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Reaction of the Oxygen Molecule at the Si(100)-SiO$_2$ Interface During Silicon Oxidation

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Using constrained *ab initio* molecular dynamics, we investigate the reaction of the O$_2$ molecule at the Si(100)-SiO$_2$ interface during Si oxidation. 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, irrespective of the O$_2$ spin state or of the amount of excess negative charge available at the interface. The reaction evolves through the generation of network coordination defects associated with charge transfers. Our investigation suggests that the Si oxidation process is fully governed by diffusion.

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The oxide thickness in current Si-based electronic devices has dropped below 20 Å [1]. In this regime, optimal device performance requires controlling the oxide growth at the atomic scale. Further progress therefore requires a detailed understanding of the fundamental processes responsible for silicon oxidation [2,3]. Since the work of Deal and Grove [4], the silicon oxidation process is generally assumed to occur sequentially through (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 characterized both experimentally [3,5] and theoretically [6], and its description nowadays meets a large consensus. At variance, the oxidation reaction has remained far less understood. This is related to the failure of the Deal-Grove model in describing the oxidation kinetics for thin films, the regime dominated by the oxidation reaction at the interface [4,7]. Kinetics models accounting for the thin-film regime separate into those preserving the activated oxidation reaction [8,9] and those relying uniquely on spatially varying diffusion properties [8,10]. However, no direct observations can at present distinguish among these modelling schemes. Furthermore, such models remain limited at reproducing the kinetics of the silicon oxidation process. A deeper understanding of the atomic-scale processes at the Si(100)-SiO$_2$ interface appears at present only accessible within density-functional investigations [11–13]. However, difficulties in modeling the structure of the Si(100)-SiO$_2$ interface have hitherto prevented the study of the oxidation reaction directly at the interface.

In this Letter, we use a constrained first-principles molecular dynamics approach 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, including photoemission and ion scattering [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. Calculated energy barriers are of the order of a few tenths of eV, implying that the reaction proceeds 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.

We here used three interface models taken from previous work [14–16]. They consist of disordered, topologically perfect oxide networks matching the Si substrate without coordination defects [14]. We retained 5 to 6 Å of oxide and seven monolayers of the Si substrate, the extremities being saturated by H atoms. The structures are periodic in the plane of the interface, with a $\sqrt{8} \times \sqrt{8}$ Si repeat unit. The transition region at the interface extends over about two Si monolayers and shows several in-plane Si-Si dimers [15]. These interface models reproduce the amount, the distribution and the location of partially oxidized Si atoms, the mass density profile across the oxide layer, and the distortions propagating into the Si substrate, as derived from photoemission, *X*-ray reflectivity, and ion-scattering data, respectively [15].

The electronic structure and the atomic forces in our simulations [17] were obtained within a spin-polarized generalized gradient approximation to density-functional theory [18]. Technical details in the electronic-structure calculations were set as in previous studies [14].

We first considered the case of the neutral O$_2$ molecule in the triplet spin state, which corresponds to the lowest-energy state of the molecule in both the vacuum and the interstitials of the oxide [6,19]. We started our simulations by locating the O$_2$ molecule on top of the oxide component, at the oxide-vacuum interface. We then adopted a constrained molecular dynamics approach, in which the distance between the O$_2$ molecule and the Si(100)-SiO$_2$ interface is gradually decreased, while 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 [20]. In this way, we obtained reaction pathways and energy profiles. Our observations are based on reaction pathways generated by starting the dynamics from 15 different locations in our three model interfaces [16]. Our simulations show that when the molecule approaches the Si(100)-SiO_2 interface the O_2 species attacks a Si atom in an intermediate oxidation state and incorporates in a Si-Si bond near the Si substrate. One of the recorded trajectories is illustrated in Fig. 1, where both the energy profile and the structure of the incorporated molecule (panel B) are shown. 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 (Table I).

