## Defects involving interstitial boron in low-temperature irradiated silicon

L. I. Khirunenko,<sup>1,\*</sup> M. G. Sosnin,<sup>1</sup> A. V. Duvanskii,<sup>1</sup> N. V. Abrosimov,<sup>2</sup> and H. Riemann<sup>2</sup>

<sup>1</sup>Institute of Physics, National Academy of Sciences of Ukraine, Prospekt Nauki 46, 03028 Kiev, Ukraine

<sup>2</sup>Leibniz Institute for Crystal Growth, Max-Born Strasse 2, D-12489 Berlin, Germany

(Received 19 August 2016; revised manuscript received 28 October 2016; published 30 December 2016)

Interstitial boron-related defects in silicon subjected to irradiation with 5 MeV electrons at a temperature of 80 K are investigated by Fourier-transform infrared absorption spectroscopy. This study demonstrates the radiation-enhanced annealing of interstitial boron during irradiation. We have revealed the interaction, which occurs in the course of irradiation, of diffusing interstitial boron atoms with one another and with interstitial oxygen. The local vibrational modes associated with these defects are identified, and the thermal stability of the defects is determined.

DOI: 10.1103/PhysRevB.94.235210

## I. INTRODUCTION

Boron is the acceptor impurity most widely used at the present time in the fabrication of silicon devices. In the development of contemporary submicron Si devices, the key problem is the attainment of a high level of doping with boron in the extremely narrow Si regions. Most frequently, this problem is solved with the use of ion implantation. During the implantation, as with the irradiation by high-energy particles, a lot of damages (Frenkel pairs, complexes arising as a result of the interaction of intrinsic vacancies and interstitial atoms with one another and with impurities) appear in the crystal, which can significantly affect the properties of a material and the diffusion of implanted impurities. To remove the damages and to activate the implanted boron, the material should be annealed. A number of undesirable effects, such as the transient-enhanced diffusion of boron at large distances for a very short time, and the formation of electrically inactive boron-interstitial clusters, which reduce the efficiency of the doping with boron, can appear upon annealing [1]. Therefore, studies of boron-related defects induced by ion implantation or irradiation and the subsequent anneals are of great importance to modern microelectronics. This information is also required for the comprehension of the processes of diffusion and activation of implanted dopants. However, in spite of numerous studies, the available information on the properties of boronrelated radiation defects has been insufficient up to now.

One of the dominant defects produced in boron-doped Si by electron irradiation at cryogenic temperatures is interstitial boron (B<sub>i</sub>) [2–4]. At low-temperature irradiation, the selfinterstitial atom (I) interacts efficiently with substitutional boron and ejects it into interstitial site in accordance with the Watkins replacement mechanism [5]. B<sub>i</sub> has three charge states (B<sup>0</sup><sub>i</sub>, B<sup>+</sup><sub>i</sub>, and B<sup>-</sup><sub>i</sub>) and forms two levels in the band gap of silicon. The energy of the donor level (0/+) estimated in different studies [4,6] lies between  $E_c - 0.13$  and  $E_c -$ 0.15 eV, whereas the energy of the acceptor level (-/0) is evaluated to be from  $E_c - 0.37$  to  $E_c - 0.45$  eV [3,4,6]. B<sub>i</sub> is a negative U-center, since the acceptor level is lower than the donor one, and the transition of B<sup>-</sup><sub>i</sub> into B<sup>+</sup><sub>i</sub> occurs in the following way: B<sup>-</sup><sub>i</sub>  $\rightarrow$  B<sup>0</sup><sub>i</sub> +  $e^- \rightarrow$  B<sup>+</sup><sub>i</sub> + 2 $e^-$ , i.e., the charge According to the available data,  $B_i$  is annealed by diffusion at about 240–250 K [2,4]. It is assumed that diffusing interstitial boron atoms can interact with one another, with substitutional boron atoms, and with the main impurities of Si such as oxygen and carbon [2,4,8–12]. The authors of Refs. [2,4,6] showed with the use of deep-level transient spectroscopy (DLTS) and electron paramagnetic resonance (EPR) that under the injection of minority carriers, a significant enhancement in the rate of annealing of  $B_i$  is observed according to the Bourgoin-Corbett mechanism. The enhanced migration involves complete cycle alteration between  $B_i^+$  and  $B_i^-$  and vice versa via the intermediate state  $B_i^0$ .

