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Reactive molecular dynamic simulations of early stage of wet oxidation of Si (001) surface

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We have investigated the initial stage of oxidation of Si (001) surface by water (H_2O) molecules using *reactive* molecular dynamics (MD) simulation at 300 K and 1200 K without any external constraint on the water molecules. Previously, reported water reaction behaviors on silicon surface by *ab initio* calculations or experimental observations were reproduced by the present MD simulation. The present simulation further revealed that the hydrogen atom in H_2O is more attractive than oxygen atom in O_2 to bond with Si, such that it accelerates the dissociation process of H_2O. It was also observed that the oxidation reaction was enhanced with increased number of the supplied water molecules. It was suggested that the repulsion between water molecules and their fragments facilitates the dissociation of both water molecules and hydroxyl decomposition on the Si surface. Therefore, the wet oxidation behavior appeared to have more temperature dependence even in the early stage of oxidation. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4818941]

I. INTRODUCTION

Silicon dioxide is preferred as a gate dielectric of CMOS transistor owing to its good interface properties with silicon. Interface between silicon and its oxide is a non-stoichiometric oxide (suboxide), whose structure and electric properties differ from those of amorphous silica.[1,2] As a result of shrinkage of the dielectric layer thickness, the fraction of the suboxide layer consisting of various oxidation states of Si becomes so significant since the performance of the device is affected by the quality of the suboxide layer. Recently, alternative high dielectric constant (high-*k*) materials were suggested to be used for the dielectric gate to prevent the uncontrollable effects caused by the scale-down.[3] However, silicon oxide layer inevitably exists at the interface between the high-*k* dielectric layer and the silicon substrate. The silicon oxide interfacial layer is also considered to improve the interfacial quality of high-*k* dielectric stack of the CMOS devices. Therefore, the initial stage of oxidation of Si has drawn much attention, and the precise control of the oxidation process at atomic scale has been a major issue in Si-CMOS technology.

Structure evolution of the suboxide layer has been studied extensively in both experimental and theoretical aspects. Several experimental observations using methods such as X-ray absorption near-edge spectroscopy (XANES), X-ray Photoelectron Spectroscopy (XPS), Extended X-ray Absorption Fine Structure (EXAFS), Elastically Scattered Electron Spectra (ESES), and Ultraviolet Photoelectron Spectroscopy (UPS), have been carried out to describe the structure of SiO_x. There are two proposed models, the random bonding model (the basic units of this structure are Si tetrahedral of the type $Si\text{-}Si_{4-y}O_y$, which are statistically distributed to form random network) and the random mixture model (global structure of SiO_x is mixture of randomly arranged cluster of amorphous Si and amorphous SiO_2).[4] Numerous photoelectron spectroscopy studies have been performed to characterize the composition and the atomic structure of the interfacial layer.[5] The theoretical investigations of the oxidation behaviors, *ab initio* molecular dynamics (MD) or classical MD simulations, were carried out to provide the more fundamental understanding of the interface.[1,6–9] However, in those theoretical studies, oxidized silicon surface was generated by artificially inserting oxygen atoms into the Si-Si network, which would be far from a realistic oxide layer. Recently, the present authors reported MD simulation results of the early stage of dry oxidation of Si without any constraint to the oxygen molecules.[10] The simulation revealed the more realistic oxidation behaviors that formed a suboxide layer of thickness of $\sim$1 nm.[10] The simulation results were in a good agreement with the previous experimental and *ab initio* calculation results. In this work, we extended the reactive MD simulation method to understand the atomic scale behaviors of the early stage of wet oxidation of Si (oxidation by water molecules).

In the last three decades, many theoretical studies were devoted to elucidate the water molecule reactions on the silicon surface. Interaction of a single water molecule with a cluster of small number of silicon atoms was frequently studied by *ab initio* calculations.[11–13] Most of the theoretical studies were carried out to provide the most feasible pathway of the water molecule adsorption on the silicon surface by comparing the barrier energies of the various possible reaction paths. It is now widely accepted that a water molecule

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dissociates into one hydrogen atom and one hydroxyl molecule, when the water molecule is adsorbed onto silicon surface. The hydroxyl molecule is further decomposed into hydrogen and oxygen atom to oxidize Si.[11] Recently, an *ab initio* MD simulation that involved several water molecules of water reaction on previously oxidized Si (001) surface was reported. The simulation revealed the dynamics of the reaction and the enhanced dissociation of water by the tensile strain on the surface, even though the time scale and the size of the system was quite limited due to the costly *ab initio* calculation.[14]

In the present work, simulations of single, double, and many water molecules adsorption were performed to elaborate all interactions involved in the wet oxidation processes. The present simulation has revealed that the behavior of wet oxidation is different from those of dry oxidation due to the repulsive reaction between water molecules and their fragments on the surface.

