JOURNAL OF APPLIED PHYSICS 119, 125305 (2016)

Early stage oxynitridation process of Si(001) surface by NO gas: Reactive molecular dynamics simulation study

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(Received 2 February 2016; accepted 10 March 2016; published online 24 March 2016)

Initial stage of oxynitridation process of Si substrate is of crucial importance in fabricating the ultrathin gate dielectric layer of high quality in advanced MOSFET devices. The oxynitridation reaction on a relaxed Si(001) surface is investigated via reactive molecular dynamics (MD) simulation. A total of 1120 events of a single nitric oxide (NO) molecule reaction at temperatures ranging from 300 to 1000 K are statistically analyzed. The observed reaction kinetics are consistent with the previous experimental or calculation results, which show the viability of the reactive MD technique to study the NO dissociation reaction on Si. We suggest the reaction pathway for NO dissociation that is characterized by the inter-dimer bridge of a NO molecule as the intermediate state prior to NO dissociation. Although the energy of the inter-dimer bridge is higher than that of the intra-dimer one, our suggestion is supported by the *ab initio* nudged elastic band calculations showing that the energy barrier for the inter-dimer bridge formation is much lower. The growth mechanism of an ultrathin Si oxynitride layer is also investigated via consecutive NO reactions simulation. The simulation reveals the mechanism of self-limiting reaction at low temperature and the time evolution of the depth profile of N and O atoms depending on the process temperature, which would guide to optimize the oxynitridation process condition. © *2016 AIP Publishing LLC*.
[http://dx.doi.org/10.1063/1.4944707]

INTRODUCTION

Silicon (Si) oxynitride film has been considered as an alternative dielectric layer to replace the conventional Si oxide layer of MOS FET devices. Si oxynitride film resolves the major problems of the thin Si oxide layer, including gate current leakage or boron diffusion to a Si channel from highly doped gate materials.[1] Moreover, Si oxynitride films have a high quality interfacial structure with a Si channel.[2] The film is thus considered as a buffer layer between the HfO_2 high-k dielectric layer and the Si channel that improves the quality of the interface.[3] It has also been reported that silicon oxynitride film can reduce the interfacial stress between a dielectric layer and a Si channel or suppress hydrogen defect formation at the interface.[4] Silicon oxynitride film is typically grown via the thermal oxynitridation of Si using nitrous oxide (N_2O) and nitric oxide (NO) gases.[5,6] However, NO is believed to be a primary precursor of nitrogen.[7,8] Therefore, a systematic study on the adsorption and dissociation behavior of a NO molecule on a Si surface is essential for understanding and controlling the initial stage of dielectric layer growth or interface formation.

Many experimental works have been reported regarding the NO molecule reaction on a Si surface. Scanning tunneling microscope (STM) analysis of the surface reaction revealed that the Si surface is chemically very active and the NO molecules can be dissociated even at 90 K.[9] They reported the self-limiting reaction at low temperature, which was confirmed by the following experimental works.[7,10,11] The initial growth behavior, governed by two dimensional nucleation, was also reported based on surface reflection electron microscopy (SREM) and reflection high energy electron diffraction (RHEED).[12] It was also suggested that nitrogen is incorporated in the Si substrate, bonding with three Si atoms nearby. The similar incorporation behavior of N in the Si structure was reported through the combined research of experiment and theory.[13] The atomic scale mechanism of NO adsorption on a Si(001) surface was investigated using high resolution photo emission spectroscopy (PES).[14] They suggested the dissociative adsorption of a NO molecule with a very low energy barrier involving either single or double Si dimers. Many experimental studies mainly focused on the surface reaction at low temperature because the atomic scale analysis of the surface reaction is considerably difficult at high temperature.

Most theoretical investigations of NO dissociation were based on the first principle total energy calculation.[15–19] Early theoretical studies employing the cluster calculations reported the barrier-less dissociative adsorption of NO molecules on a Si surface at low temperature.[15] However, further investigations suggested that the molecular adsorption on the surface Si dimer is followed by the dissociative incorporation of N and O.[16,17,19] They assumed the intra-dimer adsorption of a NO molecule based on the energetics calculations. Note that the previous first principle calculations were

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applied to a system of small size, where only a few dimers of Si were included.[16] It was thus difficult to consider the reactions involving multi-dimers. Dynamics of the reaction were investigated by using the first principle molecular dynamics (MD) method.[20] This study explored the dissociation kinetics for some initial configuration of the NO molecule on the Si surface. However, the first principle MD simulations considered a limited number of events due to the high cost of computation. Note that the reaction pathway in a real situation is to be characterized by the statistical analysis of the reaction.

In the present work, we employed the reactive MD simulations for the statistical analysis of the oxynitridation behavior on a relaxed Si(001) surface. The present simulations, using the reactive force field (ReaxFF), enabled us to simulate the reactions at a reasonable cost without substantial loss of accuracy. In contrast to the previous theoretical works, we found that the inter-dimer bridge configuration of the adsorbed NO molecule is the most probable intermediate state before its dissociation. This observation is consistent with the energy barrier calculations of the reaction path, showing that the total energy calculation is not sufficient to understand the reaction behavior. Consecutive NO reaction behaviors at various temperatures were also simulated to understand the initial stage of the film growth and the composition variation in the oxynitride film.

