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Electronic absorption of interstitial boron-related defects in silicon

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We report the data on the electronic absorption of interstitial boron-related defects in silicon, irradiated with 5 MeV electrons. Two new electronic absorption features have been revealed in the spectrum of boron-doped Si. The sharp line at 4385.2 cm^{-1} is detected in Si irradiated at 80 K and subjected to the subsequent annealing up to 300 K. The emergence of the registered line depends on the concentration of boron and does not depend on the presence of oxygen and carbon in the samples. The revealed line is associated with B_iB_s complex. It is shown that the presence of oxygen in the samples inhibits the formation of B_iB_s defects. The disappearance of the 4385.2 cm^{-1} line upon annealing is accompanied by the emergence of a line at 7829.5 cm^{-1} in the spectrum. The appearance of the 7829.5 cm^{-1} line depends on the presence of carbon in the samples. The registered 7829.5 cm^{-1} line is ascribed to B_iC_s complex. It is argued that, in the oxygen-rich material, B_i liberated as a result of the dissociation of both B_iO_i and B_iB_s defects are involved in the formation of B_iC_s. In oxygen-lean Si, only B_i liberated at the dissociation of B_iB_s participate in the formation of B_iC_s.

1 Introduction Boron is a most commonly used impurity in the manufacture of silicon-based devices today. Silicon doped with boron is widely applied to the fabrication of solar cells as electric power sources in space vehicles. Solar inverters are affected by ionizing radiation of the outer space. Damages, appearing owing to the irradiation, result in a degradation of solar cells. Therefore, the investigations of radiation defects responsible for the degradation of cells are of great importance for the provision of a reliable performance of the equipment of space vehicles under the influence of ionizing radiation. The knowledge of reactions appearing in boron-doped Si upon the irradiation and the subsequent annealing is also important for the technologies using the ion implantation to understand the processes of diffusion and activation of implanted boron in detail. But, in spite of numerous studies, the identification of the boron-related defects in Si is unsolved till now.

The investigations of the boron-related radiation defects in Si have been done in the main by deep level transient spectroscopy (DLTS) and electron paramagnetic resonance (EPR) [1–10]. The main defect appearing in boron-doped Si under the irradiation is known to be interstitial boron (B_i), which is created through the interaction of a self-interstitial atom (I) with substitutional boron [1–4]. Two levels, $E_c - 0.13$ eV and $E_c - 0.37$ eV, were attributed to B_i [2, 3, 5]. B_i is annealed by the diffusion at about 240–250 K [1, 3]. Under the injection of minority carriers, the enhanced migration of B_i atoms can be observed [1, 3, 5]. It has been shown that B_i is highly active in the formation of radiation defects. Diffusing B_i atoms can interact with one another with the formation of B_iB_i defects. B_i can be trapped by substitutional boron (B_s) and by the main impurities of Si such as oxygen and carbon with the formation of B_iB_s, B_iO_i, and B_iC_s complexes, respectively [1, 3, 6, 7, 11–14]. The level at $E_c - 0.23$ eV is ascribed to B_iO_i defect due to the correlation of its formation with the boron and oxygen concentrations in samples [3, 5, 7–10]. The defect consisting of interstitial boron and oxygen was believed to be also responsible for the light-induced degradation of Si solar cells [15–18].

B_iO_i complex dissociates upon annealing at 150–200 °C, and its annealing is accompanied by the appearance of a level at $E_v + 0.29$ eV identified as B_iC_s complex [6, 7, 13, 19, 20]. The level $E_v + 0.30$ eV detected in boron-doped Si irradiated at room temperature is associated with B_iB_s defects [7].

