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Structure and diffusion of excess Si atoms in SiO_2

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Using gradient corrected density functional theory calculations, we have investigated the structure and diffusion of excess Si atoms in amorphous SiO_2, with comparisons to their behavior in α-quartz. From the first principles calculations of their configuration, bonding, and energetics, we find that excess Si atoms can be fully incorporated into the amorphous oxide network while yielding oxygen vacancies. The incorporation turns out to gain energy as high as about 1.8 eV, relative to the bond center state where the excess Si atom is located at a Si-O bond center. Based on the results, we propose a novel mechanism for Si diffusion in amorphous SiO_2 in the presence of excess Si atoms, which involves the fourfold-coordinate Si^{2+} state creation via oxygen vacancy diffusion and pairing and its reconfiguration to the bond center state. The overall diffusion barrier is approximated to be 4.5–5.0 eV, in good agreement with recent measurements. Our calculation results also predict that excess Si atoms, if they exist, may undergo diffusion with a moderate barrier of <3.0 eV in α-quartz.

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I. INTRODUCTION

Atomic-level understanding of the behavior and properties of defects and impurities in oxide layers and their interfaces is crucial in the evolution of silicon semiconductor technology. In particular, the behavior of excess Si atoms in SiO_2 is of great interest as they can directly influence the fabrication and performance of Si-based electronic and photonic devices, such as the synthesis and structure of oxide-embedded Si nanocrystals,[1,2] and the evolution of dopant profiles in ultrashallow junction formation.[3,4]

Herein, our particular interest lies in understanding the structure and dynamics of Si atoms introduced in an amorphous SiO_2 layer, related to the synthesis of oxide embedded Si nanocrystals. Thus far, the nanocrystal formation has been described by a sequence of fundamental processes such as nucleation, growth, and Ostwald ripening of Si precipitates in silicon suboxide $[SiO_x(x<2)]$.[5] This model however often fails to explain experimental observations,[5] including strong dependence of Si cluster size on initial Si supersaturation and rapid formation of Si clusters at the early stages of annealing with very slow ripening. Therefore, a better understanding of the behavior of excess Si atoms is necessary to develop an improved growth model for oxide-embedded Si nanocrystals.

In this paper, we present the structure, diffusion, and bonding mechanisms of single Si atoms introduced in amorphous SiO_2 as well as crystalline quartz based on density functional theory calculations. Si diffusion in SiO_2 has been extensively studied both experimentally and theoretically,[6–11] but the underlying diffusion mechanism is still unclear. Recent experiments[9,10] have shown that Si diffusion coefficients under equilibrium conditions are two orders of magnitude lower than those under nonequlibrium conditions (where Si atoms are presented in excess). Si diffusion (under equilibrium) in thermally grown a-SiO_2 has been described taking into account SiO molecules generated at the Si/SiO_2 interface.[11] However, the influence of excess Si atoms on the Si diffusion coefficient has not yet been fully clarified. In addition, to the best of our knowledge no measurement of Si diffusion in α-quartz under nonequilibrium conditions is available. In reality, indeed introduction of excess Si atoms in crystalline quartz seems rather unlikely. Nonetheless, this comparative investigation between amorphous SiO_2 and α-quartz will assist in better understanding the behavior of excess Si atoms in amorphous oxide layers.

II. COMPUTATIONAL DETAILS

Crystalline SiO_2 (α-quartz) is modeled using a 72-atom supercell with lattice constants of $a=4.917$ Å and $c=5.430$ Å. Amorphous SiO_2 (a-SiO_2) is constructed using a continuous random network (CRN) model.[12] Starting with randomly distributed 25 Si and 50 O atoms in the supercell with a fixed experimental density of 2.2 g/cm^3, the SiO_2 system is relaxed via a sequence of bond transpositions using the Metropolis Monte Carlo method based on Keating-type[13] interatomic potentials. The amorphous structures are further relaxed using density functional theory calculations (as detailed below). The average Si-O-Si bond angle and the bond angle deviation of computed a-SiO_2 structures are $\approx 136°$ and $\approx 15°$, respectively, in good agreement with experimental measurements.[14]

All atomic structures and total energies reported herein are calculated using a planewave-basis pseudopotential method within the generalized gradient approximation (GGA) (Ref. 15) to density functional theory (DFT), as implemented in the Vienna *Ab-initio* Simulation Package (VASP).[16] We use Vanderbilt-type ultrasoft pseudopotentials,[17] with a planewave cutoff energy of 300 eV. The convergence of atomic structure and energetics

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with respect to the plane-wave cutoff energy is carefully checked by increasing to 400–450 eV, but the variation of relative energies turns out to be less than 0.1 eV, with unnoticeable changes in atomic structure. We use a $(2\times2\times2)$ mesh of k points in the scheme of Monkhorst-Pack[18] for the Brillouin zone sampling, yielding well-converged results. All atoms are fully relaxed until all residual forces on each constituent atom become smaller than 0.02 eV/Å.

