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Mechanism of initial adsorption of NO on the Si(100) surface

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High-resolution photoemission study of the adsorption of NO molecules on the Si(100)2×1 surface at 150 K is performed using undulator synchrotron radiation. N $1s$, O $1s$, as well as Si $2p$ core-level spectra are measured for the series of NO exposures from the very initial adsorption to the full monolayer coverage. The metastable adsorption species are observed with N $1s$ binding energies of 396.4 and 395.8 eV, along with the stable major adsorption species of $N\equiv Si_3$ at 397.4 eV. Both of the metastable species are ascribed to the intermediate reaction species of $N=Si_2$ with a dangling bond. In the O $1s$ spectra, the major O species at 532.4 eV is found to shift toward high binding energies with increasing NO exposures or increasing substrate temperature. This shift is explained by the changes in bonding configurations induced by the active oxygen agglomeration. From these results, it is concluded that NO adsorption above 150 K is completely dissociative without any metastable molecular adsorption species. Instead, it is deduced that the dissociated N atoms metastably form twofold coordinated $N=Si_2$ species through multiple dissociation paths involving one or two Si dimer atoms.

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I. INTRODUCTION

Silicon oxynitride has been a subject of great interest with increasing technological needs for a more reliable gate dielectrics with even thinner oxide thickness. Silicon oxynitride has been a favorable alternative for the conventional SiO_2 gate dielectrics due to its superior properties in electric reliability, suppressed boron penetration, relieved interfacial strain, and hot carrier resistance.[1,2] As a method of growing silicon oxynitride, the N incorporation into a SiO_2 film has been successfully accomplished by employing the thermal reaction of nitric oxide (NO) or nitrous oxide (N_2O).[3–5] Moreover, the reaction of NO on a Si substrate draws attention due to the fact that the repeated cycles of NO adsorption and annealing is a promising nitridation process for a Si substrate with a relatively defectless interface.[6]

Besides such technological interests, the NO reaction on the Si(100) surface has been studied using many surface analysis techniques due to interesting and challenging fundamental issues in it. One of the fundamental questions to be answered was whether the adsorption of NO on Si(100) is proceeded by direct barrierless dissociation or is mediated by a metastable molecular precussor stage. Early studies suggested both the molecular[7] and the dissociative[8] adsorption at room temperature (RT). Another study reported that the dissociative adsorption occurs at RT with most of the N atoms incorporated in the subsurface sites.[9] More recently, Carbone *et al.*'s experimental results suggested the NO dissociation even at 20 K.[10] Our group recently confirmed that the RT adsorption of NO is completely dissociative and the dissociated N atoms are spontaneously incorporated into a characteristic subsurface site.[11,12] However, theoretical calculations have provided conflicting views into the detailed reaction mechanism; one theoretical study reported that the dissociation proceeds without any significant barrier,[13] while the other calculation suggests that NO is initially and metastably chemisorbed in a molecular form, which might be observed at a low temperature.[14]

Another fundamental issue in clarifying the reaction mechanism is related to the identification of reaction intermediates for the dissociated N atoms. While the theoretical calculations suggest that the dissociated N atoms initially form the twofold coordinated $N=Si_2$ species,[13–15] most of the experimental results observed only the threefold coordinated $N\equiv Si_3$ species.[16,17] That is, the microscopic reaction pathway from NO molecules to the stable $N\equiv Si_3$ adsorption species[18] is not clear at all.

In this work, we investigate the adsorption of NO on the Si(100)2×1 surface at a substrate temperature of 150 K from the NO exposure of as low as 0.1 L in order to identify the metastable reaction intermediates and to clarify the initial reaction mechanism. We employed high-resolution photoemission for N $1s$, O $1s$, as well as Si $2p$ core levels using undulator synchrotron radiation. The present high-resolution N $1s$ core-level spectra clearly show the N species with binding energies lower than 397 eV. This result indicates that the dissociatively adsorbed N atoms are in the forms of both $N=Si_2$ and $N\equiv Si_3$ at 150 K, while $N\equiv Si_3$ is the major form at RT. The $N=Si_2$ species is not stable upon annealing just above 350 K. The NO dissociation processes with possible bonding structures are discussed based on the above results as well as the O $1s$ and Si $2p$ results in comparison with the recent theoretical calculations.

