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O_2 oxidation reaction at the Si(100)-SiO_2 interface: A first-principles investigation

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We investigated the oxidation reaction of the O_2 molecule at the Si(100)-SiO_2 interface by using a constrained *ab initio* molecular dynamics approach. To represent the Si(100)-SiO_2 interface, we adopted several model interfaces whose structural properties are consistent with atomic-scale information obtained from a variety of experimental probes. We addressed the oxidation reaction by sampling different reaction pathways of the O_2 molecule at the interface. The reaction proceeds sequentially through the incorporation of the O_2 molecule in a Si—Si bond and the dissociation of the resulting network O_2-species. The oxidation reaction occurs nearly spontaneously and is exothermic, regardless of the spin state of the O_2 molecule. Our study suggests a picture of the silicon oxidation process entirely based on diffusive processes. © *2005 Springer Science + Business Media, Inc.*

1. Introduction

Present-day metal-oxide-semiconductor devices demand gate oxide films thinner than 2 nm [1]. In this regime, a significant fraction of the full oxide film is occupied by the transition layer at the Si(100)-SiO_2 interface, resulting in gate oxides with degraded dielectric properties [2, 3]. Optimal device performance requires controlling the oxide growth at the atomic scale. Further progress therefore requires a detailed understanding of the fundamental atomic-scale processes responsible for silicon oxidation [2, 3].

The silicon oxidation process is commonly described by adopting the physical picture presented by Deal and Grove several decades ago [4]. According to this picture, the silicon oxidation process is assumed to proceed through two sequential steps: (i) the O_2 diffusion through the oxide network toward the Si—SiO_2 interface, and (ii) an activated O_2 reaction with the Si substrate at the interface. The diffusion process has been extensively investigated both experimentally [3, 5] and theoretically [6] and its description nowadays meets a large consensus. At variance, the oxidation reaction process appears far less characterized and understood. This is mainly related to the fact that the Deal-Grove model fails in describing the oxidation kinetics of thin films, the regime dominated by the oxidation reaction at the interface [4]. More recently, elaborate kinetics models have been designed to account for the thin-film regime [7–9]. However, such models remain only limited at reproducing the kinetics of the silicon oxidation process. No direct information is available about the fundamental processes responsible for the oxide growth at the Si—SiO_2 interface. The understanding of these atomic-scale processes appears at present only accessible within density-functional investigations [10–12]. However, difficulties in modelling the structure of the Si(100)-SiO_2 interface have hitherto prevented the study of the oxidation reaction directly at the interface.

In this work, we use a constrained first-principles molecular dynamics approach [13] to address the oxidation reaction at the Si(100)-SiO_2 interface. We employ model interface structures reproducing atomic-scale features consistent with a broad range of experimental probes [14, 15]. The O_2 reaction is found to proceed sequentially through (i) the incorporation of the molecular species in the network and (ii) the dissociation of the network O_2-species in two neighboring Si—O—Si units. Since the calculated energy barriers are of the order of a few tenths of eV, the reaction is expected to proceed readily at the temperatures generally used during thermal oxidation. Our results suggest that the kinetics of the silicon oxidation process are dominated solely by the oxygen transport through the oxide.

2. Method

The electronic structure and the atomic forces in our simulations [13] were obtained within density-functional theory. The exchange and correlation energy was accounted for within a spin-polarized generalized gradient approximation [16]. We expanded the electron

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wave functions and density on plane-wave basis sets defined by energy cutoffs of 24 and 150 Ry, respectively. Core-valence interactions were described by a norm-conserving pseudopotential for Si [17] and an ultrasoft one for O [18]. The Brillouin zone of our simulation cell was sampled at the Γ point.

To represent the Si(100)-SiO_2 interface, we used three interface models taken from previous work [14, 15]. In particular, we adopted the models labelled B, C, and C′ in Ref. [15]. These models consist of disordered, topologically perfect oxide networks matching the Si substrate without coordination defects [14]. The transition region at the interface extends over about two Si monolayers and shows several in-plane Si—Si dimers [15]. These model interfaces reproduce the mass density profile, the amount and location of partially oxidized Si atoms, and the degree of distortions propagating in the Si substrate, as measured in X-ray reflectivity [19], photoemission [20], and ion-scattering experiments [15], respectively. The model interfaces used in the present study consist of an oxide layer about 6 Å thick and a Si substrate of 7 monolayers. The extremities were saturated by H atoms. The structures are periodic in the plane of the interface, with a $\sqrt{8} \times \sqrt{8}$ Si repeat unit.

