Pathways of nitric oxide dissociation on Si(001) and subsequent atomistic processes: a first-principles molecular dynamics study

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New Journal of Physics 10 (2008) 093029 (11pp)
Received 7 July 2008
Published 25 September 2008
Online at http://www.njp.org/
doi:10.1088/1367-2630/10/9/093029

Abstract. We present first-principles molecular dynamics (MD) simulations of the dissociation of a nitric oxide (NO) molecule on an Si(001) surface and subsequent incorporation of the nitrogen atom into the subsurface, which are important in the understanding of the synthesis of oxynitride thin films. The MD runs for different initial conditions revealed various dissociation pathways. In some, the dissociated N and O atoms bridge an Si dimer and substrate backbond. The dissociated nitrogen incorporates into the subsurface with the formation of N≡Si3. The NO dissociates across two Si dimers. All the processes finish within a couple of picoseconds at all of the temperatures considered, implying that the corresponding energy barriers are quite small (\( \lesssim 0.2 \)). Inclusion of the spin polarization increases only the energy barrier for the initial dissociation process from a molecular state, suggesting the existence of a molecular precursor state. The facile dissociation of the NO and incorporation of N are consistent with photoemission measurements.
1. Introduction

Si oxynitride, where nitrogen is introduced as an impurity into Si oxide, is now used as one of the gate materials to replace Si oxide in metal–oxide–silicon (MOS) devices showing serious electrical problems at the nanometre scale [1]–[6]. Researchers reported that the oxynitride thin films could circumvent problems such as the increase of leakage current [1, 2] and penetration of dopants from highly doped gate materials. Nitric oxide (NO) adsorption, followed by thermal processes, is one of the methods for synthesizing oxynitride films. Thus, it is important to understand the adsorption and dissociation of NO at the initial stages of the oxynitridation process using NO.

NO adsorption on Si has also been studied extensively as a prototype of a molecule adsorption on Si surfaces [7]–[16]. Since the report of NO dissociation at 90 K [7], subsequent experiments have confirmed the dissociation at relatively low temperatures [9]–[12]. Using valence-band photoelectron spectroscopy, Carbone et al [10] observed the dissociation of NO even at 20 K. According to a photoemission experiment by Kim et al [12], the dissociation of NO takes place at 150 K. The chemical states of nitrogen are N≡Si₃ and N≡Si₂. Further annealing of the sample increases the amount of N≡Si₃ with the disappearance of N≡Si₂. But the realistic atomistic processes for N incorporation into the subsurface after NO dissociation and for N≡Si₃ formation have not been clarified yet [12, 13].

From the theoretical perspective, two studies on NO dissociation provided contradicting results. In their recent first-principles calculation for NO dissociation, Kato, Nakasaki and Uda (KNU) [15] found a couple of metastable structures of NO adsorption including both the molecular and dissociated forms. Then, using a nudged-elastic band (NEB) method [17], they assigned 0.07 eV to the dissociation energy barrier, which is the energy difference between the molecular state far from the surface (as in p1 of figure 1) and the transition state of the direct dissociation A → D in figure 2. Even though the initial kinetic energy (the energy difference between the molecular state far from the surface and the metastable adsorbed state) could affect a structural transformation, the energy barrier for the structural transformation is the energy difference between the transition-state and the initial metastable structures. In this case, the dissociation energy barrier should be 1.60 eV. At this barrier, the dissociation is rarely observed at room temperature. In the other cluster calculation, Korkin et al [14] suggested a different dissociation pathway following A → B → C → D in figure 2. Unlike the result of KNU, the energy barrier for the dissociation process is marginal, which is more consistent with experiments. They further performed supercell calculations showing the formation of N≡Si₃ on the surface (not in the subsurface). However, their results of the supercell calculations do not appear to describe the situations correctly, because the calculations are not based on the parameters with full convergence (a small supercell and a small number of k points)\(^1\). Therefore, to elucidate the detailed processes of the formation of threefold nitrogen and N incorporation into the subsurface and to solve the discrepancies between the theories, we need to reinvestigate the NO dissociation processes based on a different method. For this purpose, first-principles molecular dynamics (MD) could be a good choice since we can, in an unprejudiced manner, observe structural evolution from a given initial condition. The usual method of first finding

\(^1\) The metastable structure A in figure 4 was reported to be unstable in [14] in contrast with the present paper and [15]. Furthermore, in solid-state calculations with the periodic boundary condition of [14], it does not seem that the supercell is treated correctly, i.e. the bottom-most atoms are not in their bulk positions as displayed in figure 7 of [14].
Nitrogen Oxygen Silicon

**Figure 1.** Initial structures for MD simulations. p1: the NO lies above an Si dimer parallel to it. p2: the NO is parallel to the surface dimer rows in between two Si dimers. v1: the NO points to the surface just above an Si dimer.

