Irradiation-induced defects in Ge studied by transient spectroscopies

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Irradiation-induced impurity-point defect complexes have been investigated in *n*-type germanium crystals that were doped with either antimony or oxygen. Several majority-carrier traps and one minority-carrier trap are characterized by means of deep-level transient spectroscopy and minority-carrier transient spectroscopy. The antimony-vacancy complex (*E* center) $E_{0.37}$ is found to anneal in a way that is fundamentally different from that in silicon, since it is retarded under reverse bias. Temperature-dependent carrier capture cross sections of the *E* center are an order of magnitude lower than those of the oxygen-vacancy complex (*A* center) $E_{0.27}$ ($\sigma_n \sim 1.5\times10^{-18}$ and 2×10^{-17} cm^2, respectively). A trap $E_{0.23}$ which is antimony related grows in at room temperature, seemingly by interstitial capture. A trap $E_{0.29}$ is assigned to the divacancy, since it is observed after proton irradiation but not after electron irradiation. A minority-carrier trap $H_{0.30}$, displaying a strong Poole-Frenkel effect, is Sb related and possibly related to the *E* center. In view of the experiments, we comment on a range of diverging results in the literature.

I. INTRODUCTION

For the last couple of decades the dedication to understanding point defect and impurity point defect interactions in Ge has been at a large deficit relative to that in Si. This unfortunate circumstance is naturally related to the overwhelming success of Si in applied fields; Ge has not been used extensively in devices, but primarily in high-purity form as detector material. A recent trend, however, is that of venturing from Si into $Si_{1-x}Ge_x$.[1] This trend originated in improved epitaxial growth techniques and the promise of very fast devices.[2] Needless to say, a satisfactory description of carrier, defect, and band-gap issues calls for good understanding in the full composition range $0 \leqslant x \leqslant 1$. At the same time it is a misfortune that Ge, so similar to Si, has not been used to its full potential as a test ground for a range of fundamental defect properties.

Investigations of irradiated *n*-type Ge have employed electronic techniques such as Hall measurements[3] or deep-level transient spectroscopy (DLTS).[4–8] Electron paramagnetic resonance unfortunately has only limited applicability in Ge, but infrared-absorption spectroscopy has been applied to O-doped Ge.[9,10] From DLTS investigations in the literature one sees, however, that considerable scatter exists in reported energy levels, defect annealing behavior and microscopic interpretation of those defects that dominate after sample irradiation.

In this paper we show that the reverse-bias annealing of the Sb *E* center in Ge is fundamentally different from that in Si. Different annealing mechanisms are considered, as is the likelihood of a double-negative *E* center charge state. It turns out that several defects evolve strongly at room temperature. By comparing electron with proton irradiation, we are able to manifest the level of the divacancy. We also make an attempt at clarifying and unifying, where possible, experimental results from the literature.

II. EXPERIMENTAL DETAILS

Three types of material were employed, they will be denoted *Sb*1, *Sb*2, and *Ox*. Czochralski-Ge *Sb*1 and *Sb*2 from Union Miniere, Belgium, contain respectively 3.5×10^{14} Sb and 1.4×10^{15} cm^{-3} Sb, and *Ox* contains, from growth, a concentration of interstitial O of 7×10^{16} cm^{-3} (measured with infrared absorption). O-doped Ge is known to acquire its *n*-type nature from thermal, oxygen-related donors;[11] for *Ox* we measured carrier concentrations between 4 and 8×10^{14} cm^{-3}, depending on the sample.

Schottky barriers were fabricated by electron-gun evaporation of either Au, Pd, or Pt, or by thermal evaporation of Au. Immediately before diode evaporation, crystals were dipped in HF. Some *Ox* samples had been etched with CP4 with no apparent effect on the spectra. At room temperature (RT) typical leakage currents at -10 V were ~ 4 mA/cm^2 on *Sb*2 material and a bit less on *Sb*1. *C-V* characteristics were ideal. On *Ox* Ge the diode quality was less reproducible, with RT leakage currents often a factor of 2–3 higher. A few of these diodes required slight cooling ($\sim$30–50 K) below RT to display ideal *C-V* characteristics.

Defects were introduced by irradiating the diodes at RT with either 2-MeV electrons or 2-MeV protons. Beam intensities were typically ~ 100 nA cm^{-2} for electrons and ~ 0.5 nA cm^{-2} for protons, and it was ascertained that the beam induced no sample heating.

Electron traps were characterized with DLTS in a lock-in amplifier setup. Hole traps were studied in a double-boxcar system with either injection-pulse (i.e., forward bias pulse) DLTS or minority-carrier transient spectroscopy (MCTS). MCTS enables one to probe minority-carrier traps by excitation of electron-hole pairs with the use of above-band-gap light. For this purpose a GaAs diode laser was applied to the front of semitransparent Schottky barriers (typical metal

TABLE I. Properties of all electron and hole traps presently observed.

Label	E_{na} (eV)	σ_{na} (cm^2)	Annealing (°C)[a]	Identification	Occurrence	
$H_{0.30}$	0.30[b]	1.6×10^{-13}[b]	↑150	Sb related	*Sb*1, *Sb*2	H,*e*
$E_{0.37}$	0.37	1.1×10^{-14}	↓150	*E* center	*Sb*1, *Sb*2	H,*e*
$E_{0.23}$	0.23	2.0×10^{-15}	↑ RT, ↓ 110	Sb and *I* related	*Sb*1, *Sb*2	H,*e*
$E_{0.19}$	0.19	1.5×10^{-14}	↑ RT, ↓ RT	Sb and *I* related	*Sb*1, *Sb*2	H,*e*
$E_{0.13}$	0.13	3.2×10^{-15}	↑ RT, ↓ RT	Sb and *I* related	*Sb*1, *Sb*2	H,*e*
$E_{0.21}$	0.21	7.1×10^{-14}	↑ 90, ↓ 180	Sb related?	*Sb*1, *Sb*2	H,*e*
$E_{0.29}$	0.29	2.1×10^{-15}	↓ 180	Divacancy	*Sb*1, *Sb*2 (, *Ox*?)	H
$E_{0.30}$	0.30	2.9×10^{-14}	↑ RT, ↓ 110	*I* and impurity related?	*Sb*2	H,*e*
$E_{0.28}$	0.28	6.2×10^{-15}	↑ 190, ↓ 270	*O*-impurity complex?	*Sb*1	H,*e*
$E_{0.27}$	0.27	2.6×10^{-15}	↓ 150	*A* center	*Sb*1, *Ox*	H,*e*
$E'_{0.19}$	0.19	2.2×10^{-15}	↑ 130, ↓ 190	O related	*Ox*	H,*e*
$E_{0.14}$	0.14	1.3×10^{-16}	↑ 130, ↓ 190	O related	*Ox*	H,*e*

[a]After 2-MeV proton irradiation.
[b]E_{pa} and σ_{pa} at -1 V bias.

thickness ~ 100 Å). In Ge the penetration depth $(1/e)$ at an appropriate wavelength of 870 nm is approximately 0.5 μm, which is considerably less than in, e.g., Si. Therefore one must be aware that MCTS probes a region that is very close to the interface.

Temperature scans with DLTS and injection-pulse DLTS showed that all unirradiated materials were defect free when prepared with thermally evaporated diodes. When prepared with electron-gun diodes, a hole trap ($H_{0.30}$) was detected in unirradiated *Sb*1 and *Sb*2.

