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Potential energy landscape of an interstitial O_2 molecule in a SiO_2 film near the $SiO_2/Si(001)$ interface

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Potential energy distribution of interstitial O_2 molecule in the vicinity of $SiO_2/Si(001)$ interface is investigated by means of classical molecular simulation. A 4-nm-thick SiO_2 film model is built by oxidizing a Si(001) substrate, and the potential energy of an O_2 molecule is calculated at Cartesian grid points with an interval of 0.05 nm in the SiO_2 film region. The result shows that the potential energy of the interstitial site gradually rises with approaching the interface. The potential gradient is localized in the region within about 1 nm from the interface, which coincides with the experimental thickness of the interfacial strained layer. The potential energy is increased by about 0.62 eV at the SiO_2/Si interface. The result agrees with a recently proposed kinetic model for dry oxidation of silicon [Phys. Rev. Lett. **96**, 196102 (2006)], which argues that the oxidation rate is fully limited by the oxidant diffusion.

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I. INTRODUCTION

Thermal oxidation of silicon is an indispensable process in the fabrication of silicon devices to form an excellent interface to silicon substrate. The kinetics of the silicon oxidation has long been believed to be described by the Deal-Grove model,[1] but recent theoretical studies[2–7] require a serious reconsideration of it. The Deal-Grove model has served also as a basis for the oxidation kinetics of other group-IV materials such as SiGe (Ref. 8) and SiC,[9] which are extensively studied owing to their applicational importance, so that the reconstruction of the fundamental model of the silicon oxidation is a pressing issue.

It is generally accepted that the oxide film grows via i) oxidant diffusion through the SiO_2 film already formed and ii) the subsequent oxidation reaction at the SiO_2/Si interface. For relatively small oxidation times, oxide thickness increases linearly with time, and this is called linear regime. The activation energy of the oxidation rate constant in the linear regime (linear constant) has been measured as about 2 eV for oxidations in both dry and wet ambients.[1] In the Deal-Grove model, it is explained that the activation energy corresponds to the barrier for the interfacial oxidation reaction. At longer oxidation times, the thickness increases parabolically with time. This is called parabolic regime. The activation energy of the parabolic rate constant has been measured as 1.24 eV for the oxidation in dry oxygen ambient (dry oxidation). This can be compared to the value of 1.17 eV for the diffusivity of O_2 molecules through fused silica.[10] Similarly, the activation energy of the parabolic constant for the oxidation in wet ambient (wet oxidation) is known to be close to that for the diffusivity of H_2O molecules through fused silica.[11] Therefore, the rate limiting process in the parabolic regime is regarded as the diffusion process of oxidant through the existing oxide film.

However, recent theoretical studies have pointed out that, at least for the dry oxidation, the linear regime seems limited by the oxidant diffusion rather than the interfacial oxidation reaction. First-principles calculation studies[4–6] have revealed that the activation barrier for the interfacial oxidation reaction is negligibly small. Furthermore, it has been found that the layer-by-layer oxidation of silicon surfaces, which was observed by various experimental methods,[12–14] is reproduced by a diffusion-limited oxidation model which supposes that the reaction occurs immediately upon the arrival of the oxidant at the SiO_2/Si interface.[7]

In our previous studies,[2,3] we proposed a new kinetic model for the dry oxidation of silicon. The new model does not involve the rate-limiting process of the interfacial oxidation reaction, instead it is supposed that the diffusivity is suppressed in a strained oxide region near the SiO_2/Si interface. The new model derives a linear-parabolic rate equation analogous to the Deal-Grove equation. The activation energy of the linear constant corresponds to the diffusion barrier just in front of the SiO_2/Si interface, that is increased by the interfacial stress from the value in the bulk oxide film. Experimental linear constant is quantitatively reproduced by the new equation with the assumption that the potential energy for interstitial O_2 molecule gradually increases with approaching to the interface in a strained oxide layer with about 1 nm thick. However, the potential energy distribution in the proximity of the SiO_2/Si interface is unclear, so that the assumed potential profile in the previous work should be verified to substantiate our oxidation model.

