Oxygen Migration, Agglomeration, and Trapping: Key Factors for the Morphology of the Si-SiO_2 Interface

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The measured activation energies for oxide growth rates at the initial and late stages of oxidation of Si are 2 and 1.2 eV, respectively. These values imply that oxidation can proceed at temperatures much smaller than the 800 °C normally used to obtain devices with exceptionally smooth Si-SiO_2 interfaces. Here, we use first-principles calculations to identify the atomic-scale mechanisms of the 2 eV process and of additional processes with higher barriers that control the interface morphology and ultimately provide for smooth layer-by-layer oxide growth, as observed at high temperatures.

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The Si-SiO_2 interface is among the most studied solid-to-solid boundaries, mainly because of its paramount significance for electronic devices. It has long been possible to produce Si-SiO_2 interfaces with very low roughness and defect densities. Even though the need for further device miniaturization favors replacement of the oxide or the substrate with novel materials, this prototype is a paradigm for controlled growth of smooth substrate-dielectric interfaces.

The oxidation rate and the morphology of the Si-SiO_2 interface have been the focal points of many studies. Two distinct activation energies (E_a) of 2 and 1.2 eV have been extracted from measured oxide growth rates. These values were attributed by Deal and Grove [1] (hereafter denoted as DG) to an initial reaction-limited phase and a late diffusion-limited phase, respectively. The atomic-scale details of the initial phase have been the subject of extensive investigations [2–6]. It is well known that optimal conditions for growth of smooth interfaces are achieved only at temperatures T_{th} that are significantly higher (typically $\geq$ 800 °C) than those needed to activate the 1.2 and 2 eV processes. Other processes with higher activation energies must, therefore, control the morphology of the interface, and specifically the observed [7] abruptness of the near interfacial layer (NIL). Numerous calculations [2,4,8–11] have probed the NIL structural details and identified possible key features, such as ordered Si-O-Si bridges [9,10] and the energy penalty [10,12] associated with suboxide bonds and interface O protrusions [2]. Most of the calculations thus far have focused, however, on static configurations.

In this Letter we examine thermal oxidation of Si by analogy with the deposition of films on crystalline substrates (the "gas" is O_2 molecules and the film now grows into the substrate). Thus, we study nucleation, lateral migration, and "desorption or readsorption" processes. Knowledge of pertinent activation energies is indispensable in order to determine the relative significance of these processes and ultimately the interface morphology. We use first-principles calculations on model interfaces to extract binding energies, reaction, and diffusion barriers for processes present during oxidation in the (001) direction. The main findings are (i) there is an effective barrier of about 2 eV for O_2 molecules to cross the NIL and arrive at the substrate. This value is consistent with the 2-eV activation energy of the "reaction"-limited regime of the DG analysis. (ii) The oxidation reaction of Si-Si bonds is almost barrierless and strongly exothermic. This fact alone favors random deposition (RD) with large roughness, contrary to the smoothness of the interface that can be achieved at typical T_{th}'s. (iii) Diffusion of O atoms along the oxidation front is activated at typical T_{th}'s. (iv) In certain cases, Si-O-Si bridges are energetically favored to agglomerate pointing to nucleation and growth of oxidized interface islands. (v) Migration of O in bulk Si is also activated at T_{th}, raising in principle the possibility of O solvation in Si. We show, however, that errant O species in Si stick back to the interface and relax in configurations consistent with a smooth front. Occasional desorption into Si, which is a high-barrier process that requires high T_{th}, facilitates reorganization of the oxidation front decreasing the interface roughness. The processes described in (iii)–(v) cancel the RD character of the oxidation front inferred from (ii), providing for overall smoothness, as observed.

The calculations were performed within density-functional theory (DFT), with a generalized-gradient corrected (GGA) exchange-correlation functional [13], a plane wave basis set with a cutoff of 400 eV, two k points for Brillouin zone sampling [14], and ultrasoft pseudopotentials [15], as implemented in the VASP code [16]. Barriers were obtained with the elastic band method [17]. We used Si-SiO_2 supercells with quasiordered quartz (Q), cristobalite (C), and tridymite (T) SiO_2 bonding arrangements [10]. We fixed the in-plane supercell dimensions to the experimental values of bulk Si and we allowed cell relaxation in the growth direction. The obtained density for

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the Q-NIL (T-NIL) is 2.31 (2.30) g/cm^2, in agreement with experimental findings [18]. The calculated density in the C-NIL case is too low (2.06 g/cm^3) to provide for a realistic description of the NIL. We therefore report results based mostly on the Q-NIL structure and selected results for T-NIL. The Q-Si-SiO_2 supercell consists of 9 layers of Si and 6 layers of SiO_2. The initial configuration contains a checkerboard pattern of Si-O-Si bridges [9,10] described previously [9] as a "canonical" interface (CI) structure. Each Si layer contains 12 atoms for the studies of O agglomeration and trapping, and 6 atoms for barrier calculations.

