First-Principles Study of Oxide Growth on Si(100) Surfaces and at $SiO_2/Si(100)$ Interfaces

Hiroyuki Kageshima and Kenji Shiraishi
NTT Basic Research Laboratories, 3-1 Morinosato-Wakamiya, Atsugi, Kanagawa, 243-0198, Japan

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The energetics of the atomic process of Si-oxide growth on Si(100) surfaces and at $SiO_2/Si(100)$ interfaces are theoretically studied by first-principles calculation. It is found that the stress induced during the growth plays a crucial role in the growth procedure itself. The preferential growth direction of the oxide nucleus on the surfaces is vertical to the substrate, whereas that at the interfaces is lateral. Moreover, Si atoms are inevitably emitted from the interface to release the stress induced during Si oxide growth. [S0031-9007(98)08059-4]

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The oxidation of Si has been a general problem for researchers in both engineering and scientific fields. Recent radical advances in the down scaling of Si devices have led to the need for fine control techniques to form oxide layers as thin as 1 nm or less. Therefore, an atomic-scale understanding of Si oxidation is strongly demanded by industry as well as in materials science. Although the Si oxidation process has been intensively investigated [1–7], this level of understanding has not yet been reached.

During oxidation, the size of the Si region decreases as the size of the oxide region increases. This feature is quite striking compared with ordinary epitaxial growth processes where only the size of the newly formed region increases, or ordinary etching processes, where only the size of the substrate region decreases. Furthermore, since the volume of the increased oxide region is larger than that of the decreased Si region, the total volume increases as oxidation proceeds. The volume per Si atom in the SiO_2 crystal is about twice that in the Si crystal. Because the reaction of Si to oxide is thought to occur at the Si-oxide/Si interface, this expanded volume should result in high stress there. However, this stress has been offered only as the reason for the creation of Si self-interstitials at the oxide/Si interfaces in explaining oxidation-induced stacking faults (OSF) [8], oxidation-enhanced diffusion (OED), and oxidation-reduced diffusion (ORD) [9].

This study aims to theoretically clarify the energetics of the atomic process of Si oxide growth on Si(100) surfaces and at $SiO_2/Si(100)$ interfaces by first-principles calculation, and to further our understanding of the effect of the stress induced during the oxidation process. While dynamical effects, such as adsorption, dissociation, and diffusion of the oxidant, are also important in the oxidation process, they are beyond the scope of this paper. First, we will show how the stress induced by the oxidation is related to the growth direction. Second, we will show how the accumulated stress is released.

The calculations were done according to the Vanderbilt ultrasoft pseudopotential method [10]. The exchange-correlation potential was treated within the ordinary local density approximation [11]. Plane waves up to 20.25 Ry were used for the bases. Eight k points in the 1×1 lateral unit cell were used for the Brillouin zone integrals. Freedom of spin was not considered. The lateral sizes of the unit cells were $c(4 \times 4)$ for the investigation of the growth direction on the surfaces and $c(2 \times 2)$ for the investigation of the growth direction at the interfaces and the release of the stress. We used the repeated slab geometry with a thick enough vacuum region. Surfaces of no interest on the slab were simply terminated by H atoms. The initial slab for the surface model typically has five and nine Si atomic layers for the $c(4 \times 4)$ and $c(2 \times 2)$ unit cells, respectively. The initial slabs for the interface model consist of two SiO_2 molecule layers and seven Si atomic layers [12]. The most stable atomic structures and their total energies were calculated with the lateral unit cell size kept constant. In the optimization, we fixed only Si atoms on the other side of the slab and made no assumptions about structural symmetry. After optimization, the force on any atom was smaller than 3×10^{-3} HR/a.u.

First, we studied the growth directions of an oxide nucleus on Si surfaces and at Si-oxide/Si interfaces. We investigated the growth direction on clean surfaces using the Si(100) surface model with buckled dimers as the initial surface. For this surface, the most stable adsorption site of the initial O atom is the backbond of the lower dimer atom [7]. We placed the first O atom at that site and added another one between the Si-Si bonds neighboring the first Si-O-Si bond. Second, we ascertained the most stable adsorption site for the second O atom. The candidates are shown in Fig. 1(a). The calculated total energies are 0.10, 0.02, -0.33, and -0.61 eV/unit cell, for the sites B, C, D, and E, respectively, relative to the total energy of the site A. Using the dihydride Si(100) surface model [13] as the initial surface, we also investigated the growth direction for a H-terminated surface. The most stable adsorption site for the initial O atom is the outermost Si-Si bond. We placed the first O atom at that site and added another one between the Si-Si bonds neighboring the first Si-O-Si bond. Then, we calculated the most stable adsorption