In this work, we investigate the potential energy landscape for interstitial O_2 molecule around a SiO_2/Si interface by means of classical molecular simulation. Based on the potential energy landscape, we discuss validity of our new kinetic model for the thermal oxidation of silicon.

II. COMPUTATIONAL METHOD

In order to build a SiO_2/Si structure model large enough to describe the amorphous nature of the oxide film, we employ an empirical interatomic potential function designed for Si, O mixed systems.[15] The potential function is an extended version of the Stillinger-Weber potential for pure Si systems,[16] which comprises of two- and three-body potential energy terms. The extended potential has successfully realized large-scale modeling of SiO_2/Si structures. The interface models showed a compressively strained oxide region near the interface,[7,17] and reproduced x-ray diffraction peaks compatible with experimental results.[18–20] The molecular oxygen, however, cannot be treated by the potential. In this work, we prepare an additional parameter set for interstitial O_2 molecules in the SiO_2 film. This section provides detailed information about the building procedure of the $SiO_2/Si(001)$ interface model, calculation method of the potential energy distribution, and the new parameter set for O_2 molecules.

A. Building $SiO_2/Si(001)$ interface model

Building the SiO_2/Si interface structure is started from the preparation of a single-crystal Si(001) substrate. The initial structure is (001)-terminated Si model (2800 atoms) of 3.81 nm thick in $[001]$ and 3.84 nm long in $[1\bar{1}0]$ and $[110]$. Figure 1(a) shows the initial structure of the Si(001) substrate. Two-dimensional periodic boundary condition is adopted in the parallel directions to the surface. The simulation cell size and the atoms at the bottom layer are fixed, but this constraint does not prohibit expansion toward the surface-normal direction.

Next, the SiO_2 film part is formed by inserting O atoms one by one into the Si-Si bonds from the surface. The insertion site is randomly chosen from all possible Si-Si bonds at the interface, but the oxidation of the next monolayer is suppressed until the upper monolayer is fully oxidized. After each insertion of an O atom, the structure is optimized by Polak and Ribiere's conjugate gradient method.[21] At every interval of 20 insertions (0.1 monolayers of O atom), a molecular-dynamics calculation is performed for 20 000 steps keeping the system temperature at 1073 K by the Nose thermostat method.[22] A time step of 2.30×10^{-5} ps is used with fifth order of the Gear algorithm[23] to solve numerically the Nose equation of motion. The molecular-dynamics calculation anneals the structure and promotes bond breaking and recombination, leading to amorphization and the restoration of defects.

Figure 1(b) shows the $SiO_2/Si(001)$ structure obtained after the oxidation of 19 layers. The thickness of the SiO_2 film is about 4 nm.

B. Calculating the potential energy distribution

Potential energy distribution of interstitial O_2 molecule is calculated by putting an O_2 molecule into the oxide region of the $SiO_2/Si(001)$ model. The energy calculation is performed at Cartesian grid points with an interval of 0.05 nm.

Upon each calculation of the potential energy, the orientation of the inserted O_2 molecule is optimized. During this optimization, one of the O atom in the O_2 molecule is fixed at a grid point, and the other O atom position is adjusted so as to minimize the total potential energy. All the other atoms composing the SiO_2 film and the Si substrate are also fixed.

The potential energy E of the interstitial O_2 molecule is measured from a reference energy of an isolated state from the SiO_2/Si substrate, i.e.,

$$E = E_{\mathrm{complex}} - (E_{O_2} + E_{SiO_2}), \tag{1}$$

where E_{complex} is the total potential energy of the complex structure of SiO_2/Si substrate model including the interstitial O_2 molecule, E_{O_2} the potential energy of a lone O_2 molecule, and E_{SiO_2} the potential energy of SiO_2/Si substrate model without the interstitial O_2 molecule, respectively.

