Oxidation at the Si/SiO_2 Interface: Influence of the Spin Degree of Freedom

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We show, using first-principles spin-polarized total-energy calculations, that depending on the spin configuration of the system, the reaction of an O_2 molecule with a Si-Si bond in a suboxidized region might result either in a peroxy linkage defect (for a singlet spin state) or in a perfect Si-O-Si bond plus an interstitial O atom (for a triplet spin state). Even though the singlet has a lower energy than the triplet configuration, we find a rather small probability for triplet to singlet conversion. Therefore, as the O_2 in an SiO_2 interstitial site has a triplet configuration, this reaction spin dependence may have a strong influence on the high quality of the Si/SiO_2 interface.

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All the amazing advances in the information technology are to a great extent related to the continuous increase in the number of devices per chip. However, this drive towards ever smaller silicon-based electronic devices requires the gate dielectric oxide to become extremely small (< 4 nm) [1]. To achieve this task it is fundamental to have a detailed microscopic understanding of the structure of the Si/SiO_2 interface [2,3] and of the Si oxidation process occurring at the Si/SiO_2 interface. Even though this interface is one of the world's most important material interfaces, both from an economical as well as a technological viewpoint [4], we still do not have a basic understanding of the incorporation reactions of the oxidizing species in SiO_2.

Even though the possibility that atomic oxygen in a peroxy linkage (PL) configuration might be an important diffusing species has been considered in some recent theoretical studies [5–7], it is widely believed that molecular oxygen is the promoter of the oxide growth after its diffusion through the silica network [8–12]. As is well known, the ground state of the oxygen molecule in the gas phase is a triplet state ($^3\Sigma_g^-$) [13]. It has been recently shown by us [9,14] and by other theoretical calculations [7,10–12] that the lowest energy configuration for an interstitial O_2 in SiO_2 is also a triplet state, a result that is also experimentally supported [15]. Moreover, it has also been shown that during the oxidation of the Si(100) surface there is a triplet-to-singlet conversion [16,17], which is a crucial ingredient to explain how the sticking probability depends on the incident O_2 energy.

Hence, it is not only a valid but also a very important question to ask if there is also a triplet-to-singlet conversion inside the SiO_2 in any process in which the oxygen molecule is involved. Whenever there is a strong interaction of the oxygen molecule with the lattice, one would expect the singlet state to be stabilized with respect to the triplet state. In fact, we have found that whenever an oxygen molecule is incorporated into the silica network, such as a PL defect, the lowest energy configuration is a singlet state [14]. After the arrival of an O_2 at the Si/SiO_2 interface, the following possibilities might happen: (i) it reacts with an already formed Si-O-Si bond, forming a so-called ozonyl linkage [12]. This is unlikely since this reaction would be endothermic [12,14] by more than 1 eV; (ii) the O_2 could somehow break and react with two perfect Si-O-Si bonds, forming two PLs. Again this would be a highly endothermic reaction (we estimate [14] an energy variation of approximately 1.7 eV); (iii) at the interface there are many suboxidized Si atoms, which implies that there are Si-Si bonds there. Therefore, the O_2 could be incorporated into such a Si-Si bond, forming one PL. This reaction would now be exothermic. However, the final result is a defect at the interface. To explain the high quality of the interface, a further migration of the PL has to happen until the extra O atom is annihilated at a Si-Si bond; (iv) the O_2 molecule could somehow dissociate and react with two Si-Si bonds, forming two perfect Si-O-Si bonds. This final situation would be the best scenario to explain the high quality of the Si/SiO_2 interface. However, it begs the question of how the O-O bond could be broken. We show below, based on *ab initio* model calculations, that the fact that the interstitial O_2 has a triplet ground state, plus the low probability for a triplet-singlet exchange, leads to a situation where the O-O bond is naturally broken.

All our calculations are performed in the framework of the density functional theory [18] using numerical orbitals as basis sets. We have used the SIESTA code [19], which performs a fully self-consistent calculation solving the Kohn-Sham equations. For the exchange-correlation potential we adopt a generalized gradient approximation [20], and standard norm-conserving Troullier-Martins pseudopotentials [21] are used. In all calculations we employ a split-valence double-zeta basis set with polarization function with a confining energy shift of 0.2 eV [22]. We used a 72-atom α-quartz supercell and the Γ-point for the Brillouin zone sampling. The positions of all the atoms in the supercell were relaxed until all the force components were smaller than 0.05 eV/Å. The

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quality of the present results is similar to our previous plane wave calculation [9,14].