II. EXPERIMENT

The photoemission experiments were performed on a soft x-ray beam line (8A1) connected to an undulator (U7) at Pohang Accelerator Laboratory in Korea.[19,20] This beam line covers the photon energy range of 90–1500 eV with an optimum resolving power of 7000. The well-ordered Si(100)2×1 surfaces were obtained by repeated flash annealing up to 1250 °C, while the temperature was monitored by optical pyrometer. The Si substrate was cooled down to 150 K using liquid nitrogen throughout the whole experiment. The NO exposures to the Si surface were carried out by backfilling the chamber with a NO partial pressure of 1.0×10^{-8} torr while the substrate was held at 150 K. Each

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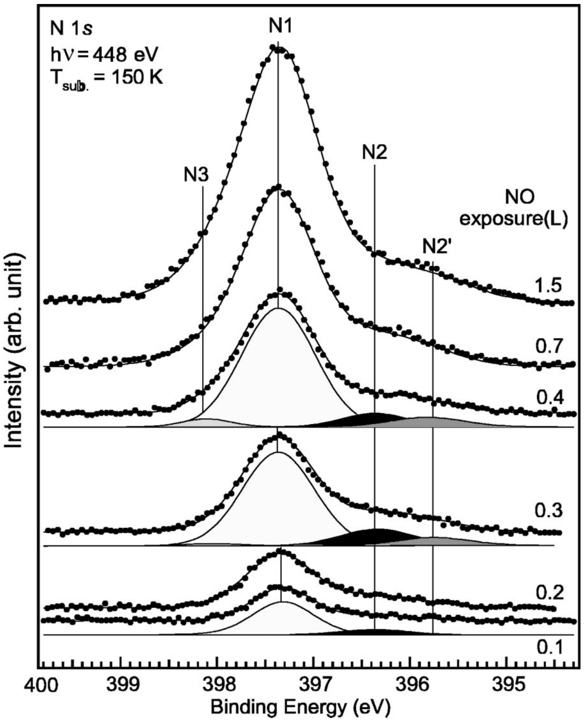

FIG. 1. N 1*s* core-level spectra for the Si(100) surface with increasing NO exposures at 150 K. The spectra were taken with a photon energy of $h\nu = 448$ eV along the surface normal and were normalized by the incident photon flux. The decomposition of the spectra through curve-fitting analyses are given together. The broad features below 397 eV as well as the main peak at 397.4 eV increase with increasing NO exposures.

NO exposure was performed on to a freshly obtained clean Si(100) surface. All spectra were taken using a high performance electron analyzer (SES-200, Gamma Data, Sweden) which exhibits the overall instrumental resolutions (the analyzer and the photon beam in total) of 350 meV for N 1*s* (O 1*s*) with a photon energy ($h\nu$) of 448 eV (584 eV) and of 60 meV for Si 2*p* with $h\nu = 145$ eV. The decomposition of each core-level spectra was accomplished through a standard least-squares fitting scheme after removal of a Shirley-type background for the Si 2*p* core levels. For the N 1*s* or O 1*s* core-levels, the background spectra of the same kinetic energy range were obtained from a clean Si(100) surface. For the Si 2*p* core-level spectra, the spin-orbit splitting and the branching ratio were fixed to 0.602 eV and 0.5, respectively. A Gaussian and Lorentzian product function was used as an approximation of a Voigt function.[21] The binding energies (E_b's) of the photoemission spectra were calibrated by referring the position of the Si $2p_{3/2}$ level of bulk Si atoms at 99.20 eV.

III. EXPERIMENTAL RESULTS

Figure 1 shows N 1*s* core-level spectra taken for a series of NO exposures on a clean Si(100) surface at 150 K with a photon energy of 448 eV. The spectra consist of a distinguished peak at 397.4 eV and a broad feature extending toward lower binding energies. It is evident that the lower binding energy feature as well as the main peak at 397.4 eV grow with increasing NO exposures. Note that no previous N 1*s* studies on Si surfaces reported a spectral feature with a binding energy smaller than 397 eV. For a more detailed analysis, each spectrum was subject to a standard curve fitting procedure described above. The Gaussian and Lorentzian widths were set to 0.6 ± 0.05 and 0.2 eV, respectively, for the N 1*s* core-level spectra. The curve fitting indicates that the N 1*s* spectra consist mainly of four different components as shown in Fig. 1. The main peak, denoted as N1, is located at 397.4 ± 0.05 eV and the two small components at 396.4 ± 0.10 and 395.8 ± 0.15 eV constitute the broad low binding energy feature. The two small components are denoted as N2 and N2′, whose binding energies are shifted by about -1.0 and -1.6 eV from N1, respectively. The two components of N2 and N2′ instead of one are evident from the changes of the shape as well as the peak position of the lower binding energy tail with increasing NO exposures. In addition, yet another component N3 is needed to fit the high binding energy tail for a coverage larger than 0.3 L, which is centered at 398.1 ± 0.05 eV and is shifted by 0.7 eV from N1.

The N1 component at $E_b = 397.4$ eV was unambiguously ascribed to the bonding configuration of $\mathrm{N}\equiv\mathrm{Si}_3$ where the fully dissociated N atoms are bonded directly with three neighboring Si atoms.[11,16–18,22,23] A similar N 1*s* binding energy was observed also for NH_3 dissociation on Si(100) and for the interfacial N species at the SiON/Si interface.[12,18,24,25]

Since a NO molecular adsorbate is expected to have a distinctively larger binding energy of 400 eV or so,[26] it is obvious that the NO adsorption is fully dissociative even at 150 K in consistency with the previous photoemission study at 20 K.[10] However, it is surprising that the highly coordinated N1 ($\mathrm{N}\equiv\mathrm{Si}_3$) is the major adsorption species even at the substrate temperature of as low as 150 K; throughout the whole NO coverages under investigation (1.5 L is close to the full monolayer saturation as discussed below), the relative population of N1, N2, and N2′ is nearly constant with a percentage ratio of $78 \pm 5 : 13 \pm 3 : 7 \pm 3$, respectively. This suggests the energy barrier for the dissociation of NO and even that for the formation of $\mathrm{N}\equiv\mathrm{Si}_3$ being fairly low.

