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Features of the Formation of the B_iB_s Defect in Si

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The data on the features of the electronic absorption in boron-doped silicon irradiated at 80 K with 5 MeV electrons are presented in this paper. The electronic transition at a frequency of 4296.8 cm^{-1} is revealed in the absorption spectra of as-irradiated boron-doped Si samples. The intensity of the registered line grows with the boron concentration. The formation of defect responsible for the 4296.8 cm^{-1} line is independent of the presence of oxygen and carbon in the samples. The investigations show that the vacancies are not components of the defect related to the 4296.8 cm^{-1} line. The study of the thermal stability of the revealed defect shows that the disappearance of line at the annealing is accompanied by the synchronous development of the 4385.2 cm^{-1} absorption line associated with the B_iB_s defects. The revealed defect is identified as a precursor of a stable configuration of the B_iB_s complex.

1. Introduction

The engineering of defects is a key factor of the manufacturing of microelectronic devices. The development of silicon-based devices with specified characteristics requires the control over the level and type of doping and the detailed knowledge of the influence of the dopants on the defect–impurities interaction during the making of an initial material, as well as in the process of production of devices on its basis. One of the main problems arisen at the doping by the implantation and at the subsequent annealing is the formation of complexes. The defects with the participation of impurities such as oxygen and/or carbon, which are the main technological impurities of silicon, appear. Many defects also arise in devices operating under conditions with high levels of radiation. The excitation of the electron subsystem under the action of radiation can induce the enhanced diffusion of impurity atoms and point-like defects and result in the formation of recombination complexes, which can affect the degradation of electric parameters of silicon and the characteristics of devices produced on its basis. A fundamental understanding of these defects and their properties is essential in defect engineering.

Boron is one of the dopants most widely used in the devices manufacture on the basis of p-silicon. The doping with boron is applied in microelectronics based on the mono- and multi-silicon and as well as in the creation of modern submicronic Si devices. However, in spite of the widespread use of Si:B, the identification of boron-related defects in silicon doped with high boron concentration remains insufficiently investigated till now. There are current debates in the silicon community about the evolution of boron-related complexes.

One of the dominant defects produced in boron-doped Si by electron irradiation at cryogenic temperatures is interstitial boron (B_i). At low-temperature irradiation, the self-interstitial atom (I) interacts efficiently with substitutional boron (B_s) and ejects it into interstitial site.[1–4] Interstitial boron (B_i) is annealed by the diffusion at about 240 K.[1–3] B_i is known to be very active in the processes of defect formation in Si under influence of irradiation.[5,6] The diffusing during annealing B_i atoms can interact with one another,[5,7] with substitutional boron,[7,8] and with the main impurities in silicon such as interstitial oxygen[5,9] and substitutional carbon,[5,10,11] by forming the B_iB_i, B_iB_s, B_iO_i, and B_iC_s complexes, respectively. The boron-containing radiation defects were mainly identified using deep-level transient spectroscopy and electron paramagnetic resonance methods. The levels at $E_c - 0.25$ eV and $E_v + 0.29$ eV were associated with the B_iO_i and B_iC_s defects, correspondingly.[8,11,12] The level at $E_v + 0.3$ eV was attributed to B_iB_s defect.[8] But, latter it was shown that the B_iB_s complex is electrically inactive.[13–16] The properties of B_iO_i defects were studied in many works. The B_iO_i defect has been of significant interest to the photovoltaic community because the light-induced degradation of solar cells is associated with the boron–oxygen-related defect.[17–19] The available information about properties of the B_iC_s, B_iB_s, and B_iB_i complexes is yet insufficient.

A few works have been devoted to the investigation of local vibrational modes (LVMs) of B_i-related defects by infrared spectroscopy. Two LVMs at 730 and 757 cm^{-1} have been attributed to interstitial ^{11}B and ^{10}B atoms, respectively.[7,20] The LVMs at 903, 912, 928, 613, and 599 cm^{-1} (S lines) were ascribed to an interstitial B_iB_i pairs.[7] Two LVMs at 733 and 760 cm^{-1} were assigned to the B_iB_s complex.[7,21] A new set of absorption bands positioned at about 538, 550, 688, 721, 756, and 991 cm^{-1} was identified as LVMs of the B_iO_i complex.[22]

