Nitridation of Si(1 1 1) for growth of 2H-AlN(0 0 0 1)/β-Si$_3$N$_4$ /Si(1 1 1) structure

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ABSTRACT

Using various nitrogen active species with different chemical and physical activities, nitridation of Si(1 1 1) was studied for the growth of group III nitrides and their alloys using a radio frequency molecular beam epitaxy. Nitrogen inductive coupling discharge produced dissociated active nitrogen atoms (N+N*), which are ground state atom N and excited atom N*, excited molecules N$_2^*$, and molecule ions N$_2^+$. The surface morphology of β-Si$_3$N$_4$ was affected by the kind of nitrogen species. Flat surface was obtained by using only (N+N*) with slow nitridation of 0.02 ML/s. When nitridation was performed by (N+N*) and N$_2^*$, many steps and many 10 nm height spikes were observed. It was essential for nitridation to eliminate nitrogen ions (N$_2^+$). In comparison with this result, when N$_2^*$ were used, the island size of β-Si$_3$N$_4$ became bigger without detachment from upper terrace. This island size affected successive surface structure of AlN. It is a key technique to achieve flat surface of β-Si$_3$N$_4$ that N+N* flux was used for nitridation. The growth of 2H-AlN(0 0 0 1)/β-Si$_3$N$_4$/Si(1 1 1) structure was also performed. RMS value of AlN grown on β-Si$_3$N$_4$ which was formed by (N+N*) became 0.88 nm.

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1. Introduction

Hexagonal 2H-AlN is an attractive material for fabrication of ultraviolet light emitting diode (UV LED) or laser diode (LD) because of their physical property [1]. AlN grown on a Si substrate is very important because of low cost, large area and high thermal conductivity of Si. Therefore, a lot of researches about AlN grown on a Si substrate have been conducted [2–5]. However, AlN on a Si substrate is low crystal quality compared with AlN on SiC and sapphire substrates because of large lattice mismatch between AlN and the Si substrate.

Recently, hexagonal SiN (β-Si$_3$N$_4$) was used as an intermediate layer when AlN was grown on Si [6–8]. Nitridation was performed by various methods, such as using NH$_3$ [9,10], NO [11] and N atoms[12]. When N atoms reacted with Si surface, the honeycomb like ("8 × 8") structure was observed by STM [12]. As a template for growth of group III nitrides, SiC film on Si was used [13,14]. However, β-Si$_3$N$_4$ on Si is much advantage because the atomic nitrogen source was available to use for successive the group III nitrides and without contamination of carbon. Radio frequency (RF) discharge is a best nitrogen source to produce active nitrogen atoms (N+N*), where N and N* are ground and excited atoms, respectively. Induction coupling (ICP) RF discharge has two

discharge modes such as low brightness (LB) and high brightness (HB) discharge modes [15]. The HB mode generates mainly active (N+N*) atoms, and excited molecules N$_2^*$ and molecule ions N$_2^+$. The LB mode generates mainly excited nitrogen molecules N$_2^*$ and molecule ion N$_2^+$ and not (N+N*). The discharge modes are controlled by changing inner discharge tube pressure and input RF power. The chemical reaction is performed by using (N+N*) and chemical activity of N$_2^*$ is very small.

In this study, the relationship between the surface of β-Si$_3$N$_4$ layer and successive grown initial AlN layer was investigated through observation of the surface of β-Si$_3$N$_4$ formed by various nitridation species.

2. Experimental procedure

Nitridation of Si and growth of AlN were performed by using a VG80H MBE system with IRFS-501 RF nitrogen radical source made by Arios Inc. Prior to insert into the MBE chamber, Si(1 1 1) substrate of 2 or 3 in was rinsed with SEMICOCLEAN23 for 5 min. A Si(1 1 1) substrate was thermally cleaned at 870 °C (reflection high energy electron diffraction (RHEED) pattern showed 1 × 1 pattern) and cooled down to 830 °C to get 7 × 7 pattern before the nitridation. After thermally cleaning the Si substrate, nitridation was performed by various chemical and physical activities of nitrogen species. Four nitridation species such as (N+N*), (N+N*) +N$_2^*$, only N$_2^*$, and (N+N*) +N$_2^*$ +N$_2^+$, were shown in Fig. 1. The kinds

