

Spontaneous N Incorporation onto a Si(100) Surface

J. W. Kim,¹ H. W. Yeom,^{1,*} K. J. Kong,² B. D. Yu,³ D. Y. Ahn,² Y. D. Chung,¹ C. N. Whang,¹ H. Yi,⁴ Y. H. Ha,⁵ and D. W. Moon⁵

¹*Institute of Physics and Applied Physics, Yonsei University, Seoul 120-749, Korea*

²*IQUIPS, University of Seoul, Seoul 130-743, Korea*

³*Department of Physics, University of Seoul, Seoul 130-743, Korea*

⁴*Supercomputing Center, KISTI, P.O. Box 122, Yusong, Taejeon 305-600, Korea*

⁵*Nano Surface Group, Korea Research Institute of Standards and Science, Taejeon 305-606, Korea*

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Initial nitridation of the Si(100) surface is investigated using photoemission, ion-scattering and *ab initio* calculations. After dissociation of NO or NH₃, nitrogen atoms are found to spontaneously form a stable, highly coordinated N≡Si₃ species even at room temperature. The majority of the N species is incorporated into the subsurface Si layers occupying an interstitial site, whose atomic structure and unique bonding mechanism is clarified through *ab initio* calculations. This unusual adsorption behavior elucidates the atomistic mechanism of initial silicon nitride formation on the surface and has important implication on the N-rich layer formation at the SiO_xN_y/Si interface.

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Ultrathin films of silicon nitride (SiN_x) or oxynitride (SiO_xN_y) have been extensively studied since they play a key role in the present and near future metal-oxide-semiconductor devices [1]. In growth of such dielectric films with nanoscale thickness, the microscopic understanding of the interface-formation and the initial-growth mechanism is crucial. For example, in the SiO_xN_y/Si system, N atoms accumulated at the interface are thought to be responsible for low leakage current and high electrical reliability [1–3]. However, the present understanding in atomic scale of the SiO_xN_y/Si interfacial structure and of the nitridation structures and processes on Si surfaces is very much limited.

Typically, nitridation of the silicon surfaces and interfaces employs thermal reaction of N-containing gas molecules and the NO/Si and NH₃/Si systems have been extensively studied. Previous studies showed that NO molecules dissociate easily on Si(100) even at a very low temperature of 20 K [4–6]. In contrast, the adsorption of NH₃ on Si(100) produces Si-NH₂ and Si-H at room temperature (RT) and an annealing to 600–800 K is needed for further N-H bond cracking [7,8]. In spite of the partial success of such studies for the very early stage of the reaction, *the incorporation structure and process* of the dissociated N atoms into Si surface layers to form SiN_x alloy is not at all clear in atomic scale. Such incorporation structure and process is the crucial link between the surface chemical reaction of molecules and the initial film and interface formation.

In this work, through combined experimental and theoretical investigations, we clearly show that N adsorption occurs extraordinarily; not through surface adsorption but mainly through *spontaneous interstitial incorporation below* the second Si layer, where the N atoms are

stabilized through a noble bonding mechanism involving surface dangling bonds. Such characteristic N incorporation may also explain the mechanism of the SiO_xN_y/Si(100) interface formation with N-rich Si layers. This result suggests a possibility of new *low-temperature* process design for ultrathin oxynitride/nitride dielectric layers.

NO or NH₃ gas was introduced onto the clean Si(100)-(2 × 1) surface at RT. High-resolution photoemission spectroscopy (PES) was performed on the soft x-ray undulator beam line (8A1) at Pohang Accelerator Laboratory in Korea, in order to probe the chemical states of N atoms [9,10]. In medium-energy-ion-scattering (MEIS) measurements for structural studies, a H⁺ beam of 101.3-keV kinetic energy was incident from [11 $\bar{1}$] direction and was analyzed around [111]. To simulate the incorporation of N, we used a repeating slab structure consisting of nine Si layers, whose bottom layer was terminated by H atoms, within the first-principle density functional scheme. A c(4 × 4) surface unit cell was used and a summation over a uniform mesh of 4 k points was done for the k-space integration.

We first approach the issue of the structure of dissociated N on Si(100) from a chemical point of view. Figure 1(a) shows a reference N 1s photoemission spectra taken from a standard SiO_xN_y/Si(100) film grown by rapid thermal annealing with a thickness of 1.4 nm. The spectrum consists of two components with similar intensity. Through recent theoretical and experimental studies, it has been well established that these two components commonly correspond to the N species bonded with three Si nearest neighbors (NN's) and the binding energy difference between them is due mainly to the second NN effect [3,11–13]. That is, the N1 component represents the

N atoms in the Si-rich interfacial region with mostly Si second NN's and N2 those within the SiO₂ matrix with oxygen second NN's. As indicated in the figure the direct N-O bonding would induce a binding energy shift as large as 1.5 eV from N1 [12,13].

