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ELECTRONIC PROPERTIES OF SEMICONDUCTORS

Interaction Rates of Group-III and Group-V Impurities with Intrinsic Point Defects in Irradiated Si and Ge[1]

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Abstract—A comparative study of interactions of shallow impurities with primary defects in oxygen- and carbon-lean moderately doped Si and Ge subjected to irradiation with 0.9 MeV electrons, ^{60}Co gamma-rays, and 15 MeV protons at room temperature is presented and discussed. For the quantitative characterization of such interactions, changes in the total concentration of the original shallow group-V donor or group-III acceptor impurities in the irradiated materials are determined by Hall effect measurements over a wide temperature range. Losses of the shallow donor or acceptor states in the irradiated Si and Ge are indicative of their removal rates that can be used for estimation of production rates of primary defects interacting with the dopants. Some important factors affecting the interactions between primary defects and shallow impurities in Si and Ge are highlighted.

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1. INTRODUCTION

Radiation-produced defects in Si and Ge form an important field of our knowledge having fundamental and application aspects. Because of this a great body of information about their electrical and optical properties as well as dynamical characteristics and so on has been collected in the literature so far; see for instance [1, 2]. On the one hand, such data lie at the basis of defect engineering in semiconductor technology. On the other hand, they are indicative of degradation processes in semiconductor devices under irradiation conditions. Defect production in irradiated Si and Ge has received much attention, since this is a starting point in consideration of radiation damage. Actually, if the energy transferred to a host atom during the scattering of incident particles by regular atoms in the crystal lattice exceeds a minimal energy threshold E_{th}, being enough to dislodge it from the lattice sites, a pair of intrinsic defects is produced. This primary defect, called a Frenkel pair, consists of a self-interstitial I bound to its parent vacant site, a vacancy V. These defects are known to be unstable in Si and Ge at room temperature: they are annihilated if the distance r between the components is less than a critical one, $r \leq r_c$, or they are separated into isolated defects V and I if $r > r_c$. Isolated vacancies and self-interstitials in Si and Ge are highly mobile at room temperature and while migrating through the crystal lattice they can be trapped by other structural defects, thus giving rise to formation of secondary defects. There are varieties of secondary defects in both semiconductors, among them impurity-related defects and complexes as well as complexes of intrinsic defects like divacancies, di-interstitials and so on [1, 2]. Changes in the electrical and optical properties of irradiated materials are controlled by the type and concentration of the dominating secondary radiation defects.

Contrary to the formation of secondary defects stable at room temperature, it is not possible to keep track of what is going on with Frenkel pairs and other intrinsic defects with the aid of electrical and optical techniques on the scale of real time. Their production processes in Si and Ge irradiated with various particles can however be visualized in models using a Non-Ionizing Energy Loss (NIEL) approach. Such an approach has been applied to detector-grade Si materials [3, 4]. The effective production rate of primary defects in Si and Ge irradiated at room temperature may be assessed by summing the formation rates of impurity-related secondary defects and stable intrinsic complexes like divacancies and so on; see for instance [5]. However, it is known that the impurity content of initial detector-grade materials is usually specific, i.e., very small concentrations of electrically active group-III and group-V impurities as compared to concentrations of electrically inactive oxygen and carbon.

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On the other hand, it would be of keen interest to get insight into interactions of primary defects with group-III and group-V impurities commonly used in doped Si and Ge. Despite a lot of data on radiation-produced defects in both semiconductors a comprehensive comparison presents a real challenge due to the fact that various electron accelerators with different regimes of pulsed irradiation have been used for materials with distinct impurity content. Because of this preference in the present work is given to the experimental method that allows one to see how the concentration of shallow donor or acceptor states of the dopants is decreased in the course of irradiation. Actually, any interplay of the impurity atoms with vacancies and self-interstitials gives rise to loss of their shallow donor or acceptor states, thus changing the electrical parameters of irradiated materials. An important point is that a marked decrease in the concentration of the shallow states can be reliably determined, no matter which kinds of secondary impurity-related defects are then formed and which charge states they acquire. The subject of the present communication is a comparison of the removal rates of shallow donor and acceptor states in electron- and proton-irradiated Si and Ge. A combination of new results and our earlier data obtained by means of the same technique allows one to provide a closer look at the production of primary defects in them.

2. EXPERIMENTAL

Square-shaped samples were cut from slices of moderately doped Si and Ge. The concentrations of group-III and group-V impurities in oxygen- and carbon-lean Ge and Si were mostly in a range of $1 \times 10^{14} \le N_{A,\,D} \le 3 \times 10^{16}$ cm^{-3}. The Si ingots were grown by the floating zone technique (FZ).

Irradiation with fast electrons at 0.9 MeV was performed in a resonant transformer accelerator on a target in a water stream. The electron energy was kept relatively low to suppress the direct production of complex intrinsic defects like divacancies and so on. The frequency of a pulsed beam was $f = 490$ cps and the pulse duration was $\tau = 330$ μs. The average intensity of electron irradiation didn't exceed $J = 7.5 \times 10^{13}$ electrons/(cm^2 s), so the irradiation temperature was lower than $T < 30$°C. The parameters of another pulsed accelerator for 3.5 MeV electrons were $f = 200$ cps, $\tau = 5$ μs, and $J = 2 \times 10^{12}$ electrons/(cm^2 s). Some samples were irradiated with gamma-rays of ^{60}Co at 1.25 MeV. The dose intensity of gamma-irradiation was 1×10^{12} gamma-quanta/(cm^2 s). The irradiation temperature was $T \approx 10$°C. Under such irradiation conditions, the main damaging factor represents both by photoelectrons and Compton electrons in Si or Compton electrons in Ge at an average energy of 760 keV.

