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Oxygen complexes in silicon

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Ab initio total-energy calculations are performed to investigate the initial stages of oxygen aggregation in silicon. Since the volume per SiO_2 unit in silicon dioxide is approximately twice the volume per silicon atom in crystalline silicon, it is generally believed that oxygen clustering in silicon will require the creation of self-interstitials. In a similar vein, it is generally believed that neighboring interstitial oxygen configurations are unbound in a weakly distorted silicon lattice. In this work, several interesting phenomena that are associated with aggregation and do not require the creation of silicon self-interstitials are predicted. These predictions are (1) oxygen atoms can cluster with large binding energies of about 1 eV; (2) this clustering can only occur for very specific geometries; and (3) the geometries are chainlike arrangements of oxygen bridging configurations. Indeed, it is the quasi-one-dimensional nature of the proposed oxygen clusters that allows the complexes to form without the accompanying large lattice stress that can lead to the ejection of silicon interstitials. The thermal treatment necessary for aggregation is identified, and predictions of the observable effects are made.

I. INTRODUCTION

Silicon is probably the most important electronic material today. Most silicon crystals are grown by the Czochralski process, in which a seed crystal is lowered into a silicon melt and slowly withdrawn. Because a quartz crucible is used, oxygen diffuses into the silicon crystal in concentrations of 10^{18} cm^{-3}. The ubiquitous presence of oxygen impurities in silicon has led to an extensive study of these defects by a wide variety of experimental techniques since the 1950s.[1-13] It is believed that oxygen breaks a silicon-silicon bond and forms two silicon-oxygen bonds to exist as an isolated "bridging" interstitial.[5,6,10,14-16] Previous calculations have found that adjacent oxygen atoms are marginally bound at best.[17-19] However, we find very strong oxygen-oxygen attraction, but only in one specific orientation for the oxygen atoms. To our knowledge, this configuration has not been previously examined for oxygen binding.

Because of volumetric considerations, it is generally believed that oxygen aggregation *necessarily* entails the creation of silicon self-interstitials. The reasoning is that the volume per silicon atom in SiO_2 is twice the volume in crystalline silicon. However, we find that the proposed quasi-one-dimensional orientation of the oxygen atoms can lead to several-atom complexes that are energetically favorable even without the ejection of silicon atoms from the lattice. Of course, as aggregation continues, volumetric considerations will eventually come into play. Consequently, silicon self-interstitials will then be necessarily created. In this paper, when we refer to oxygen clusters and their stability, we will be referring only to the *initial* quasi-one-dimensional clustering stage.

This paper is divided up in the following manner. In Sec. II, we briefly describe our calculational methodology. In Sec. III, we review previous experimental and theoretical results. In Sec. IV, we present the results of our calculations and in Sec. V discuss their implications.

II. CALCULATIONAL METHOD

We performed *ab initio* total-energy calculations using density-functional theory[20,21] and the local-density, pseudopotential, and supercell approximations. In particular, we used (1) a quantum-molecular dynamics approach[22] to relax the atomic and electronic degrees of freedom according to the respective forces on them; (2) the Ceperly-Alder parametrization[23] of the Perdew-Zunger form[24] for the exchange and correlation energy in the local-density approximation; (3) nonlocal, norm-conserving pseudopotentials of the Kleinman-Bylander[25,26] form with oxygen core radii of 0.8 and 0.8 bohr for the s and p angular momentum orbitals,[27] respectively, and silicon core radii of 1.17, 1.35, and 1.17 bohr for the s, p, and d orbitals; and (4) a Keating model[28] to include long-range geometric relaxation.

We performed extensive checks of our controlled approximations. The supercell size was varied from 16 to 32 to 64 silicon atoms. Up to second-nearest-neighbor silicon atoms were allowed to relax in the 16- and 32-silicon-atom supercells and up to third-nearest-neighbor atoms in the 64-atom supercell. Because of the strength

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of the oxygen pseudopotential, the cutoff energy for the plane-wave expansion was chosen to be 40 Ry, leading to about 550 plane waves per atom. We varied the cutoff from 30 to 80 Ry and found that energy differences were converged to 0.06 eV at 40 Ry. Brillouin-zone integrations were performed using a special k-point scheme.[29,30] Because of the presence of the oxygen atom(s), the size of the irreducible Brillouin zone is much larger than in the case of an equivalent bulk system. Therefore the number of k points at which we have to calculate explicitly the charge density is larger than in the bulk case. Convergence in the number of k points used was checked in the 16-atom unit cell by going from the Balderschi k point,[29] which leads to six k points, to the Chadi-Cohen "two-k-point" scheme,[30] which leads to ten k points. Energy differences changed by 0.04 eV or less.