III. EXPERIMENTAL RESULTS: OVERVIEW

The individual electron trap is defined by its electronic signature, i.e. $\log[e_n(T)/T^2]$ vs $1/T$, where $e_n(T)$ is the electron emission rate per trap. With the usual symbol meanings[12] the signature of an electron trap is determined by the apparent capture cross section at $T=\infty$,

$$\sigma_{na}=\sigma_\infty\frac{g_0}{g_1}e^{\Delta S/k}, \tag{1}$$

and the apparent enthalpy (according to which trap labels are chosen in this paper)

$$E_{na}=\Delta H+E_\sigma. \tag{2}$$

Here we assumed a thermally activated cross section for carrier capture,

$$\sigma_n(T)=\sigma_\infty e^{-E_\sigma/kT}, \tag{3}$$

and the trap energy level E_t is defined by

$$E_c-E_t=\Delta G=\Delta H-T\Delta S. \tag{4}$$

Similar expressions apply for hole traps.

Before discussing the individual traps, an overview is presented of the occurrences of traps and their annealing behavior. Of main concern will be the *E* center $E_{0.37}$, and the *A* center $E_{0.27}$, as well as the level $E_{0.29}$ that we propose to be related to the divacancy, and $H_{0.30}$ and $E_{0.23}$ that we propose to both be Sb related, the latter in connection with an interstitial Ge atom *I*. Properties of the observed traps are summarized in Table I.

Figure 1 shows DLTS temperature scans from materials *Sb*1 and *Sb*2, recorded three days after 2-MeV electron irradiations. The following traps were present in both materials: $E_{0.37}$, $E_{0.23}$, $E_{0.19}$, $E_{0.13}$, and, after a ~ 100 °C anneal, $E_{0.21}$. $E_{0.27}$ occurred only in *Sb*1, as did a trap $E_{0.28}$ which grew up after a 190 °C anneal. A trap $E_{0.30}$ occurred only in *Sb*2. Irradiating *Sb*1 and *Sb*2 materials with 2-MeV protons resulted in almost identical spectra, except for the pronounced occurrence of $E_{0.29}$, of which merely a hint was seen upon electron irradiation. This trap, partly hidden beneath others, becomes particularly visible upon annealing, as seen in Fig. 2, where spectra are shown of 110 °C annealed *Sb*2 samples that had been either electron or proton irradiated.

When applying MCTS or injection-pulse DLTS to *Sb*1 or *Sb*2, the hole trap $H_{0.30}$ is predominant after both electron and proton irradiation. This is shown in Fig. 3 for *Sb*2 material.

A DLTS scan from a proton-irradiated *Ox* sample is presented in Fig. 4. $E_{0.27}$ strongly dominates the spectrum, and two traps $E_{0.14}$ and $E'_{0.19}$ are found.

The inset of Fig. 4 shows a DLTS scan from the *Ox* material recorded with injection pulse. Three hole traps are present, and none of them is $H_{0.30}$. Presumably, reports of the *Ox* hole traps have not been made in the literature, but in this study focus will be solely on $H_{0.30}$.

Electronic signatures of electron traps are displayed in Fig. 5. Electric-field (Poole-Frenkel) effects were not exhibited by any of the electron traps that occurred at room temperature in Sb-doped Ge, and we infer that the electron traps probably have an acceptor character.

The hole trap $H_{0.30}$, on the other hand, exhibits a clear Poole-Frenkel effect: The $H_{0.30}$ signatures in Fig. 6 were obtained under reverse biases of 1, 8, and 20 V, respectively, and they demonstrate that for $H_{0.30}$ hole emission is stronglyenhanced with increased electric field. Thus $H_{0.30}$ is believed to create an acceptor level.

We find that dramatic evolution of defect concentrations takes place at RT in Sb-doped Ge. As a consequence, details of the defect dynamics that would normally be lost if proceeding upon irradiation with a standard annealing series

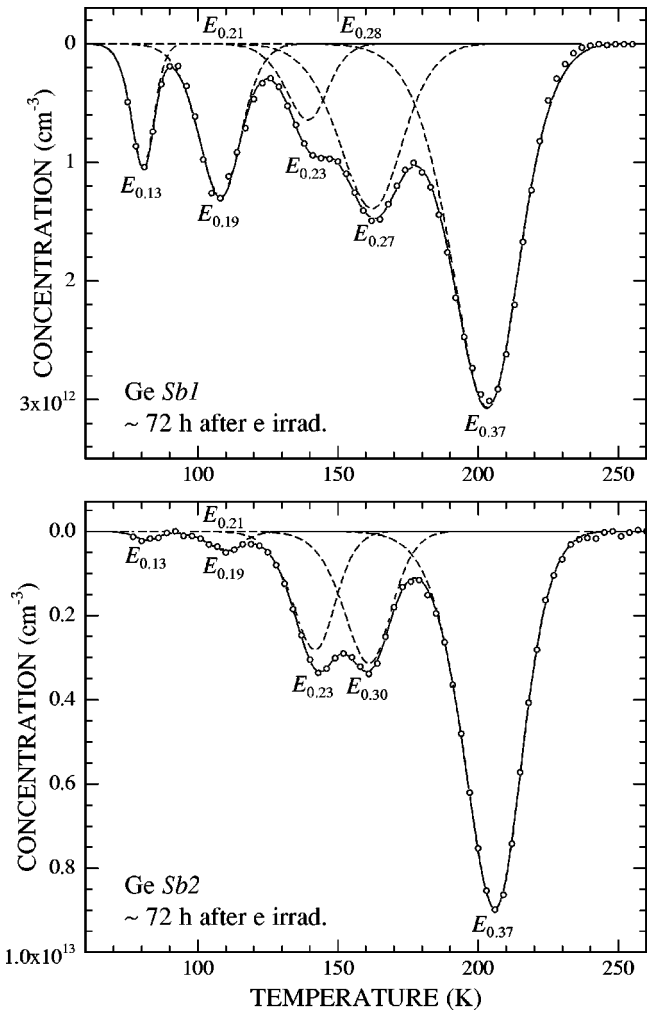

FIG. 1. DLTS spectra from $Sb1$ and $Sb2$, recorded three days after $4\times10^{13}\,\mathrm{cm}^{-2}$ electron irradiations (we have also indicated where $E_{0.21}$ and $E_{0.28}$ grow in *after* annealing). For clarity only every third data point has been drawn here and in all other plots. The solid-curve fit is a sum of the dashed curves. Settings were $e_n=542\ \mathrm{s}^{-1}$, bias $-10\rightarrow-5$ V, and pulse duration 100 μs.

