Al(111) nitridation below 473 K induced by supersonic N$_2$ molecular beam as observed by synchrotron radiation photoemission spectroscopy

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Abstract. The Al(111) surface has been directly nitrided using a supersonic N$_2$ molecular beam at a sample temperature region below 473 K. The translational kinetic energy threshold for nitridation is 1.8 eV. The nitrogen uptake curve obtained at a translational energy of 2.0 eV showed a linear dependence on dose, indicating the formation of a non-protective layer. Nitrogen diffusion into the bulk has been confirmed by a depth profile analysis using angle-resolved photoemission spectroscopy in conjunction with the maximum entropy method. The Al-2p photoemission spectra showed shoulder structures only slightly shifted to higher binding energies, suggesting that sub-nitride components are predominant in the nitride layer. The N-1s photoemission spectra confirm that the three-coordinated nitrogen (N$^3$) dominates among the four chemical state components (N$^n$; n=1-4).

1. Introduction

We have developed a supersonic molecular beam (SSMB) apparatus equipped with capabilities for photoemission spectroscopy (PES) at the high brilliance and high energy-resolution soft x-ray synchrotron radiation (SR) beamline BL23SU in the SPring-8 facilities to study surface chemical reaction dynamics [1]. Real-time photoemission spectroscopic measurements during SSMB irradiation are possible using the apparatus. Using a high temperature nozzle and seeded molecular beam techniques, translational energies greater than 1 eV can be achieved for beams of O$_2$ (2.3 eV) and N$_2$ (2.0 eV). The use of such high speed molecular beams has contributed to the elucidation of new schemes for many chemical reactions on silicon and metal surfaces [2-7].

Although there have been a few studies previously reported on the surface chemical oxidation reactions of aluminum single crystals, nitridation does not take place upon exposure to N$_2$ gas near room temperature. We have conducted a study on direct nitridation of the Al(111) surface by irradiation of inert N$_2$ SSMB from the view point of pure surface science and also from an applications point of view. An ultra-thin film of AlN can be grown by various methods including plasma ion immersion implantation [8], plasma-assisted gas-source molecular beam epitaxy [9] and metal-organic vapor phase epitaxy (MOVPE) [10]. In order to form very thin films on the nanometer scale, the MOVPE method using tri-methyl aluminum and ammonia gases has been reported as a typical method.
for AlN layer formation on SiC(0001) surfaces [10]. This method, however, requires high temperatures and careful gas handling.

We have conducted direct nitridation of the Al(111) surface by the action of the translational energy of an inert N$_2$ molecular beam at a surface temperature lower than 473 K. Although aluminum metal does not react with N$_2$ gas under ambient conditions in this temperature region, and no N-1s photoemission peak could be observed even using high brilliance synchrotron radiation for translational energies lower than 1.6 eV, nitridation of Al(111) was successfully observed using an N$_2$ SSMB with a translational energy higher than 1.8 eV. In this report, we show evidence for Al(111) nitridation by inert N$_2$ SSMB at 473 K and discuss the mechanisms of the nitridation on the basis of photoemission spectroscopy with high brilliance and high energy-resolution synchrotron radiation.

2. Experimental

All of the experiments described here were conducted at the surface chemistry experimental station (SUREAC2000) of BL23SU in the SPring-8 facilities. The SUREAC2000 apparatus was designed to promote applications of photoemission spectroscopy with synchrotron radiation and SSMB techniques in surface chemical reaction dynamics research. A detailed description of the experimental station can be found in previous reports [1], and only a brief description is given here. The surface reaction analysis chamber is pumped by two turbo-molecular pumps in tandem fashion in conjunction with a titanium sublimation pump so that a base pressure of 7×10$^{-9}$ Pa is obtained. When liquid nitrogen is fed into the manipulator and the chamber trap, a base pressure of 5×10$^{-9}$ Pa can be achieved. The chamber is equipped with a concentric hemispherical electron energy analyzer (Omicron EA125-5MCD).

