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LETTER TO THE EDITOR

***Ab initio* calculation of the local vibrational modes of the interstitial boron–interstitial oxygen defect in Si**A Carvalho¹, R Jones¹, J Coutinho² and P R Briddon³¹ School of Physics, University of Exeter, Exeter EX4 4QL, UK² Department of Physics, University of Aveiro, Campus Santiago, 3810-193 Aveiro, Portugal³ School of Natural Sciences, University of Newcastle upon Tyne, Newcastle upon Tyne, NE1 7RU, UK

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Online at stacks.iop.org/JPhysCM/17/L155**Abstract**

The first stage in the anneal of interstitial boron below room temperature in Czochralski-grown Si (Cz-Si) is the formation of the interstitial boron–oxygen (B_iO_i) defect. First principles modelling show that this defect has a structure similar to the interstitial carbon–oxygen complex. However, whereas the latter defect has been characterized by local vibrational mode infra-red spectroscopy, there is no information on the local vibrational modes of B_iO_i even though the defect is known to be a dominant interstitial boron defect in irradiated Cz-Si. Here, we carry out density functional calculations to determine its vibrational modes and respective isotope shifts, concluding that it possesses six local vibrational modes. As in the case of C_iO_i , we find an oxygen-related vibrational mode with frequency far below the 1136 cm^{-1} of the oxygen interstitial, characteristic of the three-fold coordinated oxygen.

Ion implantation is a favoured way for selective area doping of Si, but it is associated with the formation of interstitial clusters whose growth and dissolution lead to unwanted dopant, and especially of boron diffusion. The interstitial boron defect has been considered to be active in the diffusion of boron. This defect has been studied by electron paramagnetic resonance (EPR) [1], deep level transient spectroscopy (DLTS) [2], and optical absorption spectroscopy [3], as well as by theory [4–9]. The different structures found in the positive and negative charge states account for its negative- U properties, and estimates of the donor and acceptor levels at $E_c - 0.05\text{ eV}$ and $E_c - 0.33\text{ eV}$ are in excellent agreement with experimental values at 0.13 and 0.37 eV below the conduction band bottom, respectively [2]. The structure of the positively charged interstitial boron defect is shown in figure 1(b). It is made of a nearly substitutional boron atom bound to a Si self-interstitial (I), resulting in a $\langle 111 \rangle$ -split BI unit with C_{3v} symmetry. Local vibrational mode (LVM) frequencies for BI^+ were calculated at 697

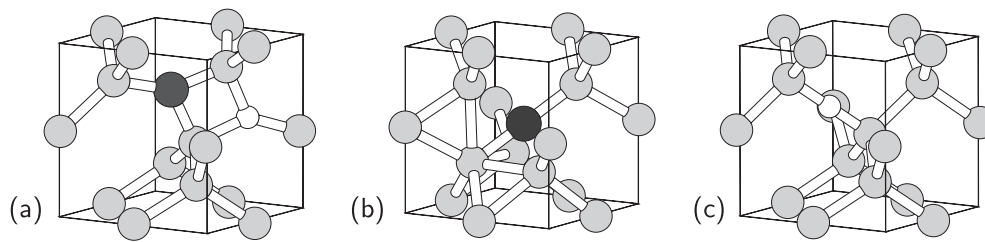


Figure 1. Ground state structures of (a) B_iO_i , (b) BI^+ and (c) O_i (D_{3d} symmetry) complexes in silicon. Si, B and O atoms are shown in grey, black and white, respectively.

and 726 cm^{-1} for ^{11}B and ^{10}B , respectively [10]. These are within 30 cm^{-1} of the R-lines, attributed to the defect, at 730 and 757 cm^{-1} and exhibit, within 2 cm^{-1} , the same isotopic splitting.

Interstitial boron disappears around 240 K at a rate given by $\nu \exp(-0.6\text{ eV}/kT)$, where $\nu \sim 10^7\text{ s}^{-1}$. The energy and prefactor suggest a loss mechanism where BI diffuses to a trap of density $\sim 10^{17}\text{--}10^{18}\text{ cm}^{-3}$, which in Cz-Si can only be linked to the abundant interstitial oxygen defects. Simultaneously to the anneal of BI, DLTS studies show the correlated growth of a level at $E_c - 0.23\text{ eV}$ [11]. Similar levels with identical annealing properties are found in room-temperature e -irradiated Cz-Si and have been attributed to an interstitial boron–oxygen complex (B_iO_i) [12, 13]. Its introduction rate increases with $[O]$ and varies as $[B]^{1/2}$ [12], or $[B]$ at low concentrations and $[B]^{-2}$ otherwise [13]. Its observation in p-type Si by minority carrier injections suggests a $(0/+)$ donor level although a second donor $(+/+)$ level cannot be excluded [12]. Modelling studies [14] show that the defect has a structure similar to C_iO_i , but although detailed vibrational studies have been made for this defect [15], none have been reported for B_iO_i . According to theory, C_iO_i and B_iO_i have C_{1h} symmetry with trivalent oxygen atoms. The local vibrational modes, along with other experimental evidence, reveal that in C_iO_i , the carbon interstitial is weakly perturbed by the oxygen atom, but the oxygen atom is strongly affected by carbon [15]. The aim of the present letter is to report on the local vibrational modes of B_iO_i .