To understand the interaction of an O_2 molecule with a Si-Si bond, which will be present in suboxidized regions, we have performed *model calculations* for an idealized system. The Si-Si bond is modeled by an oxygen vacancy in an otherwise perfect α-quartz structure. An interstitial oxygen molecule is then placed beside this Si-Si bond, and their interaction is studied both for a triplet as well as a singlet spin state. Even though this simple model may not be good for the precise determination of the energetics and/or dynamics of a reaction between an O_2 molecule and a Si-Si bond at the Si/SiO_2 interface, it should suffice to provide the correct *qualitative* physical picture for such a reaction. In particular, *the analysis of the dependence of this reaction on the spin of the system* is most certainly well treated in our model, and all our main conclusions related to this effect will not be changed by a more elaborate model [23].

We initially determined the lowest energy configuration for an interstitial O_2 close to the Si-Si bond, for both the triplet as well as the singlet state (configurations *A* in Fig. 1). Overall, both geometries are similar. For the triplet spin state the Si-Si bond length is 2.57 Å and the O-O bond length, called *d* from now on (see the inset in the top right of Fig. 1) is 1.24 Å. The distance between the center of the Si-Si bond and the O_2 center of mass, called *D* from now on (see the inset in the top right of Fig. 1), is 2.81 Å. In the singlet configuration, the equivalent distances are 2.64 Å, 1.27 Å, and 2.63 Å, respectively. As expected, the triplet state is found to be 0.8 eV lower in energy than the singlet state (see Fig. 1). This value is slightly reduced when compared to the singlet-triplet energy difference for the free molecule, which we have found to be 1.2 eV.

In order to determine a possible pathway for the O_2 + Si-Si reaction, we used the following procedure: we positioned the O_2 molecule closer to the Si-Si bond, and then let it move along the potential energy surface (PES) (for a given fixed spin state) according to the atomic forces. Depending on the initial geometry, this resulted in two types of displacements, one towards the Si-Si bond, and another back to the interstitial site. We then refined the path around the initial geometries that generated these two different behaviors, determining in this way the top of the barrier along the reaction pathway. It is important to stress the fact that we have found only one possible reaction pathway, and our barriers should be seen as upper bounds.

In Fig. 1 we see the result of the above procedure for both spin configurations, where we have displayed the calculated total energies (the singlet PL is chosen as the energy reference since it was found to have the overall lowest energy among the studied configurations) along the reaction pathways using the previously defined *D* and *d* coordinates. As can be seen in Fig. 1, the variations of *D* and *d* are very different along the triplet (black curve)

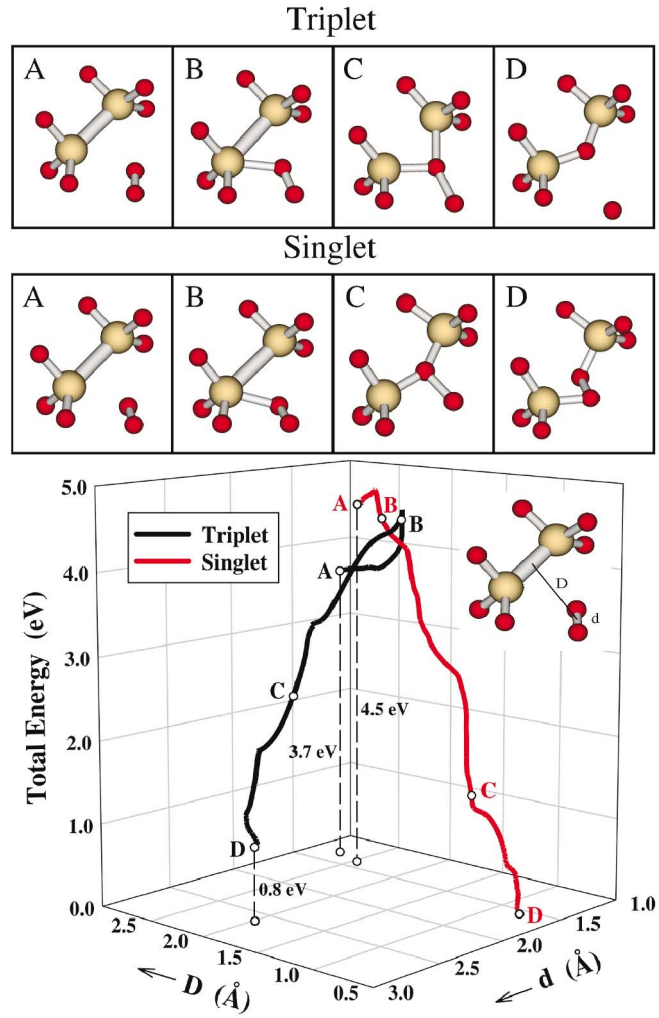

FIG. 1 (color). Triplet (black curve) and singlet (red curve) total energies along the reaction pathways for an O_2 approaching a Si-Si bond, plotted as a function of the *D* and *d* coordinates (see inset in the upper right). Configurations *A* through *D* are representative geometries along the triplet and singlet pathways. Small red spheres are O atoms and the large mustard spheres are Si atoms.

and singlet (red curve) pathways. The four configurations around the Si-Si bond shown for each spin state (*A*–*D*) are representative geometries along the pathways (also marked in the total-energy curves by the letters *A*–*D*).