In the case of proton irradiation the samples were irradiated with a pulsed beam of protons at 8 and 15 MeV. The frequency of the pulsed beam was $f = 100$ cps and the duty cycle was $\tau = 2.5$ ms. The irradiation temperature didn't exceed $T = 20$°C, because the average current was low, in an interval of 10 to 100 nA/cm^2. The accuracy of radiation dosage was about 15 percent. The samples for proton irradiation were prepared thin enough, so the protons went out of the irradiated samples. In this way it was possible to investigate the damaging factor of 8 and 15 MeV protons, without marked passivation effects of hydrogen. To provide a higher degree of reliability of data on radiation damage the above mentioned irradiation facilities were used for the most part, since strong changes in the parameters of a pulsed beam of bombarding particles may also produce some unwanted effects. Hall effect and conductivity measurements on initial and irradiated samples were taken in the van der Pauw geometry over a temperature interval of $7 \le T \le 300$ K and $20 \le T \le 300$ K for Ge and Si samples, respectively. Curves of the charge carrier concentration against reciprocal temperature, n, $p(1/T)$, were then analyzed making use of relevant equations of charge balance based on the statistics of charge carriers in non-degenerate semiconductors [6, 7]; see also some explanation for Si and Ge [8, 9].

Let's shortly outline the analysis procedure. The temperature intervals indicated above fit well the area of extrinsic conductivity in n-Ge and n-Si where ionization of the shallow states of group-V dopants takes place up to a saturation plateau $n_{\mathrm{sat}} = N_D - N_A$, where N_D and N_A are the total concentrations of the shallow donor states of group-V impurities and compensating acceptors, respectively. The equation of charge balance in n-Si and n-Ge can be written in the form

$$\frac{n + N_A}{N_D - N_A - n} = N_C T^{3/2} \frac{\exp\left(-\dfrac{E_D}{kT}\right)}{g_1^{-1} + g_2^{-1}\exp\left(-\dfrac{\delta}{kT}\right)}.$$

Here, n is the concentration of electrons in the conduction band; N_C is the effective density-of-states of the conduction band; E_D is the ionization energy of the $1s(A_1)$ state of the shallow donors; δ is the splitting of the ground state of the shallow donors, i.e. the splitting between the $1s(A_1)$ and $1s(T_2)$ states in Ge and the splitting between the $1s(A_1)$ and $1s(E) + 1s(T_2)$ states in Si; g_1 and g_2 are the degeneracy factors (including the electron spin) of the $1s(A_1)$ and $1s(T_2)$ states in Ge and the $1s(A_1)$ and $1s(E) + 1s(T_2)$ states in Si (the relevant data on the splitting are taken from optical spectra [10]); the splitting between $1s(E)$ and $1s(T_2)$ states in Si can be neglected in calculations; other symbols have their usual meanings. Going to p-type materials the equation of charge balance in p-Si and p-Ge takes the form

$$\frac{p + N_D}{N_A - N_D - p} = g_A^{-1} N_V T^{3/2} \exp\left(-\frac{E_A}{kT}\right).$$

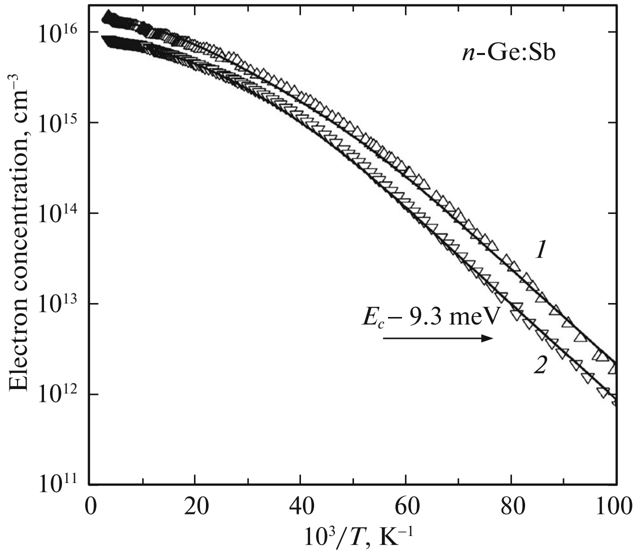

Fig. 1. Electron concentration against reciprocal temperature for the oxygen-lean n-Ge:Sb sample irradiated with 15 MeV protons. Dose, protons/cm^2: *1*—0, *2*—2 × 10^{13}. Points, experimental; curves, calculated. Ionization energy of the shallow donor states is indicated. Loss of the shallow donor states of the antimony impurity atoms in the irradiated sample is 5 × 10^{15} cm^{-3}.