At $150\text{--}200^\circ\text{C}$ in Cz-Si, the $E_c - 0.23\text{ eV}$ level disappears and a new level appears at around $E_v + 0.29\text{ eV}$. The growth of this new level has an identical activation energy and pre-exponential factor as the decay of the $E_c - 0.23\text{ eV}$ level [12], and the production rate of this new level has been shown to be independent of $[O]$ but directly proportional to $[C]$ and inversely proportional to $[B]$ [13]. If we assume that the $E_c - 0.23\text{ eV}$ level arises from B_iO_i , the above evidence strongly suggests that when B_iO_i dissociates at $\sim 150^\circ\text{C}$, BI is trapped by substitutional carbon giving rise to B_iC_s with a level at $E_v + 0.29\text{ eV}$. However, as mentioned in [16], there are some difficulties in this interpretation. In floating-zone silicon (Fz-Si), one anticipates that B_iC_s could form at room temperature when BI or C_i become mobile. However, experiments show that in carbon-rich Fz-Si the $E_v + 0.29\text{ eV}$ does not form until about 120°C [17, 18], possibly because of the preferential formation of a metastable precursor labelled $B_iC_s^*$, which has so far evaded detection in DLTS studies [9].

We carried out a density functional modelling study of the B_iO_i defect in silicon using the AIMPRO code [19]. Dual space separable pseudopotentials by Hartgwissen, Goedecker and Hutter were utilized [20], together with atom-centred Cartesian–Gaussian basis sets consisting of $(4, 12, 12)$ independent s-, p-, and d-like functions on each Si atom. For O and B we used 40 and 22 functions, respectively. A 64 atom supercell was used throughout the study and a Monkhorst–Pack $MP-2^3$ special \mathbf{k} -point scheme [21] enabled an efficient integration over the

Table 1. Calculated local vibrational mode frequencies for the B_iO_i defect (ν_{calc}), assuming the most abundant ^{28}Si , ^{11}B and ^{16}O isotope masses. Isotope shifts associated with ^{18}O , ^{10}B and ^{30}Si substitutions are reported under $\delta\nu(^{18}\text{O})$, $\delta\nu(^{10}\text{B})$, and $\delta\nu(^{30}\text{Si})$, respectively. All frequencies are in cm^{-1} .

Mode	ν_{calc}	Symmetry	$\delta\nu(^{18}\text{O})_{\text{calc}}$	$\delta\nu(^{10}\text{B})_{\text{calc}}$	$\delta\nu(^{30}\text{Si})_{\text{calc}}$
1	539.7	A''	0.0	0.0	-18.3
2	545.9	A''	-0.1	+0.1	-18.4
3	556.9	A'	-5.7	0.0	-14.3
4	716.3	A'	+1.5	+26.5	-7.7
5	736.2	A'	-35.2	-2.4	-4.6
6	1009.9	A'	-1.1	+41.6	-4.5

Table 2. Calculated vibrational modes (ν_{calc}) along with ^{18}O and ^{30}Si isotopic shifts ($\delta\nu(^{18}\text{O})_{\text{calc}}$ and $\delta\nu(^{30}\text{Si})_{\text{calc}}$) for the D_{3d} configuration of O_i . The calculated combined mode $A_{1g} + A_{2u}$ frequency and respective isotope shifts are estimated by summation of frequency and shifts of one-phonon frequencies. Experimental data were taken from [25, 26]. All frequencies are in cm^{-1} .

Mode	ν_{calc}	Symmetry	$\delta\nu(^{18}\text{O})_{\text{calc}}$	$\delta\nu(^{30}\text{Si})_{\text{calc}}$	ν_{exp}	$\delta\nu(^{18}\text{O})_{\text{exp}}$
1	519.8	E_u	0.0	-9.0	517	0.0
2	615.5	A_{1g}	0.0	-10.8	618	~ 0
3	1160.6	A_{2u}	-53.4	-3.8	1136	-51.4
4	1776.0	$A_{1g} + A_{2u}$	-53.4	-14.6	1749	-52.6

Brillouin zone to be carried out. It was found that an MP-4³ mesh did not change the calculated local vibrational mode frequencies by more than 3%.

The dynamical matrix entries connecting pairs of atoms in the core of the defect were found from the energy second derivatives. These are given by the derivative of the force on atom i when atom j is displaced along the three Cartesian directions. Other entries in the dynamical matrix were found from a previously derived Musgrave–Pople potential [22]. Further details have been reported elsewhere [23]. Convergence tests were carried out with respect to the number of sampling \mathbf{k} -points, and number of atom shells surrounding the defect used on the second derivatives calculation. We used 6 core atoms for the B_iO_i defect and 27 for O_i .

The most stable configuration of B_iO_i has C_{1h} symmetry and is shown in figure 1(a) [14]. In this configuration all Si atoms are four-fold coordinated, and both B and O are three-fold coordinated.