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The studies performed by deep-level transient spectroscopy and electron paramagnetic resonance methods indicate that, at the injection of minority carriers, a significant increase in the rate of annealing of B_i can be observed in accordance with the Bourgoin–Corbett mechanism.[4,23] Recently, it was shown that the enhanced diffusion of interstitial boron can occur also during the irradiation of samples at a temperature of 80 K.[24,25] The absorption spectra of the as-irradiated samples contain no LVMs associated with interstitial boron, but the LVMs of defects, whose composition includes interstitial boron, were registered. The revealed LVMs at 739.4, 759.6, and 780.9 cm^{-1} were assigned to the B_iB_i defect. The registered line at 923.5 cm^{-1} was identified as the B_iO_i-related defect.[24]

To our knowledge, practically no information about the electronic absorption features, which can be associated with B_i-related defects, is available. This is crucial for the comprehension of the influence of defects on the electric and optical parameters of silicon and devices produced on its basis. Recently, it was shown that the absorption lines at 4385.2 and 7829.5 cm^{-1} are associated with the electronic transitions of the B_iB_s and B_iC_s complexes, respectively.[25] In the present work, we present the new data on the specific features of the electronic absorption associated with the B_iB_s defects in silicon.

2. Experimental Section

The samples of boron-doped Si used in the study were grown by the Czochralski (Cz-Si:B) and float-zone (Fz-Si:B) methods. The concentration of boron (N_B) in samples was determined from Hall effect measurements and was varied in the interval $(0.5-3.6) \times 10^{16}$ cm^{-3}. The content of oxygen (N_O) in Cz-Si:B was determined at room temperature by the intensity of the absorption band at 1107 cm^{-1} and was changed in the range $(5.0-9.9) \times 10^{17}$ cm^{-3}. The carbon concentration (N_C) in samples was defined by the intensity of the absorption band at 605 cm^{-1} and was ranged from 1×10^{15} to 7.4×10^{16} cm^{-3}. For comparison, the phosphorous-doped Cz-Si sample was studied. 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 conditions for irradiation were similar to those described in previous study.[24] The samples were irradiated in a flow of liquid nitrogen supplied at an excess pressure. The irradiated samples were transferred without heating into a cryostat for infrared absorption measurements. The doses of irradiation were $(5–6) \times 10^{17}$ cm^{-2}.

Table 1. The parameters of samples used in the study.

No	N_B [10^{16} cm^{-3}]	N_O [10^{17} cm^{-3}]	N_C [10^{16} cm^{-3}]	N_P [10^{16} cm^{-3}]
1	3.6	9.9	7.4	–
2	2.6	0.003	<0.1	–
3	1	5	7.1	–
4	1	0.003	3.2	–
5	0.5	6	0.8	–
6	–	9.7	5	1

To study the thermal stability of radiation defects, isochronal anneals of samples for 20 min were carried out in the range of 80–330 K with the temperature increments of 10 K. 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^{-1}. The absorption spectrum of a nonirradiated high-purity Fz-Si was subtracted from each spectrum.

3. Results and Discussion

As in previous studies,[24,25] no LVMs related to the interstitial boron were registered in the absorption spectra for as-irradiated at 80 K Si:B samples due to the enhanced annealing of B_i under conditions of the experiment. The LVMs of defects involving interstitial boron and oxygen atoms (923.5 cm^{-1}) as well as B_iB_i complexes (739.4, 759.6, and 780.9 cm^{-1}) were observed in the spectra. When studying the absorption spectra of as-irradiated samples in the range of electronic transitions, we have detected the electronic transition not previously observed with maximum at 4296.8 cm^{-1}. The registered absorption spectra for Cz-Si:B samples with different concentrations of boron are shown in **Figure 1**. The half-width of the revealed line is about 0.3 cm^{-1}. As is seen from Figure 1, the intensity of the 4296.8 cm^{-1} line grows with the boron concentration. The revealed line is not observed for the phosphorous-doped sample (Figure 1, spectrum 1). This allows us to assume that an interstitial boron atom enters the composition of the defect with which the observed line is associated.

We have studied the dependence of the formation of a defect responsible for the revealed line on the oxygen and carbon contents. The absorption spectra for Si:B samples with different concentrations of oxygen and carbon are shown in **Figure 2**a,b.