III. REVIEW OF PREVIOUS STUDIES

In order to appreciate why oxygen binding is of interest, we first need to review the evidence that oxygen occurs as an isolated interstitial. The simplest question one could ask is whether the oxygen occupies an interstitial or a substitutional site. By analogy with SiO_2, one would expect it to occupy an interstitial site, as shown in Fig. 1, and several types of evidence support this hypothesis. First, careful measurements of the lattice constant of oxygenated silicon indicate that the lattice constant increases with increasing oxygen content.[4] Since the Si—O bond length is shorter than the Si—Si bond length, one would expect the lattice constant to decrease if oxygen atoms were replacing silicon atoms. Thus it is believed oxygen occurs interstitially. In particular, it is believed that the oxygen atom breaks a silicon-silicon $\langle 111 \rangle$ bond and forms two silicon-oxygen bonds in a bridging configuration, slightly displaced from the Si-Si axis. This conclusion is supported by evidence from infrared absorption: by the position of ir absorption peaks,[16] by the magnitude of the isotopic shifts of these peaks,[6,10] and by stress-induced dichroism measurements.[5] There are several distinct ir absorption peaks in silicon associated with interstitial oxygen. The strongest is at 9 μm. This is a very strong peak and is in fact used as a calibration standard for measuring the oxygen concentration.[7] Recently, Yamada-Kaneta *et al.* [16] calculated the vibrational excitations for an isolated bridging oxygen atom from first principles and obtained very good agreement with experimental ir absorption spectra. Using a Keating force constant model[28] with the oxygen atom at an interstitial site, Pajot and Cales[10] calculated the isotropic shifts for the 9-μm line and compared the predictions to their experimentally measured shifts. The model's predictions agree very well with their experimental results.

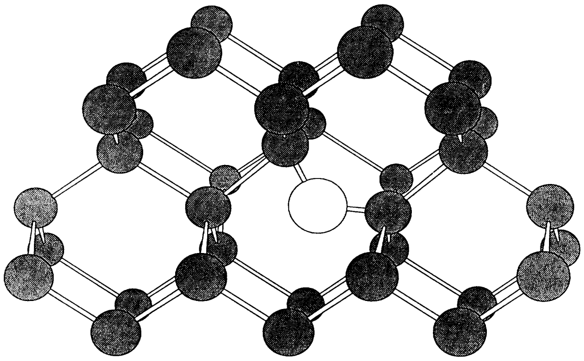

FIG. 1. Structure of bridge oxygen configuration. The oxygen atoms are shown in white; the silicon atoms are shown in gray.

The third type of experiment used to study oxygen defects in silicon needs to be explained in more detail. Stress-induced dichroism experiments can be used to determine the overall symmetry of these oxygen defects in silicon. Briefly, an external stress is applied to the silicon crystal and then the crystal is heated to allow the oxygen atoms to reorient. Finally, the absorption of light polarized in different directions is measured to determine the direction of one or more of the optically active vibrations of the oxygen defects. Thus a dichroism experiment effectively determines the number of oxygen atoms bonded in various directions relative to the stressing direction. This classic experiment was performed 25 years ago by Corbett, Mac Donald, and Watkins.[5] They measured the absorption of light polarized parallel to and perpendicular to the stressing direction for a variety of stressing and of viewing axes. They then computed the dichroic ratio, which is the ratio of absorption between the two polarizations, using a model with one bridging oxygen atom. There is one free parameter in the model, which is the difference in energies for stressed and unstressed directions divided by kT. This energy difference is fit by setting one of their predicted dichroic ratios to the respective experimentally measured one. They assumed that the dipole moment of their bridging oxygen configuration has a $\langle 111 \rangle$ orientation (any oxygen motion along another direction would average to zero because the oxygen also rotates around the broken Si—Si bond) and they obtained good agreement between the measured and predicted dichroic ratios. This good agreement has been interpreted as proof that the interstitial defect has a $\langle 111 \rangle$ orientation and is in fact an isolated interstitial oxygen atom. Thus, from these experiments and others,[2,8] the ground state for oxygen has been identified as an isolated bridging configuration.