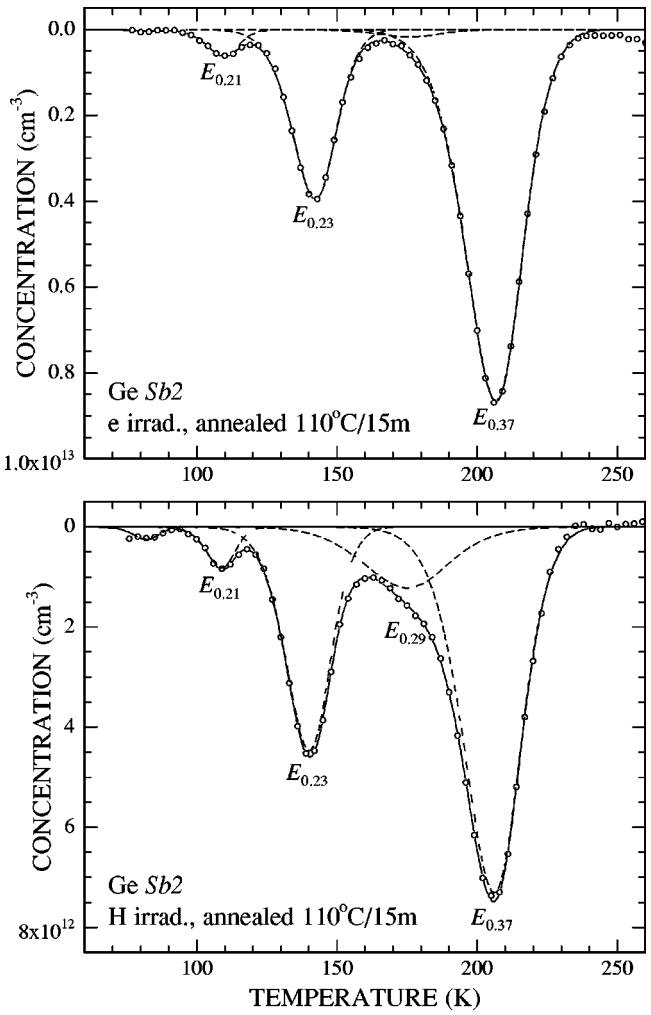

FIG. 2. DLTS spectra from $Sb2$, irradiated with $2\times10^{13}\mathrm{cm}^{-2}$ electrons (upper panel) or $1.7\times10^{11}\,\mathrm{cm}^{-2}$ protons (lower panel) and annealed at 110 °C for 15 min. The $E_{0.29}$ defect is seen clearly only after proton irradiation. Settings as in Fig. l1.

may be revealed by monitoring defect concentrations first as a function of storage time at RT, and subsequently as a function of annealing temperature. Results of such a study, on proton-irradiated $Sb1$ and $Sb2$, are plotted in Fig. 7. Apart from slight quantitative differences, the defects that occur in both materials, viz. $E_{0.37}$, $E_{0.29}$, $E_{0.23}$, $E_{0.21}$ $E_{0.19}$, and $E_{0.13}$, indeed have the same annealing behavior in both materials.

The annealing series for proton-irradiated, O-doped Ge is plotted in Fig. 8, and the observed annealing behavior of $H_{0.30}$ in $Sb2$ is reported in Fig. 9. It turns out that this is not independent of the method of observation (injection-pulse DLTS or MCTS). The annealing behavior of the individual defects shall be discussed in Sec. IV below.

IV. EXPERIMENTAL RESULTS: ANALYSIS AND DISCUSSION

In the following, for the sake of clarity, designated names of defects that are reported in the literature will be additionally indexed with author name. In accordance with the discussion below, an overview is given in Table II of some of these defects. Unless otherwise stated, defect energy levels are referred to in terms of the apparent ionization enthalpies [Eq. (2)].

A. Level $E_{0.27}$

$E_{0.27}$ strongly dominates after irradiation of O-doped Ge (Ox), and it is also present in $Sb1$. $E_{0.27}$ anneals abruptly at 150 °C in the Ox material, but the annealing starts at a lower temperature in $Sb1$. $E_{0.27}$ is identical to $E(0.25)_{Fuk}$ (at $E_c-0.25$ eV, anneals at $T_{ann}\sim150\,^{\circ}\mathrm{C}$) reported by Fukuoka and Saito,[6] and to $E_{3,Nag}(0.27\ \mathrm{eV}, T_{ann}\sim90\,^{\circ}\mathrm{C})$ reported by Nagesh and Farmer.[7] These levels were found to dominate in irradiated O-doped Ge and they were indeed assigned to the *A center*.

The electron-capture cross section was measured by varying the filling pulse duration at different, fixed temperatures. This is demonstrated in Fig. 10. We obtain

$$\sigma_n^{E_{0.27}}(T)=1.37\times10^{-16}\exp\left(-\frac{0.023\ \mathrm{eV}}{kT}\right)\ \mathrm{cm}^2$$
$$\approx(1.8-2.9)\times10^{-17}\ \mathrm{cm}^2 \qquad (5)$$

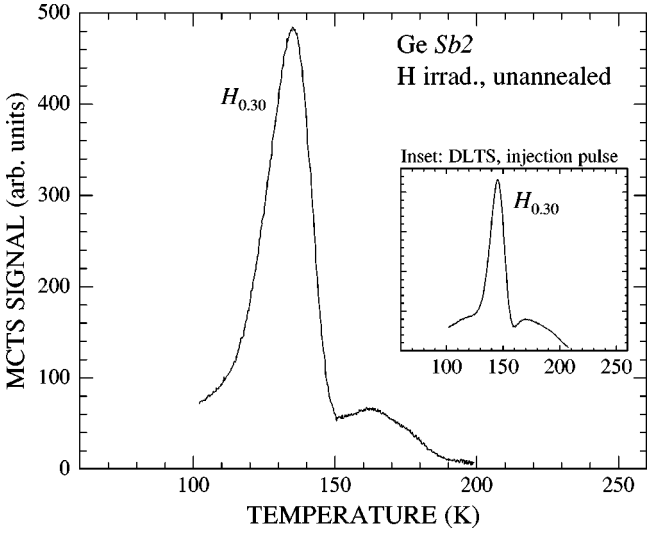

FIG. 3. Double-boxcar MCTS spectrum from a thermal Au diode on $Sb2$ material, irradiated with $5\times10^{11}\,\mathrm{cm}^{-2}$ protons. Settings were $e_n=50\ \mathrm{s}^{-1}$ and bias -2 V. Inset: double-boxcar DLTS spectrum with the use of an injection pulse. Settings were $e_n=80\ \mathrm{s}^{-1}$, and bias $-2\rightarrow+2$ V.

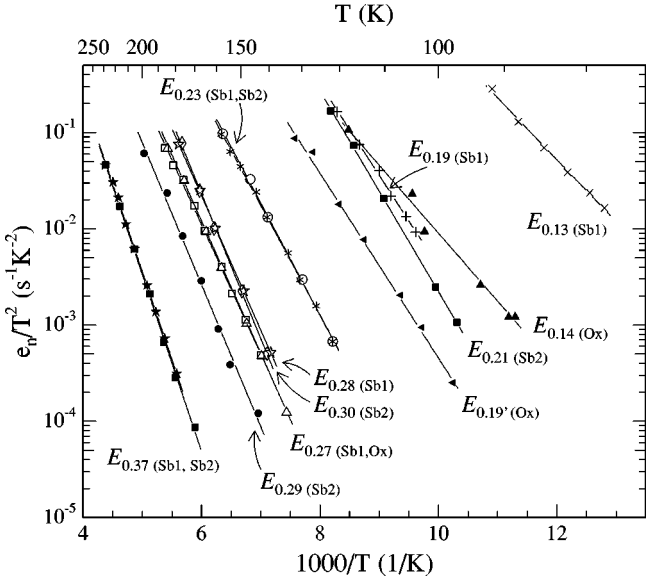

FIG. 5. Electronic signatures of all observed electron traps. For some of those traps that are present in more than one material, the signatures from both materials are presented; this is indicated in parentheses.

in the 130–170-K range. The value of the capture cross section is discussed below in connection with that of $E_{0.37}$.

