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Boron-doped silicon: a possible way of testing and refining models of non-ionizing energy loss under electron- and proton irradiation

© V.V. Emtsev¹, N.V. Abrosimov², V.V. Kozlovski³, S.B. Lastovskii⁴, G.A. Oganesyan¹, D.S. Poloskin¹, A.A. Aref'ev⁵

 ¹ loffe Institute, Russian Academy of Sciences, 194021 St. Petersburg, Russia
² Leibniz-Institut für Kristallzüchtung (IKZ), 12489 Berlin, Germany
³ Peter the Great St. Petersburg Polytechnic University, 195251 St. Petersburg, Russia
⁴ Scientific-Practical Materials Research Center of NAS of Belarus, 220072 Minsk, Belarus
⁵ Saint Petersburg Electrotechnical University "LETI", 197022 St. Petersburg, Russia
E-mail: emtsev@mail.ioffe.ru
Received September 3, 2022
Pavised September 5, 2022

Revised September 5, 2022 Accepted September 3, 2022

In this paper formation and annealing of boron-related defects in p-type silicon grown by the floating zone technique and subjected to electron and proton irradiation at room temperature are discussed. The defect model suggested earlier has provided fresh insight into the nature of two dominant complexes containing boron in irradiated p-Si, among them boron-divacancy complexes and interstitial boron-substitutional boron pairs. In the present work the same material is irradiated with 6 MeV electron and 8 MeV protons providing additional electrical data to test this model. Additionally new information on boron-related defects in heavily doped p-Si subjected to irradiation with 2.5 MeV electrons at 4.2 K and then subjected to isochronal anneals above room temperature is also discussed. The results obtained on proton irradiated p-Si(FZ) testify that the annealing behavior of boron-divacancy complexes appears to be complicated, in contrast to the behavior of substitutional boron-interstitial boron pairs. The defect model based on the experimental information furnished so far may be used for testing and refining computerized simulations of Non-Ionizing Energy Loss (NIEL) in irradiated silicon.

Keywords: silicon, boron impurity, electron- and proton-irradiation, impurity-related complexes.

DOI: 10.21883/PSS.2022.12.54380.469

1. Introduction

In contrast to fast neutron irradiation of crystalline silicon, it is widely believed in literature that irradiation with several MeV electrons and protons produce mainly similar structural defects being largely distinctive by their production rates only [1]. This concept has been served as a guide for predicting changes in electrical and other important properties of detector-grade materials under irradiation. These degradation processes are the focus of attention of investigators involved in fundamental research of nuclear physics and technical applications. This brings up the first question of non-ionizing energy loss (NIEL) of energetic protons that is responsible for defect formation in weakly doped n-Si. As a case in point, an extensive model of NIEL was based on well-known quasi-chemical defect reactions in irradiated n-Si [2]. From such a modeling it was inferred that there are marked deviations of the predicted and observed degradation of n-Si in the case of proton irradiation at E < 100 MeV. In succeeding years NIEL models were substantially improved by applying molecular dynamics calculations [3]. By this means it is possible to

take into consideration effects of collective atomic motion, in contrast to the classical NIEL model using the binary code approach. Together with this a detailed study of point and extended defects in p^+-n-n^+ planar pad Si diodes irradiated with electrons at 1.5 to 27 MeV has enriched our knowledge of defect generation and formation processes. However, the discussion points are mostly concerned with formation of oxygen- and carbon-related defects as well as multivacancy complexes, since the doping concentration in detector-grade materials was much less than $1 \cdot 10^{14}$ cm⁻³. In other words, in such a case a contribution of defect reactions with dopants like phosphorus is not a principle one among many electrically active complexes formed.

When facing NIEL issues in strongly doped and degenerate Si materials it is necessary to deal with the same dominating defect reactions in electron- and protonirradiated Si in order to give an accurate account of NIEL. By way of a concrete example, it has been demonstrated that defect production in moderately doped n-Si under electron and proton irradiation at room temperature may reportedly be different, as evidenced in the defect annealing studies [4,5]. It might be well to seek for doped Si material where prevailing radiation defect reactions of intrinsic point defects with impurity atoms appear to be nearly the same in a qualitative sense. Investigations of electron- and protonirradiated boron doped *p*-Si [6] allows one to suggest that this impurity may be appropriate for testing NIEL models where similar dopant-related defects play a leading role. The present work is aimed at providing support for this suggestion making use of strongly doped and degenerate *p*-type Si under various irradiation conditions. In addition to our previous paper devoted to studies of radiation effects of 3.5 MeV electrons and 15 MeV protons in boron-doped Si [6], new radiation experiments involving 6 MeV electron- and 8 MeV proton irradiation help one to take a searching look at some similar features of defect reactions.

