Vacancy–group-V-impurity atom pairs in Ge crystals doped with P, As, Sb, and Bi

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The electronic properties and thermal stability of centers incorporating a vacancy and a group-V-impurity atom (P, As, Sb, or Bi) in Ge crystals have been investigated. The vacancy-group-V-impurity atom pairs (*E* centers) have been induced by irradiation with ^{60}Co γ rays and studied by means of capacitance transient techniques with the use of Au-Ge Schottky barriers. It is argued that the *E* centers in Ge have three charge states: double negative, single negative and neutral, and introduce two energy levels into the gap. There are pronounced changes in the activation energies of charge carrier emission for the particular states with the changes in the type of impurity atoms. The emission of an electron from the doubly negatively charged state of the centers is accompanied by a large change in entropy (ΔS), so, the free energy of the electron ionization, $\Delta G(--/-)=\Delta H(--/-)-T\Delta S(--/-)$, changes significantly with temperature. Consequently, the position of the second acceptor level of the *E* centers $\{E(--/-)=E_c-\Delta G(--/-)\}$ is temperature dependent. In Ge crystals having shallow donor concentrations in the range 10^{13}–10^{15} cm^{-3} at equilibrium conditions half-occupancy of the doubly negatively charged state of the vacancy-group-V-impurity atom pairs occurs when the Fermi level is at $E_c-(0.18-0.22)$ eV. Changes in the entropy of ionization and the energy of electron emission for the double negative state of the *E* centers follow the Meyer-Neldel rule. It has been shown that the directly measured capture cross sections of electrons at the singly negatively charged *E* centers are temperature dependent and can be described by the multiphonon-assisted capture model. The first acceptor level of the *E* centers is in the lower part of the band gap. The formation of one vacancy–group-V-impurity atom complex results in the removal of at least two electrons from the conduction band in *n*-type Ge. It is thought that the *E* centers are responsible for the fast free carrier removal and $n\rightarrow p$ conversion of the conductivity type in oxygen-lean Ge crystals upon electron- or γ-irradiation at room temperature. The thermal stability of the *E* centers in Ge has been found to increase with an increase in the size of donor atoms.

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I. INTRODUCTION

The properties of intrinsic defects (vacancies and self-interstitials) and their interactions with impurity atoms are poorly understood in crystalline germanium compared to silicon. The recent interest in SiGe alloys and heterostructures and the possibility of using Ge in ultrafast complementary metal-oxide-semiconductor devices has brought renewed attention to the need to study the electronic and thermal properties of defects in Ge crystals.[1,2]

According to recent theoretical calculations, the structure and electronic properties of the vacancy in Ge are similar to those of the vacancy in Si: the vacancy in Ge being predicted to exist in five charge states (++), (+), (0), (−), and (−−).[3,4] However, the magnitudes and energies of Jahn-Teller distortions were found to be smaller for the vacancy in Ge compared to Si. Comparison with the results for silicon showed that the vacancy formation energies in germanium (about 2 eV) are significantly smaller than those in silicon (about 3.5 eV), for all charge states, which makes the vacancy much more important for diffusion in Ge than in Si.[3] Indeed there is strong evidence that the diffusion of all shallow donor dopants (P, As, Sb, and Bi) in Ge crystals is vacancy mediated.[5] So, the knowledge of details of interactions of Ge vacancies is extremely important for understanding implant defect removal and the diffusion of shallow donor dopants in crystalline Ge and Ge-rich SiGe alloys.

The electronic properties and structure of complexes incorporating a vacancy and a group-V-impurity atom (P, As, Sb, or Bi) in Ge crystals are not well understood [see Ref. 6 as a recent survey of deep level transient spectroscopy (DLTS) studies on radiation-induced defects in Sb-doped Ge crystals, and references therein, and Ref. 7 as a review of early results on radiation-induced defects in Ge obtained by electrical measurements]. The vacancy-group-V-impurity atom pairs in Ge will be referred thereafter as E centers in analogy with similar centers in silicon.[8]

It has been argued in a recent article that the Sb-vacancy pair in Ge has three charge states: double negative, single negative, and neutral.[9] Consequently, the pair introduces two energy levels into the band gap. The free energy of electron ionization for the second acceptor level of the complex has been found to be $\Delta G(--/-)=\Delta H(--/-)-T\Delta S(--/-)=0.294-4.2kT$ (eV), where $\Delta H(--/-)$ is the enthalpy of ionization, $\Delta S(--/-)$ is the entropy of ionization, and k is Boltzman's constant. Because of the rather large $\Delta S(--/-)$ value the position of the second acceptor level of the E center $\{E(--/-)=E_c-\Delta G(--/-)\}$ is temperature dependent. In Sb-doped Ge crystals with $N_{Sb}=10^{13}-10^{15}$ cm^{-3} at equilibrium conditions half occupancy of the doubly negatively charged state of the Sb-V complex occurs when the Fermi level is at about $E_c-0.21$ eV. The first acceptor level of the E center is in the lower part of the band gap. The activation energy of hole emission from the $E(-/0)$ level has been determined as 0.31 eV. The formation of one Sb-V defect results in the removal of two charge carriers in lightly Sb-doped Ge at room temperature. It has been proposed that this is one of the main reasons for the fast free carrier removal and $n\rightarrow p$ conversion in Ge:Sb upon electron- or γ-irradiation at room temperature.[9] The Sb-V complex has been found to anneal out in the temperature range 140–180 °C upon 30-min isochronal annealing.[9]