The N3 component was observed for the saturation-coverage RT adsorption earlier,[11,27,28] and the oxygen SNN effect on $\mathrm{N}\equiv\mathrm{Si}_3$, that is, $\mathrm{N}\equiv(\text{-Si-Si-})_{3-x}(\text{-Si-O-})_x$ ($x = 1$–3), was attributed to the N3 component above 398 eV.[11,29] The theoretical study Cerofolini *et al.* supported this assignment fully by reporting that nitrogen atoms in $\mathrm{N}\equiv[\mathrm{Si}(\text{-O-})_3]_3$ have a peak centered on 398.3 ± 0.2 eV.[30]

In order to understand the origin of different N species further, especially N2 and N2′, the thermal evolution of the N 1*s* core-level spectra were investigated with a series of annealings for the 0.7-L exposure at 150 K as shown in Fig. 2. It is found that the N2 and N2′ species are very unstable since they decrease drastically in intensities even after a mild annealing at 350 K and almost completely disappear above 450 K. The apparent observation of N2 remaining even after an annealing up to 350 K may be due to the kinetic effect since we did not observe it before for an oversaturated coverage at RT.[11] N3 also decreases with increasing annealing temperature, but partly survives to a much higher temperature.[11] These results clearly indicate that N2 and N2′

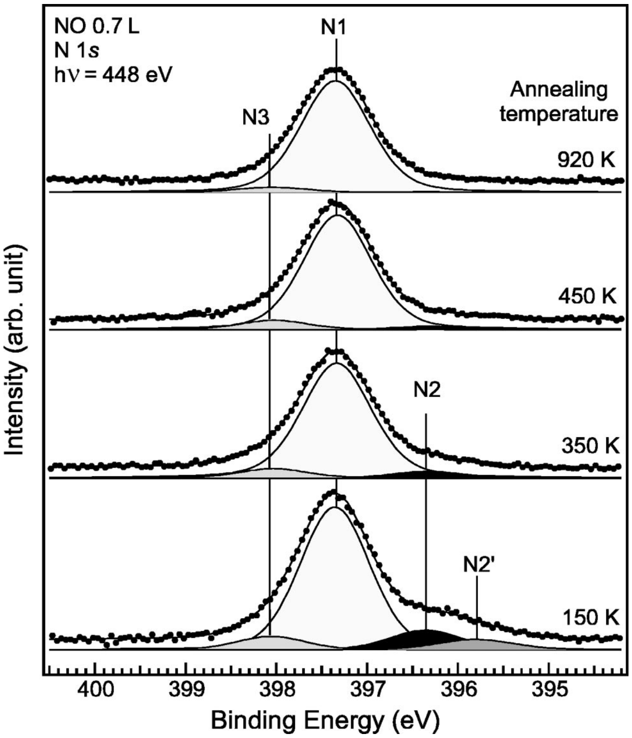

FIG. 2. N 1s core-level spectra and the corresponding decompositions for the Si(100) surface exposed to 0.7 L NO at 150 K and after subsequent annealings at the given temperatures. The spectra were taken with a photon energy of $h\nu = 448$ eV along the surface normal and were normalized by the incident photon flux. N2 and N2′ disappear just above 350 K while N3 still remains up to 920 K with reduced intensity.

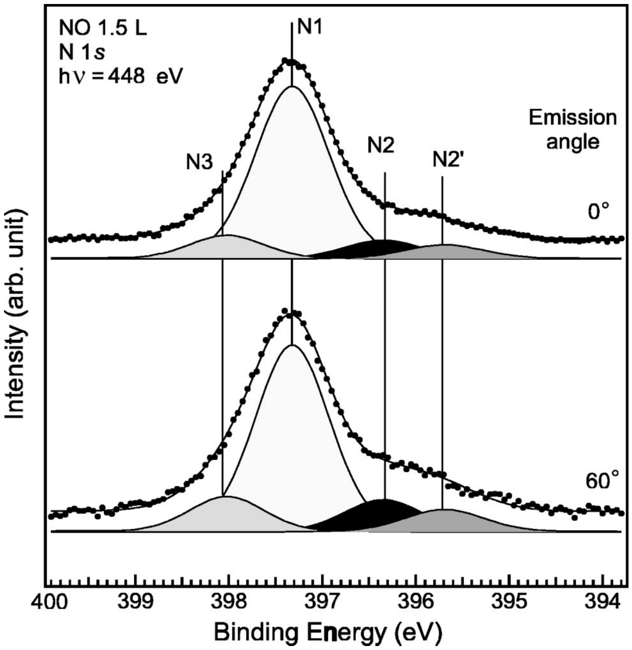

FIG. 3. N 1s core-level spectra and the corresponding decompositions for the Si(100) surface exposed to 1.5 L NO at 150 K as in Fig. 1. The spectra were taken with emission angles of 0° (normal emission) and more surface-sensitive 60°. The decomposition of the spectra through curve-fitting analyses are given together.