II. COMPUTATIONAL DETAILS

We performed MD simulations of oxidation behavior on Si (001) surface by water molecules at two different temperatures, 300 K and 1200 K. We used the reactive force field (ReaxFF) developed by Van Duin *et al.*,[15] that is integrated in "Large-scale Atomic/Molecular Massively Parallalized Simulator" (LAMMPS) code.[16] ReaxFF was selected from many available potential for Si and SiO_2 owing to its capability to describe chemical reaction (forming and breaking of bonding as well as charge transfer between constituent atoms), which should be considered in simulating oxidation process.

Slab model of single crystal Si was used as the substrate after relaxing 300 K for 10 ps. The Si substrate of diamond structure was built with the size of $5.43 \times 5.43 \times 9.77$ nm^3. Some of the slab of thickness 1.62 nm was cut in $\langle 001 \rangle$ direction to create the Si (001) surface. The number of Si atoms involved was 24 000. A periodic boundary condition was applied in the lateral directions. The atomic position of the bottommost layer was fixed to simulate a thick substrate. Temperature of the bottom layers of thickness 3.31 nm was fixed at the oxidation temperature to provide a thermal bath in the system. Temperature of the thermal bath was rescaled at every time step of 1 fs during the simulation. All the other atoms above the thermal bath were unconstrained with NVE ensemble. The substrate was equilibrated with a thermal bath for 20 ps before starting the oxidation simulation. Arrays of the Si dimers are developed as a result of surface reconstruction with Si-Si dimer bond length in the range of 2.28 Å–2.48 Å. That range of values encompasses the results of DFT calculation,[17] Elastic Low-Energy Electron Diffraction (ELEED),[18] and UHV Transmission Electron Diffraction (TED) measurements.[19]

Procedure and route of the simulations are similar to the previous dry oxidation simulation.[10] The present oxidation simulation was done by placing H_2O molecules at the distance 0.12 nm above the surface, without any external constraint and without initial velocity (with initial velocity = 0). We only defined the initial position and the initial orientation of water molecule on the Si surface. In order to compare the oxidation behavior with the previous *ab initio* calculations or the experimental results, single water molecule reaction was investigated on randomly selected surface positions with various water molecule configurations for 20 ps. For statistical analysis of the single molecule reaction, 500 independent single molecule reactions were analyzed. Second, we simulated consecutive 600 water molecules reactions on the Si surface to investigate the early stage of wet oxidation process.

III. RESULTS AND DISCUSSION

A. Single water molecule reaction

In order to observe the details of the interaction between water molecule and Si surface, single water adsorption simulation was performed with various initial pose and position of water molecule. Typical examples of 300 K reaction are presented in Figure 1 to Figure 3. The oxygen atom is presented by a dark blue ball, while two hydrogen atoms are represented by small red and orange balls, respectively. In the substrate, Si atoms composing the dimer row are denoted by green balls, and other Si atoms are presented by bright blue balls. In Figure 1, two hydrogen atoms are on the left hand side, and oxygen atom is on the right hand side of a water molecule. Figure 2 is the case when two hydrogen atoms are on the top of a water molecule, and an oxygen atom is on the bottom of the molecule. Figure 3 is the opposite case, where two hydrogen atoms are on the bottom of water molecule and an oxygen atom is on the top of water molecule.

Although the reaction kinetic is dependent on the position and the orientation of water molecule, most water molecules were dissociated in two steps: water dissociated into atomic hydrogen and hydroxyl (OH), followed by the dissociation of the hydroxyl into another hydrogen and oxygen atoms. The oxygen atom then reacts with Si and placed in the back bonds of the dimers. For example, Figure 1(b) shows that the water molecule dissociated into atomic

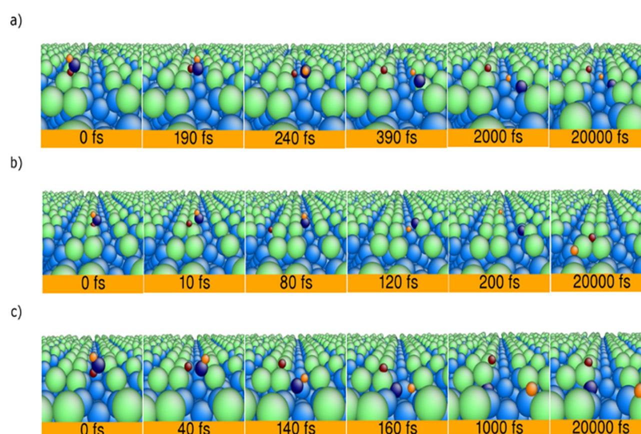

FIG. 1. Time evolution of single water molecule reaction at 300 K when the water molecule, with two hydrogen atoms on the left side and oxygen atom on the right side of the molecule, is placed (a) on the middle of the dimer row, (b) above one of the dimer atom, and (c) on the channel between the dimer row.