In the present paper results of a comprehensive deep level transient spectroscopy study of electronic properties of dominant radiation-induced defects in oxygen-lean Ge crystals doped with different group-V-impurity atoms (P, As, Sb, and Bi) are given. It has been found that in these Ge crystals the vacancy-group-V-impurity atom complexes are the dominant radiation-induced defects and possess similar electronic properties. There are some differences, however, in the values of enthalpy and entropy of defect ionization and in thermal stability for E centers incorporating different impurity atoms.

II. EXPERIMENTAL DETAILS

Samples for this study were prepared from n-type oxygen-lean Ge crystals doped with P, As, Sb, and Bi. Concentrations of shallow donors were in the range $(1-2)\times10^{14}$ cm^{-3} in the samples. Concentrations of defects with deep levels were found to be less than 5×10^{10} cm^{-3} in as-grown materials.

Schottky diodes for capacitance measurements were fabricated by thermal evaporation of Au on surfaces etched in a $1HF+10HNO_3$ acid mixture. Current-voltage (I-V) and capacitance-voltage (C-V) measurements at different temperatures were carried out in order to check the quality of Au-Ge Schottky barriers and to determine concentration of noncompensated shallow donors. Deep electronic levels were characterized with conventional DLTS and Laplace DLTS techniques.[10] Hole traps were studied with the application of injection pulses (i.e., forward bias pulses). It has been shown in a recent study that the barrier height for the

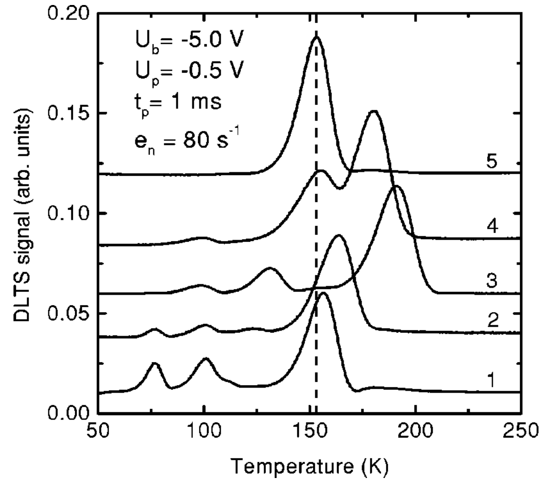

FIG. 1. DLTS spectra for gamma-irradiated oxygen-lean Ge crystals doped with (1) P, (2) As, (3) Sb, and (4) Bi. Spectrum 5 was recorded on a γ-irradiated oxygen-rich Ge sample. The spectra have been vertically displaced for clarity. Measurement settings were $e_n=80$ s^{-1}, bias $-5\rightarrow-0.5$ V, and pulse duration 1 ms.

Au-Ge Schottky diodes is close to or exceeds the band gap value.[9] Such a high barrier results in the appearance of an inversion layer with a high concentration of holes near the semiconductor surface. Application of forward bias to such Au-Ge diodes results in a flux of holes from the inversion layer to semiconductor bulk, thus explaining the possibility of recharging of hole traps in the lower part of the band gap of n-type Ge samples with Au Schottky barriers.[9]

The samples were irradiated with γ rays from a ^{60}Co source. The irradiation temperature was about 10 °C. Doses of irradiation were in the range of $(1-4)\times10^{16}$ cm^{-2}. Variations in the concentration of group-V-impurity atoms were taken into account and the doses were chosen so that the concentrations of radiation-induced defects were in the range of 3–5 % of the shallow donor concentration. Such concentration ratio of deep-to-shallow defects enables careful Laplace DLTS measurements to be done.[10] Isochronal annealing of the irradiated samples has been carried out in the temperature range 80–300 °C with increments of 20 °C.