In comparison, Fig. 1(b) shows the N 1s spectrum after the RT dissociation of NO on Si(100) [4–6,10]. The spectrum also consists of two components at very similar binding energies as N1 and N2 for SiO_xN_y/Si(100). The major component N1 is stable up to 1100 K, above which the stoichiometric Si₃N₄ islands are formed. In contrast, the adsorption of NH₃ at RT yields only single and well-defined component due to the H₂=N-Si species (data not shown). An annealing to 500–700 K leads to further dissociation of the H₂=N-Si species. Then, one can observe three different N 1s components corresponding to H₂=N-Si, H-N=Si₂ and N≡Si₃ [Fig. 1(d)]. The binding energies of these components agree well with a recent *ab initio* theoretical prediction [14]. In order to fully dissociate H₂=N-Si and H-N=Si₂, an annealing to 800–1000 K was required. The resulting spectrum [Fig. 1(e)] is essentially the same as that for the NO dissociation, especially for the major N1 component.

While the origin of the minor component N2 can be different for SiO_xN_y/Si(100), NO/Si(100), and

NH₃/Si(100) systems, we focus on the dominant and stable N species represented by N1, which is common to all three systems. From the binding energy, it is clear that N1 represents the N≡Si₃ species. That is, *N atoms dissociated from the gas molecules form readily and spontaneously a highly coordinated N≡Si₃ species with three Si NN's* even at RT. Such bonding configuration is very unusual as a surface adsorption species since the possible surface bonding geometries are chemically N-Si or N=Si₂ [15,16]. While no experimental investigation is available on the detailed atomic structure of N adsorbates, most of the recent calculations introduced the N=Si₂ configuration with N inserted into the Si-Si surface dimer bond as the stable configuration [15,16]. This cannot explain the major N species observed presently. A recent theoretical study, however, considered two different N≡Si₃ adsorption configurations, where N is inserted between the first and the second Si layers (taking two back-bonds of a Si-dimer) or N replaces a Si-dimer atom (the down dimer atom) [17]. Other highly coordinated N≡Si₃ configurations are also possible when N is incorporated in deeper subsurface layers.

Thus, in order to clarify the structure of the N≡Si₃ species, the depth distribution of N atoms is crucial. This task was done through MEIS measurements, where the direct scattering of N adsorbates and the energetic H⁺ beams are probed. Figure 2 shows a MEIS spectrum of the NO/Si(100) surface prepared *in situ* at RT as that for Fig. 1(b), where the H⁺ signals scattered by Si, O, and N atoms are distinct. The energy spectrum, representing directly the depth profile, was fitted by a well-established kinetic simulation for thin crystalline Si layers with varying N and O densities in each layer [18]. Before and after the NO dose, the spectral width of the Si peak remains nearly the same, which suggests only marginal disruption of the Si lattice by NO adsorption. Thus, in the simulations, the change of Si crystalline structure was not included. In the inset, the relative distribution of O and N atoms is given, which is determined by optimizing the fits between such simulations and the experimental data [18]. The error in the relative distribution could be rigorously estimated to be around 10% due mainly to the rather poor signal to noise ratio for O and N.

This result clearly shows that O atoms reside mostly on the surface or between the first and second Si layers. The latter and major species obviously corresponds to the O atoms inserted into the back-bonds of Si surface dimers, which has been well established for RT adsorption [19]. In sharp contrast, N atoms are mostly populated (64%) *at the subsurface sites between the second and the fourth layers*. This depth profile was qualitatively confirmed by the angle-dependence measurements of N 1s photoemission intensity (data now shown here). Similar N 1s measurements also indicate that the depth distribution of the N1 species dissociated from NH₃ [for the surfaces of Figs. 1(d) and 1(e)] is similar to the NO case. It is thus

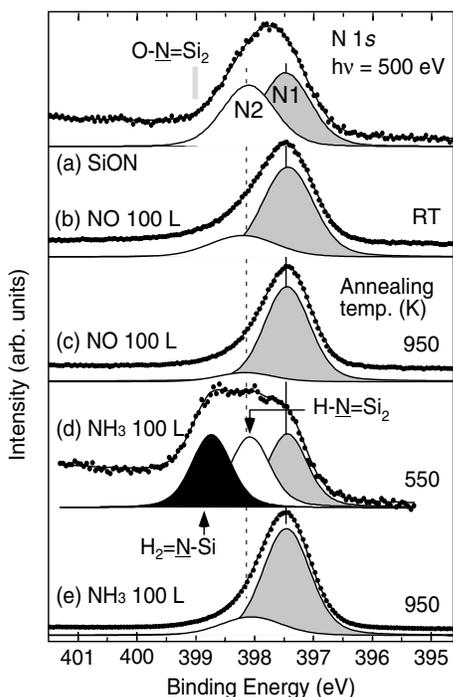


FIG. 1. N 1s photoemission spectra for (a) a standard oxynitride thin film (1.4 nm thick), (b) a Si(100) surface dosed with NO (100 L) at RT, (c) the surface as in (b) after an annealing at 950 K, (d) a NH₃-dosed Si(100) surface (100 L) annealed at (d) 550 K and at (e) 950 K. The spectra are taken at a photon energy ($h\nu$) of 500 eV. The reported energy for an O—N=Si₂ species is marked with a gray bar.

