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# The Features of Infrared Absorption of Boron-Doped Silicon

*Lyudmila Khirunenko,\* Mikhail Sosnin, Andrei Duvanskii, Nikolai Abrosimov, and Helge Riemann*

Herein, the influence of heat treatment at 400 °C on the spectrum of boron intracenter transitions in silicon using IR absorption spectroscopy is investigated. In the transition region from the ground $1\Gamma_8^+$ state associated with the $p_{3/2}$ valence band of Si to the odd-parity excited states of boron, a new absorption line with its maximum at 261.3 cm$^{-1}$ is observed in the thermally treated boron-doped Cz-Si. Oxygen is a component of defect that is responsible for the detected absorption line. Perturbation of boron atoms due to the inhomogeneous stress effect from neighboring oxygen atoms results in a frequency shift in the main boron transition. The defect associated with 261.3 cm$^{-1}$ line is also observed in as-grown silicon. The defect disappears during annealing at 550 °C. The concentration of defects and binding energy of the $1\Gamma_8^+$ ground state are estimated assuming that the line observed belongs to the transition of boron $1\Gamma_8^+ \rightarrow 2\Gamma_8^-$, subjected to the perturbation from a neighboring oxygen atom.

## 1. Introduction

Dopants determine many parameters of Si and silicon-based devices, such as electron mobility, lifetime, optical and thermal properties, and speed of operation. Boron doping is widely used in mono- and multisilicon-based microelectronics, as well as in creation of modern submicron Si devices. Therefore, understanding the role of boron in defect formation in silicon and devices made on its base is essential.

Investigating the interaction of boron with oxygen, which is known to be the main technological impurity of silicon, is particularly interesting. Both impurities actively participate in the defect formation process, and the resulting defects can affect the concentration of optically and electrically active boron. Although boron- and oxygen-related defects in Si have been investigated for many years, new defects including in their

L. Khirunenko, M. Sosnin, A. Duvanskii
Institute of Physics
National Academy of Sciences of Ukraine
Prospekt Nauki 46, Kiev 03028, Ukraine
E-mail: lukh@iop.kiev.ua

N. Abrosimov, H. Riemann
Leibniz-Institut für Kristallzüchtung
Department of Classical Semiconductors
Max-Born Str. 2, 12489 Berlin, Germany

composition boron and oxygen have been detected in the past decade.[1–4]

Boron is a substitutional, electrically active hydrogen-like impurity in a silicon lattice, described in the effective mass approximation theory.[5–11] Similar to other hydrogen-like impurities in semiconductors, boron is characterized by the line absorption spectrum caused by intracenter transitions between the ground and excited states.[11–13] For boron in the 240–350 cm$^{-1}$ spectral region, the transitions from the $1\Gamma_8^+$ ground state related to the $p_{3/2}$ ($\Gamma_8^+$) Si valence band to the $1\Gamma_8^-$, $2\Gamma_8^-$, $3\Gamma_8^-$, and other odd-parity excited states are observed.[11,13–15]

The absorption spectra of hydrogen-like impurities are highly sensitive to internal perturbations.[11,16–22] Perturbations arise from deviations in the ideal homogeneous distribution of impurities or defects, from defects resulting in local volume changes. Moreover, internal electric perturbations can also arise from fluctuations in the concentration of impurities or due to the compensation of inhomogeneities. Perturbations result in the shift of spectral lines, inhomogeneous broadening of lines, elimination of level degeneration, and consequently, splitting of absorption lines. The highly sensitivity of intracenter transitions of hydrogen-like impurities to perturbations can be used to detect possible interactions between boron and impurities or defects in the silicon lattice.

Despite the numerous studies conducted on boron-related defects, to our knowledge, only one has considered the influence of the boron-oxygen interaction on the intracenter transitions spectrum of boron.[23] Claybourn et al. carried out complex studies of the intracenter transitions and vibrational absorption bands of boron, oxygen concentration, and the specific resistance for boron-doped silicon subjected to the heat treatments at 450 °C. During the heat treatment, the intensity of boron intracenter transitions and vibrational absorption lines decreased due to the compensation of the silicon caused by the formation of thermal donors at this temperature. Furthermore, it was observed that the boron concentration continued to decrease even after reaching of the maximum concentration of thermal donors, which indicated that the boron concentration decreases not only due to the compensation of the material by thermal donors but also the additional interaction during heat treatment. However, the authors observed no appearance of absorption in the intracenter transitions region associated with new boron complexes. To the best of our knowledge, no other studies have

analyzed the impact of heat treatments on the spectrum of the intracenter transitions of boron.