The N$_2$ SSMB was continuously generated by the adiabatic expansion of a mixture of N$_2$, He and Ar. The nozzle, made of pyrolytic boron nitride, can be heated to a temperature of about 1400 K by using a specially-made heater. The translational energy is varied by varying the gas mixing ratio, keeping the nozzle temperature at 1400 K. The upper limit of the translational energy for N$_2$ molecules is 2.0 eV, as calculated on the basis of the enthalpy conservation law. Some fraction of N$_2$ molecules must be vibrationally excited since the nozzle temperature is 1400 K. The vibrational distribution is assumed to be constant irrespective of translational energy due to the constant nozzle temperature. Under typical operating conditions, the N$_2$ beam flux density is estimated to be about 2×10$^{14}$ molecules·cm$^{-2}$·s$^{-1}$ on the sample surface. According to rarefied gas dynamics studies, a velocity width ratio $\Delta v/v_p$ is expressed as 1.65$/S$, where $v_p$ is a peak velocity and $S$ is a velocity ratio. $S$ is expressed as $M(\gamma/2)^{1/2}$, where $\gamma$ is a specific heat ratio and $M$ is the Mach number. The $\gamma$ value of 2-atomic molecule is 7/5. Therefore, an energy width ratio $\Delta E/E$ is expressed as $(\Delta v/v_p)^2 + (\Delta v/v_p) \cdot 2v_L/v_p$, where $v_L$ is a lower side velocity in the half maximum of velocity. The $\Delta E/E$ can be approximated as $(\Delta v/v_p)^2 + 2(\Delta v/v_p)$ because the factor of $v_L/v_p$ is nearly one. For example, when $M$ is 30 and $\gamma$ is 7/5, the $\Delta E/E$ is estimated to be 0.13. This estimation indicates that an energy width $\Delta E$ is 13% of a peak energy $E$. As we used N$_2$ molecular beam of 2.0 eV, the energy width (FWHM) is estimated to be 0.26 eV. Actually, as mentioned in the section of 3.1.N$_2$ translational energy threshold for nitridation, a small amount of N-1s photoemission peak was observed in the N$_2$ energy setting of 1.8 eV although no signal was detected in the 1.6 eV setting. A clear nitrogen uptake curve was obtained in the 2.0 eV setting. These facts suggest that the FWHM of N$_2$ molecular beam we used is nearly 0.2 eV as estimated above.

The sample cleaning method is as follows. Firstly, the sample was ultrasonically cleaned in acetone for 5 min, ethanol for a further 5 min, rinsed in de-ionized water, dried with compressed pure nitrogen gas on a filter paper, and placed in the load-lock chamber of the SUREAC2000 apparatus. In order to remove the native oxide layer on the Al(111) surface, the surface was irradiated for 15 min with an Ar$^+$ ion beam using an acceleration energy of 1 keV, and then thermally annealed up to 773 K in the surface cleaning chamber. The sputtering and anneal cycle was repeated several times. A low energy electron diffraction pattern of 1×1 was observed in the cleaning chamber.
After confirming no detection of C-1s, O-1s, and other contaminant photoemission peaks by the SR-PES, the N\textsubscript{2} SSMB with a fixed translational energy was irradiated on the clean surface. The incident angle of the molecular beam was -10 degrees with respect to the surface normal. The photoelectron detection was +30 degrees. The SR photon energy was selected to be 686.8 eV, and the total spectral resolution was about 0.24 eV. After irradiation with the N\textsubscript{2} beam for several seconds or minutes, photoemission spectra of the Al-2p, N-1s, and O-1s core levels were recorded. This irradiation and measurement cycle was repeated several tens of times. The time evolution, that is, the N\textsubscript{2} dose dependence, of the photoemission peaks were obtained with this successive N\textsubscript{2} beam irradiation and photoemission measurements. The photoelectron detection depth is estimated to be about 3.9 nm (Al-2p), 2.7 nm (N-1s), and 2.0 nm (O-1s) [11], assuming that photoelectrons emitted from depths of up to around three times the inelastic mean free path are detectable. The surface temperature was kept at 300 K, 373 K, or 473 K following flash annealing at 773 K.