CALCULATION DETAILS

Molecular dynamics simulation of the oxynitride reaction on a Si surface requires an interatomic potential appropriate for both covalently bonded Si and all forms of ionic silicon oxynitrides. The potential should also handle the charge distribution between oxygen, nitrogen, and silicon atoms to investigate the oxynitridation process. We employed a ReaxFF of Si-O-N developed by Hudson *et al.* to investigate the formation of intergranular glassy films (IGFs) in β-silicon nitride.[21] Two concepts implemented in the ReaxFF distinguish it from other conventional non-reactive potentials: self-consistent bond order (BO) and charge equilibration (QEq).[22,23] It is thus possible to describe the reaction process by allowing dynamic bond formation and breaking via continuously updated bond order during the simulation. Atomic charge is a variable parameter that depends on the atomic configuration to match the electrostatic equilibrium using the electronegativity equalization scheme. The integrated potential was benchmarked with not only a NO molecule and crystalline Si but also amorphous SiO_2, Si_3N_4, and Si_2N_2O because the NO dissociation on Si results in an amorphous Si oxynitride layer. See the SI-1 section of the supplementary material for the details of the benchmark test.[24] "Large-scale Atomic/Molecular Massively Parallelized Simulator" (LAMMPS) code was used for the MD simulations.[25]

Figure 1(a) shows the side view of the simulation box. A slab model of single crystal Si(001) was used as the substrate after relaxing at the reaction temperatures for 10 ps. Dimensions of the silicon slab are 2.256 nm $\times$ 2.256 nm $\times$ 5.282 nm (total number of Si atoms is 1476.). A vacuum of an approximately 1.1 nm thickness was introduced to the above the Si substrate to generate the Si(001) surface. The orientation of the dimer row was set as parallel to the x axis in the simulation box, as shown in Fig. 1(b). Hence, the axes of the simulation box correspond to the $[1\bar{1}0]$, [110], and [001] directions, respectively. The periodic boundary condition was applied in two lateral directions of the substrate. The substrate was composed of three regions. To mimic a thick substrate, Si atoms in the bottom two layers (thickness: 0.27 nm) were fixed. Atoms of the 29 layers (thickness: 3.85 nm) above the fixed layer were kept at constant temperature during simulation to provide a thermal bath in the system. The temperature of the thermal bath layer was rescaled in every time step (0.5 fs) to effectively dissipate the heat generated by the surface reaction. However, no constraint was applied to the topmost 10 layers (thicknesses: 1.33 nm), where the oxynitridation reaction may occur.

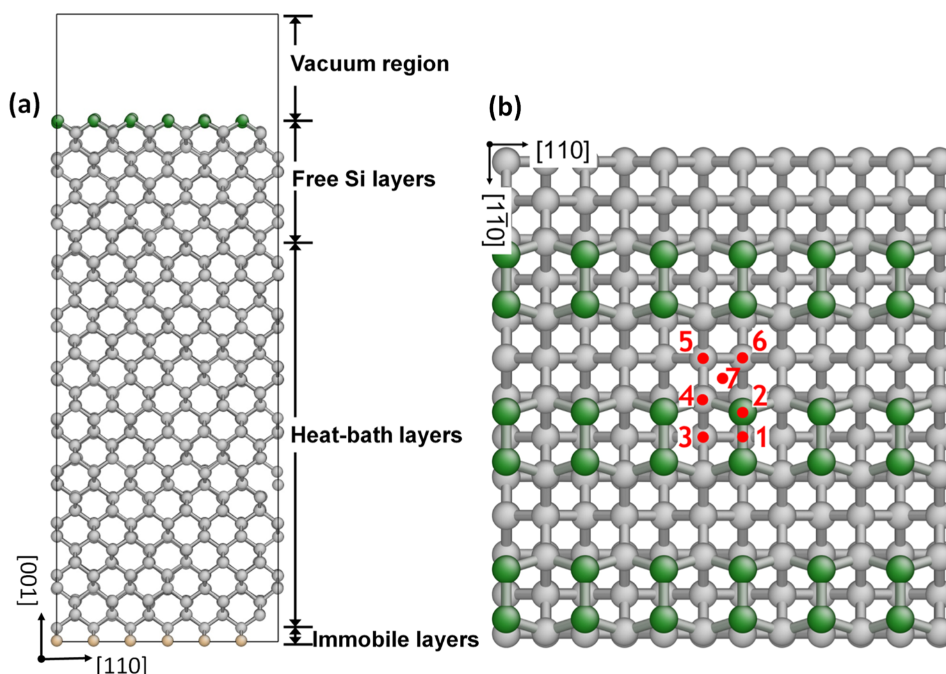

FIG. 1. (a) Side view of the simulation system in this work and (b) top view of the fully dimerized Si(001) surface used in the present work. Three coordinated Si, i.e., surface dimer atoms, are highlighted in green. Red dots represent the seven surface sites where NO molecules were placed for the reaction simulation.

