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Bismuth-related defects in n-type silicon irradiated with protons: A comparison to similar defects formed under electron irradiation

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ABSTRACT

Electrical properties of defects produced in strongly bismuth-doped silicon by 15 MeV protons are investigated in detail. Electrical measurements on irradiated samples by means of the van der Pauw technique are conducted over a wide temperature range of 20–300 K to furnish information on radiation-produced complexes. It is shown that the properties of the dominant bismuth-related defects are the same as earlier found in the electron-irradiated material. These complexes are tentatively identified as bismuth–vacancy pairs being deep donors. Their atomic configuration appears to be radically different from what is known about similar vacancy-related defects with other group-V impurities. These bismuth-related pairs are stable up to $T \approx 300\,°C$. Some special features of defect formation and annealing processes of radiation defects in bismuth-doped silicon subjected to electron and proton irradiation are discussed. This information may be of advantage in modeling impurity-related complexes containing oversized impurity atoms in silicon.

I. INTRODUCTION

Phosphorus as the principal donor impurity in commercial silicon has been much studied. This is also true for phosphorus-related defects in Si. Among them, there are phosphorus–vacancy pairs [P–*V*], whose deep acceptor states are primarily responsible for electrical properties of moderately and strongly doped materials subjected to irradiation with MeV electrons and protons. The bismuth dopant has recently attracted considerable interest because of its unique characteristics. The presence of a large nuclear spin together with a high hyperfine splitting of these impurity atoms may be particularly inviting for silicon-based quantum information processing; cf $I = 1/2$ and $A = 117.53$ MHz for P against $I = 9/2$ and $A = 1475.4$ MHz for Bi. However, our knowledge of the nature of bismuth-related defects in Si is modest up to now. By way of illustration, theoretical consideration put forward some solid arguments that the atomic structure of bismuth–vacancy pairs, [Bi–*V*], may be rather different from what is known for similar vacancy complexes with other group-V impurities in Si (cf Fig. 1, left and right).

Very recently, we touched on this issue by carrying out the Hall effect and conductivity measurements on Bi-doped silicon samples irradiated with fast electrons.[2] Such electrical measurements taken over a wide temperature range where shallow donors are gradually ionized up to their saturation plateau furnish a research tool for studying changes in the total concentrations of the shallow donor states and compensating acceptors. Some important conclusions based on the analysis of experimental data have been drawn. First, heavy losses of the shallow donor states were found in electron-irradiated n-Si:Bi. Similar effects are also observed in electron-irradiated n-Si doped with phosphorus.[3] It is generally thought that this observation is brought about by interactions

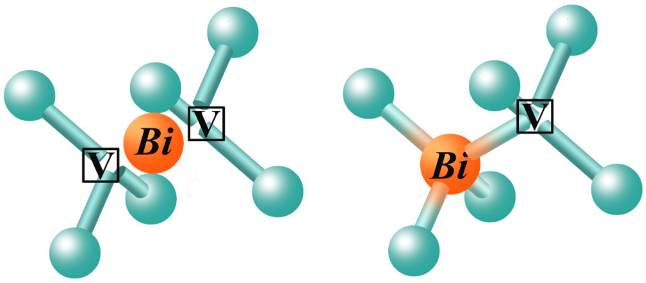

FIG. 1. The impurity atom-vacancy pair in two possible atomic configurations incorporating a split vacancy (left) and a full vacancy (right). The latter atomic configuration has been established for phosphorus–vacancy, arsenic–vacancy, and antimony–vacancy pairs in Si. The former one is considered to be preferable for an oversized bismuth impurity atom in Si.[1]

between positively charged donors and negatively charged vacancies, mobile at room temperature, where the resulting product may be visualized as phosphorus–vacancy complexes, [P–V]. The latter defects have been reliably established and investigated by Electron Paramagnetic Resonance (EPR) and Electron-Nuclear Double Resonance (ENDOR).[4] Later, the vacancy-related family in electron-irradiated n-Si was supplemented with arsenic–vacancy pairs and antimony–vacancy pairs, [As–V] and [Sb–V], respectively.[5] In all the complexes, the vacancy assumes the nearest lattice site with respect to the impurity atom in the so-called full vacancy configuration (see Fig. 1, right). The defects under discussion have single net acceptor levels around $\approx E_C - 0.4$ eV, where E_C is the bottom of the conduction band. As a consequence, they are electrically active in the n-type material. This makes them readily accessible for investigation by Deep Level Transient Spectroscopy (DLTS) (see, for instance, Refs. 5–9).

