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Electron- and proton irradiation of strongly doped silicon of p-type: Formation and annealing of boron-related defects

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ABSTRACT

A detailed study of boron-related defects in strongly doped *p*-type silicon subjected to irradiation with 3.5 MeV electrons and 15 MeV protons are carried out by means of electrical measurements over a wide temperature range of $25 \leq T \leq 300$ K. Investigations are aimed at taking a close look into the nature of radiation-produced defects that are stable at room temperature. Data obtained allow one to reveal two types of dominant boron-related complexes, which are attributed to the substitutional boron-interstitial boron pair being neutral in *p*-type Si and the substitutional boron-divacancy complex displaying donor activity. The first type of the defects is very stable and its annealing runs in a temperature region of 500–700 °C. Another type of defect turned out to be stable up to 300 °C. The formation and annealing processes of the boron-related defects appear to be very similar for electron and proton irradiation of *p*-type Si.

I. INTRODUCTION

Most up-to-date dopants in commercial silicon are phosphorus and boron in n- and p-type materials, correspondingly. Both shallow donor and shallow acceptor impurities are well known to be prone to interacting with intrinsic point defects like free vacancies and self-interstitials as primary defects, which can be generated in crystals under external conditions such as heat-treatment, plastic deformation, and irradiation with nuclear particles. These quasi-chemical defect reactions with the primary defects bring up an acute problem of materials science, since electrical and optical properties of silicon materials subjected to fast electron irradiation and energetic protons are changed due to the formation of impurity-related defects, which is called the first-generation complexes, not to mention losses in the dopant concentration pertaining to the impurity interplay, too.

In irradiated *n*-type silicon doped with phosphorus, the impurity atoms form predominantly phosphorus-vacancy pairs stable at room temperature; there is no reliable evidence of the appearance of phosphorus interstitials in electron- and proton-irradiated *n*-Si. In sharp contrast, boron impurity atoms display complicated behavior in *p*-type material. It has long been known that such radiation-produced defects like boron-vacancy pairs and boron interstitials turned out to be unstable at room temperature. As a consequence, experimental studies of these radiation-produced defects in boron-doped Si are usually carried out at cryogenic temperatures. From the aforesaid, it is apparent that electrical properties of *p*-Si subjected to MeV electron irradiation and energetic protons under normal conditions are bound to be determined by other defects, what may be termed the second-generation complexes. However, the annealing behavior of such complexes is as yet little investigated and understood. Nonetheless, some important properties of the boron-interstitial and boron-vacancy pair should be touched on in the introductory section since they are the reactants in formation processes of complexes stable at room temperature.

The model of an interstitial boron in the neutral charge state was first put forward while studying by electron paramagnetic resonance (EPR) radiation-produced defects in boron-doped Si irradiated with 1.5 MeV electrons at 20.4 K.[1] The appearance of these defects in one-to-one correspondence with immobile isolated vacancies suggests dissociation of Frenkel pairs as primary defects and free migration of isolated self-interstitials during the irradiation accompanied with their trapping at substitutional boron atoms. A very similar effect of impurity replacement was observed earlier in the case of irradiated aluminum-doped Si.[2] The impurity replacement of this type has been labeled as the Watkins model. In succeeding years refinement of the experimental techniques[3] as well as the progress of theoretical methods,[4,5] several microscopic models of the boron-interstitial B_i consistent with the EPR results for its intermediate neutral configuration have been considered. It has been established in deep level transient spectroscopic (DLTS) studies that this defect features a negative-U order of its acceptor level at E_C −0.37 eV and donor level at E_C −0.13 eV[3] leaving the neutral charge state as a metastable one. The configuration of interstitial boron $B_i^+ \rightarrow B_i^0 \rightarrow B_i^-$ is associated with some atomic rearrangements, being especially considerable in the negative charge state.[3] This implies an impact upon diffusion processes of boron impurity atoms in Si including the effects under charge carrier injection conditions.[3–6] The annealing kinetics of these defects in p-Si under normal conditions indicate an activation energy close to 0.6 eV that allows their long-range diffusion to sinks or traps.[1,7] The anneal kinetics in irradiated degenerate p-Si ($p > 10^{19}$ cm^{-3}) may be something other than that observed in non-degenerate material.[7]

