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H_2O and O_2 molecules in amorphous SiO_2: Defect formation and annihilation mechanisms

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Interstitial water and oxygen molecules are ubiquitous impurities and participate in various defect formation processes in thermally grown SiO_2 films and synthetic silica glass. Using results of first-principles calculations we report the types of defects (including different possible charge states) that H_2O and O_2 molecules may form in bulk amorphous SiO_2. We calculate their formation energies and, in the most interesting cases, the energy barriers in order to map out the most likely defect formation scenarios. In particular, we show that water molecules may form double silanol groups (Si-OH) as well as H_3O^+ and OH^- ions at a low energy cost with a barrier of about 1.5 eV. The formation energies of other defects emanating from H_2O interstitials are, however, too high to be thermally activated. We found that O_2 molecules may form ozonyl (Si-O-O-O-Si) linkages with an energy barrier of ~ 2.4 eV. An explanation for the oxygen isotope exchange observed in thin SiO_2 films near the Si-SiO_2 and SiO_2-vacuum interfaces is suggested based on the energy barrier for ozonyl formation being commensurate with the O_2 diffusion barrier close to the Si/SiO_2 interface and the O_2 incorporation energy from vacuum. We also explain the different creation rates of E' centers in wet and dry oxides by studying the annihilation mechanism of neutral and charged oxygen vacancies.

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I. INTRODUCTION

The presence of H_2O and O_2 molecules is known to affect the nature and the density of defects that form during SiO_2 glass synthesis, thermal oxidation of silicon, irradiation of SiO_2, or subsequent mechanical or thermal treatment. For example, water incorporation into silica glass reduces the viscosity, index of refraction, acoustic velocity, and density of the glass, while it causes an increase in the thermal-expansion coefficient and crystallization rate.[1,2] Additional water diffusion into silica glass also reduces the static fatigue life[3] and accelerates structural modification of the glass.[4] When water molecules are present in the oxidation ambient, the rate of silicon oxidation also increases.[5]

Despite the wide interest in the behavior of O_2 and H_2O molecules in bulk SiO_2, the understanding of the atomic scale processes remains limited. For example, water molecules are known to form silanol (Si-OH) groups in the oxide,[6] but the relative concentration of silanol to interstitial water depends on the way the oxide was manufactured and subsequently treated, raising questions about the most stable form of water in the oxide. Exposure of SiO_2 to water vapor results in the appearance of various OH vibrational bands (SiOH, hydrogen bonded OH, H_2O, hydrogen bonded water), the Si-H band,[6] and also in a shift of the SiO_2 structural bands.[4] There is also significant oxygen exchange between H_2O and SiO_2 over the entire volume of the oxide as shown by ^{18}O tagged water diffusion experiments.[7] These data suggest that water is highly reactive, while other experiments and the analysis of water diffusion[8] provide evidence that it also exists as an interstitial molecule in the oxide.

Oxygen molecules are more inert than H_2O in bulk SiO_2, i.e., they are less likely to form defects that alter the properties of the oxide. The main interest in studying the behavior of O_2 molecules in SiO_2 is due to its role in the silicon oxidation process. Thus most of the work was focused on the reactions of O_2 at the Si-SiO_2 interface.

Reactions of O_2 molecules with the SiO_2 structure were observed at the vacuum-SiO_2 and the Si-SiO_2 interfaces of thin films when the oxide is exposed to $^{18}O_2$.[9] The ^{18}O exchange was found to be small in between the film surfaces, although the film thickness in these experiments did not exceed 80 Å.[10] The presence of interstitial (i.e., intact) O_2 molecules is also observed by infrared photoluminescence.[11] As a contrast, it was suggested based on *ab initio* calculations that the oxygen molecule might break up into two O atoms that diffuse in an atomic form via peroxy (Si-O-O-Si) linkages.[12] Another possibility for the reaction between O_2 and SiO_2 is the formation of an ozonic bond (Si-O-O-O-Si).[13] The existence of interstitial ozone (O_3) molecules was confirmed by the photostimulated phosphorescence of excited O_2 molecules created by the UV dissociation of interstitial O_3.[14]

In addition to the reactions of H_2O and O_2 with the perfect amorphous SiO_2 network, several other reactions may take place at defect sites. For example, infrared measurements confirm that water molecules react with dangling Si bonds created by neutron irradiation.[15] The concentration of charged oxygen vacancies (E' centers) in irradiated oxides was suggested to decrease due to their reaction with interstitial O_2 and H_2O molecules.[16]

As it was indicated above, the behavior of water and oxygen in amorphous bulk SiO_2 is very versatile and not devoid of controversies. In this paper we attempt to provide a systematic first-principles study of the various defect formation mechanisms involving interstitial O_2 and H_2O molecules and the amorphous SiO_2 network. In particular, we investigate the possible defects that may form also taking into account the different possible charge states. We provide the formation energies and geometrical structure of these defects and map

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out the most probable defect formation scenarios. For the reactions with the lowest formation energy ($H_2O + \text{Si-O-Si} \leftrightharpoons 2\ \text{SiOH}$, $2\ H_2O \leftrightharpoons OH^- + H_3O^+$, $O_2 + \text{Si-O-Si} \leftrightharpoons \text{Si-O-O-O-Si}$), we calculate the reaction barrier and—in some cases—the variation of the formation energy due to inequivalency of atomic sites within the amorphous medium.