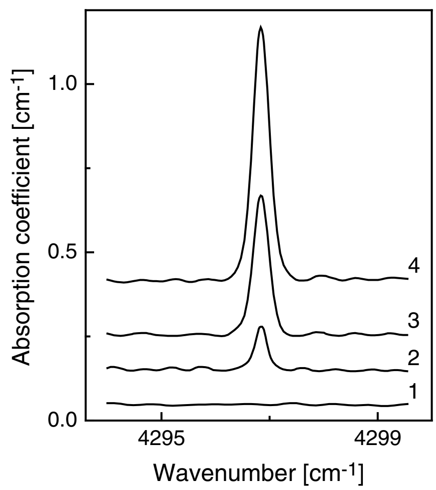

Figure 1. Fragments of the absorption spectra measured at 10 K for the as-irradiated at 80 K boron-doped Cz-Si samples. The initial boron concentrations in the samples N_B, $\times 10^{16}$ cm^{-3}: 1 – 0; 2 – 0.5; 3 – 1; 4 – 3.6. N_O, $\times 10^{17}$ cm^{-3}: 1 – 9.7; 2 – 6; 3 – 5; 4 – 9.9. The spectrum (1) corresponds to the phosphorous-doped Si. Irradiation dose was $\Phi = 6 \times 10^{17}$ cm^{-2}. The spectra are shifted along the vertical axis for clarity.

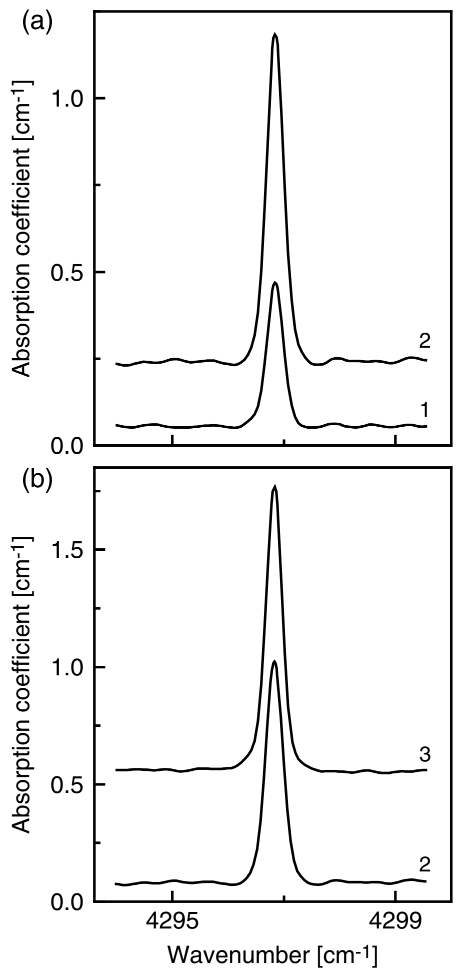

Figure 2. Absorption spectra measured at 10 K for boron-doped Si samples with comparable concentrations of boron and different oxygen content (a) and samples with comparable content of oxygen but different carbon concentrations (b). The initial boron concentrations in samples N_B, $\times 10^{16}$ cm^{-3}: 1, 2 – 1; 3 – 2.6. N_O, $\times 10^{17}$ cm^{-3}: 1 – 5; 2, 3 – 0.003. N_C, $\times 10^{16}$ cm^{-3}: 1 – 7.1; 2 – 3.2; 3 – <0.1. Irradiation dose was $\Phi = 6 \times 10^{17}$ cm^{-2}.

Figure 2a shows the spectra for the samples with comparable concentrations of boron, but differing by more than three orders in the oxygen content. Figure 2b demonstrates the spectra for the samples with comparable concentrations of oxygen (Fz-Si:B) but with different carbon contents. As can be seen from Figure 2, the registered line is observed in all types of samples. This implies that the formation of a defect responsible for the 4296.8 cm^{-1} line is independent of the presence of oxygen and carbon in the samples, i.e., the composition of a found defect do not involve these impurities. Thus, we can assume that only a boron atom enters the composition of the defect with which the observed line is associated.

Figure 2a indicates also that the intensity of the 4296.8 cm^{-1} line in oxygen-rich silicon is much lower than in the oxygen-lean material at the equal boron contents. This testifies that oxygen is the main competitor in the formation of a registered defect in Cz-Si:B.