We calculate diffusion pathways and barriers under the static approximation using the nudged elastic band method (NEBM).[19,20] We first consider sixteen images along a diffusion path for the initial sampling, and then apply the climbing NEBM method[21] to determine the saddle point precisely. We analyze bonding mechanisms using the electron localization function (ELF) as proposed by Becke and Edgecombe.[22] The ELF represents the probability of electron pair localization and can take on values ranging from 0 to 1, where ELF=1 corresponds to perfect electron pair localization and ELF=1/2 corresponds to homogeneous electron gaslike pair probability.

III. RESULTS AND DISCUSSION

A. Defect-free crystalline SiO_2 (α-quartz)

As illustrated in Fig. 1, we identify three stable configurations of a single Si atom introduced in α-quartz:

(1) Fourfold coordinate (FC) where the Si atom is bonded to neighboring two Si and two O lattice atoms by breaking two Si-O bonds;

(2) Bond center (BC) where the Si atom is located at the center of a Si-O bond; and

(3) Ring center (RC) where the Si atom is located at the center of a six-member ring by weakly interacting with neighboring Si and O lattice atoms.

Figures 1(a) and 1(b) show two different FC structures, associated, respectively, to the *third* [C and F] and the *second* [A and C] Si neighbors on a six-member ring. Hereafter the former [(a)] and the latter [(b)] are referred to as FC_I and FC_{II}. The FC_I structure causes less lattice distortions than the FC_{II} structure, thereby 0.34 eV more favorable energetically. The α-quartz structure yields two slightly different Si-O bond lengths, e.g., D-1 (d=1.62 Å) and C-1 (d=1.61 Å), as shown in Figs. 1(c) and 1(d). Hereafter Si atoms placed at the centers of the longer and shorter bonds are referred to as BC_I [(c)] and BC_{II} [(d)], respectively. It turns out that the BC_I and BC_{II} structures are nearly degenerate, and they are about 0.57 eV less favorable than the most stable FC_I structure. The placement of an excess Si atom at the center of a six-member ring results in a noticeable inward displacement of neighboring Si and O lattice atoms [Fig. 1(e)]. The RC structure is predicted to be 1.8 eV less stable than the FC_I structure. It is apparent that FC structures yield a larger strain energy than BC and the RC structures. However, their energy gain over the others by bond formation with adjacent Si and O lattice atoms appears to exceed the strain energy difference, making the FC_I structure most favorable energetically.

We analyze bonding mechanisms for FC, BC, and RC structures based on electron localized functions (ELFs), local densities of states (LDOS), and decomposed charge densities, as shown in Figs. 2 and 3. For FC_I, the ELF analysis [Fig. 2(a); left panel] clearly demonstrates the excess Si atom bonds covalently with neighboring Si atoms and ionically with O atoms. The LDOS on excess Si exhibits two sharp peaks above the valence bond maximum of α-quartz [Fig. 3, FC_I], which mainly originate from Si-Si bonds (as demonstrated by corresponding decomposed charge densities [Fig. 2(a); right panel]). The decomposed charge density analysis also shows that some partial charge is delocalized to populate the lower energy states of neighboring Si and O lattice atoms, indicating the valence electrons of excess Si are not fully involved in the formation of new Si-Si and Si-O bonds. In fact, this is not surprising considering significant lattice distortions induced by the excess Si insertion. For BC_I, the ELF analysis [Fig. 2(b); left panel] clearly demonstrates the formation of covalent and ionic bonds respectively with Si and O neighbors. Local strain makes the newly formed Si -Si bond highly distorted, and therefore the Si-Si bond center is displaced away from the atomic interaction line while moving towards the lattice Si atom. The remaining two valence electrons of excess Si are localized to form a lone pair, which is evidenced by the sharp 3p band near the Fermi level [Fig. 3, BC_I] and corresponding decomposed electron densities [Fig. 2(b); right panel]. The RC Si weakly interacts with neighboring Si and O lattice atoms [Fig. 2(c)].