Pathways and energy profiles for the O_2 oxidation reaction are obtained using a constrained molecular dynamics approach. In particular, during the molecular dynamics simulations we favor the course of the oxidation reaction by varying an appropriate reaction coordinate. All the other coordinates are free to vary according to the calculated atomic forces. During the evolution, we prevented the system from leaving the Born-Oppenheimer energy surface by damping the electronic degrees of freedom [21]. Using this procedure we generated, for each model interface, 15 different reaction pathways for the O_2 molecule in both the triplet and singlet spin state. The results of this study do not depend on the specific model used for the calculations. Hence, hereafter we will not refer to a specific model interface.

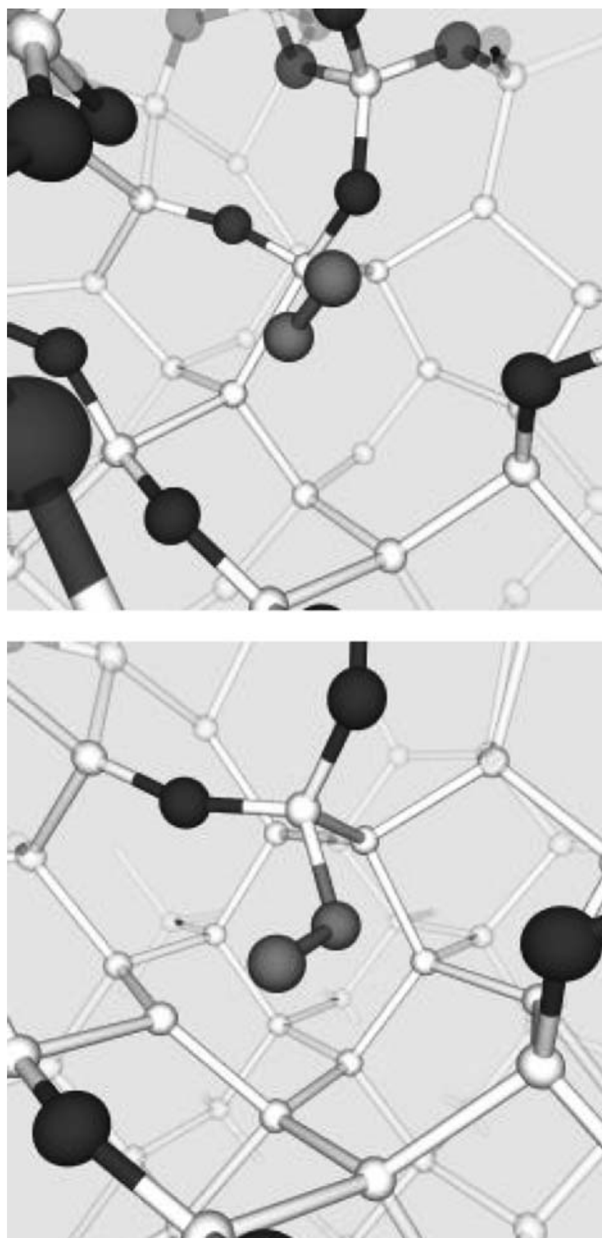

Figure 1 Neutral O_2 molecule in the triplet spin state (top) diffusing through the oxide and (bottom) incorporating in a Si—Si bond.

3. Results

The lowest-energy electronic configuration for the O_2 molecule in both the vacuum and the interstitials of the oxide corresponds to a triplet spin state [6, 22]. Hence, we started our simulations by locating the O_2 molecule in the triplet state on top of the oxide component, at the oxide-vacuum interface. At this stage, we favored the progress of the oxidation reaction by gradually decreasing the distance between the O_2 molecule and the Si(100)-SiO_2 interface. Our simulations show that the O_2 molecule approaches the interface by diffusing through neighboring interstices (Fig. 1, top panel) [6]. In the proximity of the Si(100)-SiO_2 interface, the O_2 molecule attacks a Si atom in an intermediate oxidation state and incorporates in the corresponding Si—Si bond near the Si substrate. Our simulations show that network incorporation corresponds to an exothermic process with an energy release ranging between 1.0 and 1.5 eV and proceeds by crossing energy barriers of only 0.1–0.2 eV.

