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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_{2i}-O_{2r} chain to TDD1 and the O_i-O_{nr}-O_i chains to TDDn ($n>1$) (O_i is an interstitial oxygen and O_r a threefold coordinated oxygen belonging to a ring).

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.[2,5] The structures of TDD's have long remained unclear but are commonly believed to consist of aggregated oxygen due to oxygen supersaturation in Czochralski-grown silicon. An important achievement in finding these structures as well as in clarifying the consecutive mechanism between the TDD's was the assignment of the infrared absorption local vibrational modes (LVM's) of 975, 988, 999, and 1006 cm^{-1} to TDD1, TDD2, TDD3, and TDD4, respectively.[6–8] Also the isotopic shifts when ^{16}O is replaced by ^{18}O have been measured: the shifts are -43–-44 cm^{-1}.[8] The LVM frequencies on one hand act as useful fingerprints in following the kinetics of TDD's, and on the other hand serve as a stringent test for structural models for TDD's.

It has been suggested both experimentally[9] and theoretically[10] that an interstitial Si atom should be involved in the cores of the TDD's. However, more recent total-energy calculations indicate that oxygen-only structures for TDD's are those energetically most favorable.[8,11–13] On the basis of accurate total-energy calculations we recently put forward an oxygen-chain-like model for TDD's.[13] This consists of adjacent four-member rings (R's) and flanking interstitial oxygens (O_i's). The R unit consists of two threefold coordinated O atoms (O_r's) bonded to two common Si atoms.[14] The O chains obtained by us for TDD0, TDD1, and TDDn ($n>1$) are O_i-O_{2r}, O_{2i}-O_{2r}, and O_i-O_{nr}-O_i ($n>1$), respectively.[13]

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 form[19] 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 [1$\bar{1}$0] direction of the O chains. All ionic coordinates are allowed to relax without any constraints until the largest remaining Hellmann-Feynman force component is less than 0.1 meV/Å. However, in the case of the O_{2i}-O_{2r} chain we had difficulties in stabilizing the ground-state structure for reasons that are not clear to us. Therefore, in this case we use an elongated 108-atom-site supercell that gives an intercell distance of 22 Å along the [1$\bar{1}$0] direction. The procedure and program by Köhler *et al.*[21] used earlier for O_i and vacancy-oxygen complexes,[22–24] 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 Hellman-Feynman forces are calculated. The coupling constants for the dynamical matrix are formed from these forces and displacements. Since we are interested in localized modes 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_{3i}, O_i-O_{2r}, and O_{2i}-O_{2r}. It turns out that the inclusion of only the flanking Si-O_i-Si-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_i-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}1098→1138 cm^{-1} (experiment 1136 cm^{-1}) and for O_{2i},^{0}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_i-O_{5r}-O_i^{++} chain is an estimate.

Structure	This work	Experiment	Coutinho et $al.$[a]
O_i^0	1138	1136[b]	
O_{2i}^0	1043(-48)	1060(-48)[c]	
	1013(-44)	1012(-43)[d]	
O_{3i}^0	1072(-49)		
	987(-45)	1005[e]	
	945(-41)		
O_i-O_{2r}^{2+}	973(-43)		
O_{4i}^0	1010(-46)	1020[f]	
	955(-44)		
	920(-41)		
O_{2i}-O_{2r}^{2+}	978	975[g] (TDD1)	940 (O_5)
	942		
O_i-O_{2r}-O_i^{2+}	992(-45)	988(-43)[g] (TDD2)	951 (O_6)
O_i-O_{3r}-O_i^{2+}	988(-45)	999(-44)[g] (TDD3)	963 (O_7)
O_i-O_{4r}-O_i^{2+}	1000(-45)	1006[a] (TDD4)	969 (O_8)
O_i-O_{5r}-O_i^{2+}	$\approx$1006		

[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.

FIG. 1. The calculated highest local vibrational modes for the staggered O_{3i} chain: (a) 1072 cm^{-1}, (b) 987 cm^{-1}, and (c) 945 cm^{-1}. Oxygen atoms are drawn in darker gray, silicon atoms in lighter gray.