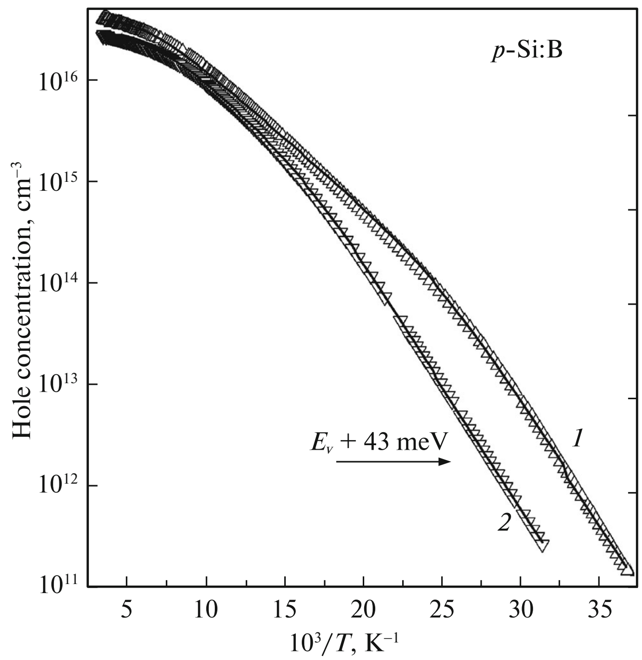

Fig. 2. Hole concentration against reciprocal temperature for the oxygen-lean p-Si:B sample irradiated with 15 MeV protons. Dose, protons/cm^2: *1*—0, *2*—1 × 10^{14}. Points, experimental; curves, calculated. Ionization energy of the shallow acceptor states is indicated. Loss of the shallow acceptor states of the boron impurity atoms in the irradiated sample is 1.1 × 10^{16} cm^{-3}.

Here, p is the concentration of holes in the valence band; N_A and N_D are the total concentrations of the shallow acceptor states of group-III impurities and compensating donors, respectively; N_V is the effective density-of-states of the valence band; E_A is the ionization energy of the shallow acceptors; g_A is the degeneracy factors (including the electron spin) of the acceptor states taking into account that the light and heavy hole mass subbands in **k**-space are degenerate at $\mathbf{k} = 0$; the contribution of the spin-orbit split-off valence band in p-Ge can be neglected at $T \leq 300$ K, whereas in p-Si it becomes pronounced with increasing temperature. Similarly to n-type materials, in this case of extrinsic conductivity the saturation plateau is defined by $p_{\rm sat} = N_A - N_D$. By way of example, several experimental and calculated curves of n, $p(1/T)$ are displayed in Figs. 1, 2.

It should be reminded that values of N_D and N_A in n-type and p-type samples, respectively, represent the total concentrations of shallow states of dopants, no matter whether they are neutral or compensated at $T = 0$ K. Therefore, the difference between the total concentrations before and after irradiation, $N_D = N_D^0 - N_D^{\rm irr}$ and $N_A = N_A^0 - N_A^{\rm irr}$, indicates directly the loss of the shallow energy states of dopants due to interactions of the impurity atoms with intrinsic defects produced by the irradiation. This has been a focus of attention in the present communication. Analysis of how the concentration of compensating secondary defects is changed in the irradiated material will be given in a separate paper.

3. RESULTS AND DISCUSSION

3.1. Electron Irradiation of Si and Ge

By analyzing the electrical data obtained on various samples of Si and Ge doped with group-V and group-III impurities some interesting features of their interactions under electron irradiation have been revealed; see Fig. 3. Based on these data one can roughly estimate the fraction of Frenkel pairs subjected to dissociation into isolated vacancies and self-interstitials, relying on removal rates of the shallow donors and acceptors in irradiated Si and Ge. Active interest is being shown in estimates of how this fraction is changed with increasing energy of fast electrons; for detector-grade Si the experimental and modeling information can be found in [4]. Such information is also essential to modeling the production and spatial distribution of primary defect in Si and Ge irradiated with heavy particles and ions. This brings up another challenging point of the threshold energy $E_{\rm th}$ for elastic displacement of regular atoms in the crystal lattice. Low values of $E_{\rm th} \approx 12$–14 eV has been often used in simulations of radiation damage in Si and Ge by ion implantation; see for instance [11]. These values