Network incorporation of the O_2 molecule in the triplet spin state gives rise to network O_2 species ranging from the peroxyl linkage to a non-bridging O_2 complex accompanied by a Si dangling bond (Fig. 1, bottom panel). These structures all correspond to metastable states. In fact, our electronic structure calculations show that spin conversion to the singlet spin state always lowers the energy, with energy gains ranging between 0.1 and 1.0 eV. Furthermore, upon spin conversion the atomic structure generally undergoes an important relaxation favoring the formation of a more symmetric peroxyl linkage (Fig. 2, bottom panel).

To further investigate the role of spin, we repeated our set of 15 simulations setting the O_2 molecule in the spin singlet state from the outset, while keeping otherwise identical conditions. In this case, the trajectories of the molecule through the oxide are very similar to those followed by the O_2 molecule in the triplet spin state and the incorporation in the Si—Si bond directly gives a

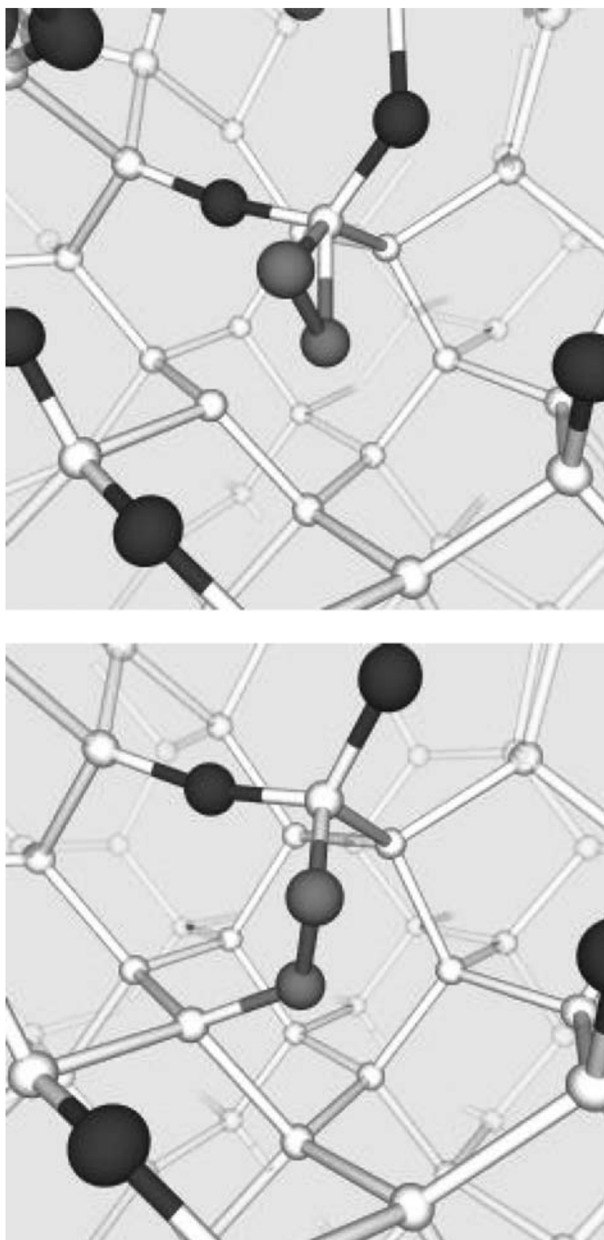

Figure 2 The spin conversion to the singlet state is energetically favorable and drives (top) the O_2 molecule incorporated in the network towards the completion of the incorporation process by forming a peroxyl linkage (bottom). The top panel corresponds to the transition state for the incorporation process of an O_2 molecule in the singlet spin state.