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_i 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_i and the right flanking O_i 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_i-O_{2r}^{2+} 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
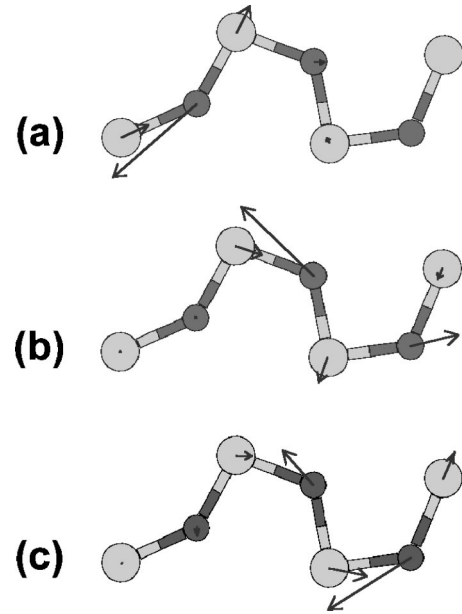
may be due to the fact that the O_i-O_{2r}^{2+} chain has about 0.4 eV higher formation energy than the staggered O_{3i}^0 chain for values of the electron chemical potential above 0.48 eV.[13,31]

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_{4i}^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_i 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_{2i}-O_{2r}^{2+} 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).[7,8] This agreement is thus consistent with our assignment of the O_{2i}-O_{2r} chain to TDD1.[13]

The highest LVM's of the O_{2i}-O_{2r}^{2+} chain resemble those of the staggered O chains as follows. The O_{2i}-O_{2r}^{2+} 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_r) is threefold coordinated which softens
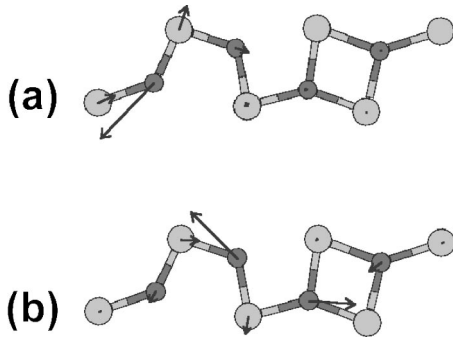
FIG. 2. The calculated highest local vibrational modes for the O_{2i}-O_{2r}^{2+} chain (TDD1): (a) 978 cm^{-1} and (b) 942 cm^{-1}. Oxygen atoms are drawn in darker gray, silicon atoms in lighter gray.

the third highest mode of the O_{2i}-O_{2r}^{2+} chain down to 866 cm^{-1}.

The calculated highest LVM for the O_i-O_{2r}-O_i^{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).[7,8] This agreement is thus consistent with our assignment of the O_i-O_{2r}-O_i chain to TDD2.[13] 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_r'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_{2i}-O_{2r}^{2+} chain.

In the same way, also the next O_i-O_{nr}-O_i^{2+} chains (TDDn, $n > 2$) 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_i-O_{3r}-O_i^{2+} chain (TDD3). The highest calculated LVM frequencies for the O_i-O_{3r}-O_i^{2+} and O_i-O_{4r}-O_i^{2+} chains are 988 and 1000 cm^{-1}, respectively (Table I). The calculated LVM frequencies agree closely with the corresponding experimental values of 999 and 1006 cm^{-1} (Table I).[7,8] This agreement is consistent with our assignment of the
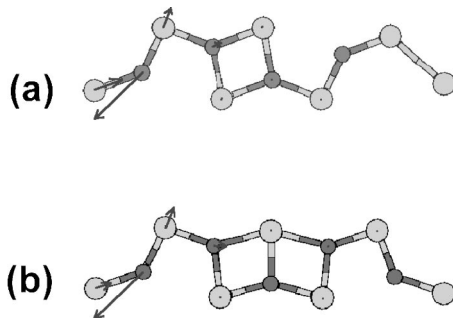

FIG. 3. The calculated highest local vibrational modes for the O_i-O_{2r}-O_i^{2+} chain (TDD2, 992 cm^{-1})(a) and the O_i-O_{3r}-O_i^{2+} chain (TDD3, 988 cm^{-1})(b). Oxygen atoms are drawn in darker gray, silicon atoms in lighter gray.