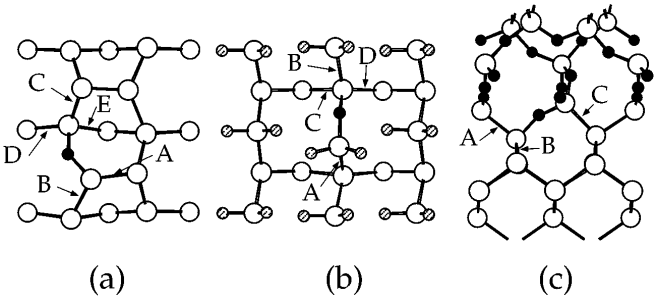

FIG. 1. Atomic structures for studying the oxide nucleus growth. (a) Top view for the clean surface, (b) top view for the dihydride surface, and (c) side view for the oxide/Si interface with the less-stressed quartzlike oxide. The filled circles are O atoms, the empty circles are Si atoms, and the small hatched circles are H atoms.

site of the second O atom. The calculated total energies are -0.12, -0.22, and -0.59 eV/unit cell, for the sites B, C, and D, respectively, relative to the total energy of the site A [Fig. 1(b)]. These calculations indicate that the oxide nucleus on the (100) surface preferentially grows vertically into the substrate, being independent of the surface reconstruction.

For the investigation of the growth direction for interfaces, we used the quartz/Si(100) interface model as the initial interface [Fig. 1(c)] [14]. While the real oxide layer formed by oxidation is amorphous, we modeled the oxide by a crystal SiO_2 because amorphous interfaces cannot be calculated with our first-principles approach. However, our model certainly has a perfect bond network without large stress, which is an important feature of the real amorphous oxide interface. We first introduced one O atom to the interface and ascertained the stable structure. Then, we introduced the second and third O atoms to the interface, assuming that all of the formed Si-O-Si bonds are connected. The calculations show that the structure, in which the second O atom is inserted into the site A, is energetically more stable (by 0.29 eV/unit cell) than the structure in which the second one is inserted into the site B. Moreover, the structure in which the second and third O atoms are inserted into the sites A and C is more stable (by 0.05 eV/unit cell) than the structure in which the second and third ones are inserted into the sites A and B. These results indicate that the oxide nucleus at the Si-oxide/Si(100) interface preferentially grows laterally, parallel to the interface [15].

The preferential growth direction of the oxide nucleus for the (100) substrate is, thus, different between "on the surface" and "at the interface." Since the vertical oxide growth on the surfaces is independent of the surface reconstruction, stress (rather than the bonding nature or the charge transfer) seems to govern the growth direction. Actually, it is easy for Si-O-Si bonds on the surfaces to expand vertically because the surface atoms in the Si region can move upwards with almost total freedom, while it is not easy for the bonds to expand laterally. Thus, the initial oxide nucleus on the surface should grow vertically in order to minimize the stress. In the case of the interface, the vertical expansion of Si-O-Si bonds is not easy because their movement is restricted by the covered oxide layer. Therefore, the energy gain due to the stress release by vertical growth is quite restricted. On the other hand, to minimize the interface energy, the initial oxide nucleus at the interface should grow laterally. We have confirmed these results by examining the stress distribution of the calculated atomic structures estimated from the shortening of the Si-Si bond lengths. These findings show the importance of the stress in determining growth direction.

Our calculations agree with the experimental results fairly well. A previous measurement, using scanning tunneling microscopy (STM), of the oxide growth on a clean Si(111) surface [3] showed that oxide islands are formed in the initial stage at 600 °C. The depth of the islands reaches several atomic layers at the very initial stage. Furthermore, recent experiments clearly show that the oxide grows atomically layer by layer at the Si-oxide/Si(100) and (111) interfaces [4–6]. These are consistent with our results.

Our results indicate that a uniform oxide layer can be obtained with any thickness by thermal oxidation once a uniform surface oxide layer is formed. Therefore, the preparation of the initial surface oxide is crucial for obtaining a uniform oxide layer with atomically controlled thickness. Although our results also indicate that the initial growth direction of the oxide nucleus on the surfaces is vertical into the substrate, this is true only when the energetics govern the oxidation process. Actually, the STM measurement showed that oxidation does not form islands, but instead forms an atomically thin surface oxide layer from the very initial stage at room temperature, where the oxidant cannot diffuse into the substrate easily [3]. It has been reported that the O_2 adsorption in the second layer of the clean Si(100) surface has a nonzero barrier of about 0.3 eV, while the adsorption in the outermost layer is barrierless [6]. Therefore, thermal oxidation at a lower oxidant pressure and lower temperature could result in the formation of a well-controlled atomically thin uniform oxide layer. The efficiency of these oxidation processes is supported by recent experiments [5,6].

