Reactions of Water Molecules in Silica-Based Network Glasses

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Given that H_2O dissolves minimally in quartz, the mechanism for the ubiquitous dissolution of H_2O in silica glasses has been a long-standing puzzle. We report first-principles calculations in prototype silica glass networks and identify the ring topologies that allow the exothermic dissolution of H_2O as geminate Si-O-H groups. The topological constraints of these reactions explain both the observed saturation of Si-O-H concentrations and the observed increase in the average Si-Si distance. In addition, calculations of H_2O and Si-O-H dissociation account for the observed response to radiation by wet thermally grown SiO_2.

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Silica-based network glasses, including synthetic silica [1–3], thermally grown SiO_2 [4], and aluminosilicate [5,6] glasses have long been known to dissolve significant amounts of water. Absorption of water leads to a wide range of interesting phenomena. For instance, the viscosity, density, and topology of the glass can be fundamentally altered. In addition, the optical and electrical properties can change significantly. Technological implications abound within the glass industry and in microelectronics. In addition, the presence of water in optical fibers and in thermal gate oxides in transistors significantly alters the response of these devices to ionizing radiation [4,7,8].

Extensive experimental investigations, using infrared and NMR spectroscopy, have established that some water molecules entering a silica glass remain intact, while others interact with the network and form silanol (Si-O-H) groups [1,5]. In fused silica and aluminosilicate glasses [1,2,5,6], the silanol concentration reaches a plateau, while the concentration of intact interstitial H_2O molecules is observed to increase unabated. X-ray absorption studies of silica glasses containing a range of silanol concentrations have revealed a correlation between Si-O-H concentration and average Si-Si distance [3]. In thermally grown oxides (Si-SiO_2 structures), the presence of water can lead to a short-term suppression and a long-term enhancement of the usual radiation-induced interface defect density [4,8]. Microscopic explanations for the above observations are lacking. Finally, the robust dissolution of H_2O in silica-based network glasses is in sharp contrast to the observation that crystalline forms of silica, e.g., quartz, absorb minimal amounts of water, mainly at defects [1,9,10].

There exist a few theoretical papers that have contributed to understanding aspects of water incorporation in silica [8,11,12]. In particular, it has been found that incorporation of interstitial H_2O is endothermic for quartz. In amorphous SiO_2, exothermic incorporation of water as geminate silanol groups has been found in special cases [8,12], but the topological conditions for such incorporation have not been identified. In this Letter, we report extensive new first-principles calculations for the reactions of water with amorphous silica networks. Based on these results, we find that the key feature of amorphous networks that enables exothermic hydrolysis is the existence of small rings, especially those comprising three or four Si-O-Si units. In quartz, all rings have 6 Si-O-Si units, which then naturally accounts for the absence of hydrolysis. In silica-based glass networks, there is a distribution of ring sizes. We find that, by fusing smaller rings into a large ring, hydrolysis results in a larger average Si-O-Si bond angle and larger average Si-Si distance, in agreement with experimental data [3]. Furthermore, since the average density of small rings is low, the present results provide a natural explanation for the saturation of the silanol concentration in both pure and fused silicates [5,6]. Further calculations of H_2O and Si-O-H in silica networks in the presence of holes are used to develop a microscopic theory for the behavior of wet oxides in microelectronics under the influence of ionizing radiation [4,8].

Density-functional calculations were performed using the local-density approximation with generalized-gradient corrections [13] as implemented in the VASP code [14]. A projector augmented-wave [15] basis with an energy cutoff of 400 eV was used. Three amorphous SiO_2 supercells were used (see below) with cubic edges of 9.61, 12.03, and 12.03 Å. Brillouin-zone integrations were carried out using two and one special k points [16], respectively. Atomic relaxations were performed until the maximum forces on atoms became less than 0.05 eV/Å; reaction barriers were calculated using the elastic-band method. Convergence tests indicate that the energies reported have an uncertainty of less than 0.1 eV.

The three amorphous SiO_2 supercells used in this study were generated with an empirical-potential Monte Carlo bond-switching method [17]. Some properties of these models are listed in Table I. Silica model 1 (model 1) has 24 SiO_2 units, whereas models 2 and 3 both have 38 SiO_2

TABLE I. Data are reported for the insertion of an H_2O from vacuum into SiO_2 at a Si-O-Si site to form two Si-O-H bonds. The second row lists the number of SiO_2 units in each supercell. The third row lists the energy per SiO_2 for each silica model using quartz as the reference. The fourth row lists the number of three Si-O-Si membered rings in the model. The last three rows contain the reaction energy where the left column lists the smallest Si-O-Si ring associated with the reaction site.