3. Results and discussion

3.1. N\textsubscript{2} translational energy threshold for nitridation

An N-1s photoemission peak was not observed for translational energies below 1.6 eV at a surface temperature of 473 K, even following the N\textsubscript{2} dose of 1.12\times10\textsuperscript{18} molecules \cdot cm\textsuperscript{-2}. This dose corresponds to 1836 monolayer (ML) of N atoms when the atomic density of the Al(111) plane in the bulk (1.22\times10\textsuperscript{15} atoms \cdot cm\textsuperscript{-2}) is defined to be 1 ML. A small N-1s peak was detected following the dose of 1.28\times10\textsuperscript{18} molecules \cdot cm\textsuperscript{-2} with a translational energy of 1.8 eV. The N\textsubscript{2} dose of 1.28\times10\textsuperscript{18} molecules \cdot cm\textsuperscript{-2} is corresponding to 2098 ML of N atoms. If the detection limit of N atoms on the surface is assumed to be 0.1 ML, the reaction probability is estimated to be 5\times10\textsuperscript{-5}. At 2.0 eV, the N-1s peak intensity increased with increasing N\textsubscript{2} dose. Figure 1 shows the uptake of the N-1s SR-PES spectra recorded at various doses between 0 and 1.2\times10\textsuperscript{19} molecules \cdot cm\textsuperscript{-2} with the incident energy of 2.0 eV. The energy scales are calibrated assuming that the binding energy of Al-2p\textsubscript{3/2} component is 72.5 eV [12] for the clean surface. Since very slight nitridation could be observed for a kinetic energy of 1.8 eV, we concluded that the translational energy threshold for the direct nitridation of Al(111) surface by N\textsubscript{2} molecular beams is 1.8 eV.

\[\text{Figure 1.} \text{ N-1s SR-PES spectra recorded during N}_2 \text{ beam irradiation from 0 to } 1.2\times10^{19} \text{ molecules } \cdot \text{cm}^{-2} \text{ with the incident energy of 2.0 eV.}\]

3.2. Chemical bonding states of aluminum

The N\textsubscript{2} dose dependence of the Al-2p photoemission peak profile is shown in figure 2. The total energy resolution is about 0.24 eV, enough to resolve the spin-orbit splitting (0.4 eV) of the Al-2p\textsubscript{3/2} and Al-2p\textsubscript{1/2} peaks. The two main peaks are due to contributions from the bulk aluminum under the nitride layer. The Al-2p photoemission peaks show a well-known asymmetric profile tailing to the
higher binding energy side due to the induction of electron-hole pairs during photoelectron emission [11]. At increasing N₂ doses a shoulder structure appears on the high binding energy side at around 73 eV to 74.5 eV, overlapping with the high binding energy side tail. This shoulder is attributed to chemical shifts of the Al-2p core levels due to bonding with mainly nitrogen and partly oxygen, as discussed below.

It has been reported [13] that an AlN layer can be formed on an Si(111) substrate by applying the plasma-source molecular beam epitaxy technique. The binding energy values for the Al-N, Al-O (alumina domains and grain boundaries), and Al-O (surface only) bonds were reported to be 73.5 eV, 74.7 eV, and 76.7 eV, respectively. In the spectra recorded here, therefore, we could expect to see satellite peaks or shoulders for these bonds in the region from 73.5 eV to 76.7 eV. In particular, any uptake was not observed in the binding energy region larger than 74.5 eV. Therefore, the shoulder structure shown in the region smaller than 74.5 eV in figure 2 is almost corresponding to Al-N bonds. We thus conclude that Al-N nitride is probably not a complete crystal, but also consists of sub-nitrides in the nitride layer observed here due to the broad shoulder structure.