B. Level $E_{0.37}$

$E_{0.37}$ is present in both kinds of Sb-doped Ge. The introduction rate increases with Sb concentration, but the level is absent in oxygen-doped Ge. In highly Sb-doped Ge ($Sb2$) $E_{0.37}$ is in fact the sole observed defect very shortly after electron irradiation; all other defects in $Sb2$ are secondary defects that grow in with time.

Sb is expected to bind vacancies in Ge, and our data confirm the conclusion by Nagesh and Farmer[7] that the corresponding level $E_{4,Nag}$ (at $E_c-0.35$ eV, seen in both P- and Sb-doped Ge after neutron and after γ irradiation, T_{ann} $\sim$125 °C) is the E center. Moreover, $E_{0.37}$ is identical to the level $E(0.40)_{Fuk}$ observed by Fukuoka and Saito.[13,5] Fukuoka and Saito did not conclude that $E(0.40)_{Fuk}$ was the E center, but $E(0.40)_{Fuk}$ dominated the spectra in two kinds of 1.5 MeV e irradiated, Sb-doped Ge, and it annealed over several hours at 97 °C.

Let us briefly point out that in two kinds of As-doped material the level $E(0.40)_{Fuk}$ was replaced by $E(0.27)_{Fuk}$.[5] Thus it is evident that $E(0.27)_{Fuk}$ is the As E center, but it is interesting that the enthalpy differs markedly from those of the Sb and P E centers.

A fraction of $E_{0.37}$ disappears already at RT, but the major fraction anneals at $\sim$150 °C. Thermally activated dissocia-

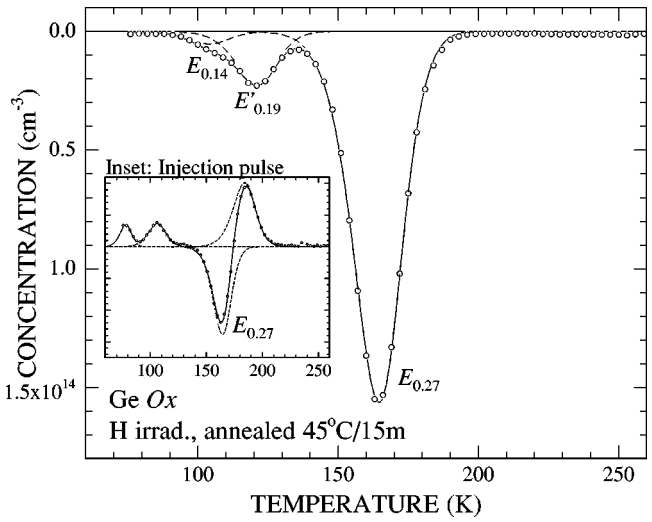

FIG. 4. DLTS spectrum from an Ox sample, irradiated with $6\times10^{10}\,\mathrm{cm}^{-2}$ protons and annealed at 45 °C for 15 min. Settings as in Fig. 1. Inset: DLTS spectrum from an Ox sample under injection pulse. $H_{0.30}$ is not present in the O-doped material.

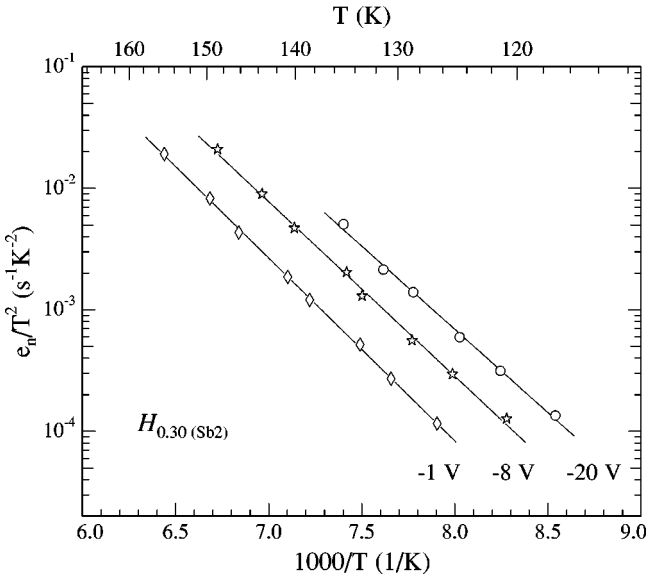

FIG. 6. Electronic signature of the $H_{0.30}$ hole trap in $Sb2$ material, extracted from MCTS spectra at reverse biases of 1, 8, and 20 V, respectively.

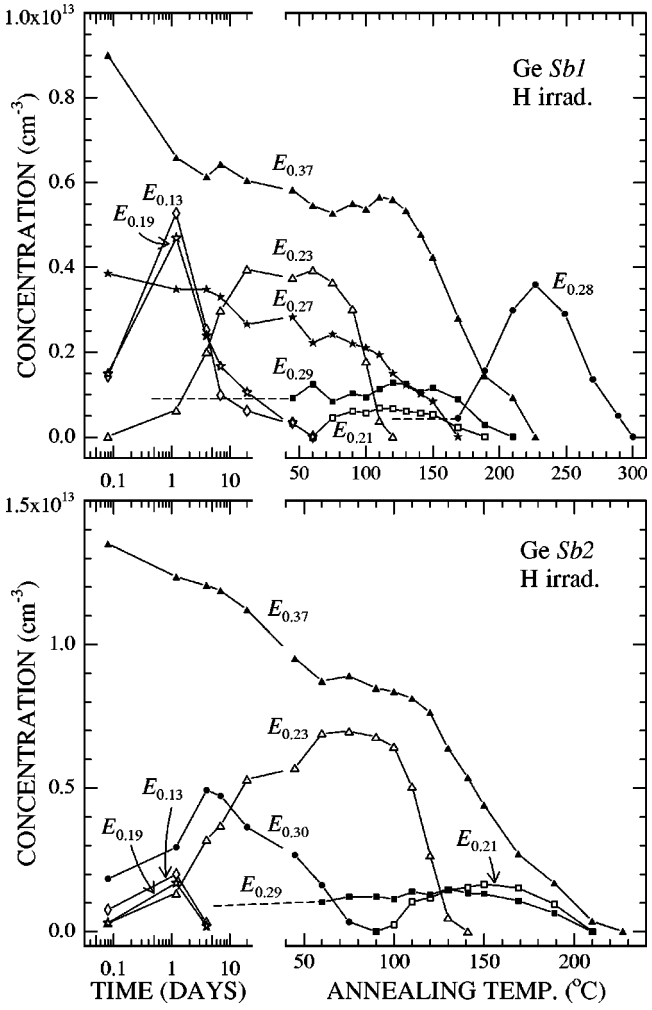

FIG. 7. Annealing series of proton-irradiated materials $Sb1$ and $Sb2$. After irradiation the defect concentrations were followed first as a function of time at RT, and subsequently as a function of 15-min isochronal anneals. The initial concentrations of $E_{0.29}$ and $E_{0.28}$ are somewhat uncertain, since the peaks are overlapped with those of $E_{0.30}$ or $E_{0.27}$.

tion or diffusion would not proceed over such a wide temperature span. Hence if we trust that the $E_{0.37}$ peak did not contain a very large contribution from other defects, some mobile species that consumes E centers must be released at RT from an unstable source that was created during irradiation. Judging from the annealing curves, this source simultaneously causes the growth of new defects. Note that the Ge self-interstitial itself has become mobile at a much lower temperature, probably around 200 K.[14] In Si a common contamination species, carbon, can indeed open up a manifold of electrically active defects[15] when interstitial carbon C_i becomes mobile at $\sim 50\,^{\circ}\mathrm{C}$ (C_i is formed when irradiation-induced self-interstitials kick out substitutional C_s). It would not be unreasonable that C could pair with E centers. However, the picture is not transferable to Ge, in which the C_s solubility is merely 10^8–$10^{10}\,\mathrm{cm}^{-3}$.[16] Most likely, interstitial agglomerates have been created during irradiation, and a transient release of Ge self-interstitials I takes place at RT.