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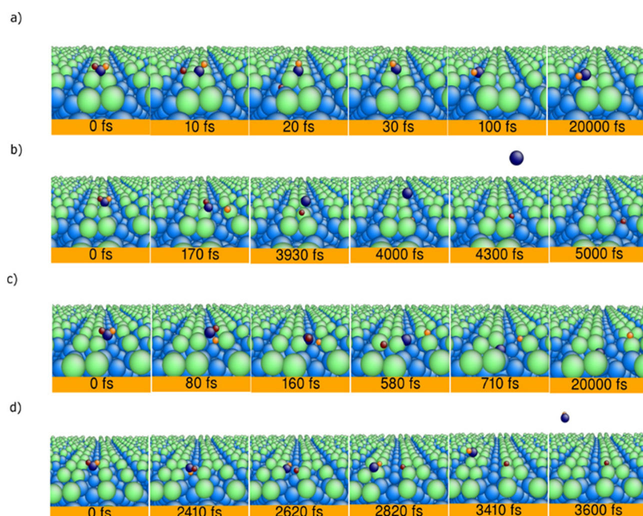

FIG. 2. Time evolution of single water molecule reaction at 300 K when the water molecule, with two hydrogen atoms on the top and oxygen atom on the bottom of the molecule, is placed (a) on the middle of the dimer row, (b) above one of the dimer atom, and (c) on the channel between the dimer row.

hydrogen and hydroxyl group within a few 10 fs. The hydroxyl group was later dissociated into atomic hydrogen and oxygen (see the snapshot at 120 fs of Figure 1(b)). The dissociated oxygen atom reacted with Si and positioned at the back bonds of the dimer as shown in the snapshot at 20 ps. In the present simulation, no case was observed where water molecule dissociates directly into an oxygen atom and two hydrogen atoms. These results agree well with the previously suggested reaction model,[20] validating the interatomic potential used in the present work. Similar two step reaction was observed in many simulation cases: Figures 1–3(b) and 3(c). However, in rare cases, water molecule remains without reaction in 20 ps (see Figures 3(a) and 3(d)). We also observed that the dissociated oxygen or hydroxyl desorbed from the surface as shown in Figures 2(b) and 2(d). Statistical analysis of the reaction behaviors during wet oxidation will be discussed later in this paper.

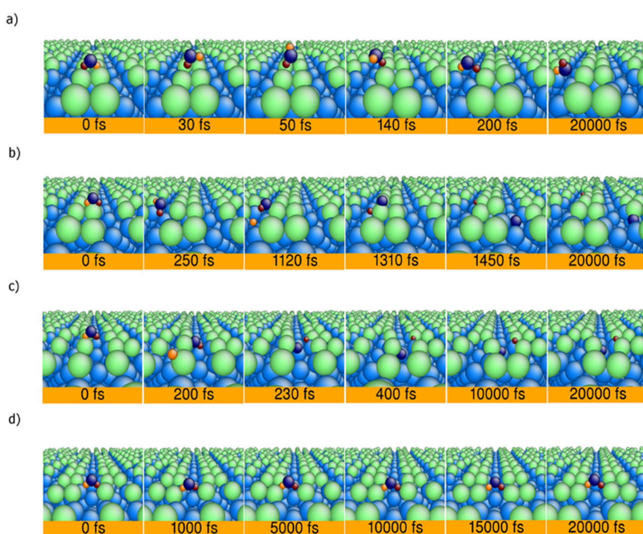

FIG. 3. Time evolution of single water molecule reaction at 300 K when the water molecule, with two hydrogen atoms on the bottom and oxygen atom on the top of the molecule, is placed (a) on the middle of the dimer row, (b) above one of the dimer atom, and (c) on the channel between the dimer row.

