitative information.

The paper is organized as follows. In Sec. III we detail the sample preparation and experimental conditions. In Sec. IV, the experimental results are divided into two parts. In a first subsection we discuss the data collected in *n*-type material where we analyze the signal attributed so far to the Frenkel pair, followed by a description of the *E* center resulting from a pairing of the vacancy with the group-*V* dopant. Then we describe the data related to the two coupled levels that the present study assigns to the single and double donors of the self-interstitial. The second subsection of the experimental results is devoted to the study of *p*-type germanium, where the unstable level assigned to the vacancy on one hand and a midgap level, which we assign to the gallium interstitial, on the other hand are analyzed. In Sec. V we confront our findings to the main results described much earlier but also found in more recent literature. We will reexamine some key features either because they are put in a new perspective or because they highlight fundamental controversies keeping some questions still open. Finally a summary and some concluding remarks will follow in Sec. VI.

III. EXPERIMENTAL CONDITIONS

In this study we use *n*- and *p*-type (001)-oriented Ge single crystals from UMICORE. The wafers are doped with antimony (Sb) or gallium (Ga) at concentrations of 1.4×10^{15} cm^{-3} and 1.8×10^{15} cm^{-3}, respectively. The residual concentration of oxygen is below 10^{15} cm^{-3} whereas the one for carbon is below 10^{14} cm^{-3}. Schottky contacts were evaporated onto *n*-type samples after standard chemical cleaning of the surface. This approach does not work on highly doped *p*-type samples as is also the case with any conventional method of making a n^+p junction either by implantation or diffusion. A detailed report on the formation of n^+p diodes of good quality on such low-resistivity *p*-type Ge was published recently[3] by some of the present authors. Here we shall briefly review some details of the technological procedure. The n^+ top layer of the diodes is a 0.8 μm-thick epitaxial, Sb-doped Ge layer grown by molecular beam epitaxy (MBE) in which a sufficiently high concentration of Sb is incorporated during the growth. As a result of the different thermal steps, a significant fraction of antimony diffuses into the *p*-type substrate beyond the junction, leading to a counter doped area. Thus, Sb-related signals can be expected to appear in the DLTS spectra from the *p*-type region under certain conditions. In the same time both *C* and *O* contaminants may diffuse, however, much less than Sb. Therefore, we do not expect any significant contribution of these species as will be demonstrated below. The resulting current-voltage IV characteristics of the so manufactured n^+p diodes are very good as described in Ref. 3. Finally, as a consequence of the very shallow acceptor levels of Ga and Sb in Ge (about 11 meV above the valence band or below the conduction band, respectively), the carrier freeze-in temperature is much lower as compared to silicon. This allows the DLTS scans to start at ~20 K.

The diodes were irradiated with 1 to 3 MeV electrons at 22 K with different doses around 5×10^{14} cm^{-2} and subsequently studied by conventional DLTS and Laplace DLTS *in-situ* following the irradiation. This facility offers the possibility to study the primary defects and their dynamics before they interact with each other or with existing foreign species such as Sb and Ga. It is well established that infrared light plays a fundamental role in the stability of the defects generated by electron irradiation at low temperature.[20] Nielsen and Andersen[21] have shown that at ultimately low temperatures the thermal radiation originating from the vacuum chamber walls affects the electronic population of the defect related levels. This effect of thermal radiation vanishes when the diode is fully encapsulated enabling thermal equilibrium with the radiation field. All our experiments have been carried out in these strict conditions. In our setup the encapsulation consists of a copper movable slit (kept at the same temperature as the diode). Immediately after irradiation, the slit is moved leading to a full encapsulation of the diode. The Laplace DLTS turned out to be very helpful in these experiments as the observed primary defects are unstable, making their analysis by conventional DLTS very difficult. This technique allows obtaining the main information in a single scan whereas, conventional DLTS requires several reversible scans, a procedure not possible when the signal disappears during or after the first scan as will be shown below.

IV. EXPERIMENTAL RESULTS

A general comment should be made before describing the experimental results. It should be clear that the techniques used in the present investigation are solely based on carrier capture-emission processes from levels located in the band gap, producing the fingerprints of point defects. Strictly speaking, these techniques are unable to give any structural information or identification of the observed defects. An approach in the following could be to use some ways of labeling the levels under investigation and to postpone a discussion of possible models until enough information are collected. We believe that this approach complicates unnecessarily the description. Instead we use below the opposite approach, which consists of attributing to each subsection the identity of the defect we propose in the present work, bearing in mind that the various identifications remain in principle open and subject to debate as they rely on indirect arguments based on a cross-checking with the available literature.

A. Low-temperature irradiation of *n*-type germanium

1. Frenkel pair

There is a general consensus that the sharp transition occurring at 65 K in the conductivity change produced by electron irradiation of germanium is due to the generation of close vacancy-interstitial of Frenkel pair.[4,7] The change in conductivity was inferred to correspond to a double acceptor

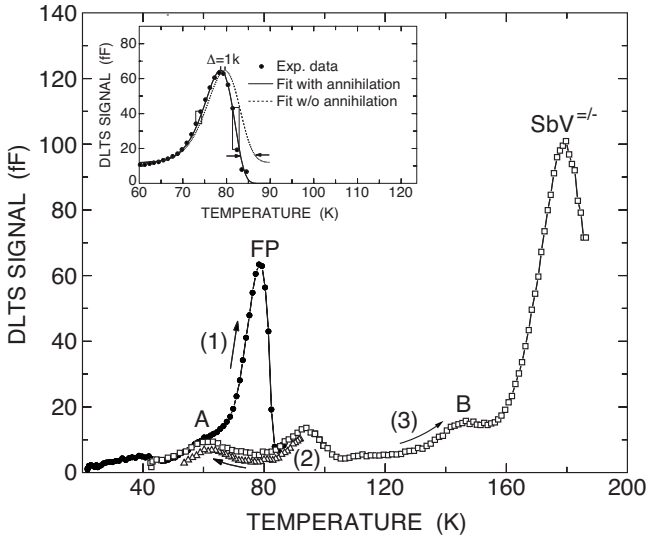

FIG. 1. Laplace DLTS step-by-step isothermal measurements (see text). The diode is an *n*-type Schottky barrier and the irradiations were performed at 22 K with a 1-MeV electron beam and a dose of 5×10^{14} cm^{-2}. The three spectra were recorded successively starting with spectrum (1), which immediately followed the irradiation. The inset focuses on the peak labeled FP. The fitting curves incorporate the constant base line on the left part of the signal.

state close to the conduction band. Our main objective in the present work was to seek for such a level and study its dynamics.