We also explain the difference in the E' center generation rates, that depend on the details of the oxide manufacturing process, by investigating the reactions between H_2O and O_2 interstitials and charged and neutral oxygen vacancies. While both interstitials annihilate the E' defects in an exothermic reaction, by calculating the activation barriers we show that irradiated wet oxides (e.g., Suprasil-1 with $[OH] \geqslant 10^{19}\ \text{cm}^{-3}$) are more likely to have more E' centers than dry oxides (e.g., Suprasil-W1 with $[OH] \leqslant 5 \times 10^{16}\ \text{cm}^{-3}$) as it has been found experimentally.[16,17] Neutral vacancies are, however, annihilated by a higher-energy barrier which is why both types of oxides may have the same amount of precursors prior to irradiation.

The rest of the paper is organized as follows. In Sec. II we describe briefly our computational approach. In Sec. III we present results of calculations for the formation energies, energy barriers, and the topological variations of the various reactions between H_2O and O_2 interstitials and the defect-free SiO_2 network. Subsequently, in Sec. IV we give similar data for reactions between H_2O and O_2 interstitials and oxygen vacancies and explain the dominant E' center annealing mechanisms in wet and dry oxides. A summary of the main conclusions of this work is given in Sec. V.

II. COMPUTATIONAL METHOD

The present calculations are based on density-functional theory, the generalized gradient approximation for the exchange-correlation energy, ultrasoft pseudopotentials, supercells, and plane waves.[18,19] The pseudopotentials used for the present study have been thoroughly tested in earlier work on a variety of Si-O-H systems.[20–22] As in that work, the energy cutoff for the basis set was 24 Ry, and integrations over the Brillouin zone were done using the Monkhorst-Pack scheme with only one special k-point in the relevant irreducible wedge.[23]

The calculations were performed for 72-atom amorphous SiO_2 supercells generated by using the Monte Carlo bond-switching method (see Refs. 24,25 for details) and relaxed until the total energy was minimized (the force on each atom is smaller than a tolerance, namely 0.1 eV/Å). The size of supercells (~ 10 Å) is big enough to neglect the interaction of a defect with its periodic images. Formation energies of various defects were calculated by subtracting the total energy of the supercell containing the defects from the total energy of the supercell with interstitial O_2 or H_2O molecules. For studying charged defects we introduced a homogeneous negative (positive) background when removing (adding) electrons in the supercell and added the Makov-Payne correction terms to the total energy.[26]

We have used spin-polarized calculations to take into account the effect of the spin state of the O_2 molecule on its reactions with the SiO_2 network. The nudged elastic band method[27] was used with a climbing image[28] to determine the reaction pathway and barrier of reactions involving O_2 and to clarify if triplet to singlet transitions occur along the reaction pathway. We have used eight intermediate images and relaxed the atoms until the force perpendicular to the minimum-energy pathway was below 0.2 eV/Å

III. REACTIONS BETWEEN H_2O AND O_2 INTERSTITIALS AND THE DEFECT-FREE SiO_2 NETWORK

A. Equilibrium positions of H_2O and O_2 interstitials

Amorphous SiO_2 can be viewed as a material having interconnecting voids of different sizes that are defined by rings made up of Si-O-Si bridges. We have studied the properties of H_2O and O_2 interstitials in voids that are ≈ 6 Å in diameter, which corresponds to the average intrinsic void size in vitreous SiO_2, as estimated by positronium lifetime measurements.[29] These voids are surrounded mainly by six-member rings, which is the dominant ring size in SiO_2.[30]

We have found that both H_2O and O_2 molecules have an equilibrium position in the middle of the voids of the SiO_2 network. In the case of O_2 molecules, the total energy has a global minimum in the middle of the void for both triplet and singlet spin states with no local minima (metastable configurations) elsewhere. We have found that the triplet configuration is always more stable than the singlet, regardless of the size of the interstitial void the molecule is in. The triplet-singlet gap, however, decreases with void size from 0.62 eV in the biggest (7 Å) to 0.52 eV in the dominant (6 Å) voids and 0.45–0.47 eV in the smallest (4 Å–5 Å) voids [cf. the triplet-singlet gap in the gas phase is 0.98 eV (Ref. 31)]. The same tendency has been observed for O_2 in α-quartz.[32] The reason for the decrease in the triplet-singlet gap is primarily due to crystal-field splitting between the oxygen nonbonding π_x and π_y orbitals. To lesser extent the change of the exchange integral inside the solid (exchange splitting) also contributes to the reduction of the triplet-singlet gap.[32]

For H_2O molecules there are additional interstitial configurations besides the middle of the void with a local minimum in the total energy. In these metastable interstitial configurations the oxygen of the water molecule is attracted to a network Si atom (typical Si-O distance is 1.87 Å where the O is in the H_2O molecule) and the hydrogens orient themselves in such a way that they are about 1.9–2.0 Å away from the oxygens adjacent to the network Si atom [Fig. 1(a)]. The reason for the existence of these metastable configurations is that Si atoms in SiO_2 are somewhat positively charged, thus they attract the negative (oxygen) end of the H_2O dipole molecule, whereas oxygens tend to collect most of the negative charge, therefore they attract the positive H atoms of the H_2O molecule. Such configurations of interstitial water have been suggested by infrared measurements based on the shifts in the vibrational frequency of the O-H bond.[6] The total-energy difference between the various metastable configurations and the middle-of-the-void configuration did not exceed 0.2 eV.

