Reactions and Diffusion of Water and Oxygen Molecules in Amorphous SiO_2

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Water and oxygen molecules determine many of the properties of amorphous SiO_2 used in several technologies, but the underlying atomic-scale processes remain unresolved. We report results of first-principles calculations showing that a wide range of behavior is possible in an amorphous environment, including diffusion of the molecule as a whole and various reactions with the network. Experimental data including oxygen exchange reaction and radiation sensitivity are accounted for. The possibility of H_3O^+ formation as a source of positive charge is discussed.

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Amorphous silicon-dioxide is a key component of metal-oxide semiconductor field-effect transistors, solar cells, and optical fibers, all of which are basic elements of modern technology. Practical applications are often limited by point defects that can change the mechanical, electrical [1], and optical [2] properties of the oxide. Many impurities, like hydrogen [3], alkali metals [4], or oxygen [5], are also known to affect the properties of the oxide.

Water and oxygen molecules are also known to play important roles in determining the properties of amorphous SiO_2, but the relevant atomic-scale configurations and processes remain unresolved. There exists no detailed account of whether these molecules remain intact in the interstitial regions, if they diffuse as molecules without breaking up, and if they attach whole to the network.

In the case of water, vibrational data reveal signatures of both interstitial H_2O molecules and silanol groups (SiOH) [6], with the ratios depending on sample preparation, total water uptake, and temperature. Experiments using H_2O molecules with ^{18}O found that the latter exchange with network O atoms even at 400 °C when oxidation processes are negligible [7]. Other experiments using tritiated water [8] found that tritium diffuses with an activation energy in the range of 0.6–0.8 eV, which is in agreement with the value extracted from thermal oxidation data [9], although the identification of the diffusing species is uncertain. The above experiments are consistent, but suggest a rather complex diffusing mechanism that involves reactions with the network.

^{18}O tagged oxygen diffusion experiments show that there is no oxygen exchange in bulk SiO_2 between oxygen molecules and network oxygen atoms [10]. This result means that O_2 diffuses in molecular form and does not react with a defect-free SiO_2 network. The diffusion barrier for oxygen molecules seems to be highly sensitive to the structure of the oxide and is typically between 0.7 and 1.6 eV [11] (for thermal oxides the Deal-Grove data give 1.2 eV) [9]. It was suggested that oxygen might diffuse in atomic form (with the diffusion barrier for peroxy oxygen is ~1.3 eV) [5]; however, this mechanism would not explain the absence of oxygen exchange in bulk SiO_2. Recent calculations show that oxygen diffuses in molecular form, but give slightly overestimated diffusion barriers [12].

Finally, the presence of water or O_2 molecules makes a critical difference on the radiation sensitivity of SiO_2 fibers [13,14]. It has been found that the rate of generation of O vacancies by γ irradiation is significantly higher in wet oxides. The difference has been attributed to different diffusivities of O_2 and H_2O molecules, but the precise origin has not been established.

In this Letter we report results of first-principles density-functional calculations in terms of which we elucidate the role of H_2O and O_2 molecules in amorphous SiO_2. We find that variations in the local bonding of the amorphous network result in a much wider range of phenomena than one normally encounters in crystals. For example, diffusion of H_2O is possible through six-member and larger rings with small energy barrier (~0.8 eV). In smaller rings, where the barrier is much higher, an H_2O molecule is more likely to break up at an O atom site, resulting in two silanol groups. In turn, an H_2O molecule can reform on the other side, allowing diffusion by a novel and unusual "reactive cut" through the network. In general, however, the lowest energy reaction is to form stable silanol groups. As opposed to water, oxygen molecules are more inert and do not react with the network. They diffuse as interstitial molecules with an energy barrier that is very sensitive to the local ring topology.

These and other results allow us to provide systematic answers to the questions posed by the diverse experimental data mentioned above. In particular, we are able to confirm the interpretation of the tritium-tagged water diffusion experiment and the oxygen exchange experiment in terms of the novel diffusion-reaction mechanisms. We also account for the differences in radiation response of wet and dry oxides.

The present calculations were based on density functional theory, the generalized gradient approximation for exchange correlation, ultrasoft pseudopotentials, supercells, and plane waves [15]. The pseudopotentials used for the present study have been thoroughly tested in an earlier work on a variety of Si-O-H systems [16]. The energy

cutoff for the basis set was 600 eV, and integrations over the Brillouin zone were done using the Monkhorst-Pack scheme with only one k point in the relevant irreducible wedge [17]. For studying charged defects we introduced a homogeneous negative (positive) background when removing (adding) electrons in the supercell. The calculations were performed for 72-atom amorphous SiO_2 supercells. These structures were generated by using the Monte Carlo bond-switching method [18], and relaxed until the total energy was minimized.