The levels of the A center and E center seem to roughly resemble those in Si. But in recent DLTS experiments[17] on 2-MeV α-irradiated n-type $Si_{1-x}Ge_x$, the E center stands

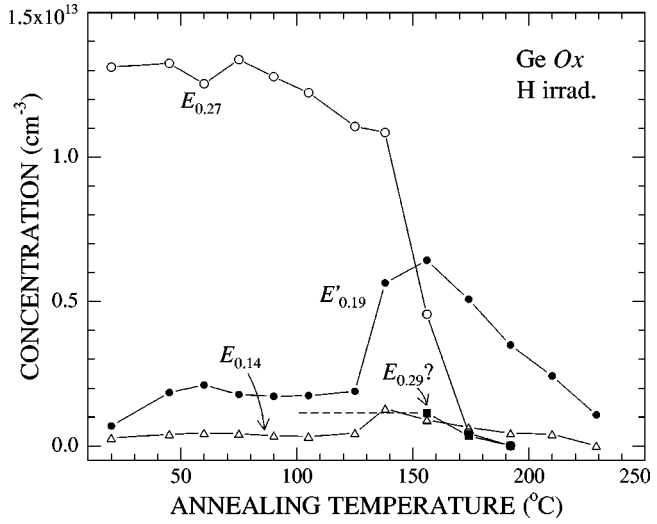

FIG. 8. 15-min isochronal annealing series of proton-irradiated material Ox. Due to the overlap with $E_{0.27}$ it cannot be decided after anneals below 156 °C whether $E_{0.29}$ exists.

out clearly for $x=0$, 0.05, and 0.15, but it has a very small amplitude for $x=0.25$ and is not detected for $x=0.35$ or 0.50.[18] Tentatively, it is deduced that the E center level moves down in the band gap with x so that for $x \gtrsim 0.25$ communication with the valence band takes over.[17] In this light it is somewhat surprising to rediscover the E center level in Ge in the upper half of the band gap. (Going from $x=0$ to 1, the conduction-band minimum is essentially fixed and identical to the Si X minimum until $x \approx 0.85$. Above this composition the Ge L conduction-band minimum moves down below X.[19] The valence-band maximum steadily rises with x, and the band gap decreases from $E_g^{Si}=1.12$ eV to $E_g^{Ge}=0.66$ eV at RT.)

Emphasizing the difference from the Si case, the E center capture cross section turns out to be lower than that of the

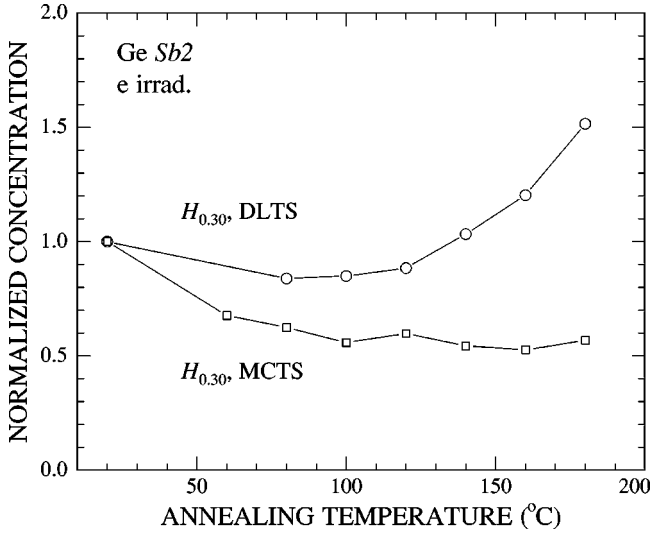

FIG. 9. 10-min isochronal annealing series of $H_{0.30}$ in material $Sb2$. The DLTS measurements were performed with an injection bias (-4 V$\rightarrow+2$ V), and the MCTS measurements were performed at a reverse bias of 2 V. It was ascertained in all MCTS measurements that the same photocurrent was generated in the diode.

TABLE II. Connection between selected deep traps from the literature. Ge was doped with either of the indicated elements and irradiated with either of the indicated species. Each entry contains designated name, apparent enthalpy (eV), apparent cross section (cm^2) at $T=\infty$, and annealing behavior (°C).

	This study Sb, O H,*e*	Bourgoin and co-workers (Refs. 4, 29, and 24) Sb, ''group V'' *e*	Fukuoka and co-workers (Refs. 13, 5, and 6) Sb, O *e*	Marie *et al.* (Ref. 8) Sb Pb, Ne	Nagesh and Farmer (Ref. 7) Sb, O, P n,γ	Zistl (Ref. 26) Sb *e*
Sb related	$H_{0.30}$ 0.30 1.6×10^{-13} ↑150	H_2 0.30 - ↑150, ↓250	$H(0.24)$ 0.24 - ↑110 (hs)			
E center	$E_{0.37}$ 0.37 1.1×10^{-14} ↓150	E_2 0.53 4×10^{-11} ↓150	$E(0.40)$ 0.40 - ↓97 (hs)	$ET5$ 0.46-0.47 $0.4–1.1\times10^{-12}$ ↓150	E_4 0.35 - ↓125	$ET5$ 0.34–0.39 - ↓150
Divacancy	$E_{0.29}$ 0.29 2.1×10^{-15} ↓180	E_4, E_5 0.46, 0.42 3×10^{-12}, 2×10^{-12} ↑90[a], ↓150		$ET4$ 0.32 1.3×10^{-14} ↓140		
A center	$E_{0.27}$ 0.27 2.6×10^{-15} ↓150		$E(0.25)$ 0.25 - ↓140		E_3 0.27 - ↓90	
Sb and *I* related	$E_{0.23}$ 0.23 2.0×10^{-15} ↑ RT, ↓110	E_1 0.32 1×10^{-13} ↓110	$E(0.23)$ 0.23 - ↑70,↓110	$ET3$ 0.29 2.2×10^{-14} ↓90	E_2[b] 0.17 - ↑ RT, ↓100	ET3 0.22-0.23 - ↑ RT, ↓110
Sb related?	$E_{0.21}$ 0.21 7.1×10^{-14} ↑90, ↓180			$ET2$ 0.27-0.28 $2.0–8.2\times10^{-12}$ ↑80, ↓160	E_6 (?) 0.15 - ↑80, ↓170	
O related	$E'_{0.19}$ 0.19 2.2×10^{-15} ↑130, ↓190		$E(0.13)$ 0.13 - ↑120, ↓200		E_5 0.17 - ↓225	

[a]Increased by 70% after 2-MeV *e* irradiation, not after 1 MeV *e* irradiation.
[b]Observed after *n* irradiation, not after γ irradiation.