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A single NO molecule reaction on the Si surface was simulated by placing a NO molecule at a distance of 0.35 nm above the surface. This distance was chosen from the preliminary simulation to find the largest distance at which the NO molecule reacts with the Si surface. The initial kinetic energy of the NO molecule was set to the thermal energy, i.e., 300 K (≈38 meV for an air molecule). To equilibrate the substrate at simulation temperatures of 300 K, 500 K, 700 K, and 900 K, the heat bath layer and the topmost free layer were coupled with a Berendsen thermostat for 10 ps before simulation. The thermostat on the free region was then removed after starting the reaction simulation under the NVE ensemble. Each simulation lasted for 20 ps, with a time step of 0.5 fs. At a given simulation temperature, NO molecules of four different initial orientations (N top, N bottom, the molecule axis parallel or perpendicular to the Si dimer) were placed at seven independent sites (see Figure 1(b)). These sites were those of unique atomic configurations on the relaxed Si(001) surface. For better statistics, ten independent events were simulated in each initial configuration, with slight variation with respect to the height of the NO molecule from the surface. In total, 1120 events of single NO molecule reactions were simulated and statistically analyzed.

The evolution of the oxynitride surface layer on Si(001) was investigated by simulating the reaction with consecutive additions of NO molecules on the Si surface at 300, 700, and 1000 K. Both the orientation and position of each NO molecule on the Si surface were randomized during the consecutive reactions simulation. The simulation box was similar to that for the single NO molecule reaction simulation, with a larger Si slab of dimensions 5.315 nm × 5.315 nm × 6.528 nm (10 000 Si atoms). The topmost 6 layers (1200 Si atoms) were defined as free layers, being on the 42 layers coupled to the Berendsen thermostat. The bottom two layers were fixed. Before consecutive NO reaction simulation, the system was equilibrated for 10 ps at the reaction temperature. NO molecules were added every 20 ps because the perturbation of the system energy by the NO molecule reaction settled down at approximately 10 ps in most cases.

The energy barrier for a specific reaction path was calculated by using the nudged elastic band (NEB) method based on the first principle calculation. We used the Vienna *ab initio* simulation package (VASP), which employs the density function theory (DFT) with a plane-wave basis set.[26] The projected-augmented wave (PAW) method and a cutoff energy of 400 eV were used. Exchange correlation energy was evaluated via the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) functional. The slab-vacuum model was used to mimic a p(2 × 2) reconstructed structure of the Si(001) surface. The supercell size of conventional unit cell, whose dimensions are 0.7734 nm × 0.7734 nm, was $\sqrt{2} \times \sqrt{2}$; two conventional unit cells were used in surface normal direction. Dangling bonds at the bottom of the slab were passivated with hydrogen. A Γ-centered $3 \times 3 \times 1$ *k*-point grid was used for Brillouin zone sampling. Six images between the initial and the final configuration were used for the NEB calculation.

RESULTS AND DISCUSSIONS

The reaction behavior of a NO molecule on a Si surface could be classified into three cases after 20 ps of simulation: (1) bounce-back NO without chemical reaction, (2) chemically adsorbed NO on the Si surface without dissociation, and (3) dissociated NO. Figure 2 shows the typical snapshots of the three cases. N atoms are denoted using blue balls, O using red balls, and Si using gray balls. Green balls represent the Si atoms in the dimer. Fig. 2(a) shows the case in which the NO molecules did not react with Si and bounced back from the surface (see also MD movie Fig. 3(a)). Once the NO molecule reached the boundary of the simulation box in the *z* direction, we removed the molecule from the system.

Un-dissociated NO adsorption is shown in Fig. 2(b) and Movie Fig. 3(b). The nitrogen atom of the NO molecule reacted

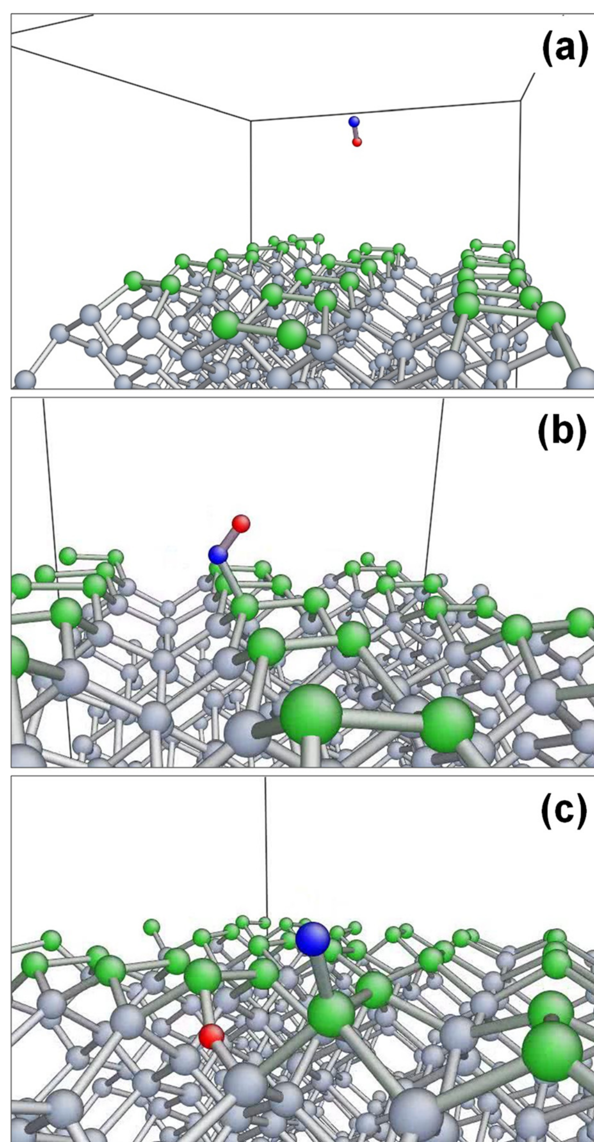

FIG. 2. Typical surface atomic structure of (a) bounced-back, (b) un-dissociated, and (c) dissociated NO reaction cases. The snapshots were taken after (a) approximately 1 ps of simulation at 700 K, (b) 5 ps of simulation at 500 K, and (c) 5 ps of simulation at 700 K. Red, blue, and gray balls represent oxygen, nitrogen, and silicon atoms, respectively. Green balls represent the Si atoms in the dimer.