C. Parameter set for O_2 molecule

The original interatomic potential for Si, O mixed systems[15] does not include the parameter set for O_2 molecules, because it is difficult to describe the covalent intramolecular O-O interaction together with the repulsive O-O interaction in the SiO_2 network. In this work, we solve this problem by treating O atoms in O_2 molecules as different type of particles from those in the SiO_2 film. This rule prohibits the exchange reaction of O atoms between an O_2 molecules and a SiO_2 network. This limitation does not matter in this work, because the O_2 molecules are almost inert in the oxide network,[24] and the reaction occurs mainly at the SiO_2/Si interface.

We denote by O_m the oxygen atom in O_2 molecule. Other oxygen atoms constituting silicon dioxide film is denoted as O. A new parameter set is determined for O_m-O_m, O_m-O, and O_m-Si two-body potential terms. Three-body terms including O_m are assumed not to contribute to the total energy, so that all three-body parameters related to O_m are set to zero.

The O_m-O_m two-body term is determined to reproduce the covalent bond interaction of O_2 molecules estimated by the first-principles calculation. We employ Becke's three parameter DFT (B3LYP) (Ref. 25) with the 6-31G^* basis set. We calculate the binding energy of an O_m-O_m molecule as a function of the O_m-O_m interval. Then the calculated plots are fitted by the Stillinger-Weber-type two-body function[16] given by

$$f_2(r) = \begin{cases} \varepsilon A(Br^{-p} - r^{-q})\exp[1/(r-a)], & r < a \\ 0, & r \geq a, \end{cases} \tag{2}$$

where r is the interatomic distance in the Stillinger-Weber length unit $\sigma(=2.0951\ \text{Å})$. $\varepsilon(=2.518\ \text{eV})$ is the energy unit used in the Stillinger-Weber potential. A, B, p, q, and a are potential parameters.

Other two-body parameters, O_m-O and O_m-Si, are determined so as to fit the repulsive interaction proposed by Wilson *et al.*,[26] which can reproduce the nuclear scattering cross section, stopping power, range, and straggling in the low energy region. Table I summarizes the parameters for O_m-O_m, O_m-O and O_m-Si two-body terms.

III. RESULTS

The calculated potential energy distribution for interstitial O_2 molecule is visualized in Fig. 2. The yellow rectangular

TABLE I. Potential parameters for O_2 molecule. O_m stands for oxygen atom in the molecular form, and O denotes oxygen atom constituting silicon dioxide film. Here, Stillinger-Weber's unit system (Ref. 16) is used: the energy unit is $\varepsilon(=2.518\ \text{eV})$, and the length unit is $\sigma(=2.0951\ \text{Å})$.

	O_m-O_m	O_m-O	O_m-Si
A	11.57	−1.91	−1.48
B	0.4598	0	0
p	3.6	0	0
q	2.63	3.0	3.6
a	1.25	1.43	1.81

frame shows the calculated space, and the bottom face corresponds to the SiO_2/Si interface. The colored part shows the lower energy region in the oxide film. Red-colored part is particularly stable for the interstitial O_2 molecule. Figure 2 shows that lower energy parts are ununiformly distributed, and the density decreases near the SiO_2/Si interface.

This image is created by dividing the calculated space into small volume elements, called voxels, and assigning a transparent color to each voxel according to the mean potential energy in it. More strictly, the color of voxel i is determined by the value $\mathcal{B}_i$ defined as the average of the Boltzmann factors of the potential energy on grid points around the voxel:

$$\mathcal{B}_i = \frac{1}{N_{\text{grid}}}\sum_k \frac{1}{(\sqrt{2\pi}\sigma)^3}\int\int\int_{\text{Voxel}_i} dxdydz \exp\left(-\frac{E_k}{k_BT}\right) \times\exp\left[\frac{(x-x_k)^2+(y-y_k)^2+(z-z_k)^2}{2\sigma^2}\right], \quad (3)$$

where N_{grid} is the number of grid points included in each voxel, k the serial number of a grid point, E_k the potential energy of interstitial O_2 molecule at grid point k, x_k, y_k, and z_k the position coordinates of the grid point k, respectively. Equation (3) means that the value of the Boltzmann factor at each grid point is spatially spread by Gaussian function, and it is integrated inside of the voxel. σ is the standard deviation of the Gauss distribution which is used as spreading parameter. We set $\sigma=0.07$ nm, and $k_BT=1$ eV to create the image. The voxel size is $0.3\times0.3\times0.3\ \text{nm}^3$, and N_{grid} is 216. To save computation time, the summation over k is restricted to the neighboring grid points within a distance 0.2 nm from the center of the voxel. The three-dimensional (3D) image of the transparent voxels is generated by using the volume rendering function of a free ray-tracing program, the Pov-Ray.[27]