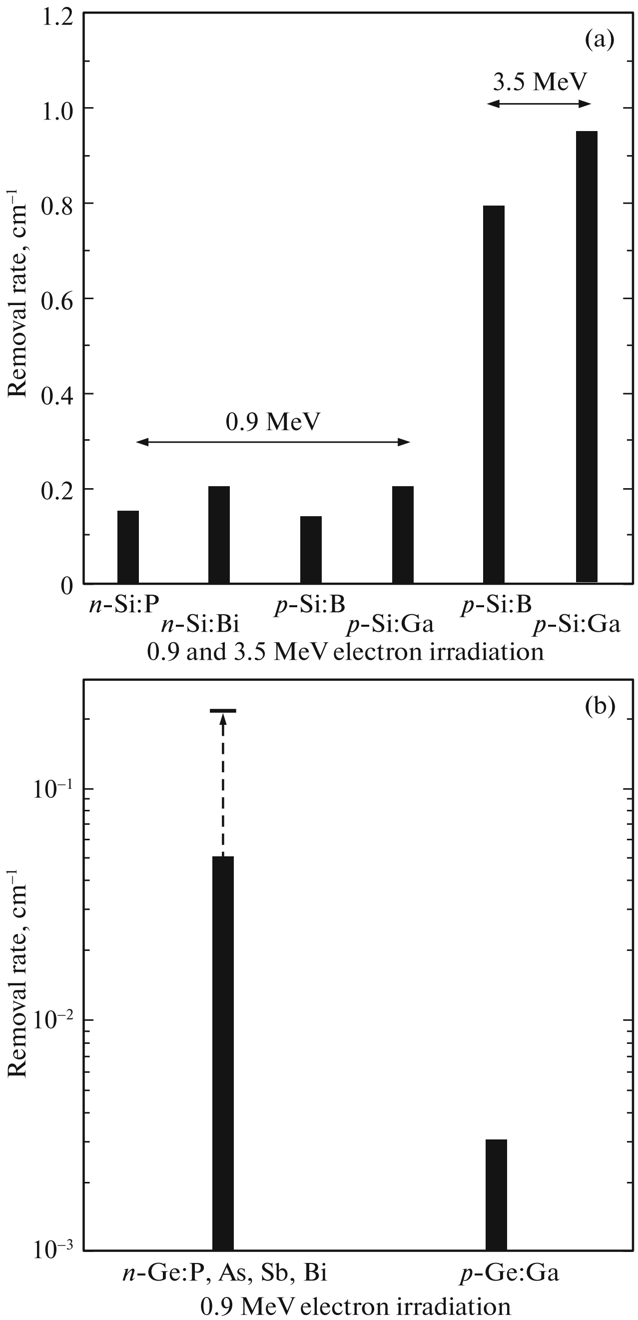

Fig. 3. (a) Removal rates of the shallow donor or acceptor states in the oxygen-lean moderately doped *n*- and *p*-Si irradiated with 0.9 and 3.5 MeV electrons, (b) removal rates of the shallow donor or acceptor states in the oxygen-lean moderately doped *n*-and *p*-Ge irradiated with 0.9 MeV electrons. Arrow shows the increase in removal rates of the shallow donor states of group-V impurities in the *n*-Ge with the increasing impurity concentration from $\approx 1 \times 10^{14}$ to $\approx 1 \times 10^{16}$ cm^{-3}.

stemmed from earlier radiation experiments where the threshold energy E_{th} was defined by means of lifetime and conductivity measurements on thin samples. The use of very thin samples of 15–60 μm thick, sometimes with the requirements of preliminary saturation of the surface states [12] for estimations of E_{th} in Si and Ge was later critically discussed taking into account that the elastic displacements of regular atoms with weakened bonds in the near-surface layers and internal regions with extended structural defects may influence the total production of primary defects [13]. In this respect, the authors made an attempt to reconsider the earlier data from this point of view [13]; see the cited literature therein. They suggested that it would be instructive to have a look at the irradiation damage in bulk Si and Ge by weakly absorbed gamma-rays of ^{60}Co which is equivalent to internal irradiation of material with photoelectrons and Compton electrons at average energies about 760 keV. It was shown that the situation with E_{th} can be better appreciated if the threshold energies in bulk Si and Ge are taken about 40 and 30 eV, respectively, with some "smeared-out" effects in the lower energy range. However, the situation with the threshold energy in Si and Ge remains somehow uncertain yet, so while modeling production of primary defects in these materials one prescribes arbitrarily E_{th} values from an energy interval of 12 to 30 eV; see also [14]. Recently, this subject for Si was comprehensively re-examined on the basis of calculations employing density functional theory (DFT) molecular dynamics (MD) [14]. It has been found that there is a global minimum of E_{th} at 12.5 eV for the [111] direction. However, the average threshold energy E_{th}^{ave} over all lattice directions turned out to be close to 36 eV. It is pointed out that modeling radiation damage in ion-implanted Si at $E_{th} \approx 25$ eV should inevitably bring about a large excess of the calculated production of primary defects. In such a case the primary defects are generally claimed to be annihilated for the most part in order to reasonably fit experimental data.

Let's briefly discuss the removal rates of the shallow donor and acceptor states in the electron irradiated *n*- and *p*-Si displayed in Fig. 3a. As is seen, the removal rates of the shallow impurity states appear to be between 0.1 and 0.2 cm^{-1} for various dopants in the materials under 0.9 MeV electron irradiation. It should be noted that the values were found to be rather comparable, though the group-III acceptor concentrations in the *p*-Si were by a factor of three higher than those of the group-V impurities in the *n*-Si being around 2×10^{16} cm^{-3}. It means that the effective concentration of isolated vacancies and self-interstitials taking part in interactions with the dopants are comparable, too. In other words, the fraction of Frenkel pairs subjected to dissociation in the 0.9 MeV electron-irradiated Si doesn't vary substantially if the Fermi level is shifted from $\approx E_C - 0.25$ eV to $\approx E_V + 0.15$ eV.