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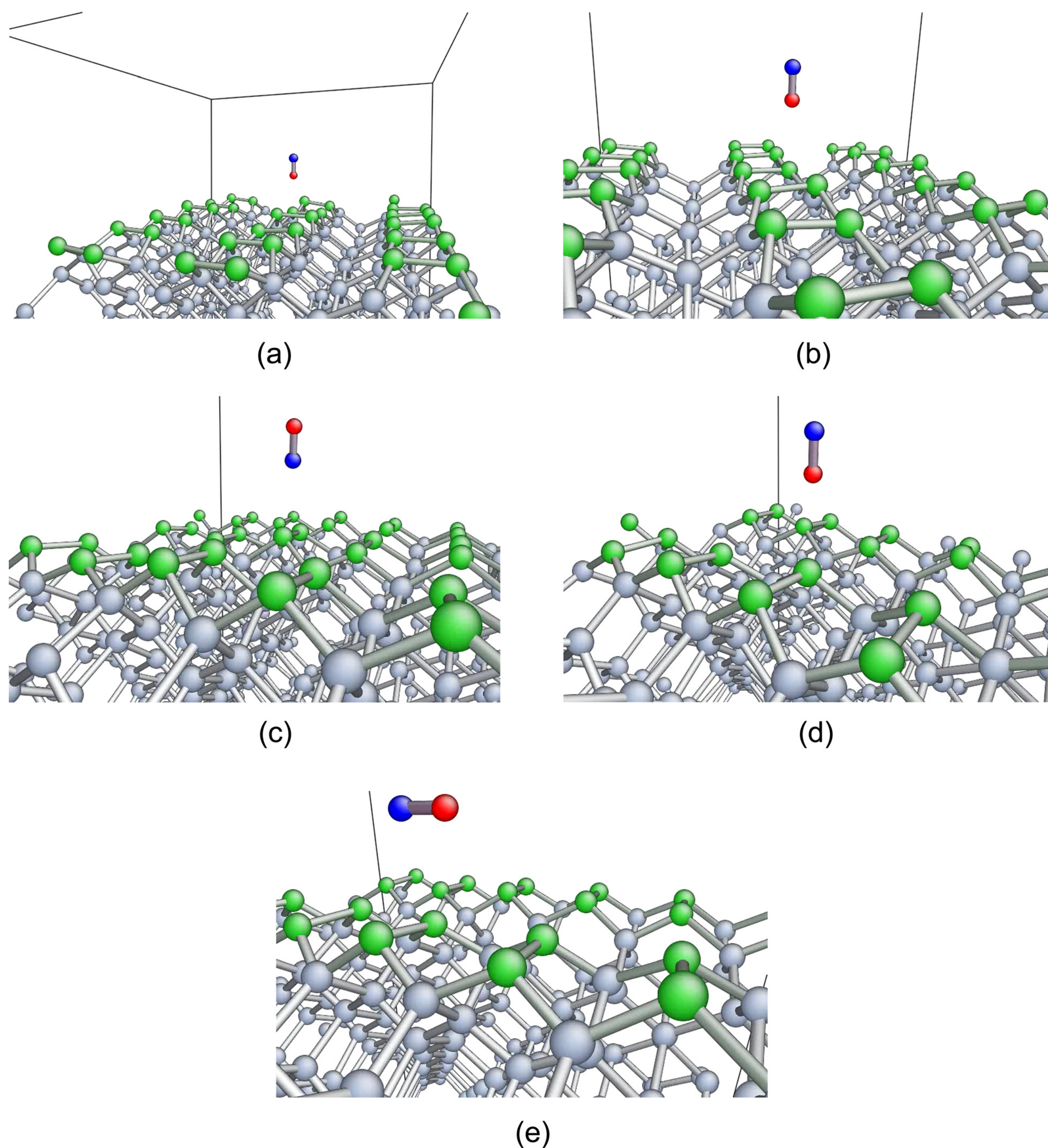

FIG. 3. Typical MD movies for various cases. (a) Bounced back of NO molecule without reaction, (b) undissociated surface adsorption of NO molecule, (c) dissociated reaction of NO (case I), (d) dissociated reaction of NO (case II), and (e) dissociated reaction of NO (case III). (Multimedia view) [URL: http://dx.doi.org/10.1063/1.4944707.1] [URL: http://dx.doi.org/10.1063/1.4944707.2] [URL: http://dx.doi.org/10.1063/1.4944707.3] [URL: http://dx.doi.org/10.1063/1.4944707.4] [URL: http://dx.doi.org/10.1063/1.4944707.5]

with the surface Si atom in the dimer (Si-N adsorption), whereas the oxygen atom was bound to the nitrogen without reacting with the surface Si. We observed that Si-N adsorption was notably preferential to Si-O adsorption regardless of the initial orientation of the NO molecule. When the oxygen atom of the NO molecule approached the surface, the molecule sometimes rotated itself, resulting in Si-N adsorption. This preferential Si-N adsorption was more significant at lower temperature. The probability of the Si-N adsorption increased from 65.5% at 900 K to 79.9% at 300 K. Similar preferential reaction was reported experimentally on the Si(111) surface by Hashinokuchi *et al.*[27] An earlier DFT calculation also revealed the more favorable Si-N bond during chemisorption of a NO molecule on a Si(111) surface.[28] This preference could correspond to the fact that Si-N adsorption can simultaneously satisfy the bond order requirements of nitrogen, oxygen, and surface Si: a N atom forms a double bond with an O atom and a single bond with the surface Si atom.