We now turn our attention to the boron-vacancy pair. The defect model has been deduced from EPR data in electron-irradiated boron-doped Si.[8] The distinguishing feature of the defect structure is that the vacancy assumes a next-nearest site to a substitutional boron atom VB_s, labeled the $2nn$ (C_1) configuration, as proposed by Watkins.[8] This is in striking contrast to a similar aluminum-related complex where the substitutional aluminum atom is a nearest neighbor of the vacancy.[9] The incorporation of boron as a constituent of the complex has later been confirmed by the electron nuclear double resonance (ENDOR) technique.[10] Low-temperature DLTS experiments on irradiated boron-doped Si revealed the radiation-produced defects having three levels at E_V +0.31, E_V +0.37, and E_V +0.11 eV.[11–13] These levels are believed to be associated with the boron-vacancy pair. DLTS measurements carried out under different recharging regimes led to the conclusion that the boron-vacancy pair is a bistable defect with two reversible atomic configurations labeled A and B. Donor levels at E_V +0.31 and E_V +0.37 eV are related to the A configuration of C_{1h} symmetry and donor level at E_V +0.11 eV belongs to the B configuration of C_1 symmetry. Theoretical treatment of the substitutional boron-vacancy pair in Si has helped elucidate its atomic configuration being dependent on the Fermi level position.[14] The calculated modeling of two next-nearest configurations of the boron-vacancy pair of C_{1h} and C_1 symmetry related to different re-bonding in the vacant site turned out to be almost equal in calculated energies. This implies that both configurations may make their appearance in a temperature interval of $T = 140–200$ K where DLTS measurements take place, thus each donor level at E_V +0.31 and E_V +0.37 eV belongs to the different configurations of the pair mentioned above. The defects are not stable at $T \cong 260$ K;[8] however, annealing details are yet unknown.[11]

From the foregoing discussion, it is readily apparent that the applied aspects of boron-doped Si concerning irradiation with nuclear particles at $T \geq 300$ K and boron diffusion processes must lean upon the second-generation boron-related complexes. Unfortunately, reliable microscopic identification of boron-related defects stable at room temperature in p-Si is lacking, so the presence of boron in radiation-produced defects may mostly be found by the indirect route only.

Some attempts to get information on the role of stable boron complexes in 1.5–2 MeV electron-irradiated degenerate p-Si have been made in extensive studies of the local vibrational modes (LVM) of substitutional and interstitial boron atoms in the Si lattice.[7,15] It has been demonstrated that the irradiation of heavily boron-doped p-Si at room temperature results in considerable losses of the boron atoms at substitutional sites, leaving only to 10% of the boron concentration originally present. This allowed then to assess the boron removal rates using the calibration procedure of the relevant IR bands. The isochronal anneals revealed one clearly defined stage around $T = 220$ °C. Further slow recovery went up to $T = 800$ °C without any individual stages. The chief drawbacks of this technique are well known, among them the total error about ±30% in concentration due to inaccuracies in the calibration of the absorption from substitutional boron and extensive use of degenerate p-Si strongly counter-doped with group-V impurities to remove the absorption due to free charge carriers.

Good indirect evidence that the formation of stable boron-related defects takes place in irradiated p-Si was furnished by detailed DLTS studies.[16–18] In the course of these investigations, the presence of boron in the forming complexes has been suggested by the dependence of their formation rates on impurity concentration, e.g., boron, oxygen, and carbon, among them. Of great importance for the aims of the present work are the proposed models of various complexes of interstitial boron with interstitial oxygen B_iO_i, substitutional carbon and boron, B_iC_s and B_iB_s, as well as their reaction branching rates taking into account that both impurities of oxygen O_i and carbon C_s are inactive in the Si lattice.[18] The model of the B_iB_s pair has been advanced keeping in mind a similar pair of Al_iAl_s in irradiated aluminum-doped p-Si.[2,19] The thermal stability of the complexes turned out to be very different, $T = 150–200$ °C, $T = 400$ °C, and $T > 400$ °C for B_iO_i, B_iC_s, and B_iB_s, respectively.[18]

The replacement reactions of boron impurity atoms in p-Si in the Watkins model awaken interest in investigations of similar reactions associated with other group-III acceptors. Using some specific hydrogen-related defect reactions in p-Si irradiated with 3 MeV electrons at room temperature, it has been demonstrated that the replacement efficiency for B, Al, and Ga appears to be alike at the beginning of the irradiation, whereas the efficiency for In is markedly higher if the impurity concentrations are comparable in a concentration range of few 10^{15} cm^{-3}.[20]

From the brief overview given above, it is apparent that the problem of stable boron-related defects in p-Si irradiated at room temperature generates a pressing need for reliable direct information on how the boron concentration is changed in the course of irradiation and subsequent anneals. It makes possible getting a closer look into the formation and thermal stability of boron-related complexes. The present work is also aimed at comparing the behavior of boron-doped p-Si under fast electron and proton irradiation, since the behavior of phosphorus-doped n-Si under the both types of the irradiation appears to be radically different.[21]

II. EXPERIMENTAL

Samples were cut from a boron-doped p-Si crystal grown by the float-zone (FZ) technique. The concentration of the dopant was about $4 \times 10^{16}\,\mathrm{cm}^{-3}$. The material studied was oxygen- and carbon-lean, their concentrations did not exceed a few $10^{16}\,\mathrm{cm}^{-3}$ to suppress a significant formation of oxygen- and carbon-related complexes with substitutional boron; this point will be discussed below in Sec. III B.