3.3. Chemical bonding states of nitrogen

The N-1s photoemission peak recorded following a dose of 1.05×10¹⁹ molecules·cm⁻² is shown in figure 3. For both the zinc-blende and wurtzite crystal structures the maximum coordination number of both nitrogen atoms and aluminum atoms is four. The N-1s peak can thus be deconvoluted into four components, corresponding to n-coordinated sub-nitride (Nⁿ n:1-3) and fully-nitrided AlN local structure (N⁴⁻). The minus is due to low electron affinity of nitrogen (-0.07 eV) than that of aluminum (0.45 eV) [12]. Good fits to the data could be obtained using four pure Gaussian line profiles and a linear background. The use of a pure Gaussian line profile is reasonable since the contribution to total energy resolution from the analyzer (0.22 eV) dominates that of the incident synchrotron radiation (about 0.1 eV). As shown in figure 3, the N³⁻ component is the most intense among the four components. This implies that the aluminum surface is not fully nitrided, the surface layers are dominated by sub-nitrides, and that AlN is barely present. This is qualitatively consistent with the observation of broad chemical shift in the Al-2p spectra (figure 2). Experimental evidence supporting the formation of sub-nitrides is also seen in the early stages of nitridation, where the N²⁻ component is dominant, as shown in figure 4(a). It can be concluded that dissociatively-adsorbed nitrogen atoms make chemical bonds between the topmost aluminum atoms to form a sub-nitride state of N²⁻. As nitridation progresses, the N³⁻ component becomes dominant, as seen in figures 3 and 4(b).

![Figure 3](image-url)

**Figure 3.** Four-component fit to N-1s SR-PES spectra recorded following a dose of 1.05×10¹⁹ N₂ molecules·cm⁻². The solid line among observed points shows the overall fit, the four lines incide the individual components in (a) and (b). (b) shows in detail the N⁴⁻ and N³⁻ components.

![Figure 4](image-url)

**Figure 4.** Comparison between fits to N-1s SR-PES spectra recorded in the early nitridation stages after doses of (a) 7.0×10¹⁶ and (b) 6.5×10¹⁷ molecules·cm⁻².
3.4. Uptake curve of nitrogen adsorption

As can be seen in figure 4, the N-1s peak profile changes with increasing N$_2$ dose. In order to make clear the evolution of the chemical bonding states of the adsorbed nitrogen, the intensity variations for the deconvoluted components of the N-1s spectra are shown in figure 5 as a function of N$_2$ dose. For doses less than $10^{17}$ molecules·cm$^{-2}$ (164 ML of N atoms), the N$^{2-}$ component dominates over the N$^{3-}$ and N$^{1-}$ components, and the N$^{4-}$ component is negligibly small. After a dose of about $10^{17}$ molecules·cm$^{-2}$, the N$^{2-}$ component begins to dominate. The N$^{2-}$ component, however, is still larger than the N$^{1-}$ and N$^{4-}$ components. After a dose of about $10^{18}$ molecules·cm$^{-2}$ (1639 ML of N atoms), the N$^{4-}$ component appears, reaching the same magnitude as the N$^{2-}$ component.

Nitrogen uptake does not saturate even after a dose of $10^{19}$ molecules·cm$^{-2}$ (16393 ML of N atoms), and linear characteristics of uptake curves are revealed not only for the total N-1s intensity but also for all components. Such linear uptakes generally indicate that the adsorbed layer does not act as a protective layer inhibiting subsequent N$_2$ adsorption. In other words, the adsorption of an N$_2$ molecule at a particular site does not protect the atomically local area from further adsorption, and a nitrided local area can again be nitried by energetic N$_2$ incidence. As seen in figure 5, surface nitridation proceeds with a constant reaction rate regardless of nitrogen coverage. This finding suggests that a proportion of nitrogen atoms adsorbed on the Al(111) surface migrate into the bulk, with the result that part of the surface remains as a clean Al(111) structure, where further nitridation can take place. The LEED patterns observed after nitridation were not clear suggesting no periodic crystal structure. In order to confirm these facts, depth-profiles of the constituent elements and nitrogen bonding states were generated by applying the maximum entropy method to angle-resolved photoemission measurements.