If the energy of bombarding electrons increases to 3.5 MeV the removal rates of the group-III acceptors go up roughly in proportion to the increased electron energy, as is seen in Fig. 3a, taking into account that in the irradiated p-Si under study both mobile vacancies and self-interstitials can interact with group-III acceptors [1]. In the light of our discussion concerning the threshold energy for elastic displacement of regular atoms it would be interesting to compare the experimental removal rates η_D and η_A with the calculated production rates of Frenkel pairs, $\eta_{FP} \approx 0.85$ cm^{-1} and $\eta_{FP} \approx 1.2$ cm^{-1} for the 0.9 and 3.5 MeV electron irradiation, respectively, taking $E_{th}^{ave} \approx 35$ eV. Thus, the fraction of dissociated Frenkel pairs in Si is increased from $\xi \approx 0.1$ to 0.35 with the increasing electron energy from 0.9 to 3.5 MeV, in accordance with the obtained data. This information may be useful for calculations of Frenkel pairs distributions over the distance between their components.

It would now be instructive for further consideration to compare the above given removal rates of the shallow impurities to the formation rate η_{VO} of oxygen atom-vacancy pairs, called the A-centers [15], in electron-irradiated oxygen-rich n-Si grown by the Czochralski (CZ) technique. The point is that isolated oxygen atoms being present in n-Si (CZ) in abundance, $\sim 7 \times 10^{17}$ cm^{-3}, are electrically inactive and, therefore, the role of charge states of primary defects in interactions with oxygen should be subtle. Earlier the formation rate of A-centers in the n-Si (CZ) subjected to irradiation with fast electrons was reported for a wide interval of electron energies [15]. It is interesting to point out that for 1 MeV electron irradiation the rate η_{VO} was found to be about 0.1 cm^{-1}; cf. Fig. 3a. Later it has been established that for pulsed electron irradiation the formation rate η_{VO} is strongly dependent on the energy and intensity of the electron beam [16]. In that work the concentration of A-centers having the well-known acceptor states at $\approx E_C - 0.16$ eV was reliably determined by Hall effect measurements. In actual fact, at irradiation intensities of $J_{pulse} \approx 5 \times 10^{14}$ to 5×10^{15} cm^{-2} s^{-1} the formation rate of A-centers in the n-Si (CZ) irradiated with 0.9 MeV electrons was observed to be about 0.07 cm^{-1} and then it reached $\eta_{VO} \approx 0.15$ cm^{-1} with the decreasing J_{pulse}, i.e. just in the same interval as was found for the removal rates of the shallow dopants in the irradiated n- and p-Si (FZ). Moreover, η_{VO} is increased in a similar way with the increasing energy of bombarding electrons from 0.9 to 3 MeV. It means that direct annihilation and dissociation processes of Frenkel pairs as primary defects in the Si during the irradiation play a decisive role, leaving other processes like indirect annihilation of isolated vacancies and self-interstitials during their migration to be of lesser importance. Turning our attention to the discussion of electron-irradiated Ge one can see a striking difference in the behavior of the n-Ge and p-Ge under 0.9 MeV electron irradiation, in a sharp contrast to the irradiated Si; cf. Fig. 3. First, the removal rate of the shallow donor states of all the V-group impurities in electron- and gamma-irradiated n-Ge shows a marked rise, nearly by a factor of five, with the increasing dopant concentration from $\approx 1 \times 10^{14}$ cm^{-3} to $\approx 1 \times 10^{16}$ cm^{-3} [17, 18]. Secondly, the removal rate of the shallow acceptor states in irradiated p-Ge appears to be extremely small taking into account that the initial concentration of Ga in the electron-irradiated p-Ge, about 2×10^{15} cm^{-3}, was by an order-of-magnitude larger than those of P and Bi in the n-Ge, shown in Fig. 3b. Similarly to electron-irradiated n-Si, the removal rate of the shallow donor states in n-Ge also grows up with the increasing energy of fast electrons [18]. A plausible cause of small removal rates in electron-irradiated p-Ge may be inappropriate charge states of primary defects. By way of example, theory predicted that the isolated vacancy in Ge has no positive charge states at all, as opposed to that in p-Si where the Coulomb attraction between positively charged vacancies and negatively charged acceptors may enhance such interactions [19–21]. Together with this, we think that the main reason is a strong suppression of dissociation of Frenkel pairs in p-Ge when compared to n-type material. An obvious hint about such behavior can also be taken from studies of gamma-irradiated Ge; see below.

3.2. Gamma-Irradiation of Si and Ge

As indicated above, ^{60}Co gamma-irradiation of Si and Ge appears to be equivalent in some respects to internal 760 keV electron irradiation. Frenkel pairs as primary defects are produced in the crystal lattice at random and, therefore, bulk samples can be used because of a weak absorbance of gamma-photons at an average energy at 1.25 MeV. In Fig. 4 some typical data on the removal rates of the shallow donor and acceptor states in the gamma-irradiated Si and Ge are displayed. It is astonishing that the situation concerning the removal rates appears to be very similar for the both semiconductors, especially for the p-type materials. Together with this, it may be worth noting that in the boron-doped Si (FZ) the removal rate of the shallow acceptor states indicated in Fig. 4a turned out to be slightly varied over a wide range of impurity concentration from 6×10^{15} cm^{-3} down to 7×10^{13} cm^{-3} [22]. Effective interactions of boron atoms with primary defects in gamma-irradiated p-Si (FZ) has been traced even at a few 10^{13} cm^{-3}, though with lower rates, $\approx 5 \times 10^{-5}$ cm^{-1}. By comparison the calculated production rate of Frenkel pairs in gamma-irradiated Si, $\eta_{FP} \approx 5 \times 10^{-3}$ cm^{-1} (taking $E_{th}^{ave} \approx 35$ eV), to the removal rates of the shallow donor and acceptor states experimentally defined one can conclude that the fraction of dissociated Frenkel pairs equals $\xi \approx 0.5$ or slightly less in the n-Si (FZ) and about $\xi \approx 0.07$ in the p-Si (FZ) when taken into account that mobile vacancies and self-interstitials are trapped by the boron impurity atoms.