Oxidation is preceded by migration of O_2 molecules from the a-SiO_2 surface towards the interface. The corresponding 1.2 eV barrier accounts for the E_a of the diffusion-limited DG regime. A fit to experimental data provides a 2 eV E_a for the other regime, commonly associated with the oxidation reaction at the interface (this 2 eV barrier is not rate limiting for a thick oxide where the random walk of O_2 controls the oxidation rate). Recent calculations [4,5] found that the oxidation barrier is much smaller than 2 eV. Bongiorno and Pasquarello [4] suggested that the 2 eV process may be related to O_2 diffusion in the NIL and corroborated their suggestion with results for a high O_2 diffusion barrier in dense silica [4]. Earlier studies also used a fit to a varying O_2 diffusivity [3] to reproduce SiO_2 growth rates. Nevertheless, no first-principles studies, such as the ones described below, for O_2 migration in a realistic interface network have been performed and the issue of the 2 eV E_a is regarded as an open question.

Figure 1 depicts selected steps of a migration pathway for an O_2 molecule in a Q-NIL. The general features are as follows: (i) there is a 1.1 to 1.65 eV energy penalty E_i to transfer the molecule from a big void in bulk a-SiO_2 to the NIL. The diffusing molecule forms peroxy bridges or extra (fifth) bonds for NIL Si atoms. O_2 triplet states are more stable than singlets (by 0.2–0.4 eV), except for configurations right before and after oxidation. (ii) The diffusion barriers are between 0.12 and 0.66 eV. Combining these values with the E_i's, we find an effective barrier of 1.8–2.05 eV for O_2 to cross the NIL and oxidize Si. The rate-limiting process in Fig. 1 is the migration between (3) and (4), with an E_i of 1.65 eV and a migration barrier of 0.4 eV. The last migration step before oxidation can, therefore, account for the 2 eV DG E_a; the reaction-limited DG phase is not a reaction *per se*, but it is consistent with a first-order kinetics process, in agreement with the standard DG analysis. (iii) In the final steps, Si-Si backbonds are broken, as shown with an arrow in panel (3) of Fig. 1. Migrating O_2 molecules, like other electronegative species such as fluorine, [19], can therefore create defects in the form of Si dangling bonds. Such configurations are metastable in our calculations, but they may be responsible for relieving long-range stress at the interface. (iv) As in previous studies [4,5], we found that the oxidation reaction has a very small barrier (0.2 eV) and it is strongly exothermic releasing 7.3 eV per O_2 molecule. These last findings show that O_2 molecules oxidize substrate Si-Si bonds almost spontaneously. The process then seems to be a case of random deposition (RD), for which large interface roughness is normally expected [20]. As discussed below, more processes involving O species at the interface are responsible to change the oxidation mode from RD to conditions that favor smooth growth.

The first key factor for smoothness is the suppression of vertical growth, originally found in the studies of Kageshima and Shiraishi [2]. We studied a number of configurations that correspond to 1–5 oxidation steps after the formation of a CI structure. For both Q-NIL and T-NIL structures we confirmed that it is energetically favorable for O protrusions to reorganize so that they become smoother, as shown, for example, in Fig. 2 for O dimer and trimer protrusions. Reorganization of dimers that result in higher O-O coordination in the sense of Si-O-Si bonds

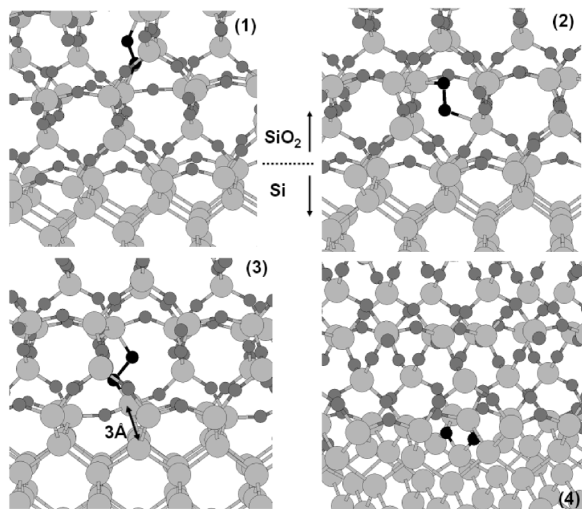

FIG. 1. Migrating steps (1)–(3) with barriers of 1.80–2.05 eV for an O_2 molecule as it moves towards Si at the Si-SiO_2 interface. The arrow in (3) shows a broken Si-Si bond. Configuration (4) with newly oxidized Si-Si bonds is rotated for clarity. (Si: gray, O: dark gray, migrating-O: black sphere).

