

## Energetics in the initial stage of oxidation of silicon

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We present microscopic calculations of the energetics in the initial stage of oxidation of Si. We find that an  $O_2$  molecule penetrates the oxygen-covered surface, dissociates near a bond-center site, and forms a peculiar bond configuration with Si atoms exothermically. We also find that the bond formation results in several oxidation states of the Si atoms at the interface and in a swelling of the Si—O—Si bond network from the surface.

Oxidation, though familiar from ancient times, is poorly understood from a microscopic viewpoint.<sup>1,2</sup> Semiconductor—in particular, Si—technology depends crucially on oxidation with an ideal insulator  $SiO_2$ , which is normally in vitreous form. With decreasing size of electron devices, it is imperative that we acquire a detailed understanding of the oxidation phenomenon and of the relation between physical properties and atomic structures of the resulting  $SiO_2$ . During oxidation reaction, the interface between Si and  $SiO_2$  propagates into the Si substrate. In terms of elementary processes, oxidation thus consists of dissociation, adsorption, penetration, and diffusion of  $O_2$  molecules through the surface, and bond formation between the Si and O atoms near the surface or the interface. It then becomes necessary to clarify the energetics in these oxidation reactions, the stability of the resulting atomic structures of O and Si atoms, and other intrinsic features of the oxidation phenomena from a microscopic viewpoint.

In this paper, we report first-principles calculations of the energetics of dissociation, adsorption, penetration, and bond formation of oxygen moving through the Si(100) surface. The results enable us to take a significant step in improving our understanding of the microscopic mechanisms of oxidation. We find (i) that an  $O_2$  molecule dissociates at any site on the surface, (ii) that after dissociation an individual O atom exhibits multistability at its adsorption site, (iii) that an additional  $O_2$  molecule penetrates the oxygen-covered surface with the aid of thermal motions and then dissociates near a bond-center site of Si, (iv) that, in the resulting atomic structure which locally resembles the crystalline form of silica, different oxidation states of the Si atoms may exist, and (v) that the Si—O—Si units formed in Si swell from the surface with increasing numbers of O atoms in the Si substrate.

The calculation is done for the repeating-slab geometry within density-functional theory. We use norm-conserving nonlocal pseudopotentials,<sup>3</sup> the local-density approximation for exchange and correlation,<sup>4</sup> and the Gaussian-orbital basis set to express the wave functions. Both the earlier calculated values with the well-converged plane-wave basis set<sup>5</sup> and the experimental data on the structural properties of Si and  $SiO_2$  are reproduced in the present scheme of the calculation.<sup>6</sup> The

total-energy optimized atomic configurations are obtained by moving O and neighboring Si atoms according to a calculated force (Helmann-Feynman force plus its correction term<sup>7</sup>) acting on each atom. To arrive at definitive conclusions, a careful examination of the calculational conditions is needed.<sup>8</sup>

On the Si(100) surface, there are several candidate sites for adsorption or dissociation of an  $O_2$  molecule (Fig. 1): between the Si dimers (site *A*), on the dimer (site *B*), and between the rows of the dimers (sites *C* and *D*). For each site, we place an  $O_2$  molecule above the surface with its bond axis arbitrarily tilted. We then look for the most favored adsorption or dissociation site by moving the O and Si atoms according to the calculated forces toward the total-energy optimized configuration (i.e., the atomic motion along the intrinsic reaction coordinates). In Fig. 2, we display the example for site *A*: First, an  $O_2$  molecule is placed above site *A* with its axis rotated by  $45^\circ$  both for [100] and [011] directions [Fig. 2(a)]. Then the molecule approaches the surface and rotates its axis so as to be parallel to the surface and perpendicular to the Si dimer axis [Fig. 2(b)]. When the molecule is between the Si dimers in the vicinity of the surface [Fig. 2(c)], the forces act on the two constituent O atoms to dissociate the molecule. After dissociation, each oxygen atom indeed settles into one of the two adsorption sites near the Si dimer that are (meta)stable for the O atom: One is a site on the dimer and the other is a site between the two Si atoms of the dimer (the bridge site).<sup>6</sup> This dissociation and subsequent atomic-adsorption reaction is exothermic. The calculated heat of formation for the reaction is 2.5 eV for adsorption at the dimer site or 3.0 eV for adsorption at the bridge site. The local vibration energy and the electron density of states for the adsorption sites obtained are consistent with the experimental data.<sup>6</sup> A mechanism of dissociation is visible in the valence-electron density shown in Fig. 2(d): More than one electron is transferred from Si to the antibonding  $\pi$  orbital of the  $O_2$  molecule so that bonding between the O atoms diminishes.