A center by more than an order of magnitude. The relevant measurements are reported in Fig. 10; the result is

$$\sigma_n^{E_{0.37}}(T)=2.55\times10^{-17}\exp\left(-\frac{0.041\ \text{eV}}{kT}\right)\ \text{cm}^2$$
$$\approx(1.1–2.4)\times10^{-18}\ \text{cm}^2 \qquad (6)$$

at 150–200 K. The very small cross section of $E_{0.37}$ hints that $E_{0.37}$ is in fact a repulsive center. That is, $E_{0.37}$ could be the double acceptor level $(-/=)$ of the Sb *E* center that has moved down from the conduction band in Si, into the gap in Ge. Indeed, that would be consistent with the above-mentioned lowering of the ''silicon'' $(0/-)$ level for $x\gtrsim0.25$.

A possible corroboration of this idea is found in annealing experiments: We demonstrate from the *E* center profiles in Fig. 11 that the application of a reverse bias (4 V) will *impede* annealing of the *E* center in Ge. This contrasts the bias enhancement of *E* center annealing in Si.[20]

The slope of the as-irradiated (+15 days) profile in Fig. 11 shows that a number of vacancies from the irradiation-generated Frenkel pairs had diffused to the surface before they could be trapped by Sb atoms. Comparing the upper and lower panels of Fig. 11, we see that the application of a -4-V bias greatly reduces the role of the surface as a sink for *E* center annealing. At an annealing temperature of 120 °C the Fermi level[21] is approximately 0.08 eV below $E_{0.37}$ [since $\Delta G(E_{0.37})=0.23$ eV if we assume $g_0/g_1=1$]. For the sake of discussion, let us assume that $E_{0.37}$ is a double acceptor $(-/=)$. In the bulk, due to the width of the Fermi level, each trap then has approximately a 9% chance of being $(=)$, but in the depleted region a trap will always be

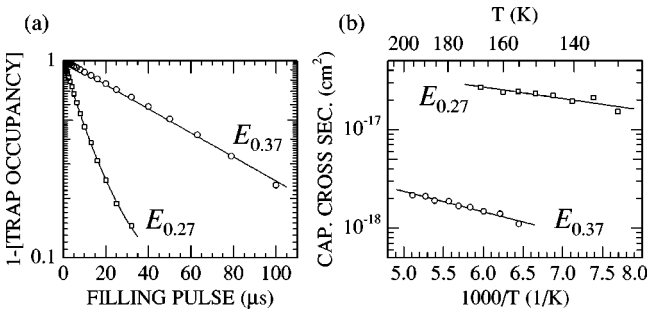

FIG. 10. (a) Fraction of the empty trap vs the filling time for the *A* center $E_{0.27}$ at $T=141$ K and $e_n=10\ s^{-1}$, and the *E* center $E_{0.37}$ at $T=186$ K and $e_n=50\ s^{-1}$. For the *A* center the filling has a slight Debye free-carrier incursion effect, and the fit has been done with the Simplex method using the complete DLTS signal: formula (8) in Ref. 32. (b) The thermal activation of the extracted electron-capture cross sections.

$(-)$. The following scenarios are then compatible with the observed depth profiles:

(i) Suppose that the *E* center anneals by *diffusion*. When migrating *E* centers approach the surface, they will be driven back at some point where the electric field is strong enough. The field acts as a barrier for outdiffusion and as a driving force toward the bulk, and only very close to the surface (in the region not probed) is the *E* center concentration expected to decrease. Note that this scenario is compatible with $(-/=)$ charge states, but not with $(0/-)$. Alternatively, migration may simply be much smaller for the *E* centers within the depletion layer (e.g., Sb$V^{=}$) than for those *E* centers in the bulk that are in a different charge state (e.g., SbV^{-}).

(ii) Suppose that the *E* center anneals by *dissociation* and vacancy loss to the surface. Dissociation should then be suppressed under reverse bias, meaning, e.g., that the $(-)$ charge state should be more stable than $(=)$. This stabilization should be stronger than the opposite tendency that the electric field will have to separate the positive Sb^{+} from the negative vacancy. Or, alternatively, the mobility of the vacancy could be reduced in the depletion region (although this opposes the Si situation where, e.g., V^{-} is more mobile than $V^{=}$).[22]

In the silicon picture[20] the annealing without bias should be slower due to the energy cost (0.23 eV) of first converting Sb$V^{=}$ into less stable SbV^{-}. From the above discussion it is clear that this picture does not hold for Sb*V* annealing in Ge—except possibly in the diffusion scenario: Even if SbV^{-} *were* more mobile than Sb$V^{=}$, the electric field could in fact retard the annealing by restraining SbV^{-} from outdiffusion.

C. Level $H_{0.30}$

This hole trap strongly dominates the minority spectra in both of the Sb-doped samples (Fig. 3), but neither before nor after anneal does it appear in the oxygen-doped Ge (Fig. 4).[23] When detected with injection-pulse DLTS the $H_{0.30}$ amplitude increases steadily for anneals above $\sim 120\,^{\circ}$C, but when applying MCTS with front-side illumination a moderate decrease is observed; see Fig. 9. To our knowledge, all studies of minority traps in irradiated Ge have hitherto been performed with injection-pulse DLTS.

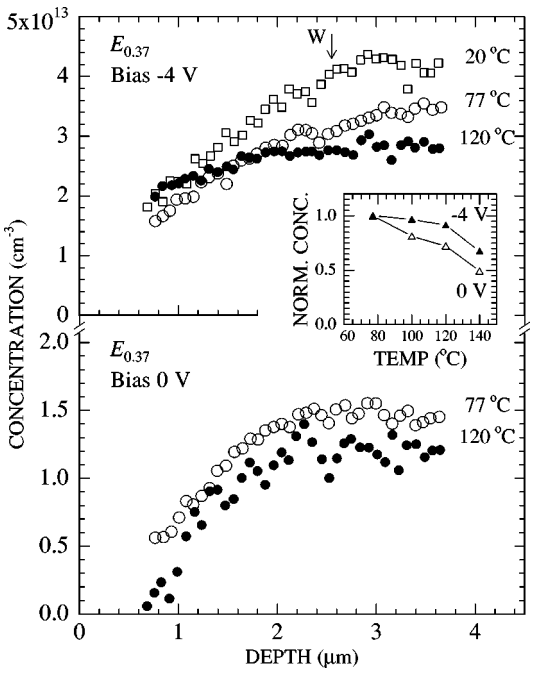

FIG. 11. *E* center depth profiles in two diodes on the same *Sb*2 sample, that were annealed either with a 4-V reverse bias or with no bias. The depletion layer width *W* at 4 V is indicated. Diodes were electron irradiated with somewhat different doses. Profiles were measured 15 days after irradiation (□), three months later after a 77 °C/5-min anneal (○), and after a 120 °C/10-min anneal (●). They were obtained at 205 K with a DLTS double-pulse technique, with a constant reverse bias of 20 V and a pulse difference $\Delta V=1.00$ V. Inserted are annealing curves with (▲) and without (△) bias, as observed by DLTS using -4 V$\rightarrow$0 V.

