

## Diffusion of Atomic Oxygen in SiO<sub>2</sub>

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Density functional calculations using an  $\alpha$ -quartz supercell as a model silica host identify the peroxy linkage as the lowest energy configuration of atomic O in SiO<sub>2</sub>, and find that its energy in this site and in interstitial molecular O<sub>2</sub> are nearly equal. Using *ab initio* molecular dynamics modified to converge to a saddle point, the barrier for concerted exchange of the peroxy linkage is found to be 1.3 eV. While O is generally believed to diffuse in molecular form in SiO<sub>2</sub>, measured diffusion activation energies are consistent with the peroxy exchange barrier. [S0031-9007(98)07404-3]

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The growth of SiO<sub>2</sub> on silicon is a key process in microelectronics technology. As dimensions of integrated circuit elements continue to shrink and oxide thicknesses of a few tens of angstroms are required, understanding this process on an atomic scale becomes increasingly important to achieve the required control. Growth kinetics are reasonably well explained by the Deal-Grove model [1], which postulates that gas-phase oxygen diffuses through the growing SiO<sub>2</sub> layer, and reacts at the Si-SiO<sub>2</sub> interface. The study of atomic O in SiO<sub>2</sub> was initially stimulated by the observation that it is more active in promoting oxide growth than molecular O<sub>2</sub> [2].

Vitreous SiO<sub>2</sub>, as well as the many crystalline polymorphs of SiO<sub>2</sub> formed at low pressures, consists of a continuous network of corner-sharing SiO<sub>4</sub> tetrahedra [3]. While the random network topology of the vitreous form may be a key feature for certain properties, diffusion barriers are likely to be dominated by local bonding effects. The present choice of a supercell based on the  $\alpha$ -quartz structure to study an "impurity" O in SiO<sub>2</sub> was motivated by this assumption and the following considerations: (i) An extended system avoids the surface effects inherent in cluster models. (ii) Elastic relaxation effects are expected to play an important role and cannot be modeled by a cluster. (iii) A supercell model of a vitreous system of computationally accessible size would of necessity contain many highly strained bonds, and be less representative of real vitreous SiO<sub>2</sub> than a crystalline model. (iv) Insofar as strained bonds may enhance diffusion, the crystalline model should provide an upper bound to the effective average vitreous energy barrier.

Even a modestly sized supercell model of SiO<sub>2</sub> has many internal degrees of freedom which need to be relaxed in the presence of the added O (henceforth O\*). SiO<sub>2</sub> models based on parametrized classical force fields are computationally efficient, but typically include only repulsive O—O interactions [4], precluding covalent O—O bonding. The Car-Parrinello *ab initio* molecular dynamics method [5] based on density functional theory [6] is to be preferred for its combination of efficiency in relaxing structural coordinates and accuracy in describing whatever bonds the system forms. This method utilizes a set of plane waves

for the expansion of wave functions, and norm-conserving pseudopotentials [7] to describe ion-core valence-electron interactions. A drawback in the application of this method to SiO<sub>2</sub> is the extremely large number of plane waves required to accurately describe the O valence wave functions due to their high degree of spatial localization.

An enhancement of the plane-wave pseudopotential approach was recently introduced by Gygi to deal with such localized orbitals [8]. Wave functions are expanded in a basis of plane waves in an adaptive curvilinear coordinate system which permits the same "plane" wave to have high spatial frequencies where needed in real Euclidean coordinates, and much lower frequencies in regions away from the atoms. The coordinate transformation itself is expressed either in terms of a general functional expansion [8] or as a superposition of parametrized atom-centered deformation functions [9]. The parameters of either representation are varied to minimize the density functional total energy, and the net effect is to concentrate the variational freedom of any given size basis in regions of space where it is most effective. The orthonormality and computational efficiency of ordinary plane waves are retained at the cost of a more complex kinetic energy operator and some additional computational overhead [8]. The adaptive coordinate method has been found to be extremely effective in application to SiO<sub>2</sub> [10].