Taking into account that the formation of a revealed defect is detected only in boron-doped samples and defect consisting of two interstitial boron atoms (B_iB_i) is observed in as-irradiated at low temperature Si:B samples, it is reasonable to assume that the registered line can be associated with B_iB_s defect. However, earlier it was shown that the electronic absorption line with a maximum at 4385.2 cm^{-1} corresponds to the B_iB_s defect which is stable up to 423 K.[25]

To determine the thermal stability of the revealed center responsible for the line at 4296.8 cm^{-1}, the isochronal annealing of the irradiated boron-doped Si samples has been carried out. No changes were observed in the intensity of 4296.8 cm^{-1} absorption line at the annealing of the samples up to the temperatures $T_{ann.} \approx 140$ K. In the temperature interval 140–180 K, some increase in the line intensity was registered. This is a testament to the additional formation of defects responsible for the 4296.8 cm^{-1} line occurs. It was shown earlier that, in the temperature interval 140–180 K, the B_iB_i complexes are annealed.[24] Although B_i should be immobile at these temperatures, it is possible that during annealing, the transformation of B_iB_i configuration into the configuration of B_iB_s precursor appears. In this case, the diffusion of interstitial boron by lattice is not required. To ascertainment of the mechanism of transformation of the B_iB_i defect into the precursor of the B_iB_s complex, the further study would be desirable.

The further increase in the annealing temperatures up to 250 K has no effect on the intensity of the detected line. Annealing at higher temperatures results in a significant decrease in the line intensity, and it disappears at about 273 K. The changes in the intensity of detected absorption line during isochronal annealing of irradiated Si:B sample in the temperature interval 180–273 K are demonstrated in **Figure 3**.

It is worth to note that in the temperature interval of the existence of the registered defect, vacancy-related reactions occur. So, the increase in the intensity of LVM at 836 cm^{-1} associated with the vacancy-oxygen (VO) defect was observed. The changes in the intensity of the VO vibrational mode upon annealing are

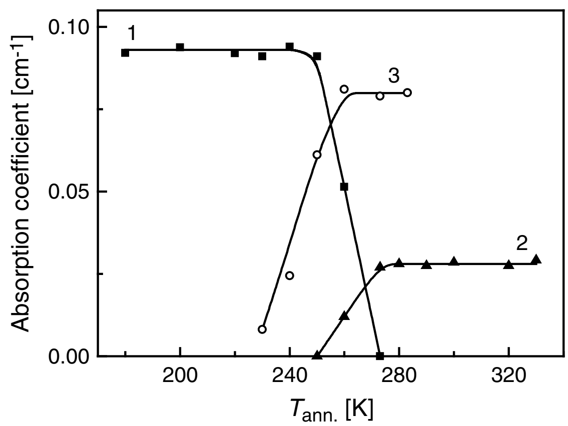

Figure 3. Changes in the intensities of the absorption lines at 4296.8 cm^{-1} (1), 4385.2 cm^{-1} (2), and 836 cm^{-1} (3) upon the 20 min isochronal annealing for the irradiated Si:B sample. $N_B = 1 \times 10^{16}$ cm^{-3}. $N_O = 5 \times 10^{17}$ cm^{-3}. The absorption coefficient for the dependences (1) and (3) has been multiplied in the ordinate by a factor of 0.2. Irradiation dose was $\Phi = 6 \times 10^{17}$ cm^{-2}.

demonstrated in Figure 3. As can be seen from Figure 3, the mode at 836 cm^{-1} develops in spectra at an annealing temperature $T_{ann.} > 220$ K and attains the maximum intensity at about 260 K. This indicates the appearance of vacancies in this temperature interval. From Figure 3, it is also seen that no changes in the intensity of 4296.8 cm^{-1} line appeared at these temperatures. This testifies that the vacancies are not components of the defect related to 4296.8 cm^{-1}. One of the well-known vacancy-related defects in irradiated boron-doped silicon is the boron-vacancy complex (BV).[26–28] The BV complex was found to anneal by dissociation in the temperature interval of 220–250 K. We can assume that the interaction of diffusing vacancies, liberated during dissociation of BV defects, with oxygen can result in the observed increase in the intensity of the LVM corresponding to the VO centers. Although it should be noted that the existence of BV complexes in Cz-Si is debatable. As previously studied by Watkins,[26] it was asserted that defect is observed only in Fz-Si with low oxygen content. Later in study carried out by Polity et al.,[29] BV defect was detected both in Cz-Si and Fz-Si. In our experiment, we observed an increase in the concentration of VO centers, which indicates an annealing of the vacancy-related defect in this temperature interval. To ascertain the nature of the defect, annealing of which leads to an increase in the concentration of VO-centers, additional researches are needed with the use of another methods.