The observed disappearance of the shallow donor states in electron-irradiated n-Si:Bi is believed to be bound by vacancy trapping, leading to the formation of bismuth–vacancy pairs. In contrast to the complexes containing the abovementioned group-V impurity atoms, theory settles a compelling argument over another possible vacancy configuration in this defect taking into account that the tetrahedral covalent radius of the bismuth atom is substantially larger than that of the silicon atom, cf $R_{\mathrm{Bi}} = 1.51$ Å against $R_{\mathrm{Si}} = 1.16$ Å.[10] The vacancy in the bismuth–vacancy pair appears energetically favorable if the impurity atom is located at the saddle point between two semi-vacancies in the so-called split vacancy configuration (see Fig. 1, left). The electrical activity of this defect remains an open question.

Detailed electrical measurements made it apparent that the dominant defects formed in electron-irradiated n-Si doped with Bi turned out to be electrically neutral in an n-type material, in sharp contrast to the known electrical activity of other vacancy-related pairs containing group-V impurities.[11] Moreover, these defects in electron-irradiated n-Si:Bi display a well-marked anisotropy of electrical conductivity, not seen in electron-irradiated n-Si:P. The experimental information provided so far bears witness to the validity of the predicted model of the [Bi–V] complex in Si. To our opinion, this complicated problem invites further investigations.

The present paper is aimed at lending additional support to the defect model earlier considered for electron-irradiated n-Si:Bi. For this purpose, 15 MeV proton irradiation is used as a different damaging factor in the production of bismuth-related complexes.

II. EXPERIMENTAL

Initial square-shaped samples of $5 \times 5\,\mathrm{mm}^2$ were cut from a strongly doped n-Si:Bi ingot of high quality earlier used in the studies of electron-irradiated samples. The charge carrier concentration prior to proton irradiation was about $n \approx 2 \times 10^{16}\,\mathrm{cm}^{-3}$. Before irradiation, the compensation ratio $K = N_D{}^0/N_A{}^0$ was very small being of a few percent. As a consequence, the electron mobility at cryogenic temperatures was found to be very high, around $4 \times 10^4\,\mathrm{cm}^2/\mathrm{V\,s}$ at $T \approx 30$ K. This fact allows one to assume that the role of residual acceptors in initial n-Si:Bi samples may be neglected.

Samples were subjected to irradiation with a 15 MeV proton pulsed beam whose frequency was 100 cps. The duty cycle was 2.5 ms. The average current was kept low, not exceeding $100\,\mathrm{nA/cm}^2$, so the irradiation temperature did not exceed 30 °C. Our estimates showed that the proton energy is high enough to pass through the irradiated samples 0.3 to 0.4 mm thick without noticeable effects of passivation.

Isochronal annealing studies of irradiated samples were carried out in steps of $\Delta T = 40$ °C and $\Delta t = 10$ min, setting the reference temperature of electrical measurements at $T = 20$ °C. It is well known that vacancy-related complexes with group-V impurity atoms of P, As, and Sb can be annealed out during isochronal anneals at temperatures around $T = 200$ °C.[11] Preliminary experiments on proton-irradiated n-Si:Bi told us that Bi-related defects are stable up to $T \approx 300$ °C and, hence, annealing studies at higher temperatures have received much consideration.

Curves of the temperature dependence of the charge carrier concentration and mobility, $n(T)$ and $\mu_e(T)$, for initial and irradiated samples were gained in the course of the Hall effect and electrical conductivity measurements over a wide temperature range of $T \approx 20$–300 K. Electrical measurements were conducted in the van der Pauw geometry. Conductivity measurements on a square-shaped sample are consecutively taken on adjacent contacts placed in the corners of the sample, i.e., in different directions; for details of electrical measurements, see Ref. 2. Conductivity values for initial samples appear to be slightly varied because of small irregularities in the shape and thickness of each sample as well as electrical contact positions. As a result, curves of conductivity vs temperature are slightly shifted relative to each other, very clearly seen at cryogenic temperatures. In all cases, such a shift of conductivity curves for samples before irradiation was found to be small, around 5%. Consequently, this is also true for the mobility data (see below). An insignificant splitting of the curves points to the fact that dopant atoms in initial samples are distributed homogeneously. Optical investigations of bismuth-doped silicon in a concentration range of 10^{14}–$10^{16}\,\mathrm{cm}^{-3}$ lend additional support for the conclusion.[12–14]