Several groups have previously investigated theoretically oxygen clustering, but in the context of the thermal donor problem or anomalous diffusion instead of clustering *per se*. Hence they did not perform a systematic study of many orientations of the clusters. Snyder and Corbett,[17] using semiempirical modified neglect of diatomic overlap cluster calculations, identified two stable clusters of two oxygen atoms. The lower energy cluster consists of oxygen atoms at adjacent bridging sites and is bound by 0.1 eV with respect to two isolated bridging oxygen atoms.

Kelly,[9] using an *ab initio* Green's-function approach to cluster calculations, also investigated clusters of two oxygen atoms. In the first cluster investigated, Kelly initially placed two oxygen atoms on adjacent bridging sites buckled inward toward each other and then relaxed the atoms, maintaining C_{2v} symmetry because thermal donors are known to have C_{2v} symmetry.[9,11] This initial configuration was unstable and the oxygen atoms relaxed outward, passing through the bond centers, until they were outwardly buckled. To the accuracy of the calculation, this configuration was not bound. The second configuration Kelly investigated was the quasimolecular O_2 molecule, originally proposed by Gösele and Tan.[7] The oxygen atoms are bound to each other and are only weakly coupled to the Si lattice. They proposed that the rapidly migrating species responsible for the "anomalous" diffusion might be this molecularlike oxygen pair. The reasoning was that since this form of oxygen was not bound to the silicon lattice, it could migrate rapidly. Additionally, O_2 molecules are known to exist in SiO_2 so it was conjectured they might also occur in crystalline silicon. Kelly finds this configuration to be unbound by 4.5 eV so any O_2 present in Si rapidly dissociates and each atom makes a bridging bond.

Investigating possible candidates for thermal donors, Saito and Oshiyama[18] looked at two clusters, each with C_{2v} symmetry, of three oxygen atoms using *ab initio* local-density-approximation (LDA) pseudopotential cluster calculations. The first cluster is reminiscent of the five-oxygen-atom model of the thermal donor proposed by Ourmazd, Schröter, and Bourret.[13] The second configuration they investigated is an oxygen atom in a "*y*-lid" configuration[17,18] stabilized by the presence of two bridging oxygen atoms. However, both of the three-atom clusters were metastable. The first is unbound by 2.1 eV with respect to three isolated bridging oxygen atoms, whereas the second is unbound by 9.7 eV.

IV. NEW RESULTS

As mentioned before, previous experimental[5,6,10] and theoretical[14,15] work shows that the minimum-energy configuration for an isolated oxygen atom is an off-center "bridge" position. We also find this to be true and plot the position of the oxygen atom in Fig. 1. We observed a large disturbance of the silicon lattice due the presence of the oxygen atom in this position. We expected this disturbance because the Si-Si distance in quartz is 3.0 Å whereas the Si-Si distance in crystalline silicon is 2.35 Å.

In order to investigate the energetics of oxygen aggregation in silicon, five classes of oxygen clusters containing two silicon atoms were studied. These include the Gösele and Tan[7] quasimolecular form (Fig. 2), a double-bridging configuration (Fig. 3), and three configurations of adjacent bridging oxygen atoms (Figs. 4–6).

A. O_2 molecule

We orient an O_2 quasimolecule along a ⟨111⟩ direction and center at the tetrahedral site, as shown in Fig. 2. We find that the relaxed O—O bond distance is 1.7 Å, which is much larger than the 1.2-Å bond length found in gaseous O_2. There is only a very small buildup of charge between the silicon and oxygen atoms indicating that any Si-O interaction is extremely weak. The energy of this configuration is 6.3 eV higher than that of two isolated bridging oxygen interstitials, which is 1.5 eV higher than the energy calculated by Kelly[19] for a ⟨100⟩ oriented molecule. The discrepancy is probably due to the difference in methods rather than the difference in orientations. Even including the effects of spin polarization and correcting for the LDA error of overestimating molecular energies,[31] this energy difference is large enough to rule out O_2 molecules in Si. We expect this configuration to be high in energy because there are four relatively strong Si—O bonds when the oxygens are in isolated bridging sites whereas there is just one O—O double bond in this molecularlike configuration.