correspond to *metastable* adsorption species. It is also evident that they are unique for the low-temperature adsorption. The first-principles calculation by Rignanese *et al.* indicates that every direct N-O bond shifts the N 1s binding energy successively by about 1.77, 3.78, and 5.55 eV, respectively,[31] which eliminates the possibility of relating N2 and N2′ with negative E_b shifts to a configurations with direct N-O bonds. Instead they can be ascribed to the bonding configurations which have a reduced number of nearest neighbors such as $N{=}Si_2$. It may also be considered that they are related to the $N{\equiv}Si_3$ species with nitrogen in the second nearest neighbors (SNN's), since the previous theoretical studies indicated that nitrogen atoms in the SNN's induces a N 1s shift toward a lower E_b.[30] However, the thermal stability shown in Fig. 2 is consistent only with the former possibility. This assignment is also supported from the fact that the N2 and N2′ species appears from the very initial stage adsorption while the occupation of SNN sites by another N is expected only at high coverages. Recent theoretical results indicate that the bonding configuration of $N{=}Si_2$ with remaining dangling bonds have a binding energy lower than $N{\equiv}Si_3$ by about -1.8 eV,[32] which corresponds well to N2′. As discussed below, the most plausible $N{=}Si_2$ adsorption structure is the N insertion into the Si dimer bond, where the electron transfer from the Si dangling bond to the N atom causes the above negative N-1s E_b shift.[14]

Then, the major remaining question is what is the difference between the bonding configurations of N2 and N2′. They may differ in the number of nearest-neighboring Si atoms, that is, N2 may be due to the bonding configurations of N-Si. However, it is very unlikely to replace the strong N-O bonds with only one N-Si bond and two dangling bonds unsaturated. Theoretical calculations also predicted that the N or O atoms bonded with only one Si atom are very unstable.[13] Thus one has to ascribe N2 and N2′ to the $N{=}Si_2$ species with different SNN atoms such as O or N. However, as mentioned above the N SNN's are unlikely for the very initial adsorption species. Then N2 is naturally assigned to the $N{=}Si_2$ species *with SNN O atoms* since the O atoms at the SNN sites are expected to increase the N-1s E_b by roughly 0.5 eV or so; the energy difference between N2 and N2′ is 0.6 eV.[30] This shift has the same origin as the E_b difference between the N1 and N3 components, which was discussed above.

The metastable adsorption species must convert to the thermodynamically stable species of $N{\equiv}Si_3$ (N1) during the annealing process since no N desorption is expected at this temperature range.[11] However, the intensity of N1 *decreases* slightly after annealing above 350 K; the intensities of N1 at 350–920 K are within 76±2% of its intensity at 150 K. The apparent reduction in the N1 intensity can only be explained by the indiffusion of the corresponding N species to the subsurface region. This is consistent with the recent experimental and theoretical work reporting that the major $N{\equiv}Si_3$ species above RT is located near the third Si layer.[12] A similar indiffusion of the dissociated N species is also observed for NH_3 adsorption on Si(100) very recently.[25]

Figure 3 shows the N 1s core-level spectra of 1.5-L NO dose at 150 K taken with different emission angles of 0° and 60°. This measurement shows the surface sensitivity of the different components, that is, the qualitative depth difference

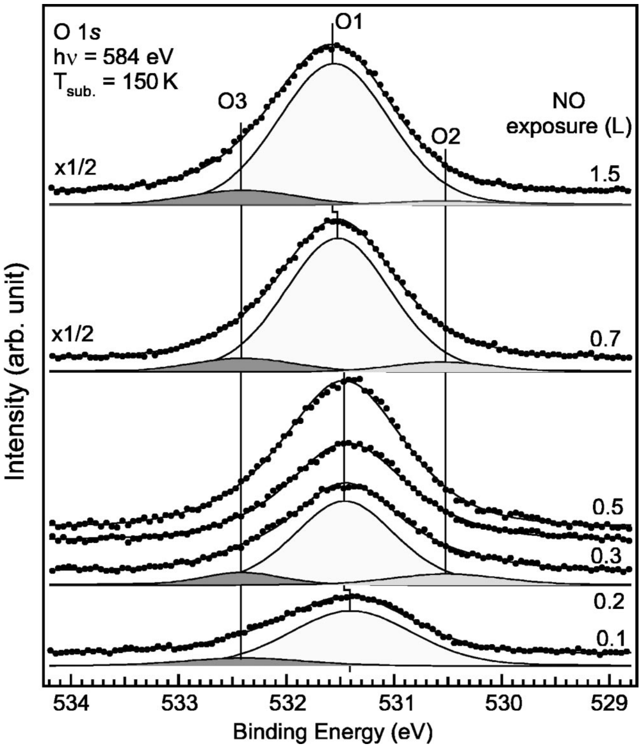

FIG. 4. O 1*s* core-level spectra and the corresponding decompositions for the Si(100) surface with increasing NO exposures at 150 K. The spectra were taken with a photon energy of $h\nu = 584$ eV along the surface normal and were normalized by the incident photon flux.