III. EXPERIMENTAL RESULTS

A. Majority carrier traps in γ-irradiated Ge samples doped with P, As, Sb, and Bi

Figure 1 shows conventional DLTS spectra for Ge crystals doped with different group-V elements after irradiation with γ rays. For the sake of comparison, a DLTS spectrum of a gamma-irradiated oxygen-rich Ge sample is also shown. It should be mentioned that no deep level defects with concentrations higher than 5×10^{10} cm^{-3} have been detected in as-grown samples. Irradiation resulted in the appearance of a number of peaks related to deep level traps in the DLTS spectra. In all the spectra there are a few minor peaks and one dominant peak, the maximum of which occurs at different temperatures for different impurity atoms. The production rates of radiation-induced defects (η) associated with

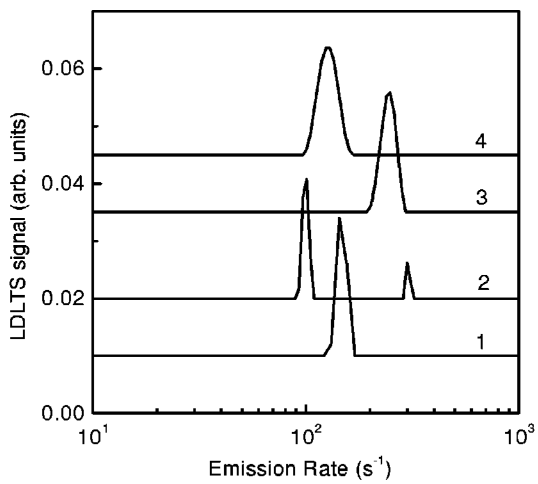

FIG. 2. Laplace DLTS spectra for γ-irradiated oxygen-lean Ge crystals doped with (1) P, (2) As, (3) Bi, and (4) Sb. The spectra were recorded at (1) 160, (2) 165, and (3) 188, and (4) 194 K. The spectra have been vertically displaced for clarity. Measurement settings were bias $-5 \rightarrow -0.5$ V and pulse duration 1 ms.

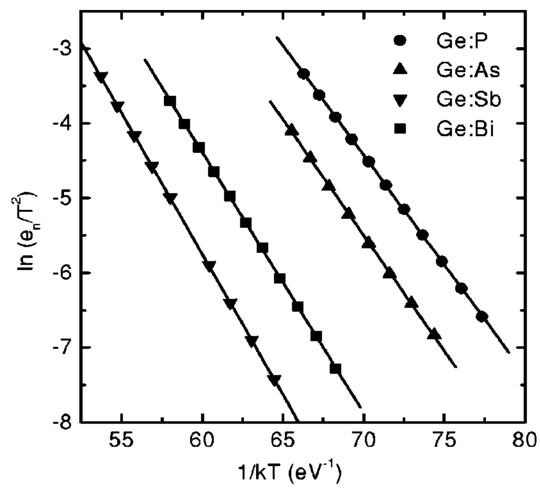

FIG. 3. Arrhenius plots of T^2-corrected emission rates for the dominant electron traps in γ-irradiated oxygen-lean Ge crystals doped with P, As, Sb, and Bi. Parameters of the traps derived from the plots are presented in Table I.

the dominant DLTS peaks have been found to be very similar [$\eta = (1-2) \times 10^{-4}$ cm^{-1}] in materials doped with various group-V impurities. In Sb-doped Ge crystals, the dominant peak with maximum at about 192 K has been identified recently as related to the second acceptor state of the Sb-V complex.[9] The DLTS spectrum for irradiated Bi-doped sample (spectrum 4) consists of a dominant peak and a rather strong low-temperature shoulder. Temperature of the peak maximum for the shoulder coincides with that for the dominant radiation-induced trap in oxygen-rich Ge crystals (spectrum 5). The latter trap has been recently identified as related to the vacancy-oxygen (VO) center.[11,12]

Figure 2 shows Laplace DLTS spectra for the γ-irradiated Ge crystals. The spectra were taken at temperatures close to the temperatures of maxima of the dominant peaks in the conventional DLTS results shown in Fig. 1. The LDLTS spectra look similar and consist of one sharp dominant peak. Only for the As-doped sample there is an additional minor peak in the close vicinity of the dominant one. These results indicate monoexponential transients related to single well-defined energy levels.

The rate of thermal emission of electrons from a deep trap can be written as[13]

$$e_n(T) = \sigma_n(T)\langle v_n(T)\rangle N_c(T)\exp[-\Delta G(T)/kT], \qquad (1)$$

where $\sigma_n(T)$ is the electron-capture cross section, $\langle v_n(T)\rangle$ is the average thermal velocity of electrons, $N_c(T)$ is the effective density of states in the conduction band, and $\Delta G(T)$ is the Gibbs free-energy change for ionization of the state $\Delta G(T) = E_c(T) - E_t(T)$, where $E_t(T)$ is the energy level of the deep state. The Gibbs free energy is related to the changes in enthalpy (ΔH) and entropy (ΔS) by

