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# Dynamic investigations of (0001) Al<sub>2</sub>O<sub>3</sub> surfaces treated with a nitrogen plasma

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We investigated the kinetics of AlN and AlNO phase formation on a sapphire substrate at different nitridation temperatures in an ultra-high vacuum. Dynamic reflection high-energy diffraction observations revealed that the growth rate of AlN decreased abruptly as the nitridation temperature increased, due mainly to the low sticking coefficient of nitrogen atoms. In addition, the formation of AlNO was enhanced by the oxidation of AlN at a high substrate temperature, which we discuss in terms of the protrusion density based on atomic force microscopy results. X-ray photoelectron spectroscopy spectra support our conclusions and indicate the importance of the metallic Al composition on the sapphire surface during the nitridation process.

Key words: Sapphire Surface, RHEED, Nitridation, Nitride, XPS.

#### Introduction

Sapphire is the most commonly used substrate for the growth of wide bandgap compound semiconductors, including GaN and ZnO, due to its low cost, high crystallinity, and ready availability. However, the direct growth of semiconductor materials on sapphire induces a high dislocation density in subsequent growing films due to the large lattice and thermal expansion coefficient mismatches between sapphire and thin films. Therefore, interfacial engineering of sapphire surfaces is considered an important step for the growth of high quality target materials on sapphire. In particular, nitridation of sapphire is performed not only to facilitate the growth of high quality III-nitrides and II-oxides [1, 2], but also to control the polarity of the films [3, 4]. Despite the many efforts made and the remarkable improvements in crystal quality obtained by nitridation of sapphire substrates [5, 6], many factors remain unknown.

In this article, we describe how we used dynamic reflection high-energy electron diffraction (RHEED) observations to monitor the surface changes of sapphire during nitrogen plasma treatments in-situ. The surface morphology and chemical properties of the Al<sub>2</sub>O<sub>3</sub> surface after the nitridation process were measured exsitu by atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS), respectively. To gain further insight into the nitridation process in an ultra-

high vacuum system, we compared the in-situ and exsitu observations.

## Experimental

Sapphire substrates (0.2 ° off toward (1-102)) were used for these experiments. Prior to nitridation, sapphire substrates were etched in a solution (H<sub>2</sub>SO<sub>4</sub>: H<sub>3</sub>PO<sub>4</sub> = 3:1) at 160 °C for 10 minutes, and rinsed with deionized water. After chemical etching of the sapphire surface, thermal cleaning was conducted under an ultra-high vacuum (about 0.13 µPa) at 900 °C for 30 minutes. Nitridation of sapphire was performed at 200 °C (sample-A), 400 °C (sample-B), and 600 °C (sample-C) for 60 minutes with a nitrogen plasma at a plasma generation power of 350 W. To investigate the changes in the sapphire surface due to exposure to activated nitrogen atoms, the sapphire surface was monitored in-situ by RHEED. The surface morphology of the nitrogen plasma-exposed sapphire surfaces at different temperatures was characterized by AFM. To prevent oxidation of the nitrided sapphire surfaces during the transfer, a vacuum transfer box was used. Chemical analysis of the sapphire surfaces was performed by XPS with a Mg  $K\alpha$  line (1253.6 eV) as an X-ray source. The core-level emission lines were calibrated using the carbon peak, which has a binding energy of 284.8 eV.

## **Results and Discussion**

The RHEED patterns of sapphire cleaned by exposure to a temperature of 900 °C for 30 minutes are shown in

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**Fig. 1.** RHEED patterns of sapphire surfaces (k//[11-20]) immediately after completion of a thermal treatment at 900 °C (a, c, and e) and after exposure to a nitrogen plasma for 60 minutes. AlN surface (k//[1100]) for (b) sample-A ( $T_s = 200$  °C), (c) sample-B ( $T_s = 400$  °C) and (d) sample-C ( $T_s = 600$  °C).

Figs. 1 a, c, and e, and the sapphire surfaces after nitrogen exposure at 200 °C (sample-A) 400 °C (sample-B), and 600 °C (sample-C) for 60 minutes are shown in Figs. 1 b, d, and f, respectively. As shown in Figs. 1a, 1c, and 1e, the annealed sapphire showed streaky RHEED patterns, indicating a smooth surface. However, after nitridation, the RHEED patterns changed into those of a wurtzite-structured AlN layers that were rotated 30° with respect to the sapphire epitaxial direction, i.e. [10-10]<sub>AIN</sub>//[11-20]<sub>Sapphire</sub>. A streaky pattern was still observed for sample-A (Fig. 1b), while the surfaces of sample-B (Fig. 1d) and sample-C (Fig. 1f) became relatively rough. The sapphire sample shown in Fig. 1f had amorphous-like features. These RHEED patterns indicate that the surface morphology of the AlN layer that formed on the sapphire was dependent on the substrate temperature. Because the thickness of the AlN layer is assumed to be just a few nm, a different surface morphology means a different crystal quality. Hence, one can imagine that the crystallinity of over-grown thin films is likely to be influenced by the nitridation temperature.