A large variation in total energies can be found, however, if we place the O_2 and H_2O interstitials into voids of different sizes in the oxide (Table I). The data show that the total

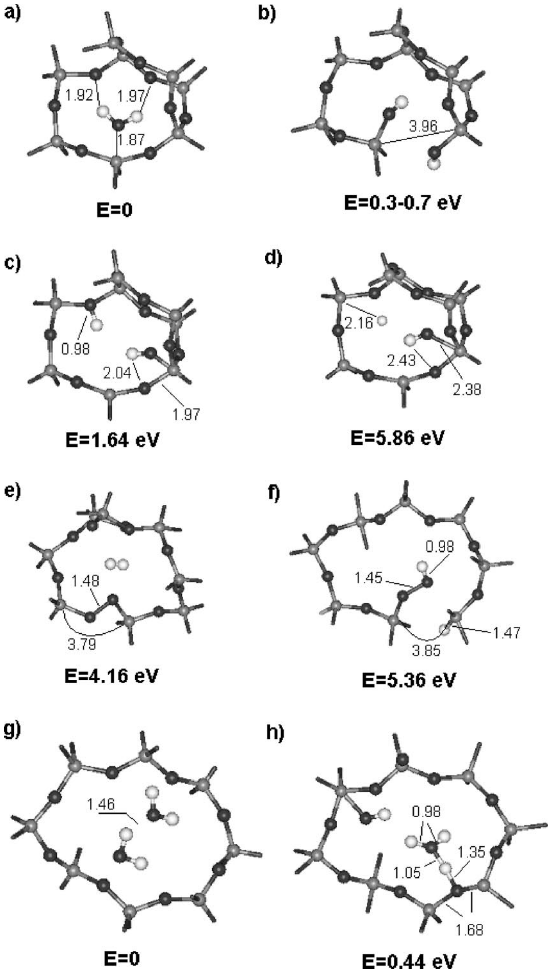

FIG. 1. Reactions of H_2O and the defect-free SiO_2 network. (a) Initial configuration of a H_2O molecule in a void bordered by a six-member ring as a part of the supercell. The H_2O molecule takes up a metastable (weakly bound) configuration prior to the reactions. The total energy of this configuration also serves as a reference point for subsequent defects [(b)–(f)]. (b) Vicinal silanol groups. The energy range shows the site dependence of the formation energies in the oxide. (c) H^+ and OH^- bound to network O and Si atoms. (d) Neutral H and OH weakly bound to network O and Si atoms. (e) Peroxy (Si-O-O-Si) linkage and interstitial H_2 molecule. (f) H-terminated peroxy radical (Si-O-O-H) and Si-H. (g) Two water molecules in a bigger (eight-member) ring. (h) H_3O^+ and OH^- bound to network O and Si atoms. Distances are shown in Angstroms.

energy increases rapidly if the void diameter decreases below ≈ 6 Å, however, it is practically constant in larger voids. Therefore, in thermal equilibrium, the H_2O and O_2 interstitials are most likely to reside in voids that are 6 Å or larger, possibly because in these voids they can be far enough (at least 2 Å away) from network atoms so that the interaction between the interstitial molecules and the network becomes small.

B. Reactions involving H_2O

TABLE I. Total energy (in eV) of interstitial H_2O and O_2 molecules in voids of different diameters (Å). We used the total energies in a 6 Å void as the reference point.

Void diameter	H_2O energy	O_2 energy
~7.0	−0.2	−0.2
~6.0	0	0
~5.0	1.2	1.5
~4.5	1.9	4.0
~4.0	2.2	4.2

In Fig. 1 we show the formation energies and relaxed geometries of several defects that may form as a result of a reaction between interstitial H_2O molecules and the defect-free SiO_2 network. The starting point is always an H_2O molecule in a metastable equilibrium position 1.87 Å away from a network Si atom [Fig. 1(a)] in a 6 Å void. The formation energy of the final reaction products depends on the local electronic environment in an amorphous solid. Here we have arbitrarily chosen a Si-O-Si segment of the six-member ring bordering the void that was replaced by the final defect complexes. The distribution of Si-O-Si angles and Si-O bond lengths in this ring is 130–170° and 1.62–1.66 Å, respectively, corresponding to typical values in a-SiO_2. The absence of large deviations from the average values means that there are no regions of extreme stress in this particular ring, therefore the formation energies calculated at different sites of this ring should be similar. We have calculated this site dependence only for one reaction ($H_2O + \text{Si-O-Si} \leftrightharpoons 2$ SiOH) and found that the extremal values of the formation energies differed by only 0.2 eV for the six-member ring shown in Fig. 1. In contrast, total energies vary by 0.4 eV in different rings.

1. Charged versus neutral species

Certain defects, which may be created by the radiation-induced splitting of H_2O and O_2 interstitials, are highly reactive radicals and will react with the network in a barrierless reaction. For example, UV irradiation may split a water molecule into H and OH or H^+ and OH^-.[33] All of these species bind to the network to some extent. H and H^+ were found to bind to network oxygens by 0.2 (Ref. 34) and 1.65 eV,[35] while our calculations show that OH and OH^- are bound to network Si atoms by ~0.3 eV in both cases. Similarly, we have found that interstitial O atoms may form peroxy linkages after overcoming a barrier of 0.61 eV. The barrier arises as the interstitial O atom in the triplet ground state excites into a singlet state while entering a Si-O bond. Negatively charged oxygen complexes bind to network silica.[36]

A further, important question is the stability of the reaction products with respect to their charge state. Generally, a defect level would be empty above the Fermi level and filled below it. In bulk a-SiO_2, unlike, e.g., in doped semiconductors, the position of the Fermi level is uncertain, because usual defect concentrations are too small to pin the Fermi level, thus different charge states may coexist.