While the local density approximation (LDA) to density functional theory [6] is widely used and gives accurate results for many materials including the low-pressure phases of SiO<sub>2</sub>, it completely fails to predict the correct energy difference  $\Delta E$  between  $\alpha$  quartz and stishovite, a metastable phase formed at high pressure characterized by 6-fold coordinated Si and 3-fold coordinated O. However, an improved density functional described as a generalized gradient approximation (GGA) [11] gives results in excellent agreement with experiment ( $\Delta E_{\text{exp}} = 0.54$  eV per SiO<sub>2</sub>,  $\Delta E_{\text{LDA}} = 0.02$  eV,  $\Delta E_{\text{GGA}} = 0.57$  eV) [12]. Implementation of GGA functionals within the adaptive coordinates framework also turns out to offer computational advantages compared to its application in standard plane wave methods [13]. Since the incorporation of O\* in SiO<sub>2</sub> and, especially, the calculation of its transition

state potentially involve coordination changes, it was considered imperative to use the GGA for the present study.

A 27 atom  $\text{SiO}_2$  supercell was constructed as a  $\sqrt{3} \times \sqrt{3} R30^\circ$  multiple of the basal-plane portion of the primitive unit cell of the hexagonal quartz lattice, keeping the  $c$  axis at its original unit length. Combined with a Brillouin zone sample consisting of three inequivalent  $\mathbf{k}$  points, this should be adequate to ensure freedom from spurious electronic interactions between neighboring  $\text{O}^*$ 's in such a wide band gap material. Interactions mediated by elastic distortions are certainly present, and have a range such that they could not be totally eliminated even with a very large supercell. However, most of the  $\text{O}^*$ -induced distortions are accommodated by rotations of the  $\text{SiO}_4$  tetrahedra and, given the soft force constant of Si—O—Si bond angle distortions [14], spurious elastic interactions probably bias the results by no more than a few hundredths of an eV. The atomic structure of the supercell is shown in Fig. 1. While the author's previous applications of adaptive coordinates to  $\text{SiO}_2$  utilized a general functional expansion for the coordinate transformation optimized simultaneously with the wave functions and atomic coordinates [10,12], the atom-based approach [9] was used here because free coordinate adaptation hindered the search for an energy saddle point. An average plane wave energy cutoff of 35 Ry was used, which was boosted to an effective cutoff of  $\sim 120$  Ry near the O atoms. Full quartz and stishovite energy-volume curves were recalculated with the atom-based adaptation, and previous results [12] were reproduced with high accuracy.

$\text{O}^*$  initially introduced at an open interstitial site migrated under the control of *ab initio* molecular dynamics