Figure 1 shows a series of three spectra recorded immediately after 1-MeV electron irradiation at 22 K of *n*-type germanium with the diode shortened. The latter condition has been used for all irradiations. Spectrum (1) is the first observed in the heating mode. It shows a dominant peak FP, which is clearly asymmetric due to an anomalous fall off of the signal on the right-hand side. The electron irradiation is performed at low temperature with a fairly low dose. By analogy with silicon, we expect thus to create the two primary defects, namely the self-interstitials and the vacancies, among which a non-negligible fraction could possibly remain close enough to bind and form the Frenkel pairs. The temperature range of stability of the peak labeled "FP" matches surprisingly well with the transition in conductivity observed in the early days and mentioned above. The observed peak is thus very likely the finger print of the Frenkel pair and thus of that transition in conductivity. In this context the observed asymmetry would be due to a local annihilation process. The barrier for annihilation of close-correlated vacancy and its counterpart, the self-interstitial, must be small enough to account for the irreversible loss of the pair at such low temperatures. This makes a quantitative analysis of the peak very difficult. In conventional DLTS several scans are indeed necessary to construct the Arrhenius plot from which the defect energy level and capture cross section could be extracted, and this is clearly not possible even though we repeat the irradiation process. The instability below 80 K forbids the use of higher experimental emission rates, which aims at shifting the peak to higher temperatures. Conventional DLTS is therefore of no help in the present situation. Laplace DLTS has in this respect a distinct advantage as it allows the recording of the full emission transient at fixed temperature, repeating this procedure at equally spaced temperatures. Therefore, restricting ourselves to a series of transients on the left-hand side of the peak, where we assume a negligible annihilation, allows at least an estimate of the defect parameters. This approach has led to an energy level of 0.166 eV below the conduction band and an emission rate prefactor of $\approx10^7$ K^{-2} s^{-1}. Because of the very narrow investigated temperature range (~10 K), the latter parameter suffers quite a large uncertainty.[22] However, these values can be refined and the annihilation parameters estimated by a fitting of the whole signal based on relation (5). In the inset we show the dominant peak with the best fit ignoring the annihilation process (dashed curve) and another fit accounting for a first-order annihilation mechanism (solid curve). To obtain the best fit, we have used the values above as starting parameters. A number of features can be highlighted from this inset. First, the data are taken by Laplace DLTS along a single scan as mentioned above. They are equidistant ($\Delta T=1$ K) and each point required $\Delta t=20$ s before it is generated, making the fitting process straightforward. Here the heating rate appearing in relation (5) is $\alpha_{\text{rate}}=0.05$ Ks^{-1}. The two rectangles taken from each side of the signal illustrate the impact of the annihilation. They would have been of the same size if the defect was perfectly stable, leading thus to a perfectly symmetric peak. Second, although the left part of the signal only could be used to extract approximate defect parameters, we clearly see that the annihilation process starts well below 80 K making the fitting of the whole signal necessary. This procedure helps in correcting the values above, leading finally to $E_c-0.14$ eV with an emission rate prefactor of about 10^6 K^{-2} s^{-1}, which we retrieve in Table I reporting numerical values of all the defects studied in the present work. The prefactor value is about an order of magnitude lower than suggested from the first estimate but this is not surprising for the reasons already mentioned.[22] In this model we also assume implicitly simple atomic jump for the mobile species governed by the Debye frequency,[23] which in the case of germanium is about 7×10^{12} K^{-2} s^{-1}. We obtain with these considerations a barrier for annihilation of 0.28 eV, which is in very good agreement with the value of 0.30 eV suggested by Wertheim.[24] However, although the fitting looks fairly good it might need further refinements. Two main unknowns would actually need to be taken into account: the role of the charge state on the annihilation rate, especially when large pulse widths are used. A deviation from a first-order annihilation process [Eq. (4)] may result. A second unknown is related to the capacitance change induced by the drift of negatively charged vacancies toward the outer edge of the depletion region, responsible for the formation of the *E* center (Fig. 1). According to Eq. (6) this effect, which occurs at fairly low temperature, might be significant, disturbing thereby the electron-emission-induced transient capacitance. Finally, the two calculated curves were normalized to the experimental data. But if we consider the absolute amplitude of the unstable signal it is actually seven times larger than shown. This is not surprising as the annihilation process starts at much lower temperatures than 80 K. The irreversible loss of the signal is illustrated by spectrum (2),

TABLE I. Electronic parameters for the radiation-induced primary defects observed in *n*- and *p*-type Ge crystals doped with, respectively, antimony (Sb) and gallium (Ga). The secondary defects, mainly *E*-centers, have already been analyzed in detail (Refs. 3, 8, and 9). The activation enthalpies for electron, respectively, hole, emission ($\Delta H_{n/p}$), pre-exponential factor ($A_{n/p}$) have been derived from the Arrhenius plots of T^2-corrected emission rates determined from conventional or Laplace DLTS measurements (see text and corresponding figures). The hole capture cross section σ_p for the midgap level in *p*-type Ge has been determined from direct capture measurements using the peak height versus pulse width variation, an approach not used for the other defects.

DLTS peak	Nature	$\Delta H_{n,p}$ eV[a]	$A_{n,p}$ $K^{-2}\ s^{-1}$	σ_p cm^2	Temp. of anneal K
FP	$(V-Ge_i)^{=/-}$	0.14	10^6		~65
A	$Ge_i^{0/+}$	0.08	5.2×10^4		~200
B	$Ge_i^{+/++}$	0.24	3.2×10^5		~200
V	$V^{=/-}$	0.14	2×10^6		~200 [b]
Ga_i	$Ga_i^{0/+}$	0.33	2.9×10^7	$7.5\times10^{-14}\exp(-0.29/kT)$	<300 [c]

[a]For the Frenkel pair the value includes both the enthalpy of ionization and the barrier for trapping (see Sec. V).
[b]The temperature of anneal should not be confused with the temperature of drift, the latter being much lower (see text).
[c]Under hole injection, otherwise the level is stable well above 300 K.

which was recorded in the cooling mode after scan (1) was stopped at about 90 K. Clearly, the peak assigned to the Frenkel pair is no longer present. This irreversible loss is once more confirmed in spectrum (3) recorded in the heating mode following spectrum (2). It shows a new dominant peak at about 180 K. This peak has already been identified elsewhere[8,9,25] as being due to the double negatively charged state of the *E* center or $SbV^{=/-}$, which is a secondary defect resulting from the trapping of a mobile vacancy (primary defect) by antimony. This complex is very stable well above room temperature.[8,9] If we assume that the assignment of the signal "FP" to the Frenkel pair is correct, then comparing the real heights of the *E* center and the Frenkel pair signals, the latter being seven times higher than shown, we obtain a concentration of vacancies close to their counterparts about three times larger than the concentration of uncorrelated vacancies; the former leading to Frenkel pairs and the latter to the *E* center. In other words, at low temperatures the larger fraction of primary defects tends to agglomerate into Frenkel pairs. This would be the first marked difference with silicon in which neither the correlated pairs nor the self-interstitials have ever been observed.

As discussed in Sec. I, the relative stability of the Frenkel pairs may strongly be affected by the irradiation temperature. Figure 2 shows a comparison of three DLTS spectra recorded after a 2-MeV electron irradiation at three different temperatures, 24, 44, and 54 K, respectively. If we consider the formation of the *E* center as a marker for the vacancy production, an interesting feature emerges. For all three irradiation conditions the concentration of the *E* center, whose formation results from long-range diffusion of vacancies, remains almost unaffected, whereas a dramatic drop of the signal "FP" is observed when the irradiation temperature increases. The drop would thus correspond more to a local annihilation process than to a release of more vacancies which would participate in the formation of more *E* centers. This result indicates that the temperature of irradiation does not influence the balance between close and far more distant uncorrelated vacancy-interstitial pairs, the vacancy being the only species responsible for the formation of the *E* center. However, this may seem in contradiction with the results depicted in Fig. 1. The fitting, shown in the inset of Fig. 1, indicates indeed that the annihilation process is negligible below 70 K. We may thus need to re-examine the situation in the light of further refined investigations. It should be noted, however, that the irradiation is not an equilibrium process, whereas the DLTS scan is supposed to be slow enough to fulfill the equilibrium conditions.[13] For the time being, we are left to speculate on a subtle coupling between the temperature and the ionization mechanism during the irradiation, which could be responsible for the strong annihilation observed in Fig. 2. It should also be noted that the data displayed in Fig. 1 correspond to a reverse bias applied to the diode immediately

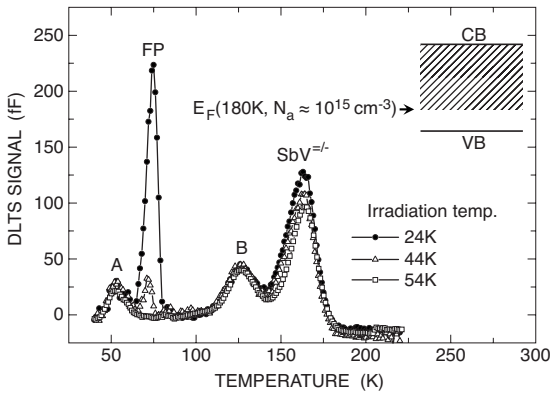

FIG. 2. DLTS spectra immediately following irradiations performed with the same dose as in Fig. 1 but with a higher energy (2 MeV) while the diode was shortened. All three spectra were launched from 22 K, which requires a cooling of the diodes irradiated at 44 and 54 K.