Figure 3 shows the histogram of the calculated potential energy on the grid points. Here the grid points are split into three regions with respect to the distance z from the SiO_2/Si interface: Region A is $0\ \text{nm}\le z<0.83$ nm, region B is $0.83\ \text{nm}\le z<1.67$ nm, and region C is $1.67\ \text{nm}\le z<2.50$ nm, respectively. Each region has the same volume and contains 103 248 grid points. In region A, the frequency of potential energies less than 3 eV is smaller compared to the other regions. Especially, number of stable grid points within the energy range from 0 to 0.3 eV is only five in region A, which is about 20 times smaller than the other regions. Thus the number of low potential energy sites decreases near the SiO_2/Si interface.

Kageshima *et al.*[28] has theoretically pointed out that, in the oxide film, there must be stable interstitial sites with almost zero incorporation energy of O_2 molecule from the vacuum. The present calculation backs up their argument; there are 30 grids points with potential energies lower than 0.1 eV, and the minimum value is 0.0156 eV.

Figure 4 shows the energy distribution of local minima. The local minimum point is defined as the grid point at which the potential energy is smaller than any other grid points locating within a distance of $\sqrt{2}\delta$. δ is the interval of Cartesian grid points, i.e., $\delta=0.05$ nm. The histograms of region B and C decrease monotonically as the potential energy increases. In region A, the peak of the histogram shifts to a higher energy by about 1 eV.

Similar energy distributions of local potential minima were obtained by Bongiorno *et al.* in their molecular-dynamics study on amorphous silica.[29] According to their report, in relaxed amorphous SiO_2 models with the density of $2.2\ \text{g/cm}^3$, local potential minima of interstitial O_2 molecule show monotonically decreasing histogram, such as those of regions B and C in Fig. 4. They investigated also the case with compressively strained amorphous SiO_2 models with higher density of $2.4\ \text{g/cm}^3$, and obtained a histogram peaked at around 1 eV, which is similar to that of region A in Fig. 4. These consistent results indicate that the potential energy of the interstitial O_2 molecule is increased in the oxide structure near the SiO_2/Si interface due to the compressive stress, while it is almost relaxed in the oxide region over 1 nm away from the interface.

Figure 5 shows the calculated potential energies versus z axis. In this figure, the plots fill the higher energy region above the lowest energy surface. Namely, the boundary of the plotted and empty areas corresponds to the depth profile of the lowest energy surface of the interstitial O_2 molecule. The undulated shape of the boundary reveals that local potential minima periodically appear with an interval of about 0.3 nm. The potential profile reflects that the thermally grown SiO_2 film retains a residual order originating from the parent silicon crystal.[18–20]

Here we label the local minima as a, b, c, d, e, f, and g in the order of the distance from the interface, as shown in Fig. 5. We define the exact position of the SiO_2/Si interface as the depth where the potential profile has maximum value just in front of the Si substrate. The origin of the z coordinate is set to this position. The local minimum around $z=-0.15$ nm is no longer in the oxide region, because the O_2 molecule at the position meets the interfacial Si-Si bonds. According to the first-principles calculations,[4–6] the O_2 molecule in such situation is immediately consumed in oxidizing the Si-Si bonds with almost no energy barrier.

