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Local vibrations of thermal double donors in silicon

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The local vibrational modes (LVM’s) of the oxygen chains assigned to thermal double donors (TDD’s) and other related oxygen defects in silicon are studied using accurate total-energy calculations. We find that the calculated LVM frequencies as well as their isotopic shifts and charge-state dependences (temperature dependences) for the oxygen chains agree closely with the corresponding experimental quantities, which supports our assignments of the O_{2r}-O_{2r} chain to TDD1 and the O_{2r}-O_{2r}-O_{2r} chains to TDDn (n>1) (O_{r} is an interstitial oxygen and O_{i} a threefold coordinated oxygen belonging to a ring).

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Local vibrations of thermal double donors in silicon

Since their first discovery in 1954 (Ref. 1) thermal double donors (TDD’s) in silicon have attracted constant interest due to their peculiar properties and technological importance. TDD’s form a family of at least 17 closely related members (TDD0–TDD16) (Refs. 2–4) and appear consecutively under thermal heating at 350–550°C.2,3,5 The structures of TDD’s have long remained unclear but are commonly associated with the experimental LVM frequencies quoted in the literature.10 That an interstitial Si atom should be involved in the bonding of the consecutive mechanism between the TDD’s was the achievement in finding these structures as well as in clarifying the bonding between the oxygen chains obtained by us for TDD0, TDD1, and TDD2. Our oxygen-only models for TDD’s.13 This consists of adatoms bonded to two common Si atoms. 14 The O_{i} atoms (O_{i}) bonded to two common Si atoms. 14 The O_{i} chains obtained by us for TDD0, TDD1, and TDDn (n>1) are O_{i}-O_{2r}, O_{2r}-O_{2r}, and O_{2r}-O_{2r}-O_{2r} (n>1), respectively. 15

We have shown that a rate-equation model for the O chains is able to produce the experimentally observed annealing kinetics of the TDD’s.15,16 However, the agreement may depend on the parameters we use in the kinetic model. It is therefore of paramount importance to compare the calculated LVM frequencies and modes of the O chains directly with the corresponding experimental quantities for the TDD’s.

The aim of this paper is to report calculated LVM’s for the O chains. We find that the relevant calculated LVM frequencies originate from the asymmetric stretching vibrations of the flanking O_{i}’s of the O chains and agree systematically with the experimental LVM frequencies quoted above.

The total-energy calculations are performed using the self-consistent plane-wave pseudopotential method (PP).17 For Si we use the norm-conserving Hamann PP.18 The PP is of the fully separable Kleinman-Bylander form19 and the s component is used as the local one. For O we use the ultrasoft Vanderbilt PP.20 A kinetic-energy cutoff of 28 Ry and the Γ-point sampling are used. We use an elongated 162-atom-site supercell that gives an intercell distance of 35 Å along the [110] direction of the O chains. All ionic coordinates are allowed to relax without any constraints until the largest remaining Hellmann-Feynman force component is less than 0.1 meV/Å. However, in the case of the O_{2r}-O_{2r} chain we had difficulties in stabilizing the ground-state structure for reasons that are not clear to us. Therefore, in this case we use an elongated 108-atom-site supercell that gives an intercell distance of 22 Å along the [110] direction. The procedure and program by Köhler et al.21 used earlier for O_{i} and vacancy-oxygen complexes22–24 are used in calculating the present LVM’s. Every atom vibrating in an LVM is displaced to all six Cartesian directions from its equilibrium position, the electronic structure for this configuration is optimized, and the resulting Hellmann-Feynman forces are calculated. The coupling constants for the dynamical matrix are formed from these forces and displacements. Since we are interested in localized models it is sufficient to include in the calculations only those atoms that have a significant vibrational amplitude. We have tested this approximation systematically for O_{3r}, O_{i}-O_{2r}, and O_{2r}-O_{2r}. It turns out that the inclusion of only the flanking Si-O_{i}-O atom group results in an error less than 2 cm^{-1}. At least these four atoms are always included in the LVM calculations.

The calculated highest LVM frequencies for the O chains are given in Table I together with the experimental frequencies and the frequencies calculated by Coutinho et al.8 The calculated LVM frequencies related to TDD’s are given for the doubly positive charge state of the corresponding O chain because almost all TDD’s have donated two electrons to the conduction band at temperatures T>100 K (for the O_{2r}-O_{2r} chain T>200 K). We first note that by increasing the size of the supercell from 32 to the present 162 atom sites we find a closer agreement with the experimental LVM frequencies for monomers and dimers: for O_{i} (0.59098–1138 cm^{-1} (experiment 1136 cm^{-1}) and for O_{2r} (1033, 984–1043,
TABLE I. High-lying LVM frequencies (cm$^{-1}$) for thermal double donors and related oxygen chains in silicon. The isotopic shifts, when $^{16}$O is replaced by $^{18}$O, are given in parenthesis. The value for the $O_2^-$-$O_{2r}^+$ chain is an estimate.