2. Experimental

Square-shaped samples of $7 \times 7 \text{ mm}^2$ and about 0.4 mm thick were prepared from a *p*-type Si crystal doped with boron in concentration of around $4 \cdot 10^{16} \text{ cm}^{-3}$. The oxygen- and carbon-lean ingot was grown by the floating zone technique. Metallic electrical contacts were applied at the corners.

Hall effect and conductivity over a temperature range of $T \approx 20$ to 300 K were measured with the help of the conventional Van der Pauw technique; see for instance [7]. In such a way temperature-dependent charge carrier concentration $p(10^3/T)$ and mobility $\mu(T)$ curves were obtained prior to and after energetic electron and proton irradiation as well as in the course of isochronal annealing.

Irradiation with 6 MeV electrons was carried out at a linear accelerator. The parameters of the accelerator are as follows: the frequency of the pulsed electron beam is 200 cps, and the duty cycle is $5 \mu s$. Going to the case of 8 MeV proton irradiation it should be noted that the irradiated samples were thin enough, so the incident protons passed through the samples and, hence, any effect of passivation of boron can be disregarded. Irradiation of samples with protons at a small size cyclotron is characterized by the frequency of the pulsed proton beam of 100 cps. The duty cycle is 2.5 ms. The average current during the electron and proton irradiation was kept low, so the irradiation temperature did not exceed 30°C. The isochronal anneals were carried out in steps of $\Delta T = 40^{\circ}$ C and $\Delta t = 10$ min setting the reference temperature at T = 300 K. Defect annealing studies up to $T = 700^{\circ}$ C were performed in steps of $\Delta T = 40^{\circ}$ C and $\Delta t = 10$ min setting the reference temperature at T = 300 K.

It has been known that experimental curves $p(10^3/T)$ spanning (covering) a wide temperature range from low cryogenic temperatures like in the present work can furnish reliable information on the total concentration of shallow acceptor states of substitutional boron, N_A , as well as their compensation, that is the total concentration of compensating donors, N_D . What counts is a separate assessment of the both values. Their changes in the course of irradiation and

annealing are closely tied to formation and breakdown of boron-related defects. A careful analysis of $p(10^3/T)$ curves in non-degenerate Si is based on the statistics of charge carriers and relevant equations of charge balance taking proper account of the complexity of the valence band and electronic structures of the group-III shallow acceptor states in Si. The equation describing how the shallow acceptor states of boron are ionized up to the saturation plateau takes 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, $N_v = N_v(T^{3/2})$ stands for the effective density-ofstates in the valence band; k is Boltzmann's constant. Values of N_v at low cryogenic temperatures stem from the contributions of the valence subbands of light and heavy holes. The contribution of the split-off valence subband becomes prominent at elevated temperatures, $T \le 100$ K, too. E_A represents the ionization energy of the ground state of the substitutional boron which can be determined from the slope of experimental $p(10^3/T)$ curves at cryogenic temperatures. The degeneracy factors g_A of the ground state including the electron spin is also taken into consideration. Other details of such calculations can be found in the literature [8,9].

In the framework of the calculation model outlined above, one can keep track on how the total concentrations of N_A and N_D are varied in the course of irradiation and subsequent isochronal anneals. It might be well to point out that for our experimental conditions the Hall factor was assumed to be unity. A good fit of the above equation to the experimental data obtained points to the fact that this assumption appears to be sensible.

3. Results and Discussion

3.1. Initial material

All the initial *p*-Si samples studied were weakly compensated having the compensation ratio $K = N_D/N_A$ around a few percent only. Because of this the hole mobility before irradiation was high at low cryogenic temperatures, $\mu_h \approx 10^4 \text{ cm}^2/\text{V}\text{ s}$ at $T \approx 30 \text{ K}$. The shapes of the initial $p(10^3/T)$ and $\mu_h(T)$ curves are in line with the known literature data [10].