Figure 4 shows the details of charge variation during the reaction of a water molecule. The atoms are colored by the Mulliken charge in the scale of the scale bar on the right hand side. When the water molecule was dissociated into hydrogen and hydroxyl group (see snapshot at 30 fs of Figure 4), Si atom, indicated by an arrow, is positively charged by transferring the electron to the dissociated hydrogen atom (indicated by a broken line arrow). At 40fs, the hydrogen atom was neutralized by incorporating itself into the Si substrate, and the negatively charged oxygen in hydroxyl is bound to the positively charged Si by exchanging electrons. Figure 4(b) shows the second step of the reaction, where the hydroxyl was dissociated into hydrogen and oxygen atoms. At 120 fs, the hydroxyl started to dissociate into hydrogen and oxygen atoms. Hydrogen atom changed to neutral, while the Si atom (indicated by an arrow) on the substrate is more positively charged. As the dissociation occurred, the bond length between O and Si decreased from 1.66 to 1.40 Å, indicating a stronger chemical reaction. After dissociation, oxygen atom was positioned at the back bond of the dimer (Oxygen atom was not shown in the 20 ps snapshot of Figure 4(b). See Figures 1(c) and 2(c)).

Difference between wet and dry oxidation was evidently shown, when the oxygen or water molecule was placed on the channel between two dimer rows. As shown in Figure 1(c), where a water molecule positioned on the channel between two dimer rows dissociated within few 10 fs. In the case of dry oxidation, much longer period is required before the molecular dissociation (see Figure 4 in Ref. 10). Considering the similar bond-dissociation energy of OH-H (493.4 kJ/mol) and O=O (497 kJ/mol), this result would suggest that hydrogen is more reactive than oxygen on the Si surface. This suggestion would be also supported by the result in Figure 2(d), where the simulation started with the oxygen atom facing towards the Si surface. It should be noted that the dissociation of water started, when hydrogen atom started to react with Si atoms after rotating the water molecule. In this case, it took about 2 ps before the dissociation.

Our simulation also revealed the possibility of hydroxyl and hydrogen species to react with Si in different dimers or

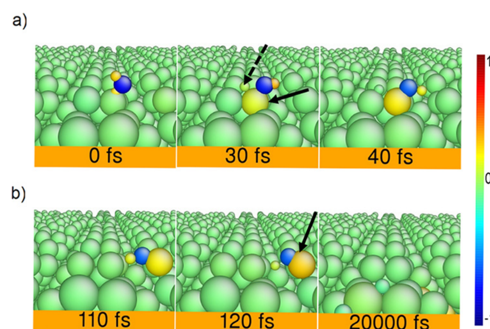

FIG. 4. Time evolution of single water molecule reaction when the water molecule adsorbed on a silicon dimer atom at 300 K, with two hydrogen atoms on the left side and oxygen atom on the right side of the molecule.

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even in the different dimer rows (for example, see Figure 2(c)). By high resolution infrared spectroscopy, it was reported that after a water molecule dissociates into hydroxyl and atomic hydrogen, the species bind to adjacent Si atoms of the same dimer, the so called on-dimer (OD) configuration.[21] However, later works using STM suggested the intra dimer (ID) configuration, where hydroxyl and atomic hydrogen bind to two neighboring dimers in the same dimer row.[22] More recent STM study further demonstrated the coexistence of the two configurations.[23,24] Our simulation results would support the recent STM study.[22–24] Furthermore, our results suggest that the hydrogen and hydroxyl can react with different dimer rows at 300 K.

Molecular adsorption of water was also observed in some cases. Figure 3(d) shows the typical examples of the molecular adsorption. It is worth noting that hydrogen atoms are always bound to Si in the case of molecular adsorption. This tendency of the molecular adsorption might be associated with the higher reactivity of hydrogen. Figure 5 shows the Mulliken charge of atoms during molecular adsorption. Two hydrogen atoms seem to be physically bound to the surface Si without notable charge transfer between them. The present simulation would explain the previous experimental report[25] that the kinetics is described by a mixture of dissociative chemisorption and non-dissociative chemisorption with the binding enthalpy of just −6 kJ/mol (−0.06 eV/molecule). Recent theoretical study also showed that molecular adsorption is more favorable on hydrogenated Si surface.[26]

Almost identical behavior of the surface reaction was observed at higher temperature of 1200 K. Water molecules dissociated into an atomic hydrogen and a hydroxyl, followed by the dissociation of the hydroxyl molecule. The reaction behavior of single water molecule appeared to be independent of the temperature, indicating a small energy barrier of water dissociation on Si surface. By the first principle calculations, Cho *et al.* showed that the energy barrier of water dissociation on Si surface is only of 0.15 eV,[27] which is even lower than that of oxygen molecule dissociation (0.25 eV).[10,28] They also reported that the dissociation of water molecule on Si surface lowers the energy by 1.8 eV. This energy gain will generate "hot atoms" that can provide enough kinetics for the dissociation of water molecular both at 300 and 1200 K. Esteve *et al.* suggested another possible hot atoms mechanism that may arise from oxygen insertion.[29] By this additional energy oxygen atom can perform backbond to backbond hopping.