In this study, we present new data on the influence of heat treatment at 400 °C on the intracenter transitions of boron. The diffusion of oxygen and oxygen dimers is known to occur at this temperature, which can result in interactions between oxygen and boron atoms. We believe the acquired data are essential for understanding the effect of such defects on the electrical and optical properties of silicon and devices produced on its base.

## 2. Results and Discussion

The typical absorption spectrum of boron in the 225–335 cm$^{-1}$ spectral region for a sample with boron concentrations of $4 \times 10^{14}$ cm$^{-3}$, is shown in **Figure 1** (spectrum 1). The spectrum was recorded with a 0.2 cm$^{-1}$ resolution. The observed absorption lines corresponded with the dipole allowed transitions from the $1\Gamma_8^+$ ground state related to the $p_{3/2}$ valence band of Si to the odd-parity excited states of $1\Gamma_8^-$ (244.95 cm$^{-1}$), $2\Gamma_8^-$ (278.29 cm$^{-1}$), $3\Gamma_8^-$ (309.5 cm$^{-1}$), $1\Gamma_6^-$ (319.4 cm$^{-1}$), $1\Gamma_7^-$ (320 cm$^{-1}$), and $4\Gamma_8^-$ (321.9 cm$^{-1}$).[11,13] The energies of transitions to the $1\Gamma_6^-$, $1\Gamma_7^-$, and $4\Gamma_8^-$ states are close in value; therefore, their spectral lines overlap.

The absorption spectrum for a Cz-Si:B sample with a boron concentration of $2.2 \times 10^{16}$ cm$^{-3}$ recorded with a resolution of 1 cm$^{-1}$ is shown in Figure 1 (spectrum 2). As can be seen, an increase in the boron concentration caused a significant broadening in the absorption lines and weak spectral components near the 250.7 and 261.5 cm$^{-1}$ appear in spectrum.
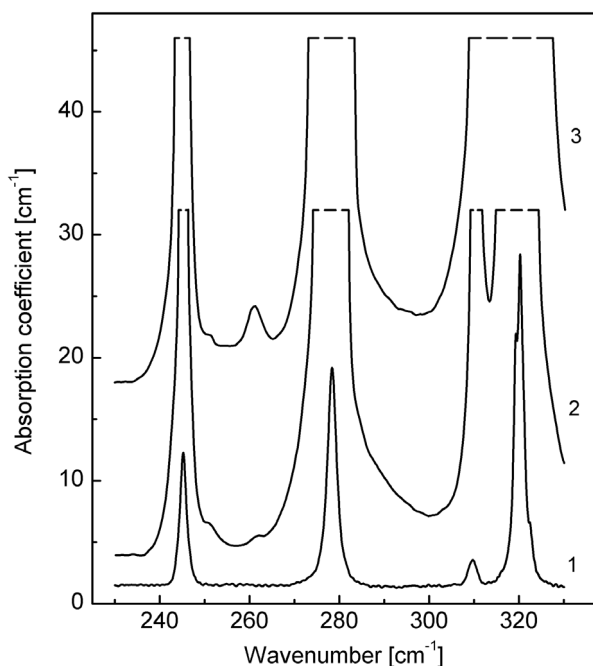
The Cz-Si:B sample with a boron concentration of $2.2 \times 10^{16}$ cm$^{-1}$ was then subjected to heat treatment at 400 °C for 10 h. The absorption spectrum of the annealed sample is shown in Figure 1 (spectrum 3). In addition to the main transitions, a not previously observed absorption line with a maximum at 261.3 cm$^{-1}$ appeared in the spectrum after thermal treatment, which overlapped with absorption line at 261.5 cm$^{-1}$. The appearance of new line in spectrum may indicate that the boron atoms have been subjected to perturbation from the environment. Moreover, the heat treatment slightly decreased the intensity of the main transitions of boron because of material compensation caused by the formation of thermal donors during heat treatment.

Studies showed that the intensities of the detected line as well as of the main transitions of boron depended on the concentration of boron in the samples. **Figure 2** shows the dependence of the detected line at 261.3 cm$^{-1}$ on the boron concentration for the samples having comparable oxygen contents. The intensity of the detected line increased as the boron concentration increased, confirming that the identified line is associated with boron.

Investigations of samples with different carbon content have shown that the intensity of the detected line is independent of the carbon concentration in the samples.