In Czochralski silicon, the annealing of  $B_i$  is accompanied by the appearance of a defect with the level at  $E_c - 0.23$  eV, which was identified as  $B_iO_i$  complex due to the correlation of its formation with the boron and oxygen concentrations in the samples [4,6]. Note that the levels at  $E_c - 0.27$  eV [10] and  $E_c - 0.26$  eV [11] were also associated with this defect. At the annealing in the temperature interval 150–200 °C, the level  $E_c - 0.23$  eV disappears, which is accompanied by the formation of a level at  $E_v + 0.29$  eV identified as the complex  $B_iC_s$  [10–13]. As is seen, the determination of the energy levels for identified  $B_i$ -related defects is somewhat ambiguous.

At present, there is only a little information available on local vibrational modes (LVMs) of B-related radiation defects in Si. Only a few works have been devoted to the investigation of those defects by infrared spectroscopy [8,9,14,15]. While studying the infrared absorption of B-doped Si subjected to irradiation with 2 MeV electrons at T = 110 K, two absorption bands at 730 and 757 cm<sup>-1</sup> (R lines), which were assigned to the local vibrational modes of  $B_i$ , were observed [8]. The subsequent annealing at T > 200 K resulted in a gradual decrease in the intensities of the LVMs at 730 and  $757 \text{ cm}^{-1}$ , and the lines disappeared at a temperature of about 250 K. The disappearance of the R lines coincided with the growth of lines at 903, 912, 928, 599, and  $613 \text{ cm}^{-1}$ (S lines), which were initially associated with vibrations of  $B_i B_i$  pairs. The defect responsible for these modes exists in a narrow temperature interval. As room temperature was attained, the S lines were transformed into LVMs at 733 and 760 cm<sup>-1</sup> (Q lines) [8,14], which were ascribed to clusters

states of a defect differ by two electrons [3,4,6,7].  $B_i^0$  is an intermediate metastable state between  $B_i^+$  and  $B_i^-$ .

<sup>\*</sup>lukh@iop.kiev.ua

of three or more  $B_i$  atoms. Later, the Q and S lines were reassigned, respectively, to the LVMs of  $B_i B_s$  complexes and to the precursors to the Q lines formed during the conversion of  $B_i$  to  $B_i B_s$  [16,17]. It should be noted that the identification of all the absorption bands executed in work [8] was carried out in the samples doped with boron in very high concentrations and simultaneously codoped with phosphorus or arsenic with the same concentrations  $(1-5) \times 10^{19} \text{ cm}^{-3}$ . To remove residual free carriers, the samples were irradiated at high doses  $[(5 \times 10^{18}) - (6.7 \times 10^{19}) \text{ cm}^{-2}]$  with 2 MeV electrons at room temperature. Then, before investigations were performed, the samples were reirradiated at T = 110 K at a dose of  $(5-9) \times 10^{17}$  cm<sup>-3</sup>. It was noted [8] that, after the first irradiation at room temperature, the samples contained local domains of *n*- or *p*-type due to the impurity striations produced by nonuniformities in the growth rate of crystals. The samples were also characterized by significant internal stresses related to a high content of impurities, which led to a broadening of the two-phonon absorption bands. The high concentration of doping impurities, the inhomogeneity of their distribution over the samples, the defects formed due to the primary irradiation, and the significant internal elastic stresses can essentially affect the defect formation processes upon reexposure, as well as the transformation of defects at the subsequent annealing of irradiated samples. The formation of more complex defects (clusters) is also expected. Therefore, a more reliable identification of B<sub>i</sub>-related defects requires study of the samples doped only with boron at its lower concentration.

It is worth noting that the mentioned studies were performed both on oxygen-rich and oxygen-lean samples, but none of the LVMs was associated with the  $B_iO_i$  complex, although the optical activity of  $B_iO_i$  centers was theoretically predicted [16,18,19]. Up to now, no electronic or vibrational absorption feature, which could be related to the enhancement in the rate of annealing of  $B_i$ , has been reported.

Thus, as is seen from the above, the identification of  $B_i$ -related defects requires further investigations. In the present work, we report new additional data on the formation of interstitial boron-related defects in silicon irradiated with 5 MeV electrons at temperature of T = 80 K. The data have been obtained with the use of Fourier-transform infrared (FTIR) absorption spectroscopy.

