

Structure and dynamics of silicon-oxygen pairs and their role in silicon self-diffusion in amorphous silica

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Based on gradient corrected periodic density functional theory calculations, we present the formation, structure, and diffusion of SiO pairs in *a*-SiO₂. We find that a SiO pair preferentially undergoes transformation into an O vacancy through a twofold-coordinated Si atom. We determine the pathways for SiO pair → divalent Si → O vacancy transformation and divalent Si diffusion, along with O vacancy diffusion. Based on these results, we also discuss how the presence of SiO pairs can enhance Si self-diffusion in *a*-SiO₂. © 2008 American Institute of Physics.

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I. INTRODUCTION

Defect structure and diffusion in thermally grown silica (SiO₂) on silicon (Si) has long been a subject of great interest because of their important role in development of silicon-based devices, particularly for complementary metal oxide semiconductor (CMOS) transistors. With continued scaling of CMOS devices, a mechanistic understanding of the atomic and molecular diffusions of defects and impurities in an ultrathin SiO₂ layer becomes an important issue. In addition, a better description of defect formation and diffusion during Si oxidation can contribute to the advance of not only CMOS technologies but also future nanoscale Si-based device applications.

It is now well established that a large fraction of Si lattice atoms are emitted during thermal Si oxidation or high-temperature thermal treatment, due to a volume mismatch (of 50% per Si atom) between crystalline Si (*c*-Si) and amorphous SiO₂ (*a*-SiO₂). A series of previous experiments¹⁻³ have evidenced that Si self-diffusion in thermally grown *a*-SiO₂ is strongly influenced by the presence of SiO pairs (which are assumed to be emitted from the Si/SiO₂ interface and diffusing into SiO₂). For instance, the Si self-diffusivity increases by about an order of magnitude, as the amount of SiO pairs increases as a result of SiO₂ thickness reduction from 650 to 200 nm.² It is also interesting to note that the diffusivity increase is mainly attributed to the increase in the prefactor, rather than in the activation energy.^{1,3-5} In addition, SiO pairs generated at the Si/SiO₂ interface may cause gate oxide degradation in MOS devices,^{6,7} and also their presence has been found to enhance diffusion of dopants such as boron in *a*-SiO₂.^{8,9} Despite its increasing importance in the fabrication and performance of ever smaller Si-based devices, the fundamental behavior of SiO pairs in *a*-SiO₂ and their role in Si and dopant diffusion remain unclear.

In this paper, the fundamental behavior of SiO pairs and their role in Si self-diffusion in *a*-SiO₂ are presented based on gradient corrected density functional theory calculations. We first determine the structure of a single SiO molecule,

and its transformation into other related defects such as divalent Si and O vacancy. Then, we calculate the diffusion pathways and barriers of the SiO related defects. Based on these results, we also discuss how Si self-diffusion can be influenced by the presence of SiO pairs in the *a*-SiO₂ matrix.

II. COMPUTATIONAL METHOD

All atomic structures and energies reported herein were calculated using a plane-wave-basis set pseudopotential method within the generalized gradient approximation of Perdew and Wang¹⁰ to density functional theory (DFT), as implemented in the well-established Vienna *ab initio* simulation package (VASP).¹¹ Vanderbilt-type ultrasoft pseudopotential¹² were used for core-electron interactions. A plane-wave cutoff energy of 300 eV was used. Brillouin zone sampling was performed using a (2 × 2 × 2) mesh of *k* points in the scheme of Monkhorst-Pack, sufficient for the disordered SiO₂ structures considered in this work. We checked carefully the convergence of atomic configurations and relative energies with respect to the plane-wave cutoff energy and the *k*-point mesh size. All atoms were fully relaxed using the conjugate gradient method until residual forces on constituent atoms become smaller than 5 × 10⁻² eV/Å. We calculated the diffusion pathways and barriers of SiO pairs and O vacancies under the static approximation using the nudged elastic band method, which allows systematic search for a minimum energy pathway between two local minima with no prior knowledge about a potential energy surface.