For the other sites, *B*, *C*, and *D*, we have also found that an  $O_2$  molecule approaching the surface rotates its axis, and that the electron is transferred from Si to the  $O_2$  so that the molecule dissociates.<sup>9</sup> Moreover, we have found that the adsorption site for the resulting oxygen atom depends on where the preceding  $O_2$  molecule disso-

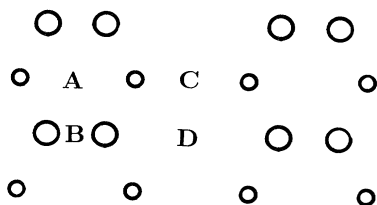


FIG. 1. Top view of the Si(100) surface. The top-layer Si (large circles, forming the dimers) and the second-layer Si (small circles) atoms are shown.

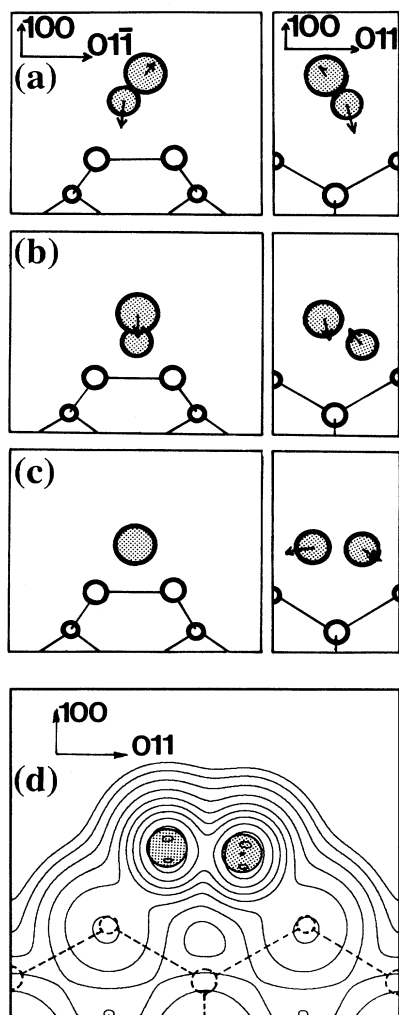


FIG. 2. Dissociation of an  $O_2$  molecule (dotted circles) approaching the Si(100) surface directly above site *A* [from (a) to (c)]. (a) At first, the center of the molecule is placed  $2.2 \text{ \AA}$  above the surface, and the forces (the arrows) of  $0.05 \text{ Ry/a.u.}$  and  $0.09 \text{ Ry/a.u.}$  act on the two constituent O atoms of the molecule. (c) In the geometry, the forces of  $0.09 \text{ Ry/a.u.}$  and  $0.07 \text{ Ry/a.u.}$  act on the O atoms which then reach one of the two (meta)stable adsorption sites: a site  $1.5 \text{ \AA}$  above the Si dimer or the bridge site. The contour plot of the valence-electron charge density in the geometry (c) is shown in (d). The maximum value of the contour is  $1.1 \text{ electrons/(a.u.)}^3$  and the subsequent lines differ by a factor of 2.

ciates: If the molecule approaches the surface above site *A* or *B*, the resulting O atom is adsorbed after dissociation at the site on the Si dimer or at the bridge site, as stated above. On the other hand, if the  $O_2$  molecule approaches a site between the dimer rows (i.e., site *C* or *D*), the molecule dissociates and each of the resulting two O atoms is adsorbed at a site away from the Si dimer. An example for O adsorption at site *C* after  $O_2$  dissociation is shown in Fig. 3. The dissociation and adsorption reaction shown in Fig. 3 is exothermic and the calculated heat of formation is  $1.4 \text{ eV}$  per O atom.

It is known<sup>2,10</sup> that both a rapid and a subsequent slow process occur in the oxygen uptake in the initial stage of the oxidation. The two processes are occasionally interpreted as due to the coexistence of molecular- and atomic-adsorption sites.<sup>10</sup> The present calculation, however, shows that there is no (meta)stable molecular-adsorption site but rather three atomic-adsorption sites. Therefore, for the Si(100) surface, the rapid and the slow processes observed may be due to the coexistence of the several metastable atomic-adsorption sites, rather than a combination of atomic- and molecular-adsorption sites.