The limited information on local vibration modes (LVMs) of interstitial boron-related defects is available. The absorption bands positioned at 730 and 757 cm^{-1} were assigned in [11] to LVMs of interstitial boron in Si. The bands at 733 and 760 cm^{-1} were identified as LVMs of B_iB_s complex, and the lines at 903, 912, 928, 599, and 613 cm^{-1} were tentatively ascribed to the precursor of B_iB_s defects [11, 21–23]. It should be noted that the identification of all absorption bands in study [11] was carried out for the samples doped with boron in very high concentrations, $(1-5)\times10^{19}\,cm^{-3}$, and simultaneously co-doped with phosphorus or arsenic with the same concentrations. To remove residual free carriers, the samples were irradiated at room temperature with 2 MeV electrons at high doses $(0.5-6.7)\times10^{19}\,cm^{-2}$. Then, before investigations were carried out, the samples were subjected to irradiation at $T = 110$ K with a dose of $(5-9)\times10^{19}\,cm^{-2}$. The reactions between defects in such materials are, apparently, more complicated. Therefore, the interpretation of the observed bands requires additional studies. The set of LVMs at 991, 721, and 550 cm^{-1} in work [24] is associated with B_iO_i-related defects. In a recent study [25], the absorption bands at 739.4, 759.6, and 780.9 cm^{-1} were identified as LVMs associated with B_iB_i defects, and the line at 923.5 cm^{-1} was ascribed to the complexes involving interstitial boron and interstitial oxygen atoms.

The available information on the optical properties of the interstitial boron-related radiation defects in Si is yet insufficient. To our knowledge, no electronic absorption features, which could be related to the B_i-related defects, has been reported till now. This information is of great importance for understanding the influence of B_i-related defects on the electrical parameters of silicon and devices made on its base. In the present work, we report new data on the electronic absorption of interstitial boron-related defects in silicon.

2 Experimental 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 $[B_s] = (1-3.6)\times10^{16}\,cm^{-3}$. The content of oxygen ($[O_i]$) in Cz-Si was determined at room temperature by the intensity of the absorption band at 1107 cm^1 and was about $3\times10^{14}\,cm^{-3}$ in Fz-Si samples and $(5.0-10.1)\times10^{17}\,cm^{-3}$ in Cz-Si. The carbon concentration was defined by the intensity of the absorption band at 605 cm^{-1} and was varied in the interval $[C_s] = (0.1-7.4)\times10^{16}\,cm^{-3}$. The samples of Si with a low content of boron ($[B_s] \le 10^{14}\,cm^{-3}$) as well as n-silicon with concentrations of phosphorus $[P_s] \approx 10^{15}\,cm^{-3}$ were studied also for the comparison. The parameters of the investigated samples are presented in Table 1.

The samples were irradiated with 5 MeV electrons at the temperature $T = 80$ K using a Microtron M30 accelerator. The doses of irradiation were $(5–6)\times10^{17}\,cm^{-2}$. Before the investigations samples were subjected to annealing up to 300 K.

To study the thermal stability of radiation defects, 20 min isochronal anneals of samples were carried out in the range of $300-650$ K with temperature increments of 10 K. The absorption spectra of 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^{-1}. The absorption spectrum of a nonirradiated high-purity Fz-Si was subtracted from each spectrum.

Table 1 The parameters of samples used in the study.

sample	$[B_s]$, $\times10^{16}\,cm^{-3}$	$[O_i]$, $\times10^{17}\,cm^{-3}$	$[C_s]$, $\times10^{16}\,cm^{-3}$	$[P_s]$, $\times10^{15}\,cm^{-3}$
1	3.6	10.1	7.4	
2	3	0.003	<0.1	
3	1	5	7.1	
4	1	0.003	3.2	
5	0.01	8	7	
6		9.7	5	1

3 Results and discussion Two new electronic absorption features not previously reported have been revealed in the spectra of irradiated boron-doped Si. Figure 1 shows the absorption spectra in the region 4380–4390 cm^{-1} for samples irradiated at 80 K and subjected to the subsequent annealing up to 300 K. The spectra for three Cz-Si (samples 1, 3, and 5) and for Fz-Si (sample 4) with different boron contents are presented in the Fig. 1. It should be noted that the spectrum for n-type silicon coincides with that for Si with low boron concentration. As is seen, the new sharp line positioned at about 4385.2 cm^{-1}