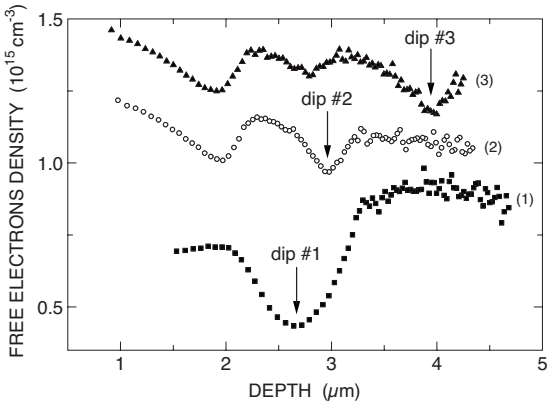

FIG. 3. The dip formation in the CV profile for the same diode (see text for more details). For the sake of clarity, the profiles were shifted in the vertical scale by 2×10^{14} cm^{-3}. It is worth mentioning that in the first profile at the bottom a larger compensation prevails after irradiation. This explains why the shallower dip No. 1 is wide and does not appear at the same position in the three profiles.

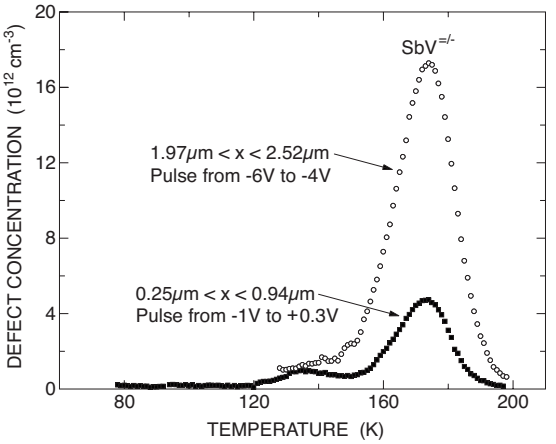

FIG. 4. Two DLTS spectra recorded in a narrow spatial window, respectively, near to the surface and at the outer edge of the space-charge region corresponding to a reverse bias of −6 V, a bias which prevailed during the first DLTS scan (larger peak).

after irradiation at 22 K. On the other hand, the data represented in Fig. 2 by the open squares were obtained for instance after irradiating the diode at 54 K while shortened and then cooled to 22 K before the reverse bias was applied and the DLTS scan launched. This may make a big difference, attributing a key role to the bias and thus to the charge state.

2. Vacancy and the E center

Most of the irradiations are performed at 22 K with a fairly low dose in moderately Sb-doped germanium. Hence we exclude the formation of the *E* center as a primary defect. The formation of this complex results rather from a diffusion, or more precisely from a drift, of mobile vacancies during the time elapsed by the DLTS scans shown in Fig. 1. The important question is obviously as to the number of charge states of the vacancy in germanium, the distribution of the corresponding energy levels in the band gap, and how this would compare to silicon. Clearly, no other signal, which could be related to the vacancy, is observed below 180 K, the temperature below which the *E* center has formed according to Fig. 1. As to the formation of an *E* center, although local atomic strain effect may need to be considered, the key role is played by the coulombic interaction between a positively charged antimony and a negatively charged vacancy.[2] It results thus that the highest vacancy level in the band gap is at least singly negatively charged when it is located below the Fermi level at 180 K in *n*-type germanium. Under these conditions, the fraction of negatively charged vacancies in germanium is maximal (=1), and because the DLTS technique requires the application of a reverse bias, those vacancies are drifted toward the edge of the depletion region where they are trapped by positively charged antimony. We should thus expect to accumulate the *E* centers at the outer edge of the depletion region and this is clearly shown in Fig. 3. In this figure we present the electrically active antimony profile in an *n*-type germanium Schottky diode after it has been subjected to electron irradiation at low temperature, followed by a DLTS scan under a bias of −2 V in the range 30–90 K [data labeled (1)]. The electric field being directed toward the Schottky barrier, the negatively charged vacancies drift toward the outer edge of the depletion region where they slow down and form the *E* centers via a coulombic interaction with positively charged antimony (Sb^+). This process results in the formation of a dip, representing the electrical deactivation of antimony in that position of the depletion region. Unless the sample is heated above 160 °C, the dip formation is an irreversible process.[8,9] The fact that the electric field plays a central role is shown by the subsequent drifts represented by the experimental profiles labeled (2) and (3). Cumulative dips are formed at different successive reverse biases. The upper profile labeled (2) followed the bottom profile after the diode has been kept at 90 K at −4 V for a few seconds. At this bias the outer edge of the SCR moved further in the bulk where we clearly see the formation of a second dip. This shows also that the source of negatively charged vacancies has not been exhausted during the first DLTS scan. Keeping the temperature at 90 K, and increasing the bias allows the formation of a third dip [labeled (3)] further away in the bulk. The DLTS spectra displayed in Fig. 4 illustrate the nonuniform distribution of the *E* center as a result of the drift. After an electron irradiation at 24 K the diode was biased at −6 V and heated up to 210 K. The two spectra then followed one in the cooling mode and the second in the heating mode with, respectively, the pulse sequence (−6 to −4 V) and (−1 to +0.3 V). The heights of the DLTS signals were converted into concentrations, taking into account the transition region and the nonuniform doping profile.[15] We clearly see that near the outer edge of the depletion region, an accumulation of the *E* centers occurs due to a drift of negatively charged vacancies, in agreement with the observed dips whose formation cannot be explained without considering negatively charged vacancies. The ratio between the concentrations of the *E* centers at the outer edge and the surface is even higher than that shown if we take into account the thicknesses of the observation areas, 0.55 μm for the former and 0.69 μm for the latter case.

Two important features emerge from these observations. First, the results displayed in Fig. 1 do not exclude the existence of vacancy-related levels in the upper half of the band gap in germanium, a situation which would then look similar to that in silicon. In this material the vacancy introduces four charge states among which the configuration $V^{=/-}$ and $V^{-/0}$ are predicted, respectively, at 0.29 and 0.45 eV below the conduction band but have never been directly observed by any thermally stimulated electrical method. The reason is that in silicon the vacancy starts moving at about 100 K, whereas the above charge states are electrically active only above 150 K.[5] Similarly, if in germanium the vacancy introduces any level in the upper half of the band gap, it would not be detectable by DLTS for the same reasons. Second, as demonstrated in Fig. 3, the vacancy being mobile already at or below 90 K in *n*-type germanium, the area of instability of the vacancy covers the range E_F(90 K)–midgap. We will show below that in *p*-type germanium, the *E* center still forms at or below 90 K, a temperature at which the Fermi level is in the lower half of the band gap closer to the valence band. The negatively charged vacancy is thus excluded from the whole shaded area displayed in the inset of Fig. 2. In particular, if the vacancy introduces more than one level, with a positive-*U* distribution, then the state $V^{-/0}$ must be even closer to the edge of the valence band if not below, in which case it becomes electrically inactive.