$$\Delta G(T) = \Delta H - T\Delta S. \qquad (2)$$

For deep-level defects with multiphonon-assisted capture process,[14] $\sigma_n(T)$ can be presented by

$$\sigma_n(T) = \sigma_{n0} \exp[-\Delta E_{n\sigma}/kT], \qquad (3)$$

where $\Delta E_{n\sigma}$ is the energy barrier for capture and σ_{n0} is the capture cross section at $1/T = 0$. Substitution of Eqs. (2) and (3) into Eq. (1) results in

$$e_n(T) = \sigma_{n0}\langle v_n(T)\rangle N_c(T)\exp[\Delta S/k]\exp[-(\Delta H + \Delta E_{n\sigma})/kT]. \qquad (4)$$

As the $\langle v_n\rangle N_c$ product has a temperature dependence on T^2 it is customary in deep level transient spectroscopy to analyze the so-called T^2-corrected emission rates in accordance with the equation

$$e_n(T)/T^2 = A_{ne} \exp(-\Delta E_{ne}/kT), \qquad (5)$$

which is based on the Eq. (4). A plot of the e_n/T^2 values versus $1/kT$ or $1/T$ (the Arrhenius plot) enables a straightforward determination of two parameters $\sigma_{n0} \times \exp(\Delta S/kT)$ and $\Delta E_{ne} = \Delta H + \Delta E_{n\sigma}$, which characterize a deep level trap.

Arrhenius plots of T^2-corrected emission rates derived from LDLTS measurements for the dominant electron traps in differently doped Ge samples are shown in Fig. 3. The values of the activation energy for electron emission (ΔE_{ne}), the pre-exponential factor (A_{ne}), and the so-called apparent capture cross section $\{\sigma_{na}, \sigma_{na} = \sigma_{n0} \times \exp(\Delta S/k)\}$ are given in Table I. The measured values of ΔE_{ne} and A_{ne} conform to the Meyer-Neldel rule,[15,16] according to which $\ln(A_{ne})$ should be a linear function of ΔE_{ne} for similar defects. Figure 4 shows a plot of measured $\ln(A_{ne})$ values vs ΔE_{ne} for the dominant radiation-induced electron traps in oxygen-lean Ge crystals together with those for the second acceptor level of the vacancy-oxygen complex in Ge.[11,12]

It was shown that the electron capture cross section of the singly negatively charged Sb-V complex is temperature dependent and can be described by an equation $\sigma_n = 9.1 \times 10^{-17} \times \exp\{[-0.083 \pm 0.001\ (\text{eV})]/kT\}$.[9] Direct capture cross section measurements have been carried out for the dominant electron traps in the irradiated Ge crystals with

TABLE I. Electronic parameters for the dominant radiation-induced electron traps in Ge crystals doped with different donor impurities. The values of the activation energy for electron emission (ΔE_{ne}), pre-exponential factor (A_{ne}), and apparent capture cross section (σ_{na}) have been derived from Arrhenius plots of T^2-corrected emission rates determined from Laplace DLTS measurements (Fig. 3). The values of the activation energy for electron capture ($\Delta E_{\sigma n}$) and capture cross section extrapolated to $1/T=0$ (σ_{n0}) have been determined from direct capture measurements using LDLTS technique (Fig. 5). The values of enthalpy (ΔH), entropy (ΔS), and free energy (ΔG) of ionization have been derived from the combined analysis of the emission and capture data.

Material	ΔE_{ne}, eV	A_{ne}, s^{-1} K^{-2}	σ_{na}, cm^2	$\Delta E_{\sigma n}$, eV	σ_{n0}, cm^2	ΔH, eV	ΔS, k	ΔG at 220 K, eV
Ge:P	0.293	9.6×10^{6}	2.7×10^{-15}	0.07	3.8×10^{-16}	0.225	1.95	0.19
Ge:As	0.310	1.1×10^{7}	2.9×10^{-15}	0.065	1.6×10^{-16}	0.245	2.9	0.19
Ge:Sb	0.377	2.1×10^{7}	5.9×10^{-15}	0.083	9.2×10^{-17}	0.295	4.2	0.215
Ge:Bi	0.349	1.5×10^{7}	4.2×10^{-15}	0.085	1.6×10^{-16}	0.265	3.3	0.20

different donor species. The capture cross sections have been found to be temperature dependent in all the samples. Figure 5 shows temperature dependencies of capture cross sections for the E centers in γ-irradiated Ge samples doped with P, As, Sb, and Bi. In all the samples the temperature dependencies of the capture cross section can be attributed to multiphonon-assisted capture processes, for which $\sigma_n = \sigma_{n0}\times\exp(-\Delta E_{n\sigma}/kT)$.[14] The values obtained for the energy barrier for capture ($\Delta E_{n\sigma}$) and the capture cross section at $1/T=0$ (σ_{n0}) are presented in Table I.