TABLE II. Calculated LVM frequency shifts (cm^{-1}) when the charge state changes from doubly positive to neutral for O_i-O_{2r} ($n = 0$), and O_i-O_{nr}-O_i ($n > 1$). The shifts for the ^{18}O isotope chains are given in parentheses.

n	0	2	3	4
Shift	5(4)	17(16)	10(9)	12(11)

O_i-O_{nr}-O_i chains to TDDn ($n > 2$).[13] However, the calculated frequency for the O_i-O_{3r}-O_i^{2+} chain (988 cm^{-1}) is lower than that for the O_i-O_{2r}-O_i^{2+} chain (992 cm^{-1}) whereas the corresponding experimental frequency for TDD3 (999 cm^{-1}) is by 11 cm^{-1} higher than that for TDD2 (988 cm^{-1}). We believe that this inconsistency is due to the insufficient **k**-point sampling (we use only Γ point).

Coutinho *et al.* have reported LVM frequencies for O chains, summarized in Table I.[8] Even though the calculated differences between the adjacent LVM frequencies agree closely with the corresponding experimental differences between TDD's in Table I, the calculated frequencies lie about 35 cm^{-1} below the experimental ones, showing a less satisfactory agreement. Coutinho *et al.* assign O_{4+n} to TDDn, which differs from our assignments given in Table I in that we have less O atoms in our corresponding chains: 4 O atoms in TDD1 *and* TDD2, $2 + n$ O atoms in TDDn for $n > 2$. The experimental kinetic study by Åberg *et al.* indicates that TDD2 forms directly from TDD1 via reconfiguration.[29] Both TDD1 and TDD2 are found experimentally to be bistable with the *same* electrically inactive X state,[30] showing that these structures are closely related and are probably different configurations of the same complex. These experimental findings are difficult to explain if TDD1 and TDD2 have a different number of O atoms as is the case in the model by Coutinho *et al.*, but are natural to understand with our O chain model where O_{2i}-O_{2r} (TDD1), O_i-O_{2r}-O_i (TDD2), and (the staggered) O_{4i} (the X state) are different configurations of the same O_4 complex.[13,15,16]

At low temperatures the electrons donated to the conduction band return to the TDD's making them electrically neutral (the TDD's change from the doubly positive state to the 0 state). It may be expected that the LVM frequencies of the TDD's undergo a positive shift when T becomes low because two more localized electrons strengthen the interatomic bonding. In fact, it is found experimentally that the 975 (TDD1), 988 (TDD2), 999 (TDD3), and 1006 cm^{-1} (TDD4) frequencies *increase* by about 3, 3, 3, and 0.5-1 cm^{-1}, respectively, when T decreases from the room temperature to 10 K (Ref. 32) whereas during the same temperature change the experimental 1060 and 1012 cm^{-1} frequencies (O_{2i}) decrease slightly (2 and 0-0.6 cm^{-1}, respectively).[32,33] This behavior may be understood qualitatively by means of the change in the charge state. The calculated frequencies for the O_i-O_{2r} (TDD0) and O_i-O_{nr}-O_i (TDDn, $n > 1$) chains all undergo—similar to the experiments—positive shifts when the charge state changes from doubly positive to neutral (Table II). On the other hand, O_{2i} does not have a donor state and O_{2i} remains, therefore, always neutral. As a consequence the calculated frequencies for O_{2i} (Table I) also remain con-

stant in qualitative agreement with the experiments[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_{2i}-O_{2r} chain to TDD1 and the O_i-O_{nr}-O_i chain to TDDn ($n>1$) as well as the staggered O_{4i} chain to the X state.

[1] C.S. Fuller, J.A. Ditzenberger, N.B. Hannay, and E. Buehler, Phys. Rev. **96**, 833 (1954).

[2] P. Wagner and J. Hage, Appl. Phys. A: Solids Surf. **49**, 123 (1989).

[3] B. Pajot, H. Compain, J. Lerouille, and B. Clerjand, Physica B & C **117B&118B**, 110 (1983).

[4] W. Götz, G. Pensel, and W. Zulehner, Phys. Rev. B **46**, 4312 (1992).

[5] *Early Stages of Oxygen Precipitation in Silicon*, edited by R. Jones (Kluwer Academic, Dodrecht, 1996).