3. Germanium self-interstitial

In this last part of the chapter devoted to the irradiation of *n*-type germanium we address the issue of the peaks labeled A and B, whose presence has already been mentioned in Fig. 1. We assigned above the signal labeled "FP" to the Frenkel pair, which then could be caught in germanium and which was not the case in silicon. However, its stability is very sensitive to the experimental conditions. In particular, we have shown that low-temperature and low-irradiation energy are the optimal conditions for their formation. Figure 5 stresses the fact that the irradiation energy is very critical as to the formation of the Frenkel pair and the defects labeled A and B. The spectrum labeled "initial" shows that a 2.7-MeV electron irradiation does not allow for the formation of the Frenkel pair but enhances the magnitudes of peaks A and B. In this study we have used the sample whose spectra are displayed in Fig. 1. In other words the same sample has been irradiated twice. A first irradiation was done at 22 K with a 1-MeV electron beam to a dose of 5×10^{14} cm^{-2}, from which the above analysis on the Frenkel pairs followed. The outcome of this first treatment is the irreversible formation of the *E* center (peak labeled SbV$^{=/-}$ in Fig. 1), the only remaining secondary defect after a full scan up to room temperature. No one of the other peaks depicted in Fig. 1 survived at room temperature. Then this same sample was cooled to 22 K and a second irradiation was performed at 2.7 MeV to the same dose. Peaks A and B are clearly much more intense than in Fig. 1 by a factor of 40, and at the end of the analysis the resulting *E* center has increased by a factor of 10 only. If we consider that the amount of unpaired vacancies has increased after the second irradiation, the factor of 10 may seem underestimated. To understand this apparent inconsistency, we have actually to keep in mind that the concentration of unpaired antimony at the outer edge of the SCR is the limiting factor. Following the first irradiation and the subsequent analysis, this concentration has decreased. Thus, although the number of available vacancies has increased after the second run of irradiation, less antimony is available for the formation of the *E* center.

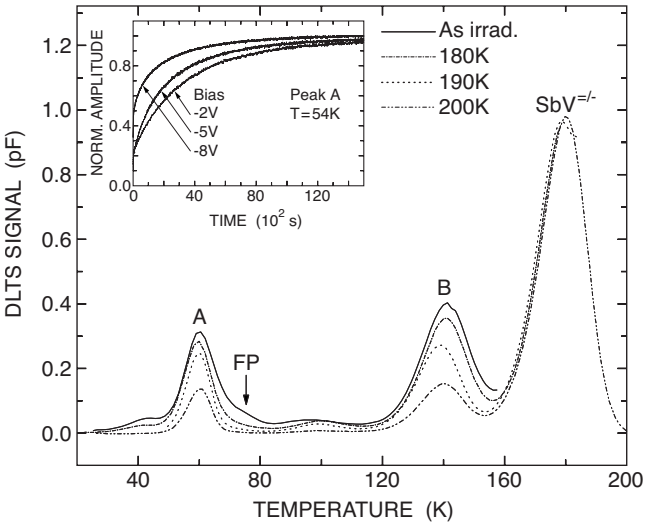

FIG. 5. DLTS scans recorded after electron irradiation at 22 K and an energy of 2.7 MeV with a dose of 5×10^{14} cm^{-2}. The solid curve represents the scan immediately following the irradiation, whereas the other spectra were recorded after successive annealings at the indicated temperatures. Note that the FP-related peak does not show up. The irradiation energy seems to be too high impeding interstitial-vacancy pairs to be correlated. The inset displays electron emission transients corresponding to peak A. A clear tendency for the Poole-Frenkel effect is observed when the reverse bias is increased. This indicates that the charge sequence of peak A is likely (0/+)

Peaks A and B are stable enough below 200 K to allow their characterization without ambiguity. The energy positions are 80 meV below the conduction band with a prefactor of their electron emission rate of 5.2×10^4 K^{-2} s^{-1} for peak A and 239 meV with a prefactor of 3.2×10^5 K^{-2} s^{-1} for peak B. These data are in remarkable match with values extracted from theory by Carvalho *et al.*,[26] who attribute 80 meV to the self-interstitial at the tetrahedral site ($I_T^{0/+}$) and 240 meV to the same species in the hexagonal site ($I_H^{+/++}$). Carvalho *et al.*[26] questioned the fact that these two levels would follow a negative-*U* distribution. If we are describing the same defects, the spectra of Fig. 5 are a clear demonstration that these two levels have a positive-*U* distribution, otherwise the shallower level would not be detectable. Within this scheme we infer that peaks A and B are likely to be related to the Ge self-interstitial, which introduces two different charge states. This assignment is further supported by the fact that both levels have the same height and decay with the same rate as it is clearly shown in Fig. 5. It is also in line with the experimental fact mentioned above that at higher irradiation energy, the FP signal vanishes while the magnitudes of peaks A and B increase. This would result from an increased separation between vacancies and self-interstitial,

leading to an increase in the concentration of uncorrelated pairs at the expense of the correlated Frenkel pairs. The charge states of these centers predicted by Carvalho *et al.*[26] suggest that the Poole-Frenkel effect should be observed. In the present work we use moderately doped substrates (10^{15} cm^{-3}), which are not the most suitable for an easy check of the Poole-Frenkel effect: The electric field achievable at the interface for such doping levels is around 1×10^5 V/cm, whereas electric fields of $(1-5) \times 10^6$ V/cm are required for the effect to be easily observed. On the other hand, although the Poole-Frenkel effect, which consists of a lowering of the barrier for carrier emission, is the same no matter the thermal depth of a defect, it is much easier to observe for shallower defects due to the fact that in the DLTS experiments, this lowering affects strongly the peaks observed at lower temperatures. A qualitative glimpse of this effect can be provided for the level located at $E_c - 80$ meV, where a series of capacitance transients measured at 54 K are reported in the inset of Fig. 5. They show a clear and substantial increase in the average emission rate when measured at larger reverse biases. In our opinion, this is an indication in favor of the donor-like character of the level as predicted by Carvalho *et al.*[26] It is worth reminding, however, that a firm statement on the Poole-Frenkel effect, thus on the donor character of peak A, requires the observation of a square-root dependence of the emission enhancement. The measurements based on the double pulse sequence, which would have led to such a behavior, have not been carried out in the present work. Finally, the annealing of these levels occurs at a temperature of about 200 K cited several times as the annealing temperature for vacancies.[11] This point, giving a further support for the assignment of peaks A and B to the germanium self-interstitial, will be discussed below. All these arguments being, however, indirect, it must be kept in mind that these identifications are tentative.

