

Backbond Oxidation of the Si(001) Surface: Narrow Channel of Barrierless Oxidation

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Oxidation of the Si(001) surface was studied by the first principles calculation technique with spin-polarized gradient approximation. We have clarified the apparent barrierless reaction mechanism of the backbond oxidation of the surface Si by incoming O₂ molecules. An O₂ molecule does not attack directly the backbond but the oxidation occurs via metastable chemisorption states on the Si surface. We have also found that the triplet-to-singlet spin conversion is crucial in explaining the incident energy dependence of the sticking probability of O₂ molecules. [S0031-9007(98)05462-3]

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The oxidation of the Si surface has been of great interest and importance in the modern Si technology. The general trend in the Si technology towards nanoscale devices requires precise control of oxidation of Si surface, which in turn requires detailed knowledge of atomic oxidation processes. Intensive studies both experimental and theoretical have been carried out and several adsorption sites of O atoms and possible adsorption channels for O₂ molecules on the Si(001) surface have been suggested [1]. Molecular beam experiments reported that the initial sticking probability S_0 of an O₂ molecule with a low incident energy ($E_i < 0.1$ eV) decreases with increasing temperature, while S_0 for a high incident energy ($E_i > 0.5$ eV) shows an opposite tendency up to 900 K, above which the desorption channel of volatile SiO opens [1–4]. The S_0 versus temperature curves for high and low incident energy regimes cross roughly at 300 K. Based on these observations Miyake *et al.* concluded that for small E_i , the precursor-mediated chemisorptions take place at lower temperatures, and that for larger E_i , on the other hand, the direct reactions with energy barriers become dominant [1,4]. This interpretation was also supported by the analysis of time-of-flight spectra and of angular distribution of scattered O₂ molecules from the Si(001) surface for various incident energies [4]. The absolute values for S_0 reported so far, however, scatter in a wide range from 2×10^{-4} to 0.2 at 300 K [1], showing that S_0 is sensitive to the surface preparation. For example, the recent scanning tunneling microscopy (STM) studies by Avouris *et al.* [5] on the initial stage of thermally oxidized Si(001) surface revealed that the oxidation occurs preferentially at the C-type defects among other defects and the perfect part of the surface appears to be rather inactive against oxidation. This suggests that the smaller values in the range cited above for S_0 will be appropriate for the ideal Si(001) surface. More recently, using scanning reflection electron microscopy (SREM), Watanabe *et al.* obtained strong evi-

dence that the oxidation of Si(001) surface proceeds in a layer-by-layer mode and that the first submonolayer including backbonds is oxidized with almost no activation energy [6]. The enhanced buckling of Si dimers after oxidation observed by the STM measurement also suggests the backbond oxidation [5].

The essential features of the initial oxidation processes on the perfect Si(001) surface suggested by the above experimental facts are summarized as follows: (i) existence of channels for almost activation barrierless dissociative chemisorption, (ii) the channels seem to be narrow and become even narrower for high incident energy O₂ molecules at low substrate temperatures, and (iii) backbond sites are mostly attacked.

The aim of the present Letter is to present theoretical interpretations to these features. Theoretical studies have been performed by several groups [7–11]. However, most of them studied the oxidation by O atoms or the stable atomic configurations after oxidation. In the present Letter, we study oxidation processes by O₂ molecules. Miyamoto and Oshiyama studied the similar problem and concluded that the dissociative chemisorption can occur without any activation energy at all sites they have studied of the substrate surface [9]. However, this conclusion may not be consistent with the very small S_0 observed experimentally. This is partly because their study did not take into account the spin degrees of freedom. We will demonstrate in the following that the chemistry depends strongly on the constraint we may impose on the spin state of the system. The ground state of an O₂ molecule is spin triplet with half-filled $2p\pi_g^*$ molecular orbital. When an O₂ molecule approaches the solid surface, the lowest energy state of the whole system becomes singlet because of the hybridization between the $2p\pi_g^*$ orbitals and the substrate states. Therefore, the process of oxidation is accompanied by the triplet-to-singlet conversion induced by the spin-orbit interaction, which is very weak in an O₂ molecule.