Model	Quartz	Silica 1	Silica 2	Silica 3
N (SiO2)	24	24	38	38
$\Delta E/SiO_2$ (eV)	0.0	$+0.24$	$+0.22$	$+0.11$
N (3-member rings)	0	1	1	0
3-ring site	$\cdots$	-1.0	-1.1	$\cdots$
4-ring site	$\cdots$	-0.7	-0.5	$+1.4$
6-ring site	$+0.7$	$+0.1$	$+1.5$	$+1.1$

units. All three models have an equilibrium density of approximately 2.17 g/cm^3. For each model, the structural properties are consistent with experimental results for pure silica glasses, although models 1 and 2 are more strained than model 3, as discussed below.

We find several configurations of nondissociated H_2O molecules in interstitial regions with positive binding energies, indicating that water absorption is an energetically favorable process. The most stable insertion configuration corresponds to an H_2O molecule inside a large ring with a diameter of 7–10 Å, as shown in Fig. 1. The average binding energy is $\sim$0.5 eV. This result contrasts with the incorporation of H_2O in quartz, where there is 0.5 eV cost for insertion. The presence of larger rings in silica glasses accounts for this difference between the glasses and quartz.

The presence of water as nondissociated molecules in silica induces minor changes in the properties of the network. More significant changes occur following hydrolytic reactions. We explore the breakup of a Si-O-Si bridge and the concomitant creation of two silanol groups. The dissociation reaction occurs at Si-O-Si sites and involves the cleavage of nine rings that connect the two silicon atoms. While many rings are involved in the reaction, the smallest rings control the reaction energy. Exothermic dissociation of H_2O is only found at Si-O-Si bridge sites involved in smaller than average rings, neighboring a relatively open interstitial region. These topological features are the key for understanding hydrolysis in silica-based network glasses.

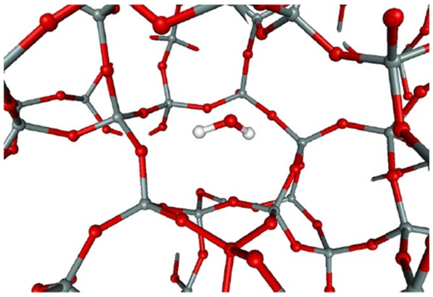

FIG. 1 (color online). Water molecule inside a void in amorphous silica model 2. The small gray spheres are Si atoms, the small dark spheres are oxygen atoms, and the small white spheres are hydrogen atoms.

In each of our structural models, several sites were examined to search for exothermic reaction sites. The results are recorded in Table I and organized according to the smallest ring associated with a site. If no exothermic sites were found for a particular ring size, then the lowest endothermic reaction energy is listed in Table I. The H_2O-induced breakup of a three-membered ring has in general the largest exothermic reaction energy. As noted in row 2 of Table I, models 1 and 2 include a single three-membered ring, whereas model 3 has none. The exothermic character of the reactions in these cases can be traced to the relief of strain, via the fusing of smaller rings into a larger ring.

Figure 2 shows one example of the microscopic structure after two Si-O-H bonds have formed cleaving a four-membered ring in the process. In models 1 and 2, there are three- and four-membered rings next to a relatively open region; these rings provide for exothermic dissolution. In model 3, a four-membered ring in the uniformly dense network does not provide an exothermic reaction site. Moreover, the endothermic reaction energies in model 3 were significantly higher than those found in models 1 and 2, consistent with model 3 having a lower energy structure (i.e., less strain is available to be relieved). In all models, reaction sites, where the smallest associated ring has 6 members, resulted in only endothermic reactions, irrespective of any neighboring large voids. In model 1, we also investigated the dissolution reaction with a silicon replaced by either boron, phosphorous, or aluminum. In each case, the three-membered ring provided an exothermic reaction, suggesting that the role of small rings in hydrolysis persists in the general class of silica glasses.