Figure 2(c) shows the dissociated NO reaction case (see also Movie Fig. 3(c)). After the NO molecules reacted with the Si atom in a dimer due to Si-N adsorption, the O atom

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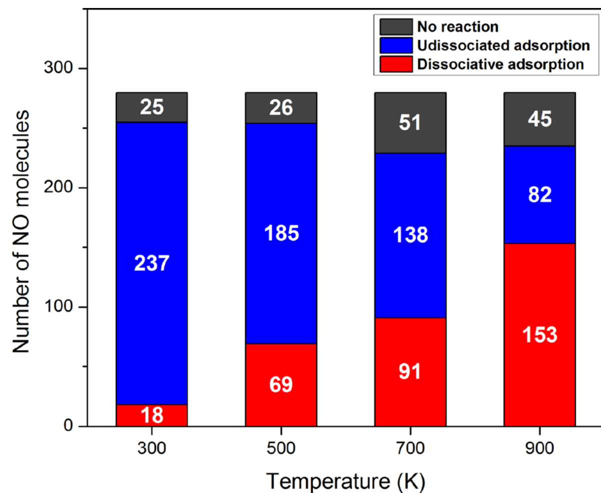

FIG. 4. The stack column plot of the statistical analysis of the NO molecule reaction with the Si surface after 20 ps of simulation at various temperatures from 300 to 900 K. At each temperature, 280 events were analyzed.

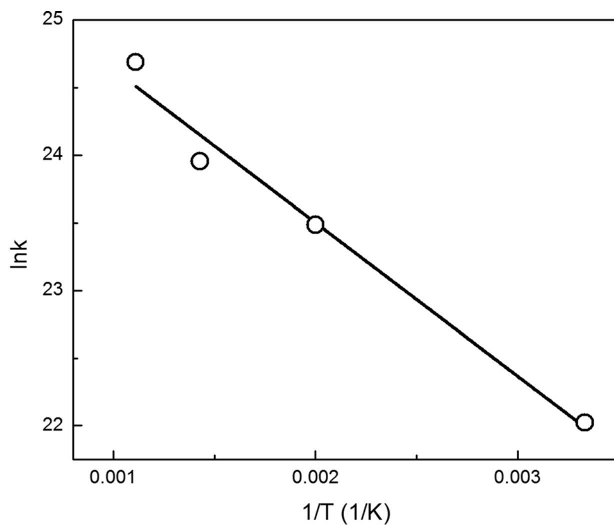

FIG. 5. Arrhenius plot of NO dissociation reaction rate constant on the Si surface. Energy barrier for the reaction was 0.1 ± 0.01 eV.

reacted with another Si atom in a neighbor dimer such that it formed an inter-dimer bridge structure. Dissociation of the NO molecule occurred immediately after formation of the inter-dimer bridge. The oxygen atom was incorporated into the back bonds of the dimer, similar to the Si surface oxidation.[29] In contrast, the N atom stayed on the surface during the present simulation period of 20 ps.

Figure 4 shows the statistical analysis of the final configuration of NO molecules after 20 ps of simulation. The number of escaped NO molecules had no evident correlation with the substrate temperature, implying that the bouncing back from the Si surface might be governed by conditions other than the temperature. Randomness of the NO orientation might be a reason for the temperature-independent bounce-back behavior. If the NO molecule arrived at the Si surface with an oxygen atom to the surface, the molecule was frequently pushed away from the substrate, as shown in the early part of Movie Fig. 3(a) or Fig. 3(b). If, by chance, there was no strong attraction to the substrate, the molecule might be bounced away from the surface.

In contrast, it is evident that the dissociation probability of the adsorbed NO molecule increased with increasing substrate temperature. The number of dissociation reactions increased from 18 at 300 K to 153 at 900 K. This temperature dependence obviously shows that the dissociation of the NO molecule on the Si surface is thermally activated. The activation energy for the dissociation process was obtained by using the Arrhenius plot shown in Fig. 5. Here, k is the reaction rate constant, defined by $\frac{1}{t}\ln\left([A]_o/[A]\right)$, where t is reaction time, $[A]_o$ is the total number of adsorbed NO molecules, and $[A]$ is the number of dissociated NO molecules. In this calculation, we used the total simulation time (20 ps) as the value of t, assuming that the time for adsorption was equal at all temperatures considered. We obtained 0.1 ± 0.01 eV as the activation energy for the NO dissociation reaction. Previous analysis of the first principle molecular dynamic simulation showed that the energy barrier ranges from 0.04 to 0.16 eV, with an assumption of attempting frequency of 10–100 THz.[20] This value quantitatively agrees with that of the present statistical analysis.