In Fig. 5, potential energies at the interfacial local minima a, b, and c monotonically decrease in this order from 0.47 to 0.056 eV. These local minima reside within about 1 nm from the SiO_2/Si interface. Such a significant potential gradient is never seen in other region. Other local minima d, e, f, and g have small energies from 0.016 to 0.11 eV. Thus the potential energy of the interstitial O_2 molecule

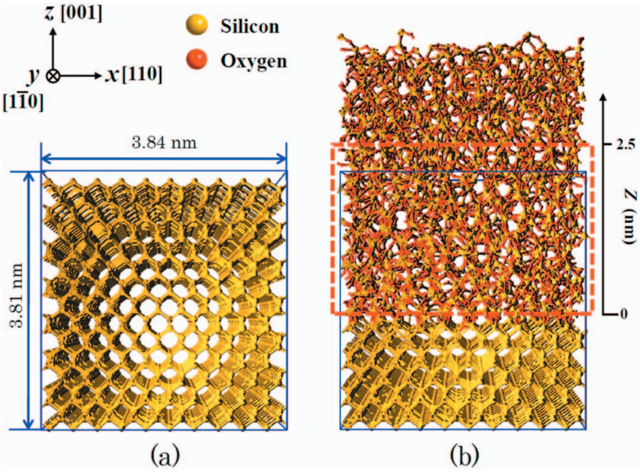

FIG. 1. (Color) (a) Si(001) substrate model with 2800 Si atoms. (b) $SiO_2/Si(001)$ interface model with about 4 nm thick oxide layer. Red broken line indicates the region where the potential energy of interstitial O_2 molecule is calculated.

gradually increases with approaching to the SiO_2/Si interface in the thin region within about 1 nm.

It was pointed out that the potential energy of the interstitial O_2 molecule has a strong correlation with the size of the interstitial void which decreases for increasing cage sizes.[29,30] To characterize the interstitial void distribution in the present SiO_2 film model, we performed a geometric Voronoi analysis.[31] The Voronoi analysis consists of partitioning the space in polyhedra, each containing the volume nearest to a given atom. The vertices of these polyhedra are equidistant to at least four atoms in the SiO_2 network, so that we can define spheres centered at the vertices which correspond to the interstitial voids. Figure 6 shows the histograms of the interstitial volumes available for O_2 molecule for regions A, B, and C, obtained by the Voronoi analysis. In region B and C, the distribution is peaked around 40–50 Å^3 and it ranges over 110 Å^3. On the other hand, the peak of the distribution in region A is shifted toward smaller volume, and the population of larger voids over 80 Å^3 is markedly smaller than that in the other regions. Thus the correlation between the potential energy of the interstitial O_2 molecule and the interstitial volume is confirmed in the present model.

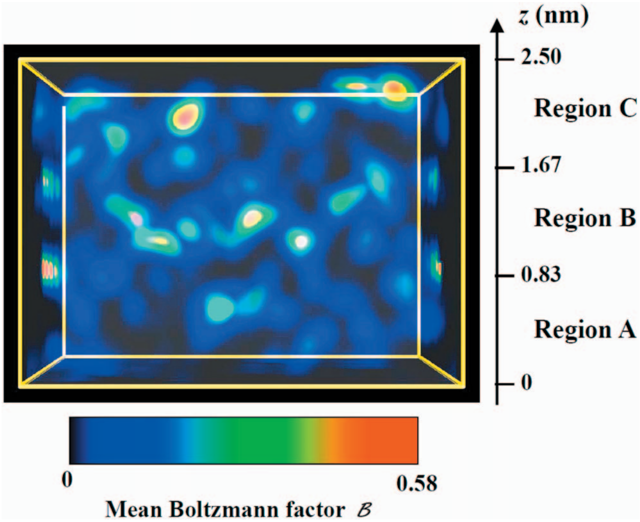

FIG. 2. (Color) Potential energy landscape of the interstitial O_2 molecule in the vicinity of $SiO_2/Si(001)$ interface. The image is created by assigning a transparent color to each voxel according to the mean potential energy in it, defined by Eq. (3). The colored part shows the lower energy region in the oxide film. Red-colored part is particularly stable for the interstitial O_2 molecule. The yellow frame show the calculated scope which corresponds to the region indicated by red broken line in Fig. 1(b). The bottom face corresponds to the SiO_2/Si interface. We analyze the obtained data by deviding the system into three regions with respect to the distance z from the SiO_2/Si interface: Region A is 0 nm$\leq z <$0.83 nm, region B is 0.83 nm$\leq z <$1.67 nm, and region C is 1.67 nm$\leq z <$2.50 nm, respectively.