#### **II. EXPERIMENTAL DETAILS**

The samples of Si used in the study were grown by the Czochralski (Cz) and float-zone (Fz) methods. The concentration of boron in samples was varied in the interval  $(0.5-3.6) \times 10^{16}$  cm<sup>-3</sup>. The content of oxygen in Cz-Si was determined at room temperature by the intensity of the absorption band at 1107 cm<sup>-1</sup> and ranged from  $2 \times 10^{14}$  to  $9.9 \times 10^{17}$  cm<sup>-3</sup>. The carbon concentration was defined by the intensity of the absorption band at 605 cm<sup>-1</sup> and varied in the interval  $(0.1-7.4) \times 10^{16}$  cm<sup>-3</sup>. We used also isotopically enriched <sup>28</sup>Si. For comparison, we studied the Cz-Si samples with a low content of boron and *n*-silicon. The parameters of the samples are presented in Table I.

The samples were irradiated with 5 MeV electrons at the temperature T = 80 K using a Microtron M30 accelerator. At the irradiation, the current density was 3  $\mu$ A cm<sup>-2</sup>. The

TABLE I. The parameters of the samples used in the study.

No.	$N_{\rm B}$ (10 <sup>16</sup> cm <sup>-3</sup> )	$N_{\rm O}$ (10 <sup>17</sup> cm <sup>-3</sup> )	$N_{\rm C}$ (10 <sup>16</sup> cm <sup>-3</sup> )	$N_{\rm P}$ (10 <sup>15</sup> cm <sup>-3</sup> )
1	3.6	9.9	7.4	
2	3.6	10.5	6.4	
3	3.6	0.003	< 0.1	
4	1	4.3	7.1	
5	1	0.003	3.2	
6	$\sim 0.9$	7	0.8	
7	0.5	6	0.8	
8	0.01	8	2	
9		9.7	5	1

samples were irradiated in a flow of liquid nitrogen supplied at an excess pressure. The temperature of the samples was controlled during irradiation by two differential thermocouples. One of the thermocouples was mounted on the rear side of a sample relative to the incident electron beam and was pressed to it with a special holder. Near the sample, the control Si sample with the same mass and size was placed. In it, a hole, into which the second thermocouple was introduced, was drilled. After irradiation, the samples together with the thermocouples were immersed in liquid nitrogen, and a check of the correctness of the temperature measurement by thermocouples was executed. The irradiation doses were  $(5-6) \times 10^{17}$  cm<sup>-2</sup>. The irradiated samples were transferred without heating into a cryostat for infrared absorption measurements.

To study the thermal stability of radiation-induced defects and their transformation, 20 min isochronal annealing of irradiated samples was carried out in the interval 80–300 K with temperature increments of 10 K. Isothermal anneals of irradiated samples were performed to determine the activation energy for the annealing of defects.

The absorption spectra of the irradiated samples were studied with the use of a Bruker IFS–113v Fourier-transform infrared spectrometer. The measurements were carried out at a temperature of 10 K with a resolution of 0.2-0.5 cm<sup>-1</sup>. The absorption spectrum of a nonirradiated high-purity Fz-Si sample was subtracted from each spectrum.

# **III. RESULTS**

The study of the Si samples with a content of boron  $N_{\rm B} \ge 5 \times 10^{15} \, {\rm cm}^{-3}$  revealed a number of specific features in infrared absorption spectra as compared with the samples with a low boron content and with *n*-silicon. It was found that the spectra of the samples irradiated at T = 80 K contain, as distinct from the previous studies, no LVMs associated with interstitial boron (730 and 757 cm<sup>-1</sup>). Instead of  $B_i$ -related lines, we detected a spectrum not previously observed in the range of 700–800 cm<sup>-1</sup> [20]. Figure 1 shows the absorption spectra for Si with different concentrations of boron. The spectrum for a sample with a boron concentration  $0.5 \times 10^{16}$  cm<sup>-3</sup> pertains to isotopically enriched <sup>28</sup>Si. As seen, three LVMs placed at comparable distances from one another with maxima, respectively, at 739.4, 759.6, and 780.9  $\text{cm}^{-1}$  are observed in the spectra. In the <sup>28</sup>Si sample, the bands shift to higher frequencies by  $\sim 0.3 \text{ cm}^{-1}$ . The positions of the revealed



FIG. 1. Fragments of the absorption spectra measured at 10 K for boron-doped Cz-Si irradiated at 80 K with 5 MeV electrons (samples 1, 4, 7, and 8). The initial boron concentrations in samples are shown on the right. Irradiation dose was  $\Phi = 6 \times 10^{17}$  cm<sup>-2</sup>. The spectra are shifted along the vertical axis for clarity.