**Figure 2.** Snapshots of the MD run at 600 K for the initial configuration p1 in figure 1. B, C and D appear at 0.036, 0.16 and 0.37 ps respectively from the appearance of A. E appears at 0.56 ps from the appearance of A at 900 K.

metastable structures and, secondly, investigating the structural changes between the metastable structures, as adopted in [15], could miss metastable structures in this complicated system and inevitably the pathways with lower activation energies.

In this paper, we perform first-principles MD simulations of NO dissociation on the Si(001) surface. We find that NO dissociates in various channels, consequently leading to various
dissociated species: a dissociated O atom, with N binding to the dimer, bridging a backbond between an Si dimer and a substrate atom; or the dissociated nitrogen incorporates into the subsurface with formation of \( \text{N} \equiv \text{Si}_3 \); or the NO dissociates across two Si dimers. All of the dissociated species appear within a couple of picoseconds at the temperatures considered, implying very small dissociation barriers. Observation of fast dissociation also suggests that easy NO dissociation is rather independent of its initial geometry with respect to the substrate. If the spin polarization of NO is taken into account, only the energy barrier of the initial stage increases by \( \sim 0.2 \text{ eV} \); however, the overall features change very little.

2. Calculation method

In the atomic structure calculations and molecular dynamics simulations, we use the Vienna ab-initio simulation package (VASP) [18]. This package incorporates ultrasoft pseudopotentials (USPP) [19] and the generalized-gradient approximation (GGA) of Perdew and Wang [20] for the exchange-correlation energy. The details of the computation parameters are the same as the previous static calculation [16]. In all of the MD simulations, the molecule is initially put about 3 Å above an Si dimer with its downward velocity calculated from \( v = \sqrt{3k_B T/m} \), where \( k_B \), \( T \) and \( m \) are the Boltzmann constant, the temperature and the mass of NO, respectively. To solve the Newton equation of ionic motion, the Verlet algorithm [21] is used with time steps of 0.3 femtoseconds (fs) (for \( T = 900 \text{ K} \)) and 0.5 fs (for \( T \leq 600 \text{ K} \)). The temperature of the system is controlled using the algorithm of Nosé [22]. The total energy of the system (the sum of the kinetic and potential energies of the ions, and the kinetic and potential energies of the thermostat) is constant within 2 meV per ion for a run over 5 picoseconds (ps) [18].

3. Results and discussion

We begin with the MD simulations of the adsorption of an NO molecule approaching the surface parallel to a dimer (p1 of figure 1). Figure 2 shows the resulting snapshots of the MD run using the p1 initial structure at 600 K. At first, the NO molecule is bound to the Si dimer just below it in a parallel configuration (p1-A). Then the molecule transforms into a more stable state as seen in figure 2(B) (p1-B). After that, the oxygen atom moves outward from the dimer with the rotation of the O–Si bond (p1-C). Finally, the oxygen atom breaks the backbond of the dimer and bridges the dimer atom and subsurface atom (p1-D), in a similar manner to \( \text{O}_2 \) dissociation on Si(001) [23]. This dissociation channel is close to the one proposed by the quantum-mechanical cluster calculation made by Korkin et al [14].

The MD simulation reveals that all of these dissociation processes take place only in 0.37 ps at 600 K, implying very small dissociation energy barriers. The time span for p1-A \( \rightarrow \) B, 0.036 ps, is extremely small. The attempt frequency for a transformation from a metastable state at temperature \( T \) is given by \( v = v_0 e^{-E_b/k_BT} \), where \( v_0 \) and \( E_b \) are the prefactor and the energy barrier from the initial state to the final state, respectively. If an event takes place within \( \Delta t \), the attempt frequency \( v \) is related to \( 1/\Delta t \). Thus, for a given \( v_0 \), the energy barrier can be estimated by \( E_b = k_B T \ln(v_0 \Delta t) \). Since \( v_0 \) is of the order of tens of THz, we can estimate the activation energies of the atomistic processes. With an assumption of \( v_0 = 10–100 \text{ THz} \), the energy barriers for the consecutive processes A \( \rightarrow \) B \( \rightarrow \) C \( \rightarrow \) D in figure 2 are estimated as \( \sim 0.06, 0.01–0.13 \) and \( 0.04–0.16 \text{ eV} \), which are comparable with the NEB values in the previous static calculations [16]. The small energy barriers are also consistent with the cluster calculation.