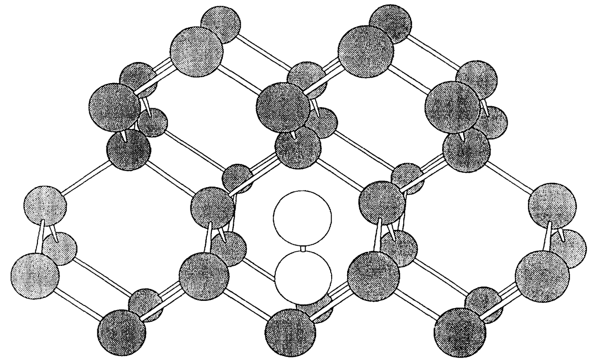

FIG. 2. Structure of molecularlike two oxygen configuration.

B. Double bridge

A second pair configuration we investigate is a double-bridging one, where the two oxygen atoms bind to the same two silicon atoms, forming a fourfield Si-O-Si-O ring, as shown in Fig. 3. In terms of the Si—O bonds, this cluster is similar to the second bound clusters found by Snyder and Corbett,[17] but the relaxation of the surrounding silicon atoms is very different. These two silicon atoms might either be four- or fivefold coordinated, depending on whether any of their Si—Si bonds break. We compute the total energy of this configuration to be

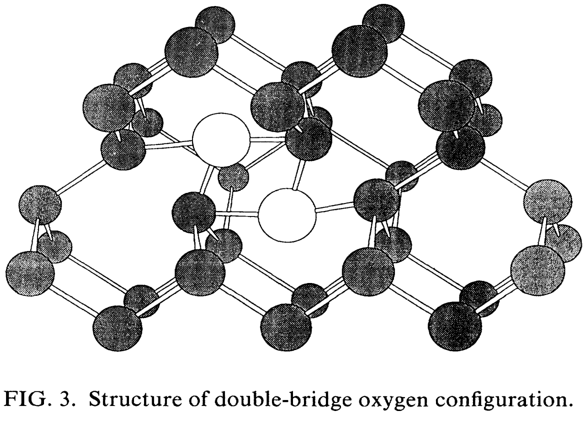

FIG. 3. Structure of double-bridge oxygen configuration.

0.1 eV higher than that of two isolated bridging oxygen interstitials, so it is marginally unstable. As illustrated in Fig. 3, this configuration looks more like a double-saddle configuration than a double-bridging configuration. The oxygens are threefold coordinated and the two adjacent Si—S bonds have been broken. Thus all silicon atoms remain fourfold coordinated.

C. C_{2v}-symmetry adjacent clusters

The next pair of configurations we study are two clusters, with C_{2v} symmetry, of two adjacent bridging oxygen atoms (see Figs. 4 and 5). Like Synder and Corbett[17] and Kelly,[19] we restricted these configurations to have C_{2v} symmetry in order to investigate these structures as possible candidates for microscopic models of a thermal donor, in addition to determining whether the oxygen atoms "bind." In agreement with Kelly, we find the configuration shown in Fig. 4 to be unstable and the atoms relax to form the configuration shown in Fig. 5. Kelly finds this configuration to be marginally bound; we now establish that it is truly unbound. The energy is 1.05 eV higher than the energy of two isolated bridging oxygen atoms.

D. Staggered cluster

Even though existing calculations find no significant binding between oxygen atoms, we have discovered one type of cluster where oxygen atoms are strongly bound. In this cluster, the oxygen atoms are staggered with respect to each other, as shown in Fig. 6, in that one oxygen atom is above and the other is below the respective Si—Si bonds they break. This cluster is bound by 1.0 eV with respect to two isolated bridging oxygen atoms. This binding energy was calculated in two ways. First, two oxygen atoms are placed as far apart as possible in the same unit cell and the atomic positions are relaxed. The energy of this configuration is compared directly to the energy of two staggered oxygen atoms in the same unit cell. In addition, we can approximately break down the total energy as being the sum of the cohesive energy of x silicon atoms, y oxygen atoms, and an additional binding energy between the oxygen atoms. Thus, by calculating the total energy per unit cell for unit cells containing zero (i.e., bulk Si), one, and two oxygen atoms, we can compute the binding energy of the pair:

$$E_{\text{bind}} = E(2\text{ oxygen per unit cell}) + E(\text{bulk Si}) - 2E(1\text{ oxygen per unit cell}) .$$

The first method has the advantage of being direct while the second has the advantage of effectively maintaining the size of the supercell. In our case the difference in the binding energy using the two methods is only 0.05 eV.