The morphological variation was further investigated by monitoring the changes in the RHEED intensity. Figure 2 shows the intensity variation of the specular spot (rectangular) and primary diffraction spot (circle)



**Fig. 2.** RHEED intensity variation of the specular spot (circle) and AlN (01) spot (square) for each sample. The time when nitrogen plasma exposure was started and the specular spot intensity reached its minimum value are indicated as N-exp. and  $t_m$ , respectively.  $t_{AIN}$  indicates the time when the AlN pattern first appeared.

of the AlN layer during nitrogen plasma exposure. The nitrogen plasma exposure was started from the time denoted as N-exp., but the AlN pattern was observed clearly from the point as denoted  $t_{AlN}$ . The specular spot intensity of all samples decreased rapidly immediately after exposure to nitrogen. The distinction ( $t_m$ ) time of the specular spot was 263, 454, and 703 seconds for sample-A, -B, and -C, respectively. The  $t_m$  values were strongly related to the nitrogen exposure temperature and decreased as the substrate temperature increased. Here, it should be noted that the successive increase in specular spot intensity after  $t_m$  was not due to recovery of the surface, but due to enhanced scattering from the rough surface.

It is well known that the evolution of the specular spot intensity is closely related to surface roughness. Because the substrate temperature during the nitrogen plasma exposure is not sufficiently high to change the surface morphology considerably by sublimation, we attributed the initial decrease in the specular spot intensity to the adsorption of nitrogen atoms on the sapphire surface, i.e. due to the formation of a AlN layer on the sapphire surface. Hence, the decrease in



**Fig. 3.** Normalized lattice constant variation of sample-C ( $T_s$  = 600 °C). I is the wavelength of electrons, L is the distance between the specimen and fluorescent screen, and D is twice the distance between the diffraction spots.

distinction time corresponds well with the fact that the sticking coefficient of atomic nitrogen is very small and strongly related to the substrate temperature [7]. The RHEED patterns collected during the nitrogen plasma exposure support the above description. We observed a mixed RHEED pattern (simultaneous observation of AlN k//[1100] and Al<sub>2</sub>O<sub>3</sub> k//[11-20] patterns) from the time when the AlN RHEED pattern emerged;  $t_{AIN}$ , just after the specular spot intensity reached its local minimum as indicated in Fig. 2. Therefore, the time delay between  $t_{AIN}$  and  $t_m$  may be due to the slow increase of AlN coverage on the surface.

Figure 3 shows variations in selected in-plane lattice constant during the nitridation process. The lattice constant was evaluated by measuring the rod-spacing between AlN (01) and (0-1) rods. The inset shows a mixed RHEED pattern, which includes AlN k//[1100] and Al<sub>2</sub>O<sub>3</sub> k//[11-20] patterns simultaneously. In terms of the large lattice misfit (13%) between AlN and Al<sub>2</sub>O<sub>3</sub>, the critical thickness of AlN on Al<sub>2</sub>O<sub>3</sub> is just a few Å; the experimental value is about 4.5 Å [8]. Hence, Fig. 3 indicates that the growth rate of AlN was extremely slow (a few Å per hour), even at a substrate temperature of 600 °C. Consequently, the RHEED observations indicate that nitridation in an ultra-high vacuum chamber using a nitrogen plasma is restricted to a relatively low temperature range due to the low sticking coefficient of atomic nitrogen.

Although the growth rate of AlN was extremely slow, the surface morphology was determined by the formation of AlN and lattice relaxation. For example, protrusion formations by nitridation may be observed [9]. Heinlein *et al.* conducted nitridation at 400 °C for longer than 300 minutes. They observed numerous protrusions from the nitrogen-exposed c-plane sapphire. Uchida et al. [10] proposed a mechanism for protrusion growth during high temperature (1050 °C) nitridation



(a) Sapphire RMS = 0.14 nm

(b) sample-A T₅=200°C RMS = 0.15 nm



(c) sample-B T<sub>s</sub>= 400°C RMS = 0.18 nm (d) sample-C T<sub>s</sub>= 600°C RMS = 0.26 nm

**Fig. 4.** AFM images of (a) a bare sapphire surface, (b) sample-A, (c) sample-B, and (d) sample-C. The density of protrusions was estimated to be  $1.2 \times 10^7$  cm<sup>-2</sup> for sample-A,  $1.6 \times 10^7$  cm<sup>-2</sup> for sample-B, and  $1.6 \times 10^8$  cm<sup>-2</sup> for sample-C.

with  $NH_3$  in a metal organic chemical vapor deposition reactor. They speculated that the cause of protrusion formation was the  $AlN_xO_{1-x}$  (aluminumoxynitride) layer formation on the sapphire surface.

