

# Local vibrational modes of interstitial boron–interstitial oxygen complex in silicon

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In the present work, we report local vibrational mode (LVM) related absorption lines which are assigned to the complex incorporating interstitial boron and interstitial oxygen atoms ( $B_iO_i$ ), a possible precursor of the center responsible for light-induced degradation (LID) in solar cells produced from boron-doped oxygen-rich silicon. Fourier transform infrared absorption (IR) spectroscopy was used for detection and analysis of absorption lines due to defects which were created in boron-doped Czochralski-grown Si samples by irradiation with 6 or 10 MeV electrons at room temperature. Changes in the IR absorption spectra upon isochronal annealing of the irradiated samples in the temperature range 75–225 °C have also been monitored. A set of previously unreported LVM

lines with the same formation and elimination behavior has been studied. The most intense lines of the set are found to be at 991, 721, and 550  $\text{cm}^{-1}$ . On the basis of an analysis of changes in intensity of the lines with the concentrations of impurities in the silicon and on the similarity of their annealing features with those for the DLTS signal due to the  $B_iO_i$  center, it is argued that the lines are related to the LVMs of this defect. The positions of the lines have been compared with the previously reported LVMs derived from *ab initio* modeling calculations for different configurations of the  $B_iO_i$  complex. A configuration having calculated LVMs close to those determined experimentally has been found and the origins of the modes are discussed.

**1 Introduction** The interstitial boron–interstitial oxygen complex ( $B_iO_i$ ) is one of the dominant defects in oxygen-rich p-type Si crystals irradiated with MeV electrons at room temperature [1–5]. It is formed as a result of an interaction of mobile  $B_i$  atoms [2] (generated via the Watkins replacement mechanism) with interstitial oxygen atoms. The  $B_iO_i$  defect appears to be a very efficient compensating center in irradiated p-type Si and can affect the parameters of silicon-based devices significantly since it removes a shallow acceptor ( $B_s$ ) and introduces a deep donor level at about  $E_C - 0.24$  eV [1–5]. Upon annealing out the  $B_iO_i$  center can either interact with interstitial oxygen atoms or release mobile interstitial boron atoms, which can interact with oxygen dimers, so forming a  $B_iO_{2i}$  complex. This complex is thought to be responsible for the light-induced degradation (LID) of some silicon solar cells [6].

However, in spite of its technological importance, the electronic properties, formation, and elimination behavior of the  $B_iO_i$  center have not been understood properly [5, 7]; local vibrational modes (LVMs) of the defect have not been identified [8] (with an exception of a tentative assignment of an absorption band at 923.5  $\text{cm}^{-1}$  to  $B_iO_i$  given recently in Ref. [9]), and there is no consensus on its atomic structure. According to previous theoretical modeling studies (Ref. [10] and references therein), the  $B_iO_i$  complex can exist in several configurations with slightly different total energies. The electronic properties of the defect in these configurations are similar, but the LVMs appear to be different. An experimental observation of the  $B_iO_i$ -related LVMs may provide a solid basis for an unambiguous identification of the center and that has been a motivation for the present study.

**2 Experimental** The samples used in the study were prepared from boron doped p-type Cz-Si crystals ( $\rho = 0.3\text{--}1\ \Omega\text{ cm}$ ). For a comparison, also a few samples from n-type Cz-Si crystals with a low concentration of substitutional carbon ( $[C_s] \leq 1 \times 10^{16}\text{ cm}^{-3}$ ) were studied. The concentration of interstitial oxygen was determined from measurements of intensity of the absorption band at  $1107\text{ cm}^{-1}$  using the calibration coefficient  $3.14 \times 10^{17}\text{ cm}^{-2}$  [11] and was in the range  $(0.9\text{--}1.15) \times 10^{18}\text{ cm}^{-3}$  in both n- and p-type Si samples. The samples were polished to an optically flat surface on two sides and the dimensions were  $10 \times 6 \times 2$  or  $10 \times 6 \times 3\text{ mm}^3$ .