From a combined analysis of emission and capture data,[13] it is possible to derive the values of enthalpy and entropy of the defect ionization for all the dominant electron traps in γ-irradiated Ge crystals. The obtained ΔH and ΔS values are presented in Table I. It should be noted that the values of entropy of ionization obtained are significantly higher than those for defects in silicon, where the absolute values of ΔS usually do not exceed k. Because of the high ΔS values, positions of energy levels of the dominant electron traps in γ-irradiated Ge crystals should be temperature-dependent **(**$E[n/(n-1)]=E_c-\Delta G[n/(n-1)]$; $\Delta G[n/(n-1)] = \Delta H[n/(n-1)]-T\Delta S[n/(n-1)]$, where n is the number of electrons at a defect; and $\Delta G[n/(n-1)]$ is a change in the free energy of a crystal accompanying the process of the defect ionization**)**.[17]

According to Hall effect measurements, ionization of the dominant radiation-induced defects occurs in the temperature range 150–300 K in oxygen-lean donor-doped ($N_d = 10^{13}-10^{15}$ cm^{-3}) Ge crystals.[18,19] These dominant defects are believed to be the E centers. For the given temperature range the values of the free energy of electron ionization are in the range of 0.18–0.22 eV for the radiation-induced electron traps considered in the present study (Table I). These values of free energy of electron ionization coincide with those derived directly from the Hall effect measurements,[7,18–20] indicating that the same electron traps have been observed by both the Hall-effect and DLTS measurements.

Figure 6 shows changes in normalized values of concentration of the dominant electron traps in the irradiated Ge crystals upon 30-min isochronal annealing with no potential

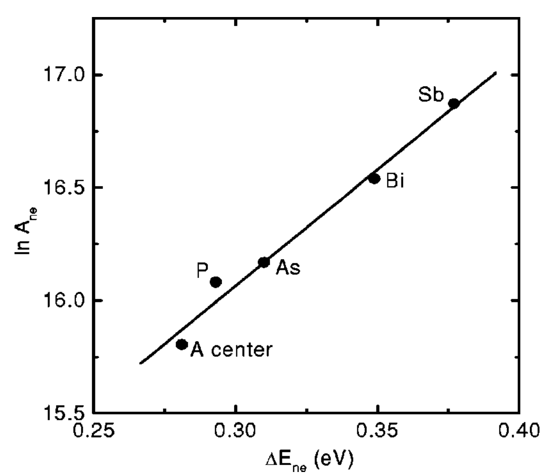

FIG. 4. Dependence of the preexponential factor (A_{ne}) vs the activation energy for electron emission (ΔE_{ne}) for T^2-corrected emission rates for the dominant radiation-induced electron traps in oxygen-lean Ge crystals doped with P, As, Sb, and Bi. The A_{ne} value for the double acceptor level of the vacancy-oxygen complex is also shown. The solid line is the linear approximation of the obtained data.

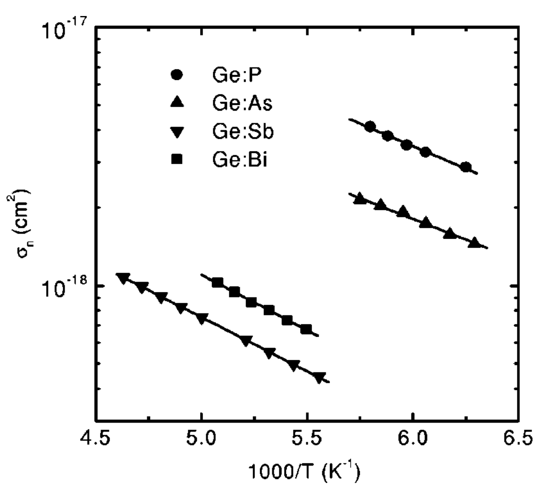

FIG. 5. Arrhenius plots of capture cross sections for the dominant electron traps in γ-irradiated oxygen-lean Ge crystals doped with P, As, Sb, and Bi. Parameters of the traps derived from the plots are presented in Table I.

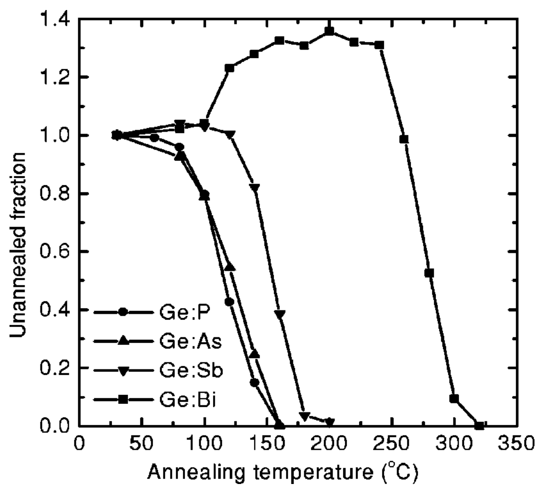

FIG. 6. Changes in normalized concentrations of the dominant electron traps in γ-irradiated oxygen-lean Ge crystals doped with P, As, Sb, and Bi upon 30-min isochronal annealing.

