

Oxygen-induced atomic desorptions in oxynitrides: Density functional calculations

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The role of atomic oxygen, O_2 , and NO molecules in the nitrogen and oxygen removal processes observed during the thermal growth of oxynitride (SiO_xN_y) films is addressed by spin density functional calculations. Our results show that the energetically most favorable N-desorption mechanism would be induced by O_2 reacting with the Si-[NO]-Si structure in SiO_2 , where nitrogen is released from the network as an interstitial NO molecule, leaving a peroxy linkage (Si-O-O-Si) in its place. Atomic O diffusing via peroxy linkage also removes nitrogen from the Si-[NO]-Si structure. However, this reaction has an occurrence rate of about 10^4 times smaller than the most favorable one. We also identify an oxygen exchange mechanism occurring through the annihilation of two peroxy O atoms when they approach each other, where oxygen is released from the network as an O_2 molecule leaving a perfect SiO_2 structure. The energetics of other possible scenarios for atomic desorptions in SiO_xN_y are also discussed.

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I. INTRODUCTION

Ultrathin films of silicon oxynitride (SiO_xN_y) are becoming increasingly important in semiconductor technology since they are replacing silicon oxide (SiO_2) for ultrathin gate dielectrics (<4 nm) in metal-oxide-semiconductor field-effect transistors. In addition to the enhanced reliability, SiO_xN_y gate dielectrics have the ability to suppress boron penetration and improve hot carrier resistance as compared to SiO_2 .¹ Although SiO_xN_y films are considered near-term solutions to the continuous scaling down of gate thickness due to their relatively low dielectric constant (κ), recent works indicate that intermediate SiO_xN_y layers between high- κ dielectric materials and silicon can improve the interfacial properties as compared to high- κ films on Si.² In particular, HfO_2 - SiO_xN_y gate stack dielectrics have shown higher resistance to leakage currents and oxygen migration as well as lower N loss due to N-O exchange reactions.^{3,4}

Whereas much progress has been made in the growth and characterization of SiO_xN_y films, some important issues regarding the incorporation reaction and the chemical stability of N atoms into the film are poorly understood. An example of that is the thermally grown mechanism of SiO_xN_y films on SiO_2 in N_2O and NO atmospheres.^{5,6} Isotopic labeling studies have shown significant O replacements as well as N removal and relocation into the films during the growth process.^{7,8} Atomic oxygen, previously incorporated in the oxide network as a peroxy defect (Si-O-O-Si), has been pointed out as the main responsible for the N-removal process. According to experimental suggestions,⁸ peroxy O atoms diffuse through the oxide until they reach incorporated N atoms, which would be removed from the network in the form of a nonreacting molecular species. In this work we investigate N- and O-desorption mechanisms as induced by peroxy oxygens and O_2 and NO interstitials, using first principles calculations. Although O_2 and NO are considered non-

reactive diffusing species in SiO_2 , their role in the N-removal process during the oxynitride growth is not yet clarified.

II. THEORETICAL APPROACH

The calculations were performed in the framework of the density functional theory, using a basis set of localized numerical atomic orbitals as implemented in the SIESTA code.⁹ We used a split-valence double- ζ basis set plus polarization (DZP) functions, and standard normconserving pseudopotentials to describe the electron-ion interaction.¹⁰ For the exchange-correlation term we adopted the generalized gradient approximation.¹¹ We used a 72-atom α -quartz supercell, considering the Γ point for sampling of the Brillouin zone (BZ) in the irreducible wedge. We have checked our results increasing to 4 k points the BZ sampling according to the Monkhorst-Pack¹² approximation, the difference in total energy between the Γ and 4 k -point calculations is found to be 0.003 eV/cell. The positions of all the atoms in the supercell were relaxed using a conjugate gradient algorithm until all the force components become smaller than 0.05 eV/Å.