Note that this staggered configuration of oxygen atoms (Fig. 6) is very similar to the arrangement of oxygen atoms in quartz and there are several reasons why it is bound. One reason is that the central Si atom is almost tetrahedrally coordinated. Another reason is that there is considerable freedom in the oxygen bond angles, which accounts for the large number of polymorphs of SiO_2. Thus the cluster could use this freedom to reduce the strain induced by the presence of the oxygen atoms. In other words, the oxygen atoms could share the strain they induce in the silicon lattice. There is only a very slight change in the valence charge density (peak and distribution) around each oxygen atom when they are

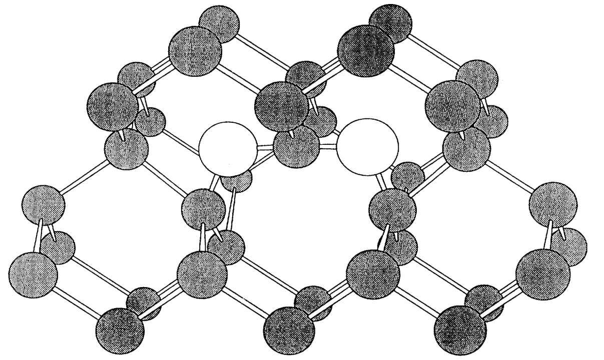

FIG. 5. Structure of double outward-buckled oxygen configuration.

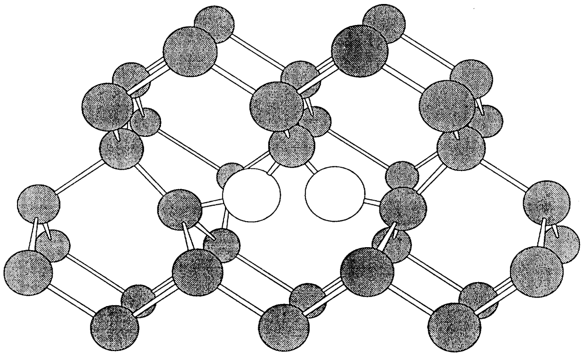

FIG. 4. Structure of double inward-buckled oxygen configuration.

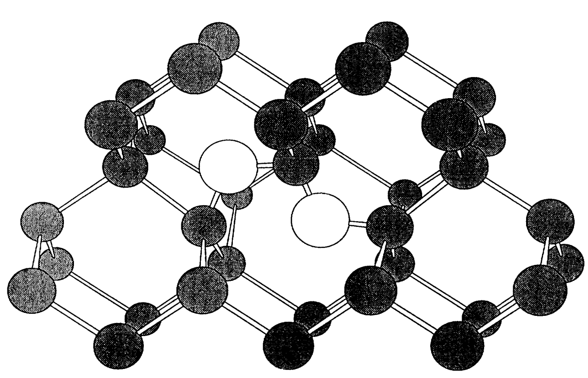

FIG. 6. Structure of staggered two-oxygen configuration.

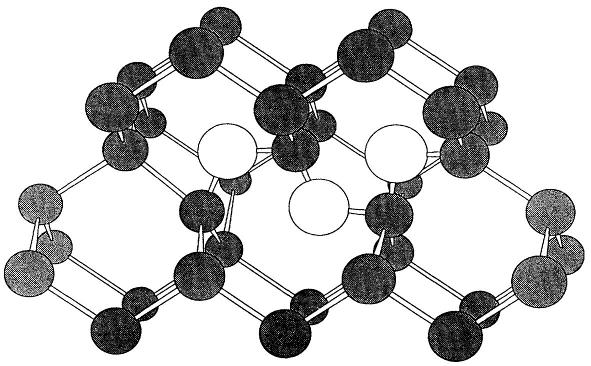

FIG. 7. Structure of staggered three-oxygen configuration.

brought together in this configuration, which may suggest that the oxygen atoms' *direct* interaction is slight. Additionally, by looking at the three-dimensional valence charge density surrounding the oxygen cluster, we can count the number of disturbed Si—Si bonds. In the staggered doublet, there are fewer disturbed bonds (change in the peak charge density) than in the case of two isolated bridging oxygen interstitials. We added a third oxygen atom similarly staggered so we had an up-down-up chain along a ⟨110⟩ direction, as shown in Fig. 7. We find that the third oxygen atom is also bound by 1.0 eV so that total binding energy for the cluster with respect to three isolated bridging oxygen atoms is 2.0 eV.

As an aside, note that in none of the three cases of adjacent bridging oxygen atoms (Figs. 4–6), were the silicon back bonds weakened. In fact, there was a small enhancement in the peak charge density because these bonds were slightly compressed.