We considered three periodic models of *a*-SiO₂, of which one consists of 24 SiO₂ units and the other two have 32 SiO₂ units, showing that there is no significant supercell size effect. The model systems have been indeed demonstrated to be sufficient in size to determine the behavior of single defects within.¹³ For good statistics, the structure and energetics of defects were calculated at more than ten different locations in the three *a*-SiO₂ supercells considered. The *a*-SiO₂ systems were constructed using a continuous random network model¹⁴ with fourfold-coordinated Si and twofold-coordinated O. Starting with randomly distributed Si and O atoms in a given supercell with a fixed experimental density of 2.2 g/cm³, the SiO₂ system was relaxed via a sequence of

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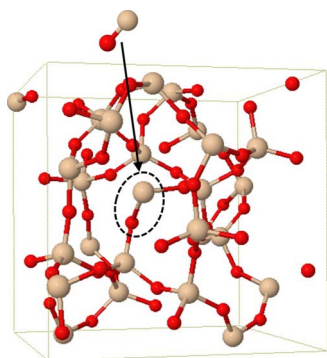


FIG. 1. (Color online) Atomic structure of a SiO pair in a -SiO₂. The enclosed shows SiO pair insertion into the a -SiO₂ matrix, resulting in the formation of a divalent Si atom. The small dark (red) and big gray (pink) balls represent O and Si atoms, respectively.

bond transpositions using the Metropolis Monte Carlo sampling method based on Keating-type interatomic potentials.¹³ The amorphous structures were further refined using DFT calculations. For the fixed density of 2.2 g/cm³, our computed a -SiO₂ structures yield the average Si–O bond length of ≈ 1.61 Å, the average Si–O–Si bond angle $\approx 136^\circ$, and the bond angle deviation of $\approx 15^\circ$. In the a -SiO₂ matrices, five- and six-member rings are prevailing with three-, four-, and seven-member rings. The calculated structural properties are in good agreement with previous experiments¹⁵ and first principles calculations.^{16–18}

III. RESULTS AND DISCUSSION

A. SiO pair structure

We first determined the structure of SiO pair in the neutral state by inserting a SiO molecule in the a -SiO₂ matrix considered. As illustrated in Fig. 1, the SiO molecule preferentially exists in the form of twofold-coordinated Si atom (=Si: where the—indicates a Si–O bond and the: designates a lone electron pair) while breaking an original Si–O bond. The resulting energy gain varies from 0.20 to 1.30 eV, depending on the local geometry.¹⁹ Here, the energy gain (ΔE) is given as

$$\Delta E = E_{a\text{-SiO}_2/\text{SiO}} - E_{a\text{-SiO}_2} - E_{\text{SiO}(g)},$$

where, $E_{a\text{-SiO}_2/\text{SiO}}$ and $E_{a\text{-SiO}_2}$ are the total energies of a -SiO₂ supercell with and without a SiO pair, respectively, and $E_{\text{SiO}(g)}$ is the energy of gas-phase SiO molecule in the singlet ground state. Given the ease of transformation, we can consider the SiO pair and the divalent Si defect to be equivalent.

As mentioned in the introduction, it is rather well established that oxidation-induced interface strain is relieved through emission of Si lattice atoms from the interface. Earlier experiments^{1–5} assumed that SiO pairs emitted from the Si/SiO₂ interface diffuse into the a -SiO₂ layer, while previous first principles studies²⁰ demonstrated emission of twofold-coordinated Si atoms from the interface during oxidation. This is, in fact, consistent with our finding of the interconversion of SiO pair and divalent Si defect (which has two Si–O bonds and an electron lone pair).