<table>
<thead>
<tr>
<th>Structure</th>
<th>This work</th>
<th>Experiment</th>
<th>Coutinho et al.$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O^0_2$</td>
<td>1138</td>
<td>1136$^b$</td>
<td></td>
</tr>
<tr>
<td>$O_2^0_{2i}$</td>
<td>1043(-48)</td>
<td>1060(-48)$^c$</td>
<td></td>
</tr>
<tr>
<td>$O_{3i}^0$</td>
<td>1013(-44)</td>
<td>1012(-43)$^d$</td>
<td></td>
</tr>
<tr>
<td>$O_{2r}^0$-$O_{2r}^+$</td>
<td>987(-45)</td>
<td>1005$^e$</td>
<td></td>
</tr>
<tr>
<td>$O_5^0$</td>
<td>945(-41)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$O_1$-$O_{2r}^+$</td>
<td>973(-43)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$O_{4r}^0$</td>
<td>1010(-46)</td>
<td>1020$^f$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>955(-44)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>920(-41)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$O_{2r}^0$-$O_{2r}^+$</td>
<td>978</td>
<td>975$^g$ (TDD1)</td>
<td>940 ($O_3$)</td>
</tr>
<tr>
<td>$O_{2r}^0$-$O_{2r}^+$</td>
<td>942</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$O_{2r}^0$-$O_{2r}^+$</td>
<td>992(-45)</td>
<td>988(-43)$^f$ (TDD2)</td>
<td>951 ($O_6$)</td>
</tr>
<tr>
<td>$O_{2r}^0$-$O_{2r}^+$</td>
<td>988(-45)</td>
<td>999(-44)$^f$ (TDD3)</td>
<td>963 ($O_7$)</td>
</tr>
<tr>
<td>$O_{2r}^0$-$O_{2r}^+$</td>
<td>1000(-45)</td>
<td>1006$^g$ (TDD4)</td>
<td>969 ($O_8$)</td>
</tr>
<tr>
<td>$O_{2r}^0$-$O_{2r}^+$</td>
<td>$\approx$1006</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Reference 8.
$^b$References 25 and 26.
$^c$References 27 and 28.
$^d$References 8, 27, and 28.
$^e$Reference 29.
$^f$Reference 30.
$^g$References 7 and 8.

1013 cm$^{-1}$ (experiment 1060, 1012 cm$^{-1}$).22–24 Also, the calculated isotopic shifts for $O_{2i}^0$ when $^{16}$O is replaced by $^{18}$O agree within 1 cm$^{-1}$ with the experimental shifts (Table I).

According to the kinetic simulations$^{15,16}$ one of the two experimental 1005 cm$^{-1}$ bands$^{29}$ should originate from an LVM of the staggered $O_{3i}^0$ chain. The three calculated high-frequency LVM’s for the staggered $O_{3i}^0$ chain are shown in Fig. 1 (we call the modes having a frequency higher than 900 cm$^{-1}$ high-frequency modes in the following). The highest frequency of 1072 cm$^{-1}$ originates from the asymmetric stretching vibration of the flanking O bowed towards the center of the chain [Fig. 1(a)]. The next highest frequencies of 987 and 945 cm$^{-1}$ originate from the coupled asymmetric stretching vibrations of the center O in the right flanking O bowed outwards from the center [Figs. 1(b) and 1(c), respectively]. The two modes in Figs. 1(b) and 1(c) resemble those of the staggered dimer.22,23 The calculated frequency of 987 cm$^{-1}$ lies closest to the experimental frequency of 1005 cm$^{-1}$ and is thus identified with this (Table I). Our calculations predict a LVM frequency of 973 cm$^{-1}$ (Table I) for the highest mode of the $O_{2r}^0$-$O_{2r}^+$ chain, assigned to TDD0.13 In this mode the flanking O$_i$ performs asymmetric stretching vibration similar to the mode shown in Fig. 1(a). To the best of the authors’ knowledge no experimental frequency is available for TDD0. This may be due to the fact that the $O_{2r}^0$-$O_{2r}^+$ chain has about 0.4 eV higher formation energy than the staggered $O_{3i}^0$ chain for values of the electron chemical potential above 0.48 eV.13,31

Hallberg and Lindström find experimentally that TDD1 and TDD2 form bistable systems with a common electrically inactive X-state configuration that has an IR absorption band at 1020 cm$^{-1}$.30 On the basis of the total-energy calculations we assign the electrically inactive staggered $O_{3i}^0 chain to the X-state configuration.13 We find that the calculated highest LVM frequency originates from the asymmetric stretching vibration of the flanking O similarly to the 1072 cm$^{-1}$ mode of the staggered $O_{3i}^0$ chain in Fig. 1(a). This highest LVM frequency is 1010 cm$^{-1}$ and agrees closely with the experimental value of 1020 cm$^{-1}$ (Table I).30 The agreement is thus consistent with our assignment of the staggered $O_{4i}^0$ chain to the X-state configuration.13 Similarly to the staggered $O_{3i}^0$ chain the staggered $O_{4i}^0$ chain has also two other high-frequency modes (Table I).