Analysis of experimental curves of $n(T)$ offers direct information on the *total* concentration of the shallow donor states belonging to the substitutional bismuth atoms, N_D, and separately the *total* concentration of all acceptors compensating these shallow donors, N_A. Variations in N_D and N_A values due to proton irradiation and subsequent annealing allow one to give a running account of quasi-chemical reactions of electrically active defects, first the substitutional bismuth atoms. The relevant equation of charge balance over a temperature interval where the shallow donors are ionized can be derived making use of the statistics of charge carriers in a non-degenerated semiconductor,

$$\frac{n + N_A}{N_D - N_A - n} = N_C\left(T^{3/2}\right)\frac{\exp\left(-\frac{E_D}{kT}\right)}{2 + 10\,\exp\left(-\frac{\delta}{kT}\right)},$$

where $N_C = N_C(T^{3/2})$ is the effective density of states in the conduction band of silicon and k is Boltzmann's constant. The $1s$ ground state of the substitutional bismuth atoms in the crystal field is known to be split into the singlet (A_1), doublet (E), and triplet (T_2) states whose energy levels with respect to the conduction band are given by optical measurements.[15] In our calculations, the ionization energy E_D of the $1s(A_1)$ states is determined from the exponential slope of experimental $n(T)$ curves at cryogenic temperatures. The value of δ, the splitting between the $1s(A_1)$ ground states and higher lying $1s(E) + 1s(T_2)$ states, is taken from optical measurements reasonably believing that an additional splitting ζ between the $1s(E)$ and $1s(T_2)$ ground states can be neglected because of $\delta >> \zeta$. In accordance with this model, the degeneracy factors $g_1 = 2$ and $g_2 = 10$ including the electron spin are referred to the $1s(A_1)$ and $1s(E) + 1s(T_2)$ ground states, respectively. Other details of measurements and calculations have comprehensively been described in the literature; see, for instance, textbooks.[16,17]

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Defects produced in bismuth-doped material under 15 MeV proton irradiation

The main effect of proton irradiation of bismuth-doped silicon is a very pronounced decrease in the charge carrier concentration at room temperature. Simple compensation of electron conductivity by radiation-produced acceptors takes place, but heavy losses of the shallow donor states of the substitutional bismuth atoms in the irradiated samples play a key role in the observed effect.

We now turn to the results of analysis of the $n(T)$ curves shown in Figs. 2(a) and 2(b). As is seen, after the 15 MeV proton irradiation at a fluence of $\Phi = 8 \times 10^{13}$ cm^{-2}, the total concentration of the shallow donor states substantially decreases from $N^0_{\mathrm{Bi}} = 1.6 \times 10^{16}$ cm^{-3} before the irradiation to $N^{\mathrm{irr}}_{\mathrm{Bi}} = 5.4 \times 10^{15}$ cm^{-3} in the irradiated n-Si:Bi, i.e., by $\Delta N_{\mathrm{Bi}} \approx 1 \times 10^{16}$ cm^{-3}. At the same time, the total concentration of all compensating acceptors increases by $\Delta N_{\mathrm{A}} \approx 3 \times 10^{15}$ cm^{-3} only. Two important conclusions can be deduced from these data. First, the observed loss of the shallow donors is brought on by interactions of the substitutional Bi atoms with primary defects (free vacancies or self-interstitials generated during the proton irradiation). Second, the dominant bismuth-related complexes were found to be an electrically neutral n-type material. Similar effects were earlier observed for electron-irradiated n-Si:Bi, too.[2]

Let us logically argue for trapping mobile vacancies by substitutional bismuth atoms in irradiated silicon. Two points should be taken into consideration. Oversized impurity atoms may be susceptible to trap a mobile vacancy, reducing a strain field associated with them in the crystal lattice. Furthermore, Coulomb attraction