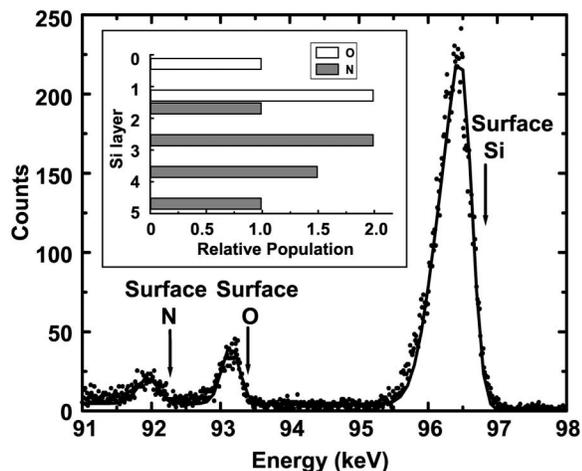


FIG. 2. Medium-energy ion scattering spectrum (dots) of a Si(100) surface dosed with NO (100 L) at RT. The best-fit simulation is shown by the solid curve and the scattering energies of the Si, N, and O surface atoms are indicated by arrows. The inset shows the relative population of N and O atoms between different Si layers determined through the simulations.

concluded that *the majority of N atoms are spontaneously incorporated into the subsurface layers to form an $N\equiv Si_3$ species.*

In order to determine the atomistic structure of the incorporated N atoms we have performed *ab initio* total-energy calculations. The Si(100) surface was simulated by using a large $c(4 \times 4)$ unit cell with a single N adsorbate (1/8 ML), as shown in Fig. 3(a). At first, possible surface adsorption sites were considered, such as those marked in Fig. 3(a). The site on top of a Si-dimer (D) is found to be most stable, lower in total-energy than other surface sites by more than 0.3 eV per N atom [20]. Within this site the underlying Si-dimer bond is broken and the N adsorbate bridges the Si-dimer atoms to form an $N=Si_2$ configuration. Previous theoretical calculations based on the cluster method also suggested site D [15,16] or TD [17] as the most stable site.

Note that the $N=Si_2$ configuration of site D is not compatible with the experimental results indicating the $N\equiv Si_3$ species as the major N species. Subsequently, we considered N atoms in the subsurface-interstitial or substitutional sites. The interstitial configurations were generated by initially putting the N atom at various subsurface sites down to the sixth surface layer. The resulting relative energies with the variation of the depth are shown in Fig. 4 for the fully relaxed geometries. The N atom is favorably incorporated into an interstitial site (HC) around the third layer, while other subsurface-interstitial sites are energetically unfavorable [HC1, HC2, and HC3 in Fig. 4]. The fully relaxed geometry of the most stable configuration HC is shown in Fig. 3(b). The N atom is bonded with the Si atoms in the second, third and fourth layers with almost equal bond lengths

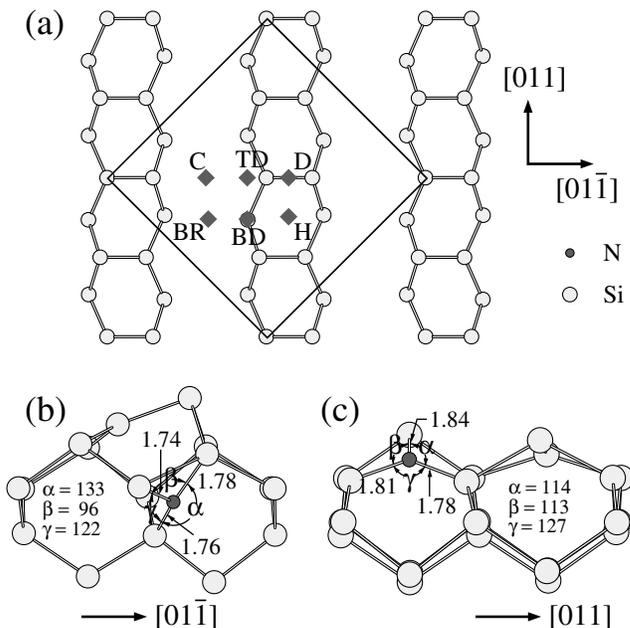


FIG. 3. (a) Top view of a Si(100) surface with a $c(4 \times 4)$ unit cell (the large square) with various nitrogen adsorption sites considered. The side views of the two stable $N\equiv Si_3$ configurations: (b) the HC configuration near the third-layer interstitial site and (c) the N_{sub} configuration with the down Si-dimer atom substituted by N. In (b) and (c), the bond lengths and angles are given in Å and degree, respectively.