B. Low-temperature irradiation of *p*-type germanium

1. Vacancy and the E center

In germanium the single acceptor state of the *E* center is a hole trap located in the lower half of the band gap at $E_v + 0.30$ eV. It thus acts as a majority trap in counter-doped *p*-type materials.[3] In this work the counter doping is unintentional but revealed to be greatly helpful. It results from our procedure of making the n^+p junctions in which a significant fraction of antimony atoms diffuse beyond the junction where they can be used as an efficient marker for mobile vacancies.[3] To maximize the defect stability we use the lowest available experimental emission rate window (4.55 s^{-1}), allowing a shift of all peaks to lower temperatures. In this case, the single acceptor state of the *E* center leads to a DLTS peak at about 120 K as shown in Fig. 6. This temperature is obviously the new upper limit for the stability of the vacancy. It is significantly lower than the value of 180 K corresponding to the position of the double negatively charged state observed in *n*-type germanium (see Fig. 1). Therefore, the shaded area of Fig. 2, illustrating the forbidden band for the vacancy, is extended even further toward the valence band. It should be noted that although the double

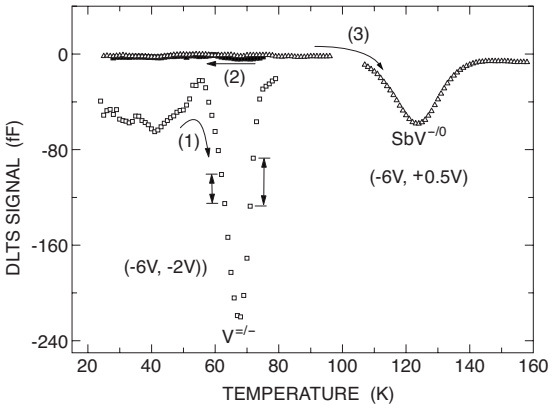

FIG. 6. DLTS spectra recorded at the lowest achievable experimental rate window (4.55 s^{-1}) on the n^+p junctions after electron irradiation at 22 K with an energy of 2 MeV, and a dose of 5×10^{14} cm^{-2}. The change of the pulse sequence allows the observation of the *E* centers, which form near the junction.

acceptor state of the *E* center appears at a higher temperature than the single acceptor state, it is closer to the conduction band than is the latter to the valence band. As we have mentioned above the reason is mainly that for the double acceptor state a correction accounting for the barrier of electron capture and the entropy accompanying the emission process is required, which is not the case for the single acceptor.[9] Figure 6 shows three temperature scans whose respective directions are indicated by the arrows. They all follow electron irradiation of a n^+p junction at low temperature. Let us first restrict our observations to the range of 22–100 K. The first spectrum labeled (1), immediately following the irradiation, displays a unique peak at 65 K, which is highly unstable already at about 70 K. It is indeed no longer present in the second run recorded in the cooling mode starting from 70 K down to 22 K. The third scan recorded in the heating mode confirms the irreversible loss of the signal, making the conventional DLTS analysis difficult. Again the Laplace DLTS reveals to be crucial as it allows an estimation of the level energy during a single scan. This approach leads to $E_v + 0.14$ eV for the shallowest and unique peak located below 120 K. The asymmetry of the signal is also clearly visible in Fig. 6, although less prominent than in the case of the signal assigned to the Frenkel pair (see Fig. 1). This asymmetry is indicated by the arrows, taken from each side of the peak, which again would have been of equal length if the peak was perfectly symmetric. Such an asymmetry, followed by the loss of the signal, is induced by the electric field as the following observation demonstrates. If at the end of the first scan, obtained under bias V_{r1}, the diode is shortened and brought back to 22 K, and a second scan launched at a higher bias V_{r2}, we observe a smaller peak in the area $W(V_{r1}) - W(V_{r2})$, previously located in the neutral region. The shallow hole trap is thus clearly associated with a defect which is negatively charged and highly mobile, thus susceptible to drift toward the junction. In the opposite case of a positively charged defect, an accumulation in the area $W(V_{r1}) - W(V_{r2})$ would have resulted. The action of the electric field must therefore be disconnected from a purely physical annealing. The second important outcome of this observation is

the fact that following the vanishing of the shallow peak, the acceptor state of the E center, located mainly near the junction, forms as shown in Fig. 6, where the third scan is extended beyond 100 K and the bias sequence changed from −6 to −2 V to −6 to +0.5 V to allow probing the narrow counter doped region near the junction. It is thus very likely that the shallow peak is the finger print of the vacancy, an identification in line with recent PAC experiments,[11] in which it is inferred that the vacancy is, however, stable up to 200 K. In our case the stability is artificially lowered below 80 K under the action of the electric field, a process out of equilibrium.

The assignment of the shallow peak to the vacancy in p-type germanium implies that the fraction of negatively charged vacancies in n-type germanium is 100%, as inferred from the formation of the dips in this material due to the E center. Consequently, in all these observations the drift process violates condition (3), and is thus clearly responsible for the observed irreversibility. The drift-induced leak of vacancies at the junction is not fully balanced by the in-diffusion of other vacancies from the neutral region through the outer edge of the SCR. The main reason is the nonuniform electric field present in the observation area, maximum at the junction and very weak at the outer edge of the SCR. It is thus not surprising that after some scans the vacancy-related signal vanishes irreversibly.

Similarly to the case of the Frenkel pairs described above, the instability of the vacancy-related signal, when subjected to the electric field, raises the crucial issue of the degree of confidence in its characteristics, and especially the energy position of $E_v+0.14$ eV extracted from the Laplace DLTS procedure. Equations (1)–(7) underline the fact that the transient capacitance of a hole trap, subjected to various kinds of instabilities, could have a more complex time constant than expected if it was stable. The slight asymmetry observed in Fig. 6 and the irreversible loss of the signal clearly means that both conditions (3) and (7) are violated. The source of this violation is twofold: (i) the drift of the vacancies due to the electric field induces by itself a transient capacitance with a time constant determined by the diffusion coefficient;[16,17] (ii) the nonconservation of the concentration of vacancies in the observation area means a loss of charges and thus the induction of another transient capacitance with its specific time constant. These two components add up to the purely conventional hole emission and it becomes questionable as to the shape of the resulting experimental transient and the weight of each specific effect. A rigorous treatment requires the knowledge of several parameters such as the diffusion coefficient, the shape of the electric field which might not only be spatially but also time dependent during the scan, and finally, the ratio between the flux of vacancies leaving the observation area at $W(V_f)$ and the flux of vacancies entering the outer edge of that area at $W(V_r)$. This means that the energy position of $E_v+0.14$ eV may only be considered as tentative. The present situation is actually fortunate as the loss of charges occurs mainly at the junction and according to relation (6) the impact should be weak. This is the main reason for the observed slight asymmetry of the peak, clearly less significant than in the case of the Frenkel pair (see Fig. 1).

As a final step in the present analysis, the charge state of the vacancy needs to be clarified. It is obvious now that the results described above cannot be consistent without assigning a negative charge state to this elementary defect. However, whether the negative charge state is single (V^-) or double ($V^=$) before the capture of a hole has still to be decided. Here we describe the main observation in favor of the charge sequence $V^{=/-}$. When the irradiation dose increases in order to produce as many vacancies as gallium atoms in p-type or even more, a huge junction capacitance appears with an apparent total negative charge in the depletion region that is much larger than the original doping level. The junction capacitance returns to initial values only after heating to about 200 K, a temperature noticed several time to be the threshold for a recovery.[11] As it has been demonstrated above, besides vacancies, the other possible defects are the Frenkel pairs, which anneal out well below 200 K, and the single acceptor state of the E center (rather neutral at low temperatures), which is confined in a narrow region near the junction. Therefore, in the space-charge region of the unbiased sample, the only defect to be considered is the vacancy. We shall see below that the signal which we attribute to the gallium interstitial, still stable at 200 K, may interfere but its charge state underlines even further the major role of the vacancy. In this context, and at very low temperature (22 K), the charge state sequence $V^{-/0}$ must be excluded as V^0 would be favored at 22 K, keeping the capacitance rather unchanged after irradiation, which is not what we observe. Therefore, we favor the configuration $V^{=/-}$ for the vacancy, a charge state sequence which was also found theoretically by Coutinho *et al.*[27] It results, by comparison with silicon, that possible donor states, if they exist, must be buried in the valence band. A final but important point is worth mentioning here. Under equilibrium at low temperature and for our gallium doping concentration, the Fermi level does not enable the charge state $V^=$. However the counter doping in the region near the junction should be included in the neutrality equation. The Fermi level will thus be shifted upwards, enabling the double acceptor to exist under equilibrium. On the other hand, if the single acceptor exists and follows a positive-U distribution, it should be between the double acceptor and the valence band, and would thus be difficult to detect for the instability reason described above.