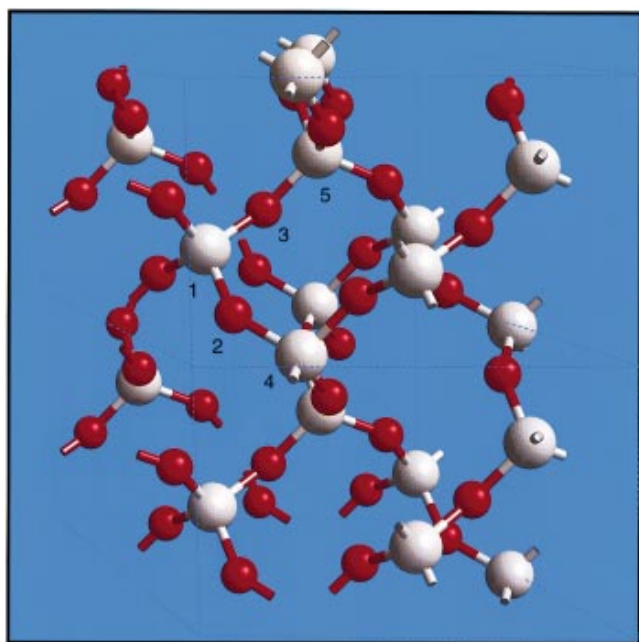


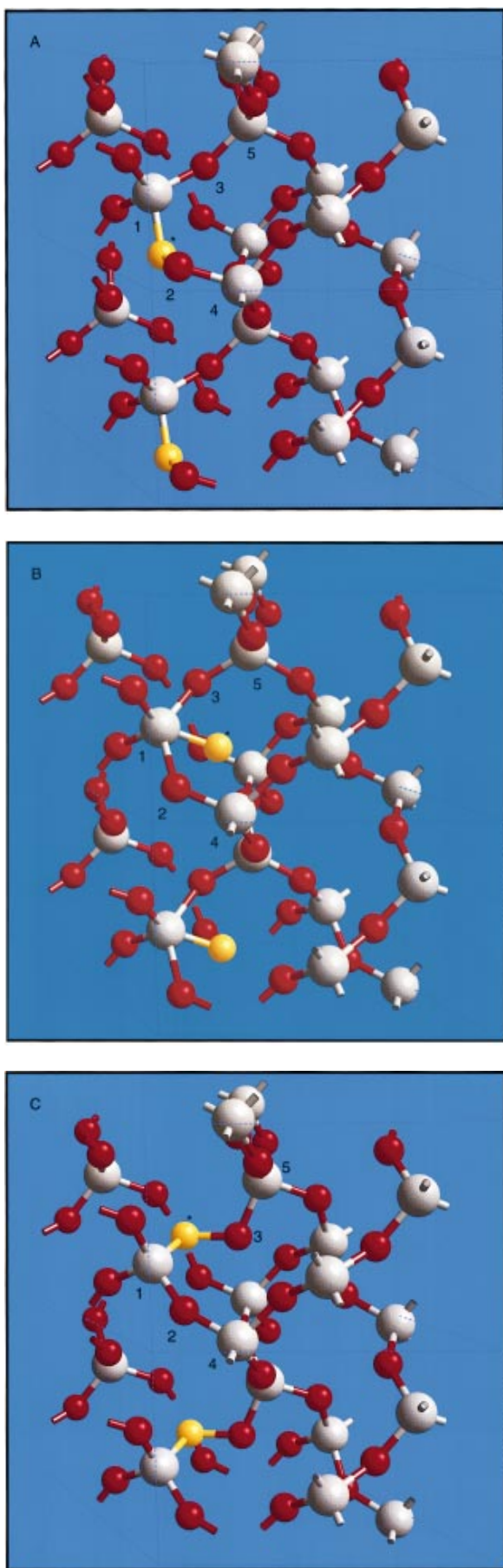
FIG. 1(color).  $\alpha$ -quartz supercell showing basic network structure of Si (gray) and O (red). Two cells along the  $c$  axis are displayed.

[5] with added viscous damping to form the peroxy linkage configuration shown in Fig. 2(A), the geometry of which is reported in Table I. The Si—O bonds participating in the peroxy linkage are  $\sim 0.04$  Å longer than those calculated for pure quartz, likely as a result of a decreased ionic contribution to the bonding, and the surrounding network has relaxed considerably outwards. A recent quantum-chemical study of the peroxy linkage using  $\text{Si}_2\text{O}_8\text{H}_6$  as a model and simulating network constraints with the terminating H's found bond lengths in excellent agreement with the present results [15]. The energy gained by incorporating gas-phase atomic O in  $\text{SiO}_2$  is calculated to be 0.86 eV in the present study and 0.7 eV in Ref. [15], which is unexpectedly good agreement given the considerable differences between the models and methods.

Completely parallel calculations were carried out for molecular  $\text{O}_2$ , which remained close to its initial  $c$ -axis interstitial site while the adjacent O's in the bonded network relaxed outwards. Using the energy of this system and an appropriate multiple of the calculated energy of bulk  $\alpha$  quartz, the energy to dissociate the interstitial molecule and place its atoms in peroxy linkages was estimated to be 0.15 eV per atom, a difference at the limit of the overall accuracy to be expected of the supercell model and density functional approximation.