(1.75 Å), forming an $N\equiv Si_3$ species. In contrast to the other interstitial sites, the Si atom in the third layer of the HC site is *newly bonded with the two Si-dimer atoms through the otherwise dangling bond electrons* at the expense of one bond towards the fourth layer. This unique local bonding configuration stabilizes the HC structure. Thus, in terms of both the energetics and the consistency with experiments, we conclude that HC site in an $N\equiv Si_3$ configuration is the most plausible configuration for the interstitial incorporation.

Other than the interstitial incorporation, the substitutional sites were also considered. However, the substitution of Si atoms in the second or deeper layers has a significant energy cost of more than 1.2 eV because of their fourfold-coordinated nature. Moreover, these sites are not consistent with the PES result showing an $N\equiv Si_3$ configuration. However, the substitution of the down Si-dimer atom on the surface [denoted as N_{sub} in Fig. 3(c)] is energetically as favorable as the HC site, 0.49 eV lower in energy than HC [21], and forms a $N\equiv Si_3$ configuration in accord with the experiments. Within this structure, the 3 N-Si bonds have an equal bond length of ~ 1.8 Å in a rather ideal planar sp^2 bonding.

The N 1s core-level shifts calculated for the HC and the N_{sub} structures are almost the same and are in good agreement with the experiment. This makes it impossible to distinguish those two sites spectroscopically. However, the MEIS result indicates that both of these species are

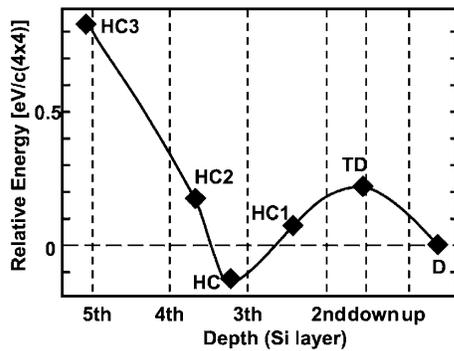


FIG. 4. Comparison of the energies calculated for various N configurations (TD and D for the surface adsorption and HC, HC1, HC2, HC3 for the subsurface interstitial incorporation) in terms of their depth from the surface Si layer (the first layer with “up” and “down” dimer atoms).

present; 18% of the total N atoms are located between the first and the second layers in agreement with the N_{sub} structure while the subsurface incorporation (the HC site) is the major species. This interpretation explains the experimental observations consistently although the detailed population balance between different sites is beyond the scope of the present work. Qualitatively speaking, the different N incorporation sites would be formed through different kinetic processes; possibly through the penetration by atomic hopping for the HC site [22] or the concerted exchange processes with complex breaking and rebonding of chemical bonds for the N_{sub} case [23].

As experimentally observed, the SiN_x (the $\text{N}\equiv\text{Si}_3$ species) structures are very stable once formed by the dissociation of NO or NH_3 . Even after oxygen (or hydrogen) desorption by heating up to 1100 K and reoxidizing the surface by O_2 doses at 900 K, the N 1s photoemission peak was intact. The resulting interfacial structure is essentially identical to the conventional ultrathin $\text{SiO}_x\text{N}_y/\text{Si}$ systems, as shown in Fig. 1, as far as the photoemission spectra of O 1s, N 1s, and Si 2p can tell. Thus, it is plausible to conclude that the spontaneous N incorporation into the Si surface during the very initial reaction stage is the origin of the N-rich layer formation at the $\text{SiO}_x\text{N}_y/\text{Si}$ interface. The present N incorporation is, however, a very low temperature process in clear contrast to the high-temperature annealing adopted conventionally in the industry. This result thus suggests a possibility of new process design for controlling N-rich layers at the oxynitride interface through low temperature gas decomposition avoiding the harmful side reactions such as etching during the conventional high-temperature procedure.

The picture for the film and interface formation deduced here is that the initial oxynitride or nitride growth follows a precursory subsurface alloying. The concept of precursory subsurface alloying may be applicable to other

thin film growth systems, for example, to the complicated initial growth of SiC on Si(100), where the C incorporation happens before SiC nucleation [24].

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*To whom all correspondence should be addressed.

Email address: yeom@phya.yonsei.ac.kr

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