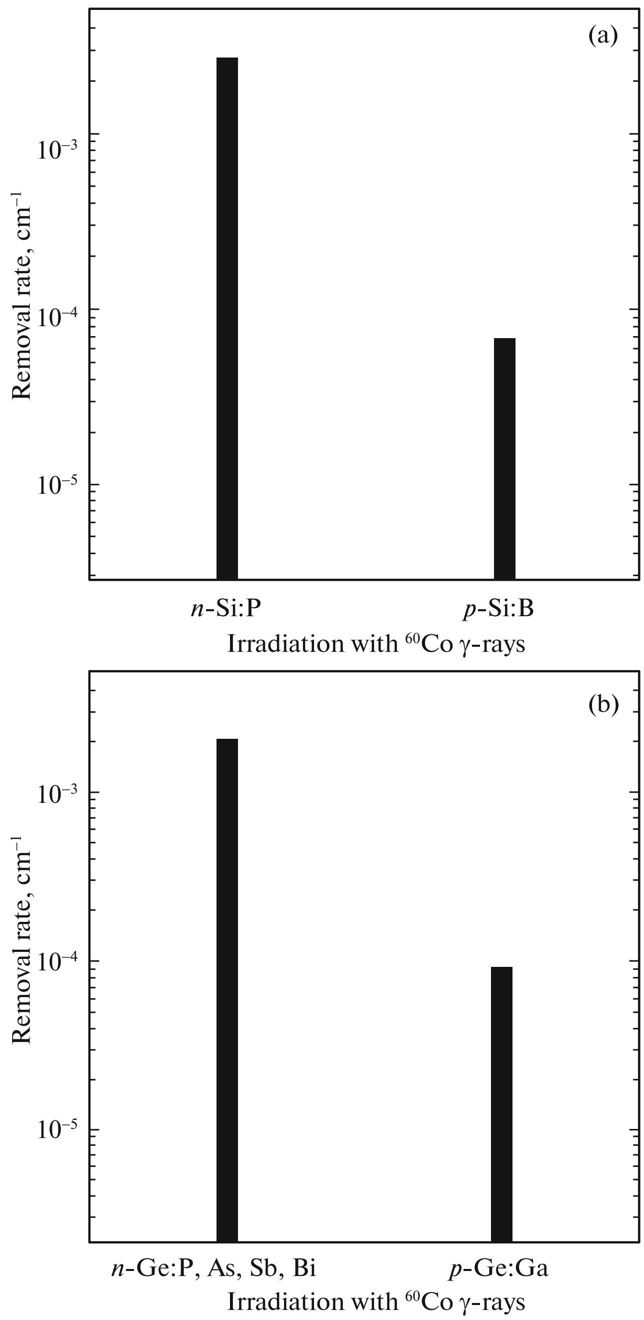

Fig. 4. (a) Removal rates of the shallow donor or acceptor states in the oxygen-lean moderately doped *n*- and *p*-Si irradiated with ^{60}Co gamma-rays. (b) Removal rates of the shallow donor or acceptor states in the oxygen-lean moderately doped *n*- and *p*-Ge irradiated with ^{60}Co gamma-rays. Removal rates in the moderately doped *n*-Ge with impurity concentrations close to $\approx 1 \times 10^{16}$ cm^{-3} are indicated.

Similarly to fast electron irradiation of *n*-Ge, in the case of the gamma-irradiated materials the removal rate of group-V shallow donor states shows a marked rise with the increasing dopant concentration, too [17, 18], so the maximal rate observed in the moderately doped *n*-Ge, $n \approx 1 \times 10^{16}$ cm^{-3}, is indicated in Fig. 4b. Unfortunately, the identification of secondary impurity-related defects in Ge is yet controversial [23]. As a consequence, the removal rates given in Fig. 4b must be taken as such. With this in mind, the maximal fraction of dissociated Frenkel pairs in the gamma-irradiated *n*-Ge taking $E_{\rm th}^{\rm ave} \approx 28$ eV is believed to be large, $\xi \approx 0.8$. In other words, in moderately doped *n*-Ge a large fraction of isolated vacancies getting free from all the dissociated Frenkel pairs with $r \geq r_c$ is believed to be trapped by the group-V impurity atoms, whereas with the decreasing concentration of the dopants this fraction for the *n*-Ge ($n \approx 5 \times 10^{13}$ cm^{-3}) drops to $\xi \leq 0.1$; the remainder is lost via indirect annihilation or at sinks.