As the O_2 approaches the Si-Si bond in the triplet state it dissociates (geometries *B* through *D*), with one O atom finally being incorporated into the silica network (forming a perfect Si-O-Si bond) and the other O atom being ejected towards the interstitial site (final equilibrium geometry *D*). The overall reaction is exothermic by 2.82 eV. We have found an energy barrier of approximately 0.85 eV to go from *A* to *D*. As mentioned before, this should be seen as an upper limit. For the singlet state, on the other hand, as the O_2 approaches the Si-Si bond (geometries *B* and *C*) it does not dissociate and is eventually incorporated as a whole into the silica network, forming a PL defect (configuration *D*). This reaction is also

exothermic, with an energy difference between the initial (A) and final (D) configurations of 4.65 eV. Along the singlet pathway we have found an energy barrier of approximately 0.2 eV to go from A to D.

To understand this different behavior between the triplet and singlet spin configurations, we present total charge density contour plots for the singlet [Fig. 2(a)] and triplet [Fig. 2(b)] C configurations, as well as a contour plot for the difference between the charge densities for the majority and minority spins for this latter geometry [Fig. 2(c)]. For the sake of comparison, we also present contour plots for the total charge density for an interstitial triplet O_2 [Fig. 2(d)] as well as for the difference between its majority and minority spin charge densities [Fig. 2(e)]. One can see comparing Fig. 2(c) with Fig. 2(e) that, as the O-O bond breaks in the triplet state, the spin polarization becomes concentrated only in the ejected O atom.

To rationalize this result, as well as the fact that in the triplet the O-O bond breaks, it is useful to think in terms of valence bonds (VB). Let us consider one VB in each Si atom (the Si dangling bonds), plus three VBs per O atom (related to the three $2p$ orbitals). Initially, we have the two Si VBs making a Heitler-London–type Si-Si bond, plus the six oxygen VBs coupled in such a way [24] to generate the triplet O_2. As the molecule approaches the Si-Si bond, the two Si VBs now couple, each pair as a singlet, to two of the VBs from the approaching O atom. This leaves a total of four oxygen VBs, three of them on the O atom farthest away from the Si atoms, and still six electrons to be distributed on these orbitals. A O-O bond is maintained if we have one electron on each VB that points towards the other O atom, coupled as a singlet (Heitler-London–type of bond). Therefore, if this is done, the remaining four electrons will occupy the two remaining VBs, resulting in two lone pairs and a bound O_2 (note that all the orbitals that are not coupled to another VB are doubly occupied), with a final singlet spin configuration. On the other hand, to have a final triplet configuration, we either couple the VBs that were performing the O-O bond as a triplet, which is not favorable [24], or we keep a lone pair on the O atom bound to the two Si atoms and have four electrons on the four VBs of the farthest O atom coupled as a triplet, as in an isolated O atom. This will result in the breaking of the O-O bond, as is observed in our calculations, and in the spin polarization being concentrated on the ejected O atom, as is seen in Fig. 2(c).

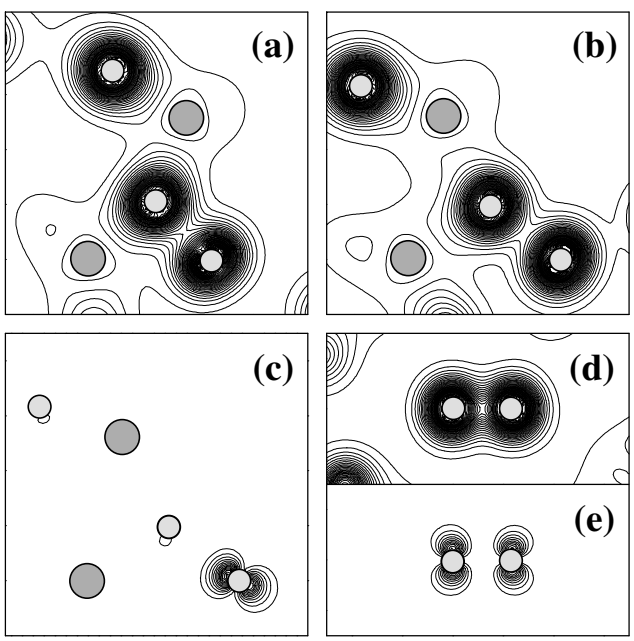

FIG. 2. Contour plots for (a) singlet and (b) triplet total charge density C configurations in a plane that passes through the incoming O_2 and the atoms that formed the initial Si-Si bond. (c) Difference between the charge densities for the majority and minority spins for geometry in (b); (d) and (e) are the total charge density and the difference between charge densities for the majority and minority spins, respectively, for the triplet interstitial O_2. The small and large circles represent O and Si atoms, respectively. For all plots the contour spacing is $0.2e/\text{Å}^3$.