While diffusion of  $\text{O}^*$  via complete removal from the peroxy linkage would appear to entail breaking two bonds and a high energy barrier, concerted exchange of the linkage to a neighboring Si—Si pair might entail a considerably lower barrier. A set of atomic coordinates in which the peroxy linkage has migrated can be generated by applying a symmetry operation of the quartz host to the calculated coordinates of the initial configuration. A 3-fold rotation followed by a  $c/3$  nonprimitive translation generates the configuration shown in Fig. 2C.

The earliest *ab initio* calculations of diffusion barriers in solids searched for energy maxima on 1D lines or 2D grids chosen on the basis of symmetry [16]. The low symmetry and complex geometry of the present case precluded such methods. A plausible approach to follow an unknown path over the saddle point is to slowly “drag” the entire  $N$  atom configuration on a hypersphere in  $3N$  dimensional space from the initial toward the final configuration. Such calculations did not reach the saddle point, however, displaying a mode of failure observed in studies of certain molecular reaction paths [17]. As an alternative approach, the (damped) *ab initio* molecular dynamics was modified in such a way that a configuration started near a saddle point should converge to that point. This can be accomplished by reversing the direction of the force along a  $3N$ -dimensional unit vector aligned with the principal axis of negative curvature at the saddle point, causing the configuration to dynamically evolve as if the saddle were a minimum [18]. The vector from the initial to the final configuration was used as a trial approximation to the direction of the negative curvature axis, and a configuration generated by the drag approach and believed



to be near the saddle point was evolved using the modified dynamics. The time dependence of the reversed component of the force and of the energy during this calculation are shown in Figs. 3(A) and 3(B), and are consistent with oscillations back and forth over the top of a ridge above the saddle accompanied by gradual relaxation toward the saddle and damping of the oscillations. Absent a proof based on the matrix of second derivatives of the energy with respect to the coordinates, this behavior provides persuasive evidence that the configuration to which the modified dynamics relaxed is, in fact, the desired saddle point. The period of the saddle-point oscillations is  $\sim 150$  fs, long compared to an Si—O breathing-mode period of  $\sim 28$  fs, and the latter undoubtedly followed the former adiabatically during the simulation.

It is important to note that the modified molecular dynamics method would not have converged in the observed manner if the direction of the initial to final state vector had not been sufficiently parallel to the principal axis of negative curvature. A general approach which should find both a starting configuration near the saddle and a good approximation to the direction of the principal axis should be given by a molecular dynamics adaptation of the method of Ref. [17].

The saddle point is energetically 1.3 eV above the minima [19]. Its highly symmetric configuration is shown in Fig. 2(B), and its geometry is given in Table I.  $O^2$  and  $O^3$  are weakly bonded to  $Si^1$ , with bonds  $\sim 0.05$  Å longer than those of 6-fold O-coordinated Si in stishovite [13].  $O^*$  has moved closer to  $Si^1$ , attaining a bond length nearly equal to that in unperturbed quartz. The  $O^*—O^2$  and  $O^*—O^3$  distances of 1.95 Å are too long to consider that any significant bonding exists. Hence the transition state found here consists of broken peroxy bonds, two weakened Si—O bonds prepared to incorporate  $O^*$  on either side of the saddle, and a strengthened Si— $O^*$  bond. The calculated barrier is slightly lower than the empirical O—O single bond energy of 1.44 eV [20].

There is extensive experimental literature on O diffusion in  $SiO_2$  which is summarized in a recent review [21]. O is generally considered to diffuse as molecular  $O_2$ , and gas transport experiments give activation energies in the range of 1.17 to 1.35 eV [21]. Experiments analyzing isotope exchange between the network O and the gas phase  $O_2$ , however, yield similar values (0.86, 1.15, 1.25, and 1.48 eV) [21]. (The considerable spread in values may reflect the presence of trace impurities such as  $H_2O$ .) The presence of peroxy linkages in  $SiO_2$  has been inferred from EPR evidence for peroxy radicals (broken linkages), and UV absorption spectra indicate significant concentrations of intact peroxy linkages in the presence of excess O [22] on the basis of a predicted gap state [23]. The present

FIG. 2(color). Supercell with  $O^*$  (yellow). (A) Initial peroxy linkage configuration. (B) Transition state configuration. (C) Final peroxy linkage configuration.