Square-shaped samples of $7 \times 7\,\mathrm{mm}^2$ were about 0.4 mm thick. Hall and conductivity measurements in a conventional design of the Van der Pauw technique were carried out over a temperature range of $T \approx 25$ to 300 K; see for instance Ref. 22. Experimental data of the free hole concentration and mobility, $p(1/T)$ and $\mu_h(T)$, respectively, were obtained in this way. Analysis of $p(1/T)$ curves with the help of relevant equations of charge balance taking into consideration the statistics of charge carriers in non-degenerate semiconductors furnishes an opportunity to determine the *total* concentration N_A of the substitutional boron, no matter they are neutral or negatively charged at $T = 0$ K, together with the *total* concentration N_D of all compensating donors being positively charged at $T = 0$ K. Taking proper account of the complexity of the valence band of Si and electronic structures of the group-III shallow acceptor states the relevant equation of charge balance can be written in the form

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

Here $N_V = N_V(T^{3/2})$ is the effective density-of-states in the valence band; it is a power function of temperature; k is Boltzmann's constant. E_A is the ionization energy of the ground state of the substitutional boron; it is determined from the slope of experimental $p(1/T)$ curves at cryogenic temperatures. Together with the contributions of the valence subbands of light and heavy holes, the contribution of the split-off valence subband to the effective density-of-states of the valence band at elevated temperatures is taken into consideration too. In accordance with this model the degeneracy factors g_A of the ground state including the electron spin is also taken into consideration. Other details of calculations have comprehensively been described in the literature.[23,24] Based on this calculation model, the *total* concentrations of N_A and N_D and their changes in the course of irradiation and subsequent isochronal anneals can be traced. Taking into account our experimental conditions, the Hall factor was assumed to be in accord, and the good agreement observed with values computed by means of the equation of charge balance suggests that this assumption is justified.

For comparison purposes, samples were bombarded with fast electrons and energetic protons.

Irradiation with 3.5 MeV electrons was performed at a linear accelerator. The frequency of the pulsed electron beam was 200 cps, and the duty cycle was 5 μs. In the case of 15 MeV, proton irradiation samples were thin enough, so the incident protons passed through the samples without noticeable effects of passivation. The samples were irradiated with a pulsed beam of protons at a small-size cyclotron. The frequency of the pulsed proton beam was 100 cps and the duty cycle was 2.5 ms. To prevent heating the samples in the course of electron and proton irradiation, the average current was kept low, so the irradiation temperature did not exceed 30 °C.

The isochronal anneals were carried out in steps of $\Delta T = 40$ °C and $\Delta t = 10$ min setting the reference temperature at $T = 20$ °C.

III. RESULTS AND DISCUSSION

A. Initial material

The electrical parameters of all the initial samples were weakly compensated. The compensation ratio $K = N_D/N_A$ was about a few percent, and the hole mobility μ_h at $T \leq 30$ K was close to $1 \times 10^4\,\mathrm{cm}^2/\mathrm{V\,s}$. In general, the shape of the experimental curves is consistent with what is known for strongly and heavily doped p-Si; see for instance Ref. 25.

B. Electron irradiation

A dramatic effect of the 3.5 MeV electron irradiation upon the electrical parameters of the boron-doped p-Si is illustrated by Figs. 1 and 2 where one can see some drastic changes in the hole concentration and mobility; cf. curves 1 and 2.