Diffusion of H_2O and O_2 in interstitial paths.— Representative results for the diffusion of H_2O through the ring structure of the SiO_2 network is shown in Fig. 1. Figure 1a shows two six-member Si-O rings. A water molecule diffuses across these rings along the shaded path. These rings constitute the bottlenecks of the diffusion channel, with a 0.84 eV barrier in this particular channel. Since total energies depend on the local bonding environment in an amorphous solid, we have calculated the barrier for both H_2O and O_2 diffusion in channels of different sizes. The results are summarized in Table I, showing that the two molecules behave very differently.

Water molecules exhibit a barrier of 0.8–0.9 eV in all the six- and seven-member rings that increases abruptly to more than 2 eV for smaller rings. If we assume that there are continuous diffusion paths made up by six- and higher-member rings, the diffusion activation energy would be 0.8–0.9 eV. Such an interpretation is fully consistent with the activation energies obtained in tritiated-water experiments [8] and thermal oxidation of Si [9]. This mechanism is similar to that elucidated in previous calculations in quartz [19].

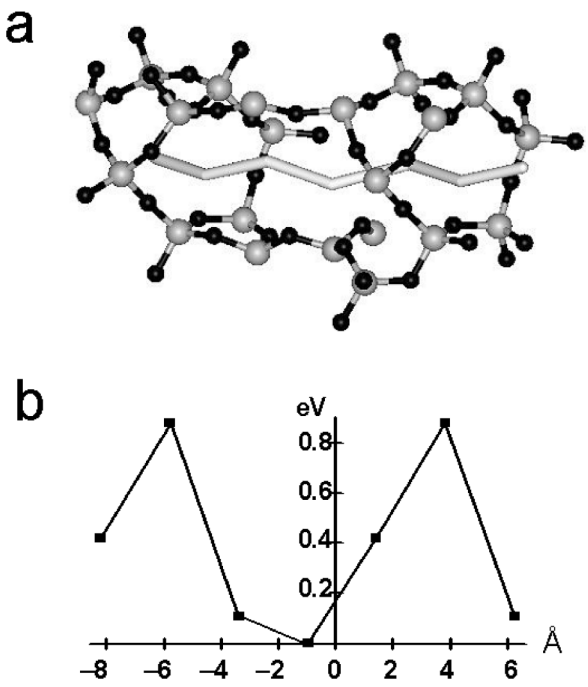

FIG. 1. (a) H_2O diffusing through two six-member Si-O rings. (b) Total energy variation along the above path. Black spheres are oxygen, gray spheres are silicon atoms.

The results for O_2 molecules are very different. The diffusion barrier is extremely sensitive to the local topology and varies almost continuously from 0.6 to 1.5 eV for seven- and six-member rings with different topologies. This wide variation is consistent with the experiments where activation energies in the range 0.7–1.6 eV were found in oxides grown in different ways [11]. Deal and Grove [9] and others [20] extract an activation energy of 1.2–1.3 eV from oxidation data, but this energy includes the "incorporation energy" for oxygen molecules which was recently reported to be 0.4 eV [12]. These experiments suggest that there are diffusion paths along which the barrier does not exceed 0.9 eV. Our amorphous cells are not large enough to allow calculation of the statistical distribution of different types of six-member rings. Ultimately, only finite-temperature simulations in large cells can produce reliable theoretical predictions of the effective activation energy in different oxides. Such calculations are not currently practical.

Reactions of H_2O with the network.—It has been suggested that the most likely reaction between H_2O and SiO_2 is the formation of adjacent SiOH groups [21]. We have calculated the activation barrier for this reaction following the scenario described by the IR observations of Davis and Tomozawa [6] (Fig. 2): the oxygen atom of the water was placed next to a network Si while one of the hydrogen atoms gets attached to one of the oxygen atoms from the network. The configuration shown in Fig. 2c corresponds to the saddle point of the reaction.

Figure 3 shows the reaction energies (the total energy differences between the final and initial products of reaction) for different possible reactions between H_2O and SiO_2. The final product with the lowest energy is two silanol groups (Fig. 3b). The range 0.3–0.7 eV corresponds to different local environments. The reaction barrier is 1.5 eV, but there is a corresponding variation in the reaction barriers as well.

Combining the above results on diffusion and reactions, we infer the following.

Water molecules diffuse freely through interconnected networks of six-member rings with an activation energy of 0.8–0.9 eV, confirming the interpretation of the diffusion experiments using tritiated water. When a water molecule

TABLE I. H_2O and O_2 diffusion barriers (in eV) as a function of ring size (number of members) and ring diameter (in Å). For ~6 Å and ~4 Å rings the barriers in several different rings are included.