The calculated two highest LVM’s for the $O_{2r}^0$-$O_{2r}^+$ chain (TDD1) are shown in Fig. 2. They are qualitatively similar to the two highest LVM’s of the staggered $O_{3i}^0$ chain in Fig. 1. The higher frequency of 978 cm$^{-1}$ originates from the asymmetric stretching vibration of the flanking O$_i$ and agrees closely with the experimental value of 975 cm$^{-1}$ for TDD1 (Table I).2,8 This agreement is thus consistent with our assignment of the $O_{2r}^0$-$O_{2r}^+$ chain to TDD1.13

The highest LVM’s of the $O_{2r}^0$-$O_{2r}^+$ chain resemble those of the staggered O chains as follows. The $O_{2r}^0$-$O_{2r}^+$ chain has two adjacent flanking O$_i$’s that can generate two high-frequency modes (compare Figs. 1 and 2). However, a third high-frequency mode is not allowed because the third O atom (O$_i$) is threefold coordinated which softens...
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The calculated highest LVM for the O$_2$-O$_2^+$ chain (TDD2) is shown in Fig. 3(a). The LVM originates again from the asymmetric stretching vibration of the flanking O$_i$. The corresponding LVM frequency is 992 cm$^{-1}$ and agrees closely with the experimental value of 988 cm$^{-1}$ for TDD2 (Table I). This agreement is thus consistent with our assignment of the O$_2$-O$_2^+$ chain down to 866 cm$^{-1}$.

The calculated highest LVM for the O$_2$-O$_2$-O$_2^+$ chain (TDD2) is shown in Fig. 3(a). The LVM originates again from the asymmetric stretching vibration of the flanking O$_i$. The corresponding LVM frequency is 992 cm$^{-1}$ and agrees closely with the experimental value of 988 cm$^{-1}$ for TDD2 (Table I). This agreement is thus consistent with our assignment of the O$_2$-O$_2$-O$_2^+$ chain down to 866 cm$^{-1}$.

The calculated highest LVM for the O$_4$-O$_4$-O$_4^+$ chain (TDD2) is shown in Fig. 3(a). The LVM originates again from the asymmetric stretching vibration of the flanking O$_i$. The corresponding LVM frequency is 992 cm$^{-1}$ and agrees closely with the experimental value of 988 cm$^{-1}$ for TDD2 (Table I). This agreement is thus consistent with our assignment of the O$_4$-O$_4$-O$_4^+$ chain down to 866 cm$^{-1}$.

The highest calculated LVM frequencies for the O$_4$-O$_4$-O$_4^+$ and O$_4$-O$_4$-O$_4^+$ chains are 988 and 1006 cm$^{-1}$, respectively (Table I). The calculated LVM frequencies agree closely with the corresponding experimental values of 999 and 1006 cm$^{-1}$ (Table I). This agreement is consistent with our assignment of the O$_4$-O$_4$-O$_4^+$ chain down to 866 cm$^{-1}$.

The structure in Fig. 3(a) is symmetric and the asymmetric stretching vibrations of both flanking O$_i$’s give the same frequency. Since the two flanking O$_i$’s are coupled to the threefold coordinated O$_i$’s other high-frequency modes do not occur and the next highest LVM frequency is softened down to 788 cm$^{-1}$ as in the O$_2$-O$_2^+$ chain.

In the same way, also the next O$_2$-O$_{nr}$-O$_2^+$ chains (TDD$n$; n>2) have two similar symmetric flanking O$_i$’s whose asymmetric stretching vibrations give rise to one high-frequency LVM. This is shown in Fig. 3(b) for the O$_2$-O$_{nr}$-O$_2^+$ chain (TDD3). The highest calculated LVM frequencies for the O$_2$-O$_{nr}$-O$_2^+$ and O$_2$-O$_{nr}$-O$_2^+$ chains are 988 and 1006 cm$^{-1}$, respectively (Table I). The calculated LVM frequencies agree closely with the corresponding experimental values of 999 and 1006 cm$^{-1}$ (Table I). This agreement is consistent with our assignment of the O$_2$-O$_2^+$ chain down to 866 cm$^{-1}$.
stant in qualitative agreement with the experiments\textsuperscript{32,33}. (We do not expect here a quantitative agreement because all calculations are performed at 0 K.)

In conclusion, we find that the calculated LVM frequencies as well as their isotopic shifts and charge-state dependences (temperature dependences) for the oxygen chains agree closely with experiments and support our assignments of the O$_2^-$-O$_2^-$ chain to TDD1 and the O$_1^-$-O$_n^-$-O$_1^+$ chain to TDD$n$ ($n>1$) as well as the staggered O$_4^-$ chain to the X state.

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