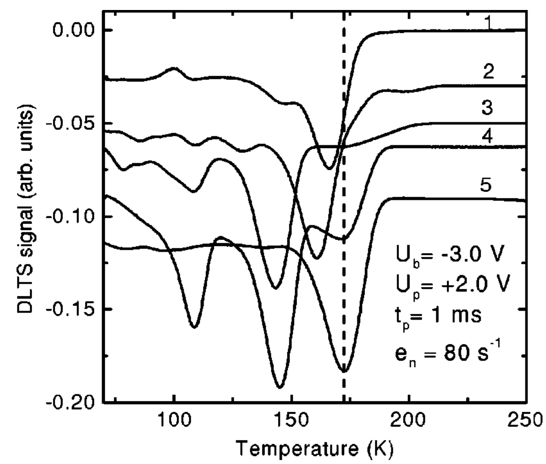

FIG. 7. "Injection" DLTS spectra for γ-irradiated oxygen-lean Ge crystals doped with (1) P, (2) As, (3) Sb, and (4) Bi. Spectrum 5 was recorded on a γ-irradiated oxygen-rich Ge sample. The spectra have been vertically displaced for clarity. Measurement settings were e_n=80 s^{-1}, bias $-3 \rightarrow +2.0$ V, and pulse duration 1 ms.

applied across the layer being annealed. The temperatures at which the traps anneal out differ in differently doped crystals. An increase in the trap concentration in Bi-doped samples upon annealing in the temperature range 120–160 °C occurs together with the annealing stage of the vacancy-oxygen complexes (*V*O),[11,12] whose energy level has been identified as responsible for a low-temperature shoulder of the dominant peak in irradiated Bi-doped samples (spectrum 4 in Fig. 1). This increase is therefore attributed to the vacancies liberated from unstable *V*O complexes and then captured by Bi. The *V*O complexes in small concentrations, $\leqslant$5% of the concentration of dominant radiation-induced traps, have been detected also in P- and As-doped Ge samples. In these samples the *V*O complexes and the dominant radiation-induced traps disappeared in the same temperature range upon isochronal annealing.

It should be mentioned that a similar trend in the annealing behavior (an increase of thermal stability with increasing atom size of the dopant) was observed for the vacancy-group-V impurity atom pairs in Si.[21,22] However, it is worth noting that contrary to the Si case,[23] annealing out of the dominant radiation-induced electron trap in Sb-doped Ge crystals was found to be retarded under the application of reverse bias.[6] It was argued that such an effect in Ge could be explained assuming that the dominant electron trap is related to the second acceptor level of the Sb-*V* pair.[6]

B. Minority carrier traps in γ-irradiated Ge samples doped with P, As, Sb, and Bi

Figure 7 shows DLTS spectra recorded with the application of forward bias minority carrier injection pulses on γ-ray-irradiated Ge samples. No deep level traps with concentration higher than 5×10^{10} cm^{-3} have been observed in the lower part of the gap in as-grown samples. Irradiation resulted in the appearance in the "injection" DLTS spectra of a dominant peak and a few minor peaks for all the samples. The production rates of dominant hole traps due to irradiation have been found to be similar in *n*-Ge with different dopants and close to the production rates of dominant electron traps [$\eta = (1-2) \times 10^{-4}$ cm^{-1}]. In Sb-doped Ge crystals, the dominant peak with maximum at about 143 K has been identified recently as related to the first acceptor state of the Sb-*V* complex.[9] The dominant radiation-induced hole trap in oxygen-rich Ge crystals (spectrum 5) is related to the vacancy-oxygen complex.[11,12] The high-temperature shoulder of the dominant trap in the DLTS spectrum for irradiated Bi-doped sample (spectrum 4) has been assigned to the *V*O complex as the electronic characteristics and annealing behavior of this shoulder coincide with those for the *V*O in irradiated oxygen-rich Ge crystals.