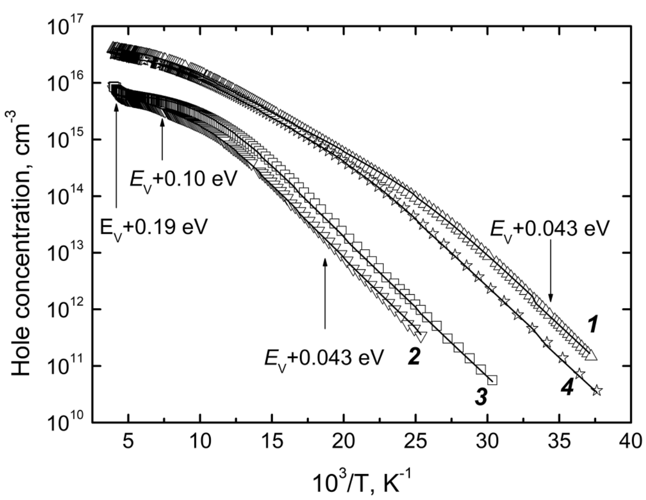

FIG. 1. Charge carrier concentration vs reciprocal temperature for the p-Si(FZ) irradiated with 3.5 MeV electrons at room temperature and then subjected to isochronal annealing. Points, experimental; curves, calculated. Fluence Φ, electrons/cm^2: 4×10^{16}. Points: 1, initial; 2, irradiated; 3, annealed at $T = 380$ °C; 4, annealed at $T = 620$ °C. Effective ionization energies of shallow acceptors as well as radiation-produced defects are indicated.

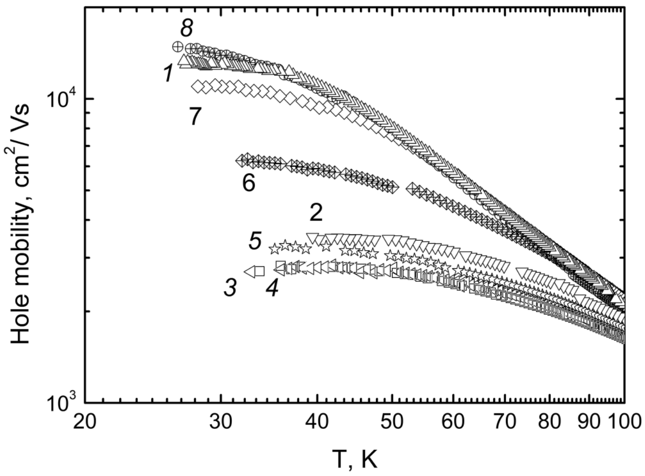

FIG. 2. Charge carrier mobility vs temperature for the *p*-Si(FZ) irradiated with 3.5 MeV electrons at room temperature and then subjected to isochronal annealing. Fluence Φ, electrons/cm^2: 4×10^{16}. Points, experimental: 1, initial (triangles up); 2, irradiated (triangles down); 3, annealed at $T = 220\,°C$ (triangles left); 4, annealed at $T = 260\,°C$ (squares); 5, annealed at $T = 300\,°C$ (stars); 6, annealed at $T = 420\,°C$ (rhombi crossed); 7, annealed at $T = 500\,°C$ (rhombi); 8, annealed at $T = 660\,°C$ (circles crossed).

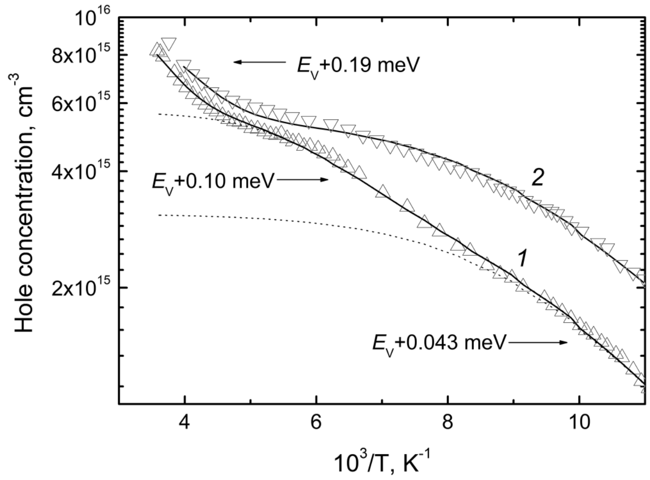

FIG. 3. Charge carrier concentration vs reciprocal temperature for the *p*-Si(FZ) irradiated with 3.5 MeV electrons at room temperature and then subjected to isochronal annealing. Fragments of the $p(10^3/T)$ curves are shown on the expanded temperature scale at $T > 78$ K; see also Fig. 1. Points, experimental; curves, calculated. Fluence Φ, electrons/cm^2: 4×10^{16}. Points: 1, irradiated; 2, annealed at $T = 340\,°C$. Effective ionization energies of shallow acceptors as well as radiation-produced defects are indicated. The dotted line displays the saturation plateau of $(N_A - N_D)$ at Φ; see text. The broken line shows the contribution of acceptor defects at $\approx E_V$ +0.10 eV. Analysis of curve 2 does not detect the presence of acceptor defects at $\approx E_V$ +0.10 eV in concentration about 1×10^{15} cm^{-3}.