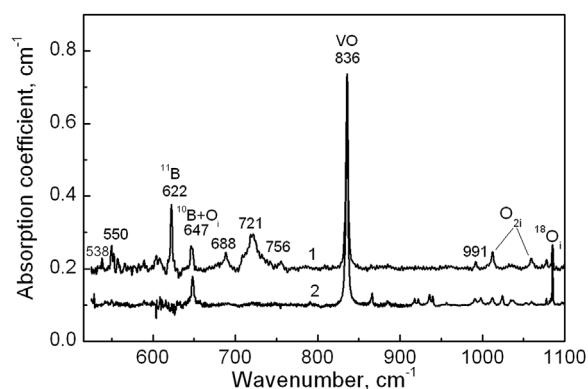
Irradiations with **10** and **6 MeV electrons** were performed at nominal room temperature with fluences in the range  $1 \times 10^{16}\text{--}5 \times 10^{17}\text{ cm}^{-2}$ . Some of the irradiated samples were subjected to 30-min isochronal annealing in the temperature range  $75\text{--}200\text{ }^\circ\text{C}$  with  $25\text{ }^\circ\text{C}$  increments.

IR absorption analysis was carried out using a Bruker IFS 113v spectrometer. A spectral resolution of  $0.5$  or  $1.0\text{ cm}^{-1}$  was used and the samples were measured at about  $20\text{ K}$  and at room temperature (RT).

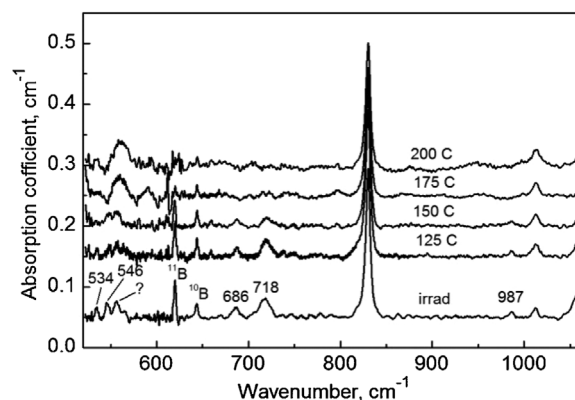
**3 Results and discussion** Figure 1 shows absorption spectra in the wavenumber range  $525\text{--}1100\text{ cm}^{-1}$  measured at  $20\text{ K}$  for p- and n-type Cz-Si samples irradiated with  $10\text{ MeV}$  electrons to a fluence of  $3 \times 10^{17}\text{ cm}^{-2}$  under identical conditions. For the n-type Si, all the observed radiation-induced LVM lines (spectrum 2) have been detected and identified previously. The main absorption band at  $836\text{ cm}^{-1}$  is related to the well-known vacancy-oxygen defect (A-center) [8, 12]. The minor bands located in the region of  $865\text{--}1040\text{ cm}^{-1}$  are associated with the interstitial type defects involving the Si self-interstitial (I), interstitial carbon ( $C_i$ ), and oxygen atoms [8, 13–20]. In particular, the well-known band at  $865\text{ cm}^{-1}$  is related to the  $C_iO_i$  complex [8, 13, 14], a pair of bands at  $917$  and

$1034\text{ cm}^{-1}$  is associated with the  $IO_{2i}$  defect, while another pair of lines at  $922$  and  $1037\text{ cm}^{-1}$  has been assigned to the  $I_2O_{2i}$  complex [15, 16]. It should be mentioned that the appearance of the bands due the  $IO_{2i}$  and  $I_2O_{2i}$  defects is consistent with a significant decrease in the intensity of the LVM bands related to “as-grown” oxygen dimer (bands at  $1012$  and  $1060\text{ cm}^{-1}$  [17]). The band at  $936\text{ cm}^{-1}$  has been assigned earlier to an  $I_2O_i$  defect [18], while a pair of the bands at  $939$  and  $1024\text{ cm}^{-1}$  to an  $IC_iO_i$  complex [19, 20]. The bands at  $991$  and  $998\text{ cm}^{-1}$  are, most likely, related to  $I_3C_iO_i$  and  $I_2C_iO_i$  defects, respectively [20]. The band at  $648\text{ cm}^{-1}$  is a combination mode related to vibrations of single  $O_i$  atoms [21].