$H_{0.30}$ resembles $H(0.24)_{Fuk}$ ($E_v+0.24$ eV). This level, present as the only minority trap after 1.5-MeV electron irradiations of 1.5×10^{14} and 2.5×10^{15}cm^{-3} Sb-doped Ge,[5] had a small decrease upon 70 °C annealing but increased in amplitude during several hours at 107 °C. $H(0.24)_{Fuk}$ was found in neither of two As-doped samples; instead what was prominent was $H(0.29)_{Fuk}$, which we propose to be the As analog. The annealing behavior of $H(0.29)_{Fuk}$ was not reported. Also similarly, the level $H_{2,Bou}$ at $E_v+0.30$ eV in 2-MeV *e*-irradiated, $10^{13}-$cm^{-3} *n*-type Ge increased above $\sim 120\,^{\circ}$C, and finally annealed at $\sim 250\,^{\circ}$C.[24] From irradiation-energy threshold experiments it was excluded that $H_{2,Bou}$ originated from two-atom displacements.[25] Hence, by combining our observations with those from the literature, strong indications arise that $H_{0.30}$ is formed when one or more simple defects, i.e., vacancies or interstitials, meets with an Sb atom.

We demonstrate in Fig. 6 that $H_{0.30}$ is strongly attractive to holes, i.e., it is an acceptor level. Bearing in mind the analysis of Sec. IV B, it is tempting to propose that $H_{0.30}$ is the $(0/-)$ transition of the *E* center: If the *E* center level $E_{0.37}$ were indeed $(-/=)$, of which we pointed out indications, then $(0/-)$, with a stronger Coulomb binding of the electron, is expected to be present below $E_{0.37}$, very likely within the band gap.

Against this picture apparently speaks the different annealing behaviors of $E_{0.37}$ and $H_{0.30}$ (Figs. 7 and 9). But one must be cautious here, since $H_{0.30}$, probed with a hole con-

centration that decays exponentially from the interface, is detected with particularly high sensitivity very near the interface.[23] When observed with injection-pulse DLTS, the $H_{0.30}$ amplitude increases above $\sim 120\,^{\circ}$C which is the temperature at which $E_{0.37}$ starts to anneal. The possibility must therefore be considered that $H_{0.30}$ and $E_{0.37}$ are related, and that the $H_{0.30}$ increase is a consequence of the abnormal E center redistribution, combined with a different annealing characteristics of the particular E center charge state that prevails very near the interface. Certainly, different annealing behaviors are exposed with MCTS and with injection DLTS.

If it is not a coincidence that $H_{0.30}$ increases when $E_{0.37}$ starts to anneal, other candidates for $H_{0.30}$ are defects that are formed from SbV migration. An example could be Sb_2V, which would have a relatively low abundance directly after irradiation. As detailed earlier, an interstitial flux seemed to appear at low temperature, and this did not cause a $H_{0.30}$ increase.

D. Level $E_{0.29}$

In $Sb2$ Ge, $E_{0.29}$ cannot be positively detected at any time after electron irradiation. But following proton irradiation, $E_{0.29}$ stands out after a 110 °C anneal when $E_{0.30}$ has disappeared. This was demonstrated in Fig. 2. The linewidth is $\sim 65\%$ larger than expected for a 0.29-eV line, so $E_{0.29}$ is in fact a sum of two close-lying levels. The concentration of $E_{0.29}$ prior to heating of the sample is somewhat uncertain; we can only estimate that the amplitude must have been $\lesssim 75\%$ of the amplitude after 110 °C.

In $Sb1$ Ge, $E_{0.29}$ is almost hidden under the A center $E_{0.27}$ or under $E_{0.28}$. Upon proton irradiation and a 110 °C anneal (giving a slight A center decrease), the existence of $E_{0.27}$ is clear, but before sample heating we can only say that the amplitude must have been $\lesssim 120\%$ of the amplitude after 110 °C. In electron-irradiated $Sb1$ a systematic annealing series was not performed.

In proton-irradiated, O-doped Ge a small shoulder to the A center can be seen when the A center has strongly decreased after a 156 °C anneal. The shoulder is possibly, though not certainly, $E_{0.29}$.

Thus the introduction rate of $E_{0.29}$ relative to other defects in $Sb2$ Ge is multiply enhanced with proton relative to electron irradiation. $E_{0.29}$ is most likely present immediately after proton irradiation (but hidden beneath other peaks). It is also introduced in $Sb1$, and possibly in Ox. Hence $E_{0.29}$ meets the requirements, as the only level, of a defect that is related to a displacement of more than one host atom and probably does not involve a dopant atom. We propose that $E_{0.29}$ belongs to a divacancy or a di-interstitial.

E. Levels $E_{0.13}$, $E_{0.19}$, and $E_{0.23}$

These defects appear in $Sb1$ and $Sb2$ after both electron and proton irradiation, but not in Ox. At RT, $E_{0.13}$ and $E_{0.19}$ transiently grow in with almost identical concentrations, and anneal again over a few days. Most likely, $E_{0.13}$ and $E_{0.19}$ are therefore different (close-lying) charge states of the same defect. $E_{0.23}$ grows in after longer time at RT, and anneals at $\sim 110\,^{\circ}$C.

$E_{0.13}$ and $E_{0.19}$ were also observed by Zistl[26] in 1.2-MeV e-irradiated, 2×10^{15}-cm^{-3} Sb-doped Ge: The levels $ET1_{Zis}$ and $ET2_{Zis}$ are at 0.14 and 0.19 eV, and both anneal at RT. Moreover, in a temperature scan down to 100 °C a defect $E_{3,Bou}$ (Ref. 27) that was unstable at RT appeared close to the position of $E_{0.19}$.

$E_{0.23}$ matches $E(0.23)_{Fuk}$ (Ref. 5) which grows in during a couple of hours at $\sim 70\,^{\circ}$C and anneals at $\sim 110\,^{\circ}$C. This level was seen in 1.5×10^{14} and 2.5×10^{15}cm^{-3} Sb-doped Ge after 1.5-MeV electron irradiations. It also matches $ET3_{Zis}$ at 0.22–0.23 eV.[26] $ET3_{Zis}$ grows in at RT, anneals at $\sim 110\,^{\circ}$C and is seen in 2×10^{15} and 1×10^{16}cm^{-3} Sb-doped material.

These observations very strongly suggest that $E_{0.23}$ is Sb related. In As-doped Ge, Fukuoka and Saito[5] did not detect a level that resembled $E(0.23)_{Fuk}$, but annealing experiments were not reported.

Since $E_{0.13}$, $E_{0.19}$, and $E_{0.23}$ are not produced in the collision cascade, they must be formed from thermal transformation of one defect species and/or from capture of defects that are released from another. From the time and temperature evolutions in both $Sb1$ and $Sb2$, it appears that the same defect source (presumably interstitials) as that which reduces $E_{0.37}$ at RT is responsible for the growth of $E_{0.13}$, $E_{0.19}$, and $E_{0.23}$. Hence we arrive at the conclusion that $E_{0.23}$ contains a Sb atom, very likely in relation with an interstitial-related defect.

Formation of $E_{0.13}$ and $E_{0.19}$ *precedes* the formation of $E_{0.23}$. It is possible that a small energy barrier exists to the formation of $E_{0.23}$, and $E_{0.13}$ and $E_{0.19}$ may even be two levels of a metastable ''precursor'' configuration to the former.

$E(0.23)_{Fuk}$ was speculated to be created from a vacancy flux at $\sim 70\,^{\circ}$C and to be Sb_iV.[5] However, that does not fit with the foregoing discussion. In particular, it can be seen that a vacancy injection which would have increased the E center concentration is not supported by our annealing curves (Fig. 7).