One must note that the overall singlet reaction pathway is somewhat artificial, since when the O_2 molecule is in an interstitial geometry, it has a triplet configuration. However, as the oxygen molecule evolves along the triplet reaction pathway, it may very well change to the singlet one. Therefore, it is fundamental to have an estimate of the probability for this triplet-singlet exchange. The crossing between the two curves occurs approximately for $D = 2.2$ Å and $d = 1.3$ Å, before the O-O bond starts to break in the triplet state. The probability that a system will change from the triplet to the singlet PES may be *estimated* [25] by the Landau-Zener theory[16,26]. Considering that the O_2 is initially in the triplet PES and is evolving towards the crossing region with a velocity v, the probability P_{ts} that it will end up at the singlet PES may be approximated by $P_{ts} = 2[1 - \exp(-V^2/hv|F_1 - F_2|)]$ where V is the small perturbation that couples the two PESs, h is the Planck's constant, and F_1 and F_2 are the slopes of the two PESs at the crossing point. F_1 and F_2 can be obtained from the triplet and singlet paths at the crossing region, and v can be estimated from the O_2 center-of-mass thermal energy [27]. Using for V the spin-orbit matrix element of 122 cm^{-1} between the triplet and singlet states [16,17] for the O_2, the probability is finally obtained as $P_{ts} \simeq 0.001$. Such a small value implies that, even though the singlet state becomes a lower energy configuration along the reaction pathway, there is a large probability for the reaction to proceed along the triplet PES. The analysis of a similar type of reaction, involving O_2 and the Si(100) surface, showed that the difference between our method of estimating P_{ts} and a more accurate theory results only in an increase of P_{ts} by a factor of 2 [16,17].

Finally, one has to note that this is the probability for the triplet-singlet exchange along a single passage along the PES. As the reaction along the triplet PES is thermally

activated, many passages across the crossing point will have to be performed until the final products are obtained. To estimate the ratio between the reaction rates along the triplet and singlet pathways, we assume that the rates for the reaction along the triplet and singlet channels are approximately $\Gamma_t = \Gamma_0[\exp(-\Delta E_t/k_B T)](1 - P_{ts})$ and $\Gamma_s = \Gamma_0[\exp(-\Delta E_{ts}/k_B T)]P_{ts}$, respectively, where Γ_0 is a frequency prefactor, ΔE_t is the energy barrier along the triplet PES ($\Delta E_t = 0.85$ eV), ΔE_{ts} is the energy difference between the singlet-triplet crossing point and the interstitial triplet O_2 configurations ($\Delta E_{ts} = 0.53$ eV), and k_B is the Boltzmann constant. For a temperature of 1200 K, we obtain for our calculated P_{ts} that $\Gamma_t/\Gamma_s \simeq 45$, which clearly indicates that the reaction will most likely proceed along the triplet pathway. Finally, one should note two things: (i) even if P_{ts} is higher by a factor of 10, we would still have the triplet channel as the most favorable one by a factor of approximately 5 and (ii) lower temperatures favor the singlet channel (P_{ts} increases as T decreases), which indicates that one would probably have a worse quality interface at lower T.

The implications of this result for the understanding of the oxidation process at the Si/SiO_2 cannot be underestimated. If there were always a switch to a singlet PES the oxidation would surely involve the PL defect. This would imply that either the interface would contain a large number of defects or the extra oxygen at the PL would have to migrate from one Si-O-Si bond to another until it would reach a Si-Si. However, to have a high quality interface this O migration must somehow happen preferentially in a direction parallel to the interface. On the other hand, the fact that the oxidation proceeds with a high probability along the triplet PES implies that the O-O bond is naturally broken as a perfect Si-O-Si bond is formed. The O atom ejected towards the interstitial site will have a high probability of being incorporated into a nearby Si-Si bond, forming in this way another perfect Si-O-Si bond. Therefore, the spin degree of freedom may be one of the important factors determining the high quality of the Si/SiO_2 interface. Finally, it should be noted that such an effect is very likely to be present in many other reactions involving either O_2 molecules or O atoms, indicating that they are very important not only for the microscopic understanding of the Si oxidation process, but also for the understanding of many other oxidation reactions in condensed phases.

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