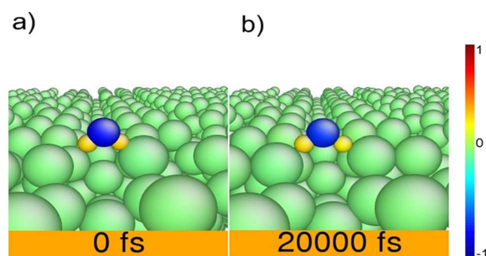

FIG. 5. The snapshot of the physically absorbed water molecule on Si surface at 300 K. (a) Initial absorption configuration (b) after 2 ps. Atoms are colored by the Mulliken charge.

TABLE I. Total uptake fraction of oxygen and the depth distribution of the oxygen obtained by statistical analysis of 500 independent events of single H_2O molecule reaction.

Oxidation position after 20 ps	300 K	1200 K
Depth 1 (0.0–0.2 nm)	95.60%	97.79%
Depth 2 (0.2–0.4 nm)	3.91%	1.47%
Depth 3 (0.4–0.6 nm)	0.49%	0.25%
Total fraction of adsorbed oxygen	81.80%	81.40%

B. Statistical independent single water molecule reaction simulations

Statistical analysis of 500 independent single water molecule reactions was summarized in Tables I and II. Table I shows the probability for oxygen atom to be adsorbed in Si for various values of depth. Similar values of the total oxygen uptake probability were observed regardless to the reaction temperature (81.8% at 300 K and 81.4% at 1200 K). No considerable difference was also observed in the oxygen uptake position: most oxygen atom was bound to the first layer of Si at both 300 K and 1200 K. This observation would result from the low energy barrier of the water adsorption process on Si.[27] However, it must be also noted that the time scale of the present simulation was just 20 ps, where thermally activated diffusion cannot be sufficiently considered. In contrast to that of oxygen, early stage of hydrogen absorption behavior was strongly dependent on the reaction temperature (see Table II). As can be seen, the uptake probability decreased from 64.1% to 51.8% as the temperature increased from 300 to 1200 K. This difference would originate from the higher probability of hydrogen desorption at higher temperature. Furthermore, hydrogen penetrated deeper at higher temperature even for the simulation period of 20 ps.

C. Consecutive multiple water molecules reaction

As a next step, we performed 600 water molecules reaction by consecutively supplying the individual water molecule of randomly chosen pose on randomly selected position of the Si surface. The interval between two consecutive

TABLE II. Total uptake fraction and depth distribution of hydrogen obtained by statistical analysis of 500 independent events of single H_2O molecule reaction.

Hydrogen position after 20 ps	300 K	1200 K
Depth 1 (0.0–0.2 nm)	76.755%	70.849%
Depth 2 (0.2–0.4 nm)	8.736%	10.039%
Depth 3 (0.4–0.6 nm)	3.588%	5.598%
Depth 4 (0.6–0.8 nm)	3.120%	4.440%
Depth 5 (0.8–1.0 nm)	3.120%	3.088%
Depth 6 (1.0–1.2 nm)	1.716%	2.123%
Depth 7 (1.2–1.4 nm)	1.404%	1.158%
Depth 8 (1.4–1.6 nm)	0.936%	0.386%
Depth 9 (1.6–1.8 nm)	0.156%	0.772%
Depth 10 (1.8–2.0 nm)	0.156%	0.772%
Depth 11 (2.0–2.2 nm)	0.156%	0%
Depth 12 (2.2–2.4 nm)	0.156%	0.193%
Total fraction of adsorbed hydrogen	64.1%	51.8%