Laplace DLTS measurements with the application of "injection" pulses have been carried out for the dominant hole traps in all the irradiated Ge sample. Figure 8 shows Arrhenius plots of T^2-corrected emission rates of holes for the domi-

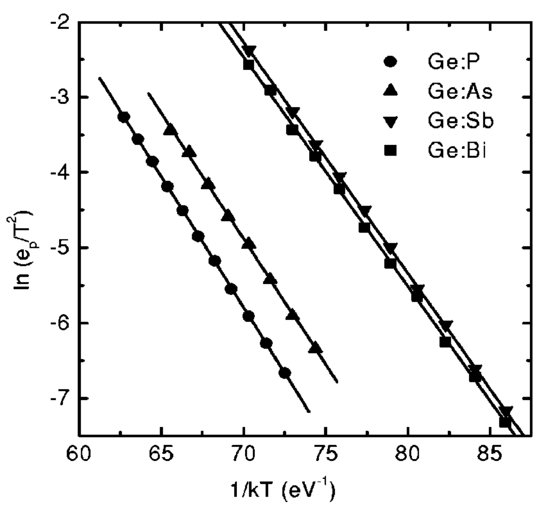

FIG. 8. Arrhenius plots of T^2-corrected emission rates for the dominant hole traps in γ-irradiated oxygen-lean Ge crystals doped with P, As, Sb, and Bi. Parameters of the traps derived from the plots are presented in Table II.

TABLE II. Electronic parameters for the dominant radiation-induced hole traps in Ge crystals doped with different donor impurities. The values of the activation energy for hole emission (ΔE_{pe}), pre-exponential factor (A_{pe}), and apparent capture cross section (σ_{pa}) have been derived from Arrhenius plots of T^2-corrected emission rates measured by Laplace DLTS technique (Fig. 8).

Material	ΔE_{pe}, eV	A_{pe}, s^{-1} K^{-2}	σ_{pa}, cm^2
Ge:P	0.348	1.1×10^8	9.2×10^{-14}
Ge:As	0.334	1.05×10^8	8.75×10^{-14}
Ge:Sb	0.307	2.2×10^8	1.8×10^{-13}
Ge:Bi	0.305	1.5×10^8	1.25×10^{-13}

nant holes traps. The derived values of the activation energy for the hole emission (ΔE_{pe}), preexponential factors (A_{pe}), and the apparent capture cross sections (σ_{pa}), are given in Table II. Unfortunately, because of very fast filling of the traps with holes under application of "injection" pulses and uncertainties in the absolute value of the hole flux, we could not determine the values of hole capture cross section and enthalpy and entropy of ionization for these traps.

It was shown in our previous article that the dominant electron and hole traps disappeared simultaneously upon isochronal annealing of γ-irradiated Ge:Sb crystals.[8] It has been found in the present study that the annealing behavior of the dominant hole traps is essentially the same as the annealing behavior of the dominant electron traps in Ge samples doped with P, As, and Bi. For example, Fig. 9 shows changes upon isochronal annealing in magnitudes of DLTS peaks related to the dominant electron and hole traps in a γ-irradiated Ge:Bi sample. The results of the isochronal annealing study suggest that the dominant electron and hole traps should be related to two energy levels of the same defects in irradiated Ge crystals doped with P, As, Sb, and Bi.

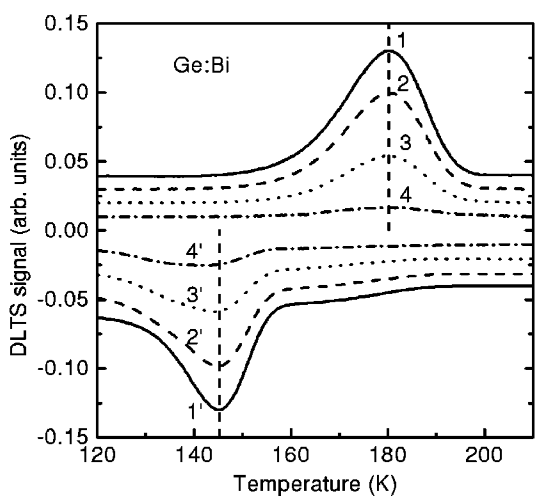

FIG. 9. DLTS spectra of Bi-doped Ge crystals after γ-irradiation and subsequent 30 min annealing at temperatures (1, 1′) 240 °C, (2, 2′) 260 °C, (3, 3′) 280 °C, and (4, 4′) 300 °C. Measurements settings were $e_n=80$ s^{-1} and pulse duration 1 ms for all the spectra. Bias sequences were (1–4) $-5.0\rightarrow -0.5$ V and (1′–4′) $-3.0\rightarrow +2.0$ V.