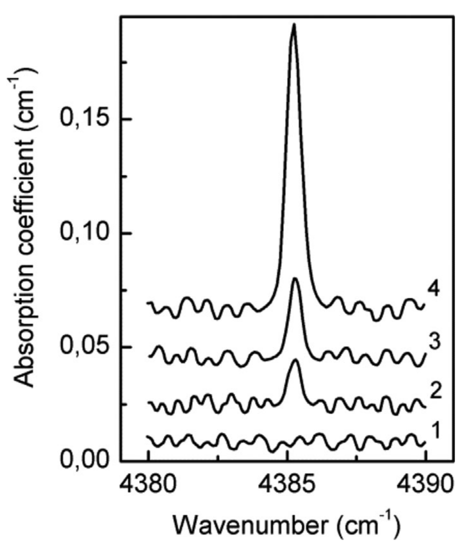

Figure 1 Fragments of the absorption spectra measured at 10 K for boron-doped Cz-Si and Fz-Si samples irradiated at 80 K with 5 MeV electrons and subjected to subsequent annealing up to 300 K. The initial boron concentrations in samples $[B_s]$, $\times10^{16}\,cm^{-3}$: 1 – 0.01; 2, 4 – 1; 3 – 3.6. $[O_i]$, $\times10^{17}\,cm^{-3}$: 1 – 8; 2 – 5; 3 – 10.1; 4 – 0.003. Irradiation dose was $\Phi = 5\times10^{17}\,cm^{-2}$. The spectra are baseline corrected and shifted along the vertical axis for clarity.

appears in Si samples with the content of boron $[B_s] \geq 1 \times 10^{16}\,cm^{-3}$ as compared with the samples with low boron content and with n-silicon. The half-width of the detected line is $0.5\,cm^{-1}$. Figure 1 demonstrates that the emergence of the detected line is observed for both Cz-Si and Fz-Si, i.e., its appearance is independent of the presence of oxygen in the samples. The investigations of samples with different carbon concentrations have shown that the appearance of the line at $4385.2\,cm^{-1}$ is independent also of the carbon content in samples. The comparison of the intensity of the detected line for Cz-Si samples with different boron contents (spectra 2 and 3) shows that it grows with the boron concentration. This implies that a boron atom enters the composition of the defect responsible for the revealed line.

Two B_i-related defects (B_iO_i and B_iB_s) have been detected earlier by DLTS in boron-doped Si samples irradiated at room temperature [6, 7, 13]. The observed dependence of the intensities of the revealed line at $4385.2\,cm^{-1}$ on the boron concentration and the independence of its appearance of the presence of oxygen and carbon in the samples can testify that the detected line corresponds to B_iB_s complex.

As seen from Fig. 1, the efficiency of the formation of B_iB_s defects in oxygen-rich silicon is much lower than in the oxygen-lean material at the equal initial boron contents (spectra 2 and 4). The simultaneous presence of B_iB_s (level $E_v + 0.30\,eV$) and B_iO_i (level $E_c - 0.23\,eV$) defects registered by DLTS in boron-doped Cz-Si [7] and a significant reduction observed by us in the rate of B_iB_s formation in oxygen-rich samples in comparison with Fz-Si imply that the efficiency of the interaction of B_i with interstitial oxygen is rather higher. Thus, O_i is the main competitor of B_s for the interaction with B_i, as it was assumed in Ref. [7].

To determine the thermal stability of B_iB_s defects, the isochronal anneals have been carried out. Figure 2 shows the changes in the intensity of the $4385.2\,cm^{-1}$ absorption line upon the annealing of Fz-Si (sample 4). No changes in the intensity occurred at a temperatures up to 353 K. The further increase in the annealing temperature ($T_{ann.}$) results in a decrease in the line intensity, and the line disappears at about 423 K. In Cz-Si, line anneals in the same interval of temperatures.