3.2. Irradiation of strongly boron-doped *p*-Si(FZ) with 6 MeV electrons

In Fig. 1 some experimental and calculated curves of $p(10^3/T)$ are displayed to show the range where the hole concentration in one of the boron-doped Si samples was changed in the course of the electron irradiation and subsequent isochronal annealing. The electron fluence was relatively low, so the Fermi level shift down in the upper half of the band gap didn't allow to detect radiation defects whose energy levels lie deeper than $\approx E_V + 0.1$ eV. However, from



Figure 1. Charge carrier concentration *vs* reciprocal temperature for the *p*-Si(FZ) irradiated with 6 MeV electrons at room temperature and then subjected to isochronal annealing. Points, experimental; curves, calculated (in colors online). Fluence Φ , electrons/cm²: 2 · 10¹⁶. Points: *I* — initial (blue triangles up); *2* — irradiated (red triangles down); *3* — annealed at *T* = 300°C (crosses); *4* — annealed at *T* = 420°C (rhombi); *5* — annealed at *T* = 520°C (squares); *6* — annealed at *T* = 580°C (stars). Effective ionization energies of shallow acceptors are indicated.

our earlier experiments with 3.5 MeV electron irradiation of the same material [6] the important information on deeper defects is available; see Fig. 2. Together with this, it has been argued that donor levels at $\approx E_V + 0.19 \,\mathrm{eV}$ belong to the substitutional boron-divacancy complexes. It means that in our case they are responsible for compensation of the shallow acceptor states of the substitutional boron as well as for a strong scattering of charge carriers by ionized centers at $T \leq 40$ K when most of the shallow acceptor states are neutral; see Fig. 1 and 3. Annealing of these compensating substitutional boron-divacancy complexes around $T \approx 400^{\circ}$ C brings about a complete recovery of the hole mobility, as is seen in Fig. 3 taking into account that the remaining fraction of interstitial boron-substitutional boron pairs are electrically neutral [11]. The changes of the total concentration N_A and N_D displayed in Fig. 4 lend additional support to the model of radiation-produced defects discussed in [6].

Let us to give a glimpse at most important features of the model. It has been known for a long time that the both kinds of boron-related defects, the interstitial boron atom and substitutional boron atom-vacancy pair, produced during electron irradiation are stable at low cryogenic temperatures only [12–14]. Irradiation of strongly borondoped p-Si(FZ) at room temperature gives rise to the formation of other stable boron-related complexes. Mobile interstitial boron atoms B_i^+ are trapped at substitutional boron atoms B_s^- resulting in appearance of interstitial boron-substitutional boron pairs $[B_s^-B_i^+]$. Concurrently substitutional boron atoms B_s^- can trap mobile vacancies Vand these $[B_s^-V]$ pairs can survive if in their lifetime they trap additional free vacancies $[B_s^-V] + V \rightarrow [B_sVV]$ resulting in appearance of substitutional boron atomdivacancy complexes stable up to $T \approx 300^{\circ}$ C. In general, the latter defect retains electrical activity characteristic for the divacancy $[VV]^+$ in *p*-type Si.

Recovery of electrical properties of irradiated materials involves two consecutive annealing stages over a temperature interval of $300^{\circ}C \leq T \leq 420^{\circ}C$ and $420^{\circ}C \leq T \leq 700^{\circ}C$. Boron-divacancy complexes are destroyed at the first annealing stage. Boron ion pairs $[B_s^-B_i^+]$ turned out to be more stable and they are decayed at higher temperatures. By and large the suggested model of formation and annealing of the boron-related defects appears to be adequate for description of radiation damage of *p*-Si(FZ) induced by 3.5 to 6 MeV electron irradiation.



Figure 2. 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. Points, experimental; curves, calculated (in colors online). Fluence Φ , electrons/cm²: $4 \cdot 10^{16}$. Points: I — irradiated; 2 — annealed at $T = 340^{\circ}$ C. Effective ionization energies of shallow acceptors as well as radiation-produced defects are indicated. The dotted red line displays the saturation plateau of $(N_A - N_D)$ at Φ ; see text. The broken red line shows the contribution of acceptor defects at $\approx E_V + 0.10$ eV. Analysis of red curve 2 doesn't detect the presence of acceptor defects at $\approx E_V + 0.10$ eV in concentration about $1 \cdot 10^{15}$ cm⁻³. Data are taken from [6].