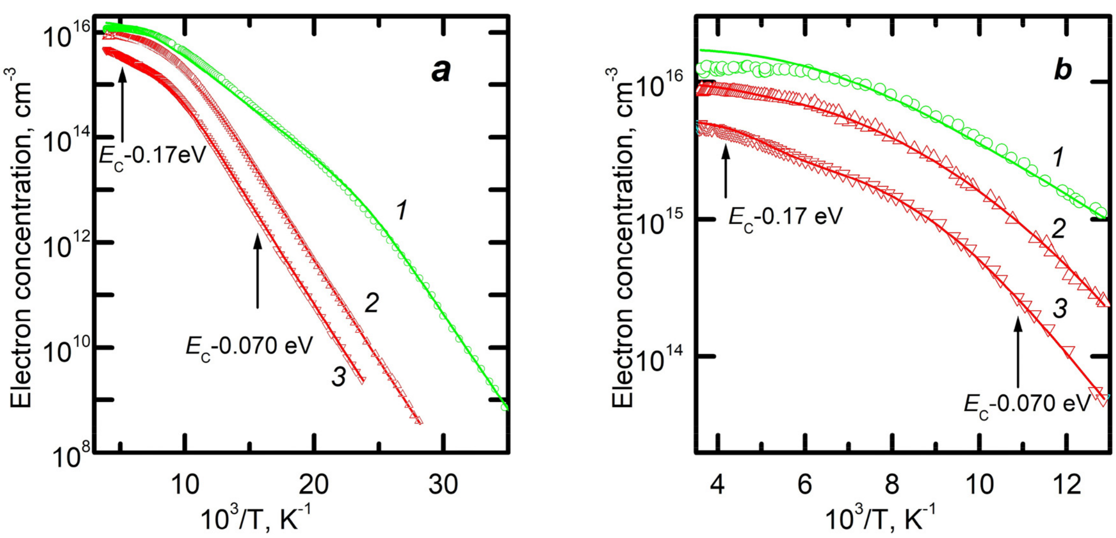

FIG. 2. Charge carrier concentration vs reciprocal temperature for the strongly doped *n*-Si(FZ):Bi irradiated with 15 MeV protons at room temperature (a). Fragments of the $n(10^3/T)$ curves are shown on the expanded temperature scale at $T > 78$ K (b). Points, experimental (in color online); curves, calculated. Points: *1*, initial (green circles); *2*, irradiated at a fluence of $\Phi = 4 \times 10^{13}$ protons/cm^2 (red triangles up); *3*, irradiated at a fluence of $\Phi = 8 \times 10^{13}$ protons/cm^2 (red triangles down). Effective ionization energies of shallow donors as well as radiation-produced defects are indicated.

between negatively charged vacancies and positively charged impurity atoms can greatly enhance the formation of such bismuth–vacancy pairs. This concept has been widely used as a starting point for modeling electrically active defect complexes in irradiated n-Si with group-V impurities.[4–9] With one exception, these bismuth-related pairs do not possess any deep acceptor levels, presenting a striking contrast to other vacancy-related pairs containing group-V impurities (P, As, and Sb).

One more remark needs to be made in relation to free isolated self-interstitials concurrently produced with free vacancies because of the dissociation of primary radiation defects (Frenkel pairs). These defects are mobile at room temperature. Their interactions with residual substitutional oxygen and carbon atoms in floating-zone n-Si may assume a secondary role owing to their low concentrations. In addition, they are known to be electrically inert in the Si crystal lattice. Theoretical calculations suggest that they can form pairs of two self-interstitials and other complexes that are predicted to be electrically neutral in n-Si.[18] Their presence is conceivably manifested itself by the formation of deep acceptors at high annealing temperatures, at $T \geq 400$ °C (see below).

The next point of interest is the nature of the radiation-produced defects whose energy levels around $E_C - 0.17$ eV are clearly detected in n-Si:Bi (see Fig. 2). It is thought that they are oxygen-vacancy complexes (the so-called A-centers), taking into account the presence of residual oxygen in noticeable amounts. It is well known that oxygen atoms can trap mobile vacancies forming oxygen-vacancy pairs whose acceptor states are just placed at $\approx E_C - (0.16 \pm 0.01)$ eV.[19–21] Earlier, we have presented evidence that similar defects in electron-irradiated n-Si:Bi were proved to be of acceptor type. Together with this, they appear to be dominant among all radiation-produced acceptors. Their contribution in the proton-irradiated n-Si:Bi is also very much more pronounced, up to 80% of the N_A values.

Of course, a marked difference between two kinds of the damaging factors manifests itself in the removal rates of the shallow donor states under discussion, $\eta_{Bi} = \Delta N_{Bi}/\Phi \approx 320\ \mathrm{cm}^{-1}$ and $\eta_{Bi} \approx 0.3\ \mathrm{cm}^{-1}$ for 15 MeV proton and 0.9 MeV electron irradiation, respectively. It is pertinent to note that these removal rates η_{Bi} are referred to the beginning of the proton and electron irradiation. For prolonged proton irradiation, the averaged removal rate is usually decreased, say, to $\eta_{Bi} \approx 120\ \mathrm{cm}^{-1}$ at $\Phi = 8 \times 10^{13}\ \mathrm{cm}^{-2}$. Such an effect may be expected because of the dwindling reservoir of free substitutional Bi atoms as traps for intrinsic defects in the course of irradiation. A similar effect of the removal rate decreasing from $\eta_{Bi} \approx 0.3$ to $0.08\ \mathrm{cm}^{-1}$ at $\Phi = 8 \times 10^{16}\ \mathrm{cm}^{-2}$ was noted for electron irradiation, too.[2]

The production rate of A-centers under the proton irradiation was found to be close to $\eta_A \approx 30\ \mathrm{cm}^{-1}$ over the whole fluence range used, since the residual oxygen concentration may be larger than the concentration of the shallow donors by a factor of 2 or 3.

