Vibrations of the Interstitial Oxygen Pairs in Silicon

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First-principles methods are used to calculate the structures and local vibrational modes of interstitial oxygen pairs in silicon. The staggered O_i-Si-Si-O_i and skewed O_i-Si-Si-O_i structures are nearly degenerate in energy. The calculated local vibration frequencies and their pure and mixed $^{18}O \rightarrow {}^{16}O$ isotopic shifts agree closely with experiments: the highest frequency is assigned to the skewed and the four lower ones to the staggered structure. This result may clear up the controversy of oxygen dimers in silicon, and also suggests a mechanism for fast oxygen diffusion. [S0031-9007(99)09205-4]

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Approximately 10^{18} oxygen atoms/cm^3 appear in as-grown Czochralski silicon, supersaturated and highly inhomogeneously distributed. During subsequent heat treatments oxygen atoms become mobile at temperatures $>350\,^{\circ}$C and begin to cluster. Individual oxygen atoms occupying interstitial bond center positions (O_i) are known to diffuse by hopping between the neighboring bond center sites with an activation energy of 2.54 eV in a large temperature range of 300–1200 °C [1,2]. However, aggregation of oxygen takes place at a much lower activation energy of about 1.8 eV [3] and oxygen-containing fast diffusing species are needed to explain the aggregation [4,5]. The interstitial oxygen pairs (O_{2i}) have been suggested to be a fast diffusing species [4,5]. The local vibration (LV) frequencies of the structures of O_{2i} can play an important role as fingerprints in clarifying the aggregation mechanisms of oxygen.

When two O_i's approach each other their mutual interactions cause splittings in the LV frequencies of O_i at 1136 and 517 cm^{-1} [6,7]. Four LV frequencies at 1060, 1012, 690, and 556 cm^{-1} assigned to the same configuration of O_{2i} were recently detected and identified experimentally by Hallberg *et al.* [8] and Murin *et al.* [5]. Murin *et al.* [5] also detected an LV frequency at 1105 cm^{-1} which they associated with another configuration of O_{2i}. The subsequent study by Öberg *et al.* [9] using the mixed and pure $^{18}O \rightarrow {}^{16}O$ isotopes actually proved that the defect giving rise to the four LV frequencies above contains at least two coupled O atoms.

The lowest-energy configuration of O_{2i} has earlier been assigned to the staggered one [two O atoms having a common Si atom located in the same (110) plane; see Fig. 1] [10]. Recently, Öberg *et al.* [9] reported their finding that a *skewed* O_i-Si-Si-O_i configuration [two O atoms separated by two Si atoms located in different (110) planes; see Fig. 2] is, in fact, the ground state. They assigned the four measured LV frequencies (see above) to the LV's of the skewed O_i-Si-Si-O_i configuration. The purpose of the present Letter is to report LV frequencies for these two configurations of O_{2i} calculated using accurate density-functional-theory [11] based methods. The calculations give rise to a new interpretation for the measured LV frequencies and the structure of O_{2i}. We find that the four measured frequencies originate from the *staggered* configuration and the frequency at 1105 cm^{-1} from the *skewed* O_i-Si-Si-O_i one. Especially, we find a *new* local oxygen-induced silicon mode that explains the vanishing of the $^{18}O \rightarrow {}^{16}O$ isotopic shift of the lowest measured frequency. This is the first time that *all*