We now present results on penetration of the  $O_2$  molecule through the oxygen-covered surface and successive bond formation between the O and Si atoms. In the case of one-monolayer coverage of oxygen, the most energetically favorable site for oxygen adsorption is found to be a bridge site in which the Si dimer is decomposed by the intervening O atom.<sup>11</sup> We then place an oxygen molecule above the O-covered surface, and seek the path of penetration of the  $O_2$  molecule. We have found that the calculated forces acting on the  $O_2$  molecule are repulsive from the surface unless the O atoms are already adsorbed and the top-layer Si atoms are dislodged; i.e., there is an energy barrier for  $O_2$  penetration if there is no relaxation of the neighboring atoms. When the top-layer O and the Si atoms are moved along the  $[011]$  direction by  $0.5 \text{ \AA}$ ,

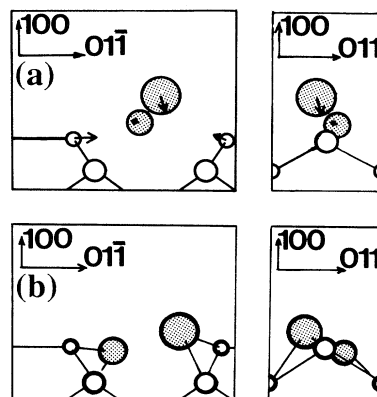


FIG. 3. Dissociation of an  $O_2$  molecule (dotted circles) approaching from the Si(100) surface above site *C*. At first, the center of the molecule is placed  $1.1 \text{ \AA}$  above the surface, and the forces of  $0.06$  and  $0.03 \text{ Ry/a.u.}$  (the arrows) (a) act on the two O atoms. The molecule dissociates near the surface (not shown here), and the final geometry after dissociation is shown in (b).

however, the  $O_2$  molecule is found to penetrate through the oxygen-covered surface. After penetration, the molecule dissociates in the vicinity of the bond-center site of top- and second-layer Si atoms. The dissociation is again caused by electron transfer from the Si bonds to the  $\pi$  orbital of the  $O_2$  molecule. This suggests that, in the oxidation reaction, dissociation of the  $O_2$  molecule occurs not on the O-covered surface or in the  $SiO_2$  film but at the interface where the electrons triggering the dissociation can be donated by the Si—Si bonds. The final stable geometry that we have found is shown in Fig. 4 along with the valence-electron charge density. We can see a peculiar bond formation of Si and O after  $O_2$  penetration and dissociation. This penetration, dissociation, and bond-formation reaction is exothermic: The calculated heat of formation is 1.2 eV per O atom. A most remarkable feature of this stable geometry is its local structure. The Si—O bond length (1.6 Å) and the Si—O—Si bond angle ( $144^\circ$ ) obtained in Fig. 4 are surprisingly close to values observed in  $\alpha$  quartz, the most stable crystalline form of  $SiO_2$ . The Si and the O atoms strongly favor this local bonding configuration in many cases.<sup>12</sup> Yet the O—Si—O bond angle ( $81^\circ$ ) is much smaller than the corresponding value (about  $110^\circ$ ) in crystalline  $SiO_2$  under low pressures (i.e., quartz, cristobalite, or coesite).<sup>13</sup> Under high pressures, however,  $SiO_2$  has another crystalline form, stishovite. The value of the O—Si—O angle in stishovite ranges from  $81^\circ$  to  $98^\circ$ , and is comparable to the value obtained in the geometry in Fig. 4. This coexistence of the low- and high-pressure crystalline forms is a consequence of the local strain due to a sizable difference in Si—Si distance between  $SiO_2$  and the Si substrate.