By comparing total energies of different charge states after allowing the charged defect to relax, we have found that OH molecules are more stable in the negative, while H atoms are more stable in the positive charge state in concordance with earlier work.[35] In both cases there are substantial relaxations from the positions of the neutral defect as mentioned earlier. However, this result is only valid if there is a source of electrons/holes for charging the OH/H. The higher stability of OH^- and H^+ versus the neutral species is also consistent with the observation that splitting up H_2O molecules into charged species is favored by 5.8 eV–1.6 eV = 4.2 eV [cf. Figs. 1(c) and 1(d)]. Moreover, H^+ in SiO_2 has been observed, e.g., via the dynamics of interface trap formation,[37] whereas shifts in the OH vibrational bond due to charging were seen in the infrared spectra of SiO_2.[38]

The reaction with the lowest formation energy that results in the production of charged species starting from a single water molecule is the splitting of H_2O into H^+ and OH^- [Fig. 1(c)]. Right after the reaction both the OH^- and the H^+ are interstitials, however they relax towards the network and bind to Si and O atoms, respectively. The total-energy difference between the interstitial H_2O and the relaxed reaction products is 1.6 eV; however, right after the H_2O split, while the OH^- and H^+ are interstitial (unrelaxed configuration), the total energy of the products is higher. We can calculate this energy and use it as a lower estimate for the energy barrier of this reaction.

We found that the binding energy for OH^- is only 0.3 eV; this much energy is required to move the molecule into the middle of the 6 Å void from its relaxed position only 1.8 Å away from a network Si atom. For H^+ the binding energy was found to be 1.65 eV.[35] Therefore, right after the H_2O is split, the total energy of the interstitial OH^- and H^+ complex can be estimated to be 1.6 eV+0.3 eV+1.65 eV = 3.55 eV. The actual barrier is probably higher, but for our purposes it suffices to note that this energy is already too high to be overcomed in a thermally activated process. Therefore, we assume that this reaction channel may only be open in oxides exposed to radiation. Indeed, UV radiation is known to split water molecules,[33] and neutron irradiation releases hydrogen in the oxide. One possible source of this hydrogen may be the interstitial H_2O molecule.[37]

In thin films, where neutral hydrogen is unstable versus H^+,[35] OH molecules may act as electron traps, i.e., they may immediately capture an electron from the Si valence band. Once an OH molecule is negatively charged, it binds to a Si atom making it fivefold coordinated. Before capturing an electron, the OH has an energy level about 1.3 eV above the SiO_2 valence band and this level drops below 0.9 eV in the negatively charged state after binding to the Si atom. Based on the location of this energy level, we suggest that OH^- bound to Si may be one of the water-related electron traps observed in as-grown SiO_2 films.[39]

2. Vicinal silanol groups

Based on formation energies, the most likely reaction between an interstitial H_2O and the defect-free SiO_2 network is the formation of two adjacent (vicinal) SiOH groups [see Fig. 1(b)]. By putting the water molecule into different voids and picking different locations for the silanol groups, we found that formation energies vary between 0.3 eV–0.7 eV, where the lower values are obtained in the 6–8 member rings. The positive formation energies mean that water is most stable as an interstitial molecule, seemingly contradicting the observation that most of the "wet"oxides contain water in the form of silanols.[6] The reason for this contradiction may be that, upon the oxidation process, SiOH groups are predominantly formed in the vicinity of the Si/SiO_2 interface that is rich in oxygen vacancies and usually accumulates some stress and is therefore different from the defect-free and unstrained bulk oxide used in our calculations. Indeed, H_2O-related vibrational bands appear in the infrared spectra if water is introduced into the bulk oxide at low temperatures.[6] For this reaction with H_2O initially in a six-member ring we have calculated a 1.5 eV reaction barrier which can easily be overcome at oxidation temperatures.[22]

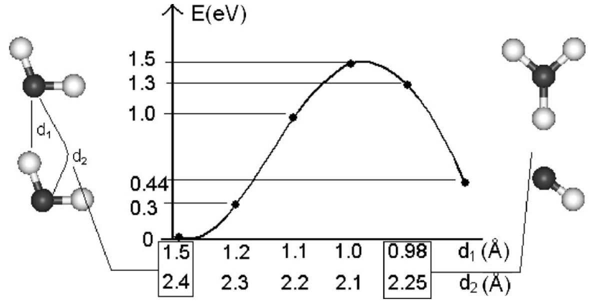

FIG. 2. Energy barrier of the 2 $H_2O \leftrightharpoons H_3O^+ + OH^-$ reaction. At left is the initial configuration as in Fig. 1(g). The total energies were obtained by fixing d_1 at different values and relaxing the entire supercell at each value. The final reaction products (H_3O^+ and OH^-) are to the right.

Subsequent reactions have formation energies exceeding 4 eV [Figs. 1(d)–1(f)]. We did not, therefore, calculate reaction barriers or site-dependent formation energy variations in these cases. Because of the high energy of the reaction products, these reactions are unlikely in defect-free oxides.

3. Reaction of two water molecules

Water molecules may cluster in the bigger voids of the oxide,[40] i.e., form hydrogen-bonded complexes with each other and network O atoms. In such cases two H_2O molecules may react with each other forming OH^- and H_3O^+ only at a cost of 0.44 eV [Fig. 1(h)].