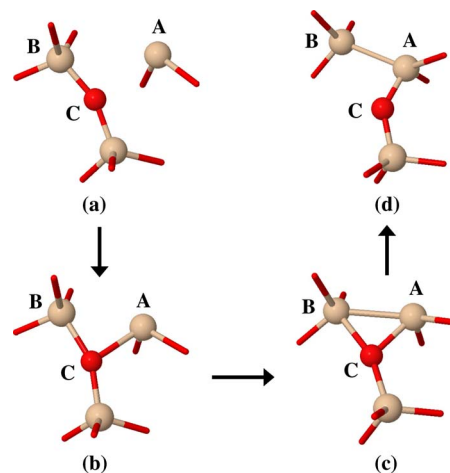


FIG. 2. (Color online) Predicted path for transformation of a divalent Si (a) into an O vacancy (d), which involves the dative interaction between the divalent Si atom A and the neighboring O atom C (b), followed by the interaction of the negative lone pair of divalent Si atom A with the adjacent Si atom B (c). The small dark (red) and big gray (pink) balls represent O and Si atoms, respectively.

Our calculations also show that a divalent Si defect may further undergo transformation into an O vacancy by breaking a Si–O bond, i.e., =Si: + –O–Si≡ → ≡Si–Si≡, with an energy gain of around 1.0–2.0 eV. As shown in Fig. 2, this transformation is initiated by the dative interaction of the empty p orbital of the divalent Si atom (indicated as A) with a lone pair of the neighboring O atom (indicated as C). This is almost simultaneously followed by the interaction of the negative lone pair of the divalent Si (A) with an adjacent Si (indicated as B), leading to O vacancy formation while breaking the original Si–O bond.

The energy barrier for the divalent Si → O vacancy transformation turns out to be a strong function of the =Si: plane orientation with respect to the direction of O lone pairs. This is not surprising considering the importance of the dative interaction between the divalent Si empty p orbital and a neighboring O lone pair. Furthermore our extensive density functional calculations show that this transformation barrier is also highly correlated with the dihedral angle ϕ (created by two intersecting planes) and the bend angle θ ($\angle BCA$), as indicated in Fig. 3. When the bend angle θ is smaller than 95° and the dihedral angle ϕ ranges from 30° to 45° , the lone pair of the divalent Si (A) can easily interact with the adjacent Si (B) to break the Si–O bond (B–C), leading to the formation of a stable O vacancy. When the dihedral angle ϕ and the bend angle θ are within this range, the energy barrier for the divalent Si → O vacancy transformation is predicted to be lower than 1.6 eV. Here, we consider the nature of a neutral SiO pair that favorably exists as a dicoordinated Si (=Si:) or an O vacancy (≡Si–Si≡). It might be also worthwhile to note that the diamagnetic oxygen deficient centers can be converted to paramagnetic E' centers (≡Si·, threefold-coordinated Si with an unpaired electron) upon UV irradiation in a -SiO₂. In addition, E'_g centers (≡Si· + Si≡) can be created by irradiation-induced positive ionization of O vacancy and divalent defects.

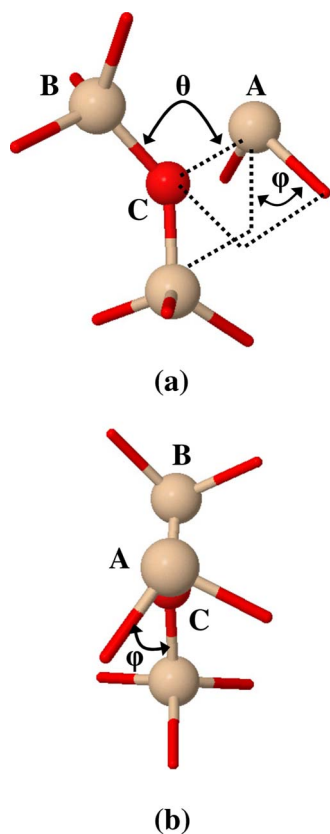


FIG. 3. (Color online) The relative position of a divalent Si (indicated as A) with respect to the neighboring Si lattice atom B and O lattice atom C, defined in terms of the bend angle θ and the dihedral angle ϕ as indicated. The small dark (red) and big gray (pink) balls represent O and Si atoms, respectively.