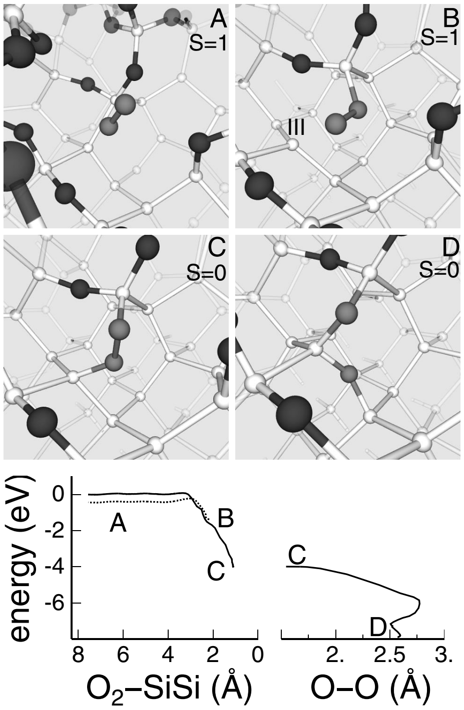

FIG. 1. Top: Neutral O_2 molecule in the triplet spin state ($S = 1$), (A) diffusing through the oxide and (B) incorporating in a Si-Si bond. The incorporation leads to the formation of a threefold Si atom (III). Spin conversion to the singlet state ($S = 0$) gives (C) a symmetric peroxyl linkage. Its dissociation gives (D) two neighboring Si-O-Si units. Light (black) spheres correspond to Si (O) atoms. A gray color is used for the O_2 molecule. Bottom: 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. Both the triplet (A → B, dotted line) and singlet spin states (A → C, solid line) are considered. For the dissociation (C → D), the energy is given with respect to the O_2 bond length.

The network incorporation of the O_2 molecule in the triplet spin state gives rise to network oxygen species ranging from the peroxyl linkage to a nonbridging O_2 complex accompanied by a Si dangling bond (Fig. 1, panel B). These structures all correspond to metastable states, since spin conversion to the singlet state always lowers the energy, with energy gains ranging between 0.1 and 1.0 eV. Upon spin conversion, the atomic structure generally undergoes an important relaxation favoring the formation of a more symmetric peroxyl linkage (Fig. 1, panel C). 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 trajectory of the molecule through the oxide is similar to that for the triplet spin state, and the incorporation in the Si-Si bond directly gives a symmetric peroxyl linkage (Fig. 1, panel C). 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. 1). 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 [21].

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 were constrained until the transition barrier was overcome 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 (Table I). 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.

To validate our results, it is important to assess the absolute accuracy of the energy barriers in Table I. At the transition state associated to the incorporation in a Si-Si

TABLE I. Range of values found for the energy barriers (B) and energy gains (E) associated to the O_2 incorporation (i) and dissociation (d) processes, for different spin (S) and charge states. Energies are in eV.

	B_i	E_i	B_d	E_d
O_2, $S = 1$	0.1–0.2	1.0–1.5	–	–
O_2, $S = 0$	0.0–0.4	2.8–4.8	0.1–0.4	4.0–5.0
O_2^-	0.0–0.0	2.0-4.0	0.0–0.5	4.0-8.0
O_2^{2-}	0.0–0.0	2.0-4.0	0.0–1.0	4.0-8.0

bond, the O_2 molecule approaches an electron-rich environment. An estimate of the involved error can therefore be obtained by considering the electron affinity of the isolated O_2 molecule. We calculated an electron affinity of 0.22 eV, to be compared with the experimental value of 0.45 eV [22]. This comparison suggests that the transition barrier for incorporation is described within an error of only ~0.2 eV, thereby confirming the nearly spontaneous evolution of the reaction. The error associated to the ensuing dissociation process can be estimated from a comparison between the calculated and measured binding energies of the isolated O_2 molecule. With our approach, we obtained a binding energy of 5.8 eV, larger by 0.7 eV than the respective experimental value (5.1 eV [22]). Consideration of this error might lead to energy barriers for dissociation as high as 1 eV. However, these barriers are not expected to hinder the dissocciation process in view of the sensibly larger energy (2.0–4.8 eV, Table I) released upon incorporation. Hence, the present assessment of involved errors corroborates the picture emerging from our density-functional calculations.

In the vicinity of the Si(100)-SiO_2 interface, electrons can tunnel from the silicon substrate to the approaching O_2 molecule giving rise to negatively charged oxygen species [23]. Hence, we extended our investigation of the O_2 molecule at the interface to cases with either one or two excess electrons in the simulation cell[24]. Following a similar procedure as for the neutral molecule, we generated a set of 15 pathways for each of the two charge states by starting the dynamics from interstitials located in the neighborhood of the interface. Our simulations show that the availability of excess negative charge favors the spontaneous incorporation of the O_2 molecule in the network, as shown for a specific case in Fig. 2. The incorporation of the molecule occurs through the attachment of either one or both of its O atoms to Si atoms of the oxide, which thus become fivefold coordinated (Fig. 2, panel A). Indeed, the localization of the excess negative charge favors the formation of these new Si-O bonds with bond lengths of about 1.8 Å. These observations are consistent with previous theoretical studies on various charge states of the O_2 molecule in bulk SiO_2 [23,25]. For both charge states considered here, the energy released upon incorporation ranges between 2 and 4 eV, sufficiently large for overcoming the transition barrier associated with the ensuing dissociation (Table I). Overall, these results suggest that the availability of additional electrons further favors the course of the O_2 oxidation reaction at the Si(100)-SiO_2Si(100)-SiO_2 interface.