Only very weak traces of the bands related to complexes involving the Si self-interstitial and/or  $C_i$  atoms can be detected in the spectrum of irradiated p-type Si. This observation indicates that in this material there are some other traps, which are more efficient in capturing mobile radiation-induced Si self-interstitial atoms than oxygen- and carbon-related centers, and the appearance of some new complexes is expected. These complexes can give rise to vibrational absorption bands. Indeed, as one can see in Fig. 1 (spectrum 1) in irradiated p-Si, a new set of radiation-induced absorption lines is appearing. The most intense of them are positioned at about  $538$ ,  $550$ ,  $688$ ,  $721$ ,  $756$ , and  $991\text{ cm}^{-1}$  (the latter band cannot be related to the  $I_3C_iO_i$  defect since the other bands related to the  $I_nC_iO_i$  complexes with  $n < 3$  are absent). All the bands except the one at  $756\text{ cm}^{-1}$  are also clearly observed in the absorption spectrum of irradiated p-type Si measured at RT (Fig. 2). At room temperature, the band positions are shifted to lower frequencies by about  $3\text{--}5\text{ cm}^{-1}$  and such shifts are typical for the LVMs due to radiation-induced defects in silicon [13–16, 18–20]. Inspection of Fig. 2 indicates similar annealing behavior of the lines, so suggesting that they can be related to the same defect.



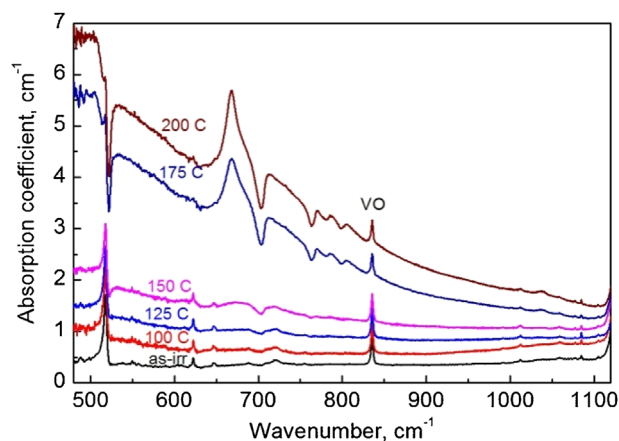
**Figure 1** Fragments of absorption spectra measured at  $20\text{ K}$  for Cz-Si samples irradiated with  $10\text{ MeV}$  electrons to a fluence of  $3 \times 10^{17}\text{ cm}^{-2}$ . Spectrum (1) p-Si ( $[O_i] = 1.0 \times 10^{18}$ ,  $[C_s] \leq 5 \times 10^{15}$ ,  $[B_s] = 8 \times 10^{16}\text{ cm}^{-3}$ ); spectrum (2) n-Si ( $[O_i] = 1.15 \times 10^{18}$ ,  $[C_s] = 5 \times 10^{15}$ ,  $[P] = 6 \times 10^{14}\text{ cm}^{-3}$ ). The spectra are base line corrected.



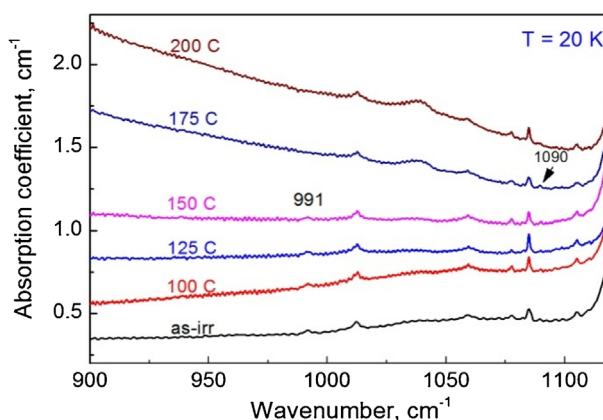
**Figure 2** Fragments of absorption spectrum measured at room temperature for p-Cz-Si sample ( $[O_i] = 1.0 \times 10^{18}$ ,  $[C_s] \leq 5 \times 10^{15}$ ,  $[B_s] = 8 \times 10^{16}\text{ cm}^{-3}$ ) irradiated with  $10\text{ MeV}$  electrons to a fluence of  $3 \times 10^{17}\text{ cm}^{-2}$  at RT and then subjected to 30 min isochronal anneals with the last steps at the temperatures indicated above the curves. The spectra are base line corrected.