Figure 3. Charge carrier mobility *vs* temperature for the *p*-Si(FZ) irradiated with 6 MeV electrons at room temperature and then subjected to isochronal annealing. Fluence Φ , electrons/cm²: $2 \cdot 10^{16}$. Points, experimental (in colors online) *I* — initial (blue triangles up); *2* — irradiated (red triangles down); *3* — annealed at $T = 300^{\circ}$ C (rhombi); *4* — annealed at $T = 380^{\circ}$ C (circles); *5* — annealed at $T = 600^{\circ}$ C (stars).



Figure 4. Total concentrations of the shallow acceptor states (N_A) and deep donor states (N_D) for the *p*-Si(FZ) irradiated with 6 MeV electrons vs annealing temperature at some steps. Fluence Φ , electrons/cm²: $2 \cdot 10^{16}$. Concentrations of N_A and N_D are indicated by blue and red bars, respectively. The dashed arrow shows the change in the total concentration of the shallow acceptor states of the substitutional boron atoms after the irradiation.

3.3. Irradiation of heavily boron-doped *p*-Si with 2.5 MeV electrons

Earlier we have investigated the annealing processes of defects in heavily boron-doped and degenerate *p*-Si following fast electron irradiation at T = 4.2 K [15]. Then we kept track of how the resistivity of irradiated samples was changed in the course of isochronal anneals up to room temperature. Above this temperature point the recovery processes of the charge carrier concentration were carefully studied under isochronal annealing in steps of $\Delta T = 100^{\circ}$ C and $\Delta t = 20$ min making use of Hall effect measurements. The annealing behavior of such defects is shown in Fig. 5.

Though it is impossible in this case to extract direct information on changes of the concentration of the shallow acceptor states in heavily doped p-Si(CZ) as we did it for strongly doped materials of p-Si(FZ) [6], the shape of the annealing curves looks very similar to those obtained for materials with much lesser doping levels. Let's clarify some important points concerning the defect formation and annealing processes under consideration.

It has long been known that under electron irradiation of p-Si the generation of free vacancies and self-interstitials in p-Si takes place as a result of dissociation of primary defects, i.e. Frenkel pairs $[VSi_i]$ consisting of a vacancy V and an self-interstitial Si_i . In our case of electron irradiation at $T = 4.2 \,\mathrm{K}$ the formation of boron-related defects goes in several stages. First interstitial boron atoms are produced via trapping of extremely mobile selfinterstitials Si_i at substitutional boron atoms accompanied by a replacement reaction $Si_i + B_s \rightarrow [Si_iB_s] \rightarrow Si_s + B_i$, known as the Watkin's reaction [12,14]. With increasing temperature of irradiated *p*-Si to $T \approx 180$ K isolated vacancies become mobile and they are trapped at substitutional boron atoms. As a result, new boron-related complexes appear, $B_s + V \rightarrow [B_s V]$. Further annealing of irradiated p-Si around room temperature leads to the formation of boron-related ion pairs $[B_s^-B_i^+]$, whereas unstable $[B_sV]$ pairs can be converted in stable $[B_sVV]$ defects by trapping additional free vacancies. This is a marked distinction between the source of free vacancies available for such a transformation of boron-vacancy pairs under electron irradiation at room temperature and under low cryogenic conditions. In the last case it means that the maximal concentration of boron-divacancies can't exceed one half of the concentration of boron-vacancy complexes already available, because there is no external source of free vacancies. It may be slightly less if some other effective sinks for free vacancies exist, aside from the boron-vacancy pairs. The concentration of boron ion pairs allows one to assess the concentration of self-interstitials involved in the formation of interstitial boron atoms. It should be equal to the concentration of vacancies involved in the formation of boron-vacancy pairs. This is substantiated by the estimations made in [6]. Hence, the concentration of charge carriers that ought to be freed at the end of isochronal annealing of boron-divacancies at $T \approx 420 - 450^{\circ}$ C is twice as large,



Figure 5. Charge carrier concentration vs annealing temperature for the heavily boron-doped *p*-Si irradiated with 2.5 MeV electrons at T = 4.2 K and then subjected to isochronal anneals. Above room temperature the reference point was set at T = 300 K. At higher temperatures the annealing step was kept at $\Delta T = 100^{\circ}$ C for $\Delta t = 20$ min. Initial hole concentration, cm⁻³: $a = 7.32 \cdot 10^{17}$; $b = 4.77 \cdot 10^{18}$; $c = 2.52 \cdot 10^{19}$. Fluence, electrons/cm²: $a = 1.58 \cdot 10^{17}$; $b = 1.9 \cdot 10^{18}$; $c = 1.8 \cdot 10^{19}$. Estimations of the $[B_s VV]$ and $[B_s^- B_i^+]$ concentrations are based on two annealing intervals: $300 \le T \le 420^{\circ}$ C (indicated by arrows) and $420 \le T \le 700^{\circ}$ C for the first and second kinds of the defects, respectively.

taking into account that each defect $[B_sVV]$ compensates one shallow acceptor state of the substitutional boron atoms [6].