LVMs coincide with none of the known absorption bands, which were observed earlier in silicon highly doped with boron [8,14,21]. Figure 1 demonstrates also the dependence of the revealed LVMs on the boron concentration: the higher the boron content in the samples, the more intense are the absorption bands. This implies that a boron atom enters the composition of the defect with which the observed spectrum is associated.

The dependence of the detected spectrum on the oxygen and carbon contents, which are known to be the main impurities in silicon, is shown in Fig. 2, where the spectra for the samples with comparable concentrations of boron, but differing by more than three orders in the oxygen content and by two orders in the carbon concentration (samples 1 and 3), are demonstrated. It is seen that the appearance of the revealed spectrum is independent of the oxygen and carbon contents in the samples.

The study of the thermal stability of the revealed defect showed that it is annealed at a sufficiently low temperature. The changes in the intensities of detected absorption lines during isochronal annealing of irradiated boron-doped Si are demonstrated in Fig. 3. No changes occurred for temperatures up to  $\sim$ 130 K. The further increase in the annealing temperature results in a decrease in the intensity of the lines, and they disappear about  $\sim$ 180 K. No new absorption bands were found to arise synchronously with the disappearance of the detected lines. At the annealing, the defect transforms, obviously, into an optically inactive complex.

In addition to the above-described feature in the absorption spectrum, we found also a boron-related peculiarity in the spectral range 910–950 cm<sup>-1</sup>. Four well-known absorption lines are typically observed in this spectral region for Si with a low boron content (lower spectrum in Fig. 4) and for *n*-type Si irradiated at low temperatures. Two absorption lines at 922.1 and 932.1 cm<sup>-1</sup> arise from local vibrational modes due to the interstitial carbon [22], the 935.8 cm<sup>-1</sup> line is associated with





FIG. 2. Dependence of the detected spectrum on the oxygen and carbon content in Si samples. The concentration of boron in the untreated samples was  $N_{\rm B} = 3.6 \times 10^{16} \, {\rm cm}^{-3}$ . The oxygen content in samples is shown on the right side of the spectrum. Carbon concentrations were  $N_{\rm C} < 1 \times 10^{15} \, {\rm cm}^{-3}$  in the oxygen-lean sample and  $N_{\rm C} \approx 7.4 \times 10^{16} \, {\rm cm}^{-3}$  in the oxygen-rich sample. Irradiation dose was  $\Phi = 6 \times 10^{17} \, {\rm cm}^{-2}$ .

the LVM of the I<sub>2</sub>O<sub>*i*</sub> defect [23], and the line at 944 cm<sup>-1</sup> is related to vibrations of defect IO<sub>*i*</sub> [24]. We found that, as the boron concentration increases ( $N_B \ge 5 \times 10^{15} \text{ cm}^{-3}$ ), the band at 922.1 cm<sup>-1</sup> is gradually widened, and the new component with a maximum at 923.5 cm<sup>-1</sup> develops in the spectrum (Fig. 4). The detected component intensity grows with increasing boron concentration.

Figure 5 demonstrates the dependence of the revealed line at 923.5 cm<sup>-1</sup> on the oxygen and carbon contents in the samples. The results obtained for Si samples with comparable concentrations of boron ( $N_{\rm B} \approx 1 \times 10^{16}$  cm<sup>-3</sup>), but differing



FIG. 3. Changes in the intensities of revealed absorption lines at the 20 min isochronal annealing of the irradiated boron-doped Si (sample 2). The concentration of boron in the untreated sample was  $N_{\rm B} = 3.6 \times 10^{16}$  cm<sup>-3</sup>. Irradiation dose was  $\Phi = 5 \times 10^{17}$  cm<sup>-2</sup>.



FIG. 4. Fragments of the absorption spectra measured at 10 K for the as-irradiated at 80 K boron-doped Cz-Si (samples 2, 4, and 8). The spectra are shifted along the vertical axis for clarity. The initial boron contents in the samples are shown on the right. Irradiation dose was  $\Phi = 5 \times 10^{17}$  cm<sup>-2</sup>.

by more than three orders in the oxygen content [Fig. 5(a)] and by nine times in the carbon concentration [Fig. 5(b)], are shown. The spectrum for the sample with low carbon



FIG. 5. Dependence of the 923.5 cm<sup>-1</sup> absorption line (a) on the oxygen (samples 4 and 5) and (b) carbon (samples 4 and 6) contents in Si. The oxygen and carbon concentrations for initial samples are shown on the right. The irradiation dose was  $\Phi = 5 \times 10^{17}$  cm<sup>-2</sup>.