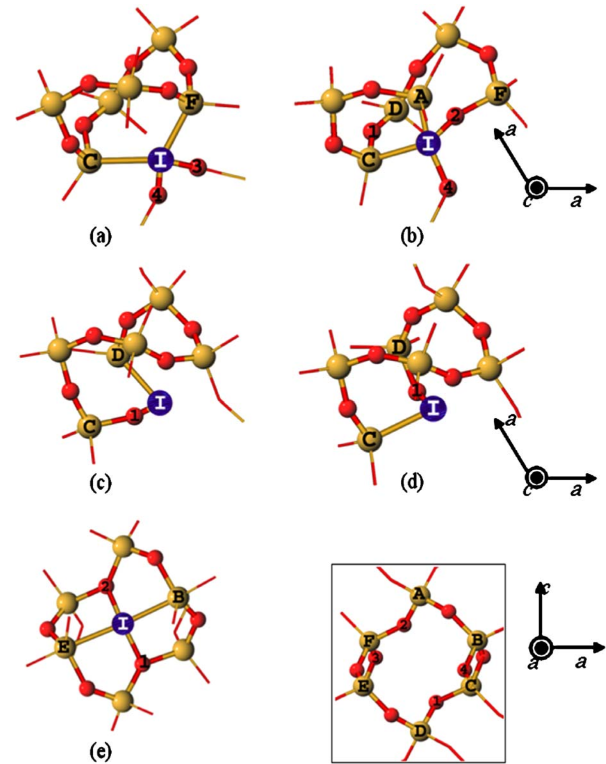

FIG. 1. (Color online) Configurations of excess Si in α-quartz: (a) FC_I; (b) FC_{II}; (b) BC_I; (d) BC_{II}; (e) RC. The inset shows the structure of α-quartz. [The fourfold coordinated (FC) and bond centered (BC) structures are projected on a plane perpendicular to the c-axis, while the ring centered (RC) and α-quartz structures are on a plane perpendicular to the a-axis.] An excess Si atom is indicated I, and its neighboring Si [in yellow (light)] and O [in red (dark)] lattice atoms are also indicated accordingly.

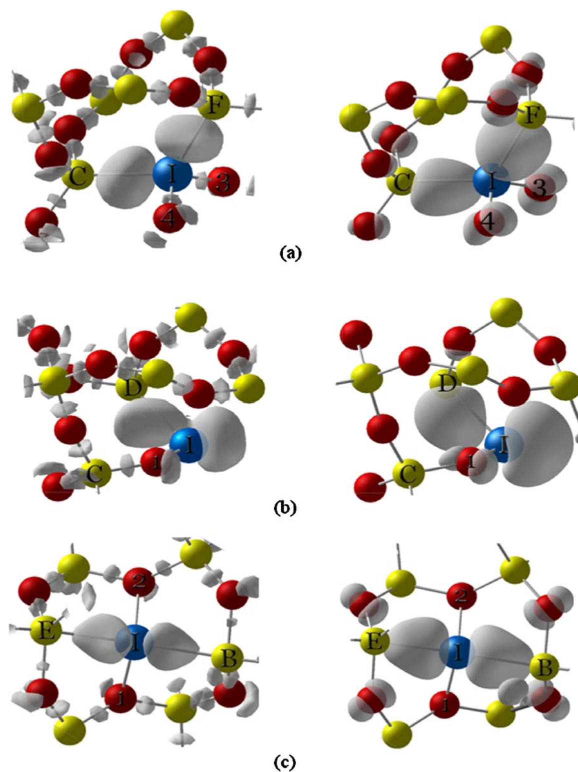

FIG. 2. (Color online) Isosurfaces of electron localization functions (at the value of 0.82) (left panels) and decomposed charge densities (right panels) of (a) the FC_I, (b) BC_I, and (c) RC state of excess Si in α-quartz. The decomposed charge densities represent the energy ranges where two shaded sharp peaks appear in the plot of densities of states (Fig. 3) for corresponding excess Si states.