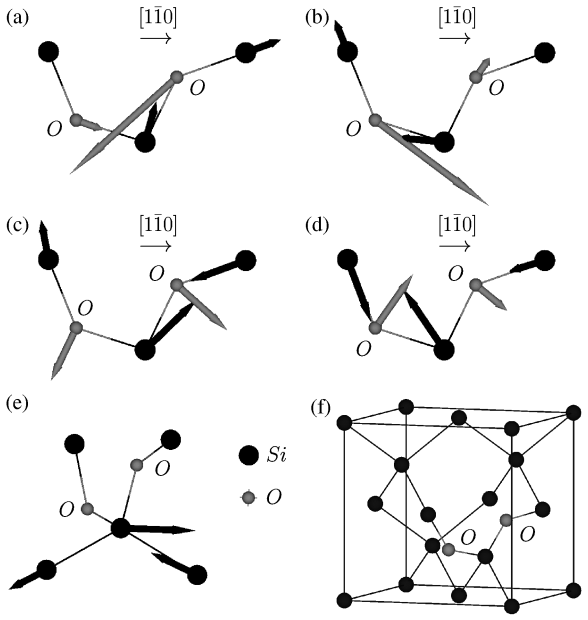

FIG. 1. Calculated vibrational modes for the interstitial oxygen pair in the staggered configuration. Black and grey circles denote silicon and oxygen atoms, respectively. The types and frequencies of the modes are as follows. Asymmetric stretching-type local vibrational modes: (a) 1033 cm^{-1} and (b) 984 cm^{-1}; symmetric stretching-type local vibrational modes: (c) 697 cm^{-1} and (d) 661 cm^{-1}; and (e) oxygen-induced asymmetric silicon vibrational mode: 566 cm^{-1}. (f) Schematic conventional Si unit cell with two O_i's. (a)–(d) are in the (110) plane. (e) is slightly tilted for clarity.

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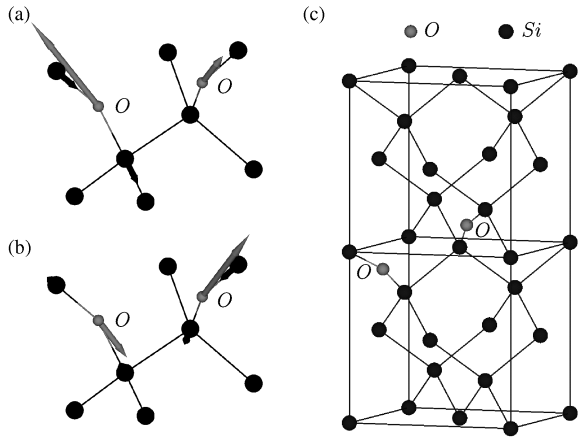

FIG. 2. Calculated asymmetric stretching-type local vibrational modes of the interstitial oxygen pair in the skewed O_i-Si-Si-O_i configuration: (a) 1104 cm^{-1} and (b) 1091 cm^{-1}. (c) Two schematic conventional Si unit cells with two O_i's. Black and grey circles denote silicon and oxygen atoms, respectively.

experimental frequencies for O_{2i} can be explained within one and the same theoretical approach.

The total energy calculations are performed in the local density [12] approximation using a self-consistent plane-wave pseudopotential method. The Perdew-Zunger [13] parametrization of the Ceperley-Alder data [14] is used for the exchange-correlation energy. For silicon we use the norm-conserving Hamann pseudopotential [15]. The pseudopotential is of the fully separable Kleinman-Bylander form [16] and the *s* component is used as the local one. For oxygen we use the ultrasoft Vanderbilt pseudopotential [17]. The valence-electron wave functions are expanded in a plane-wave basis set up to a kinetic-energy cutoff of 28 Ry. We use the Monkhorst-Pack 2^3 **k**-point sampling [18] and a 32 atom-site supercell in calculating the LV modes. The total energy is minimized by allowing all ionic coordinates to relax without any constraints until the largest remaining Hellman-Feynman force component is less than 3 meV/Å. The LV calculations are always performed in the zero pressure configuration using the procedure and program by Köhler *et al.* [19]: Every atom is displaced to all six Cartesian directions from the 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 calculated by finite differences using these forces and displacements.