To study the reaction of two water molecules, we first put them into the biggest void in our supercell [Fig. 1(g)]. The O-H distance between the two molecules was initially 1.46 Å. The small distance means that they were "squeezed" together by the surrounding solid even prior to the reaction. (As a comparison, the bond length of hydrogen bonding in ice is 1.8 Å.) We found that, by putting two H_2O molecules into one void [like the one in Fig. 1(g)] as opposed to having them in two separate voids, the total energy increases by 0.8 eV. To calculate the reaction barrier we approximated the O atom of the first H_2O molecule to the H atom of the second by keeping them fixed and varying the distance d_1 between them (Fig. 2). The supercell was relaxed in each configuration with the above constraint. We have also monitored the distance of the two oxygens (d_2) to ascertain the saddle point of the reaction (in the saddle point d_2 has a minimum).

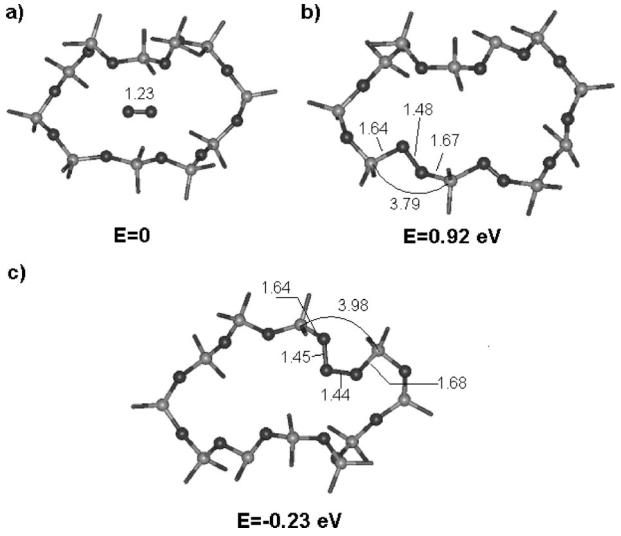

FIG. 3. Reactions of O_2 and the defect-free SiO_2 network. (a) Initial position of an O_2 molecule in the middle of an 11-member (only 6 Å in diameter) ring. (b) Two adjacent peroxy linkages. (c) Ozonyl linkage. Note that the Si-Si distance increases from 3.2 Å to 3.79 Å and 3.98 Å to accommodate the strain, but the Si-O distances remain little changed. Distances are shown in Angstroms.

The two water molecules break up into H_3O^+ and OH^- complexes at about $d_1 = 1.0$ Å. The moderate 1.5 eV barrier means that, if the oxide is exposed to water vapor at high temperatures, this reaction may contribute to the formation of oxide trapped charges in as-processed oxides. The final reaction products relax and bind to network atoms as seen on Fig. 1(h).

C. Reactions involving O_2

A medium-energy-ion-scattering spectroscopy study[9,10] has shown evidence for reactions between O_2 and a-SiO_2 at oxide surfaces. We have investigated two reactions between interstitial O_2 and the defect-free SiO_2 network [Fig. 3(a)]: the formation of adjacent peroxy linkages [Fig. 3(b)] and the formation of an ozonyl linkage [Fig. 3(c)].

In all the reactions involving O_2 and a defect-free network, the overall spin multiplicity of the system changes. Both atomic and molecular oxygen have a triplet ground state (see Sec. III A), however the reaction products (peroxy or ozonyl linkages) have a singlet ground state. To account for the presence of a triplet to singlet transition in these reactions we have carried out spin-polarized calculations.

Our results for the formation energies of peroxy and ozonyl linkages are consistent with those of Chelikowsky *et al.*,[13] who calculated them for a quartz cluster. We find the formation energy of two peroxy linkages to be 0.92 eV [or 0.46 eV per peroxy unit, Fig. 3(b)], as opposed to 0.6 eV per peroxy unit in Ref. 13. The higher value probably occurs because interstitial O_2 introduces less strain in an amorphous material that has larger voids and a more flexible structure; therefore, it has a lower total energy in its initial configuration. We also confirm that an ozonyl linkage has lower energy than the interstitial O_2 molecule in bulk amorphous SiO_2 by 0.23 eV; see Fig. 3(c) [the result for quartz is 0.3 eV (Ref. 13)].

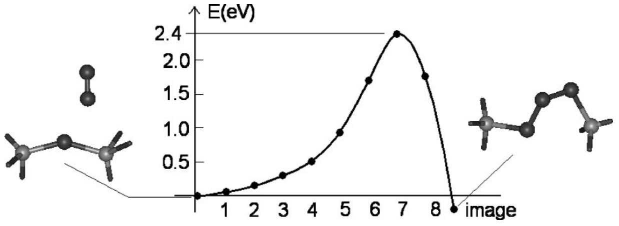

FIG. 4. Energy barrier of the $O_2 + \text{Si-O-Si} \leftrightharpoons \text{Si-O-O-O-Si}$ reaction. At left is the initial configuration as in Fig. 3(a) (image 0), at right is the ozonyl linkage as in Fig. 3(c) (image 9).

The data show that the formation of ozonyl linkages is energetically favorable. This reaction would, however lead to an isotope exchange between interstitial O_2 and the SiO_2 network throughout the bulk oxide, contradicting experimental data.[9,10] To explain the lack of oxygen exchange in the bulk oxide, we have calculated the energy barrier for the formation of ozonyl using the nudged elastic band method with eight intermediate images and one climbing image. The reaction proceeds as follows (Fig. 4). First, the O_2 molecule is bound to a Si atom making it fivefold coordinated (images 1–5). In the second step, a neighboring Si-O bond is broken (image 6) and the dangling oxygen binds to the O atom of the O_2 molecule that is further away from the Si atom, thus forming an ozonyl bond (image 7). This intermediate step is also the saddle point of the reaction, and the point where the triplet to singlet transition occurs. Finally, the ozonyl bond relaxes to its equilibrium configuration (images 8 and 9). The calculated activation barrier for this reaction is 2.4 eV. This barrier takes into account the necessity of a triplet-singlet transition at the saddle point of the reaction pathway.