2. Gallium interstitial

When we proceed with the DLTS scan to temperatures above 150 K, as shown in Fig. 7, a third hole trap appears at room temperature with about the same height as the vacancy peak. However, if we apply larger pulse widths, which enable the injecting of more holes, an unexpected increase in the peak amplitude is observed. This defect, which we assign below to Ga_i, should therefore have a very low capture cross section. The Arrhenius plot of its emission rate, displayed in the inset, gives the activation energy of 0.62 eV. This value is very close to the band gap of germanium and cannot be entirely assigned to the hole binding energy, otherwise the emission process would not be possible below room temperature. Such a peculiar behavior has already been reported several times in other materials such as GaAs,[28] where large

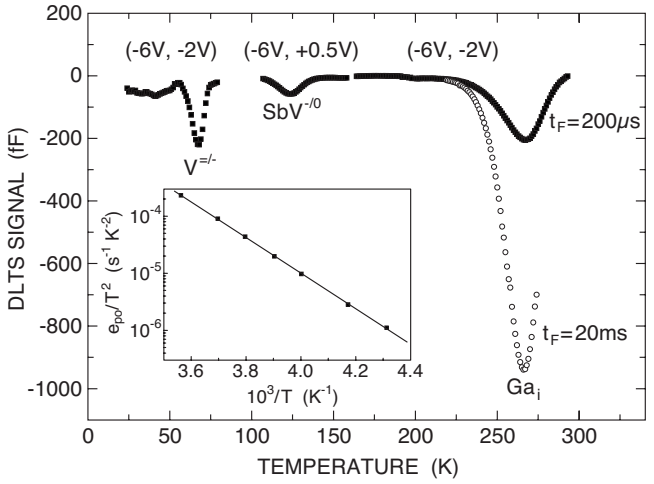

FIG. 7. Similar measurements as in Fig. 6 but extended up to the room temperature. The inset displays the Arrhenius graph extracted from the hole emission rates of the deepest level. The activation energy of 0.62 eV is very close to the band gap, indicating the presence of a strong relaxation of the defect.

activation energies were shown to be composed of at least two contributions; the activation enthalpy ΔH_p for hole emission expressing the level position in the band gap (provided the accompanying change of entropy is weak[29]) and a barrier energy for hole trapping ΔE_σ. The magnitude of the capture cross section is limited by the barrier for trapping, suggesting a multiphonon process, which may lead to a strong relaxation with severe implications as will be demonstrated below. It should be noted that unlike ionic materials,[28] defects exhibiting large lattice relaxation were not expected to occur in perfectly covalent materials until Baraff *et al.*[30] provided theoretical basis in the case of the vacancy in silicon, later on confirmed experimentally for both the vacancy and the boron interstitial by Troxell *et al.*[31,32] Figure 8 shows the capture data from which we extract indeed the large expected activation energy ΔE_σ=0.29 eV, responsible for the observed low capture cross section near room temperature. It follows from a simple calculation that the activation enthalpy for hole emission is ΔH_p=0.33 eV.

One of the main consequences of the large lattice relaxation involving several phonons is raised by the energy dissipation issue when the process of hole trapping is completed. For a moderately stable defect this mechanism may be detrimental. A large dissipation can be entirely converted into a transformation of the defect. We show in Fig. 9 that if the hole injection exceeds a few tens of seconds, a very important and irreversible decrease in the peak height is observed. A quantitative analysis is reported in the inset where we show that a first-order kinetics governs what is clearly a multiphonon annealing mechanism.[28] In the present case the energy dissipation is very likely directed toward a migration process if we assume that the defect in question is elementary instead of being complex, in which case a dissociation mechanism should be considered. The strong coupling between the local vibrational modes and the hole is taken up by anharmonic modes whose main effect is to convert the free hole energy into heat responsible for the observed instability. Figure 10 shows the annealing parameters where two points are worth emphasizing. First, the extracted activation annealing energy of 0.35 eV, which in fact represents the migration

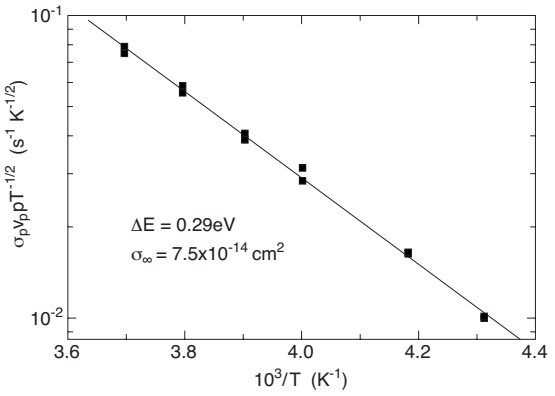

FIG. 8. The Arrhenius plot representing the thermal activation of the capture cross section of the deep level shown in Fig. 7.

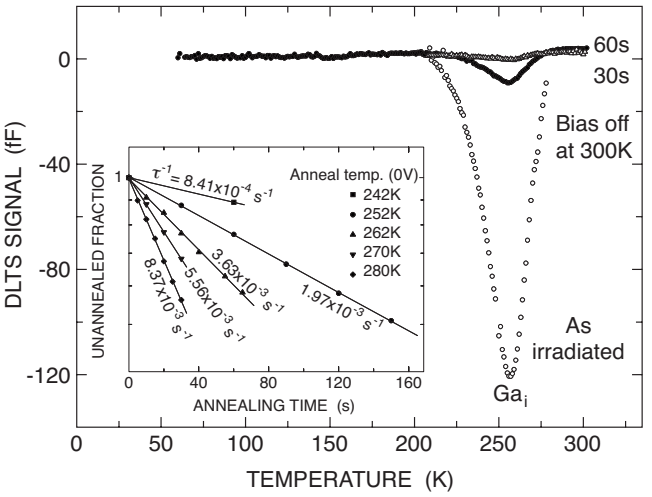

FIG. 9. DLTS spectra of the *p*-type germanium sample after electron irradiation. They show the instability of the defect under hole injection. The inset displays quantitative data related to the decay of its amplitude, which is clearly of a first-order type.

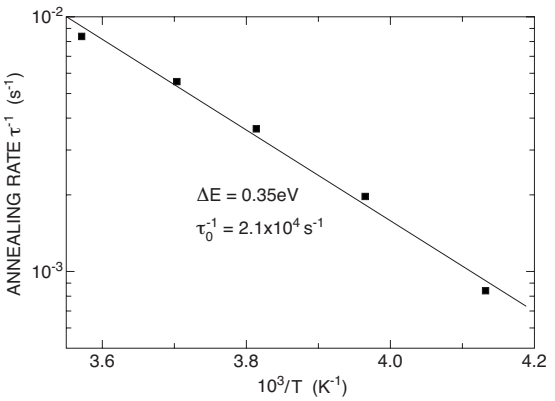

FIG. 10. The Arrhenius plot of the annealing rate of the deep hole trap. The extracted activation energy represents the migration energy of the corresponding defect, which is very likely interstitial gallium (see text).