Next, we look at the diffusion of excess Si atoms in α-quartz taking into account the local minimum states identified above, such as FC↔BC, BC↔BC, BC↔RC. The FC↔BC hopping may occur in two ways: $FC_I \leftrightarrow BC_{II}$ and $FC_{II} \leftrightarrow BC_I$. The corresponding forward/backward barriers are predicted to be 1.8/1.3 eV and 1.7 eV/1.5 eV, respectively. We also checked $FC_{II} \leftrightarrow BC_{II}$, but it turns out to be unlikely. For the BC↔BC hopping (over a lattice Si), three different channels are identified: $BC_I \leftrightarrow BC_I$, $BC_I \leftrightarrow BC_{II}$, and $BC_{II} \leftrightarrow BC_{II}$, with corresponding barriers of approximately 2.6 eV, 1.9 eV, and 2.1 eV. Recall that BC_I and BC_{II} are degenerate, so the forward and backward barriers are identical. The BC↔BC barrier appears to be a function of the bond topology of O-Si-O neighbors (that are directly involved in the Si diffusion.) For instance, in the $BC_I \leftrightarrow BC_I$, $BC_I \leftrightarrow BC_{II}$, and $BC_{II} \leftrightarrow BC_{II}$ cases, the O-Si-O bond angles (prior to the excess Si insertion) are 109.7°, 108.5°, and 109.1°, respectively. This suggests the barrier can be a strong function of the O-Si-O angle. We also calculate a barrier of 1.9 eV for exchange between the BC Si and adjacent O atoms. Our calculations also predict that BC↔RC hopping may occur by crossing forward/backward barriers of approximately 1.8/0.6 eV while leading to Si diffusion in the c-axis direction.

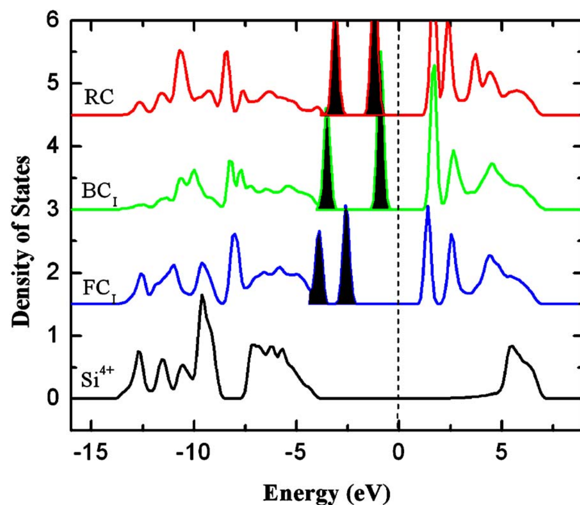

FIG. 3. (Color online) Local density of states of excess Si in the FC_I, BC_I, and RC states, together with that of lattice $Si(Si^{4+})$ in defect free α-quartz. The Fermi level for Si^{4+} is set at 0 eV, and excess Si DOS plots are aligned at the O $2s$ band of Si^{4+}.

Based on these results, we suggest three possible diffusion pathways for excess Si atoms between two FC_I states (that are the possible lowest energy states):

(1) $FC_I \rightarrow BC_{II} \rightarrow BC_{II} \rightarrow FC_I$;
(2) $FC_I \rightarrow BC_{II} \rightarrow RC \rightarrow BC_{II} \rightarrow FC_I$; and
(3) $FC_I \rightarrow BC_{II} \rightarrow BC_I \rightarrow BC_{II} \rightarrow FC_I$.

Corresponding overall barriers are predicted to be 2.6 eV, 2.2 eV, and 2.4 eV, respectively, under the steady state approximation. Note that these diffusion barriers are much smaller than recent experimental estimations of 5–7.6 eV (Ref. 6, 8, and 10) and 4.7–5 eV,[9] respectively, for Si diffusion in stoichiometric SiO_2 (under equilibrium) and Si-rich amorphous SiO_2 (under nonequilibrium). This suggests that excess Si atoms in α-quartz, if they exist, could be more mobile.

B. Defect-free amorphous SiO_2

We identify stable FC and BC structures of excess Si in a-SiO_2. However, the RC state turns out to be unfavorable simply because of the lack of *symmetric* six-member rings in the amorphous layer. For good statistics, we examine the structure and energetics of excess Si at many different locations using five different (72-atom) a-SiO_2 supercells. We find that the amorphous network can render very stable FC structures with minimal strain. However, such stable FC sites may not exist as many as FC sites in crystalline quartz because of the sparse/disordered nature of amorphous oxide structures. Depending on the local bonding environment, there is a significant site-to-site variation in the eneregtics of BC sites, as much as 1.5 eV among sampled sites in this work. Nonetheless, knowing that the energy gain of the FC state over the BC state is mainly attributed to formation of additional Si-Si and Si-O bonds, we can approximate the energy difference between fully relaxed FC and BC structures using cluster model calculations (which may yield minimal strain energies). Thus, as illustrated in Fig. 4, we calculate a model reaction of $(OH)_3Si\text{-}Si\text{-}O\text{-}Si(OH)_3$ and $(OH)_3Si\text{-}O\text{-}Si(OH)_3$ to form $(Si(OH)_3)_2\text{-}Si\text{-}(O\text{-}Si(OH)_3)_2$,