We have not yet touched on why the initial removal rate of shallow donor states in n-Si:Bi turned out to be substantially larger than that observed in n-Si:P under the same irradiation conditions. In actual fact, the ratio of η_{Bi}/η_P is about 3 in the case of 0.9 MeV electron irradiation. A similar ratio was found to be around this value for the 15 MeV proton irradiation as well. We do not think that it may be accidental in all strongly doped samples, $n \geq 10^{16}\ \mathrm{cm}^{-3}$. Two competitive processes of the production of free mobile intrinsic defects and their indirect annihilation by the encounter of opposite intrinsic defects or defect complexes take place during electron or proton irradiation at room temperature. Defect complexes, say, vacancy-impurity pairs, may have an energy barrier for the trapping of self-interstitials. A strain field associated with [Bi–V] pairs due to their specific atomic configuration is thought to hinder the trapping of self-interstitials, and, therefore, it enhances the pair formation (see Fig. 1, left).

B. Charge carrier mobility in bismuth-doped n-Si subjected to 15 MeV proton irradiation

We are coming now to the discussion of the behavior of the charge carrier mobility, $\mu_e(T)$, in the proton-irradiated n-Si:Bi. Our concern is only a temperature range of $25\ \mathrm{K} < T < 78\ \mathrm{K}$ where the scattering of charge carriers by acoustic phonons takes on a secondary role as compared to that by ionized centers if their concentration appears to be sizeable. It is just the case of the irradiated samples where the concentration of negative charged A-centers compensating the shallow donors was found to be of order of $10^{15}\ \mathrm{cm}^{-3}$. As a consequence of the increasing Coulomb scattering, a marked drop in the mobility after the irradiation of n-Si:Bi is observed. This effect is reasonable to expect.

Figure 3 (red circles) displays the behavior of the charge carrier mobility at cryogenic temperatures in n-Si:Bi prior to and after proton irradiation. As already stated in Sec. II, a marginal

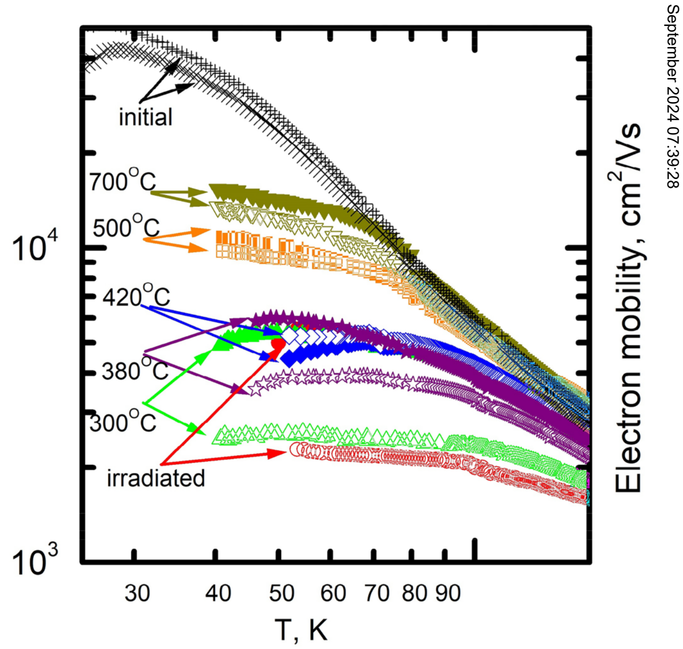

FIG. 3. Charge carrier mobility vs temperature for the strongly doped n-Si(FZ):Bi irradiated with 15 MeV protons at room temperature and then subjected to isochronal annealing. Fluence Φ, protons/cm^2: 8×10^{13}. Points at some annealing steps, experimental (in color online): the annealing temperatures at the steps are given on the left.

splitting of the mobility curve before the irradiation is due to the known irregularities of the sample being inherent in the van der Pauw technique. A dramatical feature of the $\mu_e(T)$ curve being split into two branches just after the proton irradiation is of particular interest. There can be no doubt that the observed splitting is radiation-induced. Annealing steps at $400\,°C \leq T \leq 500\,°C$ bear a direct relation to a progressive recovery of the mobility accompanied with the pulling of both branches together. The complete disappearance of bismuth–vacancy pairs at $T \geq 500\,°C$ regains the splitting of the mobility branches to their original shape. It has been just the issue that helped us in revealing a pronounced anisotropy of the mobility after the electron irradiation of the same Bi-doped material, too.[2] This component of the scattering is believed to be related to a strain field associated with bismuth–vacancy complexes, which were proved to be an electrically neutral n-type material. It will be recalled that in the case of phosphorus, the impurity atom in the complex is known to hold its substitutional position and no noticeable anisotropy of the charge carrier mobility is observed, whereas the atomic configuration of bismuth atom-vacancy pairs is suggested to be rather different and a profound anisotropy effect is produced (see Fig. 1 and Ref. 2).