Analysis of curves 1 and 2 in Fig. 1 betokens the observed damage: a marked loss of the shallow acceptor states of the substitutional boron, $\Delta N_A = N_A(\Phi) - N_A{}^0 = -3.16 \times 10^{16}\ \mathrm{cm}^{-3}$ at a fluence of $\Phi = 4 \times 10^{16}$ electrons/cm^2, where $N_A{}^0$ and $N_A(\Phi)$ are the total concentrations of the shallow boron acceptor states before and after irradiation, respectively. It means that the total removal rate is $\eta_A \approx 0.8\ \mathrm{cm}^{-1}$. Together with this, the hole mobility at cryogenic temperatures drops by a factor of 2.5. However, the surprising thing is that the increase in the total concentration of all compensating donors, N_D, turned out to be by a factor of six smaller than the loss of the shallow boron states in the irradiated sample, $|-\Delta N_A| \gg \Delta N_D = N_D(\Phi) - N_D{}^0 = 4.9 \times 10^{15}\ \mathrm{cm}^{-3}$. In other words, the dominant boron-related defects proved to be electrically neutral, e.g., they may be deep acceptors; see below.

The shape of $p(1/T)$ after the irradiation shown on the expanded scale in Fig. 3 (curve 1) stated that there are also radiation-produced defects at $\approx E_V$ +0.10 eV whose concentration was estimated as $N_{0.1} \cong 2.1 \times 10^{15}\ \mathrm{cm}^{-3}$.

Moreover, the hole concentration starts to grow at $T \geq 200$ K indicating the presence of other radiation-produced defects at $\approx E_V$ +0.19 eV. A tentative estimate of their concentration reasonably correlates with the *total* concentration of compensating donors. This, in turn, suggests that defects at $\approx E_V$ +0.10 eV are of acceptor type.

We are coming now to the discussion of how the boron-related defects stable at room temperature can be annealed out. To this end, the analysis of electrical data with the help of the equation of charge balance has been extended to most steps of isochronal annealing. The results obtained are depicted in Fig. 4.

As is seen in this figure, there are no sensible changes in the concentrations of N_A and N_D up to $T \approx 300\,°C$. The hole mobility does not show any significant recovery too; see curves 2–5 in Fig. 2. Acceptor defects $\approx E_V$ +0.10 eV disappear around $T \approx 340\,°C$; see Fig. 3, curve 2. After that point, a minor annealing stage accompanied with a partial recovery of the boron-related defects takes place

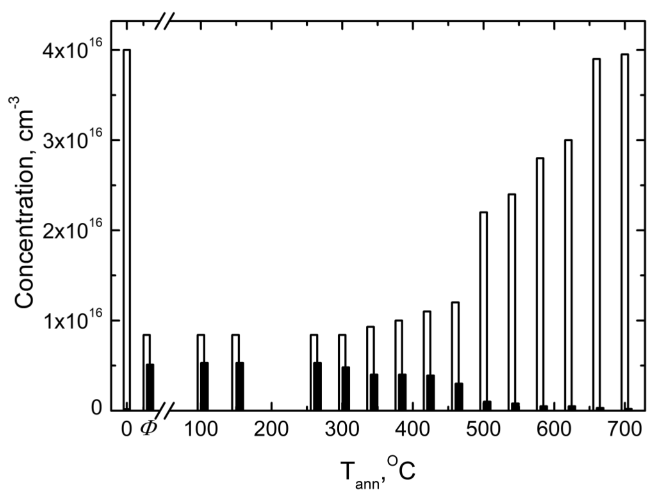

FIG. 4. Total concentrations of the shallow acceptor states (N_A) and deep donor states (N_D) for the *p*-Si(FZ) irradiated with 3.5 MeV electrons vs annealing temperature at some steps. Fluence Φ, electrons/cm^2: 4×10^{16}. Concentrations of N_A and N_D are indicated by white and black bars, respectively.

in a temperature range of $T \approx 340$–460 °C. The behavior of the hole mobility substantiates our conclusion concerning a complete disappearance of the radiation-produced donors in this temperature range. In actual fact, the hole mobility at cryogenic temperatures being very sensitive to the scattering by ionized centers is returned to the initial values in spite of a substantial amount of the neutral boron-related defects; cf. curves 1 and 7 in Fig. 2.

A prominent recovery stage of these neutral defects is developed at $T \geq 500$ °C. After an anneal step at $T = 700$ °C, the concentration of the shallow acceptor states of substitutional boron appears to be very close to its initial concentration $N_A{}^0$.

The discussion given in Sec. I points to the fact that none of the two basic boron-related defects, the vacancy-substitutional boron atom pair VB_s and the interstitial boron atom B_i, could be responsible for a substantial loss of the shallow acceptor states of the substitutional boron shown in Figs. 1 and 4 as a result of the electron irradiation at room temperature.