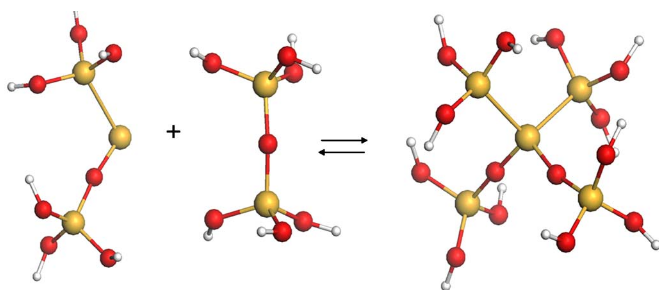

FIG. 4. (Color online) Cluster model used to examine the relative stability of BC and FC structures of excess Si in amorphous SiO_2 where the structures are assumed to be fully relaxed. Big yellow (light), small red (dark), and small white balls represent Si, O, and H atoms, respectively.

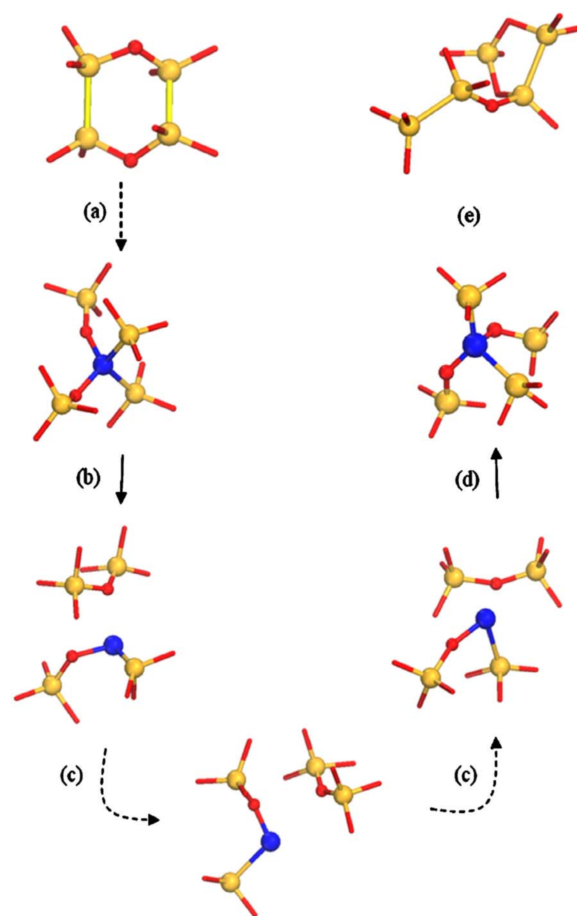

FIG. 5. (Color online) Proposed diffusion mechanism for an excess Si atom in amorphous SiO_2: (a) O hopping to a Si-Si BC site (or O vacancy diffusion); (b) Si hopping from a FC site to a BC site, (i.e., FC-to-BC reconfiguration of excess Si); (c) Si hopping from a BC site to a BC site; (d) Si hopping from a BC site to a FC site, (i.e., BC-to-FC reconfiguration of excess Si); (e) O hopping to a Si-Si BC site (to create two separate Si^{3+}-Si^{3+} charge configurations, i.e., two separate oxygen vacancies). Big yellow (light) and blue (dark) balls represent lattice Si and excess Si atoms, respectively, and small red (dark) balls indicate lattice O atoms. Solid arrow indicates single step events and dashed arrows represent multiple step events (or a series of single step events).

which may mimic the transformation of BC to FC by forming new Si-Si and Si-O bonds while breaking one Si-O bond. In the exothermic reaction, the energy gain is predicted to be 1.8 eV. This suggests the possible existence of very stable FC structures which can be about 1.8 eV more stable than fully relaxed BC structures. Indeed, such stable FC and BC structures (with a nominal strain energy) could be generated by lattice relaxation in the (rather flexible) amorphous oxide network. Recall that, in α-quartz (which has a rigid lattice structure,) the FC state is only about 0.57 eV more stable than the BC state due to larger strain resulting from greater lattice distortions.