We studied the reaction pathway by analyzing all dissociation cases in Fig. 4 (331 cases). Figure 6 shows the typical reaction pathway through which the adsorbed NO molecule is dissociated into N and O atoms. The representative dissociation reactions of NO molecules of various orientations are presented in Movies Figs. 3(c), 3(d), and 3(e). When NO molecules approached the surface (Fig. 6(a)), most of them aligned themselves such that the nitrogen reacted with the surface Si atoms. Rotation of the molecule was frequently

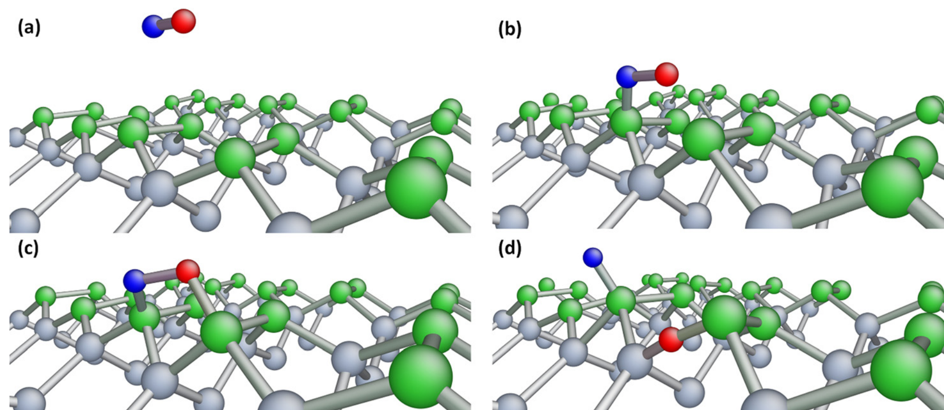

FIG. 6. Typical reaction path of single NO molecule on the Si(100) surface. The NO molecule forms a Si-N bond, followed by the formation of an inter-dimer bridge prior to dissociation.

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observed when nitrogen in the initial position of the NO molecule was further away from the surface than oxygen. Figure 6(b) shows the molecular adsorption, where the NO molecule was anchored onto a surface Si by the Si-N adsorption.

After the molecular adsorption, the oxygen-end rotated around the Si-N sigma bond and explored the adjacent Si sites suitable for a Si-O bond. We found that some delay of the reaction occurred at this stage. If the oxygen atom reacted with a Si surface atom, the NO molecule would form a bridge between two surface Si atoms. Three possible bridges could form between the surface Si atoms. The most frequently observed configuration was the inter-dimer bridge between Si atoms of the adjacent dimers in the same dimer row (see Fig. 6(c)). The second possible configuration is that in which the NO molecule reacted with two Si atoms of the same dimer to form an intra-dimer bridge. This configuration was considered as the most probable intermediate state in the previous theoretical studies,[16,17] where only the energetics of the intermediate atomic configurations were considered. However, the intra-dimer bridge was hardly observed in the present MD simulations. This discrepancy will be discussed later in Fig. 7. In the last possible case, the NO molecule forms bonds with two Si atoms in two adjacent dimer rows by bridging across the channel between them. However, this bridge could not be found in the present work because the distance between the Si atoms (0.52 nm) was much larger than the equilibrium distance of the N-O bond (0.12 nm for a double bond or 0.14 nm for a single bond).

After the NO molecule formed an inter-dimer bridge, dissociation of the molecule occurred immediately (Fig. 6(d)). After dissociation, the oxygen atom rapidly incorporated into the back bonds of the dimer row, which is known to be the most preferable site of the surface oxygen. In contrast, nitrogen stayed on the dimer bond site where it first bonded. Inward diffusion of the nitrogen was observed at high temperature. The incorporated nitrogen was coordinated by three Si atoms, as in the previous reports:[7,20] two surface Si atoms and a subsurface Si. This reaction can be considered as the first inward diffusion step of nitrogen during the oxynitridation process.

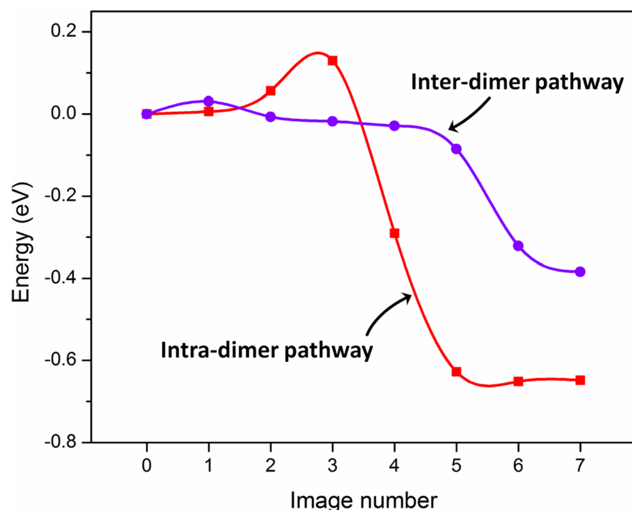

FIG. 7. Energy barriers used to form inter-dimer or intra-dimer bridges, starting from the adsorbed NO molecule on the Si atom in a dimer.