While modeling other boron-related complexes and taking into account the charge states of interacting defects, one should in the first place consider ion pairing when mobile B_i^+ atoms are trapped at $B_s{}^-$. The prominent annealing stage observed at $500° \leq T \leq 700$ °C is consistent with what is expected for ion pairs $B_i^+B_s{}^-$. The Coulomb attraction between the components is the driving force for the defect formation, on the one hand, and the main contribution being of 1.3 eV to the binding energy of the ion pair, on the other hand.[26] The capture radius r_c for this reaction may be many tens of an Å, whereas it is $r_c \leq 5$ Å for electrically inactive substitutional carbon C_s and interstitial oxygen atoms O_i. A large difference of r_c dictates a significant value of the relative reaction branching ratios for reaction products in p-Si, say, $[B_i{}^+B_s{}^-]/[B_i{}^+O_i] \approx 12$; see the discussion in Ref. 18. A similar situation is true for carbon.[18] Owing to this factor, boron-related defects in p-Si studied are strongly dominant over other complexes containing background impurities.

Based on earlier DLTS studies, it has been suggested that these ion pairs may possess energy levels at E_V +0.3 eV. A tentative identification was made, since the production rate of the traps was found to be proportional to the initial boron concentration squared.[17] The annealing temperature of the defects has not been determined.[17,18] It should be noted that theoretical studies of diboron defects, with symmetry D_{2d}, demonstrates that it is the lowest-energy structure of the B_iB_s pair whose LVM Q_1 at 733 cm^{-1} and Q_2 at 760 cm^{-1} are related to the boron isotopes of ^{11}B and ^{10}B, correspondingly.[26] Both lines make their appearance in p-Si irradiated at $T = 110$ K and subsequently annealed at $T \approx 230$ K when interstitial boron atoms become mobile.[7] However, the conclusion[26] that the complex would not survive anneals above $T \approx 400$ °C has been misjudged.

We are now going to discuss the minor annealing stage between $T \approx 340$ and 460 °C. Earlier it has been reported that a pronounced annealing stage of conductivity was observed around 220 °C in heavily doped p-Si subjected to electron irradiation at room temperature.[15] This stage is believed to be associated with mobile divacancies trapped at B_i via the reaction path of $V_2 + B_i \rightarrow B_s + V$ (mobile). In connection with this model, one important point should be kept in mind. The initial material was heavily doped with boron (5×10^{18} cm^{-3}). Conversion of any changes in conductivity after the electron irradiation and subsequent isochronal anneals into hole concentration values should be used with caution because of unknown compensation ratios of substitutional boron.

The production rate of divacancies in Si irradiated with fast electrons at 3 MeV is reported to be $\eta_{VV} \approx 0.01$ cm^{-1}.[27] In accordance with this, in our case, the concentration of divacancies produced by successive displacement of two lattice atoms should be less than 5×10^{14} cm^{-3} at a fluence of $\Phi = 4 \times 10^{16}$ cm^{-2}, so their annealing could scarcely be detected. As a reasonable explanation of the observed annealing of radiation-produced deep donors accompanied with a partial restoration of the substitutional boron, a new model is put forward. Electron irradiation of boron-doped Si samples at room temperature gives rise to the formation of unstable vacancy-substitutional boron pairs VB_s in the $2nn(C_1)$ configuration; see Sec. I. If during the lifetime of this defect it traps a free vacancy, a new complex is produced $VB_s + V \rightarrow VVB_s$, the divacancy-boron centers. Interestingly, the latter complex in the $2nn$ configuration is predicted to be most stable in all charge states, $E(2-/-)$, $E(-/0)$, and $E(0/+)$, like the isolated divacancy in Si.[14] Together with this, it has been found that the perturbation of the levels of the divacancy by the presence of a substitutional boron atom is small, so the charge state $E(0/+)$ of the VVB_s complex in the $2nn$ configuration is associated with a level at E_V +0.15 eV. Moreover, the dissociation of boron-divacancy defects is predicted at around $T = 300$ °C. The findings of the above theoretical consideration correlate reasonably well with the proposed model based on our experimental data concerning the boron-related defects annealed between $T \approx 340$ and 460 °C.

The last point to touch on is the fate of free vacancies taking into account the equal concentration of self-interstitials and vacancies being liberated after dissociation of Frenkel pairs as the primary intrinsic defects. Making a conservative estimate of the concentration of self-interstitials based on the data shown in Fig. 4, the concentration of free vacancies may also be about 1×10^{16} cm^{-3}. Taking into consideration that the formation of divacancy-boron complexes requires two vacancies for each defect, nearly all vacancies available appear to be bound up in these complexes present in a concentration of 4.9×10^{15} cm^{-3}.