Next we studied how the accumulated stress during oxidation is released. Stress release was investigated using a dihydride Si(100) surface as the initial surface. We sequentially inserted O atoms between Si-Si bonds from the surface, assuming atomical layer-by-layer oxide growth. This assumption simplifies the analysis of the accumulated stress, as will be shown below. When eight O atoms per unit cell are introduced [Fig. 2(a)], the formed oxide has a Si-O-Si network similar to that of the cristobalite of crystal SiO_2 [16]. However, the structure is highly compressed compared to that of the cristobalite. The a

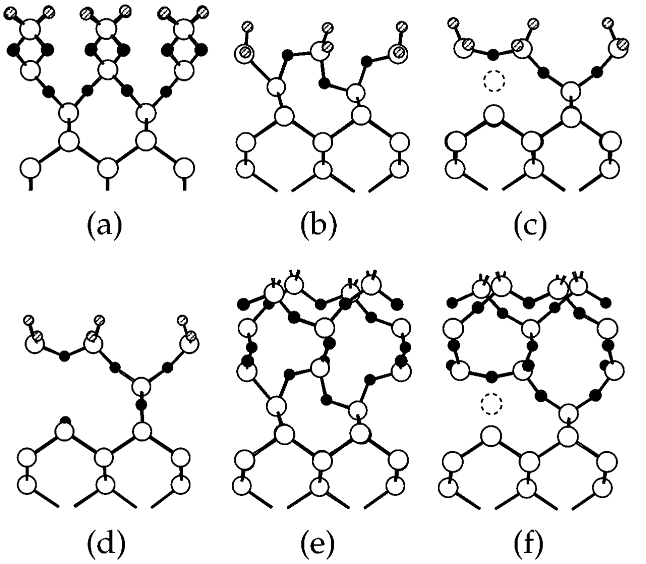

FIG. 2. Side views of the atomic structures for studying the accumulation and the release of the stress. (a) The structure after sequential oxidation by two Si atomic layers; (b),(c) the structures before and after the Si emission on the dihydride surface; (d) the structure with the Si emission after oxidation by two Si atomic layers; (e),(f) the structures before and after the emission at the oxide/Si interface with the less-stressed quartzlike oxide. The broken circles indicate the position where the Si atom is emitted.

and *b* axes of the obtained oxidized region, which are parallel to the interface, are 23% shorter than the corresponding axes of the α-cristobalite. Despite the elastic theory, the *c* axis, which is perpendicular to the interface, is only 20% longer than the corresponding axis of the α-cristobalite. Thus, the structure is largely compressed to about 3/4 the volume of that of the α-cristobalite. This suggests some mechanism for reducing the accumulated stress during the oxide growth. One possibility is the breaking, deformation, and rebonding of the formed Si-O-Si network, which would correspond to the viscous flow of oxide. However, bond breaking and deformation after oxide formation require a lot of energy. Therefore, there must be some other mechanisms that work to release the stress before the compressed oxide is formed.

We found that the atomic structure, when three O atoms per unit cell are introduced, is the key to the stress release [Fig. 2(b)] [17]. In this structure, an O atom is quite close to a surface Si atom, which has only one Si-O bond. Thus, these two atoms can form a bond by breaking the bonds with the second-layer Si atom. Moreover, the second-layer Si atom, whose two bonds were broken, could be emitted from the surface because of laterally compressed stress on it [Fig. 2(c)]. We calculated the total energy of such a Si-emitting structure and found that the total energy of the emitting structure is only 0.04 eV/unit cell higher than that of the nonemitting structure, though there remain two dangling bonds. This structure resembles the well-known *A* center (or the VO center) in bulk Si crystal [18]. In addition, when we sequentially insert O atoms, the total energies for all of the emitting structures are more stable than those for the corresponding nonemitting structures [Fig. 3]. The energy advantage is up to 2 eV/unit cell. This is because the two remaining dangling bonds first form a weak bond by laterally compressed stress, and are finally terminated by forming a Si-O-Si bond. This also indicates that the Si emission scarcely results in the creation of the interfacial gap states. Moreover, when six O atoms per unit cell are introduced to the emitting structure [Fig. 2(d)], the resulting bond network resembles the quartz structure of crystal SiO_2 [16]. [This corresponds to the quartz/Si(100) interface model mentioned above.] The *a* axis of the obtained oxidized region is only 8% longer than the corresponding axis of the β-quartz. The *b* and *c* axes are only 1% and 0.2% shorter, respectively, than the corresponding axes of the β-quartz. Thus, the volume of the structure is expanded by only 8%. In addition, this 8% expansion is due to the small size of the unit cell of our models. The remaining stress in the formed oxide would be completely released after the Si emission if we could use a larger unit cell. Si emission is thus significant for releasing the induced stress during oxide growth.