FIG. 6. Evolution of the absorption spectrum at the 20 min isochronal annealing in the temperature interval from 80 to 270 K for irradiated <sup>28</sup>Si (sample 7). Irradiation dose was  $\Phi = 6 \times 10^{17}$  cm<sup>-2</sup>. The spectra are vertically shifted for clarity.

content corresponds to isotopically enriched <sup>28</sup>Si. The revealed component for <sup>28</sup>Si shifts slightly to higher frequencies by  $\sim 0.23 \text{ cm}^{-1}$ . Figure 5 demonstrates that the component at 923.5 cm<sup>-1</sup> is not observed for the oxygen-lean sample, which testifies that the interstitial oxygen atom is involved in the defect. Figure 5 also shows that the appearance of the LVM is independent of the carbon concentration in the sample, and the revealed component becomes dominant in intensity for the sample with a low carbon content.

To determine the thermal stability of the revealed complex responsible for the line at 923.5  $\text{cm}^{-1}$ , isochronal annealing of the irradiated samples has been done. Figure 6 shows the obtained results. The annealing up to 170 K has no effect on the intensity of the 923.7  $cm^{-1}$  line. In the temperature interval 170-190 K, some increase in the line intensity is observed. This is a testament to the additional formation of defects responsible for the line. Further annealing at higher temperatures (T > 210 K) results in a significant decrease in the line intensity, and it disappears at about 260 K. Only the LVM associated with interstitial carbon (922.3 cm<sup>-1</sup>) remains in the spectrum. The isothermal anneals of irradiated samples performed at 220 and 230 K have shown that the annealing activation energy of the defect responsible for the 923.5  $\rm cm^{-1}$ line is about 0.77 eV. The carried out investigations showed no absorption features in the spectral range  $550-4000 \text{ cm}^{-1}$ for samples annealed up to 400 K, except for those mentioned above, which could be attributed to defects formed with participation of interstitial boron.

# **IV. DISCUSSION**

As was mentioned in the Introduction, the previous studies showed that  $B_i$  is annealed at a temperature of about 240-250 K. The studies performed with the use of DLTS and EPR indicate that, at the injection of minority carriers, a significant increase in the rate of annealing of  $B_i$  can be observed [2,4]. However, no vibrational absorption features related to the enhanced migration of  $B_i$  have been observed up to now. The absence of the LVMs associated with  $B_i$  just after the irradiation of samples at 80 K in our study indicates that the annealing of interstitial boron occurred during the irradiation. Note that in Refs. [2-4], the enhanced annealing of  $B_i$  was observed after the irradiation of samples, and the rate of annealing was proportional to the square of the injection level. The fact that those studies did not detect the enhanced annealing of  $B_i$  during irradiation, which was found in our work, can probably be explained by the different conditions of irradiation of the samples. As is known, enhanced annealing is determined by the concentration of minority carriers. The degree of ionization (and, respectively, the concentration of minority carriers) upon irradiation is proportional to the energy of particles and the current density. In Refs. [2–4], the samples were irradiated with electrons whose energy was much less, 1-1.5 MeV, than that in our studies (5 MeV). Thus, the degree of ionization under the conditions of our experiment is much higher than that in Refs. [2-4]. Therefore, obviously, enhanced annealing of  $B_i$  in Refs. [2–4] was observed only at the injection of minority carriers. Unfortunately, the values of the current density at irradiation were not given in these studies.

The appearance of the new LVMs at 739.4, 759.6, and 780.9 cm<sup>-1</sup> in as-irradiated samples instead of  $B_i$ -related lines suggests that  $B_i$  is involved in the composition of a defect responsible for these lines. The revealed absorption lines show identical behaviors upon annealing, and they disappear simultaneously, which indicates their conformity to one center. The observed dependence of the intensities of LVMs on the boron content and their independence of oxygen and carbon concentrations is a testament to the fact that the composition of the defect responsible for these lines includes only the boron atom.