V. DISCUSSION

In order to verify this prediction of oxygen clustering, we need to understand how these clusters might be created and observed. In this section, we will discuss first the temperature range where these clusters predominate, assuming thermal equilibrium; second, the annealing conditions under which oxygen atoms could aggregate on a reasonable time scale; and finally, how these clusters could be observed experimentally. Specifically, we will discuss ir absorptions measurements, dichroism measurements, and migration activation energy studies in terms of oxygen clusters.

Since the third oxygen atom is strongly bound to the chain (even in our 16-atom unit cell, where the periodicity is four Si—Si bonds), we believe it is plausible that a fourth and subsequent oxygen atoms would also be strongly bound. At low temperatures, the free energy of the system would be minimized when the oxygen atoms aggregate into small one-dimensional chains that we imagine would snake through the crystal.

We have performed a simple calculation to see under what thermodynamic conditions such clusters remain bound. Because calculating the internal entropy of a cluster is difficult, we did not include it in this estimate. We computed the percentage of oxygen atoms in clusters assuming two different *Ansätze*: (a) oxygen singlets and doublets only are present, and (b) oxygen clusters of all sizes are present. These assumptions lead to simple, closed-form solutions and also form upper and lower bounds for the percentage of atoms in clusters. The percentage is found to increase monotonically with the maximum allowed chain length. We assumed a constant binding energy per additional atom in the chain; i.e., the energy of a cluster of n atoms, with respect to n isolated bridging atoms, is $(n-1)$ eV. For a total oxygen concentration of 10^{18} cm^{-3}, we plot the fraction of oxygen atoms in clusters as a function of temperature in Fig. 8. This concentration is above the solubility limit for most of the temperature range plotted. However, at lower temperatures, the crystal will not necessarily be in thermal equilibrium. As can be seen by the curves, the equilibrium fraction of oxygen atoms in clusters is large up to 1050–1150 K. Of course, including the effects of internal entropy will increase both the number of oxygen atoms in clusters and the above temperature.

To study the annealing conditions that would give rise to the clustering, we assumed that oxygen atoms enter the Si melt or crystal randomly. Since the oxygen concentration is 2×10^{-5}, it should take at least on the order of 5×10^{4} hops for an appreciable number of oxygen atoms to find each other. We performed Monte Carlo calculations to estimate directly the number of hops it takes for atoms randomly placed in a crystal to find each other. We varied the oxygen concentration from 0.125 to 1.1×10^{-5} by varying the number of oxygen atoms from 2 to 16 in Si supercells varying in size from 64 to $8(50^3)=1\,000\,000$ atoms. We performed 100 simulations for a given number of oxygen atoms in a given Si supercell by randomly placing the oxygen atoms in the unit cell and letting them hop sequentially in a random direction. For each of the runs there was a different set of random initial positions and a different sequence of random hops. Furthermore, we assumed no dissociation occurs once the oxygen atoms cluster. This is a reasonable assumption because the frequency of dissociation should be

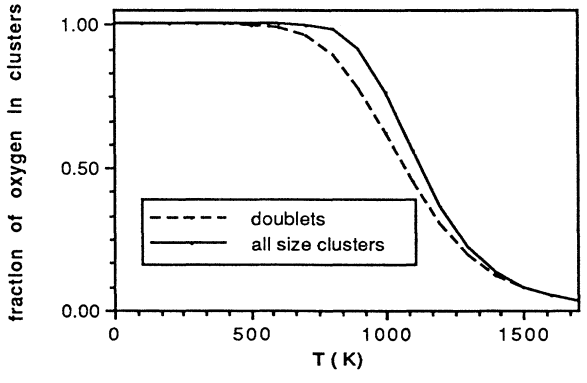

FIG. 8. Fraction of oxygen atoms in clusters as a function of temperature.