Spin-polarization effects are included throughout the calculation since they are important for the correct description of the reactant species (O atom and O_2) inside SiO_2 .¹³ We consider the neutral reactants O_2 and NO since they are able to diffuse through SiO_2 with lower energy barriers with respect to charged ones, as recently suggested by first-principles calculations.¹⁵ Two bonding configurations around the N atom are considered as our local oxynitride model (hereafter incorporated N structures): (i) the N atom binds to two Si atoms forming the Si-N-Si structure, and (ii) the N atom binds to two Si and one O atom, forming the Si-[NO]-Si structure. Si-[NO]-Si is commonly found at near interface regions of SiO_xN_y thermally grown on SiO_2 in N_2O and NO atmospheres.^{16,17} Although Si-N-Si seems to be less favorable due to the undercoordinated nitrogen, we find that

this structure is energetically stable, thus we cannot exclude its occurrence as a possible oxynitride geometry. The reaction paths were found by mapping the different transition regions, searching for the energetically favorable saddle point geometries. Initially, the reactants were placed at several positions around a saddle point, allowing the system to relax. Once the saddle-point geometry is optimized, the reactant is left to evolve from this point to the minima driven by the force field.

III. RESULTS AND DISCUSSION

A. O₂ and NO molecules reacting with the incorporated N structures

Results for the total-energy variations along the reaction paths for NO and O₂ interstitials reacting with incorporated nitrogen in SiO₂ are shown in Fig. 1. The atomic structures in the figures represent the local equilibrium geometries at their respective minima. Figure 1(a) shows the reaction path between a NO molecule approaching the Si-N-Si structure. The starting position in the reaction path represents the NO molecule in a noninteracting interstitial site [A in Fig. 1(a)]. We observe that the NO binds strongly to the N atom of Si-N-Si, with a binding energy of 1.94 eV. The overall N-removal reaction $\text{Si-N-Si} + \text{NO} \rightarrow \text{Si-O-Si} + \text{N}_2$ is exothermic, with an energy gain of 3.55 eV. The energy barriers through the reaction path are found to be approximately 1.8 eV and 1.5 eV [C and E in Fig. 1(a), respectively]. We also find that the NO molecule approaching with its O atom facing the Si-N-Si structure is repelled. It is important to note that the whole reaction occurs in a spin singlet ($S=0$) reaction path. We also investigate other reactions involving the NO molecule with the Si-[NO]-Si structure (not shown). A stable geometry is found when the N atom of NO binds to the O atom of Si-[NO]-Si. The binding energy of the NO molecule in this configuration is found to be 1.92 eV. However, after considering several geometries that might initiate NO incorporation reactions, no energetically favorable N-removal processes were found. This result suggests that interstitial NO does not remove nitrogen from Si-[NO]-Si structures in SiO_xN_y, supporting available experimental data.^{7,18}

Figure 1(b) shows another possible N-removal mechanism from Si-N-Si as induced by an interstitial O₂. Here the oxygen molecule, initially in a noninteracting interstitial site, binds to nitrogen, forming a stable structure with a binding energy of about 1.1 eV [B in Fig. 1(b)]. The N-removal reaction $\text{Si-N-Si} + \text{O}_2 \rightarrow \text{Si-O-Si} + \text{NO}$ is exothermic, with an energy gain of 3.57 eV and it occurs in a spin doublet ($S=1/2$) reaction path. The energy barrier for the N-removal process is found to be ~ 1.6 eV [C in Fig. 1(b)]. However, as this barrier is higher than the O₂ binding energy to the Si-N-Si structure (1.1 eV), it is more likely that a thermally activated O₂ desorbs from the Si-N-Si than initiates a N-removal process. Finally, Fig. 1(c) shows that the most probable N-removal process occurs when an interstitial O₂ reacts with the Si-[NO]-Si structure, where the final product is a peroxy linkage plus an interstitial NO molecule. The reaction $\text{Si-[NO]-Si} + \text{O}_2 \rightarrow \text{Si-O-O-Si} + \text{NO}$ is exothermic,