As is known, natural boron consists of two isotopes (80.1% of isotope <sup>11</sup>B and 19.9% of isotope <sup>10</sup>B). The presence of three absorption lines in the spectrum rather than two, as is observed for substitutional or interstitial boron, can provide evidence that the center responsible for the revealed LVMs includes two boron atoms. Therefore, LVMs at 739.4, 759.6, and 780.9 cm<sup>-1</sup> can be attributed to vibrations of the pairs <sup>11</sup>B +<sup>11</sup>B, <sup>11</sup>B +<sup>10</sup>B, and <sup>10</sup>B +<sup>10</sup>B, respectively. The performed analysis of the intensities of LVMs with regard to this assumption shows that the ratio of contributions from <sup>11</sup>B and <sup>10</sup>B to the intensities of spectral lines is close to 4:1 in the limits of experimental errors, as it should be in view of the isotopic composition of boron.

Two defect structures can be assumed for the defect responsible for the appearance of observed lines. The interstitial boron atoms diffusing during irradiation can interact with one another, forming the  $B_i B_i$  complex, or the migrating  $B_i$  atom can be trapped by substitutional boron with the formation of the  $B_i B_s$  center. However, the  $B_i B_s$  complex has been observed previously and is known to be stable up to  $220 \,^{\circ}\text{C}$  [14,21], far exceeding the temperature 180 K at which the defect responsible for the spectrum observed in our investigations disappears. Therefore, we can suppose that the interaction of diffusing interstitial boron atoms with one another occurs at irradiation, which results in the formation of the B<sub>i</sub>B<sub>i</sub> complex.

The appearance of the line at 923.5  $\text{cm}^{-1}$  in boron-doped Si irradiated at 80 K, and the dependence of its formation on the concentrations of boron and oxygen, make it possible to assume that both of these components are involved in the composition of the defect responsible for this line. The performed isochronal and isothermal anneals of the irradiated samples have shown that the detected centers are annealed at about 260 K with an annealing activation energy of  $\sim$ 0.77 eV. No additional modes that can be correlated with the 923.5  $\text{cm}^{-1}$  line were found in the investigated samples. The presence of only one line in the spectrum rather than two, as it should be due to the isotopic composition of boron, can testify to the fact that the interaction between the boron and oxygen atoms in the complex is weak. In other words, the boron and oxygen atoms form no direct bonds with each other. In such a structure, the isotope substitution of boron does not result in a significant change in the vibrational frequency of the defect. The similar structure has some oxygen-related radiation defects in Si. Direct bonds did not form, for example, between oxygen and self-interstitials in the supposed model of the  $I_2O_i$  defect [25], or between the oxygen and carbon atoms in the  $C_i O_i$  complex [26].

As is known, the level at  $E_c - 0.23$  eV is associated with the B<sub>i</sub>O<sub>i</sub> complex [4,10,11]. However, the LVM revealed by us has no relation to the defect associated with that level. The B<sub>i</sub>O<sub>i</sub> complex has a high thermal stability, as distinct from the defect registered by us, and it is annealed at a temperature much higher (150–200 °C) than the found defect. According to Refs. [4,6], the level  $E_c - 0.23$  eV arises synchronously with the annealing of B<sub>i</sub>. The annealing temperature for B<sub>i</sub> is close to that of the defect observed by us. Therefore, it is possible that the formation of a defect with the level  $E_c - 0.23$  eV can occur both as a result of the interaction of diffusing B<sub>i</sub> with oxygen and due to the temperature-induced transformation of the defect revealed by us. To resolve this question, further study would be desirable.

The defect that we revealed is not also a precursor of complex observed in very recent work by Murin et al. [27]. A new set of absorption bands were observed in this study. The defect responsible for these lines has the same thermal stability as the defect responsible for the level  $E_c - 0.23 \text{ eV}$ , and detected bands were identified as local vibrational modes of the  $B_iO_i$  complex. It should be noted that LVMs were observed in Ref. [27] only after the irradiation of samples with 10 MeV electrons. The irradiation with electrons with a lower energy (6 MeV) caused no formation of the defect responsible for those LVMs, while the appearance of the level  $E_c - 0.23 \text{ eV}$  was registered [4,6,10,11,28] in boron-doped Si irradiated with electrons with any energies in the interval 1-4 MeV. When the LVM registered by us disappeared at annealing, we observed neither the spectrum presented in Ref. [27] nor other LVMs, which would be transformed in this spectrum at subsequent annealing in the temperature interval 260-400 K.