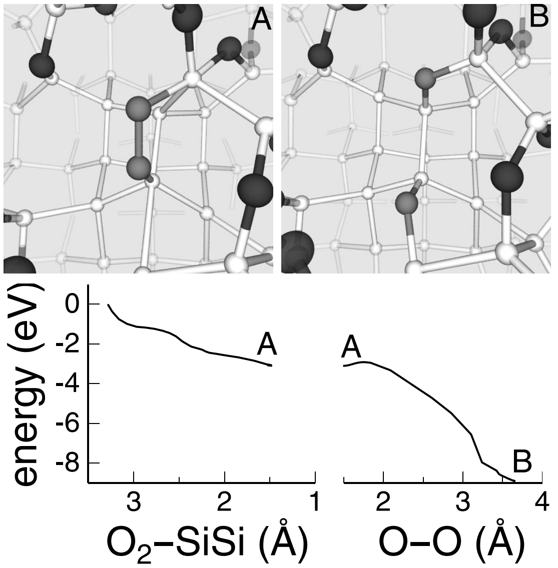

FIG. 2. Top: equilibrium configurations resulting from (A) the incorporation and (B) the dissociation of a O_2 molecule at the interface in the presence of one excess electron in the simulation cell. Bottom: Respective energy profiles. Same conventions as in Fig. 1.

The facilitated formation of Si-O bonds in the presence of excess negative charge hints at the importance of charge fluctuations during the oxidation reaction [11,26]. In fact, also in the case of the neutral O_2 molecule, charge fluctuations provide a basis for interpreting the sequence of observed defect configurations. The formation of a Si-O bond between one of the Si atoms forming the targeted Si-Si bond and one of the O atoms of the molecule (Fig. 3, left panel) is a source of charge accumulation, generally at the expense of the weaker Si-Si bond. As a consequence, the latter bond is weakened and can more easily break, leaving the other Si atom forming the original Si-Si bond in a threefold coordinated, positively charged state. The breaking of the Si-Si bond confers an enhanced flexibility to the network, which can lead to the formation of a bond between the latter Si atom and a neighboring bridging O atom. This process is illustrated in Fig. 3 (right panel), which shows the threefold coordinated oxygen center observed during the dissociation process shown in Fig. 1. The present simulations show that the reaction of the O_2 molecule at

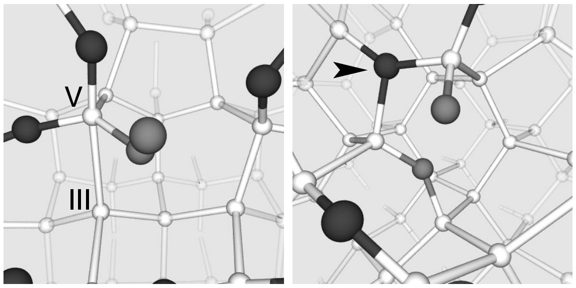

FIG. 3. Transition states during the oxidation reaction of a neutral O_2 molecule at the Si(100)-SiO_2 interface, corresponding to the case in Fig. 1. The incorporation (left) occurred via the formation of a fivefold Si atom (V) and a threefold Si atom (III). During dissociation, a threefold O atom (arrow) was observed (right). Same conventions as in Fig. 1.

the interface evolves through the generation of network coordination defects associated with charge transfer processes. Furthermore, the associated higher propensity for rearranging the network structure suggests a possible mechanism for the amorphization of the oxide occurring during oxidation.

Our study provides strong evidence against an activated O_2 reaction at the interface which severely influences the kinetics of the oxidation process [4]. However, our results are consistent with a picture of the oxidation fully governed by diffusion properties. Diffusion models require a decrease of the O_2 diffusion rate near the interface to match kinetics data [8,10]. Such an effect is achieved by the occurrence of a thin interfacial oxide layer of higher density [27], which has indeed been observed in X-ray reflectivity experiments [28].

The present findings do not preclude that other mechanisms are concomitantly operative during silicon oxidation. For instance, the O_2 molecule approaching the interface could capture an electron [23] and give rise to a double-bridge network O ion [25]. The latter species then continues the diffusion process with an activation barrier of 0.2 eV [25] and oxidizes a Si-Si bond by crossing a barrier smaller than 0.4 eV (Table I) [25]. Another channel of oxidation consists in assuming that the O_2 molecule incorporates in a Si-Si bond within the suboxide but separated from the substrate. As found in this Letter, this process occurs by crossing vanishingly small energy barriers [21]. The further diffusion of the resulting peroxyl linkage to the interface proceeds with an activation energy of about 1.3 eV [29]. Despite the higher activation energy, this process could become a viable alternative in case the diffusion of the O_2 molecule is suppressed by an interfacial oxide layer of higher density [27].

In conclusion, we investigated the reaction of the O_2 molecule at the Si(100)-SiO_2 interface, providing an atomic-scale picture of a key aspect of the silicon oxidation process. We found that this reaction is not hindered by any significant barrier, favoring a picture of the oxidation mechanism fully governed by diffusion.

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