IV. DISCUSSION AND CONCLUSION

It has been argued previously that the dominant electron and hole traps produced in oxygen-lean Sb-doped Ge by irradiation with ^{60}Co γ rays at room temperature are associated with the second and first acceptor levels of the Sb-*V* pair.[9] Results obtained in the present study give further support to this assignment and show that the properties and introduction rates of vacancy-group-V-impurity atom pairs are similar for the defects incorporating different atoms (P, As, Sb, or Bi). It should be pointed out that the Ge crystals, which were studied in the present work, were high quality crystals with a low concentration ($<5\times 10^{10}$ cm^{-3}) of deep level defects in as-grown materials. The group-V impurities were the impurities with the highest concentration in the Ge crystals. As group-V impurity atoms are known to be very effective traps for vacancies in Si and Ge crystals it is reasonable to expect that the introduction of the vacancy-group-V-impurity complexes dominates upon γ irradiation of oxygen-lean Ge at room temperature. Below we consider the available evidence from the present study and from previous work relating to the assignment of the dominant radiation-induced electron and hole traps in oxygen-lean donor-doped Ge crystals to the acceptor levels of the *E* centers.

(i) Concentrations of the dominant radiation-induced electron and hole traps have been found to be nearly identical after irradiation and at different stages of isochronal annealing in the same Ge crystals (Ref. 9 and this work). This suggests an assignment of the traps to two different energy levels of the same defect.

(ii) Introduction rates and electronic properties of the dominant radiation-induced electron and hole traps are similar in Ge crystals doped with different donor impurities (Refs. 7 and 9, and this work). This suggests the similar nature of the defects responsible for the traps in differently doped crystals. There are, however, pronounced changes in the values of enthalpy and entropy of defect ionization for the traps in Ge crystals doped with different donor atoms. The changes can be accounted for by the effect of donor atoms on the electronic properties of the complexes. As the changes in parameters of the traps are significant one can assume that the donor atoms should be incorporated into or to be in the close vicinity of the complexes.

(iii) The dominant radiation-induced hole trap exhibited field-enhanced hole emission in Sb-doped Ge crystals.[6] This suggests the acceptor nature of the dominant hole trap.[6]

(iv) The annealing behavior of the dominant radiation-induced electron trap in Sb-doped Ge under the application of reverse bias can be explained consistently assuming the double acceptor nature of the trap.[6]

(v) It is known that electron or γ irradiation of *n*-type Ge results in fast free electron removal and $n\rightarrow p$ conversion of conductivity.[7,18] This is consistent with the assignment of the dominant radiation-induced electron and hole traps to the acceptor levels of a defect, which results from the reaction of a vacancy with a shallow donor to produce a double acceptor. The formation of such a defect in lightly doped *n*-Ge is accompanied by the removal of two electrons from the conduction band at room temperature.

(vi) It is well known that irradiation of Si and Ge crystals with ^{60}Co γ rays at room temperature results mostly in the introduction of intrinsic point defects, vacancies and self-interstitials. The introduction rates of complex defects such as divacancies, etc., are much smaller than those of simple intrinsic defects.[7] It has been argued that the first acceptor level of the Ge vacancy should be at about $E_v+0.20$ eV, and a donor level of the Ge self-interstitial at $E_c-0.04$ eV.[24] If so, in lightly doped ($N_d=10^{13}-10^{15}$ cm^{-3}) *n*-Ge crystals at room temperature (when the Fermi level is close to the mid-gap), vacancies should be negatively charged and self-interstitials are positively charged. Consequently, the mobile negatively charged vacancies should interact effectively with positively charged group-V-impurity atoms giving rise to the vacancy-group-V-impurity atom pair. The interaction of positively charged interstitials with positively charged donor species should not be significant because of Coulomb repulsion.

There is an analogy with the established case of defect reactions in oxygen-lean *n*-Si crystals lightly irradiated with ^{60}Co γ rays at room temperature. It was found that in this case practically all vacancies react with phosphorus atoms resulting in the formation of vacancy-phosphorus pairs.[25,26]

(vii) The activation energy of the electron emission from the first acceptor level of the Sb-*V* pair was found to increase significantly in Si-rich SiGe alloys with increasing Ge content (from about 0.41 eV in pure Si to about 0.51 in $Si_{0.75}Ge_{0.25}$).[27,28] It should be pointed out, however, that it was argued in Ref. 27 that the energy level of the pair is pinned to the conduction band edge over the alloy composition range studied. In any case, if the level is pinned to the conduction band edge or if it is not, the shrinkage of the band gap with the increase in Ge content in SiGe crystals results in the movement of the first acceptor level of the Sb-*V* vacancy pair towards the valence band. This trend is consistent with the assignment of the dominant hole trap in the lower part of the band gap to the first acceptor level of the *E* center in irradiated Ge.

(viii) It was found that the thermal stability of *E* centers in crystalline silicon increases with the increase in the size of group-V impurity atoms.[21,22] A similar situation has been found to occur for the dominant radiation-induced electron and hole traps in Ge crystals doped with different donor impurities.

The above observations and arguments strongly indicate that the dominant electron and hole traps, which were observed in γ-irradiated oxygen-lean *n*-type Ge, are related to the second and first acceptor levels of the vacancy–group-V-impurity atom complex, respectively.

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