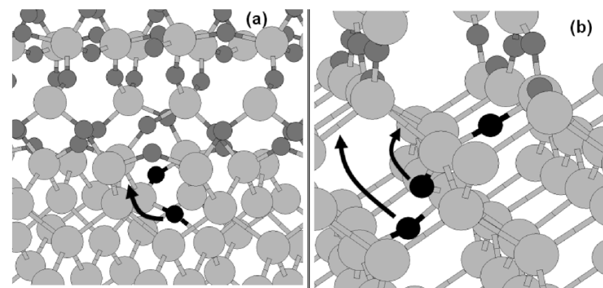

FIG. 2. Sticking and reorganization of an (a) O dimer (barrier is 2.2 eV) and a (b) O trimer at the Si-SiO_2 interface. For energy gains see Table I. (Si: gray, O: dark gray, protruding-O: black).

lead to a decrease in energy (hereafter termed reorganization energy E_r) of 1.10 eV. For trimers, the two consecutive reorganization steps shown in Fig. 2(b) have E_r's of 1.06 eV and 1.73 eV and they result in a flat 3-O atom chain in the (110) direction. The transfer of an O atom to the end of a 4-O chain from an initial position that protrudes out of the chain and towards Si decreases the energy by 0.6 eV. A large E_r of 1.2 eV was also found for dimers at a T-NIL structure. Finally, a large E_r of 1.56 eV was found when a protruding O atom moved to a neighboring suboxide bond at an otherwise abrupt CI interface.

In addition to suppression of vertical growth, we found a novel mechanism that affects the interface morphology. Specifically, we found that it is energetically favorable for protruding Si-O-Si bridges at a Q-NIL interface to agglomerate. In the following we refer to these Si-O-Si bonds as simply O atoms. In this sense, the binding energy (E_b) for two O's at the$Q$-NIL interface is 0.31 eV. For a third O atom E_b is 0.4 eV, giving an overall 3-O cluster E_b of 0.71 eV. The trend of positive E_b's persists for 4-O (5-O) clusters with E_b of 0.23 eV (0.28 eV) for the last O atom. The O atoms in these clusters form chains in the (110) direction, similar to O clusters in bulk Si [21]. For 4-O and 5-O clusters we found that a similar E_b is attained when the protruding O atoms are either in the same or in neighboring chains. Energy considerations alone favor therefore O nucleation at the oxidation front of a Q-NIL structure. For T-NIL structures with low concentrations of protruding O's, isolated dimers are the most stable configurations. For high protruding-O concentrations, however, there is an agglomeration trend similar to the Q-NIL case, with E_b's of 0.3 eV for the last O atom at 2-O and 3-O clusters, and an energy gain of 0.54 eV after the formation of a single 4-atom chain out of vicinal O dimers.

The formation of nuclei, as suggested by the agglomeration trend above, depends critically on two more factors: diffusion of species and dissociation. We studied the lateral migration of an O atom at the interface and the corresponding transition states are shown in Fig. 3. The diffusion barriers range between 2.05 eV and 2.25 eV depending on whether the migrating-O atom pivots around a Si atom in a Si^{+1} or Si^{+3} oxidation state. We note that diffusion in all directions of the oxidation front must occasionally include migration steps inside the Si layers adjacent to the interface. As explained below, such steps raise the effective lateral diffusion barrier. Typical T_{th} temperatures, however, allow for activation of processes with such elevated barriers, so that lateral diffusion is present during thermal oxidation. Such lateral diffusion could also facilitate the formation of a canonical interface.

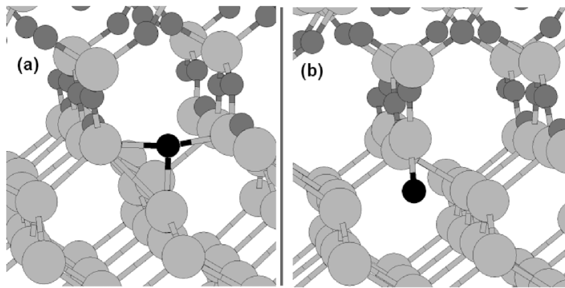

FIG. 3. O diffusion transition states at the Si-SiO_2 interface. Barriers are (a) 2.05 eV and (b) 2.25 eV. (Si: gray, O: dark gray, diffusing-O: black).