The calculations are performed using the Vanderbilt's ultrasoft pseudopotential [12] for oxygen and the Troullier-Martins' optimized norm-conserving pseudopotential [13] for silicon. We found that the cutoff energies of 25 Ry for the wave functions and 144 Ry for the augmented electron densities are sufficient. The Si(001) surface is modeled as a repeated slab with a 4×2 unit cell, consisting of 10 layers of Si atoms and a vacuum spacing of the same thickness. Inversion symmetry with respect to the center of the slab is imposed. The local density approximation (LDA) and even its spin-polarized version (LSDA) fail to reproduce the binding energy of an O_2 molecule. The experimental value is 5.11 eV, while LDA and LSDA give the considerably larger values of 8.91 and 7.19 eV, respectively. At the present stage, only the spin-polarized generalized gradient approximation (SP-GGA) [14], on which the present work is based, can give the reasonable binding energy of 5.60 eV within an accuracy of 10%.

We have studied the oxidation processes for several initial configurations with an O_2 molecule above the Si(001) surface, three cases of which are shown in Fig. 1. The O_2 molecular axis are set to be parallel to the substrate surface, because in this configuration the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of an O_2 molecule can interact efficiently with the occupied and unoccupied Si(001) surface states. As a first step, we search a local minimum structure by relaxing the coordinates of the whole system according to the force acting on each atom except for those atoms in the innermost two layers, which are kept fixed. This can be regarded as a simulation for the limit of a low temperature and low incident energy. Note that as long as the same local minimum configuration is reached, the

details of the initial configuration of an O_2 molecule will affect only the intermediate processes. In most cases, an O_2 molecule weakly attaches to the up dimer atom on the surface without noticeable changes in bond lengths, and spin polarization. The binding energies are in the range of 0.1–0.2 eV. These metastable states may correspond to precursor states as is suggested experimentally [4].

In order to study the dissociative chemisorption processes as the second step, we move the O_2 molecule towards the surface quasistatically. In this procedure, the distance between the center of the O_2 molecule and the surface is controlled artificially, while other coordinates except for those in the innermost layers were fully relaxed. The first example shown as Fig. 1(a) may be regarded as a possible process of direct backbond oxidation. With the prescription mentioned above, the initial oxygens shown by thick solid circles end up with the final ones shown by shaded circles. The O_2 molecule is dissociatively chemisorbed with one O atom sitting at the bridge site while the other is at the backbond site. The adsorption energy is as large as 6.16 eV, and the spin state becomes singlet. The triplet-to-singlet conversion takes place immediately after the displacement of O atoms from their shallow local minimum configuration obtained in the first step procedure toward the transition state explored in the second step procedure. The energy of the transition state, i.e., the activation barrier, is found to be 0.8 eV. We have studied three other different cases (not shown) and found that for all of them activation barriers of 1.0–2.4 eV are needed for direct dissociative chemisorption. It may be a fairly general feature that the direct oxidation on the Si surface needs a considerable activation energy including backbond oxidation.

However, we demonstrate below that there exist narrow channels which actually lead to apparent barrierless backbond oxidation through a two-step mechanism. One of such examples is the case in Fig. 1(b), where, as the first step, starting with the initial configuration shown by the solid circles, the O_2 molecule dissociates spontaneously, and each O atom is bonded to the bridge site of the nearest substrate dimer as shown by a shaded circle. As the adsorption energy of 5.99 eV is slightly smaller than that of the case (a), the backbond oxidation is, in fact, energetically more favorable than the bridge-site oxidation. As the second step, we consider a reaction path along which an O atom at the dimer bridge site moves toward the backbond site as shown in Fig. 1(d). The energy variation along this path is illustrated in Fig. 2, together with the local geometries at representative positions. Although there are two adiabatic energy barriers in this process, the kinetic energy for the O atom to overcome these barriers can be supplied easily from the initial dissociation energy of 5.99 eV, leading to the apparent barrierless backbond oxidation. The case 1(c) is another such example. In the local minimum configuration reached by the initial configuration of the case 1(c), the bond length between O atoms is increased by 0.3 Å, and the Si dimer underneath becomes symmetric.