of the different N species. It is evident from the figure that N2, N2′, and N3 are more surface sensitive than N1; the intensity ratios of N1, N2, N2′, or N3 between the emission angles of 60° and 0° are 0.85±0.05, 1.6±0.2, 1.5±0.1, or 1.5±0.4, respectively, at the whole range of NO exposures measured. This indicates that the bonding configurations responsible for N1 are formed mainly in the subsurface region while the other bonding structures for N2, N2′, and N3 are located near the top surface layer. This is natural since the highly coordinated $N\equiv Si_3$ species (N1) cannot easily be formed on top of the Si surface layer and is fully consistent with the above temperature dependence of the N1 intensity.

We next consider the behavior of the dissociated O adsorbates through O 1*s* photoemission. Figure 4 shows the corresponding O 1*s* core-level spectra obtained from the same NO/Si(100) surfaces as in Fig. 1. The spectra are dominated by a strong peak around 531.5 eV but one can notice that it has extending tails at both sides. The careful fittings lead to decompose these spectra into three different peaks at 531.5 eV (denoted as O1), 532.4 eV (O3), and 530.8 eV (O2). It is interesting to note that the dominant O1 peak shifts slightly toward a higher binding energy by about 0.15 eV with increasing NO exposures. As the NO exposure increases, the relative intensity of O2 decreases while O1 and O3 grow altogether. The temperature dependence of each O component was also examined for the 0.7-L NO exposure as given in Fig. 5. It can be seen that O2 disappears after annealing up to 450 K, which indicates that it is a metastable bonding state occurring only at low temperature and low coverage. In contrast, O3 grows in its intensity with increasing the substrate temperature. Yet another noticeable change is that O1 is gradually shifted to even higher binding energies, by 0.3 eV after annealing up to 920 K.

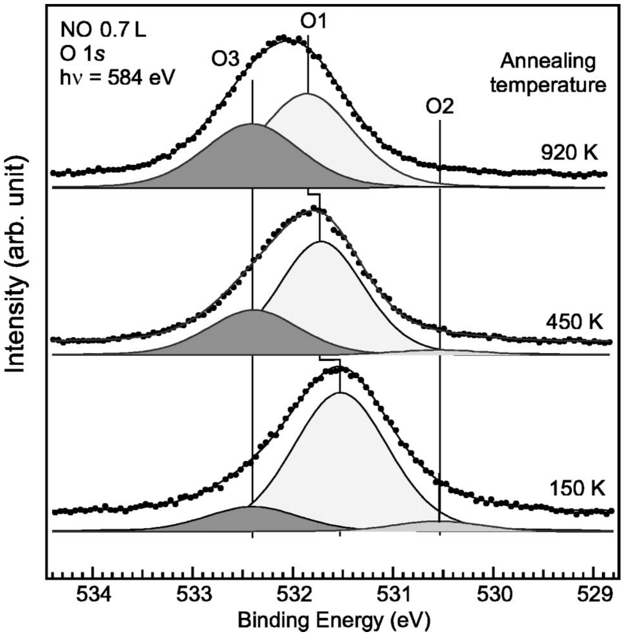

FIG. 5. O 1*s* core-level spectra and the corresponding decompositions for the Si(100) surface exposed to 0.7 L NO at 150 K and after subsequent annealings at the given temperatures.

The O1 peak at 531.5–531.8 eV is obviously related to the major adsorption species of $O=Si_2$, where the oxygen atoms are expected to occupy the backbond sites of Si surface dimers.[11] This peak was observed for RT adsorption of NO,[11] and also for the O_2 adsorption case. However, the systematic shift in the binding energy of O1 and another stable species O3 provide further complexity. The shift of the main component was also observed in the previous O 1*s* study for the NO adsorption at RT with post annealing.[33]

The O3 component at 532.4 eV has a peak position shifted by 0.7 eV from O1 and its intensity increases further upon annealing. This behavior was not noticed in the previous RT adsorption experiment, probably due to the difference in the coverage, the limited energy resolution at RT and the misalignment of the spectral energy positions.[11,33] We also performed a similar O 1*s* measurement for the O_2 adsorption on Si(100) at 150 K as shown in Fig. 6. Even in that case, the post annealing was found to induce very similar O 1*s* line shape changes, that is, the shift of O1 and the growth of O3, except that the O2 component is not observed.[33]