The exothermic nature of the dissolution reaction hinges on the release of network strain, so it is important to understand the nature of strain in our model networks. The energy per SiO_2 for each amorphous silica model relative to quartz is reported in row 3 of Table I. Models 1 and 2

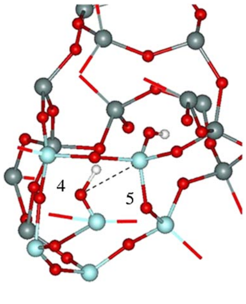

FIG. 2 (color online). The final configuration after the dissolution of H_2O forming two Si-O-H. The broken 4/5 ring is shown with a dashed line. The large gray spheres are network Si atoms. The large light spheres are network Si atoms within the 4/5 rings. The small dark spheres are oxygen and the small white spheres are hydrogen.

have sizable network strain of about 0.2 eV per SiO_2 higher than quartz, while the strain energy of model 3 is only half as large. While generating models 2 and 3, we discovered that elimination of three-membered rings allows the network to relax significantly. In models with small numbers of SiO_2 units, a single three-membered ring represents an enormous density perturbation and an important source of strain. Naturally, in small models relatively open interstitial regions occur to offset the high-density region around the three-membered rings.

To further explore the nature of three-membered rings in network glasses, we generated two amorphous silica models each with 216 SiO_2 units. One of these models has a single three-membered ring and the other has none. Since these models are too large for the calculation of dissolution reactions using density-functional theory, we use an empirical potential [17] to examine the strain energies of each Si atom. The model with a three-membered ring includes 18 silicon atoms with strain energies above 1 eV, whereas the other model had no silicon atoms with such high strain. In the center of Fig. 3 one can see a three-membered ring with a relatively open region to its left. The silicon atoms represented by large light balls are highly strained with an energy two standard deviations above the average. Importantly, only the three-membered ring includes neighboring highly strained silicon atoms. These results demonstrate that three-membered rings involve highly strained atoms, are associated with relatively open regions, and are particularly reactive sites. Therefore, our results from the 216 SiO_2 unit models are consistent with our first-principles results on smaller models.

Overall, the topological constraints discovered here provide an explanation for a variety of puzzling experiments on silica-based network glasses. In synthetic silica samples grown to maximize water dissolution, approximately 0.1% silanol incorporation has been observed [3]. Based on our results, the concentration of three- and four-membered rings sets an upper bound on the concentration of silanols that can be incorporated in silica. Indeed, recent studies place the total concentration of three- and four-membered rings at 0.6% in pure silica glass networks [18], consistent with the observed 0.1% silanol concentration. In fused and synthetic pure silica, recent x-ray scattering experiments [3] find the average Si-Si distance increases with increasing Si-O-H concentration. This result occurs because dissolution involves removing strained smaller rings. We find the release of strain is indeed evidenced by an overall larger average Si-Si distance. In alumina silicates fused from powders, recent NMR studies [5,6] find the Si-O-H concentration is initially larger than the molecular H_2O concentration until the Si-O-H concentration reaches saturation at 1%–2%, while the molecular H_2O concentration continues to increase without saturation. Our results show that H_2O exothermically incorporates into silica both in its molecular and in its dissolved form as Si-O-H. As water is introduced, since the Si-O-H structure is favored for low water concentration, the Si-O-H concentration will initially be larger as observed. Because of the limited number of small rings available, the bulk Si-O-H concentration saturates, as observed [5]. Finally, the concentration of intact H_2O molecules does not saturate because there exist plenty of large-diameter rings.

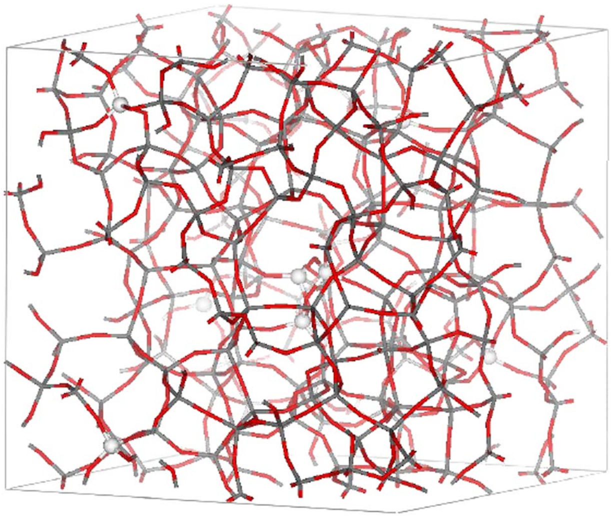

FIG. 3 (color online). A silica glass network containing 216 SiO_2 units is presented. Light balls represent highly strained silicon atoms. A 3-membered ring of highly strained Si atoms is in the center.