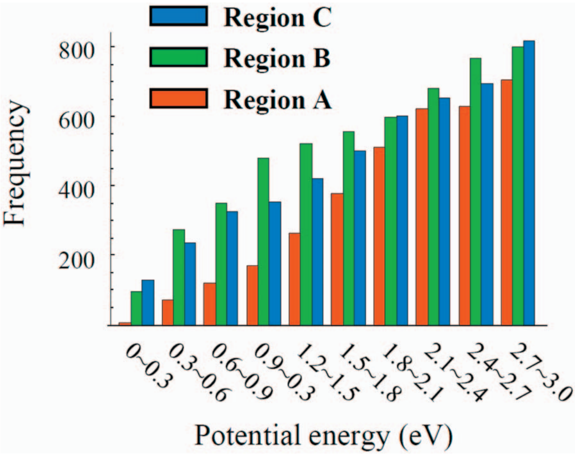

FIG. 3. (Color) Histograms of the calculated potential energy on the grid points in regions A, B, and C.

Figure 7 shows the mass density profile across the SiO_2/Si interface model. At the present model size, the density is sensitive to the local configuration and the profile is subject to sharp fluctuation. It can, however, be seen that the density of the oxide region oscillates around 2.35 g/cm^3 and is raised to about 2.45 g/cm^3 in the vicinity of the SiO_2/Si interface. This result is roughly in agreement with a previous

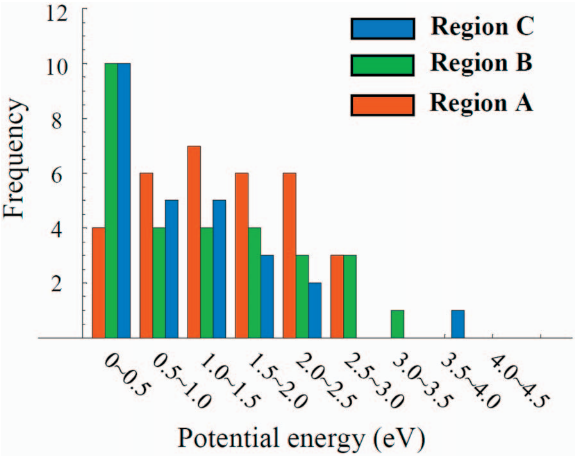

FIG. 4. (Color) Potential energy distributions of local minima included in regions A, B, and C.

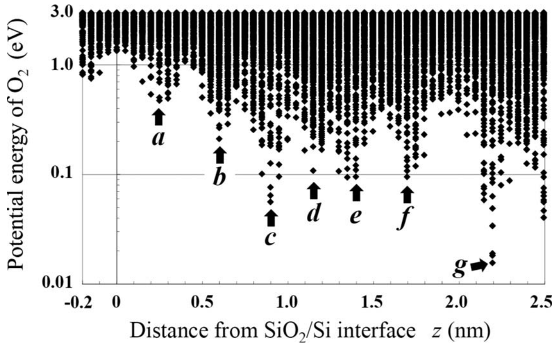

FIG. 5. Potential energies of interstitial O_2 molecule versus z axis. The boundary of the plotted and empty areas corresponds to the depth profile of the lowest energy surface of the interstitial O_2 molecule. The exact position of the SiO_2/Si interface is defined as at the highest barrier of the potential profile just in front of the Si substrate. The origin of the z coordinate is set to this position. Local potential minima in the oxide region are labeled as a, b, c, d, e, f, and g in the order of the distance from the interface.

modeling work.[32] The increase in the potential energy of interstitial O_2 molecule can be interpreted as the result that the density of SiO_2 film is increased and the volume of the interstitial void is reduced.