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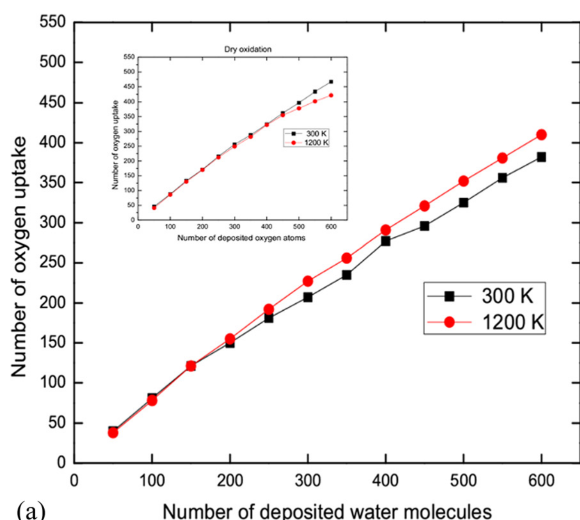
additions of the water molecule was 20 ps. Before supplying each water molecule, the temperature of the system was rescaled to the oxidation temperature. The uptake behavior of oxygen and hydrogen during oxidation simulation at 300 and 1200 K was presented in Figure 6, where it is shown in Figure 6(a) that a slightly increased amount of oxygen was adsorbed at higher temperature, when more than 200 water molecules were supplied to the Si surface. This result is in contrast to that of the dry oxidation, where more oxygen atoms were adsorbed at 300 K in the later stage of oxidation (see inset of Figure 6(a)). Enhanced oxidation at a higher temperature with the addition of larger number of water molecule would reveal the role of intermolecular interaction on the oxidation behavior, as will be discussed later. Figure 6(b) shows the hydrogen adsorption behavior that is strongly dependent on the temperature. Hydrogen desorption was enhanced at 1200 K due to significant thermal activation, resulting in the decreased amount of hydrogen adsorption. Energy barrier for hydrogen desorption is in the range of 2–3.4 eV depending on the hydrogen adsorption state.[30] Negligible amount of hydrogen desorption is thus expected at 300 K.



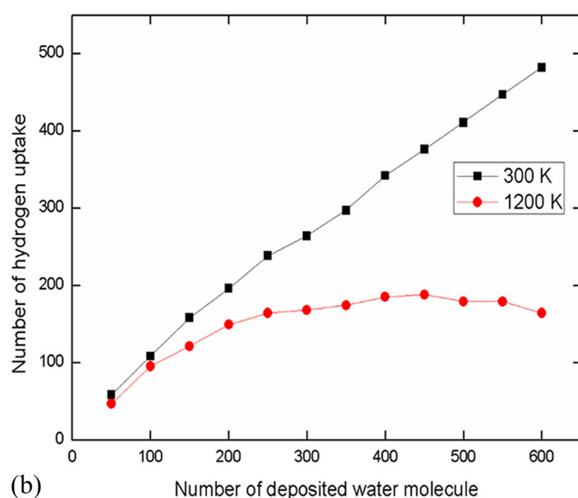


FIG. 6. (a) Time evolution of the number of adsorbed oxygen atoms during wet oxidation and dry oxidation (inset, Reprinted with permission from M. A. Pamungkas, M. Joe, B. H. Kim, and K. R. Lee, J. Appl. Phys. **110**, 053513 (2011). Copyright 2011 American Institute of Physics). (b) Time evolution of the number of adsorbed hydrogen atoms during wet oxidation.

Figure 7 shows the atomic configuration of the oxidized surface when 150 water molecules reacted with the Si substrate. Figures 7(a) and 7(b) are, respectively, the atomic configuration and the charge distribution at 300 K, while the Figures 7(c) and 7(d) are those at 1200 K. In the atomic configurations, Si, oxygen, and hydrogen are, respectively, presented by red, blue, and green balls. The charge of the atom is described by the Mulliken charge values in terms of the color scale on the right side. At 300 K, many hydroxyl groups remain intact at room temperature as indicated by arrows in Figure 7(a). It is evident in Figure 7(b) that the hydrogen bound to oxygen was positively charged, as in typical hydroxyl molecule. Because of the higher value of electronegativity of oxygen (3.44 in Pauling scale) than hydrogen (2.20) or Si (1.90), all oxygen atoms appear negatively charged up to $-1.0e$, by receiving electrons from nearby hydrogen and Si atoms. At 1200 K, it was observed that much smaller amount of hydrogen remained on the surface. The adsorbed hydrogen turned to neutral, as shown in Figure 7(d). Furthermore, no hydroxyl molecule was found on the surface in this simulation.

Figure 8 shows the same surfaces after 600 water molecules were supplied, where more significant amorphization of the surface was observed. Comparing with the case of 150 water molecule reaction shown in Figures 7(b) and 7(d), Si atoms were more positively charged as the transfer of electron occurs to the oxygen atoms nearby. If one compares the oxidized surfaces between 300 K and 1200 K, it would be apparent that the oxidation state of Si and the oxygen concentration on the surface was lower at 1200 K. Because the total amount of adsorbed oxygen is higher at 1200 K (see Figure 6(a)), this result implies that significant oxygen