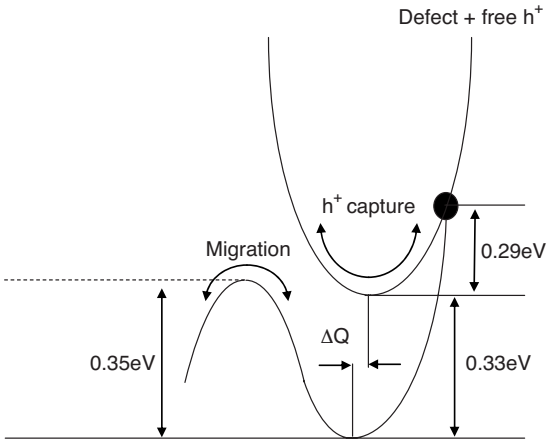

FIG. 11. A simple one-dimensional configuration coordinate diagram of trapping-induced instability. The reaction (migration) barrier is only slightly higher than the hole binding energy allowing the peak observation. However, this difference is sufficiently small to allow the observed instability. The change in the equilibrium configuration (ΔQ) stands for the relaxation.

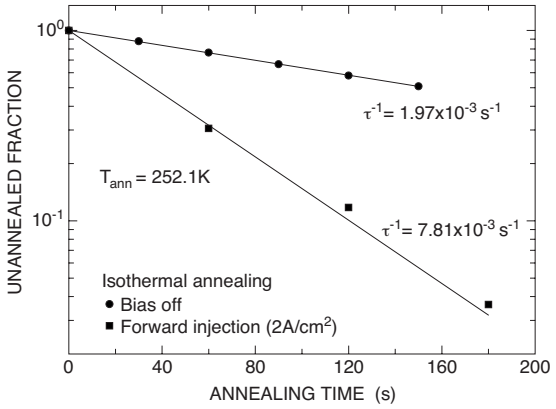

FIG. 12. Enhanced annealing rate at 252.1 K of the deep hole trap when a forward current is applied in which both types of carriers are injected. This corresponds to the so-called REDRs (Refs. 33–35). This case is compared to the annealing rate when the diode is zero biased allowing the sole injection of holes.

energy, is slightly higher than the energy position in the band gap. This slight difference explains why the level could be observed. But it is sufficiently small to make the defect unstable. Second, the frequency factor $1/\tau_0$ of about 2×10^4 s^{-1} is far below the Debye frequency.[23] Therefore, hole capture as the limiting factor in the process does not suffer any ambiguity. A comprehensive one-dimensional configurational diagram, shown in Fig. 11 and based on a single vibrational mode, represents the various numbers extracted from the present analysis.

We have seen above some marked differences between silicon and germanium. But there are also similarities and the present deep hole trap is an example. Its dynamic behavior is surprisingly similar to boron and aluminum interstitials in silicon, studied by Troxell *et al.*[31,32] As in the present case, B_i is a midgap level in silicon, unstable below room temperature and subject to hole injection enhanced annealing. The similarity between B_i in silicon and our deep level in germanium is pushed even further as both defects undergo a strong recombination enhanced defect reaction (REDR) (Refs. 33–35) as shown in Fig. 12. Under minority-carrier injection (forward bias where both electrons and holes are injected), a large enhancement in the defect annealing is indeed observed. The only test has been performed at 252.1 K, where the decay is faster than without minority injection but still thermally activated. Troxell *et al.*[31] observed that far below 150 K, the decay rate of B_i becomes relatively insensitive to temperature invoking the Bourgoin mechanism.[32,36] Although this aspect deserves further investigations, we have plenty of reasons to safely conclude that our deep level represents gallium interstitial (Ga_i). However unlike B_i in silicon, the possibility for a negative-U property is not obvious. A second coupled level seems to exist but more investigations are necessary before a final statement could be made.

V. COMPARISON WITH OTHER RESULTS IN THE LITERATURE

Our aim in this section is to clarify whenever possible some key features related to earlier results which may appear inconsistent with our findings but finally easy to reconcile in spite of the difficulties inherent to the observed instabilities. On the other hand, we will highlight the points which remain open to debate because in conflict with our inferences. Once more, we would like to point out that the assignments proposed above and stressed below cannot be considered as final because they are based on indirect evidence. But we believe that the conditions of irradiations and our knowledge of silicon offer a safe basis.

Starting with the signal displayed in Fig. 1 and 2, it is very likely that it corresponds to the Frenkel pair, assigned very early to the annealing stage that occurs at 65 K after electron irradiation of n-type Ge at liquid helium.[4] The observed peak is unstable around this temperature and its loss is irreversible, in agreement with an annihilation process. The annealing stage seems to be charge state dependent and can be made to proceed at lower temperatures by illumination (around 27 K).[20,21,37] The present study confirms qualitatively this point as a lack of encapsulation of the diode after irradiation results in a considerable reduction of the observed signal. A quantitative study would have required to access to much lower irradiation temperatures than 22 K and to use much lower emission rate windows which was not possible in the present study. But in spite of these surprising similarities, the level position in the band gap is in conflict with what has been deduced from conductivity studies.[4] We infer a position around 0.14 eV below the conduction band whereas the earlier studies converge toward a position close to 0.07 eV. Clearly, our level is deeper by a factor 2 and this is beyond the experimental uncertainty. In fact such an inconsistency can be understood if we consider the double acceptor character of the Frenkel pair ($V^{=}$-$I^{0/+}$) detailed in Emtsev's review[4] and recently predicted by Carvalho *et al.*[26] If the charge state assignment is correct our value of 0.14 eV cannot be the ionization enthalpy but must include the barrier for capture. On the other hand, the level position of 0.07 eV below the conduction band was extracted from annealing measurements carried out under thermal equilibrium, corresponding thus to the Fermi level a few kT above the level, more precisely about E_F+3kT_A, where T_A represents the an-

nealing temperature.[37] It would thus be straightforward to reconcile our findings with literature data provided the activation barrier for capture is properly determined. Unfortunately, this parameter is not easy to determine for obvious instability reasons mentioned above, among which two important features are worth recalling. First, measuring the capture cross section means using large pulse widths, especially when we suspect the defect to be a double acceptor. However, if the charge state plays an important role in the stability of the defect, the annihilation rate would become pulse width dependent, making Eq. (4) more complex and thus the fitting would no longer be straightforward. Second, the vacancies are mobile at temperatures very close to the range of investigation of the unstable "FP" signal. According to relation (6), their drift toward the outer edge of the space-charge region would cause a significant change in the capacitance and this has to be taken into account in extracting the capture cross section. The fitting would become more complex as it requires quantifying such a drift-induced capacitance change. If this could be achieved in future investigations, then our observed single peak could safely be linked to the sharp temperature-dependent transition assigned earlier to the Frenkel pair.[4] As a consequence, the presence of a single peak would indicate that the distribution of distances between the Frenkel pair counterparts is very narrow, unlike the situation encountered in compound semiconductors,[6] where several peaks have been attributed to this major defect.