New Journal of Physics 10 (2008) 093029 (http://www.njp.org/)
of Korkin et al [14], but in sharp contrast with the report of KNU [15]. The dissociation of p1-A → B is observed even at lower temperature simulations. The time spans of p1-A → B are 1.64 and 0.54 ps at 100 and 300 K, respectively. The present findings of NO dissociation at very low temperatures are in good agreement with the previous experiments [9]–[13].

At a very high temperature of 900 K, the NO dissociation takes place through rather different processes. After the p1-B configuration, nitrogen makes an additional bond with a subsurface Si atom (marked by a filled triangle in figure 3(B)), breaking the Si dimer bond and penetrating into the bulk. This results in the formation of N≡Si₃. At the same time, the O–Si bond rotates and O moves outward from the dimer as in p1-C in figure 2. The structure is further stabilized through oxygen bonding to a subsurface Si atom as in p1-E. This structure with N≡Si₃ and the backbond O has a energy higher than p1-D by 1.40 eV from the static calculations. All these processes also finish within 0.56 ps, confirming the low energy barriers of the NO dissociation.

Next, MD simulations are performed starting from the NO molecule, between two dimers, whose axis is along the dimer rows (p2 in figure 1). Figure 3 shows snapshots at 600 K for the p2 initial structure. The molecule binds with one of the two dimers and forms a metastable state (figure 3(A)), different from the parallel binding as in figure 2(A). In this structure, the three atoms binding to nitrogen (two dimer-Si and oxygen atoms) do not lie in a plane, implying the formation of an sp³ orbital hybridization in the nitrogen atom. At 3.23 ps from the appearance of the structure, the NO molecule dissociates. In the dissociated structure, unlike the dissociation in the dimer-parallel attack in figure 2, the nitrogen and oxygen atoms bind to different dimers (figure 3(B)). We estimate the energy barrier as 0.18–0.3 eV, which is again very small. The present results suggest that the dissociation of the NO molecule across two dimers could be possible although less frequent than the dissociation involving the same dimer [11, 12].

The transformation of p2-B to a more stable structure, e.g. where the oxygen atom breaks a backbond as in p1-D (N(2)-O(2b) in figure 3(b) of [16]), does not take place within 4 ps, implying a larger energy barrier for such a transformation. At 900 K, a different channel for two-dimer dissociation is observed as in figure 3(C). In this structure, O bridges a backbond between a dimer atom and a subsurface atom, as in p1-D, while N binds to two dimers, again making an
Figure 4. Snapshots of the MD run at 900 K for the initial configuration v1 in figure 1. B, C, D and E appear at 0.41, 0.66, 1.28 and 1.41 ps respectively from the appearance of A.

N≡Si₃ species. The p2-C structure is formed within 0.75 ps from p2-A, again meaning a very small dissociation energy barrier.

The vertical impingement of the NO molecule (v1 in figure 1) at 900 K takes a different channel as shown in figure 4. As guessed from the initial structure, NO forms a molecular adsorption state with only N binding with the two Si atoms. The NO axis is still perpendicular to the surface (figure 4(A)). Unlike the sp³ configuration in figure 3(A), the atoms around nitrogen lie in a plane, implying the sp² configuration. Then, in 0.41 ps, the NO molecule dissociates into a metastable structure as displayed in figure 4(B) (v1-B), similar to the dissociated structure from the parallel attack in p1-B (figure 2). After 0.25 ps from v1-B, the nitrogen makes a bond with a subsurface Si atom. Then, after 0.75 ps from v1-C, the nitrogen penetrates further into the subsurface (figure 4(E)) via v1-D. That is, the nitrogen makes bonds with a dimer atom and two subsurface Si atoms (formation of N≡Si₃). Oxygen bridges the Si dimers, saturating the Si dangling bonds. The binding energy of this structure is 5.63 eV, the most stable one found through MD simulations (more stable than p1-D by 0.18 eV). The overall time from the initial structure to the final one is only 1.41 ps. Among the elementary processes, the most time-consuming one is v1-C → D, whose energy barrier is estimated as 0.14–0.32 eV. The present result also differs from the large activation barriers (more than 2.3 eV) [15] for the threefold coordinated N and provides one of the possible channels for N incorporation along with N≡Si₃ formation, which is observed as the major species in the NO adsorption on Si(001) [12, 13].