A possible reason for the appearance of perturbation of boron atoms could be their interaction with oxygen that diffuses during heat treatment. To understand the role of oxygen in the formation of the defect that gave rise to the detected transition, we studied Si samples grown by the float-zone method, with oxygen concentrations lower than the detection level ($N_O \leq 3 \times 10^{15}$ cm$^{-3}$). The absorption spectra for the samples having comparable boron
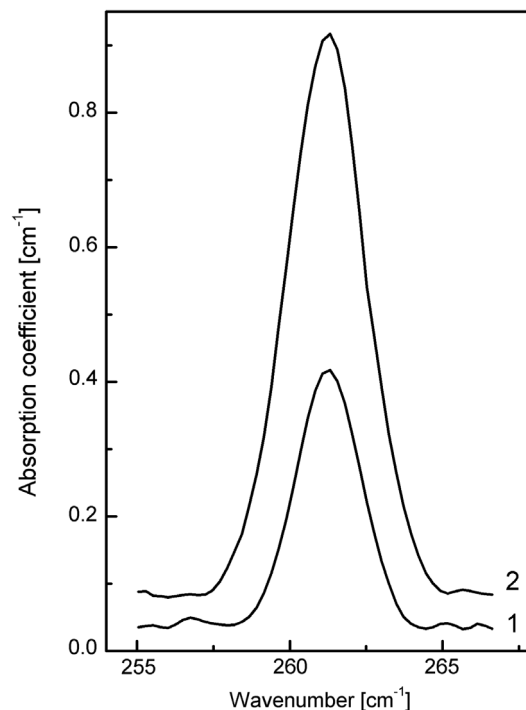


**Figure 1.** Infrared absorption spectra measured at 10 K for the Cz-Si:B. $N_B$, $\times 10^{16}$ cm$^{-3}$: 1 − 0.04; 2, 3 − 2.2. $N_O$, $\times 10^{18}$ cm$^{-3}$: 1 − 1; 2, 3 − 1.1. Spectrum (3) corresponds to the sample heat treated at 400 °C for 10 h. The spectra are shifted along the vertical axes for clarity.



**Figure 2.** Fragments of the absorption spectra detected at 10 K for Cz-Si:B samples heat treated at 400 °C for 10 h. $N_B$, $\times 10^{16}$ cm$^{-3}$: 1 − 1; 2 − 2.2. $N_O$, $\times 10^{17}$ cm$^{-3}$: 1 − 4.4; 2 − 4.6. The spectra are baseline corrected and shifted along the vertical axes for clarity.

concentrations and oxygen content differing over three orders are shown in **Figure 3**. As can be seen, the heat-treatment of oxygen-lean sample did not result in the transition detected at 261.3 cm$^{-1}$ for Cz-Si:B. This implies that the presence of oxygen atoms in the composition of the defect result in the appearance of detected line. Figure 3 also shows that two absorption lines with very weak intensities located near 250.7 and 261.7 cm$^{-1}$ are observed in the spectra of Fz-Si:B. These absorption lines appeared for both as-grown and heat-treated samples and the thermal treatment did not affect the intensity of the lines. The lines were similar to those observed for the as-grown Cz-Si:B, however, for the Cz-Si:B sample, the line shifts from 261.7 to 261.5 cm$^{-1}$.

Notably, in the spectral region under study, four lines with weak intensities relative to the main absorption lines of boron and maxima at $\sim$184, 220, 251, and 261 cm$^{-1}$ were previously observed in silicon with a high boron concentration ($9 \times 10^{16}$ cm$^{-3}$).[24] The lines were identified as components of the spectrum associated with the X-acceptor center, which includes a boron atom in its composition. The defects responsible for the lines were highly thermally stable and resistant to annealing up to the melting point of silicon. The X-center concentration measurements of both Cz-Si:B and Fz-Si:B showed that the appearance of the lines did not depend on the concentration of interstitial oxygen. Analogous absorption lines were also detected for other acceptor impurities in silicon.[11,24,25] According to a model proposed for the X-center, the defect

was an acceptor–carbon complex.[26] However, this model has been questioned,[25,27] as the defects were also observed in samples with carbon concentrations lower than the detection level ($N_C \leq 5 \times 10^{15}$ cm$^{-3}$). Subsequently, the electron Raman resonance with a maximum at 261.2 cm$^{-1}$ was registered for Si:B and identified by the transition from the ground $1\Gamma_8^+$ state to the even-parity excited $2\Gamma_8^+$ state related to the p$_{1/2}$ valence band of Si.[27]

The position of the spectral line revealed in our study is very close to the absorption line associated with the X-centers (261 cm$^{-1}$). However, as mentioned earlier, the absorption line at 261.3 cm$^{-1}$ is distinct from the X-line because it is observed only in samples with a high oxygen concentration.