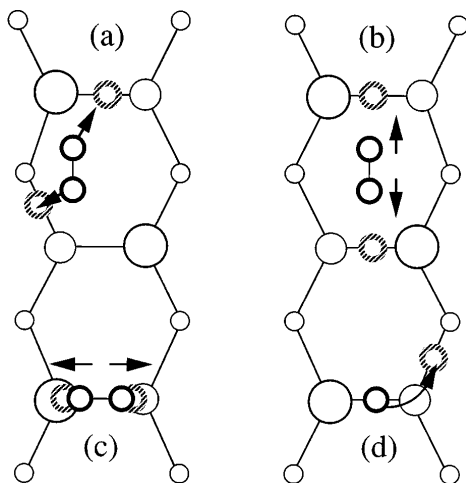


FIG. 1. (a), (b), and (c) are the initial and metastable configurations of adsorbed O_2 molecules on the Si(001) surface. Thick solid and shaded circles indicate O atoms at initial and metastable structures, respectively. Thin solid circles indicate substrate Si atoms. The larger circles are closer to the eye. (d) The diffusion path of an O atom at the bridge site to the backbond site, realizing the conversion of the metastable structure (b) to the more stable structure (a).

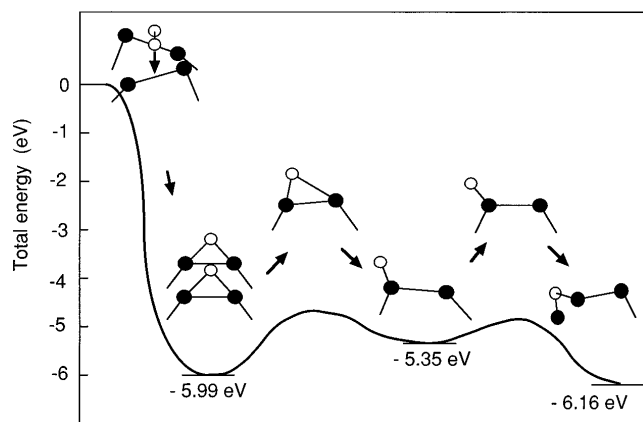


FIG. 2. Total energy variation along the diffusion path shown in Fig. 1(d). The insets are local geometries of adsorbed O atoms and a Si dimer underneath at typical points on the diffusion path. There are two energy barriers with 1.3 and 0.5 eV. The large chemisorption energy of 5.99 eV for the metastable structure (b) in Fig. 1 is large enough for an O atom to go over these barriers with no extra energy, indicating the apparent barrierless oxidation of a backbond of Si surface.

The energy gain of 2.96 eV, which is much smaller than the corresponding energy gain for the cases 1(a) and 1(b), may still be sufficient to convert the final configuration of Fig. 1(c) to a configuration of backbond oxidation. The energy variation along the diffusion path is illustrated in Fig. 3. There are no energy barriers larger than the initial dissociation energy of 2.96 eV, again suggesting a possible barrierless oxidation of a backbond.