The coverage- and temperature-dependent E_b shift of O1 suggests that the actual bonding configuration responsible for O1 evolves gradually as the coverage or the temperature is increased. It is likely that the oxygen agglomeration leading to the oxygen occupation of the SNN sites of $O=Si_2$ constitutes that evolution. Such active agglomeration of oxygen adsorbates was clearly indicated by the Si 2*p* core-level study for $O_2/Si(100)$, where the highly coordinated Si^{3+} and Si^{4+} species increase for high coverages even at 100 K and also after post annealing.[34,35] We observe a very similar trend in the Si 2*p* spectra for NO adsorption as shown below. In consistency with the above argument for the energy shift

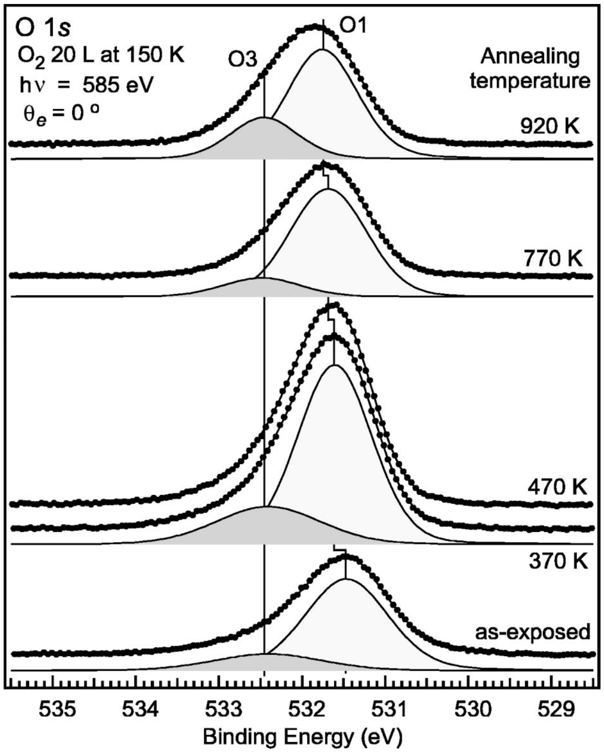

FIG. 6. O 1*s* core-level spectra and the corresponding decompositions for the Si(100) surface exposed to 20 L O_2 at 150 K and after subsequent annealings at the given temperatures.

of O1, we assign the O3 component to the $O{=}Si_2$ species with the SNN's saturated fully by O atoms, which is basically the same as the stoichiometric SiO_2. That is, as the oxygen agglomeration proceeds to form the stoichiometric SiO_2 bonding configurations (the -O-Si-O- network) locally, the O1 component gets closer to O3 and is expected to merge into a single O3 peak as observed in a full-developed SiO_2 film. On the other hand, the bonding configuration responsible for O2 is not clear but it may be related with N2, that is the $O{=}Si_2$ species with a SNN N atom (the -Si-O-Si-N-Si-configuration), since (i) O2 and N2 components disappears concomitantly after annealing and (ii) O2 is not found in the O_2/Si(100) system.

The Si 2*p* core-level spectra were also investigated after each NO exposure and post annealing, which are partly displayed in Fig. 7. The spectra were taken at a photon energy of 145 eV with an emission angle of 60° in order to enhance the surface sensitivity. All those spectra were subject to the curve fittings for detailed line-shape analyses, whose results are given in the figure for only a limited number of spectra for clarity reasons. From the raw spectra themselves, one can notice the gradual quenching of the component S for the bare Si dimer atoms upon increase of the NO exposure. The quenching of S is accompanied by the growth of broad high E_b features. The intensity of S at 1.5 L is less than one-tenth of that on the clean surface indicating that this dose is already close to the full monolayer coverage.

From this result and the almost linear growth of the N 1*s* intensity in Fig. 1, it is concluded clearly that the NO adsorption is not a self-limiting reaction up to a full monolayer in contrast to the results of an earlier experiment[10] and a recent theoretical study[14] indicating a self-limiting behavior with a maximum coverage only of 0.2 monolayer (ML). Instead the NO adsorption behavior looks very close to the case of O_2 on Si(100).[34,35]