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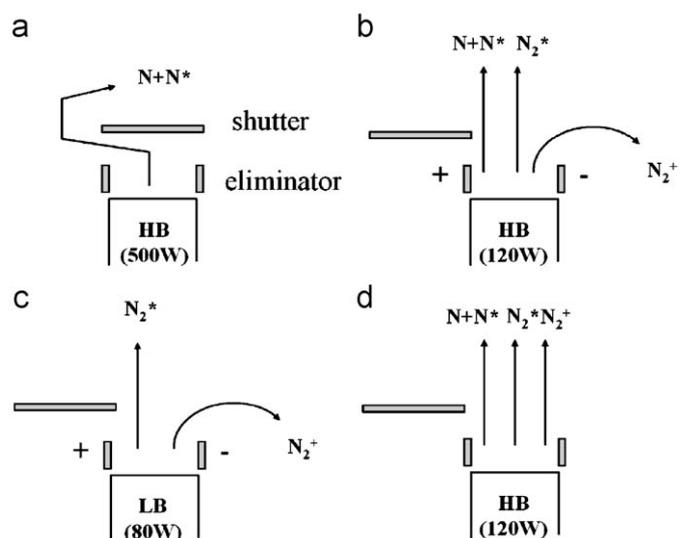E-mail address: tohachi@eml.doshisha.ac.jp (T. Ohachi).

Fig. 1. Schematic of experimental procedure: nitridation by (a) leaked N+N*, (b) N+N* and N_2^*, (c) N_2^* and (d) N+N*, N_2^* and N_2^+.

lation migration enhancement epitaxy (AM-MEE) method which changed the discharge modes by RF input power periodically between the LB discharge mode and the HB discharge mode [16,17]. Surface morphology of β-Si_3N_4 and AlN were evaluated by AFM.
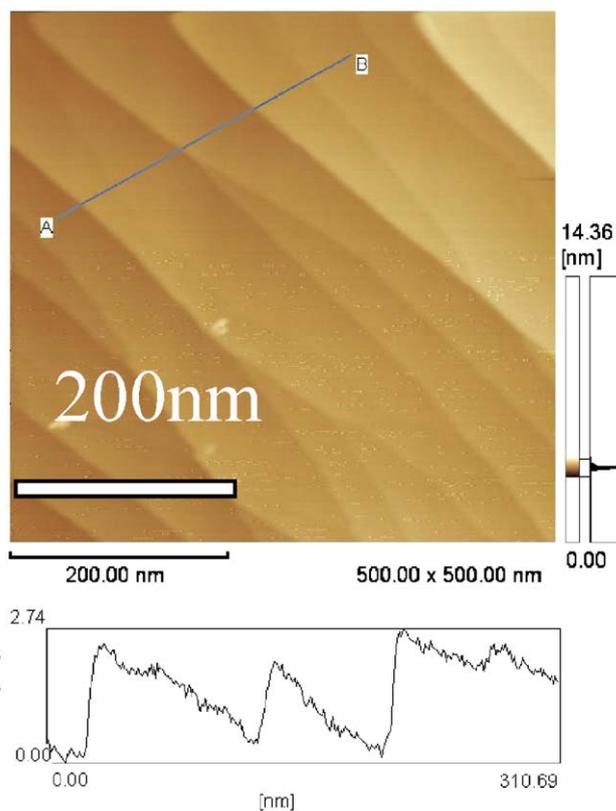

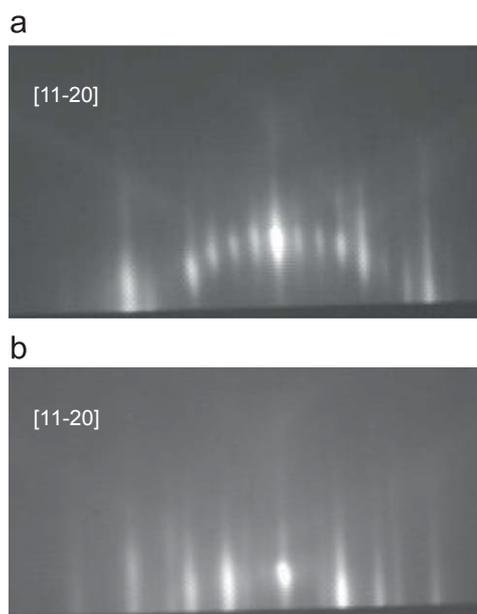**Fig. 2.** Surface of Si(111) wafer after annealing in MBE chamber. Step height is about 2.7 nm.

of the nitrogen species were controlled by the selection of discharge mode between LB discharge one and HB discharge one, the RF discharge power and inner pressure of nitrogen, the shutter position in front of the outlet of N cell, the eliminator potential. The following four nitridation experiments, which were performed at 830 °C, are shown as follows depending on various nitrogen species.