Isochronal anneals allow one to determine the temperature range when these complexes can be destroyed. Details of the annealing processes of bismuth–vacancy pairs remain unknown. During anneals, the complexes may undergo some atomic rearrangements before their dissociation. This point should be given more attention of theory. Recently, a successful example of such a theoretical approach has been provided for 2D InBi.[22] In addition, non-uniform distributions of primary defects during the irradiation of silicon with protons and electrons of high energy present some challenging questions of contemporary simulation modeling (see, for instance, Refs. 23 and 24).

C. Defect annealing in bismuth-doped n-Si subjected to 15 MeV proton irradiation

As an illustration, Fig. 4 demonstrates some $n(T)$ curves taken in the course of the 15 MeV proton irradiation and subsequent annealing.

Our analysis of the data permits us to determine how the N_{Bi} and N_A values are changed in a typical n-Si:Bi sample (see Fig. 5). The annealing stage of Bi–V complexes after the 15 MeV proton irradiation shows a pronounced recovery shift to higher temperatures by $\Delta T_{ann} \approx 80\,°C$ as compared to the annealing stage in the same electron-irradiated material. This effect may be attributed to an inhomogeneous distribution of vacancies along the proton tracks, contrary to the vacancy generation under fast electron irradiation. The observed splitting of the mobility branches upon

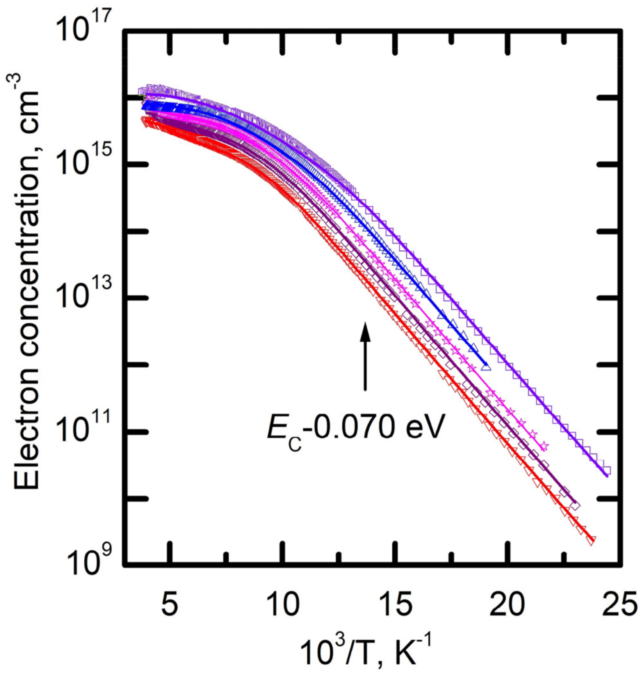

FIG. 4. Charge carrier concentration vs reciprocal temperature for the strongly doped n-Si(FZ):Bi irradiated with 15 MeV protons at room temperatures and then subjected to isochronal annealing. Points, experimental; curves, calculated. Fluence Φ, protons/cm^2: 8×10^{13}. Points: irradiated (red triangles down); annealed at $T = 260\,°C$ (purple rhombi); annealed at $T = 380\,°C$ (magenta stars); annealed at $T = 420\,°C$ (blue triangles up); annealed at $T = 500\,°C$ (violet squares). Effective ionization energies of shallow donors are indicated.