The top-layer Si atoms in Fig. 4 are surrounded by three O atoms and one Si atom. To attain a bond configuration topologically the same as in  $SiO_2$  (i.e., four

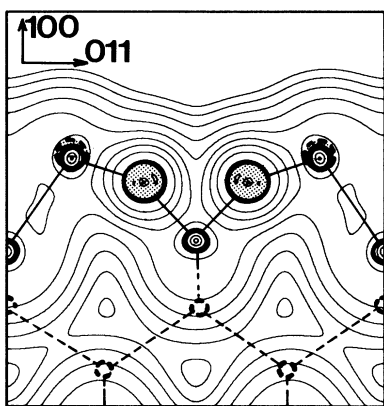


FIG. 4. The stable atomic geometry after penetration and dissociation of the  $O_2$  molecule near the Si(100) surface. The  $O_2$  molecule penetrates the 1-monolayer-oxygen-covered surface, dissociates, and forms Si—O bonds with the top- and second-layer Si atoms. We note the sizable relaxation of the first- and the second-layer Si atoms. The maximum value of the contour plot of the valence-electron charge density is 1.1 electrons/(a.u.)<sup>3</sup>, and the subsequent lines differ by a factor of 2.

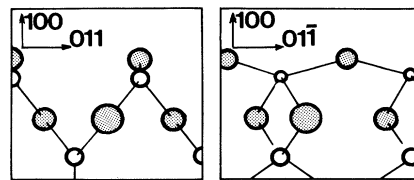


FIG. 5. Swelling of the Si—O—Si local bond network from the Si(100) surface observed in the stable atomic geometry. The O atoms (dotted circles) intervene at all the bond-center sites between the first- and the second-layer Si atoms. Because of limited space, the O atoms are squeezed so that the adjacent Si—O—Si bonds are rotated in opposite directions (represented by large and small circles).

oxygen atoms around a Si atom), additional O atoms are required to intervene at the remaining bond-center sites. In fact, due to the large upward displacement of the top-layer Si atoms (0.5 Å from the original site), the remaining bonds are weakened considerably, as is clearly seen in the contour plot in Fig. 4. Yet the resulting Si—Si distances are still too small to accommodate the additional O atoms. A natural consequence is therefore a swelling of the Si—O—Si unit from the original Si surface. In Fig. 5 the obtained metastable geometry is shown after penetration of additional O atoms, in which the top-layer Si atoms are surrounded by four O atoms and Si—O—Si units swell from the original Si surface. This reaction of oxygen uptake is again exothermic: The calculated heat of formation in the reaction adding an additional O atom is 1.5 eV. The structure in Fig. 5 is again a local mixture of the low- and high-pressure crystalline forms of  $SiO_2$ . The swelling of the Si—O—Si unit obtained in Fig. 5 corresponds to a volume expansion of the region containing the O and the top- and the second-layer Si atoms by 83%. This value can be compared with the volume difference between Si and silica (e.g., the ratio in volume per Si atom of  $\alpha$ -quartz to Si is 1.88). It is interesting to note that the expansion has begun from the very earliest stages of oxidation.

Another important finding shown in Figs. 4 and 5 is the existence of different oxidation states of Si atoms. In Fig. 4, the top-layer and second-layer Si atoms are surrounded by three and two, respectively, O neighbors; in Fig. 5, the top-layer Si atom, by four O neighbors. The difference in coordination numbers that we have found indeed results in different core-level shifts of the Si atom, which is exactly observed in the photoemission-spectroscopy measurements for the  $SiO_2/Si$  interface.<sup>14,15</sup> Moreover, in case of the Si surrounded by three O atoms, there is the imbalance in length between the two different bonds: the Si—Si and the Si—O bonds. The consequence is the significant stretching of the Si—Si bond (see the contour plot in Fig. 4). The stretching in this stable geometry causes further oxidation as is demonstrated above, and, on the other hand, reduces the formation energy of the Si self-interstitial atom at the interface. This is the microscopic origin of the observed injection of the self-interstitial atoms to the Si substrate upon oxidation.<sup>16</sup>

The intrinsic features in the initial stage of oxidation that we have found here are the following: thermal penetration of the  $O_2$  molecule, dissociation of the molecule due to electron transfer from Si, characteristic bond formation of the Si and O atoms accompanied by a large stretching of the Si—Si bond, and the resulting expansion in volume of the local atomic configurations. These features are not limited to the initial stage. If the  $SiO_2$  film has been already formed, although the thermal diffusion of the  $O_2$  molecule plays a role, the essential features of the oxidation stated above are expected to occur at the frontier of oxidation: the  $SiO_2/Si$  interface. It is further noticed that the local bond lengths and an-

gles of the Si and O atoms formed during the oxidation are similar to those in the most stable silica,  $\alpha$ -quartz. In the stable geometries of Figs. 4 and 5, however, the Si atoms near the O atom are significantly dislodged. Further, the network in the Si crystal is topologically different from the Si network in the crystalline forms of silica. Thus the vitreous form of  $SiO_2$  is realized.