We now address another mechanism that is part of the oxidation process. At 800 °C, diffusion of O in bulk Si (the experimental barrier is 2.53 eV, and our calculated value is 2.32 eV) is also activated. Why then does thermal oxidation lead to well-defined oxide-substrate boundaries as opposed to solvation of O in Si? Moreover, O species get stabilized in small clusters in Si, [21] and it is unclear why such clusters are not normally formed during thermal oxidation. Finally, it is known that oxygen is the most common impurity in Si substrates, especially for Czochralski-grown Si, and it is important to know the effect of thermal oxidation on the concentration of such impurities.

The answer to the questions above is that there is an energy gain (trapping energy E_t) when O atoms originally in Si stick to the interface. The E_t's, summarized in Table I, are 0.87 eV, 0.50 eV, and 0.45 eV for 1-O, 2-O, and 3-O species, respectively. For the latter two cases, the O atoms are aligned in the (101) direction. As stated above, there is an extra energy gain when these asperities reorganize to smoother configurations. We calculated also the reorganization barrier for an O-dimer, as shown in Fig. 2(a), to be 2.15 eV. High T_{th}'s allow therefore for the migration, interface trapping and reorganization of any errant O species in Si.

The set of mechanisms discussed above can be summarized in describing thermal oxidation as a random deposition process with relaxation. Agglomeration and less frequent in-plane dissociation of O clusters point to [20] the formation of smooth islands that grow laterally and coalesce. Since the cluster binding energies are relatively small, a critical nucleus size can be expected for typical T_{th}'s. Moreover, at these temperatures O lateral diffusion is activated, in cases facilitated by "desorption" of O species

TABLE I. Interface trapping energies E_t for O species originally in Si. E_r is the reorganization energy gain resulting in smoothening of O asperities. E_d is the dissociation energy of O dimer and trimer protrusions (for larger clusters see text).

Number of O atoms	E_r (eV)	E_t (eV)	E_d (eV)
1	—	0.87	—
2	0.00	0.50	—
2	1.10	1.60	0.31
3	0.00	0.45	—
3	1.06	1.51	—
3	1.73	2.18	0.71

to the Si layers next to the interface. A 3.4 eV value as an upper estimate for the barrier of this desorption-mediated diffusion is obtained from a combination of E_t for a single O atom and the O diffusion barrier in Si. This process does not control directly the oxide growth rate and it is therefore hidden from experiments that probe only the reaction-diffusion DG processes discussed above. Its activation, however, is a key condition for small critical roughness exponents [20], and it can be achieved only at typical $T_{\rm th}$'s, which are much higher than temperatures needed to activate the DG processes.

In terms of experiments, there is a broad consensus for a smooth layer-by-layer mode [6]. An understanding of such a generic feature can be obtained based on the set of atomic-scale mechanisms described here. For example, ordered features, such as terraces, which are a direct consequence of O agglomeration at the interface, have indeed been observed after annealing at high temperatures [22]. We should note, however, that our approach also has certain limitations. The role of stress at ranges longer than our supercells is not taken into account here. For example, we have not considered the stress-induced emission of Si interstitials [2] and the formation of stable dangling bonds. More importantly, we have described mechanisms based solely on energy considerations and for quasiordered interface structures. In reality, high $T_{\rm th}$'s and the existence of an amorphous overlayer induce unavoidably some disorder [9,11] in terms of NIL substoichiometry, and the tendency for O agglomeration may vary depending on the specific oxidation conditions. Diffusion barriers, however, are primarily controlled by the local bonding structure and the density, and we do not expect a strong effect on the calculated values if more bulk amorphous SiO_2 is included on top of our NIL. As a final note, the present study elucidates key observed features of thermal oxidation, but it also suggests that post-oxidation annealing at temperatures lower than $T_{\rm th}$ may ameliorate partly the NIL disorder as long as O migration at the oxidation front is activated.

In summary, we identified O lateral diffusion, reorganization of asperities and O interface trapping as mechanisms that result in the renowned smoothness of Si-SiO_2 interfaces after thermal oxidation. We also showed that the migration barrier of an O_2 molecule in the near interface layer is consistent with the observed early-stage activation energies of oxidation.

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