We suggest that the relatively large value of this barrier compared to the O_2 diffusion barriers is the reason for the lack of O_2 exchange in bulk SiO_2. However, as the O_2 molecule diffuses closer to the Si/SiO_2 interface, the structure of the oxide changes. Besides having more defects towards the Si-SiO_2 interface, positron annihilation spectroscopy experiments show that the density of the oxide also increases.[41] The increased density results in the dominance of smaller rings where the diffusion barrier was found to be much higher (>2.0 eV),[22] making the ozonyl formation reaction more favorable. The incorporation energy of a free gas-phase O_2 molecule into SiO_2 was found to be ~ 2 eV.[13,42] This is the energy barrier the O_2 molecule has to overcome to enter the network of interstitial voids in the oxide. The high incorporation barrier makes the formation of ozonyl linkages also at the vacuum-SiO_2 interface likely. Once ozonyl is formed, the O_2 may reform in a reverse reaction overcoming a barrier of ~ 2.6 eV. Since different O atoms may be incorporated in the reformed O_2 molecule, the ozonyl formation reaction allows for oxygen isotope exchange between the diffusing interstitial O_2 and the SiO_2 network.

In summary, the O_2 molecule may form ozonyl linkages in the oxide overcoming a barrier of ~ 2.4 eV. This barrier is higher than the diffusion barrier in the dominant voids, but commensurate with the diffusion barrier in small voids and the incorporation energy of free O_2 making reactions at the oxide interfaces more likely.

IV. REACTION OF H_2O AND O_2 MOLECULES WITH OXYGEN VACANCIES

Oxygen vacancies are ubiquitous defects in all forms of SiO_2. They are electrically active as they may capture holes and consequently modify the current-voltage characteristics of transistors that have a conduction channel at the oxide/semiconductor interface (e.g., metal-oxide-semiconductor field-effect transistors). In optical fibers the neutral vacancy or the Si-Si bond gives rise to absorption and subsequent photoluminescence bands.[43] Under intense irradiation conditions, typically with doses exceeding several Mrads,[44] oxygen vacancies may be created by dislodging network oxygens.[17] Neutral oxygen vacancies may capture holes since they have a partially occupied energy level in the band gap ~ 3.2 eV above the top of the SiO_2 valence band. This level is associated with dangling Si sp^3 orbitals. Positively charged oxygen vacancies (E' centers) are paramagnetic and can be detected by electron paramagnetic resonance (EPR) measurements.[45]

Neutron irradiation experiments show that the generation rate for E' centers is higher in "wet" synthetic silica (e.g., Suprasil-1) than in "dry" silica (e.g., Suprasil-W1) (Ref. 16,17). The wet oxide contains typically $10^{19}\ \mathrm{cm}^{-3}$ OH groups (in the form of silanol or interstitial water molecules), while the typical OH concentration in dry oxides is only $10^{16}\ \mathrm{cm}^{-3}$. Also, infrared photoluminescence measurements show that, in the same type of dry oxides as above, the concentration of interstitial O_2 molecules is $\sim 10^{18}\ \mathrm{cm}^{-3}$, while in wet oxides it is $< 10^{14}\ \mathrm{cm}^{-3}$.[11] Practically, these data mean that one has roughly 1000 times more interstitial H_2O and 1000 times less interstitial O_2 molecules in wet oxides than in dry ones.

It is straightforward to assume that in bulk oxides radiation generates oxygen vacancies by the same mechanism regardless of the processing of the oxide (i.e., the cross section for dislodging oxygen atoms depends only on the local electronic environment surrounding the O atom and not on process-specific factors such as, e.g., defect concentrations). In such case the difference in the concentration of E' centers in various oxides as a function of dose is due to the different annihilation mechanisms of the E' centers. We have studied the reactions of charged and neutral oxygen vacancies with interstitial H_2O and O_2 molecules to determine their role in the annihilation mechanism of E' centers.

1. Neutral oxygen vacancies

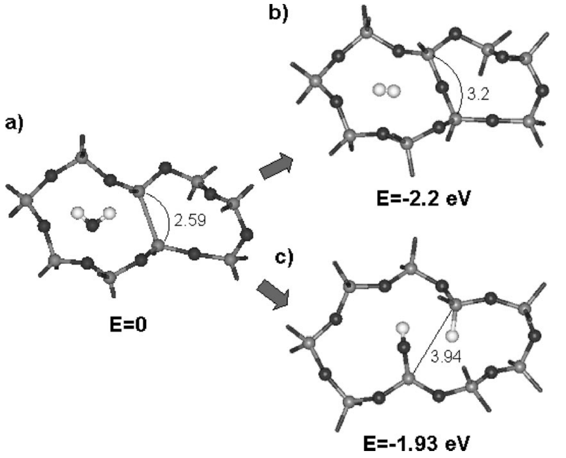

FIG. 5. Reactions of H_2O with an oxygen vacancy (Si-Si bond). (a) Initial position of a H_2O molecule in the middle of a six-member ring with an O vacancy. (b) Restored network with an interstitial H_2. (c) Adjacent Si-OH and Si-H defects. Note the relaxation of the ring in the different values of the Si-Si distance. Distances are shown in Angstroms.