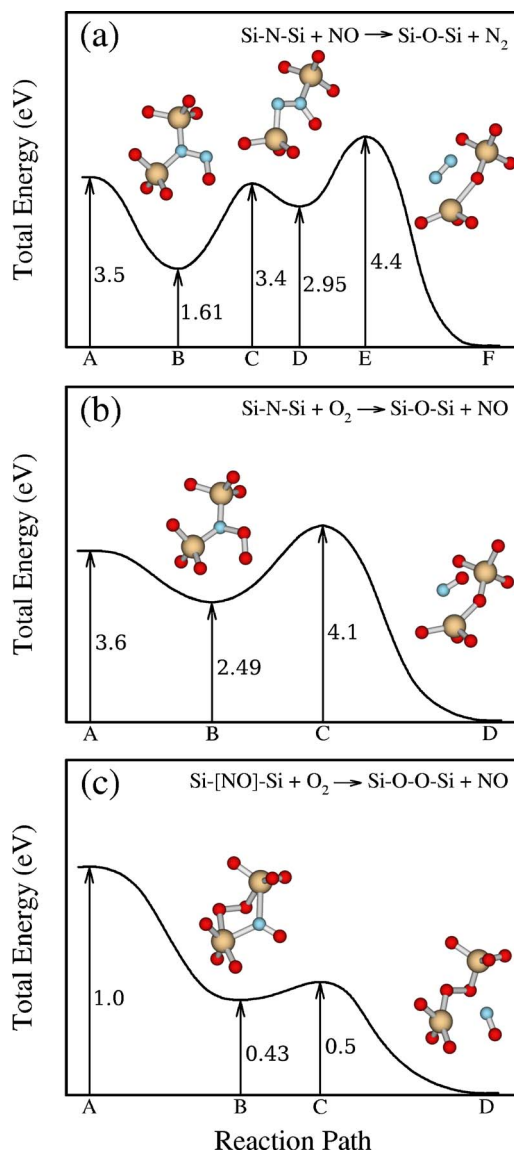


FIG. 1. (Color online) Total-energy variation along the reaction paths for different N-desorption mechanisms induced by the interstitial molecules NO and O₂. (a) NO reacting with Si-N-Si. (b) O₂ reacting with Si-N-Si. (c) O₂ reacting with Si-[NO]-Si. The reaction paths initiate with NO and O₂ at open interstitial positions in the oxide. The atomic structures represent the local equilibrium geometries at the metastable positions.

with an energy gain of 1.02 eV, and it occurs in a spin doublet reaction path. The metastable equilibrium geometry [B in Fig. 1(c)] is found when O₂ approaches the Si-[NO]-Si bonding structure from the N-atom side, otherwise O₂ is repelled. NO is removed from the oxynitride structure after overcoming a very small energy barrier of about 0.1 eV, while O₂ is simultaneously incorporated in its place. However, the energy profile of Fig. 1(c) suggests that this reaction occurs as if it is barrierless. Therefore, diffusing O₂ would be an important precursor for the nitrogen removal from Si-[NO]-Si structures as well as for the oxygen replacement during the oxynitride growth.

Figure 2 shows the energetically favorable saddle point geometries of desorption reactions induced by NO, O₂ and

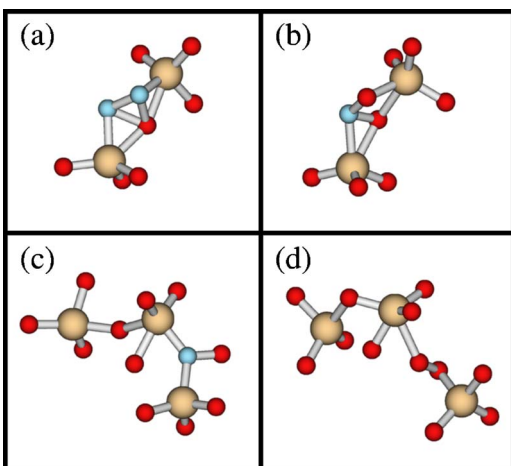


FIG. 2. (Color online) Saddle point structures of desorption reactions in nitrated SiO_2 . (a) Interstitial NO reacting with Si-N-Si [E in Fig. 1(a)]. (b) Interstitial O_2 reacting with Si-N-Si [C in Fig. 1(b)]. (c) Peroxyl oxygen reacting with Si-[NO]-Si [C in Fig. 3(b)]. (d) Peroxyl oxygen reacting with Si-O-O-Si [C in Fig. 3(c)].