We have demonstrated the existence of channels of barrierless oxidation at the backbond sites. Among several configurations studied, the two examples described above are the only possible such channels. This may suggest that the channels of barrierless oxidation will be fairly narrow. Furthermore, even if an O_2 molecule may approach the surface, the orientation of the molecular axis makes a dif-

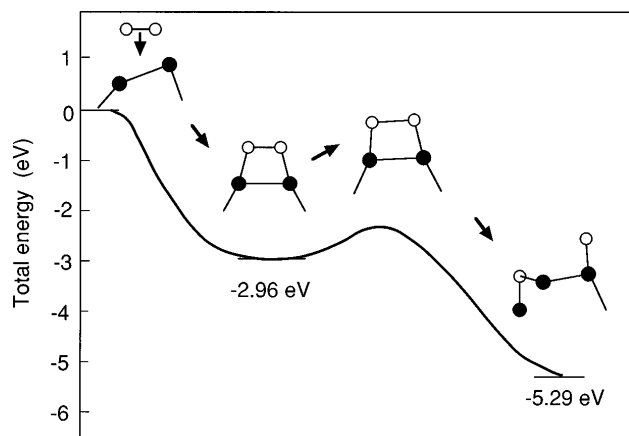


FIG. 3. Total energy variation along a path from the initial structure in Fig. 1(c) to the more stable structure with an O atom at backbond site. The chemisorption energy in Fig. 1(c) of 2.96 eV is larger than any energy barriers along the path, showing again the apparent barrierless backbond oxidation.

ference in the activation barrier. It was shown by Hoshino *et al.* that a large activation energy of 2.6 eV is needed for a triplet O_2 molecule to be dissociatively chemisorbed at the center of a Si dimer as in Fig. 1(c), if the molecular axis is kept perpendicular to the surface [10]. For an O_2 molecule with a sufficiently small incident energy, the position and the molecular orientation can be adjusted so that the molecule may trace the lowest energy path. However, as the incident energy increases, an O_2 molecule will not have sufficient time to adjust its lateral position and molecular orientation before it hits the surface. Therefore, the probability for an O_2 molecule to take the barrierless oxidation path will be further reduced. This feature known as a steering effect [15] is fairly common in many chemical reactions.

There is another controlling factor to narrow the channel. We have tacitly assumed that the triplet-to-singlet spin conversion occurs instantaneously, despite the small spin orbit interaction of an O_2 molecule. We examine in detail the spin conversion effect on the reaction probability for the barrierless oxidation for the case of Fig. 1(b) as an example. Two different total spin states ($S_z = 1$ and 0) for the initial configuration are considered. The total energies versus the distance z between an O_2 molecule and the substrate surface are shown in Fig. 4. The triangles in the region $z > 1.57 \text{ \AA}$ show ground states with $S_z = 1$, where the substrate has no spin polarization and the O_2 molecule is in the triplet state. In the region $z < 1.57 \text{ \AA}$, the ground states are realized by the configuration with $S_z = 0$, where the substrate has no spin polarization as in

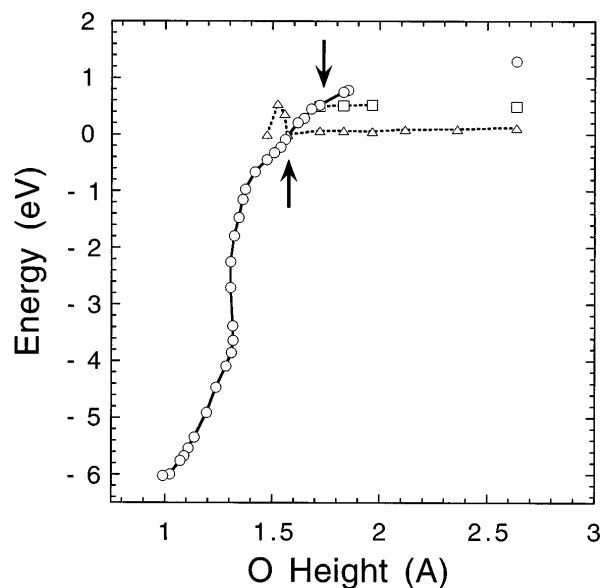


FIG. 4. The total energies of the case in Fig. 1(b) are plotted against the averaged height of two O atoms from the Si surface. The triangles show energies of triplet states. The circles and squares show those of singlet states. While the circles denote the states in which both substrate and O_2 molecule are not polarized, the squares denote the states, where both substrate and O_2 molecule have polarization, which couple antiferromagnetically leading to the $S_z = 1$ of the total system.