The study of the thermal stability of the revealed complex has shown that the disappearance of the 4296.8 cm^{-1} line is accompanied by the development of the absorption line at 4385.2 cm^{-1} in the spectrum which was associated with the B_iB_s centers.[25] **Figure 4** demonstrates the dependence of the absorption spectra on the annealing temperatures for a sample irradiated at 80 K and subjected to the subsequent annealing. The changes in the intensities of the absorption lines at 4296.8 and 4385.2 cm^{-1} upon the 20 min isochronal annealing are shown

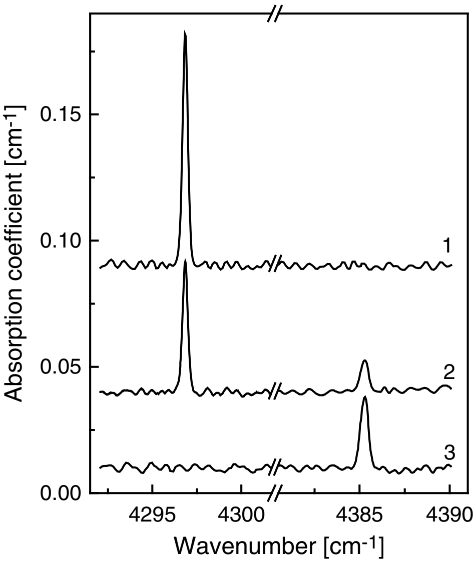

Figure 4. Evolution of the absorption spectrum upon the isochronal annealing of the irradiated at 80 K boron-doped Si. $T_{ann.}$, K: 1 − 250; 2 − 260; 3 − 280. $N_B = 1 \times 10^{16}$ cm^{-3}. $N_O = 5 \times 10^{17}$ cm^{-3}. Irradiation dose was $\Phi = 6 \times 10^{17}$ cm^{-2}.

in Figure 3. Figure 3 and 4 indicate that the 4385.2 cm^{-1} line arises synchronously with the disappearance of the 4296.8 cm^{-1} line. This allows us to assume that the revealed defect is transformed into the B_iB_s complex upon annealing.

Thus, the obtained experimental data testify the following features in the formation of the defect responsible for the 4296.8 cm^{-1} line detected in irradiated boron-doped Si: the B_i atom is involved in the defect, the appearance of the defect is independent of the presence of oxygen and carbon in the samples, the defect transforms at the annealing into the B_iB_s complex. This allows to suggest that the registered electronic transition at 4296.8 cm^{-1} may be identified as the precursor (B_iB_s*) of the B_iB_s center. The possible existence of the precursor of a stable configuration of the B_iB_s defect has been reported in previous studies.[13–15] The boron-related defects in Si, produced by irradiation or implantation, were studied in these works. According to the model, proposed for the structure of an unstable configuration of B_iB_s*, an atom of self-interstitial diffusing at irradiation locates firstly into the space between two atoms of substitutional boron forming metastable linear B_s–Si_i–B_s pair along a [111] axis. This configuration is unstable and is transformed into a stable configuration of the B_iB_s defect with rising the annealing temperature. According to the theoretical calculations, a level at $E_c - 0.2$ eV is associated with the precursor of the B_iB_s defect. The LVMs at 903, 912, 928, 613, and 599 cm^{-1} (S lines), which were initially ascribed to an interstitial B_iB_i pairs,[7] were presumably reassigned to the LVMs of the precursor of a stable configuration of the B_iB_s defects.[13–15]

4. Conclusion

In boron-doped Si irradiated at 80 K with 5 MeV electrons, we have revealed the electronic transition at a frequency of 4296.8 cm^{-1}. The intensity of detected line grows with the increasing boron concentration. The formation of a defect responsible for the 4296.8 cm^{-1} line is independent of oxygen and carbon in the samples, i.e., the composition of a found defect do not involve these impurities. The intensity of the 4296.8 cm^{-1} line in oxygen-rich silicon is much lower than in the oxygen-lean material at the equal initial boron contents. This testifies that oxygen is the main competitor in the formation of a registered defect in Cz-Si:B. The defect responsible for the observed line is thermally stable up to 250 K and disappears, as the temperature increases up to 273 K. The disappearance of the 4296.8 cm^{-1} line during the annealing is accompanied by the synchronous development in spectra of the 4385.2 cm^{-1} line associated with the B_iB_s complexes. The registered line at 4296.8 cm^{-1} is ascribed to the precursors of a stable configuration of the B_iB_s defect. Thus, the obtained data indicate that the B_iB_s-related defect in Si exists in a wide temperature interval (from 80 to 423 K) and can affect the properties of silicon and devices made on its base.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

boron, radiation defects, silicon

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