Ring size	Ring diameter	H_2O barrier	O_2 barrier
7	~7	0.8	0.5
6	~6	0.84, 0.89, 0.91	0.6, 1.0, 1.5
5	~4.5	1.8	1.9
4	~4	2.0, 2.2	2.4, 2.8

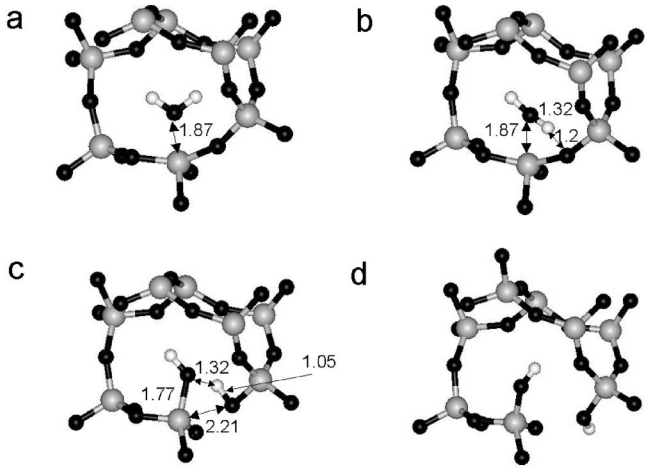

FIG. 2. Stages of the $H_2O + SiO_2 \rightarrow 2SiOH$ reaction: (a) H_2O initially in the middle of the void; (b) H_2O bends and stretches toward a network oxygen; (c) breakup occurs (saddle point); (d) final configuration: two adjacent SiOH groups. All distances are in angstroms, and white spheres are H atoms.

goes into a five-member or narrower ring, it is more likely to react with the network and form two silanol groups. The water molecule can then reform either on the same side or on the other side and continue diffusing. This reactive cut mode of diffusion involves a possible exchange between water and network oxygen atoms. Since the barrier for this process is only ~1.5 eV, the exchange can occur at low temperatures (400 °C) as has been observed [7]. If the process occurs long enough to equilibrate, the number of silanol groups would be substantial because of their low formation energy (0.3–0.7 eV). If the process is not equilibrated, the free water molecules would dominate, explaining the large variation in the observed ratio of water to silanol groups [6].

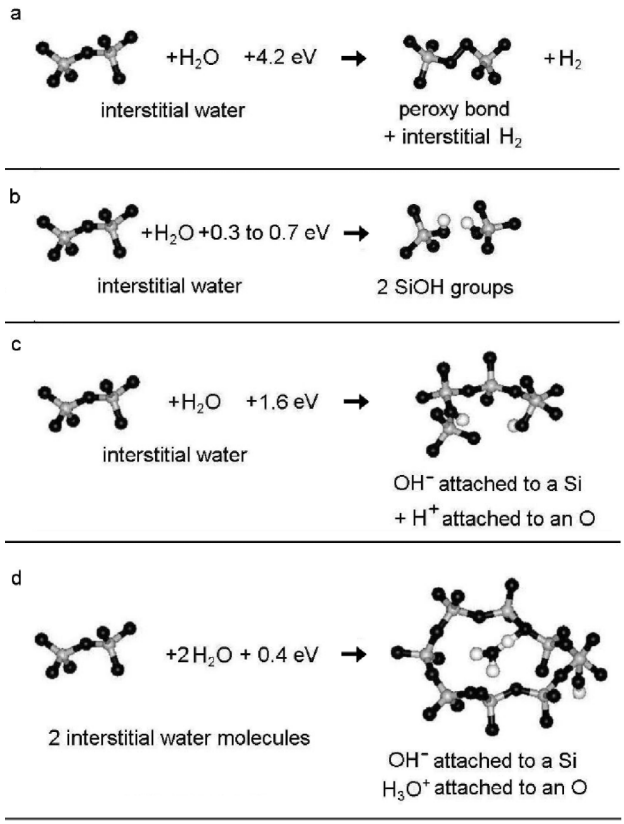

FIG. 3. Reactions between H_2O and the SiO_2 network. In the case of silanol group formation (b) the final total energy was calculated at different sites of the network.

We found that the breakup of a water molecule into neutral species other than silanol groups would cost at least 4.2 eV (Fig. 3a). Breakup into charged species is somewhat more likely: the formation energy of OH^- and H^+ is comparable to the total energy variation of interstitial H_2O throughout the oxide (Fig. 3c), but it is still too high to give a significant contribution to the as-processed oxide charge. These facts explain why water always prefers to diffuse as a single molecule.