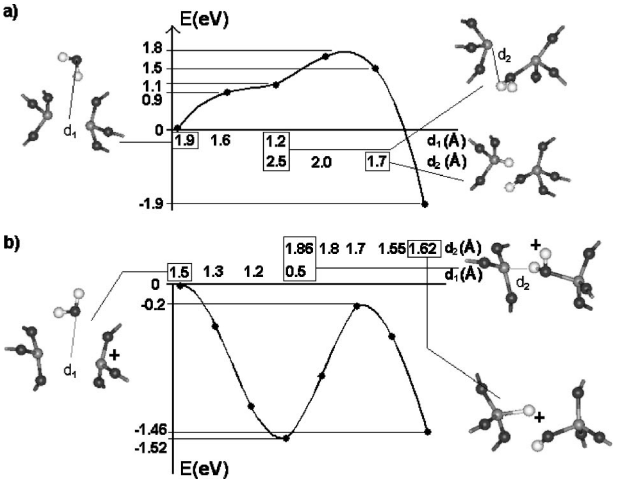

FIG. 6. Energy barrier of the reactions annihilating (a) neutral and (b) charged oxygen vacancies. (a) At left is an H_2O molecule in a void with a vacancy as in Fig. 5(a). Total energies are obtained by first reducing d_1 then, at the flat part of the total-energy curve, by keeping O of the H_2O fixed and reducing d_2. At right are the final reaction products (bottom) and the intermediate stage with the H_2O bound to a Si (top). (b) At left is an H_2O molecule in a void with an E'_δ center. First the H_2O binds to one of the silica in a barrierless reaction (right top). Then by keeping the O of the H_2O fixed and varying d_2 a Si-H^+ and a Si-OH is created (right bottom). The corresponding total energies at respective values of d_1 and d_2 are shown in the middle.

Neutral oxygen vacancies usually relax to form strained Si-Si bonds as in Fig. 5(a). A water molecule may fill up the oxygen vacancy and leave an interstitial H_2 behind [Fig. 5(b)] or create adjacent Si-OH and Si-H defects [Fig. 5(c)]. To calculate the energy barrier of these reactions we move the oxygen atom of the H_2O molecule toward the center of the Si-Si bond by varying the distance d_1 in Fig. 6(a). The water molecule first has to disrupt the strained Si-Si bond that takes place at $d_1 \approx 1.2$ Å. At this location, the whole molecule binds to one of the Si atoms creating a metastable configuration. To proceed further, we now keep O in the H_2O fixed and approximate one of the hydrogens toward the other silicon by varying the distance d_2 [Fig. 6(a)]. At $d_2 \lesssim 2$ Å the O-H bond breaks and the hydrogen binds to the adjacent Si. The total energy of the system is now lower, but it had to overcome a ~ 1.8 eV barrier to reach the final configuration. We found that filling the vacancy with an O atom and leav-

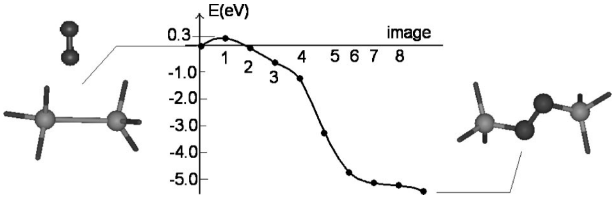

FIG. 7. Energy barrier of the $O_2 + \text{Si-Si} \leftrightharpoons \text{Si-O-O-Si}$ reaction. At left is the initial configuration: an O vacancy and an interstitial O_2 molecule (image 0). At right is the peroxy linkage as in, e.g., Fig. 3(b) (image 9).

ing an interstitial H_2 would have a much higher barrier since two O-H bonds would need to be broken in addition to the breaking of the weak Si-Si bond.

Oxygen molecules may react with the strained Si-Si bonds forming a peroxy linkage. Although the reaction results in an energy gain of 5.42 eV, the Si-Si bond must be broken and the interstitial O_2 molecule must transform from its triplet ground state to singlet state when forming the peroxy linkage. To account for the change in the overall multiplicity of the system, we have used spin-polarized calculations and the nudged elastic band method with eight intermediate images and one climbing image in calculating the formation energy and energy barrier.

The reaction proceeds as follows (see Fig. 7). As the O_2 molecule approaches the Si-Si bond, it increases the local strain resulting in the breaking of the bond and a small (0.3 eV) reaction barrier (image 1). Afterwards, the O_2 molecule binds to one of the Si atoms, but is still in the triplet configuration (image 2). The triplet to singlet transition occurs as the second O atom of the O_2 molecule binds to the second Si atom of the original Si-Si bond (image 3). In the remaining part of the reaction, the peroxy bond relaxes to its equilibrium configuration (images 4–9). These results are somewhat at variance with the reaction of O_2 with an O-vacancy in quartz[46] where one of the O atoms of the O_2 molecule binds to both Si atoms in the Si-Si bond in the first part of the reaction. The reason for the different reaction pathways most probably lies in the greater flexibility of the amorphous network (breaking the Si-Si bond may cause larger relaxations than in quartz, allowing the O_2 molecule to bind only to one Si atom in the first stage of the reaction). The above calculations show that the barrier for annihilating oxygen vacancies by interstitial O_2 molecules is significantly smaller than the diffusion barrier of interstitial O_2 (0.3 eV vs 0.6–1.5 eV in the dominant voids[22]). Therefore the rate limiting step for neutral oxygen vacancy annihilation by O_2 molecules is the diffusion of interstitial O_2.