The present observation of the preferential inter-dimer bridge state is in contrast with the previous first principle calculation results, where the intra-dimer bridge was energetically favorable.[16,17] We also obtained the same result by performing the total energy calculations using the present force field. To address this incompatibility, we conducted *ab initio* NEB calculations to obtain the energy barrier for the inter-dimer or intra-dimer bridge formation from the adsorbed NO configuration of Fig. 6(b). Six intermediate images between the initial and the final configuration are shown in SI-2 section of the supplementary material.[24] (VASP POSCAR format of the initial and two final atomic configurations are also included in the supplementary material.[24]) Figure 7 shows the energy diagram for the reaction paths, obtained from the *ab initio* NEB calculations. Intra-dimer formation has an energy barrier of approximately 0.15 eV, while inter-dimer formation has almost no energy barrier (at most, 0.04 eV). The same behavior was observed regardless of the Si atom in the asymmetric buckling structure of the dimer. This result shows that the inter-dimer bridge was mostly observed due to much lower energy barrier, although the configuration is of higher energy.

Figure 8 shows the uptake behavior of N and O atoms into the Si(001) substrate, obtained by simulating consecutive NO reactions at various temperatures from 300 K to 1000 K. The NO incorporation into Si results in an amorphous Si oxynitride layer, as in the oxidation process of Si.[29] The dashed line in Fig. 8 indicates the cumulative number of NO molecules supplied for the simulation (50 molecules per ns). At the initial stage of the NO reaction, most of the supplied molecules were dissociated and incorporated into Si at all temperatures, showing that the pristine Si(001) surface has high reactivity with the NO molecule. However, significant suppression of the uptake behavior occurred at 300 K after 1.2 ns. The self-limiting behavior occurred after approximately 6 ns of the simulation. This retarded oxynitridation process at low temperature was already reported experimentally.[9] At higher temperatures of 700 K and 1000 K, the self-limiting behavior became less significant and the uptake of N and O atoms continued to occur during simulation up to more than 10 ns.

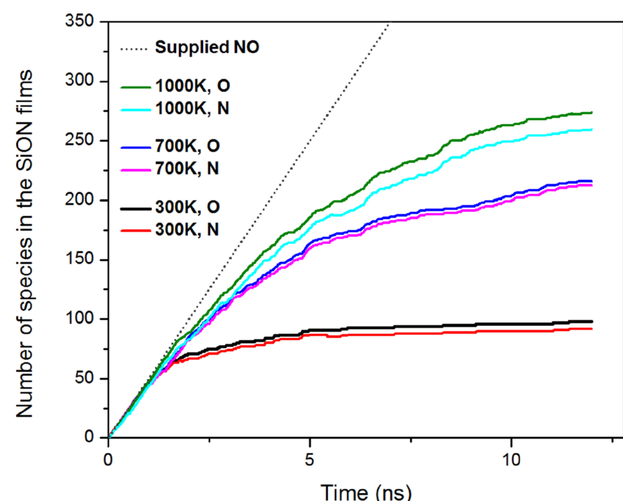

FIG. 8. Uptake behavior of N and O atoms at various simulation temperatures.

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However, a large fraction of the supplied molecules was not incorporated into the Si substrate in the later stage of simulation. The sticking coefficient at 12 ns was 0.163 and 0.457 at 300 K and 1000 K, respectively. The uptake of nitrogen always appeared lower than that of oxygen at all simulation temperatures because some dissociated nitrogen atoms remaining on the surface aggregated to form a N_2 molecule and detached from the surface.

Figure 9 shows the depth profile of N and O atoms at various temperatures during consecutive NO reaction simulation. The depth profile was characterized by the number of atoms in a slice of thickness 0.025 nm from the surface. At 300 K, oxygen was incorporated deeper than nitrogen, which could be expected based on the observations, in which the dissociated oxygen atom was placed in the back bonds of a dimer, while most nitrogen atoms are bound to the surface Si atoms. At low temperature, the depth profile did not vary during the simulation because the diffusion of N and O atoms hardly occurred. The present observation of uptake behavior and depth profile reveals that the dissociation reaction occurred only in the initial stage of simulation at 300 K. Because of negligible inward diffusion, the reactive sites of the Si surface were saturated soon after starting the simulation. The self-limiting behavior at low temperature could result from the deficiency of the reactive sites on the surface. As the temperature increased, it became notable for both nitrogen and oxygen diffusion that the depth profile was shifted inward during simulation. Note that the nitrogen profile was shifted more rapidly. This result agreed with the experimental measurement of their diffusivities in Si.[30] The nitrogen distributed more deeply than the oxygen as the reaction proceeded. Because of the enhanced inward diffusion at