In thermally grown SiO_2 used in microelectronics, the hydrogen content of SiO_2 is known to be key to understanding many radiation-induced phenomena [19]. Radiation generates electron-hole pairs; the holes release H^+ from various sites where it is bonded. The released H^+, under positive bias, migrates to the interface where it depassivates dangling bonds (the arriving H^+ pairs with the H in a Si-H interface bond, resulting in H_2 and a positively charged Si dangling bond [20]). One might expect that the presence of water and its dissolution into silanol groups simply means more bound H that can be released by holes, causing a higher-than-normal increase of the density of depassivated dangling bonds (D_{it}, density of interface traps). Experiments, however, have shown that the increase in D_{it} is suppressed in wet oxides relative to dry oxides immediately following irradiation. Only after a period of time (room-temperature annealing), D_{it} grows faster in wet oxides [4,8]. We have addressed these issues with new first-principles calculations. In particular, we investigated the stability of the geminate silanol groups introduced by the dissolution of H_2O in our pure silica models. The release of hydrogen is strongly endothermic with a reaction energy of +1.4 eV and a barrier of 1.7 eV, much higher than the reverse of the dissolution reaction. In contrast, the presence of a hole leads to the release of a H^+ with a reaction energy of only 0.55 eV and a barrier of 0.85 eV, which can be overcome at room temperature. The proton release results in the reformation of a Si-O-Si bridge and the retention of an OH group as a fifth bond for one Si atom. An example is shown in Fig. 4. This "interstitial

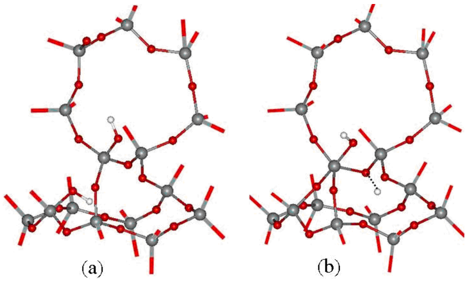

FIG. 4 (color online). Two Si-O-H complexes (a) and a loose OH complex with proton (b). The large gray spheres are Si, the small dark spheres are oxygen, and the small white spheres are hydrogen.

OH" complex involves a Si-O bond with length 1.71 Å, while the other four Si-O bonds have lengths of 1.65, 1.68, 1.72, and 1.79 Å. The interstitial OH group can hop to a neighboring site with a barrier of ~0.6 eV, and by itself is also a potential source of protons. In the presence of a hole, the OH releases an H^+ exothermically with reaction energy of -0.2 eV and a low barrier of 0.4 eV. The remaining O atom recombines with a Si-O-Si in the network to form a peroxy Si-O-O-Si structure. This reaction is illustrated in Fig. 5. These results mean that the presence of water can significantly enhance the radiation-induced increase of D_{it}.

To account for the short-term suppression of radiation response, we examined the role of interstitial H_2O molecules in the vicinity of the Si-SiO_2 interface using previously developed interface models [20]. We found the following. After a radiation-released H^+ depassivates a Si dangling bond at the interface, a nearby H_2O molecule can repassivate it via the reaction $D + H_2O \rightarrow$ Si-H + OH, where D stands for a Si dangling bond (reaction energy 0.4 eV; barrier 0.9 eV). The remaining OH can also passivate dangling bonds via the exothermic reaction $D + \mathrm{OH} \rightarrow$ Si-O-H. Thus, for some initial time after irradiation, the proton induced increase in the density of dangling bonds is suppressed by interstitial water in the interface region, consistent with experimental results [4,8]. Once this supply of H_2O molecules is depleted, H^+ that is driven by a positive bias from the bulk SiO_2 to the interface continues to depassivate dangling bonds, with the net rate being higher in wet relative to dry oxides.

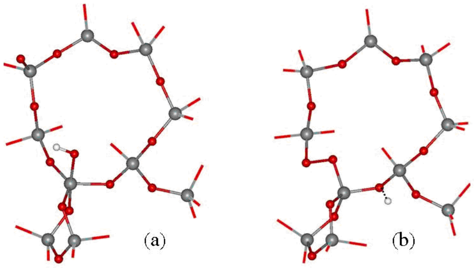

FIG. 5 (color online). Loose OH complex (a) and peroxy structure with proton (b). The large dark spheres are Si, the small dark spheres are oxygen, and the small white spheres are hydrogen.

In summary, we have used first-principles density-functional calculations to discover topological rules for the exothermic dissolution of H_2O in silica glasses. These rules provide a framework for explaining the lack of incorporation of water in quartz, the saturation observed in alumina silicates, and the structural changes observed in x-ray studies. Finally, based on new calculations, we develop a microscopic theory for the role of water in Si-SiO_2 structures exposed to ionizing radiation.

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