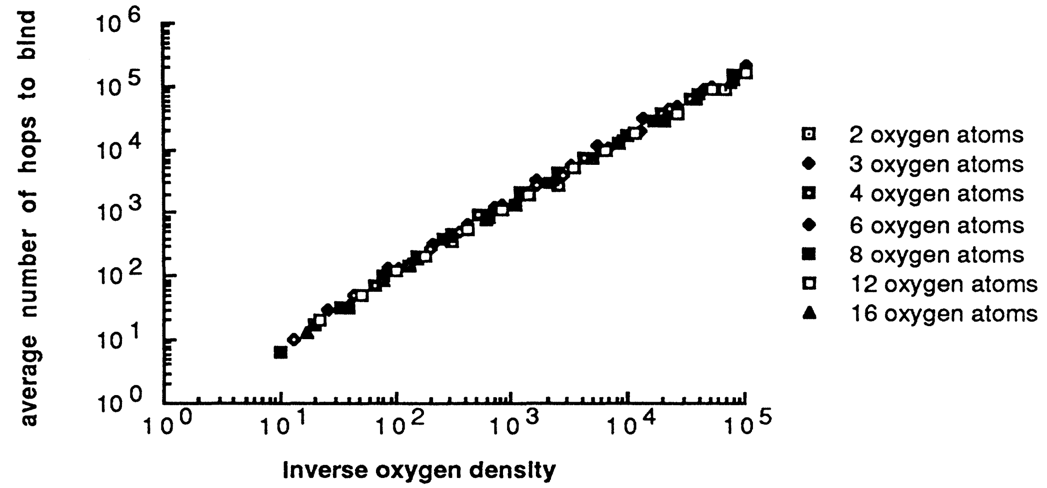

FIG. 9. Average number of hops per oxygen atom for all oxygen atoms to bind. This is the average over 100 runs.

down by a factor of $e^{-1.0\text{ eV}/kT}$ from the frequency of a hop. Even assuming that the oxygen clusters were stable up to 1200 K, this is at least a factor of 20 000. Additionally, the effects we predict are not dependent upon an equilibrium distribution of cluster sizes, which is ill defined with so few particles, but on the oxygen being bound in any size cluster. We would need to allow the clusters to dissociate if it were important to reach thermal equilibrium, but since thermal equilibrium is not necessary, allowing the clusters to dissociate would needlessly complicate the simulation.

As can be seen from Fig. 9, where we plot the average number of hops for the oxygen atoms to cluster as a function of oxygen concentration, the number of hops to cluster varies inversely as the concentration. Therefore we need to determine the time it takes for an oxygen atom to complete of order 5×10^4 hops when the barrier is 2.5 eV.[5,7,11] The number of hops completed is given by the product of the length of time with the attempt rate with the probability of success, respectively:

$$\text{No. of hops} = t(\text{sec})\times10^{13}(\text{attempts/sec}) \times e^{-2.5\text{ eV}/kT}\,,$$

where the factor 10^{13} is a typical phonon frequency. If we set the number of hops equal to the inverse density so that number of hops $\cong5\times10^4$, we can solve for the time. As can be seen from Table I, only by annealing temperatures of at least 900 K will a sizable fraction of the oxygen atoms be able to cluster within a reasonable time.

TABLE I. Annealing time necessary to form clusters.

T (K)	Annealing time for 5×10^4 hops
800	3 y
900	17 d
1000	15 h
1100	1 h
1200	6 min

Now we will discuss the ways very small oxygen clusters could be observed. Almost all ir absorption measurements have been performed at room T. Using a Born force constant model as a rough estimator, we calculate the splitting of the 9-μm modes to be about 20 cm^{-1} for a two-oxygen-atom cluster. If this simple calculation is taken seriously, it suggests the splitting is smaller than the 30–50 cm^{-1} width of the absorption curve at room temperature.[5] Therefore the experiment would have to be performed at low temperature in order to tell whether one is observing one or multiple peaks. As the clustering continues, the multiple peaks merge into one broad absorption peak. This broad peak as well as SiO_2-like features have recently been observed.[32]

Now let us reexamine the dichroism experiment. We

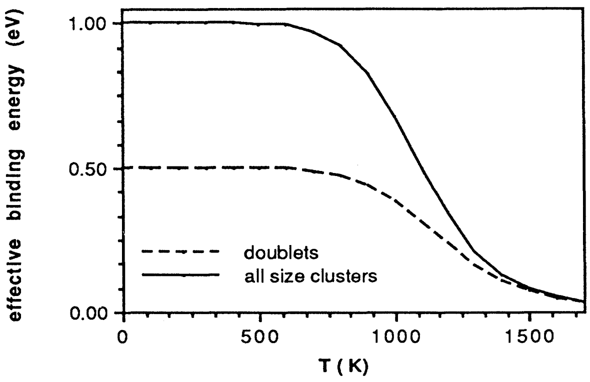

FIG. 10. Effective binding energy per atom as a function of temperature.

TABLE II. Comparison of experimentally measured stress-induced dichroic ratios to that predicted by models of chains of varying lengths.