As to the levels assigned to the self-interstitial, comparison with more recent perturbed angular correlation (PAC) measurements, carried out by Haesslein *et al.*,[11] is instructive. A detailed analysis brought Haesslein *et al.*[11] to suggest that one of the two observed signals corresponds to the self-interstitial trapped by the probe atom (^{111}In-Ge$_i$). Haesslein *et al.*,[11] carried out annealing measurements in a wide range of doping concentrations and with the help of the neutrality equation they could propose for the self-interstitial the configuration $I^{0/+}$ located at 0.04 ± 0.02 eV below the conduction band, a position half way to our DLTS peak A displayed in Fig. 5. The observation of two coupled levels A and B suggests that the self-interstitial introduces a second donor state $I^{+/++}$ deeper in the band gap in agreement with recent theoretical predictions.[26] However, both our work and that of Haesslein *et al.*[11] agree that this defect is stable up to about 200 K, in contradiction with earlier studies,[20,38] suggesting that similar to the silicon self-interstitial, Ge$_i$ migrates athermally according to the Bourgoin-Corbett mechanism.[36] We believe that our analysis, partially in agreement with the work of Haesslein *et al.* and recent theoretical considerations,[26] are in favor of a stabilization of Ge$_i$ into the lattice. This would be the second marked difference with silicon, the first one being the possibility to catch the Frenkel pair. It is however worth pointing out that the identification regarding germanium interstitial raises more question marks than in the case of the Frenkel pair calling for more attention in future investigations.

Following the same procedure described above, Haesslein *et al.*[11] attribute to another PAC signal the pair ^{11}In-V where the vacancy has the charge state sequence $V^{-/0}$, which they locate at 0.20 ± 0.04 eV above the valence band. Again this value matches fairly well with the position inferred in the present work, and the annealing temperature of the vacancy, also around 200 K, is probably in good trend with our finding. Unfortunately, the electric-field-induced instability did not allow us to come to a firm determination of its thermal stability. However, our conclusion that the vacancy has a double acceptor character ($V^{=/-}$) is clearly in conflict with the suggestion of Haesslein *et al.*[11] These authors came to the sequence $V^{-/0}$ on the basis of the trapping mechanism of the vacancy by the probe indium atom, which is negatively charged above liquid nitrogen. They excluded the trapping of a negatively charged vacancy by In$^-$ as the Coulombic repulsion demands. This important statement implies the existence of the neutral vacancy which then raises the question of lack of observation of the divacancy when light incident particles and moderate irradiations doses are used. This pair would have some chance to be formed if the neutral vacancy had a real existence, whereas it would not form according to our charge assignment. On the other hand, the lack of detection of the Frenkel pair in *p*-type germanium led earlier authors to suggest the double acceptor character of the vacancy in agreement with our result.[7] Therefore, as for the self-interstitial discussed above, whether the neutral state of the vacancy exists or not, crucial to establish the level distribution in the band gap, remains open. But in any case, the negative charge state inferred from drift measurements carried out in the present work does not suffer any ambiguity.

Finally the deep hole trap behaves clearly like the well-known boron interstitial in silicon and thus seems to be the finger print of the so-called Watkins replacement mechanism, which is active in germanium too. Again, this identification would be confirmed when the same study is carried out in materials doped with various gallium concentrations.

As a final support to the assignments proposed in this work we may notice the fact that, except the *E* center, no one of the peaks resulting from electron irradiation survives at room temperature, which is very much in favor of simple primary defects.

VI. SUMMARY AND CONCLUSION

In this study we have taken advantage of the possibility to prepare reproducible and reliable n^+p junctions, allowing the scan of the whole band gap. Some attempts to make Schottky contact on *p*-type germanium were so far not decisive.[39] The second advantage of the present work is the *in-situ* analysis in which the sample is irradiated at low temperature and analyzed on line, allowing to follow the kinetics of the primary defects. One of our objectives was to check a crucial point raised by Watkins[10] in the early days of defect studies. According to Watkins, we should expect that the same defects are produced whether at room-temperature irradiation or at low-temperature irradiation followed by anneal. This picture, which revealed fairly well valid in silicon, assumes implicitly that the temperature is the major parameter governing the branching ratio between various reactions. We have shown that after irradiating *p*-type germanium at low temperature and reaching room temperature, the annealing is complete and no other complex defects are left. The observed formation of the *E* center near the junction must be

excluded from this reasoning as the group-V atoms are not natural constituents of p-type germanium. Such a behavior may have misled some early authors when they claimed that p-type Ge is more resistant to irradiation than n-type Ge.[20,37,38] As to our objection to Watkins statement,[10] the major argument is the charge state distribution. We believe that the main defects observed in p-type are the single vacancy and the gallium interstitial. Both disappear after reaching room temperature without converting to any other defect such as divacancy V-V or $Ga_i - V$, and this is markedly different from silicon. The double acceptor character of the vacancy inferred in this work has the important implication of forbidding the formation of the divacancy either as a primary defect, resulting from the knock-out of two neighboring Ge atoms, or resulting from long-range migration of two uncorrelated vacancies. The main reason is the strong coulombic repulsion of two close negatively charged vacancies, at least as long as light irradiating particles and low or moderate doses are concerned. The pair $Ga_i - V$ does not seem to be thermodynamically stable either. The explanation is rather a recombination or site exchange between a gallium interstitial (Ga_i) and the vacancy (V) leading to a gallium substitutional (Ga_s). Again the double negative charge state of the vacancy and the positive charge state of the gallium interstitial (following hole capture when the electric field is removed) would enable a coulombic attraction between these species. This statement may seem inconsistent from the observation of Fig. 7 where clearly the heights of the vacancy and gallium interstitial signals are markedly different, unlike the 1:1 correspondence observed by Watkins between B_i and V in p-type silicon.[40] The main reason is that in silicon both species are stable at the temperature at which they are observed. We believe that in germanium the fact that $V^=$ drifts away during its analysis impedes us from observing a 1:1 correspondence. In brief, the only primary defects to be considered in p-type germanium are the germanium self-interstitials (Ge_i), the vacancies, and as a secondary defect, resulting from the Watkins replacement mechanism, the gallium interstitials (Ga_i). The E center is excluded as it is accidental in p-type germanium. Among these defects, only the vacancy and the gallium interstitial introduce levels in the lower half of the band gap. It seems an accepted fact that the Frenkel pair is much less stable in p-type germanium than it is in n-type, although in the latter material this defect remains very unstable as well. Finally, in p-type germanium, when approaching room temperature, the remaining uncorrelated vacancies react with both Ge_i and Ga_i clearing up the whole observation area in p-type material. The irradiation of the same material at room temperature leads clearly to a different picture,[3] contrary to the predictions made by Watkins.[10]

In n-type germanium we have argued that we observe the Frenkel pairs, two charge states of the germanium interstitial and the double acceptor state of the E centers, resulting from the association of the vacancies and the group V-dopant atoms. This last defect clearly obeys Watkins predictions such as a long-range migration of the vacancies resulting in their random trapping by antimony atoms. We have found that germanium self-interstitials and probably vacancies disappear at around 200 K.

Finally, two marked differences between silicon and germanium are worth mentioning. First, the vacancy seems to introduce only a single level in germanium whereas four charge states are clearly established in silicon. Surprisingly, almost the opposite is observed for the E center. Four charge states exist in germanium whereas only two charge states in silicon. Second, the Frenkel pair and the self-interstitial were never caught in silicon, whereas in germanium they seem to be easy to observe although their instabilities introduce some uncertainties on their electrical characteristics. An interesting point to be checked in the future would be the mobility of the germanium self-interstitial and its conversion to a gallium interstitial. This would be possible by carrying out photocapacitance measurements at a temperature below 200 K to follow the onset of the formation of Ga_i, an approach which would also enable the investigation of a possible relaxation effect by comparing the optical and thermal ionization energies.

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