C. Proton irradiation

In the same way as was done in the case of electron irradiation, some important data of electrical measurements on the proton-irradiated boron-doped samples are shown in Figs. 5 and 6.

Analysis of the curves $p(1/T)$ before and after proton irradiation depicted in Fig. 5 demonstrates a pronounced loss of the shallow acceptor states of the substitutional boron $\Delta N_A = N_A(\Phi) - N_A{}^0 = -1.1 \times 10^{16}$ cm^{-3} at a fluence of $\Phi = 1 \times 10^{14}$ protons/cm^2, where $N_A{}^0$ and $N_A(\Phi)$ are the total concentrations of the shallow boron acceptors before and after the irradiation, respectively. It means that the total removal rate η_A is about 110 cm^{-1} for 15 MeV protons. As in the case of electron irradiation, the increase in the total concentration of all compensating donors, N_D, was found to be smaller nearly by an order-of-magnitude than the loss of the shallow boron states in the irradiated sample, $|-\Delta N_A| \gg \Delta N_D = N_D(\Phi) - N_D{}^0 = 1.6 \times 10^{15}$ cm^{-3}.

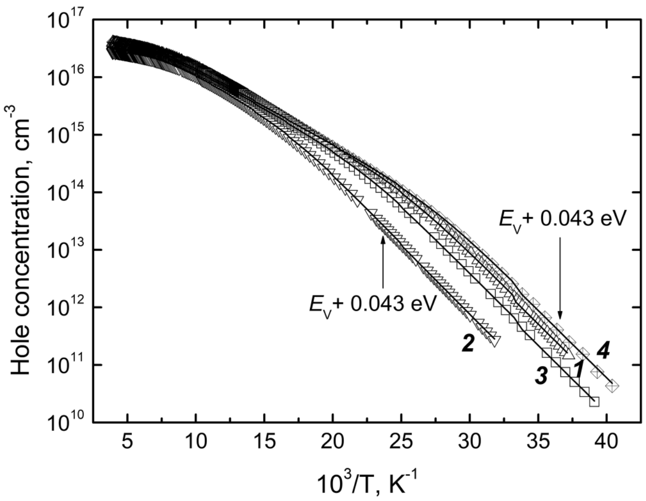

FIG. 5. Charge carrier concentration vs reciprocal temperature for the *p*-Si(FZ) irradiated with 15 MeV protons at room temperature and then subjected to isochronal annealing. Fluence Φ, protons/cm^2: 1×10^{14}. Points, experimental; curves, calculated. Points: 1, initial; 2, irradiated; 3, annealed at $T = 580$ °C; 4, annealed at $T = 700$ °C. Effective ionization energies of shallow acceptors are indicated.

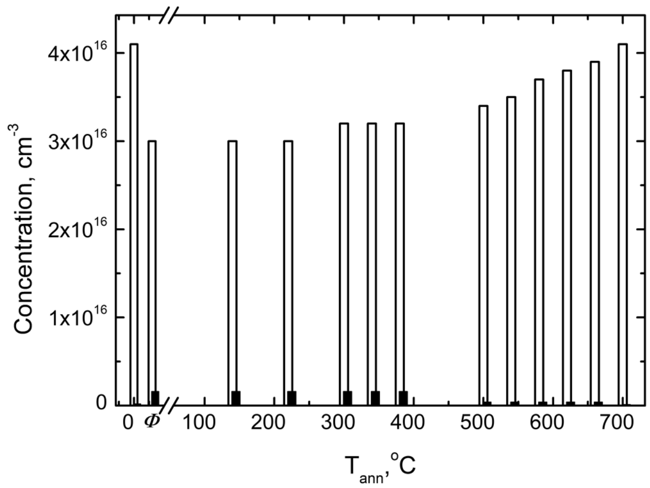

FIG. 7. Total concentrations of the shallow acceptor states (N_A) and deep donor states (N_D) for the *p*-Si(FZ) irradiated with 15 MeV protons vs annealing temperature at some steps. Fluence Φ, protons/cm^2: 1×10^{14}. Concentrations of N_A and N_D are indicated by white and black bars, respectively.

It points to the fact that the dominant boron-related defects in the electron- and proton-irradiated *p*-Si are electrically neutral. The only distinction between the two types of irradiation is that after the proton irradiation, the formation of defects at $\approx E_V + 0.10$ eV has not been observed.