AFM images of a bare sapphire surface are shown in Figure 4a, while Figs. 4b, 4c, and 4d show the nitrided sapphire surface at each temperature. The sapphire surface became rough due to nitrogen plasma exposure, and protrusions were also observed. The density of protrusions was  $1.2 \times 10^7$  cm<sup>-2</sup> (sample-A; T<sub>s</sub> = 200 °C),  $1.6 \times 10^7$  cm<sup>-2</sup> (sample-B; T<sub>s</sub> = 400 °C), and  $1.6 \times 10^8$  cm<sup>-2</sup> (sample-C; T<sub>s</sub>=600 °C). Note that these values are considerably lower than the density values reported by Uchida et al ( $10^9 - 10^{10}$  cm<sup>-2</sup>)[10]. In addition, our result indicates that the protrusion density increased abruptly over the same critical nitridation temperature.

In terms of the origin of protrusions on the sapphire surface, it appears that the formation of the  $AIN_xO_{1-x}$  layer was primarily responsible for the formation of protrusions on the surface, rather than strain relaxation of the AIN layer itself. If the lattice relaxation of AIN is the main cause for the formation of protrusions, a higher density of protrusions should have been observed in those samples treated at lower substrate temperatures.



Fig. 5. XPS spectra for N 1s and Al 2p emissions (take-off angle of  $35^{\circ}$ ).

Figure 5 shows core level spectra of N 1s and Al 2p peaks detected from sapphire surfaces nitrided at different nitridation temperatures. An Al 2p peak appeared at 74.5 eV in sample-A, but shifted to 75.9 eV and 76.0 eV in sample-B and sample-C, respectively. In the case of the N 1s peak, the spectra showed a blue-shift from 396.8 eV to 398.5 eV as the substrate temperature increased.

The dominant Al 2p emission position of sample-A can be assigned to AlN [11]; however, there was also considerable emission intensity at the peak positions of metallic Al and Al<sub>2</sub>O<sub>3</sub>. Metallic Al and AlN-related emissions were of a lower intensity in sample-B and -C than in sample-A. In sample-B and sample-C, AlN<sub>x</sub> and Al<sub>2</sub>O<sub>3</sub>-related emissions became dominant. The metallic state of Al may be formed by oxygen deficiencies on the surface that form during thermal cleaning at 900 °C. Furthermore, Losurdo et al. have observed the fingerprint of Al-Al bonds [12] on nitrided Al<sub>2</sub>O<sub>3</sub> surfaces. The concentration of oxygen deficiencies in  $Al_2O_3$  increases as the temperature increases [13]. Note that the formation enthalpy of AlN from metallic Al or Al<sub>2</sub>O<sub>3</sub> is considerably different; metallic-Al greatly facilitates the formation of AlN. The equations shown below indicate the importance of the Al-composition on the sapphire surface for nitridation, especially at low temperatures:

 $Al_2O_3$  (s) + 2N (g)  $\rightarrow$  2AlN + 3/2  $O_2$  (-213.6 kJ/mol) (1)

$$2Al(s) + 2N(g) \rightarrow 2AlN (s) (-783.8 \text{ kJ/mol})$$
(2)

Because the thermal cleaning temperatures for all samples were the same, the initial content of Al on the sapphire surface should be the same. However, during nitrogen exposure, Al has a higher vapor pressure at a higher substrate temperature, which could restrict the rate of formation of AlN on the surface. Furthermore, nitrogen atoms have a lower sticking coefficient at a higher substrate temperature; this would reduce the effective supply rate of nitrogen atoms. Hence, nitridation proceeds more slowly at higher substrate temperatures; this was confirmed by the RHEED observations shown in Fig. 2.

Furthermore, the spectra for samples-B and -C strongly demonstrate the other effect of higher temperature nitridation; a considerable amount of AlN decomposes into  $AlN_x$ , presumably due to the formation of  $AlN_xO_{1-x}$ . This is illustrated with the following formula:

$$2AIN(s) + Al_2O_3(s) \rightarrow 2AINO(s) + Al_2O_{3-x}(s) + 2N$$
  
$$\rightarrow 4AINO(s)$$
(3)

It was reported that AIN is easily oxidized to form AINO [13], especially when the substrate temperature is high enough. The Al 2p spectra indicate that AIN forms mainly due to Al-N bonding. At a low substrate temperature, the AIN remains unchanged, but when the substrate temperature increases, the formation of the AINO phase is enhanced by the oxidation of AIN. The shift of the N 1*s* core level peak supports this explanation. The N 1*s* peak shifted from the position of AIN (sample-A) to that of AINO (samples-B and C), which corresponds well with the above description. However, emission due to N-O bonds (405.4 eV) was not observed from our samples, indicating the existence of N-O bonds related to the AINO phase rather than simple N-O bonds.

### Conclusions

In conclusion, we investigated the temperature dependence of formation of AIN and AINO phases on c-sapphire substrates after nitridation at relatively low temperatures. Dynamic RHEED observations revealed that the growth rate of AIN decreased as the substrate temperature increased due to the low sticking coefficient of atomic nitrogen. Furthermore, the formation of AINO was enhanced by high substrate temperature nitridation due to oxidation of the AIN layer. XPS spectra support these conclusions and indicate the importance of the metallic Al composition on the sapphire surface in the nitridation process. The effects we observed are attributed to nitridation temperature restriction in an ultra-high vacuum system.

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