To analyze the thermal stability of the detected defects, the sample of Cz-Si:B that was initially heat treated at 400 °C for 10 h was then annealed isochronally at temperatures ranging from 500 to 650 °C at 25 °C increments. Studies showed that the defects responsible for the registered absorption line were not thermally stable. The defect disappeared at temperatures $T > 500$ ºC. **Figure 4** shows the results obtained for the sample subjected to annealing at 550 °C. The annealing process decreased the intensity of the detected absorption line at 261.3 cm$^{-1}$, and it gradually shifted toward high frequencies. After annealing for 40 min (spectrum 3), only a low intensity absorption line at 261.7 cm$^{-1}$ remained in the spectrum, similar to that observed for Fz-Si:B (see Figure 3). The subsequent

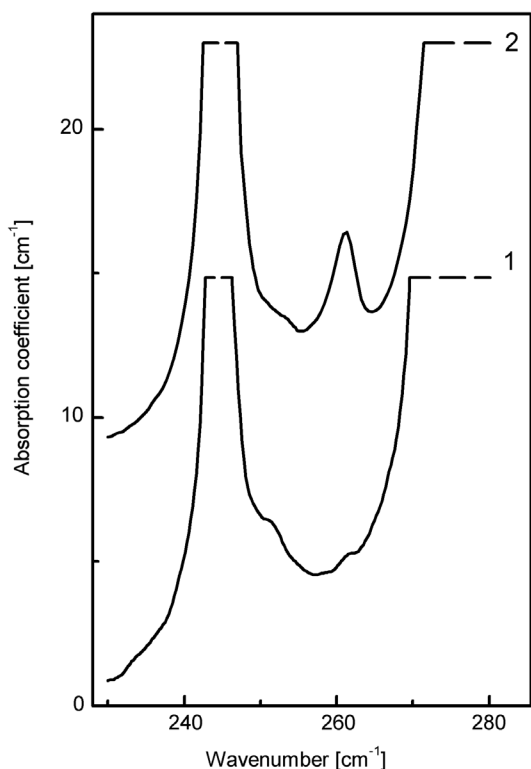**Figure 3.** Fragments of the absorption spectra detected at 10 K for Fz-Si:B (1) and Cz-Si:B (2) samples heat treated at 400 °C for 10 h. $N_B$, × 10$^{16}$ cm$^{-3}$: 1 – 2.6; 2 – 2.2. $N_o$, × 10$^{17}$ cm$^{-3}$: 1 – ≤0.03; 2 – 10.8. The spectra are shifted along the vertical axes for clarity.
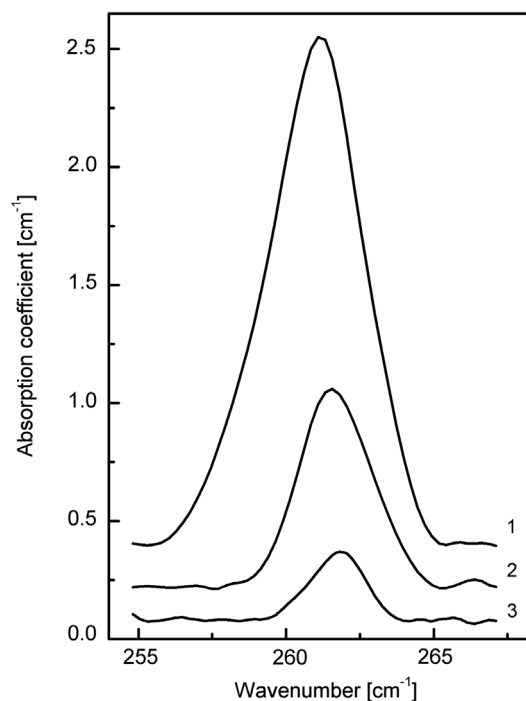
**Figure 4.** Fragments of the absorption spectra measured at 10 K for boron-doped Cz-Si sample heat treated at 400 °C for 10 h and subjected to the subsequent annealing at 550 °C. Time of an annealing at 550 °C, min: 1 – 0; 2 – 20; 3 – 40. $N_B = 2.2 \times 10^{16}$ cm$^{-3}$. $N_o = 0.93 \times 10^{18}$ cm$^{-3}$. The spectra are baseline corrected and shifted along the vertical axis for clarity.