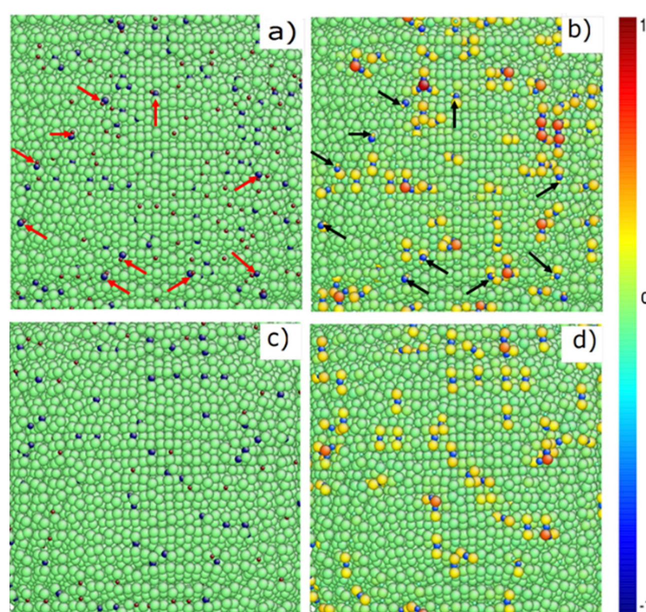


FIG. 7. Top view of the oxidized Si (001) surface by 150 water molecules at 300 K ((a) and (b)) and 1200 K ((c) and (d)). The atoms are colored by type ((a) and (c)) and the Mulliken charge ((b) and (d)).

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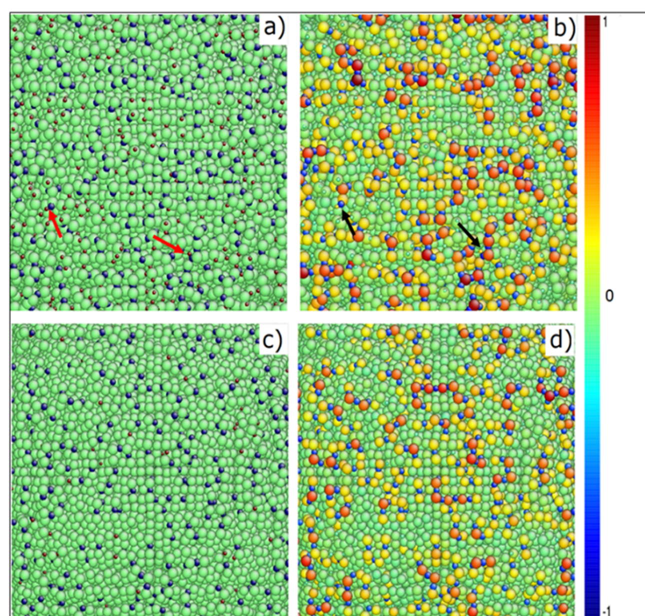

FIG. 8. Top view of the oxidized Si (001) surface by 600 water molecules at 300 K ((a) and (b)) and 1200 K ((c) and (d)). The atoms are colored by type ((a) and (c)) and the Mulliken charge ((b) and (d)).

diffusion into Si substrate occurs for the short simulation time of only 12 ns. Depth profile analysis of oxygen, shown in Figure 9, revealed that a significant oxygen diffusion occurred at 1200 K, and even at 300 K some oxygen atoms could diffuse down to 1.0 nm. The simulated depth profile of oxygen supports the ballistic diffusion model of oxygen in the early stage of oxidation, as proposed by Yasuda *et al.*[31] In the case of hydrogen, much deeper penetration of the adsorbed hydrogen was observed, which would be a natural consequence of high mobility of hydrogen in Si lattice.

It is interesting to note that most of hydroxyl molecules were decomposed on the Si surface even at 300 K (see Figures 8(a) and 8(b)). Only few hydroxyl molecules were found in the present simulation as indicated by arrows in Figure 8. A number of previous experimental works on the temperature dependence of hydroxyl decomposition on Si surface reported that the decomposition usually occurs at an elevated temperature. Schulze *et al.* reported that hydroxyl decomposes to bridge-bonded oxygen and addition silicon hydride upon heating from 300 K to 400 K.[20] An STM study has reported that hydroxyl is completely decomposed into O and H atoms at the temperature of higher than 563 K on Si (111) surface.[32] It was also reported that thermal decomposition of SiOD to form Si-O-Si and Si-D mainly occurs between 500 and 750 K, even if the decomposition starts at 300 K.[33] Other experimental works using high resolution IR spectroscopy, LEED, AES, and Photoemission yield spectroscopy (PYS) reported that the elevated temperature arouses the dissociation of OH.[21,34] However, the present simulation revealed that the decomposition of hydroxyl is also dependent on the amount of water molecules incorporated. The reaction between hydroxyl-hydroxyl or water-hydroxyl molecules may play an important role in the enhanced decomposition of hydroxyl at room temperature.