The disappearance of the $4385.2\,cm^{-1}$ line upon the annealing is accompanied by the development of a new sharp line at $7829.5\,cm^{-1}$ in the spectrum. Figure 3 shows the absorption spectra in the region $7810–7840\,cm^{-1}$ for Cz-Si (samples 1, 3, and 5) and Fz-Si (sample 4) with different boron contents. The line at about $\sim 7819\,cm^{-1}$ has been assigned earlier to C_iC_s complexes [26]. The half-width of the detected line at $7829.5\,cm^{-1}$ is $0.6\,cm^{-1}$. The coincidence of the formation of the defect responsible for the registered line with the annealing of B_iB_s defects suggests that interstitial boron liberated at its dissociation is involved in the composition of a defect responsible for the line at $7829.5\,cm^{-1}$. The comparison of the absorption

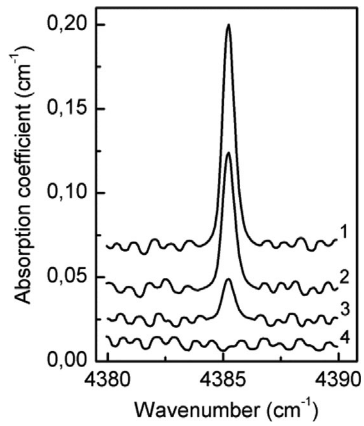

Figure 2 Evolution of the absorption spectrum upon the 20 min isochronal annealing of the irradiated boron-doped Si. $T_{ann.}$, K: 1 – 353; 2 – 383; 3 – 413, 4 – 423. $[B_s] = 1 \times 10^{16}\,cm^{-3}$. Irradiation dose was $\Phi = 5 \times 10^{17}\,cm^{-2}$. The spectra are baseline corrected.

spectra (see Fig. 3) for oxygen-rich and -lean samples demonstrates that the $7829.5\,cm^{-1}$ line is observed for both materials. This implies that the appearance of the revealed line is independent of the presence of oxygen in the samples.

The investigations have shown that the emergence of a defect responsible for the line at $7829.5\,cm^{-1}$ depends on the presence of carbon in the samples. Figure 4 shows the absorption spectra for two oxygen-lean samples, in one of which the carbon concentration is below the detection level ($\leq 1 \times 10^{15}\,cm^{3}$), and it is $3.2 \times 10^{16}\,cm^{-3}$ in the second one. As seen, the line at $7829.5\,cm^{-1}$ does not

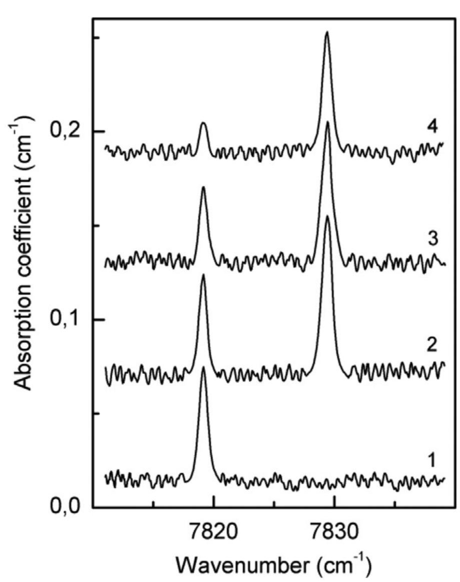

Figure 3 Fragments of the absorption spectra measured at 10 K for boron-doped Cz-Si (1–3) and Fz-Si (4) samples subjected to isochronal annealing up to 523 K. The initial boron concentrations in samples $[B_s]$, $\times 10^{16}\,cm^{-3}$: 1 – 0.01; 2, 4 – 1; 3 – 3.6. Irradiation dose was $\Phi = 5 \times 10^{17}\,cm^{-2}$. $[O_i]$, $\times 10^{17}\,cm^{-3}$: 1 – 8; 2 – 5; 3 – 10.1; 4 – 0.003. The spectra are baseline corrected.