One of the possible models of the defect responsible for the line 923.5 cm<sup>-1</sup> may be the following. Oxygen cannot diffuse during the irradiation of Si at a temperature of 80 K. This assumes that the detected complex is formed if a diffusing  $B_i$  atom is localized near a defect whose composition includes an oxygen atom. As is known, the diffusing self-interstitial atoms interact efficiently with oxygen and form the defects IO<sub>i</sub> and I<sub>2</sub>O<sub>i</sub> under irradiation at low temperatures [23,24]. In addition, IO<sub>i</sub> can be transformed into I<sub>2</sub>O<sub>i</sub> by the recapture of self-interstitials liberated at the dissociation of IO<sub>i</sub> by other IO<sub>i</sub>. Therefore, it is quite probable that the interstitials, can be localized near the IO<sub>i</sub> centers with the formation of the B<sub>i</sub>IO<sub>i</sub> complexes.

The additional formation of defects responsible for the 923.5 cm<sup>-1</sup> line in the temperature interval 170–190 K coincides with the annealing of the  $B_iB_i$  defect. This may show that the center  $B_iB_i$  is annealed by dissociation, and the liberated  $B_i$  atoms may be trapped by the oxygen-related defect with the formation of a complex responsible for the observed line.

The annealing temperature of both of the detected interstitial boron-related complexes is lower than or comparable to that for  $B_i$ . Therefore, it is obvious that the authors of the previous investigations, who had not observed the enhanced annealing of  $B_i$  during irradiation, could not observe  $B_i$ -related defects found by us, since their lifetime at these temperatures is quite low.

- N. E. B. Cowern, K. T. F. Janssen, and H. F. F. Jos, J. Appl. Phys. 68, 6191 (1990); L. Pelaz, M. Jaraiz, G. H. Gilmer, H.-J. Gossmann, C. S. Rafferty, D. J. Eaglesham, and J. M. Poate, Appl. Phys. Lett. 70, 2285 (1997).
- [2] G. D. Watkins, Phys. Rev. B 12, 5824 (1975).
- [3] G. D. Watkins and J. R. Troxell, Phys. Rev. Lett. 44, 593 (1980).
- [4] J. R. Troxell and G. D. Watkins, Phys. Rev. B 22, 921 (1980).
- [5] G. D. Watkins, A Review of EPR Studies in Irradiated Silicon, in Radiation Damage in Semiconductors, edited by P. Baruch (Dunod, Paris, 1964), pp. 97–113.
- [6] R. D. Harris, J. L. Newton, and G. D. Watkins, Phys. Rev. B 36, 1094 (1987).
- [7] M. Hakala, M. J. Puska, and R. M. Nieminen, Phys. Rev. B 61, 8155 (2000).
- [8] A. K. Tipping and R. C. Newman, Semicond. Sci. Technol. 2, 389 (1987).
- [9] K. Laithwaite, R. C. Newman, and D. H. J. Totterdell, J. Phys. C 8, 236 (1975).
- [10] P. M. Mooney, L. J. Cheng, M. Süli, J. D. Gerson, and J. W. Corbett, Phys. Rev. B 15, 3836 (1977).
- [11] P. J. Drevinsky, C. E. Caefer, S. P. Tobin, J. C. Mikkelsen Jr., and L. C. Kimerling, *Influence of Oxygen and Boron on Defect Production in Irradiated Silicon*, MRS Symposia Proceedings Vol. 104, edited by M. Stavola, S. J. Pearton, and G. Davies (Materials Research Society, Pittsburgh, PA, 1988), p. 167.
- [12] L. C. Kimerling, M. T. Asom, J. L. Benton, P. J. Drevinsky, and C. E. Caefer, Mater. Sci. Forum 38–41, 141 (1989).

Thus, the radiation-enhanced annealing of  $B_i$ , which occurs during irradiation at 80 K of boron-doped Si, has enabled us to detect  $B_i$ -related defects that have not been observed previously.

#### V. SUMMARY

The absorption spectra for as-irradiated samples contain no local vibrational modes associated with interstitial boron. This is a testament to the enhanced annealing of interstitial boron during irradiation. Instead of local vibrational modes of  $B_i$ , two new peculiarities in the absorption spectra were detected. The first is observed in the range 700–800 cm<sup>-1</sup>, and it consists of three lines located at comparable distances from one another, with their maxima at 739.4, 759.6, and 780.9 cm<sup>-1</sup>. The emergence of these lines depends only on the concentration of boron in the samples. The spectrum is identified as local vibrational modes of the complex  $B_i B_i$ . The studies indicate that defect  $B_i B_i$  is annealed at about  $T \approx 180$  K.