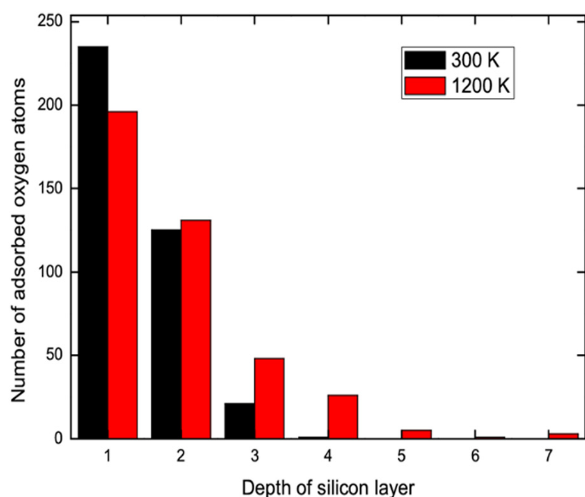

FIG. 9. Oxygen depth profile of the oxidized silicon surface with 600 water molecules. Each data were taken in the layer of thickness 0.32 nm from the surface.

D. Intermolecular interaction

Previous first principle calculation had predicted the repulsive interaction between water molecules on Si surface.[27] The repulsive interaction that causes the molecules to push each other to the Si dimers facilitating the dissociation and adsorption process. We applied the reactive MD simulation to study intermolecular interaction during oxidation. Figure 10 shows the reaction snapshots when two water molecules (Figure 10(a)), water and hydroxyl molecules (Figure 10(b)), and two hydroxyl molecules (Figure 10(c)), were supplied to the Si surface. We deliberately performed the simulation with the same initial orientations and positions of water molecule as in Figure 3(d), where molecular adsorption was observed in the single water molecule reaction. The present simulation showed that a repulsive interaction between two molecules occurred in all the combinations of Figure 10. Higher mobility of the molecule on Si surface at higher temperature would increase the chance of repulsive reaction between molecules. This repulsion will enhance the decomposition of the molecules and, thus, the oxidation of Si. The intermolecular repulsion might explain the strong temperature dependence

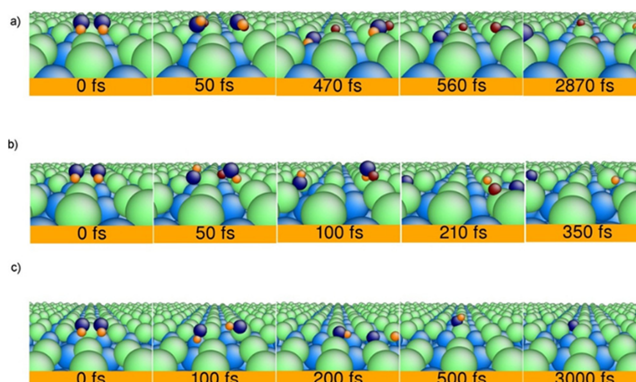

FIG. 10. Time evolution of (a) water-water molecule reaction, (b) water-hydroxyl reaction, and (c) hydroxyl-hydroxyl reaction.

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of the oxygen uptake as shown in Figure 6(a), which is in contrast to the statistical analysis of independent single water molecule reaction shown in Table I.

IV. CONCLUSION

Molecular dynamics simulation using a reactive force field enabled us to investigate the reactions of water molecules on Si (001) surface in atomic scale. The simulation results were in good agreement with the previous experimental and *ab initio* calculation studies: dissociative adsorption of water dominates to form Si-H and Si-OH surface bonds, which is followed by the dissociation of the hydroxyl into hydrogen and oxygen, and the oxygen reacted with Si at the back bonds of the Si dimer. The present simulations further suggested that the hydrogen reaction with Si enhances the dissociation of water. The most noteworthy suggestion from the present simulation is that the oxidation of Si could be enhanced by the repulsive interaction between water and its fragments. At higher temperature, the molecules move faster on the surface, increasing the chance of collision between the molecules. Therefore, temperature dependence of the oxidation behavior appeared even in the early stage of wet oxidation, which is in contrast to that of dry oxidation.[10] These results are expected to provide a novel understanding on how temperature and type of oxidants may affect the early stage of oxidation of Si, which would be useful for engineering the Si/SiO_x interface.

ACKNOWLEDGMENT

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