In the previous static calculation [16], it was argued that, despite little difference in the NO atomic distance, p1-A has molecular characteristics while p1-B is dissociated, based on the distribution of the total charge density and the values of spin polarization (a free NO molecule is spin-polarized with a magnitude of 1). That is, p1-A is spin-polarized with a large charge density between the N and O atoms, implying a bonding character, while, in p1-B, the spin polarization disappears and the charge between N and O significantly depletes. We reinvestigate the initial process of the NO dissociation, p1-A → B, since the initial and the final structures
Figure 5. Energy variation for the dissociation of NO, i.e. p1-A → B in figure 2 with (a) the initial structure, (b) the transition-state structure and (c) the final structure. The filled circles and empty boxes in the plot represent the spin-unpolarized and spin-polarized results, respectively.

have different spin polarization. We perform an NEB calculation for the spin-polarized system, where the total spin of the system is fixed at 1 during the transition. The reaction path rarely changes from the spin-unpolarized one. The energy curve along the reaction path is shown by the empty boxes in figure 5. In the final state, the spin-unpolarized one is more stable than the spin-polarized one and the interpolated curves for both cases intersect at the reaction coordinate of 0.92 Å. Thus, the energy barrier from the spin-polarized p1-A to the spin-unpolarized p1-B is 0.21 eV, the energy difference between the intersection point and the initial point. The same argument can be applied to the molecular adsorption structure v1-A with the energy gains of 0.11 due to the spin polarization. Hence, the energy barriers for v1-A → B may increase by about 0.1 eV. Nonetheless, these values are still small and can be overcome very easily at low temperatures. The results of the subsequent processes are unaffected by the spin polarization because all the initial, transition-state and final structures are clearly spin-unpolarized. For a confirmation of the low dissociation energy barrier of the spin-polarized NO molecule, the MD simulations with the inclusion of spin polarization are carried out for the parallel attack of p1
Figure 6. Simulated STM images for (a) p1-A (figure 2(A)), (b) p1-D (figure 2(D)), (c) v1-E (figure 4(E)) and (d) p2-B (figure 3(B)). The upper and lower panels of each subplot are the filled-state (bias: $-2.0$ V) and empty-state (bias: $+2.0$ V) images, respectively.

at 700 and 900 K. The dissociation process takes place within about 0.20 and 0.15 ps (judging from the magnitude of the spin polarization), respectively. The processes after the dissociation are similar to each other. Thus, the spin polarization of the NO molecule affects only the first dissociation process for the initial sub-picoseconds.

The increase of the energy barrier of the p1-A $\rightarrow$ B suggests the possibility of the precursor state p1-A lasting for a long time at low temperatures. Since the precursor state as well as other stable configurations has unique structural features, it can be identified easily by, e.g., low-temperature scanning tunneling microscopy (STM). Figure 6 shows the simulated STM images of p1-A, p1-D, v1-E and p2-B for both the filled and empty states. As expected, the STM image of p1-A shows a reflection symmetry with respect to the Si dimer bound to NO. The N atom is brighter than the O atom since it is located higher than O by 0.07 Å. In the p1-D
image, the unit of the Si dimer and the dissociated species looks darker (brighter) than the rest of the surface in the filled-state (empty-state) images. In the N-penetrated structure, an Si dimer atom binding with both N and O appears brightest in both the filled- and empty-state images. In the p2-B structure, where NO dissociates across two dimers, a pair of the brighter (due to O) and darker (due to N) features across the two dimers appears in the filled-state image. Thus, the four stable structures show distinct features in their STM images and will serve as a guide in future STM experiments.