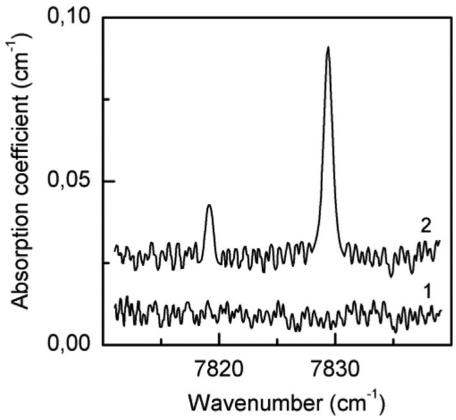

Figure 4 Fragments of the absorption spectra measured at 10 K for boron-doped Fz-Si subjected to isochronal annealing up to 523 K. The initial boron concentrations in samples [B_s], $\times 10^{16}\,cm^{-3}$: 1–3; 2 – 1. [C_s], $\times 10^{16}\,cm^{-3}$: 1 – <0.1; 2 – 3.2. Irradiation dose was $\Phi = 5 \times 10^{17}\,cm^{-2}$. The spectra are vertically shifted for clarity.

emerge in carbon-lean Si. This testifies that the carbon atom is a component of the defect responsible for the detected line.

The dependence of the emergence of a defect responsible for the revealed line on the presence of boron and carbon in the samples implies that the registered line at 7829.5 cm^{-1} is most likely related to B_iC_s complexes. Obviously, the defect is formed, when a mobile B_i atom liberated at the B_iB_s dissociation is localized near a carbon atom.

The difference in the rates of formation of B_iC_s for Fz- and Cz-Si samples is revealed in the present study. Figure 5 demonstrates the changes in the intensities of the absorption lines at 4385.2 and 7829.5 cm^1 at the 20 min isochronal anneals for oxygen-rich and -lean samples with equal boron content. From the results shown in Fig. 5, it is seen that the 7829.5 cm^{-1} line emerges at the annealing of B_iB_s defects in

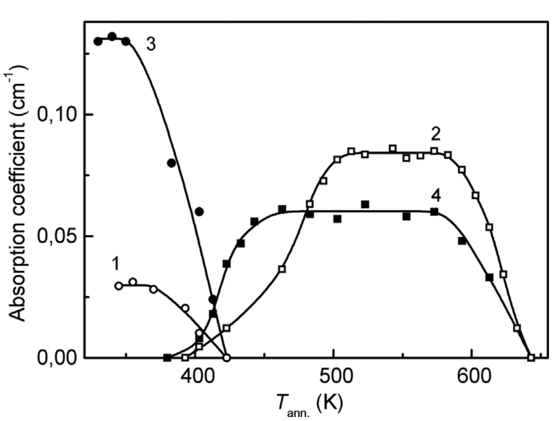

Figure 5 Changes in the intensities of the absorption lines at 4385.2 cm^{-1} (1, 3) and 7829.5 cm^{-1} (2, 4) upon the 20 min isochronal annealing for Cz-Si (1, 2) and Fz-Si (3, 4) samples with equal boron content ([B_s] = $1 \times 10^{16}\,cm^{-3}$). [$O_i$], $\times 10^{17}\,cm^{-3}$: 1, 2 – 5; 3, 4 – 0.003.

the both types of samples, but it appears in Fz-Si at temperatures slightly lower than in Cz-Si. Besides, the line intensity reaches the maximum value at 453 K in Fz-Si, whereas, in Cz-Si at 513 K. Moreover, the value of maximum intensity for the line in Cz-Si is higher than that in Fz-Si. Although, as seen from the figure, the formation efficiency of B_iB_s defects in Cz-Si is significantly lower than in Fz-Si. This implies the existence of an additional source of B_i in the Cz-material, which is involved in the formation of B_iC_s.