We find that the calculated total energy of the 32 atom-site supercell including the skewed O_i-Si-Si-O_i configuration is by 0.38 eV below that including the staggered O_i-Si-O_i configuration. However, improving the accuracy (see Ref. [20]) by increasing the supercell to 128 atom sites and using the Γ point we find that the latter configuration is by 0.1 eV more stable than the former one [21]. Thus, it is important to consider simultaneously the LV's of both configurations when analyzing the infrared (IR) absorption experiments. This result also suggests a new fast diffusion mechanism for O_{2i} provided that the diffusion barrier between the two configurations is low enough: Instead of moving both O_i's simultaneously as in the model by Ramamoorthy and Pantelides [22] one could move them alternatingly, first O_i^1 in the skewed O_i^1-Si-Si-O_i^2 configuration to form a staggered O_i^1-Si-O_i^2 configuration and then O_i^2 to form again a transferred skewed O_i^1-Si-Si-O_i^2 configuration [cf. Figs. 2(a) and 1(a)] and so on.

The results from the LV calculations are given in Tables I and II and the relevant LV modes are shown in Figs. 1 and 2.

The calculated LV's in the staggered configuration appear in pairs and bear a clear resemblance to the corresponding LV's of O_i. The two LV's of the highest frequency pair of 1033 and 984 cm^{-1} [Figs. 1(a) and 1(b)] are of the asymmetric stretching type. In the 1033 (984) cm^{-1} LV mode the oxygen atoms vibrate roughly 180° out of phase (in phase). The two LV modes of the next highest frequency pair of 697 and 661 cm^{-1} [Figs. 1(c) and 1(d)] consist analogously of coupled symmetric stretching modes of the two Si-O_i-Si groups. Finally, Fig. 1(e) shows the localized oxygen-induced Si mode of the next highest frequency of 566 cm^{-1} located just above the region of delocalized vibrations. The Si atom between the two O_i's and its two neighboring Si atoms vibrate in an asymmetric stretching mode with much larger amplitudes than the other atoms.

The calculated LV's in the skewed O_i-Si-Si-O_i configuration also appear in pairs. The LV's of the highest frequency pair of 1104 and 1091 cm^{-1} (Fig. 2) consist of two puckered Si-O_i-Si groups vibrating in asymmetric stretching modes with very different amplitude sizes such that the oxygen atoms vibrate roughly 180° out of phase and in phase, respectively. The two LV's of the next highest frequency pair of 643 and 627 cm^{-1} consist analogously of two puckered Si-O_i-Si groups vibrating in symmetric stretching modes. The mode of the next highest frequency of 558 cm^{-1} is again an oxygen-induced Si mode consisting mainly of the large vibrations of the two Si atoms between the two O_i's and their neighboring Si atoms.

We compare first the upper (asymmetric stretching-type) LV pairs. The calculated LV frequencies for the staggered configuration agree more closely with the experiments than do those for the skewed O_i-Si-Si-O_i configuration (within 30 and 80 cm^{-1}, respectively, Table I). The calculated $^{18}O \rightarrow {}^{16}O$ isotopic shifts (all silicon atoms are of the ^{28}Si isotope in this paper) for the staggered configuration (-46 and -42 cm^{-1}) agree again more closely with the experimental isotopic shifts (-48 and -43 cm^{-1}) than do those for the skewed O_i-Si-Si-O_i configuration (-50 and -50 cm^{-1}) (Table I). The calculated separation of the asymmetric LV frequency pair for the staggered configuration and the $^{18}O \rightarrow {}^{16}O$ isotopic shift of this quantity (49 and -4 cm^{-1}) agree much more closely with the corresponding experimental

TABLE I. Local vibration frequencies (cm^{-1}) of O_{2i}. S denotes the staggered configuration and SK the skewed O_i-Si-Si-O_i configuration. The symbol "18-16" denotes a mixed $^{18}O_i \rightarrow {}^{16}O_i$-type O_{2i}. All silicon atoms are of the ^{28}Si isotope. The isotopic shifts are given in parentheses in the sixth and seventh column.