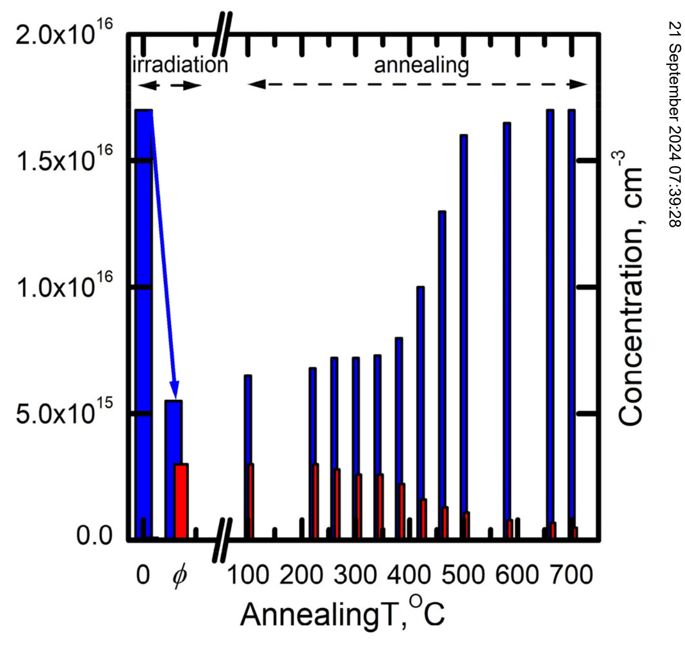

FIG. 5. Total concentrations of the shallow donor states (N_D) and deep acceptor states (N_A) for the strongly doped n-Si(FZ):Bi irradiated with 15 MeV protons vs annealing temperature at some steps. Fluence Φ, protons/cm^2: 8×10^{13}. Concentrations of N_D and N_A are indicated by blue and red bars, respectively (in color online). The arrow shows how the total concentration of the shallow donor states of the substitutional bismuth atoms dropped after the proton irradiation.

annealing is seen to retain up to $T \approx 340\,°C$. The annealing process of Bi–vacancy pairs terminates around $T = 460\,°C$. It should be noted that oxygen-vacancy pairs are known to be annealed out at $T \approx 400\,°C$. Nonetheless, the concentration of deep acceptors remains appreciable and the charged carrier mobility does not returned to the initial one even after an anneal at $T \approx 700\,°C$. A similar effect has been seen in electron-irradiated n-Si:Bi as well.[2]

To close this section, let us take an inquiring look at the present situation with oversized impurities in silicon. In this connection, it might be instructive to make mention of the paper devoted to EPR studies of the tin–vacancy complex in irradiated p-Si.[21] The tin impurity atom is large and heavy like the bismuth atom. Its tetrahedral covalent radius is $R_{Sn} = 1.39$ Å that is substantially larger than that of silicon, $R_{Si} = 1.16$ Å. In silicon crystals, tin atoms are located at the normal lattice sites being very effective traps of isolated vacancies in electron-irradiated Si. As a consequence, the formation of tin–vacancy pairs [Sn–V] displaying the distorted octahedral symmetry (D_{3d}) takes place. Theoretical calculations suggest that the defect should be amphoteric, having acceptor and donor states.[1] Similar characteristic features of the energy spectra are also predicted to be held for such tin–divacancy related defects such as [Sn–V_2] and [Sn_2–V_2].[25]

A model consistent with the EPR results for the tin–vacancy pair bears a resemblance to the atomic configuration of the bismuth–vacancy pair with one exception: there is no sign of the amphoteric behavior of the defect under discussion taking into consideration the relationship between the ΔN_D and ΔN_A values in the proton-irradiated samples, $\Delta N_D >> \Delta N_A$ (see above).

Theoretical calculations are made concerted attempts to predict a possibility of split atomic configurations with vacancies among various oversized impurities in silicon. Some logical reasons have been discussed on the basis of lattice relaxations with respect to the stability of vacancy-impurity pairs in Si and Ge.[1] Notwithstanding, it should be used with caution. To cite an example, let us mention the tin and antimony impurity atoms having the same tetrahedral covalent radii, $R_{Sn,Sb} = 1.39$ Å (see Ref. 10). It is worth noting that in electron-irradiated n-Si:Sb, the vacancy is captured by the substitutional antimony atom retaining its normal lattice site in the complex [Sb–V], whereas the tin–vacancy pair displays the split vacancy configuration. Although the calculated relaxation of the nearest neighbors of the substitutional impurity atom increases in the sequence of Sn → Sb → Bi, the configuration of their vacancy-related complexes appears to be different: the split vacancy configuration for Sn and Bi and the full vacancy configuration for Sb.

IV. CONCLUSION

The results obtained in this work demonstrated that heavy losses of the shallow donor states in n-Si:Bi under 15 MeV proton irradiation are due to the formation of bismuth-related defects whose electrical properties were found to be the same as those earlier observed in n-Si:Bi subjected to fast electron irradiation. These dominant defects tentatively identified as bismuth–vacancy pairs possess the features that appear peculiar to the well-known properties of similar vacancy-related complexes containing other group-V donor impurities (P, As, and Sb). In striking contrast, these pairs proved to be electrically neutral in the n-type material. The charge carrier mobility in irradiated samples at cryogenic temperatures displayed a very pronounced anisotropic behavior. It is believed that this effect arises from the scattering of charge carriers by a strain field associated with the neutral Bi-related complexes. The bismuth impurity atom in the pair is located at the saddle point between a pair of semi-vacancies, in accordance with theoretical expectations. This defect configuration is thought to hinder the indirect annihilation of self-interstitials during irradiation, thus substantially increasing the production rate of secondary defects. The thermal stability of bismuth–vacancy pairs was found to be much higher than those of similar complexes with other group-V impurities.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Vadim Emtsev: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Project administration (equal); Supervision (equal); Validation (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal). **Nikolay Abrosimov:** Resources (equal); Validation (equal); Writing – review & editing (equal). **Vitalii Kozlovski:** Investigation (equal); Methodology (equal); Writing – review & editing (equal). **Stanislav Lastovskii:** Data curation (equal); Formal analysis (equal); Investigation (equal); Visualization (equal); Writing – review & editing (equal). **Gagik Oganesyan:** Data curation (equal); Formal analysis (equal); Investigation (equal); Writing – review & editing (equal). **Dmitrii Poloskin:** Data curation (equal); Formal analysis (equal); Investigation (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article.