F. Levels $E'_{0.19}$ and $E_{0.14}$

These levels are detected only in the Ox material. $E'_{0.19}$ increases after 138 °C anneal, shortly before the A center anneals. $E_{0.14}$, as a small shoulder, closely follows the growth and decrease of $E'_{0.19}$. The annealing characteristics of $E'_{0.19}$ is very close to those of $E(0.13)_{Fuk}$ (Ref. 6) (created after a 120 °C anneal, and slow disappearance between 160 and 300 °C) and $E_{5,Nag}$ (Ref. 7) ($E_c-0.17$ eV, $T_{ann}\sim 225\,^{\circ}$C), that both occurred next to the A center in heavily O-doped Ge. It is unclear why there is an energy discrepancy with $E(0.13)_{Fuk}$.

G. Levels $E_{0.30}$, $E_{0.28}$, and $E_{0.21}$

$E_{0.21}$ is observed in $Sb2$ and, with a smaller amplitude, also in $Sb1$. It grows in above $\sim 90\,^{\circ}$C and anneals at $\sim 180\,^{\circ}$C. The maximum amplitude (relative to the E center) is enhanced only slightly by proton vs electron irradiation. The level may be Sb related, but other than $ET2_{Mar}$ (Ref. 8) and $E_{1,Nag}$,[7] literature reports of this defect are elusive (see Table II and Sec. IV H below).

$E_{0.30}$ is observed only in $Sb2$; it is found after both electron and proton irradiation. $E_{0.30}$ grows in and anneals again during several days at RT. Referring to Sec. IV E, this behavior may be indicative of an interstitial-related defect.

$E_{0.28}$, seen after irradiation of $Sb1$ Ge only, grows in above 170 °C, and anneals at ~270 °C. Prior to annealing, if present, $E_{0.28}$ is hidden directly below the A center $E_{0.27}$. The growth, annealing, and energy level of $E_{0.28}$ resembles that of $E(0.29)_{Fuk}$ from heavily O-doped Ge (which did peak, however, in the DLTS spectrum at a higher temperature than the A center).[6] $E(0.29)_{Fuk}$ was associated with an 819-cm^{-1} infrared-absorption band[9] that resembled a defect-dioxygen complex or a complex containing oxygen and a different impurity atom.[9] Acknowledging that $Sb1$ contains oxygen, this description, though speculative, is also not untenable for $E_{0.28}$. In any case, it is plausible that $E_{0.30}$ and $E_{0.28}$ are related to residual impurities in Ge.

H. Variations in the literature

It has now been established that several electronic levels exist in n-type Ge, for which agreement can indeed be found on energy level and annealing behavior.[5–7,26] However, extensive DLTS investigations of (0.5–3 MeV electron-) irradiated n-type Ge were performed first by the Bourgoin group,[4,24,27–29] but the remarkably large values of the enthalpies[29] render impossible a direct comparison with the enthalpies of this study. On grounds of the annealing behavior the levels $E_{2,Bou}$ (0.53 eV; T_{ann}~150 °C) and $E_{1,Bou}$ (0.32 eV; T_{ann}~110 °C) were identified, respectively, with the A center and the E center,[24] but we now see that most likely $E_{2,Bou}=E_{0.37}$ (E center) and $E_{1,Bou}=E_{0.23}$ (Sb related). This is inferred from the annealing temperatures and from the defect ordering in the spectra. Comparing still with $E_{0.37}$, it is worth mentioning that out of four defects, $E_{2,Bou}$ was found to have by far the smallest capture cross section.[29] (However, our measurement on $E_{0.37}$ now reduces the absolute value by a factor of ~25).

Further, studies of the energy threshold of defect introduction[28] lead to the conclusion that the close-lying levels $E_{4,Bou}$ (0.46 eV, T_{ann}~150 °C) and $E_{5,Bou}$ (0.42 eV, T_{ann}~150 °C) were divacancy related. Like $E_{0.29}$, the levels $E_{4,Bou}$ and $E_{5,Bou}$ appeared in the spectra at a slightly lower temperature than the E center (i.e., $E_{2,Bou}$). It seems reasonable that $E_{4,Bou}$ and/or $E_{5,Bou}$ are the same as $E_{0.29}$ that contains two close-lying levels, and which we indeed attribute to the divacancy.[30]

A word is appropriate also on the studies by Marie and co-workers.[8,31] They irradiated $2.4\times10^{14}\,cm^{-3}$ Sb-doped Cz-Ge with high-energy (~0.3–6 GeV) heavy ions, but for a reason yet to be understood the apparent enthalpies[8] of the defects so obtained differ markedly from the enthalpies obtained with electron and proton irradiation. If we reinterprettheir assignments, with an eye on the defect ordering and annealing temperatures, it now seems clear that $ET5_{Mar}$ (0.47 eV, T_{ann}~150 °C) is the same as $E_{0.37}$ (E center) and highly probable that $ET3_{Mar}$ (0.29 eV, T_{ann}~90 °C) is the same as $E_{0.23}$ (Sb related). Here we rely on the value of 150 °C, rather than 90 °C,[7] of the A-center annealing temperature—which makes it unlikely that $ET3_{Mar}$, and also $E_{1,Bou}$, should be identified with the A center $E_{0.27}$.

A divacancy level is anticipated from the heavy-ion irradiations, and a highly plausible candidate is $ET4_{Mar}$ (0.32 eV, T_{ann}~140 °C),[8] which has the proper position in the spectra. But from arguments based solely on the annealing behavior it is hard to see that $ET2_{Mar}$ (0.28 eV, amplitude doubles at ~90 °C, T_{ann}~150 °C) should in fact be related to the divacancy levels $E_{4,Bou}$ and $E_{5,Bou}$. The suggestion[31] that $ET2_{Mar}$ and $ET4_{Mar}$ are merely single and double acceptor states of the same defect is not easily justified, owing to the fact that $ET2_{Mar}$ increased strongly with a 90 °C anneal, whereas $ET4_{Mar}$ did not.[8] $ET2_{Mar}$ is positioned in the spectra at a relatively low temperature, close to $E_{0.21}$, and indeed they have a similar annealing behavior.

V. SUMMARY

Ge with three types of doping was investigated. Crystals contained $2.5\times10^{14}\,cm^{-3}$ Sb, $1.2\times10^{15}cm^{-3}$ Sb, and $7\times10^{16}cm^{-3}$ O, respectively. A strong defect evolution at RT was observed in both Sb-doped materials after 2-MeV proton or electron irradiation, and the dynamics is compatible with the existence of a source of interstitials. Contrary to the Si case, annealing of the Sb E center, $E_{0.37}$, is retarded under reverse bias. Temperature-dependent electron-capture cross sections were measured for the E center and A center, $E_{0.27}$; they are near 1.5×10^{-18} and 2×10^{-17} cm^2, respectively. It was speculated that $E_{0.37}$ is the double-acceptor level of the E center. A trap $E_{0.23}$ is related to Sb, and seemingly grows up by interstitial capture, possibly hindered by a small barrier. The amplitude of a trap $E_{0.29}$ is strongly enhanced by proton relative to electron irradiation, and $E_{0.29}$ is suggested to be divacancy related. One significant hole trap $H_{0.30}$ was present in Sb-doped material but not in O-doped material. The apparent annealing behavior of $H_{0.30}$ depends on the mode of detection (MCTS or injection-pulse DLTS). $H_{0.30}$ is strongly attractive to holes, and whereas a firm identification cannot be made, we cautiously presented the idea that it be the single acceptor level of the E center. Correspondence was pointed out between seemingly varying literature results.

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