The important issue is whether the model of radiationproduced defects suggested for moderately and strongly boron-doped p-Si(FZ) may also be true for heavily and nearly degenerate doped p-Si(CZ) grown by the Czochralski technique. The key feature of the model discussed is a relation between the concentrations of radiation-produced defects annealed out at the first and second stages, i.e. the annealing of $[B_sVV]$ and $[B_s^-B_i^+]$ complexes. As we noticed earlier, in heavily boron-doped *p*-Si(CZ) one has to deal only with the concentration of charge carriers while handling electrical data. Notwithstanding, it is possible to



Figure 6. Charge carrier mobility vs annealing temperature for the degenerate boron-doped *p*-Si irradiated with 2.5 MeV electrons at T = 4.2 K and then subjected to isochronal anneals. Above room temperature the reference point was set at T = 300 K. At higher temperatures the annealing step was kept at $\Delta T = 100^{\circ}$ C for $\Delta t = 20$ min. Initial hole concentration was $2.52 \cdot 10^{19}$ cm⁻³. Fluence, electrons/cm²: $1.8 \cdot 10^{19}$. Initial hole mobility μ_h^0 is indicated.

assess this ratio as well if one is aware of the electrical activity of radiation-produced defects. Each boron-ion pair $[B_s^-B_i^+]$ annealed returns two free holes into the valence band, since these defects considered are neutral in *p*-type Si; see also below. On the other hand, the concentration of the boron ion pairs should be equal to the concentration of boron-vacancy pairs formed below room temperature. Hence, the concentration of the boron-divacancy complexes stable at room temperature could be around one half of that of the boron-ion pairs. Each boron-divacancy complex annealed returns two free holes into the valence band taking into account its donor activity in p-type Si. Judging from the changes in the concentration of charge carriers in the electron-irradiated p-Si(CZ) under annealing it means that the ratio of the defect concentrations annealed at the two annealing stages is expected to be 1:2. Looking at Fig. 5 one should keep in mind that the annealing of borondivacancy complexes starts at $T \approx 300^{\circ}$ C and finishes at $T \approx 420^{\circ}$ C or slightly above if their defect concentration is substantial; cf Fig. 4 in [6] and Fig. 4 in the present paper. In Fig. 5 the recovery of the hole concentration in the electronirradiated *p*-Si(CZ) heavily doped with boron is displayed. One can readily see that the ratio of the changes in the hole concentration restored at the both annealing stages was found to be close to the expected one with an accuracy of ten per cent or better.

It implies that the defect model under consideration may be applied to heavily and degenerate boron-doped materials as well. Moreover, the annealing behavior of the charge carrier mobility in the degenerate p-Si(CZ) depicted in Fig. 6 offers additional evidence that the defect model discussed is true. In actual fact, the defect concentration in this electron-irradiated material is large enough to produce a marked effect upon the hole mobility even at the reference temperature T = 300 K.

The presence of a substantial fraction of neutral boron pairs $[B_s^-B_i^+]$ after the electron irradiation at T = 4.2 K and a subsequent anneal around room temperature results in a very pronounced increase of the hole mobility; see Fig. 6. There is no annealing effect up to $T \approx 300^{\circ}$ C. At higher temperatures of $350 \le T \le 550^{\circ}$ C the annealing curve of $\mu_h(T_{ann})$ shows a drop to the initial value, since the dissociation of each neutral boron pair $[B_s^-B_i^+]$ restores two ionized scattering centers B_s^- . Hence the variations of the hole mobility during the annealing are consistent with the model discussed.

3.4. Irradiation of strongly boron-doped *p*-Si with 8 MeV protons

As one might expect, an effect of the proton irradiation on electrical parameters of the *p*-Si(FZ) turned out to be much stronger that that observed for the same material irradiated with proton irradiation at 15 MeV [6]. It should suffice to compare the removal rates of charge carriers in both cases, $\eta_h (8 \text{ MeV}) \approx 260 \text{ cm}^{-1} \text{ vs } \eta_h (15 \text{ MeV}) \approx 110 \text{ cm}^{-1}$. Let's highlight most important findings.