REFERENCES

[1] H. Höhler, N. Atodiresei, K. Schroeder, R. Zeller, and P. H. Dederichs, Phys. Rev. B **71**, 035212 (2005).

[2] V. Emtsev, N. Abrosimov, V. Kozlovski, G. Oganesyan, and D. Poloskin, J. Appl. Phys. **134**, 025103 (2023).

[3] V. V. Emtsev, N. V. Abrosimov, V. V. Kozlovski, G. A. Oganesyan, and D. S. Poloskin, *Semiconductors* (Pleiades Publishing, Ltd., 2020), Vol. 54, p. 46.

[4] G. D. Watkins and J. W. Corbett, Phys. Rev. **138**, A543 (1965).

[5] E. L. Elkin and G. D. Watkins, Phys. Rev. **174**, 881 (1968).

[6] L. W. Song, B. W. Benson, and G. D. Watkins, Phys. Rev. **33**, 1452 (1986).

[7] L. C. Kimerling, H. M. DeAngelis, and C. P. Carnes, Phys. Rev. B **3**, 427 (1971).

[8]A. O. Evwaraye, J. Appl. Phys. **29**, 476 (1976).
[9]A. O. Evwaraye, J. Appl. Phys. **48**, 734 (1977).
[10]P. Pyykkö, Phys. Rev. B **85**, 024115 (2012).
[11]G. D. Watkins, in *Materials Science and Technology*, edited by R. W. Cahn, P. Haasen, and E. J. Kramer (Wiley-VCH Verlag GmbH&Co.KGaA, 2005), Vol. 4/5, pp. 107–141.
[12]T. Sekiguchi, M. Steger, K. Saeedi, M. L. W. Thewalt, H. Riemann, N. V. Abrosimov, and N. Nötzel, Phys. Rev. Lett. **104**, 137402 (2010).
[13]R. E. George, W. Witzel, H. Riemann, N. V. Abrosimov, N. Nötzel, M. L. W. Thewalt, and J. J. L. Morton, Phys. Rev. Lett. **105**, 067601 (2010).
[14]N. Stavrias, K. Saeedi, B. Redlich, P. T. Greenland, H. Riemann, N. V. Abrosimov, M. L. W. Thewalt, C. R. Pidgeon, and B. N. Murdin, Phys. Rev. B **96**, 155204 (2017).
[15]B. Pajot, *Optical Absorption of Impurities and Defects in Semiconducting Crystals. Hydrogen-Like Centers (Springer Series in Solid-State Sciences)* (Springer-Verlag, Berlin, 2010), Vol. 158, p. 182.
[16]K. Seeger, *Semiconductor Physics* (Springer-Verlag, Wien, 1973).
[17]D. C. Look, *Electrical Characterization of GaAs Materials and Devices* (Wiley, New York, 1989).
[18]A. Carvalho, R. Jones, J. Coutinho, and P. R. Briddon, Phys. Rev. B **72**, 155208 (2005).
[19]L. C. Kimerling, M. T. Asom, J. L. Benton, P. J. Drevinsky, and C. E. Caefer, in *Materials Science Forum*, edited by G. Ferenzi (Trans Tech Publications, Switzerland, 1989), Vol. 38–41, pp. 141–150.
[20]G. D. Watkins and J. W. Corbett, Phys. Rev. **121**, 1001 (1961).
[21]G. D. Watkins, Phys. Rev. B **12**, 4383 (1975).
[22]C. Lundgren, A. Kakanakova-Georgieva, and G. K. Gueorguiev, Nanotechnology **33**, 335706 (2022).
[23]M. Huhtinen, Nucl. Instrum. Methods Phys. Res., Sect. A **491**, 194 (2002).
[24]R. Radu, I. Pintilie, L. C. Nister, E. Fretwurst, G. Lindstroem, and L. F. Makarenko, J. Appl. Phys. **117**, 164503 (2015)..
[25]M. Kaukonen, R. Jones, S. Öberg, and P. R. Briddon, Phys. Rev. B **64**, 245213 (2001).