peroxyl oxygen reacting with incorporated nitrogen Si-N-Si and Si-NO-Si in SiO_2 . We find that in the saddle point geometries, interstitial NO and O_2 form triangular structures with the N atom of Si-N-Si as shown Figs. 2(a) and 2(b), respectively. The desorption occurs when an O atom find a favorable position forming the Si-O-Si bond.

B. Peroxyl O atoms reacting with the incorporated N structures

The diffusion of peroxyl O atoms in SiO_2 has been studied by Hamann using first principles molecular dynamic calculations and an α -quartz supercell.¹⁴ He found that the incorporation reaction of an interstitial oxygen into the SiO_2 network is exothermic by 0.86 eV, whereas the energy barrier for its diffusion via peroxy linkage is 1.3 eV. According to our results, the gain in energy by the O incorporation and the peroxyl diffusion barrier are found to be 1.49 and 1.9 eV, respectively. The discrepancy with the results of Ref. 14 may be attributed to spin-polarization effects, which are important to correctly describe the O atom and O_2 in SiO_2 . For instance, our results reveal that the O atom has a triplet ($S=1$) ground state inside SiO_2 , whereas the singlet state is 1.59 eV higher in energy. Similarly, a triplet ground state has been found by us and others for O_2 at interstitial sites of α -quartz and amorphous SiO_2 . The O_2 triplet-singlet gap is found to be 0.9 eV in the case of α -quartz,¹³ whereas it ranges from 0.62 to 0.45 eV in the case of amorphous SiO_2 , depending on the void size.¹⁹

Atomic oxygen is a product of the N_2O decomposition at typical oxidation temperatures. An interstitial O atom is energetically unstable being rapidly incorporated in the oxide as a peroxyl defect. Our results for the reactions between a peroxyl O atom and the N incorporated structures in SiO_2 are shown in Fig. 3. The initial position in reaction paths (A) corresponds to the O atom at the top of the peroxyl diffusion barrier. Figure 3(a) shows the reaction of a peroxyl O atom