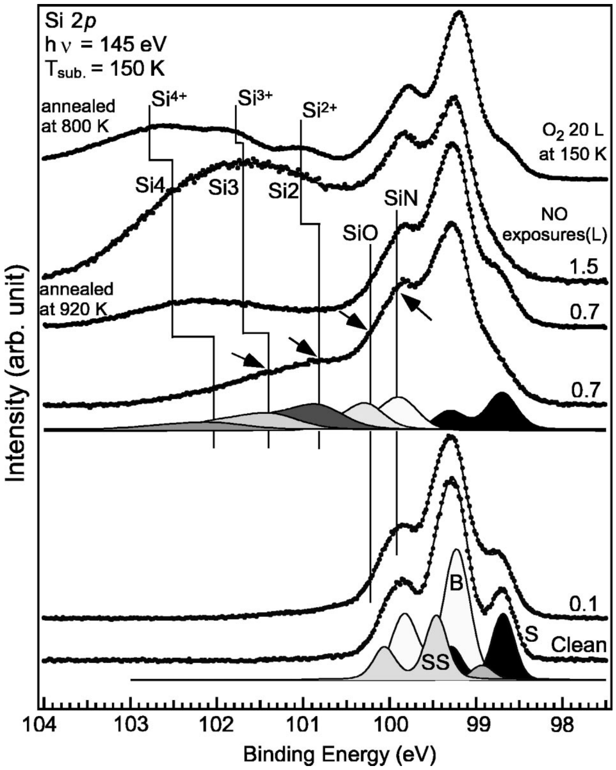

FIG. 7. Si 2*p* core-level spectra for the Si(100) surface with increasing NO exposures at 150 K. The spectra were taken with a photon energy of $h\nu = 145$ eV along the 60°-off direction from the surface normal and were normalized by the maximum peak intensity. The spectrum for the clean Si(100) surface is included for comparison. The decompositions of the spectra for the clean surface and the surface dosed with 0.7 L NO are given. See text for the detailed explanation of the spectral changes and the assignments of the components.

Though being not unambiguous, one may decompose the broad high E_b features into a few Si 2*p* doublets; note the breaking points on the spectral line shape, for example, for 0.7 L (see the arrows in the figure), which suggest the position of different component peaks within the high E_b structure. The spectrum for the 0.7-L dose could successfully be decomposed into five adsorption-induced components for the high E_b structure. These components have core-level shifts from the bulk Si 2*p* component B of 0.7, 1.0, 1.7, 2.5, and 3.2 eV. These components, especially the higher binding components at 2.5 and 3.2 eV, grow and tend to shift to yet higher E_b as the NO coverage increases.

It is well established that each Si-O (Si-N) bond induces a Si-2*p* E_b shift of about 0.9 (0.7) eV in the pure oxide[34,36] (nitride)[18] case. One should also note that these values can depend on the detailed atomic structures, local bonding configurations, and local dielectric responses.[34] Based on these core-level shift references, we assign the observed components at 0.7, 1.0, 1.7, 2.5, and 3.2 eV in Fig. 7 as due to NSi^{1+} (Si atoms bond to one N nearest neighbor), Si^{1+} (Si atoms bond to one O atom), Si atoms with two neighboring N or O atoms, Si atoms with three neighboring N or O at-

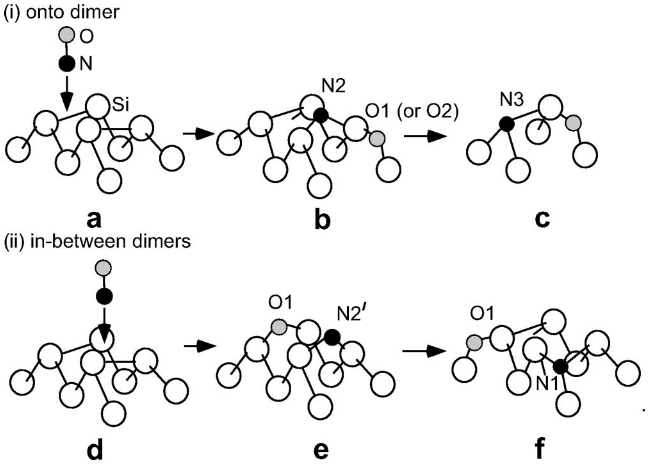

FIG. 8. Schematic illustrations for the possible bonding configurations of N and O atoms on Si(100) after the initial dissociation of NO. Two possible dissociation pathways of NO onto a Si dimer (a)–(c) and in between the dimers (d)–(f) have been considered as discussed in the recent theoretical calculations (Refs. 13 and 14) in mind.

oms, and Si atoms with four neighboring N or O atoms, respectively. The previous Si $2p$ study for the RT NO adsorption on Si(100) observed similar components at 0.8, 1.4, 2.0, and 3.0 eV, which are subject to a larger uncertainty in peak position due to the broader spectral line shape than the present low-temperature and low-coverage measurements. Considering such differences, the present and the previous RT study are qualitatively consistent for the high E_b Si $2p$ features. The main difference is the identification of the separate peaks at 0.7 and 1.0 eV for the Si-O and single Si-N configurations in the present LT work rather than a broad feature with a shift of 0.8 eV at RT.[11,18] In fact the single broad RT feature at 0.8 eV was interpreted as the mixture of the Si-O and Si-N configurations. The growth and the further shifts of high E_b features at high NO doses and high temperatures indicate the agglomeration of oxygen adsorbates as mentioned already for the O 1s spectra.