In the previous studies [7, 10, 13, 20], it was shown by DLTS that the B_iC_s complexes in boron-doped Cz-Si arise synchronously with the dissociation of B_iO_i defects. The annealing temperature for B_iO_i, according to the studies [7–10, 13, 20, 24, 27] is 150–200 °C, i.e., slightly higher than that for B_iB_s defects observed by us. Taking into account the closeness of these two annealing processes, it can be concluded that B_i atoms liberated as a result of the dissociation of both B_iB_s and B_iO_i are involved in the formation of B_iC_s defects in the oxygen-rich material. The high value of maximum intensity for the 7829.5 cm^{-1} line in Cz-Si is explained by this fact. The shift in the annealing temperatures for B_iB_s and B_iO_i complexes results in the observed shift in the temperature, at which the maximum intensity for the line at 7829.5 cm^{-1} in Cz-material is attained, in comparison with Fz-Si. As for oxygen-lean silicon, the formation of B_iC_s defects involves only B_i liberated at the dissociation of B_iB_s.

After reaching the maximum value, no changes in the intensity of the line at 7829.5 cm^{-1} are observed at annealing temperature up to 573 K. The further increase in the annealing temperature results in a decrease in the line intensity, and the line disappears at about 643 K for both Cz-Si and Fz-Si samples. It should be noted that the temperatures of the emergence and disappearance of the line at 7829.5 cm^{-1} coincide with those for the level $E_v + 0.29$ eV identified previously by DLTS [7, 13] as related to B_iC_s defects. This confirms the correctness of the identification of the line found by us.

4 Conclusions The new sharp line with a half-width of 0.5 cm^{-1} and with a maximum at about 4385.2 cm^{-1} has been revealed in the absorption spectra of boron-doped Si samples irradiated at 80 K and subjected to the subsequent annealing up to 300 K. The observed dependence of the line intensity on the boron concentration, the independence of its emergence on the presence of oxygen and carbon in the samples, and the coincidence of its appearance with this of the level $E_v + 0.30$ eV identified earlier by DLTS as related to B_iB_s defects, can testify that the detected line corresponds to B_iB_s complexes. The efficiency of the formation of B_iB_s defects in oxygen-rich silicon is much lower than in the oxygen-lean material. A significant reduction in the rate of formation of B_iB_s in oxygen-rich samples appears owing to the competition in the formation of B_iO_i and B_iB_s complexes and implies that the probability of the interaction of B_i with interstitial oxygen is rather higher.

The disappearance of the line at $4385.2\,cm^{-1}$ upon the annealing is accompanied by the development of a new sharp line at $7829.5\,cm^{-1}$ in the spectrum. The dependence of the emergence of a defect responsible for the revealed line on the presence of boron and carbon in samples, and coincidence of its appearance and disappearance with those of the level $E_v + 0.29\,eV$ identified previously by DLTS as that related to B_iC_s defects suggest that the registered line at $7829.5\,cm^{-1}$ is associated with B_iC_s complexes. The obtained data have shown that B_i atoms, liberated as a result of the dissociation of both B_iB_s and B_iO_i, are involved in the formation of B_iC_s defects in the oxygen-rich Si, whereas, in oxygen-lean Si, only B_i liberated at the dissociation of B_iB_s complexes participate in the formation of B_iC_s.

It should be noted that most of the work published during the last decades is devoted to the study of the B_iO_i defect responsible for the radiation- and light-induced degradation of solar cells. The very limited information on other boron aggregates is available. The obtained in work results are important for understanding the evolution of boron-containing defects, their interaction with each other and their influence on both the radiation- and the light-induced degradation of solar cells.

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