B. SiO pair diffusion

Figure 4 shows a viable pathway for divalent Si diffusion in α -SiO₂, which we have identified based on density functional calculations. The first step involves the dative interaction of the divalent Si atom (indicated as A) with a neighboring O lattice atom (indicated as D) to form a saddle structure where the O atom is threefold coordinated. This step is followed by an electrostatic interaction between the adjacent Si (indicated as C) and O (indicated as B) lattice atoms, resulting in an intermediate two-member ring. Subsequently, two Si–O bonds (A–B and C–D) break to yield a new divalent Si configuration where the Si atom is linked to the O atoms (D and E), as opposed to the original bonds with the O atoms (B and E). Following the mechanism, the divalent Si atom may undergo diffusion until converting to another stable O vacancy.

Like the divalent Si→O vacancy reconfiguration, the energy barrier for divalent Si diffusion is likely determined by the dihedral (ϕ) and bend (θ) angles as well as the =Si: plane orientation, with respect to the direction of O lone pairs. Our calculations show that when θ is greater than 100° while ϕ ranges from 0° to 30° the divalent Si readily interacts with the neighboring Si and O lattice atoms which are directly involved in the Si atom hopping. Therefore, the divalent Si diffusion barrier can be as low as 0.5 eV when θ and ϕ are within this range.

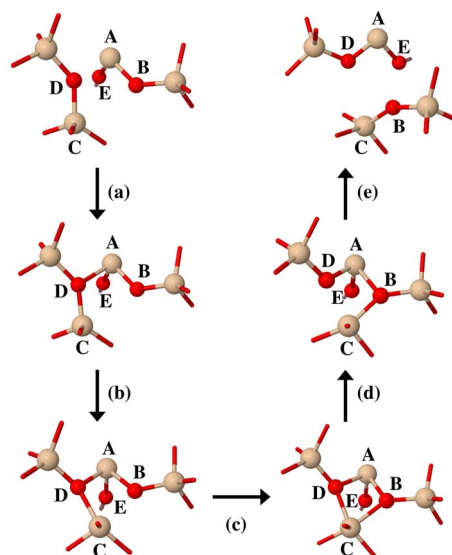


FIG. 4. (Color online) Predicted path for divalent Si atom diffusion in α -SiO₂, involving dative interaction of the divalent Si atom A with the neighboring O atom B (a); electrostatic interaction between the adjacent Si atom C and O atom B, resulting in an intermediate two-member ring [(b) and (c)]; and subsequent A–B and C–D bond break which yields a new divalent Si atom [(d) and (e)]. The small dark (red) and big gray (pink) balls represent O and Si atoms, respectively.

C. O vacancy diffusion

Since a divalent Si defect (or SiO pair) can be transformed into an O vacancy as discussed earlier, we also looked at O vacancy diffusion (which occurs by a series of O hops between adjacent O vacancy sites). Unlike crystalline silica, the O diffusion barrier in α -SiO₂ varies significantly from site to site, depending on the local geometry around the O vacancy, particularly the bend angle between the three Si atoms directly involved in the O migration, as illustrated in Fig. 5. When the bend angle is sufficiently small, the pronounced interaction of the migrating O atom with the neighboring Si atoms will significantly lower the diffusion barrier, compared to 4.6 eV as obtained for direct O hopping in crystalline SiO₂. For a few selected cases, our calculations yield diffusion barriers of as low as 2.8–3.6 eV. On the other hand, when the bend angle is as large as the crystalline SiO₂ case, O migration occurs by direct hopping to a neighboring O vacancy site. The corresponding diffusion barrier is predicted to be around 4.5–5.0 eV. Despite the significant variation of O hopping barrier with the local geometry, we can expect that the overall activation energy for O vacancy diffusion is mainly governed by the large barriers.