	$^{16}O_{2i}$ (S)	$^{16}O_{2i}$ (SK)	18-16; 16-18 (S)	18-16; 16-18 (SK)	$^{18}O_{2i}$ (S)	$^{18}O_{2i}$ (SK)
This work	1033, 984	1104, 1091	1032, 942; 993, 978	1103, 1043; 1094, 1052	987(−46), 942(−42)	1054(−50), 1041(−50)
	697, 661	643, 627	693, 655; 691, 658	641, 626; 642, 625	686(−11), 653(−8)	640(−3), 624(−3)
	566	558	566; 566	558; 558	566(0)	558(0)
Öberg *et al.* calculations[a]	1101, 926	1085, 1036	1072, 907; 1087, 895	1082, 991; 1053, 1020		1038(−47), 988(−47)
		637		634; 627		625(−12)
		581		579; 578		577(−4)
		574		570; 574		569(−5)
Experiments[a,b] (10 K)	1060, 1012	1105	~1060, 970; 1021, 1004		1012(−48), 969(−43)	
	690		686; 686		680(−10)	
	556		~556; ~556		556(0)	

[a]Reference [9].
[b]References [5,8].

values (48 and -5 cm^{-1}) than do those for the skewed O_i-Si-Si-O_i configuration (13 and 0 cm^{-1}) (Table II). Also, the calculated separations [23] of the asymmetric LV frequency pairs for the staggered mixed isotope configurations (90; 15 cm^{-1}) agree much more closely with the corresponding experimental values (90; 17 cm^{-1}) than do those for the skewed O_i-Si-Si-O_i ones (60; 42 cm^{-1}) (Table II). And finally, the calculated shift of the average of the asymmetric LV frequency pair and the change induced by the replacement of ^{16}O by ^{18}O to this quantity for the staggered configuration (-89.5 and 6 cm^{-1}) agree much more closely with the corresponding experimental values (-100 and 6.5 cm^{-1}) than do those for the skewed O_i-Si-Si-O_i configuration (-0.5 and 0 cm^{-1}) (Table II). Thus this comparison strongly suggests that the measured IR absorption peaks at 1060 and 1012 cm^{-1} are due to the *asymmetric* stretching-type LV's of the *staggered* O_{2i} [Figs. 1(a) and 1(b)].

The experimentally detected LV frequency of 1105 cm^{-1} belonging to a different configuration [5] than the other four frequencies listed in Table I occurs below the large IR absorption peak of O_i at 1136 cm^{-1} [6]. It is natural to associate the lower frequency (the calculated value of 1091 cm^{-1}) of the asymmetric stretching frequency pair of the *skewed* O_i-Si-Si-O_i configuration to the experimental frequency of 1105 cm^{-1}. The 1091 cm^{-1} frequency lies 58 cm^{-1} above the highest frequency of 1033 cm^{-1} of the staggered configuration which matches well with the corresponding experimental difference of $1105 - 1060 = 45$ cm^{-1} (Table I). The upper frequency would then be masked by the IR absorption peak of O_i (or might be seen as a weak feature on either flank of the peak).

As to the lower (symmetric stretching-type) LV pairs the calculated upper frequency of the staggered configuration of 697 cm^{-1} and its $^{18}O \rightarrow {}^{16}O$ isotopic shift of -11 cm^{-1} agree closely with the next experimental frequency of 690 cm^{-1} and its $^{18}O \rightarrow {}^{16}O$ isotopic shift of -10 cm^{-1} (Table I). Since the corresponding quantities of the skewed O_i-Si-Si-O_i configuration (643 and -3 cm^{-1}) show a less satisfactory agreement the result strongly suggests that the experimental frequency of 690 cm^{-1} is the upper frequency of the *symmetric* stretching LV pair of the *staggered* configuration.