The second peculiarity is registered in the interval 910–930 cm<sup>-1</sup> and consists of a single line with the maximum at about 923.5 cm<sup>-1</sup>. The appearance of the defect responsible for this line depends on the presence of boron and oxygen in the samples. The center is formed, if a diffusing  $B_i$  atom is localized near a defect, whose composition includes an oxygen atom. The detected complex is found to be stable up to  $T \approx 260$  K and is annealed with an activation energy of ~0.77 eV.

- [13] E. V. Monakhov, A. Nylandsted Larsen, and P. Kringhøj, J. Appl. Phys. 81, 1180 (1997); N. Yarykin, O. V. Feklisova, and J. Weber, Phys. Rev. B 69, 045201 (2004).
- [14] A. R. Bean, S. R. Morrison, R. C. Newman, and R. S. Smith, J. Phys. C 5, 379 (1972).
- [15] K. Thonke, J. Weber, J. Wagner, and R. Sauer, Physica B 116, 252 (1983).
- [16] J. Adey, R. Jones, P. R. Briddon, and J. P. Goss, J. Phys.: Condens. Matter 15, S2851 (2003).
- [17] J. Adey, J. P. Goss, R. Jones, and P. R. Briddon, Phys. Rev. B 67, 245325 (2003).
- [18] J. Adey, J. P. Goss, R. Jones, and P. R. Briddon, Physica B 340–342, 505 (2003).
- [19] A. Carvalho, R. Jones, J. Coutinho, and P. R. Briddon, J. Phys.: Condens. Matter 17, L155 (2005).
- [20] L. Khirunenko, M. Sosnin, A. Duvanskii, N. V. Abrosimov, and H. Riemann, Solid State Phenom. 242, 285 (2016).
- [21] Vibrational absorption of quasi-substitutional atoms and other centres, in *Optical Absorption of Impurities and Defects in Semiconducting Crystals: Electronic Absorption of Deep Centres and Vibrational Spectra*, edited by B. Pajot and B. Clerjaud (Springer-Verlag, Berlin, 2013), Vol. 169, Chap. 7, pp. 325–367.
- [22] R. C. Newman, *Carbon in Crystalline Silicon*, MRS Symposia Proceedings Vol. 59, edited by J. C. Mikkelsen Jr., S. J. Pearton, J. W. Corbett, and S. J. Pennycook (Materials Research Society, Pittsburgh, PA, 1986), p. 403.
- [23] L. I. Khirunenko, L. I. Murin, J. L. Lindström, M. G. Sosnin, and Yu. V. Pomozov, Physica B 308–310, 458 (2001).

- [24] J. Hermansson, L. I. Murin, T. Hallberg, V. P. Markevich, J. L. Lindström, M. Kleverman, and B. G. Svensson, Physica B 302– 303, 188 (2001).
- [25] V. P. Markevich, A. R. Peaker, B. Hamilton, V. E. Gusakov, S. B. Lastovskii, L. I. Murin, N. Ganagona, E. V. Monakov, and B. G. Svensson, Solid State Phenom. 242, 290 (2016).
- [26] L. I. Khirunenko, M. G. Sosnin, Yu. V. Pomozov, L. I. Murin, V. P. Markevich, A. R. Peaker, L. M. Almeida, J. Coutinho, and V. J. B. Torres, Phys. Rev. B 78, 155203 (2008).
- [27] L. I. Murin, S. B. Lastovskii, E. A. Tolkacheva, V. P. Markevich, A. R. Peaker, and B. G. Svensson, Phys. Status Solidi A 213, 2850 (2016).
- [28] L. F. Makarenko, S. B. Lastovskii, F. P. Korshunov, M. Moll, I. Pentilie, and N. V. Abrosimov, *Formation and Annealing* of Boron-Oxygen Defects in Irradiated Silicon and Silicon-Germanium n<sup>+</sup>-p Structures, AIP Conf. Proc. Vol. 1583, edited by A. Cavallini and S. K. Estreicher (AIP Publishing, Melville, New York, 2014), p. 123.