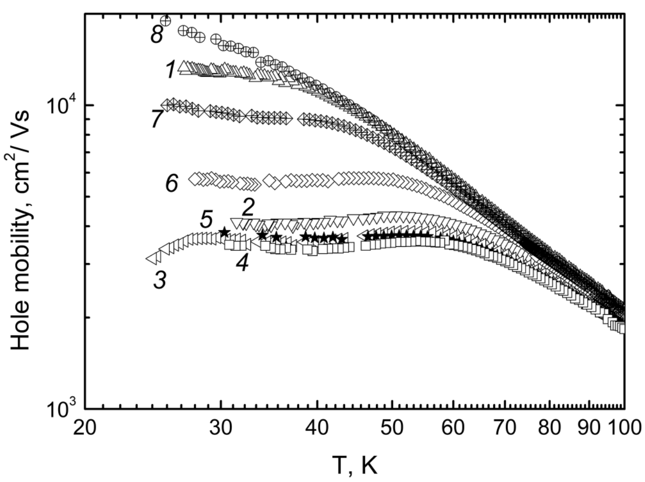

FIG. 6. Charge carrier mobility vs temperature for the *p*-Si(FZ) irradiated with 15 MeV protons at room temperature and then subjected to isochronal annealing. Fluence Φ, protons/cm^2: 1×10^{14}. Points, experimental: 1, initial (triangles up); 2, irradiated (triangles down); 3, annealed at $T = 220$ °C (triangles left); 4, annealed at $T = 260$ °C (squares); 5, annealed at $T = 300$ °C (stars); 6, annealed at $T = 420$ °C (rhombi); 7, annealed at $T = 580$ °C (rhombi crossed); 8, annealed at $T = 700$ °C (circles crossed).

Figure 7 shows how the total concentrations of N_A and N_D varied during isochronal anneals. First of all, our attention is drawn to a striking similarity of the annealing processes of the dominant radiation-produced defects in Figs. 4 and 7. The main stage where the concentration of the substitutional boron is completely restored is placed at $500 \leq T \leq 700$ °C.

A weak recovering process of the substitutional boron accompanied with a noticeable disappearance of the compensating donors is also seen over a temperature interval $400 \leq T \leq 500$ °C followed by a pronounced increase in the hole mobility like in the case of the electron irradiation; cf. curves 6 in Figs. 2 and 6. As distinct from the electron irradiation, there is an additional temperature interval of annealing at $220 \leq T \leq 300$ °C where the total concentration of the substitutional boron is slightly increased without any detectable change in the concentration of compensating donors. Interestingly, there is no annealing effect upon the hole mobility, in contrast to the above annealing stage at $400 \leq T \leq 500$ °C; cf. curves 3–6 in Fig. 6.

It is not clear why there is no indication of any annealing of the compensating donors, which could be associated with the divacancies mobile at $220 \leq T \leq 300$ °C. This is in contrast to 15 MeV proton-irradiated n-Si where the anneal of divacancies was observed over the temperature mentioned above.[21]

IV. CONCLUSION

In the past, two types of boron-related defects of the first-generation in irradiated *p*-Si, the substitutional boron atom-vacancy and the boron-interstitial, both unstable in a temperature range above room temperature, have comprehensively been studied. In the present work, investigations of the electrical properties of electron- and proton-irradiated *p*-Si allow one to get a searching look at the boron-related complexes of the second-generation stable at room temperature. A great body of direct information on variations of the total concentrations of the shallow acceptor states of substitutional boron as well as compensating donors due to formation and annealing processes provides conclusive evidence concerning the presence of two types of boron-related complexes in electron-irradiated *p*-Si. One type of the dominant boron-related defects that can be annealed at $500 \leq T \leq 700\,°C$ is attributed to substitutional boron-interstitial boron pairs. These pairs are electrically neutral in strongly doped *p*-Si. Another type of the boron-related defects is believed to be associated with substitutional boron-divacancy complexes, which are brought about when mobile vacancies are trapped at unstable substitutional boron-vacancy pairs produced during irradiation at room temperature. The divacancy as a component of the defect provides donor activity in *p*-Si. This complex displays higher thermal stability up to $T \approx 300\,°C$, in contrast to isolated divacancies annealable around $T \approx 220\,°C$. There is a clear indication that the presence of these positively charged centers has a strong impact on the hole mobility.

The formation and annealing processes of the boron-related defects in electron- and proton-irradiated *p*-Si appear basically to be very similar, in sharp contrast to some dramatical distinctions of the formation and annealing processes of radiation-produced defects in electron- and proton-irradiated *n*-Si doped with phosphorus.[21]

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Ethics Approval

Ethics approval is not required.

DATA AVAILABILITY

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

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