			Dichroic ratio Model: number of oxygen atoms per chain			
Stress axis	Viewing axis	Expt. (Ref. 5)	1	2	3	4
$\langle 100 \rangle$	$\langle 100 \rangle$	1.03 ± 0.07	1.0	1.0	1.0	1.0
$\langle 110 \rangle$	$\langle 100 \rangle$	1.31 ± 0.07	1.31	1.29	1.29	1.29
	$\langle 110 \rangle$	1.18 ± 0.07	1.16	1.15	1.15	1.14
$\langle 111 \rangle$	$\langle 110 \rangle$	1.30 ± 0.07	used to fit free parameter			

calculate the dichroic ratio of staggered doublets using exactly the same analysis as Corbett, Mac Donald, and Watkins.[5] As can be seen by comparing the dichroism measured experimentally to the dichroism predicted by the model with two oxygen atoms shown in Table II, we also obtain excellent agreement with experiment even though the staggered configuration does not have $\langle 111 \rangle$ symmetry. Going a step further, we calculated the dichroic ratio of staggered triplets and quadruplets. As can be seen from Table II, we again obtain excellent agreement to the experimental values. Thus, because of the fitted parameter in the model used to interpret the results, this experiment is much less sensitive to the overall symmetry of the defect as long as its individual dipole moments have a $\langle 111 \rangle$ orientation.

For predictions of stress-induced dichroism of clusters, two additional assumptions must be made. First, when the chain is three atoms long or longer, there are then two types of atoms: "inside" and "end." Thus the question arises whether all atoms reorient on the time scale of the experiment or just the ones at the end of a chain. Since the dichroic ratios are close to 1, the equilibrium population of oxygen atoms in the stressed direction is close to the equilibrium population before stressing. Hence, the difference in energy between stressed and unstressed directions is small. In fact, this energy difference is less than kT. Consequently, the energy gained by an inside oxygen atom moving to an unstressed direction is much less than the 2 eV it costs to break a chain, so we expect just the end atoms can move. However, even relaxing this assumption has a minimal effect on the predicted dichroic ratio. Second, one can make additional assumptions about whether or not chains "bend" and these assumptions do not appreciably affect the dichroism this simple model predicts.

Finally, we discuss experiments which determine the activation energy for oxygen hopping. For the sake of this discussion, we will assume that when oxygen is bound in chains, oxygen migration, or reorientation in the case of dichroism experiments, still takes place by the hopping of a single oxygen atom.[33] Hence migration should be a two-step process. First, an atom must dissociate from the cluster and second, hop to an adjacent site. Therefore the measured activation energy will be higher by this dissociation energy than the activation energy observed for the migration of single oxygen atoms. This should be observable even if clusters do not predominate over isolated oxygen atoms since their presence will give rise to an effective dissociation energy. In Fig. 10, we plot the effective binding energy per oxygen atom assuming clusters of all sizes form (upper curve) and only doublets form (lower curve) as a function of temperature for a total oxygen concentration of 10^{18} cm^{-3}. At low temperatures, the total migration activation energy should be the sum of the 2.5-eV normal diffusion activation energy and the 1.0-eV binding energy, or approximately $2.5+1.0=3.5$ eV. As can be seen from Fig. 10, there is a considerable difference in the binding energy, depending on whether only doublets or all size clusters form but, as can be seen from Fig. 8, the fraction of oxygen atoms in clusters does not strongly depend on the sizes of clusters that form. At higher temperatures, the binding will be less but it is significant up to 1100 K.

VI. CONCLUSIONS

Using *ab initio* methods, we have investigated the energetics of several oxygen clusters. We have identified one particular class of clusters where additional oxygen atoms bind with an energy of 1.0 eV. Cluster lengths of at least three oxygen atoms can form without the interjection of Si self-interstitials. We find that formation of these small clusters requires annealing at temperatures greater than 900 K, but that clusters are thermodynamically favored only at temperatures less than 1050–1150 K. These small clusters should be observable in low-temperature ir absorption measurements because of the splitting of symmetric and antisymmetric vibration modes. Oxygen clustering might also be observable from an increase in the activation energy for dichroism relaxation or diffusion from 2.5 to 3.2–3.5 eV (depending on temperature) if diffusion takes place by single oxygen atoms. Oxygen aggregation is not directly observable by dichroism experiments unless the sensitivity is increased.

ACKNOWLEDGMENTS

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[33] This is not necessarily the case. Oxygen migration from a cluster could occur by the migration of the entire cluster. Snyder and Corbett (Ref. 17) investigated one such possibility.