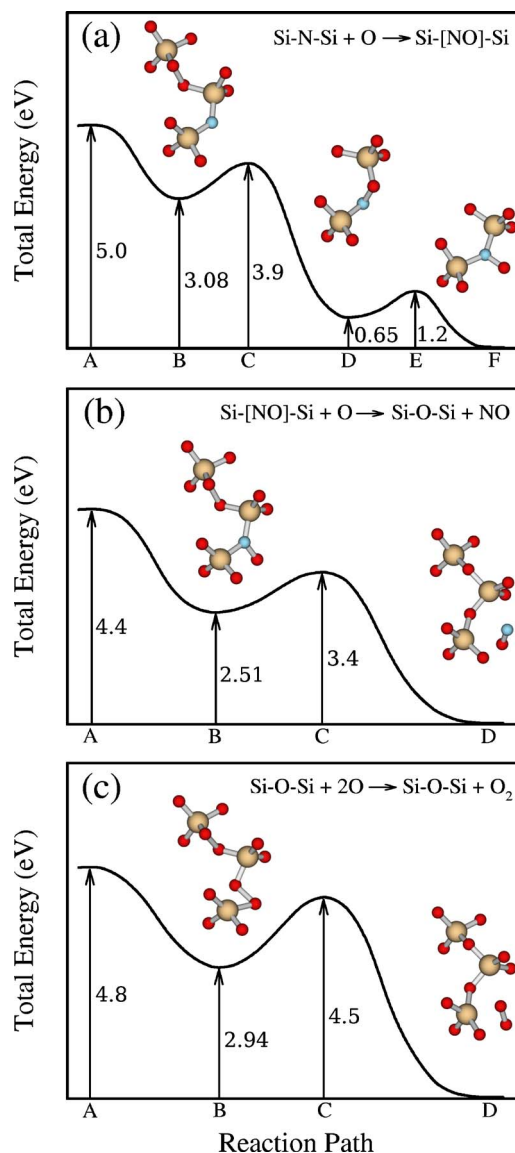


FIG. 3. (Color online) The reaction of atomic oxygen with incorporated nitrogen in SiO_2 after diffusing via peroxy linkages. (a) A peroxyl O atom reacting with Si-N-Si. (b) A peroxyl O atom reacting with Si-[NO]-Si. (c) The annihilation of two peroxyl O atoms. The reaction paths initiate with a peroxyl oxygen at the top of its diffusion barrier (A) far away from the other reactants.

with the Si-N-Si bonding structure. The result is a stable Si-[NO]-Si structure, indicating that this reaction does not remove nitrogen. The reaction $\text{Si-N-Si} + \text{O} \rightarrow \text{Si-[NO]-Si}$ is exothermic by 3.08 eV and occurs in a spin doublet reaction path. The energy barriers for a peroxyl O atom to react with an incorporated N, forming an incorporated NO are found to be about 0.8 and 0.6 eV [C and E in Fig. 3(a), respectively]. We notice that the final incorporated NO structure [F in Fig. 3(a)] is one of the most stable among other oxynitride configurations, as recently shown by first-principles calculations as having a binding energy of 3.8 eV.²⁰

Figure 3(b) shows the reaction involving a peroxyl O atom and the Si-[NO]-Si structure in SiO_2 . We find that the peroxyl O atom can effectively remove nitrogen from Si-

[NO]-Si after overcoming an energy barrier of about 0.9 eV. Nitrogen escapes from the network as interstitial NO molecules, leaving a perfect SiO₂ structure in its place. Figure 2(c) shows the saddle point geometry of the desorption reaction in which an O atom dissociates from the peroxy structure, recovering its atomic character afterward it forms the Si-O-Si bond which induces the NO desorption. The distance between desorbed O atom and the Si atom is about 1.9 Å. We note that the O atom moves off the plane of its nearest neighbors when it passes through the saddle point [Fig. 2(c)]. The reaction Si-[NO]-Si+O → Si-O-Si+NO is exothermic by 2.51 eV and it occurs in a spin doublet reaction path. We also find that when a peroxy O atom is nearest neighbor to Si-[NO]-Si [B in Fig. 3(b)], the energy of the system is lower by 0.3 eV when compared to configurations where they are farther apart, suggesting a tendency to favor the N desorption. It is noticeable that the energy barriers for a peroxy O atom to react with incorporated N in the Si-N-Si and Si-[NO]-Si structures (0.8 and 0.9, respectively) are considerably lower than the energy barriers of the O-peroxy diffusion in SiO₂ (1.9 eV), indicating that the peroxy mediated reactions are diffusion-limited processes.