In Fig. 7 several $p(10^3/T)$ curves are depicted to illustrate how the charge carrier concentration is changed in the course of the proton irradiation and subsequent anneals. Figure 8 shows some $p(10^3/T)$ curves on the expanded scale displaying these changes in detail. It is readily seen that warming-up to $T \approx 300^{\circ}$ C doesn't affect the hole concentration in the irradiated sample.

The surprising thing is that the annealing of this sample at $T \approx 420^{\circ}$ C also produced a little increase in the charge carrier concentration. A speedy recovery of the hole concentration takes place at $T \ge 460^{\circ}$ C. In other words, the annealing stage of boron-divacancy complexes appears to be strongly suppressed. Annealing at $T \approx 700^{\circ}$ C removes all produced defects in proton-irradiated samples.

The changes in the hole mobility observed in the course of irradiation and annealing of boron-doped Si(FZ) allows one to better appreciate the scattering processes of charge carriers at cryogenic temperatures; see Fig. 9.

As is seen in Fig. 8 (curve 2), at T < 60 K most of the substitutional boron atoms after the irradiation are neutral, B_s^0 , so the concentration of free holes turned out to be rather small, $p < 10^{14}$ cm⁻³, i.e. $B_s \rightarrow B_s^- + h$ (at the expense of thermal ionization). In these circumstances, the dominant scattering mechanism of charge carriers in the irradiated sample is due to the presence of the compensating radiation-produced donors D_{rad}^+



Figure 7. Charge carrier concentration vs reciprocal temperature for the *p*-Si(FZ) irradiated with 8 MeV protons at $T \le 60^{\circ}$ C and then subjected to isochronal annealing. Points, experimental; curves, calculated (in colors online). Fluence Φ , protons/cm²: $1 \cdot 10^{14}$. Points: I — initial (blue triangles up); 2 — irradiated (red triangles down); 3 — annealed at $T = 500^{\circ}$ C (rhombi). Effective ionization energies of shallow acceptors are indicated.

whose concentration is at least by an order-of-magnitude larger than that of free holes. Because the total concentration of ionized centers appears to be substantial, $N_{ion}^{total} \approx 2 D_{rad}^+ \approx 3 \cdot 10^{15} \,\mathrm{cm}^{-3}$, the hole mobility in Fig. 9 (curve 2) features a temperature dependence $\mu_h(T) \propto T^{3/2}$ being well-known as characteristic for the scattering of charge carriers by ionized centers; see for instance [9]. It is significant that this temperature dependence of the hole mobility at cryogenic temperature is retained in the irradiated samples during anneals up to $T = 420^{\circ}$ C, as is evident in Fig. 9 (curves 3 to 5). Noteworthy also is the increasing hole mobility over an annealing interval of $300 \le T \le 450^{\circ}$ C that allows one to follow the disappearance of the compensating radiation-produced donors. This temperature interval of the donors may be attributed to the annealing of boron-divacancy complexes taking into consideration their electrical activity. With further increasing temperature of the annealing the hole mobility in Fig. 9 (curves 6 to 8) doesn't display any pronounced temperature dependence at $T \leq 50 \,\mathrm{K}$ what correlates reasonably well with dissociation of electrically neutral ion pairs $[B_s^-B_i^+]$.

Although the annealing behavior of the charge carrier mobility in proton-irradiated p-Si(FZ) demonstrates the presence of both kinds of the boron-related complexes already known from our investigation of the same electronirradiated material, the changes in the total concentration of shallow acceptor states during anneals tell us that the relationship between two stages of $300 \le T \le 420^{\circ}$ C and $460 \le T \le 700^{\circ}$ C in proton- and electron-irradiated *p*-Si(FZ) proved to be rather different; *cf* Figs. 4 and 10.

As is earlier seen that in the latter case the concentration of boron-divacancy complexes $[B_sVV]$ is found to be nearly equal to one half of the concentration of ion pairs $[B_s^-B_i^+]$. Contrary, in the case of proton irradiation of *p*-Si(FZ) the first annealing stage where the boron-divacancy complexes $[B_sVV]$ are destroyed plays a marginal role whereas the second high-temperature annealing stage where the ion pairs $[B_s^-B_i^+]$ are disappeared is absolutely dominant; see also [6].