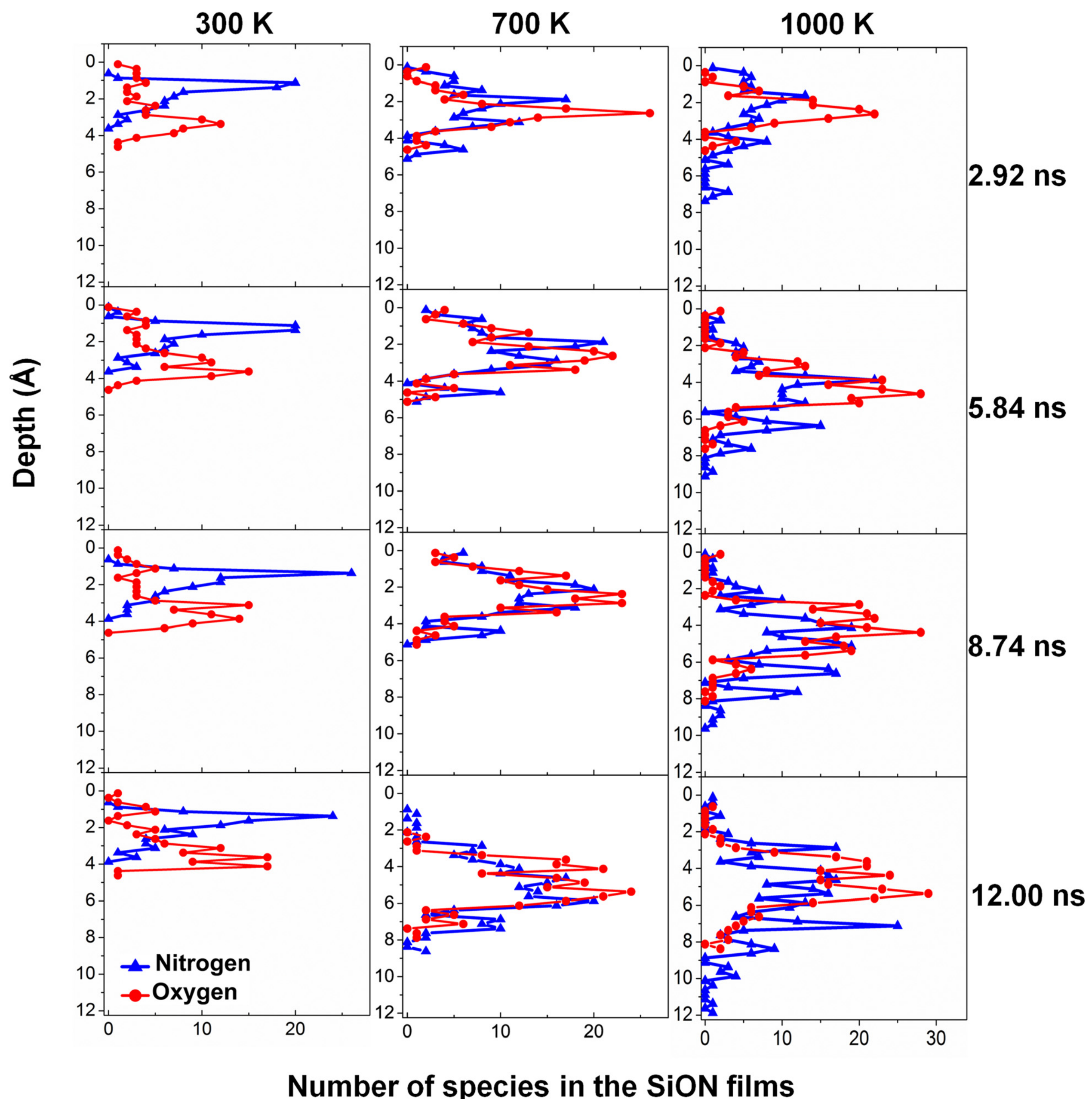

FIG. 9. Depth profile of N and O atoms at various temperatures during consecutive NO reaction simulation.

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higher temperatures, chemically active sites of the surface could be regenerated. Consequently, continuous uptake of N and O atoms occurred at higher temperature.

The present simulation works can provide a guide for optimizing the process condition of Si oxynitride growth on a Si surface. Ultra-thin Si oxynitride film of high quality can be obtained at low temperature, where self-limiting NO dissociation is expected. One of the major advantages of N incorporation into the gate dielectric is the suppression of boron diffusion into the dielectric layer. It would be desirable that a N-abundant layer would form at the interface between the dielectric layer and the poly-Si gate. Annealing at high temperature, i.e., at 1000 K, may result in a significant shift of N distribution, as shown in Fig. 9, which will undermine the performance of the Si oxynitride layer as the boron diffusion barrier.

CONCLUSIONS

The reactive MD simulations of oxynitridation of a Si(001) surface revealed the reaction behavior at an atomic scale, which were consistent with the previous experimental observations and the first principle calculation results. We also reported the small activation energy of the reaction, the preferential Si-N bond for NO molecule adsorption, and the self-limiting reaction behavior at low temperature. The consistency shows the validity of the reactive force field used in the present work. The most significant result of the present study is the suggestion of the reaction pathway of NO dissociation. We observed that the inter-dimer bridge of a NO molecule is the dominating intermediate state of the adsorbed NO molecule prior to its dissociation. Although this observation is in contrast to the previous theoretical studies based only on the total energy calculations, this suggestion was supported by the *ab initio* NEB calculations from which it could be seen that the energy barrier for the inter-dimer bridge formation was much lower than that for the intra-dimer one. This result definitely shows that the energetics of the reaction product is not sufficient to understand the reaction pathway; thus, considering the energy barrier is crucial. The growth mechanism of an ultrathin Si oxynitride layer, explored via consecutive NO reaction simulations, revealed the notable difference in depth profile of N and O atoms depending on the temperature. These results will be useful for optimizing the process condition of Si oxynitride growth.

ACKNOWLEDGMENTS

This research was supported by the KIST institutional project (Grant No. 2E25372). We gratefully acknowledge the technical support from Mr. Minho Lee and Chansoo Kim while using the high performance computing facility at the Korea Institute of Science and Technology. Part of the present work was performed by using the supercomputers at the Institute of Materials Research of Tohoku University with the help of Dr. Hiroshi Mizuseki.

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