The present MD simulations using a couple of the initial conditions reveal various pathways of NO dissociation. In all the MD simulations, the NO molecule dissociates within a couple of picoseconds at all the temperatures considered, suggesting very small energy barriers for the atomistic processes. Even with rather restrictive sets of the initial conditions in the configuration space, we argue that NO dissociates very easily irrespective of its initial geometry with respect to the surface. N≡Si₃, a major species in the experiments, is easily formed as in p1-E (figure 2), p2-C (figure 3) and v1-E (figure 4). Among them, the easy formation of p1-E and v1-E provides one of the realistic pathways for N incorporation, which was addressed in the adsorption of NO and NH₃ on Si(001) [13]. Of course, this does not mean that all of the molecules can be dissociated upon adsorption on the surface, i.e. a complete sticking. The present MD simulations, the previous static calculation [16], and the cluster calculation [14] unanimously result in very small energy barriers for NO dissociation. This is in contrast with the NEB calculation of KNU [15], where the correct transition-state structure could be missed², again supporting the necessity for using MD simulations.

4. Summary

We performed first-principles molecular dynamics calculations of NO adsorption on a Si(001) surface and the subsequent atomistic processes such as molecular dissociation and N incorporation. The NO dissociation takes place through a couple of metastable structures. Initially the NO molecule molecularly binds to an Si dimer in a parallel or vertical configuration. The molecule then dissociates into more stable forms. Each of the atomistic processes proceeds for only sub-picoseconds. All processes finish within a few picoseconds, implying low activation energies for NO dissociation (estimated as \(\lesssim 0.2\) eV). The low dissociation energies are independent of the initial geometries with respect to the surface within the present simulations. We found various dissociation channels for the initial structures and temperatures, as summarized in table 1. For the initial structure p1 at 600 K, we obtained, through p1-A, B and C, the p1-D structure (figure 2(D)) where N and O bridges an Si dimer and a backbond. At the lower temperatures of 100 and 300 K, the dissociated structure could not reach the p1-D structure within 5 ps due to low thermal energies. At 900 K, the dissociated nitrogen binds to a subsurface Si as indicated by the filled triangle in figure 2(B) (B’, not shown in the figure) and a threefold nitrogen, N≡Si₃, is formed (figure 2(E)). For the p2 initial structure at 600 K, N and O bind to two neighboring dimers (figure 3(B)). At 900 K, the dissociated nitrogen bonds to a neighboring Si dimer and N≡Si₃ is formed (figure 3(C)). When the NO molecule approaches vertically at 900 K, the dissociated nitrogen is incorporated into the

² Use of different calculation parameters cannot be the reason for the different results, because the additional calculations with the parameters of KNU (25 Ryd, 2k-points, and 4×2 supercell) show that the changes in the relative energies among the metastable structures in figures 2–4 are less than 0.3 eV.
Table 1. Summary of structural changes in the MD runs within about 5 ps according to the initial structures and the temperatures $T$. B’ at 900 K for the p1 initial structure is the structure where N binds to a subsurface Si atom as indicated by the filled triangle in figure 2(B) (not shown in figure 2).

| Initial structure | $T$ (K) | Pictures | Structural evolution |
|-------------------|---------|----------|----------------------|
| p1                | 100     | Figure 2 | A $\rightarrow$ B    |
|                   | 300     | Figure 2 | A $\rightarrow$ B $\rightarrow$ C |
|                   | 600     | Figure 2 | A $\rightarrow$ B $\rightarrow$ C $\rightarrow$ D |
|                   | 900     | Figure 2 | A $\rightarrow$ B $\rightarrow$ B’ $\rightarrow$ E |
| p2                | 600     | Figure 3 | A $\rightarrow$ B    |
|                   | 900     | Figure 3 | A $\rightarrow$ C    |
| v1                | 900     | Figure 4 | A $\rightarrow$ B $\rightarrow$ C $\rightarrow$ D $\rightarrow$ E |

subsurface and N≡Si$_3$ is again formed (figure 4(E)). The spin-polarized GGA calculation for the initial process of p1-A $\rightarrow$ B (figure 2) revealed that the spin polarization of the NO molecule disappears upon dissociation and the dissociation barrier increases to 0.21 eV. The following processes are independent of spin polarization. The present values of the small dissociation barrier are in agreement with most experiments, but in sharp contrast with the previous first-principles calculation [15]. The simulated STM images of the (meta)stable structures reflect the corresponding structural features. The present findings will stimulate further experimental efforts to identify the precursor state and will be helpful in understanding the molecule adsorption of NO on the Si surface and the following oxynitridation process using NO.

Acknowledgment

This work was supported by a Korea Research Foundation grant (R05-2004-000-10728-0).

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