Based on our calculation results, we attempt to draw a physical picture for SiO pair diffusion in amorphous SiO₂. This involves a combination of SiO pair (or divalent Si) diffusion; interconversion between SiO pairs and O vacancies; and O vacancy diffusion. The rate-determining step in the diffusion process should be O vacancy hopping which requires overcoming a barrier of as high as 4.5–5.0 eV. The energy barrier for O vacancy→SiO pair transformation is predicted to be 2.8–3.6 eV, while the SiO (or divalent Si) migration barrier is as low as 0.5 eV. This also suggests that Si self-diffusion could occur in the form of SiO pair (or

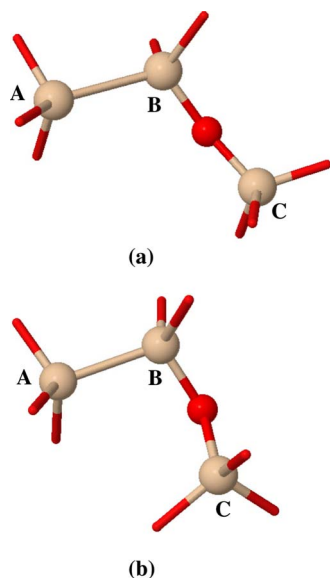


FIG. 5. (Color online) Illustrations of two different local geometries around an O vacancy site in a -SiO₂: (a) the $\angle ABC$ bend angle is greater than 110° , in which direct O hopping requires overcoming a barrier as high as in crystalline silica; (b) the $\angle ABC$ bend angle is less than 110° , in which the migrating O atom has a rather strong interaction at the saddle point with the neighboring three Si atoms (A, B, and C), thereby yielding a far lower barrier.

divalent Si), by overcoming an overall barrier of 4.5–5.0 eV while the prefactor depends on the availability of SiO pairs (or divalent Si defects).

We should point out that Si self-diffusion may also occur in the form of bond-centered (BC) Si which can be generated via pairing of two O vacancies¹³ and/or other O-vacancy related defects such as S centers (which may warrant further investigation). The BC diffusion mechanism is predicted to yield the overall barrier of 4.5–5.0 eV because it is also determined by O vacancy migration, while BC Si diffusion requires overcoming a far lower barrier (in the range of 2.2–3.2 eV, depending on the local geometry). The results suggest that Si self-diffusion can be facilitated by the presence of SiO pairs (which preferentially exist in the form of O vacancies), as a result of an increase in the prefactor while the overall activation energy remain nearly unchanged. This is consistent with existing experimental observations.^{1–3}

IV. CONCLUSION

In summary, we have examined the formation, structure and diffusion of SiO pairs in a -SiO₂ using plane-wave basis, pseudopotential total energy calculations. Our results show that in a -SiO₂ a SiO pair is easily transformed to a divalent Si defect which further converts to an O vacancy while breaking original $\equiv\text{Si}-\text{O}$ bonds, i.e., $\text{SiO} \rightarrow \equiv\text{Si} \cdot \rightarrow \equiv\text{Si}-\text{Si}\equiv$. The corresponding energy gains are predicted to

be around 0.2–1.3 eV and 1.0–2.0 eV, respectively, depending on the local geometry. Our calculations also predict that the barrier for Si diffusion in the form of divalent Si can be as low as 0.5 eV, but the overall activation barrier is primarily determined by O vacancy hopping, which is as high as 4.5–5.0 eV. This suggests that the presence of SiO pairs (equivalent to O vacancies) may facilitate Si self-diffusion by mainly increasing the prefactor, with no significant change in the overall activation energy, consistent with existing experimental observations. The improved understanding will assist in developing a predictive physical model for thermal Si oxidation as well as complex defect and dopant diffusion in the a -SiO₂ matrix.

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