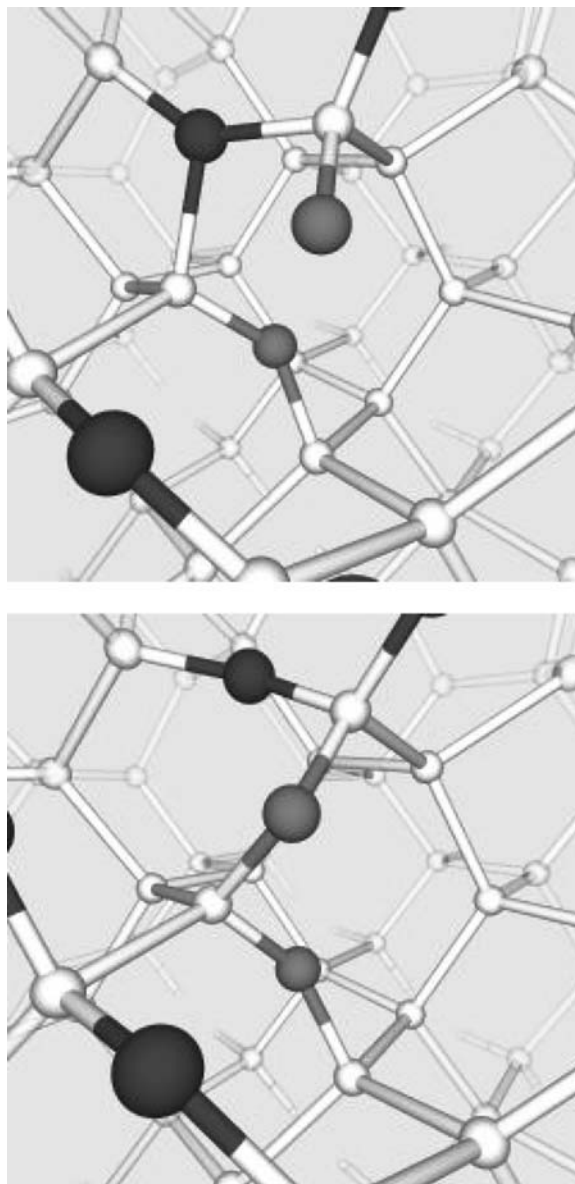

Figure 3 The top panel shows the transition state associated to the dissociation process of the network O_2 species in the bottom panel of Fig. 2. Dissociation gives two neighboring Si—O—Si units (bottom).

symmetric peroxyl linkage (Fig. 2, bottom panel). Also the energetic profile is very similar to the triplet spin case. The triplet-singlet crossing occurs in the neighborhood of the transition state (Fig. 2, top panel). Hence, regardless of the spin carried by the O_2 molecule, the oxidation reaction proceeds through barriers that can easily be overcome under the usual thermal conditions of silicon oxidation [4] and results in the formation of a peroxyl linkage.

To further investigate the oxidation reaction, we favored the dissociation of the network molecular species by taking the bond length of the molecule as the new reaction coordinate. The dynamics was constrained until the transition barrier was overcome (Fig. 3, top panel) and evolved freely afterwards. We observed that the network O_2 species dissociates by having one of the O atoms oxidize a neighboring Si—Si bond. For our set of 15 simulations, we found transition barriers of at most 0.4 eV. These barriers are noticeably smaller than the energy released during the incorporation of the O_2 molecule, suggesting that the dissociation proceeds readily. The uptake of oxygen at the interface finally results in two neighboring Si—O—Si units (Fig. 3, bottom panel).

4. Conclusions

In conclusion, we used constrained *ab initio* molecular dynamics simulations to investigate the reaction of the O_2 molecule at the Si(100)-SiO_2 interface. Our study shows that the oxidation reactions occurs in two sequential steps: (i) the incorporation in the network at a Si—Si bond, and (ii) the dissociation of the network O_2 species in two neighboring Si—O—Si units (Fig. 4). Both processes are activated with energies of a few tenths of an eV and are highly exothermic. Therefore, our study provides strong evidence against an activated O_2 reaction at the interface which severely influences

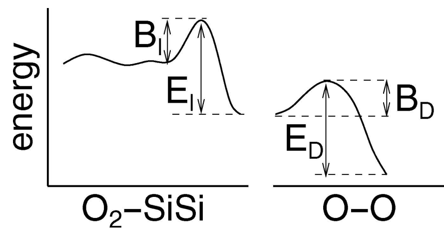

Figure 4 Schematic energy profiles during the incorporation (left) and dissociation (right) processes of the oxidation reaction. For the incorporation, the energy is given with respect to the distance between the O_2 molecule and the Si—Si bond at the interface. For the dissociation, the energy is given with respect to the O_2 bond length. E_I, E_D, B_I, and B_D refer to the energy gains and the energy barriers for the incorporation and dissociation process, respectively.

the kinetics of the oxidation process [4]. Our results are consistent with kinetics models fully relying on diffusion [9]. However, to match kinetic data in the thin oxide regime, such a description should account for a decrease of the diffusion rate near the interface [7]. According to a recent theoretical investigation [23], such an effect is achieved by the occurrence of a thin interfacial oxide layer of higher density, which has indeed been observed in X-ray reflectivity experiments [19].

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