Silicon emission also occurs at the Si-oxide/Si interfaces. We investigated Si emission from the interfaces using the quartz/Si(100) interface model. The total energy of the emitting structure [Fig. 2(f)] is more stable (by 0.41 eV/unit cell) than that of the nonemitting structure [Fig. 2(e)]. This means that, even at the oxide/Si interfaces, Si atoms are preferentially emitted during oxide growth. Moreover, although we assumed layer-by-layer oxidation above, further calculations show that the Si emission is independent of the oxide growth mode. Even after the initial vertical oxide growth on the surfaces, the emission can occur again when the oxide islands connect with each other. Since stress accumulation is inevitable in the Si oxidation process, the release of this stress by Si emission should be essential and universal.

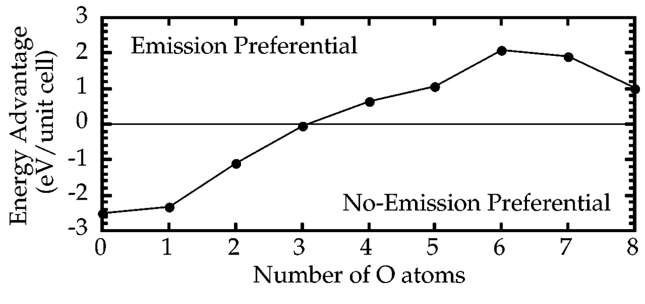

FIG. 3. Energy advantage of the Si emitting structures compared with the nonemitting structures as a function of the number of inserted O atoms per unit cell. The most stable structures for each case are compared assuming the atomical layer-by-layer oxide growth.

As discussed above, the emitted Si atoms should play an important role in the oxidation process. Since the energy advantage of the Si emission (up to 2 eV) is smaller than the formation energy of the Si interstitials (4.9 eV) [19], the Si atoms are thought to be trapped by the kink at the interface, pile up on the surface, be trapped in the oxide region, combine with Si vacancies in the Si substrate, and be emitted from the surface as SiO molecules. However, the emitted Si atoms are still the source of Si interstitials, and could induce the OSF, the OED, and the ORD. Silicon emission is also suggested by Si regrowth on the surface during the oxidation of clean Si surfaces [2,3] as well as by an anomalous loss of Si atoms when Si nanocolumns are oxidized [20].

The stress has another role in Si emission. When compressive stress remains in the grown oxide, the Si emission is reduced. Silicon emission from the interfaces with stressed surface oxide was investigated using a highly compressed $SiO_2/Si(100)$ interface of Fig. 2(a) as the initial interface. A similar comparison to Figs. 2(e) and 2(f) shows that the emitted structure is unstable (by 0.34 eV/unit cell) compared with that of the nonemitted structure. This is consistent with the experimental observation of the self-limiting of the oxidation for Si nanocolumns [20]. It is also consistent with the pattern dependent oxidation (PADOX) when nanoscale patterns are fabricated on SOI (silicon on insulator) substrates [21]. Such self-reduction of the oxidation is also a result of the stress. Thus, control of the stress is crucial in controlling oxide formation.

In conclusion, the stress induced by the Si oxidation process plays an important role in the oxidation procedure itself. Differences in the preferential growth directions of the oxide nucleus on the surfaces and at the interfaces can be explained by the stress. Furthermore, to release the accumulated stress, Si is emitted from the interface during the oxidation. Control of the stress is thus the key to controlling the growth of the Si oxide. Since we studied only limited models of surfaces and interfaces, not all of the details of the actual process are included. Nonetheless, we believe that our findings accelerate the atomic-scale understanding of the oxidation process and that they offer a universal concept of the oxidation.

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Note added.—Very recently, a dynamical study of the oxidation process at a SiO_2/Si interface was carried out by the first-principles molecular dynamics [22].

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