Consistent with a low removal rate of the shallow acceptor states in the gamma-irradiated gallium-doped *p*-Ge being close to 1×10^{-4} cm^{-1} [24], low removal rates have also been evidenced in irradiated *p*-Ge doped with transition metals. In actual fact, the first acceptor states of the copper in *p*-Ge:Cu, at $E_V + 0.04$ eV, and the first acceptor states of the gold in *p*-Ge:Au, at $E_V + 0.15$ eV, were found to be lost with the same low rates in the course of ^{60}Co gamma-irradiation [25, 26]. Another convincing evidence has been provided the behavior of *n*-Ge subjected to $n \rightarrow p$ conversion of conductivity type during ^{60}Co gamma-irradiation when the production of primary defects falls by one order-of-magnitude by shifting the Fermi level in the lower half of the band gap [22].

Taking into consideration that the removal rates in the electron-irradiated *n*-Si and *p*-Si given in Fig. 3a are significant and comparable, the small removal rate in the gamma-irradiated *p*-Si should be related to an increasing fraction of annihilated Frenkel pairs. There are grounds for believing that two factors may be responsible. First, the electronic excitation level during gamma-irradiation is lower by several orders-of-magnitude as compared to that of pulsed electron irradiation, so unfavorable charge states of primary defects may produce detrimental effects enhancing annihilation processes of Frenkel pairs and, second, the mean distance between the components of Frenkel pairs in the ^{60}Co gamma-irradiated materials is thought to get closer to the annihilation radius r_c.

3.3. Proton Irradiation of Si and Ge

Proton irradiation of Si and Ge is widely used for passivation of electrical active impurities and structural defects as well as in SMART technology. This kind of irradiation also attracts much attention of researchers who are engaged into investigations of degradation processes in detector-grade materials. Experimental information coming from studies of defects produced in Si after proton irradiation at a few MeV implies that there are much similarities in defect

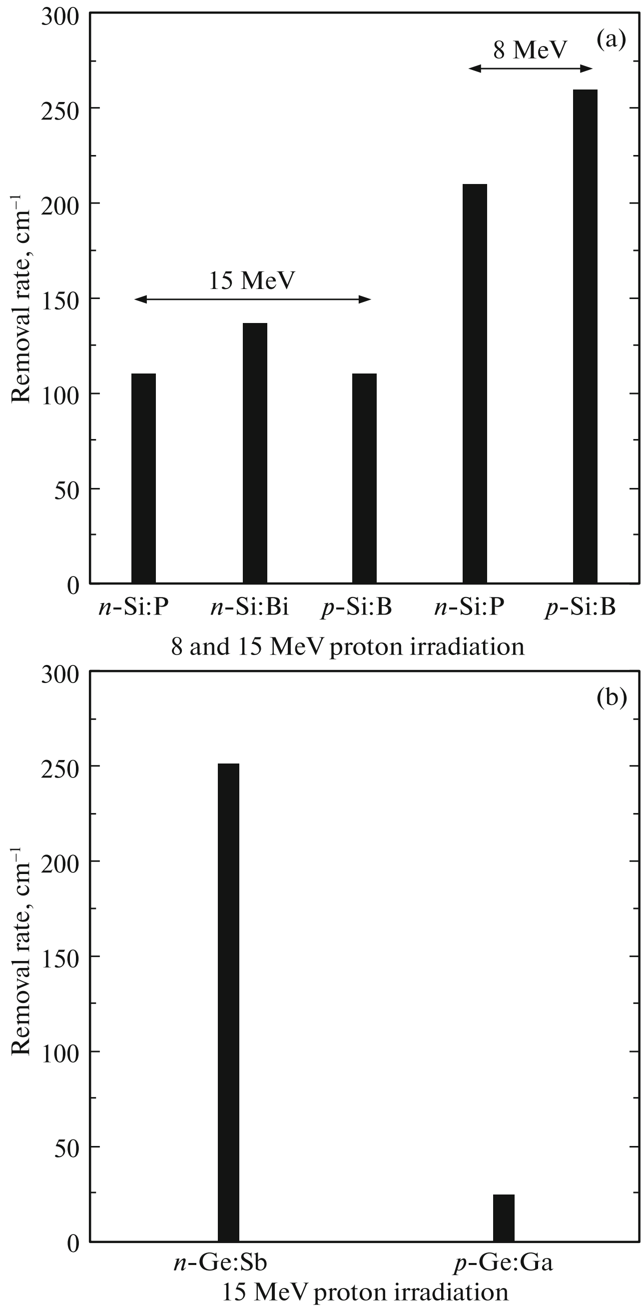

Fig. 5. (a) Removal rates of the shallow donor or acceptor states in the oxygen-lean moderately doped n- and p-Si irradiated with 8 and 15 MeV protons. The scatter in the data is within 10 percent. (b) Removal rates of the shallow donor or acceptor states in the oxygen-lean moderately doped n- and p-Ge irradiated with 15 MeV protons. The scatter in the data is within 10 percent.