TABLE I. Interatomic distances (Å). Atom superscripts in first column correspond to numbering in the ball-and-stick figures.

	Quartz Fig. 1	Peroxy linkage Fig. 2(A)	Transition state Fig. 2(B)
Si <sup>1</sup> —O <sup>2</sup>	1.624	2.599	1.880
Si <sup>1</sup> —O <sup>3</sup>	1.621	1.615	1.824
Si <sup>1</sup> —O*		1.670	1.613
Si <sup>4</sup> —O <sup>2</sup>	1.621	1.659	1.666
Si <sup>5</sup> —O <sup>3</sup>	1.624	1.634	1.674
O <sup>2</sup> —O*		1.469	1.947
O <sup>3</sup> —O*		2.678	1.945
O <sup>2</sup> —O <sup>3</sup>	2.678	3.438	3.419
Si <sup>1</sup> —Si <sup>4</sup>	3.089	3.660	3.197
Si <sup>1</sup> —Si <sup>5</sup>	3.089	3.109	3.120

results on the nearly degenerate energies of interstitial O<sub>2</sub> and O in peroxy linkages suggest that a substantial concentration of the linkages should exist in equilibrium [24]. Peroxy linkages have recently been proposed as the primary mechanism for diffusion of network-forming impurities such as B in SiO<sub>2</sub> [25]. While peroxy linkage migration has not been considered to play a major role in O transport in SiO<sub>2</sub>, this work suggests that such a possibility should be seriously considered, and experiments designed to test it. Growth of thin (50 Å) SiO<sub>2</sub> films on Si with isotopically labeled O<sub>2</sub> molecules provides evi-

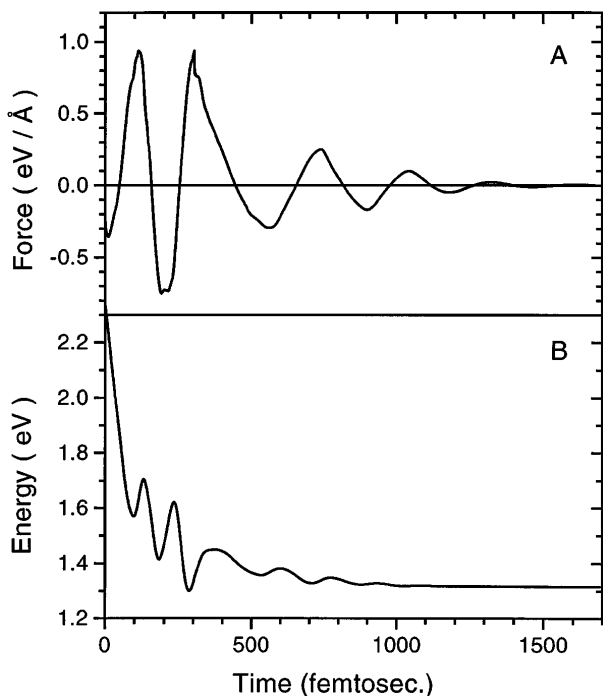


FIG. 3. Molecular dynamics evolution towards saddle point. The viscous damping was doubled at  $\sim 300$  fs. (A) Component of  $3N$ -dimensional force vector parallel to a vector from the initial to the final configuration. (B) System energy relative to the initial or the final configuration.

dence for both network exchange and molecular diffusion in that process [26]. A permeation experiment [27] introducing <sup>18</sup>O<sub>2</sub> on one side of a bulk Si<sup>16</sup>O<sub>2</sub> membrane would provide a more critical test of the proposed peroxy linkage diffusion mechanism.

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