3.5. Depth profiling

The depth-specific information present in angular-resolved PES spectra can be extracted using the maximum entropy method [14], where the sample structure is modeled as a finite number of layers containing a number of different elements or the chemical states of those elements. By recording O-1s, N-1s, and Al-2p PES spectra at a range of different takeoff angles, we have generated depth profiles of elemental N, O, and Al, and also of the four components fitted to the N-1s spectra for the AlN thin-film sample produced following exposure of the clean Al(111) surface to $1.2\times10^{19}$ N$_2$ molecules·cm$^{-2}$.

After correcting for the differing photoionisation cross sections [15], the sum of all six components was normalised to 1.0 at each angle. Figure 6(a) shows the atomic concentrations of Al, O, and N as a function of depth. Angular dependencies produced a depth profile of nitrogen concentration which extends to a depth of about 1.5 nm, and the presence of an oxide sub-layer with about 1 nm thickness was suggested. The O-1s photoemission peak was also observed during the N$_2$ molecular beam irradiation. However the N$_2$ beam was confirmed free of oxygen atoms and oxygen-containing molecules using the quadrupole mass analyzer, so it must be assumed that oxygen-containing residual gas molecules (for example H$_2$O) are adsorbed onto the nitride surface. We speculated that oxygen atoms initially-adsorbed on the surface migrated into the bulk to be trapped in the defect sites of the interface region. Incorporated oxygen in the bulk is about 1/3 comparing to nitrogen. The position of oxygen atoms is restricted near the interface so that the depth profile of oxygen is completely different.
to that of nitrogen. Although oxynitrides may exist near the interface, nitride layers are clearly formed near the surface. The profiles for the four nitrogen components are shown in figure 6(b). The fit suggests that while the N$_3^-$ component is dominant throughout the AlN film, N$_2^-$ and N$_4^-$ are only present close to the surface, and a sub-layer is suggested for N$_1^-$ in the interface.

4. Conclusions
Although the Al(111) surface does not react with thermal N$_2$ gas, we have shown that it can be directly nitrided using an N$_2$ SSMB at a translational energy larger than 1.8 eV at a sample temperature below 473 K. The nitrogen uptake curve was confirmed to be almost linear with respect to increasing N$_2$ dose, indicating that the nitridation rate is constant regardless of nitrogen coverage on the surface, and furthermore that a protective layer is not formed on the topmost nitride surface. In order to make clear the reason behind this linear uptake, depth-profiles of the constituent elements and chemical bonding states of nitrogen were calculated from angle-resolved photoemission spectra using the maximum entropy method. The Al-2p photoemission spectra showed only small shoulder structures, suggesting that sub-nitride components are predominant in the nitride layer. The N-1s photoemission spectra confirm that the three-coordinated nitrogen (N$_3^-$) dominates among the four chemical state components (N$_n^-$: n=1-4). We do not mention about penetration of N$_2$ molecules into the bulk through the Al(111) surface even if the incident energy of N$_2$ molecule is 2.0 eV. We speculate nitrogen atoms generated on the Al(111) surface by activated dissociative adsorption of high speed N$_2$ molecules may diffuse into the bulk due to the thermal energy of substrate (473 K). Actually, apparent substrate temperature dependence of nitrogen uptake curve has been observed in our recent experiments. Furthermore, incubation time for nitrogen uptake was also observed when the substrate was at a room temperature. These experimental facts suggest that the nitridation of Al(111) surface by high speed N$_2$ molecules cannot explained by the penetration of N$_2$ molecule into the bulk. Consequently, nitrogen diffusion into the bulk and the formation of sub-nitride layers was verified in our high energy resolution photoemission measurements. The study for clarifying the reasons of incubation time and temperature dependence is now on progress.

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