IV. DISCUSSION

Based on the above results, we discuss some details of the mechanism of NO decomposition on the Si(100)2×1 surface. As mentioned in the introduction, the experimental information on the detailed dissociation reaction path has been very limited. A few theoretical studies, instead, provided microscopic pictures of the reaction pathway. According to Korkin, Demkov, Tanpipat, and Andzelm, the NO dissociation occurs without any significant reaction barrier on a single Si dimer to form a $N{=}Si_2$ species with one SNN O [see Figs. 8(a) and (b)].[13] Kato, Nakasaki, and Uda's more rigorous first-principles calculation agreed that the NO dissociation on a single Si dimer is favorable, which leads to the same final state of $N{=}Si_2$ with one SNN O [Figs. 8(a) and (b)], but they showed that the molecular NO adsorbates is metastable. They further calculated on the reaction paths to the most stable $N{\equiv}Si_3$ [Fig. 8(c)] species. This species substitutes the down-dimer Si atom of the top Si layer and the conversion of $N{=}Si_2$ to $N{\equiv}Si_3$ requires a significant energy barrier of 2.3 eV.[14] However, it was found in the present experiment that the N atoms are mostly in the stable $N{\equiv}Si_3$ (N1 or N3) configuration and no molecular species is observed. This suggests that the reaction barriers, if any, both for NO dissociation and for forming a threefold N species should be very low in contrast to the theoretical prediction.[13,14]

In addition, we observe two intermediate reaction species of twofold N, $N{=}Si_2$, with or without SNN O atoms, which correspond to N2 and N2′, respectively. The former species with a SNN O (N2) can be explained by the NO dissociation involving a single Si dimer as the theory suggested [Figs. 8(b) and (c)].[14] One may consider that such SNN O atoms occur due to secondary reaction events. This explanation is not consistent with the experimental result that the corresponding N2′ species is observed from the very initial adsorption stage, where the secondary reaction would be negligible. In turn, the N2′ species without the SNN O adsorbates may indicate the NO dissociation in-between two adjacent dimers as depicted in Figs. 8(d) and (e). This reaction was considered to be unrealistic in the recent theory of Kato, Nakasaki, and Uda.[14] However, in the present experiment, the population of N2 is twice that of N2′ indicating that both reaction channels, the dissociation involving single and double Si dimers, are active.

On the other hand, the NO exposures above 0.3 L are characterized by the appearance of N3. As assigned above for N3, it can be understood from the increase of the oxygen population in the SNN's of $N{\equiv}Si_3$. It is worthwhile to note that the high-coverage or high-temperature behaviors of oxygen and nitrogen adsorbates are quite different as viewed from the O 1s and N 1s data. That is, while the major O1 component shows the gradual shift and O3 grows noticeably as the coverage or the temperature increases, the E_b of N1 is constant and the growth of N3 is marginal. This suggest that the migration of oxygen to form -O-Si-O- network (the oxygen agglomeration), which would finally evolve into SiO_2, is very active compared to the migration of N adsorbates for the -N-Si-N- or the N-Si-O network formation. The formation of N-Si-N network for stoichiometric Si_3N_4 occurs only above a very high temperature of 1100 K or so.[11]

V. CONCLUSION

We have performed a systematic high-resolution core-level photoemission spectroscopy study for the NO adsorption on the Si(100) surface at 150 K in order to elucidate the adsorption and the initial reaction mechanism of NO molecules on Si(100). From the N 1s photoemission spectra, two metastable adsorption species with N 1s binding energies of 396.4 (N2) and 395.8 (N2′) eV are observed together with the stable $N{\equiv}Si_3$ species (N1) at 397.4 eV. These two metastable species are assigned to the twofold coordinated $N{=}Si_2$ species with (N2) and without (N2′) the second nearest neighbor oxygen adsorbates in good agreement with the theoretical calculations for N 1s binding energies. The O 1s spectra also exhibit multiple oxygen bonding configurations of a very marginal metastable component at 530.8 eV (O2) and two stable species at 531.5–531.8 eV (O1) and 532.4 (O3) eV. While the origin of the metastable component O2 is not clear, the major O1 and O3 components are related to

$O{=}Si_2$ species and a similar species but with SNN oxygens, respectively. The latter species is thought to be similar to stoichiometric SiO_2 and the former species corresponds to the surface adsorbates in Si rich environment. In clear contrast to the N case, the major O1 peak shows systematic shift toward high binding energy upon the increase of coverage and temperature. This is explained by the active agglomeration of oxygen adsorbates to form the -O-Si-O- network even at a very low temperature. In the line-shape analyses of the Si 2p spectra, we could assign the Si 2p components for the Si-N and Si-O bonds in the initial adsorption studies with a core-level shifts of 0.7 and 1.0 eV, respectively, along with other highly coordinated components at 1.7, 2.5, and 3.2 eV. From these results (mainly from the N 1s result), we conclude that the NO adsorption is completely dissociative even at 150 K but the stable $N{\equiv}Si_3$ species is formed through metastable adsorption configurations of $N{=}Si_2$. The two different $N{=}Si_2$ metastable species observed is interpreted to indicate two different reaction channels; the dissociation of a NO molecule on top of a Si dimer and that between two neighboring Si dimers, which results in the $N{=}Si_2$ adsorbate configuration with and without a SNN oxygen atom, respectively.

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