IV. DISCUSSION

All aspects of the results indicate that the potential energy of the interstitial O_2 molecule increases in the oxide region within about 1 nm from the SiO_2/Si interface. It has been pointed out that the oxide layer with about 1 nm thick in the vicinity of the SiO_2/Si interface has different properties from other bulk oxide region, and it is called "structural transition layer." According to an x-ray reflectivity measurement,[33] the structural transition layer has a higher mass density of about 2.4 g/cm^3 with respect to the regular amorphous SiO_2 with a density of 2.2 g/cm^3. The existence of the compressive stress in the structural transition layer was suggested by infrared spectroscopy[34] and x-ray photoelectron spectroscopy,[35] but first-principles studies[36,37] showed the observed shift in these spectral peaks rather arises from other reasons peculiar to the vicinity of the SiO_2/Si interface. Apart from the detailed discussion on the origin of the properties, it is almost accepted that the structural transition layer is a dense and compressively strained oxide layer with about 1 nm thick. In this work, we confirm that the structural transition layer has also an impact on the potential energy of the interstitial O_2 molecule.

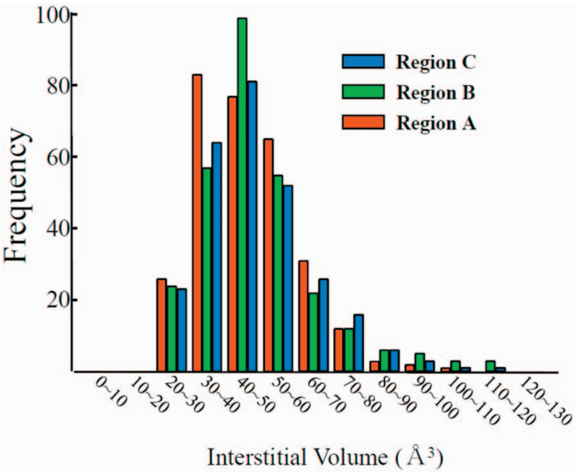

FIG. 6. (Color) Distribution of interstitial volumes available for molecular oxygen for region A, B, and C.

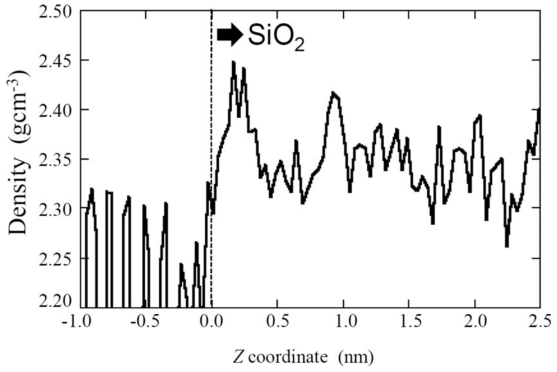

FIG. 7. Mass density profile across the SiO_2/Si interface model.

The potential energy profile of the interstitial O_2 molecule shown in Fig. 5 is very similar to that supposed in the new kinetic model of the thermal oxidation of silicon.[2] Fig. 8 shows the potential profile proposed in Ref. 2. In Fig. 8, l indicates the number of the oxide layers in the structural transition layer, A the mean interval of the adjacent interstitial sites in the SiO_2 film, and ΔE the additional potential energy at the SiO_2/Si interface induced by the interfacial stress, respectively. ΔE corresponds to the difference in the activation energies of the linear constant and the parabolic constant. In the dry oxidation, the typical activation energies are 2.0 and 1.24 eV for linear and parabolic constants, respectively, so that ΔE=0.76 eV. Local potential minima near the SiO_2/Si interface are labeled as a, b, and c in the same manner as in Fig. 5. Thus, in the new kinetic model, it is supposed that the diffusion barriers of the interstitial O_2 molecule are raised monotonically by up to 0.76 eV with

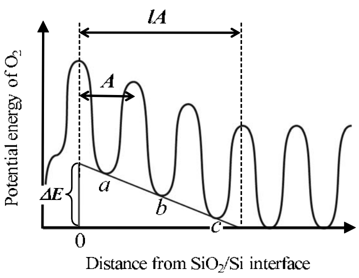

FIG. 8. Potential energy profile of the interstitial O_2 molecule proposed in the new kinetic model for the silicon oxidation (Ref. 2). ΔE is the additional potential energy at the SiO_2/Si interface induced by the interfacial stress. l is the number of the oxide layers in the structural transition layer. A is the mean interval of the adjacent interstitial sites in the SiO_2 film.