Our calculations show that B_iO_i has six local vibrational modes lying above the calculated Raman frequency of Si (511 cm^{-1}). These are reported in table 1. Four of these modes have A' symmetry and may be detected in luminescence. However, unlike C_iO_i , no electronic absorption or emission spectrum has been connected with B_iO_i . The isotope shifts of the frequencies and the localization of the calculated modes show that the lower frequency modes 1 and 2 are predominately related with the movement of Si atoms, and consequently they are not shifted by the ^{18}O and ^{10}B isotope substitution. Mode 3 is located both on oxygen and silicon, modes 4 and 6 are predominantly localized on the boron atom, while mode 5 is predominantly localized on oxygen.

Let us compare the local vibrational modes of B_iO_i with those of interstitial oxygen and interstitial boron defects shown in tables 2 and 3, respectively.

Interstitial oxygen in silicon can assume C_1 , C_{1h} , C_2 or D_{3d} symmetry. Coutinho *et al* [24] have shown that although the ground state configuration is C_2 , the low energy barrier implies that the defect is likely to tunnel between the above-mentioned configurations, assuming an

Table 3. Calculated local vibrational mode frequencies (ν_{calc}) for $^{11}\text{BI}^+$, along with ^{10}B and ^{30}Si isotopic shifts ($\delta\nu(^{10}\text{B})_{\text{calc}}$ and $\delta\nu(^{30}\text{Si})_{\text{calc}}$). Experimental data (ν_{exp} and $\delta\nu(^{10}\text{B})_{\text{exp}}$) were taken from [3]. All frequencies are in cm^{-1} .

Mode	ν_{calc}	Symmetry	$\delta\nu(^{10}\text{B})_{\text{calc}}$	$\delta\nu(^{30}\text{Si})_{\text{calc}}$	ν_{exp}	$\delta\nu(^{10}\text{B})_{\text{exp}}$
1	522.3	A_1	+1	-18		
2	696.2	A_1	+29	-3	730	+27

averaged D_{3d} symmetry. The frequencies arising from both the C_2 and D_{3d} bond centered structures are very close together and in good agreement with the experimental data. For the D_{3d} structure we find two local modes at 615.5 cm^{-1} (mode 2) and 1160.6 cm^{-1} (mode 3) and a resonant mode at 519.8 cm^{-1} (mode 1). Modes 1 and 2 involve the oscillation of Si neighbouring atoms only, whereas mode 3 is the asymmetric Si–O–Si stretch mode which is observed in the form of a prominent absorption band at 1136 cm^{-1} . The isotope shifts are supportive of these assignments. Whereas modes 1 and 2 are insensitive to the oxygen mass, mode 3 in $^{18}\text{O}_i$ decreases by 53.4 cm^{-1} with respect to $^{16}\text{O}_i$.

The calculated LVM frequencies of BI^+ (shown in table 3) account well for the measurements [3] and differ by $\sim 1 \text{ cm}^{-1}$ from similar calculations reported previously [10]. Accordingly, the I–B–Si unit has an asymmetric stretch mode at 696.2 cm^{-1} , which is to be compared with the R-line at 730 cm^{-1} . Additionally, we find a previously unreported *breathing* mode involving Si atoms only at 522 cm^{-1} . This is likely to lie below the Raman edge, in which case it may escape detection.

The oxygen-related vibrational mode in B_iO_i (see table 1) lies at 736.2 cm^{-1} , and much lower than the 1160.6 cm^{-1} stretch mode for O_i (measured at 1136 cm^{-1}). The same mode shifts by -35.2 cm^{-1} under ^{18}O substitution, which is also much lower than the isotope shift of the 1160.6 cm^{-1} stretch mode for O_i . On the other hand, the 736.2 cm^{-1} mode is close to the oxygen-related mode of C_iO_i at 759.6 cm^{-1} [15], which also has an ^{18}O shift of -35.6 cm^{-1} . This latter mode has been detected at 742.8 cm^{-1} [15]. Such low frequency oxygen modes are characteristic of three-fold coordinated oxygen atoms. We note that mode 4 has an *anomalously* positive ^{18}O isotope shift, which results from a crossover with mode 5. Analogously, a similar effect takes place under ^{10}B substitution, resulting in a negative isotope shift of mode 5. All the three B–Si bonds in the B_iO_i structure are shorter and hence stronger than the B–Si bonds in BI^+ . This explains why the two boron-related modes in the B_iO_i complex lie above those of the boron interstitial.

In conclusion, we have carried out an *ab initio* modelling study of the B_iO_i complex. Its vibrational properties were studied in detail and compared with those of interstitial oxygen and interstitial boron centres. The B_iO_i has six vibrational modes above the Raman frequency. Similarly to the C_iO_i complex, the oxygen atom in B_iO_i is strongly affected by the boron atom (when compared to its *normal* location in O_i), becoming overcoordinated, and thereby leading to an oxygen-related vibrational frequency far below the 1136 cm^{-1} mode of oxygen interstitial. The B–Si bonds, though, are shorter than those in the BI^+ structure, and account for the higher vibrational mode frequencies.

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