the region $z > 1.57 \text{ \AA}$, while the O_2 molecule is changed to the singlet state (circles), due to spin conversion. The triangles in this region show excited states with $S_z = 1$, which are obtained with constraint for spin polarization. As to the excited states in the region $z > 1.57 \text{ \AA}$, on the other hand, we have generally two spin configurations for $S_z = 0$, namely, (i) both O_2 molecule and substrate have spin polarization, which couples antiferromagnetically to result in $S_z = 0$ of the total system (squares), and (ii) both O_2 molecule and substrate have no spin polarization (circles). The energies of polarized and totally unpolarized states are 0.38 and 1.14 eV higher than the ground state, when an O_2 molecule is located far from the surface. As an O_2 molecule comes closer to the surface, the energy difference between the two states decreases, and eventually it vanishes at around 1.75 \AA from the surface. It should be stressed that in the narrow range $1.57 < z < 1.75 \text{ \AA}$, the states with spin polarization in both the O_2 molecule and the substrate do not exist. Figure 4 helps us construct the following picture for the oxidation process on the low temperature substrate. An O_2 molecule with a very small incident energy may be trapped at a shallow energy minimum at around $z = 1.6 \text{ \AA}$ along the path with $S_z = 1$. Then the reaction path may switch to another path with $S_z = 0$ due to the spin-orbit interaction and the O_2 molecule dissociates as shown in Fig. 1(b). This is an adiabatic path. On the other hand, if the incident energy becomes higher, the probability of the system tracing along the path with $S_z = 1$, i.e., a diabatic process, will increase. The competition between the adiabatic and diabatic processes at an energy crossing region can be treated by the Landau-Zener-Stueckelberg theory [16]. The probability P of an adiabatic process with a small perturbation V may be approximated by

$$P = 2 \left[1 - \exp\left(-\frac{V^2}{h\nu|F_1 - F_2|}\right) \right], \quad (1)$$

where ν is the velocity of an incident O_2 molecule, F_1 and F_2 are the slopes of two energy curves at the crossing point, and h is the Planck's constant. Using the spin-orbit matrix element of 122 cm^{-1} between the triplet and the singlet states for an O_2 molecule [17], we estimate the probability of the adiabatic process to be 0.08 and 0.025 for E_i of 0.1 and 1.0 eV, respectively. Therefore, the triplet-to-singlet conversion also contributes to narrowing the channel for the barrierless oxidation even for relatively low incident energy O_2 molecules.

Finally, we comment on the local geometry of the backbond oxidation. Uchiyama and Tsukada concluded that an O atom in the backbond site of a down dimer Si atom is more stable in energy compared with that for an up dimer Si atom [11]. We have also found that even if we put an O atom in the backbond site of an up dimer Si atom, the dimer flips to reverse the orientation of the buckling. Therefore, the backbond oxidation fixes the attached Si dimer buckling so that the nearest surface Si atom becomes the down dimer atom. These results are consistent with the

experimental STM image, indicating the enhanced buckling of the Si dimer after exposure to O_2 molecules [5].

In conclusion, the backbond oxidation may be energetically most favorable being consistent with the previous theoretical calculations and experimental observations. However, the direct processes for the backbond oxidation require 0.8 to 2.4 eV for activation barriers in contrast to the experimental evidence for the almost barrierless processes. We have proposed a two-step (indirect) mechanism for the backbond oxidation which does not require any external energy supply, meaning that the process is apparently barrierless. Among several configurations studied, only two of them lead to such apparent barrierless backbond oxidation. We have demonstrated that the spin degrees of freedom play important roles in the oxidation process. The triplet-to-singlet conversion process contributes to a narrowing of the channel.

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