In conclusion, we have presented a microscopic picture of the oxidation of Si on the basis of *ab initio* total-energy electronic-structure calculations. The results provide a firm theoretical framework for understanding the oxidation phenomenon and the atomic structures of the resulting  $SiO_2$  films.

<sup>1</sup>See the special issue in *Philos. Mag.* **55** (2 and 5) (1987).

<sup>2</sup>Much useful information may be found in pioneer experiments: see M. Tabe, T. T. Chiang, I. Lindau, and W. E. Spicer, *Phys. Rev. B* **34**, 2706 (1986), and references cited therein.

<sup>3</sup>D. R. Hamann, M. Schlüter, and C. Chiang, *Phys. Rev. Lett.* **43**, 1494 (1979).

<sup>4</sup>D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980).

<sup>5</sup>A. Oshiyama and M. Saito, *J. Phys. Soc. Jpn.* **56**, 2104 (1987); *Phys. Rev. B* **36**, 6156 (1987). For results on  $SiO_2$ , see Y. Bar-Yam, S. T. Pantelides, and J. D. Joannopoulos, *ibid.* **39**, 3396 (1989).

<sup>6</sup>Y. Miyamoto and A. Oshiyama, *Phys. Rev. B* **41**, 12 680 (1990).

<sup>7</sup>M. Saito and A. Oshiyama, *Phys. Rev. B* **38**, 10 711 (1988), and references therein.

<sup>8</sup>Most calculations have been done with a slab consisting of 4 Si atomic layers plus 11-Å vacuum layers, and the structural stability of the obtained geometry is always confirmed by repeating the calculations with the thicker slab consisting of 8 atomic layers plus 11-Å vacuum layers. Also in the lateral directions, a sufficiently long period of the unit cell is necessary to avoid a spurious interaction between the O atoms. Further, the compact nature of the O orbitals requires more than 10 mesh points per Si—O bond in performing fast-Fourier transformation.

<sup>9</sup>The effect of spin polarization has been examined by the local-spin-density calculation. We have found that, as the distance between the  $O_2$  molecule and the Si surface decreases, the en-

ergetically most favorable spin state changes from the triplet to the doublet, and that at the distance at which the dissociation of the  $O_2$  molecule occurs no spin-polarized state can be obtained.

<sup>10</sup>U. Höfer, P. Morgen, W. Wurth, and E. Umbach, *Phys. Rev. Lett.* **55**, 2979 (1985); *Phys. Rev. B* **40**, 1130 (1989).

<sup>11</sup>For the bridge site, we have optimized the locations of the O and the top-layer Si atoms, and the calculated binding energy is 7.9 eV per oxygen. These results are quantitatively different from, and qualitatively similar to, the results from the total-energy calculation by I. P. Batra, P. S. Bagus, and K. Hermann, *Phys. Rev. Lett.* **52**, 384 (1984).

<sup>12</sup>We observe this bond configuration (a Si—O bond length of 1.6 Å and a Si—O—Si angle of 144°) energetically favorable in the case of the O impurity in bulk Si (Ref. 7), and in the case of the Si/ $SiO_2$  interface [M. Hane, Y. Miyamoto, and A. Oshiyama, *Phys. Rev. B* **41**, 12 637 (1990)].

<sup>13</sup>R. W. G. Wyckoff, *Crystal Structures* (Interscience, New York, 1963), Vol. 1, p. 312.

<sup>14</sup>F. J. Grunthaner, P. J. Grunthaner, R. P. Vasquez, B. F. Lewis, J. Maserjian, and A. Madhukar, *Phys. Rev. Lett.* **43**, 1683 (1979).

<sup>15</sup>G. Hollinger and F. J. Himpsel, *Phys. Rev. B* **28**, 3651 (1983); F. J. Himpsel, F. R. McFeely, A. Taleb-Ibrahimi, J. A. Yarmoff, and G. Hollinger, *ibid.* **38**, 6084 (1988).

<sup>16</sup>See, e.g., P. M. Fahey, P. B. Griffin, and J. D. Plummer, *Rev. Mod. Phys.* **61**, 289 (1989).