[6] J.L. Lindström and T. Hallberg, Phys. Rev. Lett. **72**, 2729 (1994).

[7] T. Hallberg and J.L. Lindström, J. Appl. Phys. **79**, 7570 (1996).

[8] J. Coutinho, R. Jones, L.I. Murin, V.P. Markevich, J.L. Lindström, S. Öberg, and P.R. Briddon, Phys. Rev. Lett. **87**, 235501 (2001).

[9] R.C. Newman, J. Phys. C **18**, L967 (1985).

[10] P. Deák, L.C. Snyder, and J.W. Corbett, Phys. Rev. B **45**, 11 612 (1992).

[11] D.J. Chadi, Phys. Rev. Lett. **77**, 861 (1996).

[12] M. Ramamoorthy and S.T. Pantelides, Appl. Phys. Lett. **75**, 115 (1999).

[13] M. Pesola, Y.J. Lee, J. von Boehm, M. Kaukonen, and R.M. Nieminen, Phys. Rev. Lett. **84**, 5343 (2000).

[14] L.C. Snyder, J.W. Corbett, P. Deak, and R. Wu, in *Defects in Electronic Materials*, edited by M. Satvola *et al.*, Mater. Res. Soc. Symp. Proc. 104 (Materials Research Society, Pittsburgh, 1988), p. 179.

[15] Y.J. Lee, J. von Boehm, M. Pesola, and R.M. Nieminen, Phys. Rev. Lett. **86**, 3060 (2001).

[16] Y.J. Lee, J. von Boehm, M. Pesola, and R.M. Nieminen, Appl. Phys. Lett. **79**, 1453 (2001).

[17] S. Pöykkö, M.J. Puska, and R.M. Nieminen, Phys. Rev. B **57**, 12 174 (1998).

[18] D.H. Hamann, Phys. Rev. B **40**, 2980 (1989).

[19] L. Kleinman and D.M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).

[20] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990); K. Laasonen, A. Pasquarello, R. Car, C. Lee, and D. Vanderbilt, *ibid.* **47**, 10 142 (1993).

[21] Th. Köhler, Th. Frauenheim, and G. Jungnickel, Phys. Rev. B **52**, 11 837 (1995).

[22] M. Pesola, J. von Boehm, and R.M. Nieminen, Phys. Rev. Lett. **82**, 4022 (1999).

[23] M. Pesola, J. von Boehm, T. Mattila, and R.M. Nieminen, Phys. Rev. B **60**, 11 449 (1999).

[24] R.M. Nieminen, M. Pesola, Y.J. Lee, and J. von Boehm, in *Computer Simulation Studies in Condensed Matter Physics*, edited by D.P. Landau, S.P. Lewis, and H.B. Schüttler (Springer-Verlag, Heidelberg, 2000), Vol. XIII.

[25] H.J. Hrostowski and R.H. Kaiser, Phys. Rev. **107**, 966 (1957).

[26] H.J. Hrostowski and B.J. Alder, J. Chem. Phys. **33**, 980 (1960).

[27] L.I. Murin, T. Hallberg, V.P. Markevich, and J.L. Lindström, Phys. Rev. Lett. **80**, 93 (1998).

[28] S. Öberg, C.P. Ewels, R. Jones, T. Hallberg, J.L. Lindström, L.I. Murin, and P.R. Briddon, Phys. Rev. Lett. **81**, 2930 (1998).

[29] D. Åberg, B.G. Svensson, T. Hallberg, and J.L. Lindström, Phys. Rev. B **58**, 12 944 (1998).

[30] T. Hallberg and J.L. Lindström, Appl. Phys. Lett. **68**, 3458 (1996).

[31] Y.J. Lee, J. von Boehm, M. Pesola, and R.M. Nieminen, Phys. Rev. B **65**, 085205 (2002).

[32] J.L. Lindström and T. Hallberg, in *Early Stages of Oxygen Precipitation in Silicon*, edited by R. Jones (Kluwer Academic, Dordrecht, 1996), p. 61.

[33] T. Hallberg, J.L. Lindström, L.I. Murin, and V.P. Markevich, Mater. Sci. Forum **258-263**, 361 (1997).