approaching to the SiO_2/Si interface. The thickness of the structural transition layer lA was estimated to about 1 nm by using the expression of the new oxidation rate equation,[2,3] which compares well with the experimental value of the structural transition layer.[33]

It should be noted that the value of $\Delta E = 0.76$ eV is the maximum one in the oxidation process. Since the potential profile in the strained region continues to shift forward into the Si substrate, there must be intermediate phases with lower barriers during the period of one-monolayer oxidation. The intermediate barrier will decrease to about $\Delta E(l-1)/l$ as discussed in Ref. 2. Supposing the ideal pseudocristobalite model on Si(100) substrate,[18] the value of A, the mean distance of the adjacent interstitial sites projected to the surface-normal axis, is about 0.27 nm. l is, therefore, estimated to 3.7 (three to four atomic layers), and the minimum value of the intermediate barrier is estimated to be about 0.55 eV. Namely, it is expected that the additional potential energy ΔE at the SiO_2/Si has a value between 0.55 and 0.76 eV.

In this work, the value of ΔE is determined by the linear extrapolation of the potential energies at the local minima of a, b, and c in Fig. 5. These potential minima are well fitted by

$$f(z) = 0.622 - 0.646z, \tag{4}$$

adopting the least-square method. ΔE corresponds to $f(0) = 0.62$ eV. This value is within the expected range. The energy $f(z)$ vanishes at $z = 0.963$ nm, which coincides with the experimental thickness of the interfacial strained layer.[33] The present result attests the validity of the new kinetic model for thermal oxidation of silicon in dry oxygen ambient.

A remark which should be made here is that the potential profile depends on the structure model of SiO_2/Si interface and the interatomic interaction model. In order to draw a general conclusion, it is necessary to further confirm that the similar results are obtained irrespective of the choice of these models. It is, however, considered that the present result shows the representative picture of the transition layer near the SiO_2/Si interface, because the many aspects of the present results coincide with the other work[29] that employs a different interaction model based on first-principles calculations and various structure model of amorphous silica.

Finally we discuss the wet oxidation. Contrary to the dry oxidation, the conventional Deal-Grove model is considered to be still valid for the wet oxidation. First-principles density-functional calculations by Bakos *et al.*[24] showed that the diffusion barrier of interstitial O_2 molecules is extremely sensitive to the local topology, agreeing well with the present results. However, interstitial H_2O molecules exhibit an almost constant barrier of 0.8–0.9 eV in all models used in their calculations. Thus, it is considered that the diffusion of H_2O molecules is hardly suppressed in the interfacial strained layer. Actually, we have attempted to fit the new kinetic equation to the experimental data for the wet oxidation, but we get a meaninglessly small value of about 0.03 nm for thickness of the structural transition layer.[3]

According to the first-principles calculation by Stefanov *et al.*[38] the barrier for the oxidation reaction of the clean Si(001) surface by H_2O molecule is about 2.1–2.4 eV. Tsetseris *et al.*[39] estimated the barrier for the interfacial oxidation reaction by H_2O molecule to be about 1.5 eV. Therefore, it is considered that the rate of the wet oxidation is limited by the oxidation reaction rather than the diffusion in the strained oxide layer, and the Deal-Grove model correctly describe the wet oxidation. Although the dry and wet oxidations have been uniformly described by the Deal-Grove theory over the past 40 years, we argue that their mechanisms are essentially different from each other.

V. CONCLUSION

We have investigated the potential energy landscape around a $SiO_2/Si(001)$ interface model for interstitial O_2 molecule by means of classical molecular simulation. The potential energy gradually rises with approaching the interface in the region within about 1 nm from the interface. At the SiO_2/Si interface, the potential energy is increased by about 0.62 eV. The result agrees well with our new kinetic theory for thermal oxidation of silicon. Contrary to the conventional Deal-Grove theory, the rate of dry oxidation of silicon is considered to be fully limited by the diffusion process of O_2 molecules.

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