The same set of the new LVM bands was detected also in the irradiated p-type Cz-Si samples having lower boron concentrations,  $\rho = 0.5$  and  $1 \Omega \text{ cm}$ , but the intensities of the bands in these samples were lower than those in the samples with the highest boron content,  $\rho = 0.3 \Omega \text{ cm}$ . This finding suggests an involvement of boron atoms into the center responsible for the bands. According to an earlier study [22], irradiation of Si samples in which the boron concentration was significantly higher than the oxygen concentration did not result in an appearance of the boron-related bands mentioned above and observed by us in the oxygen rich samples with  $[\text{O}_i] > [\text{B}_s]$ . The latter fact indicates the presence of oxygen atoms in the defect, which gives rise to a new set of the LVM bands. It seems reasonable to suggest that this center can be a  $\text{B}_i\text{O}_i$  defect. Such an assignment is supported by results of the thermal stability study of the defect responsible for the bands observed.

Figures 3 and 4 show the development of the IR absorption spectra measured at low temperature for an irradiated p-type Cz-Si sample upon 30-min isochronal annealing in the temperature range 100–200 °C. After annealing in steps up to 150 °C, there are no essential changes in the spectra. However, after annealing at 175 °C, the situation changes drastically. The new lines are no longer observed, a strong increase in the absorption by free holes occurs, and a number of new rather strong peaks and dips appear in the spectra. The later features indicate the presence of neutral acceptors, which in this case are non-ionized substitutional boron atoms. The peaks positioned at about 668, 693, and 702  $\text{cm}^{-1}$  are related to transitions of holes from the boron ground  $1s$  state in the forbidden gap to the excited  $2p'$ ,  $3p'$ , and  $4p'$  states associated with the split-off  $p_{1/2}$  valence band [23]. A set of profound dips positioned at 521, 703, 765, 782, and 798  $\text{cm}^{-1}$  are due to resonant interaction of optical phonons with acceptor continuum states (Fano anti-resonance) [24].



**Figure 3** Development of the IR absorption spectra measured at 20 K for the p-Cz-Si sample, the absorption spectra of which are shown in Figs. 1 and 2, upon 30 min isochronal annealing in the temperature range 100–200 °C.



**Figure 4** Fragments of the absorption spectra, shown in Fig. 3, in the wavenumber range 900–1120  $\text{cm}^{-1}$ .

A strong absorption by free holes and the presence of intense peaks and dips related to electronic transitions prevent a definite conclusion to be drawn that all the new LVM lines disappear simultaneously upon annealing at 175 °C as they are relatively weak. However, an analysis of the spectra measured at RT (Fig. 2) shows that such disappearance actually does occur. Thus, the thermal stability of the defect giving rise to a set of new LVM lines and a partial recovery of the free hole concentration observed upon its annihilation are consistent in general with the similar features observed in deep level transient spectroscopy studies for the  $\text{B}_i\text{O}_i$  defect [1–5, 7, 25].

To suggest possible assignments of the observed  $\text{B}_i\text{O}_i$ -related LVMs to specific boron and oxygen atoms vibrations, we have compared the experimentally obtained frequencies with the results of theoretical predictions. According to previous theoretical modeling studies [10, 26], the  $\text{B}_i\text{O}_i$  complex can exist in two configurations with slightly different total energies. However, the calculated vibrational spectra related to these configurations appear to be rather different mainly because of the different positions (coordination) of the interstitial boron atom. In the configuration labeled  $\{\text{B}_i\text{O}_i\}_a$ , both B and O atoms are threefold coordinated while another configuration labeled  $\{\text{B}_i\text{O}_i\}_b$  contains a nearly-substitutional boron atom next to an interstitial oxygen atom [10, 26].

From a comparison of the experimental and theoretical data presented in Table 1, it appears that the calculated LVMs for the (a) structure (“ring”) of the  $\text{B}_i\text{O}_i$  defect are more consistent with the experimentally observed absorption lines. A prominent feature of the experimental spectrum is the most intense band at 721  $\text{cm}^{-1}$  positioned in the region where normally the LVMs of threefold coordinated oxygen atoms are observed [8, 13–16]. This fact gives a strong support for the  $\{\text{B}_i\text{O}_i\}_a$  model. A solid confirmation of the assignment of the mode at 991  $\text{cm}^{-1}$  to vibrations of an  $^{11}\text{B}$  atom requires an observation of the  $^{10}\text{B}$  related isotope analog of this mode. However, because of relatively low presence of  $^{10}\text{B}$  (~20%) and, accordingly, rather low