increase in both annealing time and annealing temperature did not result in changes to the intensity of the absorption line at 261.7 cm$^{-1}$. The thermal stability of the line above 550 °C confirmed that line 261.7 cm$^{-1}$ is associated with the X-center. Thus, the low intensity line at 261.7 cm$^{-1}$ in the Cz-Si:B sample observing after annealing at 550 °C and in the Fz-Si:B sample recorded before and after heat treatment at 400 °C were clearly related to the X-centers. Moreover, obtained results also indicate that the line 261.3 cm$^{-1}$ detected in the thermally treated Cz-Si:B is a superposition of the absorption lines located at 261.3 and 261.7 cm$^{-1}$.

The weak intensity absorption line observed at 250.7 cm$^{-1}$ in the Fz-Si:B and Cz-Si:B samples is also associated with the X-centers, given that its intensity was independent of the thermal treatments at both 400 and 550 °C.

As follows from above, the position of the detected line in the as-grown Cz-Si:B sample (261.5 cm$^{-1}$) did not coincide with the maximum of the line associated with the X-center (261.7 cm$^{-1}$). **Figure 5** shows fragments of the absorption spectrum for the sample immediately after growth and after its successive heat treatments at 400 and 550 °C when only the line associated with the X-center remains in the spectrum. The intensity of the 261.5 cm$^{-1}$ line for the as-grown sample is higher than that for the X-center, which indicated that the defect responsible for the detected transition formed as the silicon was grown. This is obviously because the ingot passes all temperatures below the growing temperature during the cooling process. Thus, the
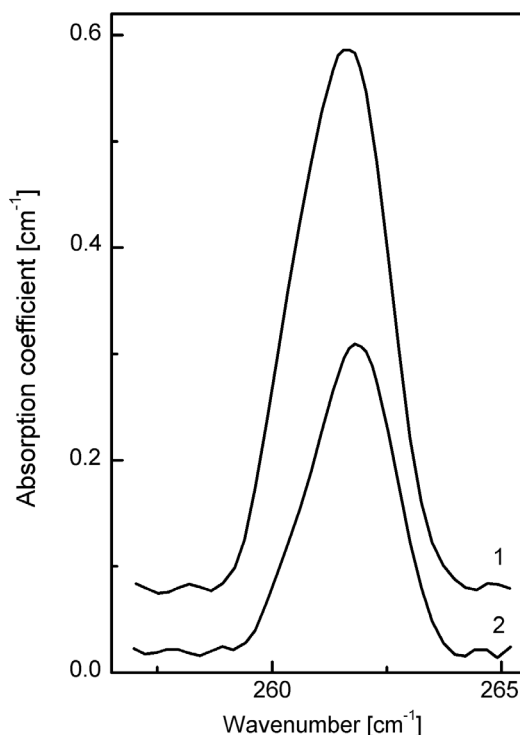
detected line in the as-grown Cz-Si:B sample is the superposition of the two spectral components located at 261.7 and 261.3 cm$^{-1}$. Low concentration of the defects in as-grown Si resulted in the line shifting only to 261.5 cm$^{-1}$.

Therefore, the revealed absorption line is associated with the spectrum characteristics of the main transitions of boron, whereas the defect responsible for the observed line formed due to the presence of oxygen atoms in the samples. This indicates that oxygen atoms diffusing during heat treatment at 400 °C localize near boron atoms and the perturbation of boron by the neighboring oxygen results in a frequency shift of the main transition of boron.

The absorption line detected at 261.3 cm$^{-1}$ is located between the two main transitions of boron $1\Gamma_8^+ \rightarrow 2\Gamma_8^-$ (278.29 cm$^{-1}$) and $1\Gamma_8^+ \rightarrow 1\Gamma_8^-$ (244.95 cm$^{-1}$). According to the literature, the transition $1\Gamma_8^+ \rightarrow 2\Gamma_8^-$ is characterized by the highest oscillator strength (769),[9,11] and the absorption line associated with this transition has the highest intensity in the absorption spectrum of boron. In comparison, the oscillator strength for $1\Gamma_8^+ \rightarrow 1\Gamma_8^-$ transition is 194, and the intensity of transition is lower than for $1\Gamma_8^+ \rightarrow 2\Gamma_8^-$ transition. In addition, the $1\Gamma_8^+ \rightarrow 2\Gamma_8^-$ transition is known to be more sensitive to the stress induced perturbations as compared with $1\Gamma_8^+ \rightarrow 1\Gamma_8^-$.[11,17] Moreover, no new absorption components were observed in the thermally treated samples above the transition 278.29 cm$^{-1}$. Therefore, we can assume that the line detected could be associated with the $1\Gamma_8^+ \rightarrow 2\Gamma_8^-$ transition shifted due to disturbances caused by neighboring oxygen atoms.