2. *E′ centers*

E′ centers have several distinct equilibrium configurations.[47] In the experimental study of Refs. 16, 17, the oxides were irradiated to several Mrad creating *E′* concentrations up to 10^{20} cm^{-3}. The absence of subsequent thermal or electrical treatment results in the most abundant precursors (Si-Si bonds) being transformed to E'_δ centers. These centers, which make up approximately 80% of the observed *E′* EPR signal, comprise of two threefold coordinated Si atoms with a trapped positive charge (Fig. 8a).[47] As opposed to the neutral case, charged oxygen vacancies do not recombine forming an Si-Si bond. The Si-Si distance now is almost 3.5 Å as can be seen in Fig. 8. The interstitial H_2O and O_2 molecules are no longer in equilibrium; they bind to one of the silicas in a barrierless reaction as shown on Fig. 8(b) for the case of H_2O. To verify the absence of a barrier we have tracked the motion of H_2O and O_2 by fixing the distance between the O of the H_2O/O_2 and the midpoint of the two silicon atoms [d_1 in Fig. 6(a), only the case of water is shown] and calculating the total energy of the relaxed supercell in each point. Both molecules are first attracted to the Si atom carrying the positive charge.

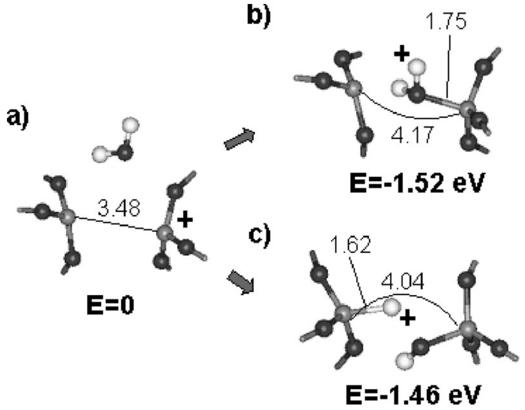

FIG. 8. Reactions of H_2O with a positively charged oxygen vacancy (E'_δ center). (a) Initial position of a H_2O molecule in the middle of a six-member ring with an E'_δ. (b) H_2O bound to a positively charged Si atom. (c) Adjacent Si-OH and Si-H^+ defects. Distances are shown in Angstroms.

For oxygen molecules, first a peroxy radical is formed, that is, a positively charged dangling O_2 molecule bound to only one silicon. The oxygen remains in the triplet configuration, though with one electron missing from its $2p$ orbital. Because of the proximity of the second Si atom from the original Si-Si bond, this peroxy radical becomes a positively charged peroxy linkage, which is the final stage of the E'-O_2 reaction.

For water molecules the intermediate configuration in Fig. 8(b) serves only as a metastable position. To arrive to the final configuration in Fig. 8(c) an O-H bond has to be broken, giving rise to a barrier. To calculate the barrier of this reaction, we have approximated one of the hydrogens of the water molecule toward the Si atom by varying the distance d_2 [Fig. 6(b)] and keeping the O of the H_2O fixed. At $d_2 \lesssim 1.7$ Å the Si-O bond breaks and the H attaches to the neighboring oxygen. The total energy of the system is almost the same as it was before the reaction, but it had to overcome a barrier of ~1.3 eV. In this final configuration there are no dangling Si bonds, and an analysis of the defect states in the gap shows that the positive charge is located on the hydrogen of the Si-H complex. After this final reaction step is completed, the *E′* center loses its EPR activity.

Comparing the above data with diffusion barriers of O_2 and H_2O through the dominant voids of the oxide, we infer that in wet oxides the E'_δ center annihilation is reaction limited (by a 1.3 eV energy barrier) and charged vacancies are annihilated easier than neutral ones whereas in dry oxides the annihilation of E'_δ centers is diffusion limited with a lower activation barrier of ~ 1 eV that corresponds to the diffusion barrier of O_2 molecules. As a result, dry oxides will have a smaller concentration of E' centers then wet oxides when irradiated with the same total dose.

V. CONCLUSIONS

In summary, we have shown that, although the most stable form of water in SiO_2 is the interstitial molecule, vicinal silanol groups may form at a low-energy cost (0.3–0.7 eV) with a barrier of 1.5 eV. H_3O^+ and OH^- complexes may form at an energy cost of 0.3 eV with a barrier of 1.5 eV in the large voids of the oxide and at high interstitial water concentrations, when clustering of H_2O molecules becomes significant. Water is more likely to split into OH^- and H^+ than neutral species if the oxide is irradiated, although this reaction—as all remaining reactions—has a too high barrier to be thermally activated.

O_2 molecules are most stable in the ozonyl linkage configuration; however, their formation is suppressed in the bulk oxide because of the high reaction barrier compared to the O_2 diffusion barrier. At the SiO_2/vacuum and Si/SiO_2 interfaces, however, ozonyl linkages may form because the incorporation energy of O_2 molecules from the gas phase and the diffusion barrier of O_2 molecules in the predominantly small rings towards the Si/SiO_2 interface becomes commensurate with the energy barrier for ozonyl formation, explaining the oxygen exchange patterns found in experiments.

Finally, we have shown that E' centers are annihilated at a faster rate in dry synthetic silica than in wet because the diffusion barrier of O_2 molecules that limits the annihilation process in dry oxides is lower than the rate limiting E'-H_2O reaction barrier in wet oxides.

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