The FC structure yields the Si^{3+}-Si^{2+}-Si^{3+} charge configuration (with two adjacent O vacancies); that is, the charge states of the introduced Si and adjacent Si lattice atoms are 2+ and 3+, respectively. Here, we can expect the migration of a neighboring O atom to a Si-Si BC site, rendering the Si^{3+}-Si^{3+}-Si^{3+}-Si^{3+} charge configuration (with two separate O vacancies). Allowing successive O migration to a Si-Si BC site (and/or O-vacancy diffusion which might not involve O migration), the introduced Si atom can be fully integrated into the amorphous network, with two separate Si^{3+}-Si^{3+} charge configurations, (i.e., two isolate O vacancies). The resulting change in the suboxide penalty energy is minimal, according to $Si^{4+}=0.0$, $Si^{3+}=0.24$, $Si^{2+}=0.51$, and $S^{i+}=0.47$ in eV, as recently reported.[23] This suggests the separate charge state is energetically comparable to the FC state, if both are fully relaxed.

Based on these fundamental findings we propose a novel mechanism for Si diffusion in Si-rich a-SiO_2. As illustrated in Fig. 5, this diffusion model involves: (a) O-vacancy diffusion and pairing to form a FC Si structure, (b) transformation from the FC state to the BC state, (c) Si diffusion jumps between BC sites, (d) transformation from the BC state to the FC state, and (e) O-vacancy separation. Due to the disordered nature of a-SiO_2, the diffusion barriers exhibit a significant site-to-site variation. However, our extensive calculations suggest that the overall barrier can primarily be determined by O-vacancy diffusion [(a)] or/and FC$\rightarrow$BC reconfiguration [(b)]. In a well-relaxed structure, the barriers for both O-vacancy diffusion (accompanied by O diffusion) and FC$\rightarrow$BC reconfiguration are predicted to be approximately 4.5 eV. (We should point out that O-vacancy migration could also occur following the bistable behavior[24] with a lower barrier than O hopping.) The barrier for Si diffusion between BC sites varies from 2.2 eV to 3.2 eV, depending on the local geometry as discussed earlier. Considering the energy difference of about 1.8 eV between fully relaxed FC and BC structures, the overall barrier for Si diffusion in Si-rich a-SiO_2 is approximated to be 4.5–5.0 eV. This is in good agreement with 4.74 ± 0.25 eV as estimated from recent experiments in which Si atoms were introduced in excess in stoichiometric SiO_2.[9] We also expect that Si diffusion could take place by forming Si-O pairs,[11] and the relative contribution between the mechanisms based on Si-O pairs and Si atoms (proposed herein) depends on the concentration of excess Si atoms, (i.e., the density of O vacancies). The detailed comparison will be reported elsewhere.

IV. SUMMARY

The structure, energetics, bonding, and diffusion of excess Si atoms in defect-free crystalline quartz and amorphous SiO_2 layers have been examined using planewave basis, pseudopotential total energy calculations. In α-quartz, three stable configurations of an excess Si atom are identified: (1) fourfold coordinate (FC) where the Si atom is bonded to neighboring two Si and two O lattice atoms by breaking two Si-O bonds; (2) bond center (BC) where the Si atom is located at the center of a Si-O bond; and (3) ring center (RC) where the Si atom is located at the center of a six-member ring by weekly interacting with Si and O neighbors. The BC and RC structures are, respectively, 0.57 eV and 1.8 eV less favorable than the most stable FC structure. Excess Si atoms in α-quartz are predicted to undergo diffusion with a moderate barrier of about 2.2–2.6 eV, while their presence and behavior have not been reported experimentally. In amorphous SiO_2, stable FC and RC structures are identified, but the RC state appears to be unlikely because of the lack of *symmetric* six-member rings. By virtue of the ease of bond rearrangement, the amorphous network can yield very stable FC and BC structures with minimal strain. The fully relaxed FC structure is predicted to be about 1.8 eV more favorable than the fully relaxed BC structure. The FC structure is further transformed to two isolated O vacancies via successive O vacancy diffusion, with no significant energy change. Through this processes, an excess Si atom can be fully incorporated into the amorphous oxide network. Based on these fundamental findings, we propose a novel mechanism for Si diffusion in Si-rich a-SiO_2, involving O-vacancy diffusion and pairing, reconfiguration between FC and BC states, and excess Si diffusion between BC sites. The overall barrier is predicted to be approximately 4.5–5.0 eV, in good agreement with recent experimental measurements of 4.74 ± 0.25 eV for Si diffusion in Si-rich amorphous SiO_2.

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