The fourth experimental frequency of 556 cm^{-1} has no $^{18}O \rightarrow {}^{16}O$ isotopic shift and is characterized as Si related [9]. We find a local *oxygen-induced* Si mode of this type just above the region of delocalized vibrations

TABLE II. Separations and shifts of averages of the asymmetric stretching-type local vibration frequency pairs (cm^{-1}) of O_{2i}. The shifts of averages are given in parentheses and are calculated from the calculated values of 1098 and 630 cm^{-1} of $^{16}O_i$ and 1048 and 628 cm^{-1} of $^{18}O_i$ [21]. S denotes the staggered configuration and SK the skewed O_i-Si-Si-O_i configuration. All silicon atoms are of the ^{28}Si isotope. The symbol "18-16" denotes a mixed $^{18}O_i \rightarrow {}^{16}O_i$-type O_{2i}.

	$^{16}O_{2i}$ (S)	$^{16}O_{2i}$ (SK)	18-16; 16-18 (S)	18-16; 16-18 (SK)	$^{18}O_{2i}$ (S)	$^{18}O_{2i}$ (SK)
This work	49(−89.5)	13(−0.5)	90; 15	60; 42	45(−83.5)	13(−0.5)
Öberg *et al.* calculation[a]	175	49	165; 192	91; 33		50
Experiments (10 K)	48(−100)[a,b,c]		90; 17[a]		43(−93.5)[a,b]	

[a]Reference [9].
[b]Reference [8].
[c]Reference [5].

at 566 cm^{-1} for the staggered configuration [Table I and Fig. 1(e)]. The facts that this frequency agrees closely with the experimental value and in agreement with the experiment shows no $^{18}O \rightarrow {}^{16}O$ isotopic shift (Table I) strongly suggest that this LV mode is seen in the experiment at 556 cm^{-1}.

The LV frequencies of the symmetric stretching frequency pair of the skewed O_i-Si-Si-O_i configuration have not been detected experimentally (see Table I). The reason for this may be as follows. The O_i's interact in this mode weakly, almost like two independent O_i's [21]. And, since the symmetric stretching vibration of O_i has not been detected because either a linear Si-O_i-Si "molecule" is infrared inactive [24] or the amplitude of O_i in a puckered case is anyway small [21], it is natural that the symmetric stretching modes of the skewed O_i-Si-Si-O_i configuration are not detected either. The absence of only the lower frequency of the symmetric stretching frequency pair of the staggered configuration (Table I) may be understood in the same way. The O_i's in the lower frequency mode vibrate roughly in phase and interact thus less than the O_i's in the upper frequency mode vibrating roughly 180° out of phase [Figs. 1(d) and 1(c)]. Thus, the symmetric stretching vibrations of the O_i's in the lower frequency mode resemble more those of a single O_i which might explain the absence.

Öberg *et al.* [9] using an *H*-terminated cluster of 88 atoms (44 Si atoms) reported that their calculated frequencies for the skewed O_i-Si-Si-O_i configuration correlate quite well with the four experimental frequencies while those for their configuration (i)—corresponding to the staggered geometry—do not (Table I). Especially the large mixed $^{18}O \rightarrow {}^{16}O$ isotopic shifts in the frequencies of 1101 and 926 cm^{-1}—reflecting an excessive interaction between the oxygen atoms—ruled out their configuration (i) (Table I). Also the large separation of 175 cm^{-1} found for the asymmetric stretching pair (Table II) reflects a large interaction. These results differ considerably from ours and more work is needed to resolve these discrepancies.

In conclusion, we find from accurate total energy pseudopotential calculations that the experimental LV frequencies of 1060, 1012, 690, and 556 cm^{-1} are the upper and lower frequencies of the asymmetric stretching-type frequency pair, the upper frequency of the symmetric stretching-type frequency pair, and the frequency of the oxygen-induced silicon mode of the staggered O_{2i} defect, respectively. The 1105 cm^{-1} frequency is assigned to the lower frequency of the asymmetric stretching-type frequency pair of the skewed O_i-Si-Si-O_i configuration of O_{2i} .

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