Based on this assumption, we estimated the concentration of the detected defects using the known values of the calibration factor associated with the integrated intensity of absorption line at 278.29 cm$^{-1}$ of boron (1.5 × 10$^{13}$ cm$^{-1}$).[11,26] For the as-grown and heat treated at 400 °C during 10 h sample with $N_B = 2.2 \times 10^{16}$ cm$^{-3}$ and $N_O = 1.1 \times 10^{18}$ cm$^{-3}$, the concentration of defects are 7.8 × 10$^{12}$ and 1.7 × 10$^{14}$ cm$^{-3}$, respectively.

The binding energy for the $1\Gamma_8^+$ ground state of the detected defect was estimated using the assumption made for the line detected in the spectrum. According to the data obtained, the energy of the detected transition is 32.39 meV. By adding the energy of the $2\Gamma_8^-$ state (11.54 meV, as calculated by effective mass theory for acceptors in silicon[9,11]) to the energy of the detected transition, a binding energy $E_{io} = 43.93$ meV was obtained for the $1\Gamma_8^+$ ground state of the detected defect.

Notably, association the identified line with the $1\Gamma_8^+ \rightarrow 1\Gamma_8^-$ transition does not significantly affect the estimations made for the $1\Gamma_8^+ \rightarrow 2\Gamma_8^-$ transition, however, this slightly increases the values of the above estimates.

Thus, the obtained results indicate that the interaction of oxygen with boron during the growth and heat treatment of the Cz-Si:B induces new defects. The defects formed are thermally stable up to 550 °C and could affect the electrical parameters of silicon.



**Figure 5.** Fragments of the absorption spectrum for the sample immediately after growth (1) and after its successive heat treatments at 400 and 550 °C. (2) $N_B = 2.2 \times 10^{16}$ cm$^{-3}$. No = 1.02 × 10$^{18}$ cm$^{-3}$. The spectra are baseline corrected.

## 3. Conclusion

In the transitions region from the ground $1\Gamma_8^+$ state related to the p$_{3/2}$ valence band of Si to the odd-parity excited states of boron, a new absorption line with its maximum at 261.3 cm$^{-1}$

was detected in the thermally treated at 400 °C boron-doped Cz-Si. The thermal treatment of Fz-Si:B having an oxygen concentration less than the detection level showed no absorption line as observed in Cz-Si:B, implying that an oxygen atom is involved in the composition of the defect. The localization of oxygen atoms diffusing at 400 °C near the boron atoms formed the defect responsible for the detected absorption line. The perturbation of boron atoms by their neighboring oxygen atoms results in a shift in the frequency of the main transition of boron $1\Gamma_8^+ \rightarrow 2\Gamma_8^-$. In addition, the defect was formed even as Cz-Si:B was grown. The estimated concentration of detected defects for the as-grown and heat-treated at 400 °C during 10 h sample with $N_B = 2.2 \times 10^{16}\,\mathrm{cm}^{-3}$ and $N_O = 1.1 \times 10^{18}\,\mathrm{cm}^{-3}$, are $7.8 \times 10^{12}$ and $1.7 \times 10^{14}\,\mathrm{cm}^{-3}$, respectively.

The acquired data are essential for understanding the influence of boron-oxygen-related defects on the electrical and optical properties of silicon and devices made on its base.

## 4. 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 ($N_B$) was $1 \times 10^{16}$ and $2.2 \times 10^{16}\,\mathrm{cm}^{-3}$ for Cz-Si:B samples and $2.6 \times 10^{16}\,\mathrm{cm}^{-3}$ for Fz-Si:B. 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 varied in the interval $(0.43–1.1) \times 10^{18}\,\mathrm{cm}^{-3}$. The carbon concentration was defined by the intensity of the absorption band at 605 cm$^{-1}$ and was varied in the interval $(8–12) \times 10^{16}\,\mathrm{cm}^{-3}$.

To study the interaction between boron and oxygen atoms the heat treatments of samples were carried out at 400 °C during 10 h. The thermal treatments were carried out in argon ambient and the annealing was completed by dropping the samples in ethylene glycol.

The absorption spectra of the 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 0.2–1 cm$^{-1}$.

## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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