formation processes under electron and proton irradiation; see for instance [27]. Based on the NIEL scaling a serious effort was mounted to construct a model that could be able to calculate, say, the leakage current constant for transistors and diodes under irradiation with various particles types and energies [3]. However, it was found that the NIEL scaling is significantly violated in the case of 10 MeV protons as suggested due to an increasing role of clustered defects. In Fig. 5a the removal rates of the proton-irradiated Si are shown. At first sight these data seem to resemble the results presented in Fig. 3a for the electron-irradiated materials, though with much enhanced removal rates. One may think that such similarities are related to the same defect reactions in proton- and electron-irradiated Si for the most part and the contribution of clustered defects is of minor importance, just in accordance with the concept often met in literature. But recent analysis of electrical data obtained on n-Si (FZ) doped with phosphorus evidenced that for the 8 and 15 MeV protons the damage model should be more complicated, since the loss of shallow donor states turned out to be much higher than the concentration of radiation-produced acceptors [28]. It means that, along with the formation of vacancy-phosphorus atom pairs, the well-known E-centers, there are other effective reaction paths of primary defects with the dopant. This may be a plausible reason why the use of the reaction scheme observed in electron-irradiated Si for the 10 to 20 MeV proton irradiation gives rise to a pronounced violation of the NIEL scaling [3].

Again, in the case of proton irradiation of Ge there is a striking difference in the removal rates of the shallow donor and acceptor states in the n- and p-type materials, as is seen in Fig. 5b, and, therefore, this distinction in the production of primary defects turned out to be characteristic for all types of irradiation. Together with this, the reaction paths of primary defects with the shallow donors were found to be rather different from what is usually observed in the case of electron- and gamma-irradiation; see for instance [29]. Thus, one can see that the proton irradiation of both Si and Ge initiate new formation processes of impurity-related defects.

4. CONCLUSIONS

A comparative study of radiation damage in Si and Ge irradiated with protons, electron and gamma-irradiation has been carried out in the present work. Losses of the shallow donor and acceptor states due to interactions of group-V and group-III impurities with vacancies and self-interstitials in irradiated Si and Ge were used for characterization of the damage. The removal rates of the shallow donor and acceptor impurity-related states in moderately doped materials under irradiation were investigated. These general characteristics allow one to get a look into interactions between primary radiation defects and impurity atoms without taking into consideration the atomic structures of secondary complexes and their charge states. This, in turn, permits one to estimate the fraction of Frenkel pairs dissociated into isolated vacancies and self-interstitials in Si and Ge under various irradiation conditions.

The removal rates of the shallow impurity states in the Si doped with P, Bi, B, and Ga turned out to be rather comparable under 0.9 MeV electron irradiation. Together with this, they proved to be comparable to the rate of interactions of vacancies with electrically inactive oxygen atoms. This allows one to reliably estimate the fraction of dissociated Frenkel pairs to be $\xi \approx 0.1$. This fraction increases to $\xi \approx 0.35$ with the increasing electron energy from 0.9 to 3.5 MeV. The situation with electron-irradiated Ge was found to be strongly different from that observed in Si. The removal rate of the shallow donor states in *n*-Ge doped with various group-V impurities is larger at least by an order-of-magnitude than that found in electron-irradiated *p*-Ge doped with Ga. It has been demonstrated that it is also true for the gamma- and proton irradiation despite an impressive difference of the removal rates in the irradiated *n*-Ge being many orders-of-magnitude. The main reason of such behavior is believed to be a leading role of spontaneous annihilation of Frenkel pairs due to unfavorable charge states of the components in material of *p*-type, no matter which acceptor states provide the hole conductivity (group-III impurities, transition metals, or radiation defects). In sharp contrast, our experimental results evidenced that primary intrinsic defects are effectively trapped by the group-V impurity atoms, so the fraction of dissociated Frenkel pairs in moderately doped *n*-Ge ($n \approx 10^{16}$ cm^{-3}) may be as large as $\xi \approx 0.8$ under the 0.9 MeV electron and ^{60}Co gamma-irradiation. In actual fact, this provides a natural explanation for an effect of $n \rightarrow p$ conversion of conductivity type observed in irradiated *n*-Ge. On the other hand, comparable removal rates of shallow impurity states in electron-irradiated Si (FZ) make possible shifting the Fermi level to the middle of the bandgap in both *n*- and *p*-type materials and, thus, generally speaking, irradiated Si is prone to being intrinsic. Nonetheless, the seemingly same behavior of both materials under ^{60}Co gamma-irradiation needs a deeper insight into the behavior of the components of Frenkel pairs. The fate of primary defects like Frenkel pairs under irradiation conditions is typically believed to be governed by Coulomb and elastic interactions between their components. We think that anisotropic strain-induced polarization effects associated with these defects should be included as an important part into consideration, too; see in this connection [18].

The removal rates of the shallow donor and acceptor states of group-V and group-III impurities in Si and Ge subjected to proton irradiation at 8 to 15 MeV turned out to be similar in their appearance to those observed in the case of electron-irradiated Si and Ge, though on a strongly increasing scale. In spite of these similarities, one should take into consideration that the processes resulting in losses of the shallow donor states in proton-irradiated oxygen- and carbon-lean *n*-Si and *n*-Ge proved to be rather different from those in electron-irradiated materials. In this respect, a sophisticated modeling of defect production processes making use of the classical NIEL model amplified by MD simulations for better description of collision cascades may be helpful [4].

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