This raises the question as to why formation of vacancyrelated defects under proton irradiation proved to be strongly suppressed. Simulations of radiation damage of Si irradiated with 10 MeV protons indicates that the production of Frenkel pairs is relatively uniform [2]. It is conceivable that isolated vacancies being created under low electronic excitation are prone to formation of stable multivacancy complexes which are electrically neutral in *p*-Si. They may be destroyed at high temperatures, together with dissociation of ion pairs $[B_s^- B_i^+]$.



Figure 8. Charge carrier concentration vs reciprocal temperature for the *p*-Si(FZ) irradiated with 8 MeV protons at $T \le 60^{\circ}$ C 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. Points, experimental; curves, calculated (in colors online). Fluence Φ , electrons/cm²: $4 \cdot 10^{16}$. Points: 1 - irradiated (red triangles down); 2 - annealed at $T = 300^{\circ}$ C (circles); 3 annealed at $T = 420^{\circ}$ C (rhombi); 4 - annealed at $T = 500^{\circ}$ C (crosses); 5 - annealed at $T = 620^{\circ}$ C (stars); 6 - annealed at $T = 700^{\circ}$ C (green triangles up). Effective ionization energies of shallow acceptors as well as radiation-produced defects are indicated.



Figure 9. Charge carrier mobility *vs* temperature for the *p*-Si(FZ) irradiated with 8 MeV protons at $T \le 60^{\circ}$ C and then subjected to isochronal annealing. Fluence Φ , protons/cm²: $1 \cdot 10^{14}$. Points, experimental (in colors online) 1 — initial (blue triangles up); 2 — irradiated (red triangles down); 3 — annealed at $T = 300^{\circ}$ C (stars); 4 — annealed at $T = 380^{\circ}$ C (squares); 5 — annealed at $T = 420^{\circ}$ C (triangles up); 6 — annealed at $T = 460^{\circ}$ C (crosses); 7 — annealed at $T = 540^{\circ}$ C (rhombi); 8 — annealed at $T = 580^{\circ}$ C (triangles left); 9 — annealed at $T = 700^{\circ}$ C (circles).



Figure 10. Total concentrations of the shallow acceptor states (N_A) and deep donor states (ND) for the *p*-Si(FZ) irradiated with 8 MeV protons *vs* annealing temperature at some steps. Fluence Φ , protons/cm²: $1 \cdot 10^{14}$. Concentrations of N_A and N_D are indicated by blue and red bars, respectively. The broken arrow shows the change in the total concentration of the shallow acceptor states of the substitutional boron atoms after the irradiation.

4. Conclusions

The present work devoted to electrical measurements on boron-doped Si(FZ) irradiated with 6 MeV electrons and 8 MeV protons at room temperature enables us to test the model of boron-related defects recently suggested for similar investigations of the same material irradiated with 3.5 MeV electrons and 15 MeV protons. The new findings lend additional support for the model based on two principal boron-related complexes stable at room temperature, among them the substitutional boron atomdivacancy $[B_sVV]$ and the substitutional boron atominterstitial boron atom $[B_s^-B_i^+]$. They display different thermal stability: $[B_sVV]$ complexes can be annealed over a temperature range of $300 \le T \le 450^{\circ}$ C, whereas ion pairs $[B_s^-B_i^+]$ are disappeared at higher annealing temperatures, $460 \le T \le 700^{\circ}$ C.

The results obtained point to the fact that the formation and annealing processes of such complexes in heavily borondoped Si(CZ) run in the same way, no matter whether electron irradiation is performed at room temperature or first at cryogenic temperatures and then accompanied with warming-up to room temperature. This experimental evidence permits one to extend the boron concentration range of *p*-Si from $\approx 10^{16}$ to $\approx 10^{19}$ cm⁻³ in computer simulations of Non-Ionizing Energy Loss (NIEL) under fast electron irradiation.

Irradiation of the same boron-doped *p*-Si with 8 and 15 MeV revealed that the formation of boron-divacancy complexes $[B_sVV]$ is strongly suppressed, whereas other known boron-related defects, boron ion pairs $[B_s^-B_i^+]$, make their appearance as a dominant component of the radiation damage. Notwithstanding the defect formation model may also be modified for simulations of NIEL in proton-irradiated boron-doped *p*-Si.

Acknowledgments

The authors would like to express their sincere thanks to Professor G.D. Watkins for reading the paper. His critical comments are greatly appreciated.

Conflict of Interest

The authors have no conflicts to disclose.

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