Figure 3(c) shows our results for the reaction involving two nearest-neighbor peroxy O atoms in the SiO₂ network. We find that the peroxy linkages annihilate themselves after one peroxy O atom overcomes an energy barrier of 1.6 eV. The neighboring peroxy oxygens rehybridize, forming an O₂ molecule which escapes from the network, leaving a perfect SiO₂ structure. The corresponding saddle point geometry is shown in Fig. 2(d). The annihilation reaction Si-O-Si+2O → Si-O-Si+O₂ is exothermic by 2.94 eV with respect to nearest-neighbor peroxy linkages. The starting point [A in Fig. 3(c)], corresponds to one O atom at the top of the peroxy diffusion barrier (~1.9 eV), far from the second peroxy linkage. We find that at nearest-neighbor sites [B in Fig. 3(c)], the peroxy O atoms increase the total energy of the system by 1.1 eV with respect to the noninteracting position (5 Å apart), suggesting that there is an effective repulsive interaction between them, which would make the annihilation reaction difficult. It is also important to note that during the annihilation reaction the system suffers a singlet-to-triplet spin exchange. The equilibrium geometry of neighboring peroxy oxygens [B in Fig. 3(c)] has a singlet ground state, whereas the interstitial O₂ [D in Fig. 3(c)] has a triplet one. We estimate that the singlet-to-triplet conversion occurs at the transition configuration, where a peroxy O atom left its peroxy linkage, recovering its atomic character before reacting with the neighboring peroxy O atom. In fact, if the reaction occurs through a singlet pathway without the spin conversion, both peroxy oxygens find each other, forming a stable ozonyl structure (Si-O-O-O-Si). The energy barrier for this reaction is found to be 2.7 eV, approximately 1.1 eV higher in energy than the barrier for the annihilation reaction, whereas the ozonyl equilibrium structure is about 2.0 eV

higher in energy than the interstitial O₂. Similar spin-dependent reaction processes have been reported recently in the nitridation of bulk SiO₂,¹⁵ as well as in the oxidation of the Si-SiO₂ interface,^{21,22} and the Si(001) surface.^{23,24}

In order to quantify the occurrence of nitrogen desorption events at a given temperature, we estimate the desorption reaction rates (Γ), assuming that the thermally activated processes follow the Arrhenius law $\Gamma = \Gamma_0 \exp(-E_b/kT)$. Here, Γ_0 is the attempt frequency, E_b the energy barrier, and kT the Boltzmann constant times the temperature. Γ_0 is estimated from the linear vibration of the O atoms in a peroxy linkage ($8 \times 10^{12} \text{s}^{-1}$) and is assumed to be the same for all the reactions under consideration. For a typical annealing temperature of 800 °C, the highest N-desorption rate is found for O₂ reacting with the Si-[NO]-Si structure, as shown in Fig. 1(c) ($\Gamma_{1c} = 0.47 \Gamma_0$). The peroxy O atom reacting with the Si-[NO]-Si structure [Fig. 3(b)] and the O₂ reacting with the Si-N-Si structure [Fig. 1(b)] are less likely N removal processes, as can be verified by the ratios $\Gamma_{2b}/\Gamma_{1c} \approx 10^{-4}$ and $\Gamma_{1b}/\Gamma_{1c} \approx 10^{-7}$, respectively. We also estimate the ratio between occurrence rates of the annihilation of two peroxy linkages (the singlet-to-triplet reaction, Γ_{st}) and the ozonyl formation (the singlet reaction, Γ_s) by $\Gamma_{st}/\Gamma_s = \exp[-(E_{st} - E_s)/kT] \times P/(1 - P)$, where P is the probability for a singlet-to-triplet conversion and $E_{st}(E_s)$ the annihilation (ozonyl) energy barrier. Using $P \approx 0.001$ as estimated in Ref. 21, we find that $\Gamma_{st}/\Gamma_s \approx 150$, which means that the annihilation reaction has an occurrence rate 150 times larger than the ozonyl formation reaction.

IV. SUMMARY AND CONCLUSIONS

We have shown that the most favorable thermally-activated N-desorption mechanism would be induced by O₂ interstitials reacting with Si-[NO]-Si structures in SiO₂, where nitrogen is released from the network as a NO molecule leaving a peroxy defect in its place. The reactions involving O atoms diffusing via peroxy linkages and the Si-[NO]-Si structure also result in a similar N desorption, but it has an occurrence rate of about 10⁴ times smaller than the most favorable one. We also identify an O-desorption mechanism occurring via the annihilation of two neighboring peroxy O atoms in SiO₂, resulting in an interstitial O₂ molecule. The above results provide an atomic-scale understanding of the probable routes for nitrogen desorption and oxygen replacement experimentally observed during the thermal growth of SiO_xN_y films.

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