**Table 1** Experimentally observed and calculated (Refs. [10] and [26]) frequencies in  $\text{cm}^{-1}$  of the LVMs due to the  $\text{B}_i\text{O}_i$  defect in the positive charge state. Calculations were carried out assuming the involvement of the most abundant silicon, boron, and oxygen isotopes,  $^{28}\text{Si}$ ,  $^{11}\text{B}$ , and  $^{16}\text{O}$ . LVMs related mainly to boron vibrations are given in bold, related mainly to oxygen vibrations in italic. Low frequency modes are predominately related to movements of silicon atoms. The measured low frequency modes were rather weak with low signal-to-noise ratios, therefore, the analysis of the changes in their intensities was not as solid as for the modes with higher frequencies and the question marks in the table indicate some uncertainty in the assignments.

$\nu_{\text{meas.}}$ @ 20 K	$\nu_{\text{meas.}}$ @ 300 K	$\nu_{\text{calc.}}$ [10] $\{\text{B}_i\text{O}_i\}_a$	$\nu_{\text{calc.}}$ [26] $\{\text{B}_i\text{O}_i\}_a$	$\nu_{\text{calc.}}$ [10] $\{\text{B}_i\text{O}_i\}_b$	$\nu_{\text{calc.}}$ [26] $\{\text{B}_i\text{O}_i\}_b$
991	987	<b>1009</b>	<b>998</b>	833	813
721	718	761	740		
688	686	<b>672</b>	<b>693</b>	<b>688</b>	<b>682</b>
?	556?	570	558	592	589
				<b>575</b>	
550	546		542	<b>549</b>	549
538	534?		537		536

intensity expected for this band, we were not able to observe clearly an appropriate band.

With the aim to detect the  $^{10}\text{B}$  related LVM, an attempt has been done to increase the concentration of the  $\text{B}_i\text{O}_i$  defect by a further irradiation. A few samples of p-Cz-Si initially irradiated with 10 MeV electrons to a fluence of  $3 \times 10^{17} \text{ cm}^{-2}$  were subjected to an additional irradiation with 6 MeV electrons to a fluence of  $2 \times 10^{17} \text{ cm}^{-2}$ . However, the FTIR measurements have shown that there are no noticeable changes in the intensity of the absorption bands assigned to  $\text{B}_i\text{O}_i$  after the additional irradiation. Another new band at  $1090 \text{ cm}^{-1}$  was found to grow up along with the well-known band at  $836 \text{ cm}^{-1}$  related to VO. Probably, the  $\text{B}_i\text{O}_i$  defect is an efficient trap for the Si self-interstitials and it can be suggested that the  $1090 \text{ cm}^{-1}$  band arises from an  $\text{IB}_i\text{O}_i$  complex. A rather similar situation (trapping of I atoms) occurs for carbon-related defects [8, 13–16, 19, 20].

As regard of an assignment of the LVM band at  $923.5 \text{ cm}^{-1}$ , which was observed recently in low temperature ( $\sim 80 \text{ K}$ ) irradiated p-type Si [9], to the  $\text{B}_i\text{O}_i$  complex it seems likely that the observed band can be related to a precursor of the stable form of  $\text{B}_i\text{O}_i$ . An occurrence of such precursors has been observed previously for the interstitial carbon-interstitial oxygen and interstitial carbon-substitutional carbon complexes [27, 28].

**4 Conclusions** A set of absorption lines, which were not reported earlier, has been observed in boron-doped Czochralski grown silicon crystals after irradiation with 10 MeV electrons at room temperature. From an analysis of changes in intensities of the lines in irradiated samples with

different impurity compositions and upon isochronal annealing of the samples, they have been assigned to local vibrational modes of the  $\text{B}_i\text{O}_i$  complex. A comparison of the line positions with the previously reported LVMs derived from *ab initio* modeling calculations for different configurations of the  $\text{B}_i\text{O}_i$  complex suggests that the structure consisting of the threefold coordinated boron and oxygen atoms is the minimum energy configuration of the defect. This configuration occurs in boron-doped p-type Si crystals and is stable up to  $175^\circ\text{C}$ .

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