Formation of H_3O^+.—The reaction of two water molecules to form an H_3O^+ and an OH^- complex involves a total energy cost of 0.4 eV (Fig. 3d). The barrier for this reaction is ~1.5 eV. The H_3O^+ ion attaches to an O atom (which becomes threefold coordinated) of the SiO_2 network via one hydrogen, while the OH^- ion attaches to a Si atom (which becomes fivefold coordinated). Such an attaching of charged complexes is similar to attaching of H^+ and H^- ions (to O and Si atoms, respectively) in SiO_2 [22]. The OH^- complex can become interstitial at an energy cost of 0.3 eV and diffuse away in the interstitial voids, but the H_3O^+ complex remains localized. This reaction, however, would start only if the two molecules are about 1.2 Å apart which has a very low probability at typical concentrations of water in amorphous SiO_2. If, however, the oxide contains bigger voids, the water molecules may cluster in these voids [23]. In such a case, H_3O^+ may contribute to the as-oxidized oxide trapped charge [24].

Reactions with oxygen vacancies.—So far we considered only water molecules in a perfect, defect-free oxide. The defects of greatest concern are the oxygen vacancies—they may trap holes (created by irradiation) and increase the fixed charge in the oxide [25]. Oxygen vacancies also introduce scattering centers in optical cables that reduce the transmission in the visible domain [26]. Under intense irradiation conditions such as in Refs. [13,14], preexisting neutral vacancies capture holes and become E' centers, and new vacancies form by dislodging O atoms (in wet oxides, possibly also by releasing silanol groups bonded to adjacent Si atoms). We may assume that these physical mechanisms are responsible for E' center generation for both wet and dry oxides. We also note that in dry oxides, the concentration of O_2 molecules is higher and the concentration of H_2O molecules is lower than in wet oxides [27,28]. The efficiency of O vacancy annihilation by H_2O and O_2 molecules, however, is determined by the rate limiting step in each case.

Figure 4 shows that the final reaction products are lower in energy than the vacancy and the interstitial molecule (in the case of H_2O, the result is an Si-H^+ and a silanol group,

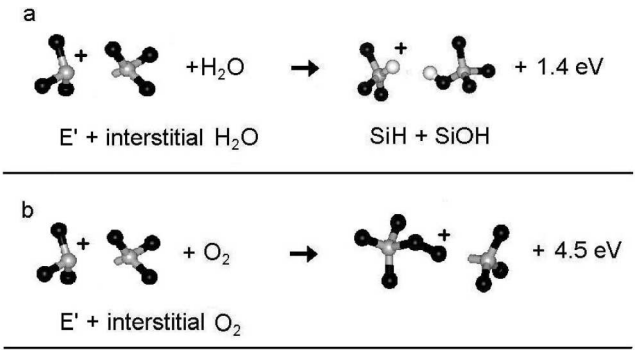

FIG. 4. Reactions involving vacancies.

in the case of O_2, a positively charged peroxy radical is formed [29]). The energy release for a positively charged vacancy is lower (4.5 eV for O_2 and 1.4 eV for H_2O) than for a neutral one (5.5 eV for O_2 and 1.9 eV for H_2O). Since the annihilation reaction itself is exothermic, it can be rate limited by diffusion or reaction barriers only.

For water molecules, the barrier for the vacancy annihilation reaction is 1.8 eV if the vacancy is neutral and 1.3 eV if it is positively charged. Comparing the reaction barrier with a diffusion barrier of 0.8–0.9 eV, we conclude that in wet oxides the E' center annihilation is reaction limited (by a 1.3 eV energy barrier) and charged vacancies are annihilated easier than neutral ones.

For oxygen molecules we found no barrier for the annihilation reaction, independent of the charge state of the vacancy. Thus, the annihilation of vacancies by O_2 is diffusion limited. As discussed earlier, the activation energy for O_2 diffusion varies over a range in both theory and experiment, but the most likely values are of order $\sim$1 eV, i.e., smaller than the barrier limiting annihilation of O vacancies by water molecules (1.3 eV). In the absence of O_2 diffusion data in the oxides used in Refs. [13,14], the best that can be said at this point is that the O_2 diffusion activation energy in these oxides is smaller than 1.3 eV. However, an interesting prediction emerges from the theoretical results: if, indeed, the vacancy production rate is the same in wet and dry oxides, the net concentration of vacancies would be the same in the two oxides if the experiments are done at low temperature.

In summary, we have found that molecular H_2O is the most stable form of water in a bulk amorphous SiO_2. Nevertheless, even at low temperatures one may find a considerable amount of SiOH groups in SiO_2 because the formation energy for the reaction between H_2O and amorphous network is low, and the reaction barrier is highly varying. Water molecules diffuse through interconnected networks of six-member rings. A charged complex, H_3O^+, can be formed in bigger voids in agreement with the observed clustering effect of water molecules. This complex may contribute to the as-oxidized oxide fixed charge. The difference in the radiation sensitivity for wet and dry oxides is also consistently explained.

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