(a) Only active atoms (N+N*), which were produced from the leaked active nitrogen atoms by the strong HB mode with a closed shutter [16], were used in Fig. 1(a) experiment. Even though the nitrogen mechanical shutter was closed under the HB mode, active atoms (N+N*) and excited molecules N_2^* could be leaked from the gap between the shutter and the outlet of a cell. The production rate of (N+N*)/N_2^*, however, is high for the strong HB than that of the weak HB discharge, the effect of N_2^* is negligibly small in this case [16]. Nitrogen atoms (N+N*) are effective for nitridation, because the chemical activity of (N+N*) is very high compared with that of N_2^*. The amount of (N+N*) was monitored the atom current, which is proposed by our group [16]. Atomic current in VG 80H as 5.5×10^{-4} ML/s/nA was obtained. The atomic current in the case of Fig. 1(a) (500 W and 75 Pa) was 35 nA, which corresponds to 0.02 ML/s.

(b) Secondly using direct exposure of (N+N*) and N_2^* under the weak HB mode with opened shutter and application of the eliminator potential. In this case discharge condition was 120 W, 26 Pa and 81 nA, which corresponds 0.044 ML/s. The amount of direct exposure of (N+N*) and N_2^* beams was controllable by input power and inner pressure. In this case chemical activity of (N+N*) and physical activity N_2^* contributed nitridation.

(c) Thirdly using only N_2^* by the LB discharge mode with application of the eliminator potential. Using an eliminator placed at the exit of N cell, charged particles were removed from the incident beam. In this case discharge RF power was 80 W. This nitridation method uses physical activity of N_2^* and small chemical activity.

(d) The effect of N_2^+ was studies in Fig. 1(c) by (N+N*) and N_2^* and N_2^+ without applying the eliminator potential. N_2^+ has high energy compared with other nitrogen species.

After the nitridation as shown in Fig. 1, a few monolayers Al were deposited on β-Si_3N_4 and form an initial Al polarity AlN layer. Successive AlN layer was grown by activity modu-

Fig. 3. RHEED patterns of (a) 7×7 clean Si surface and (b) 8×8 β-Si_3N_4 surface: Nitridation was performed by using the leaked active nitrogen atoms of the strong HB mode with a closed shutter.

3. Results and discussion

3.1. Nitridation by (N+N*) using the leak strong HB plasma with closed shutter

After Si(1 1 1) substrate was thermally cleaned, the surface with clear step pattern was observed at room temperature as shown in Fig. 2. Nitridation of Si was occurred even when an N cell shutter was closed because the leaked active nitrogen atoms and molecules from the gap of shutter could be achieved to the Si surface. Both exited atomic nitrogen (N*) and ground state atomic nitrogen (N), which were generated by a high bright mode (HB) of RF discharge, were used for the nitridation of Si. The amount of (N+N*) was so large that the effect of N_2^* was able to be negligible during the growth under the strong HB discharge. The amount of (N+N*) was also able to be measured by a Langumuir-like atom probe biased negative potential when no charged particles exist [16]. The atom current for HB discharge under 500 W RF power and 75 Pa (1.38 sccm) inner pressure was 390 nA for open shutter operation and 35 nA for closed shutter one. By closing a shutter of
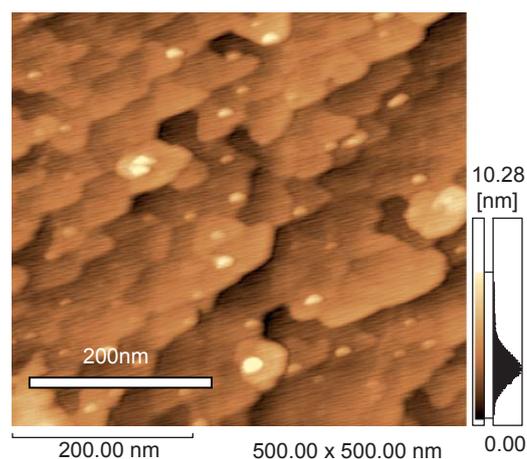

Fig. 6. Nitridation by the excited molecules N_2^* flux under LB discharge mode under 80 W for 5 min as shown in Fig. 2(c): Surface morphology of β-Si₃N₄ was observed by AFM.
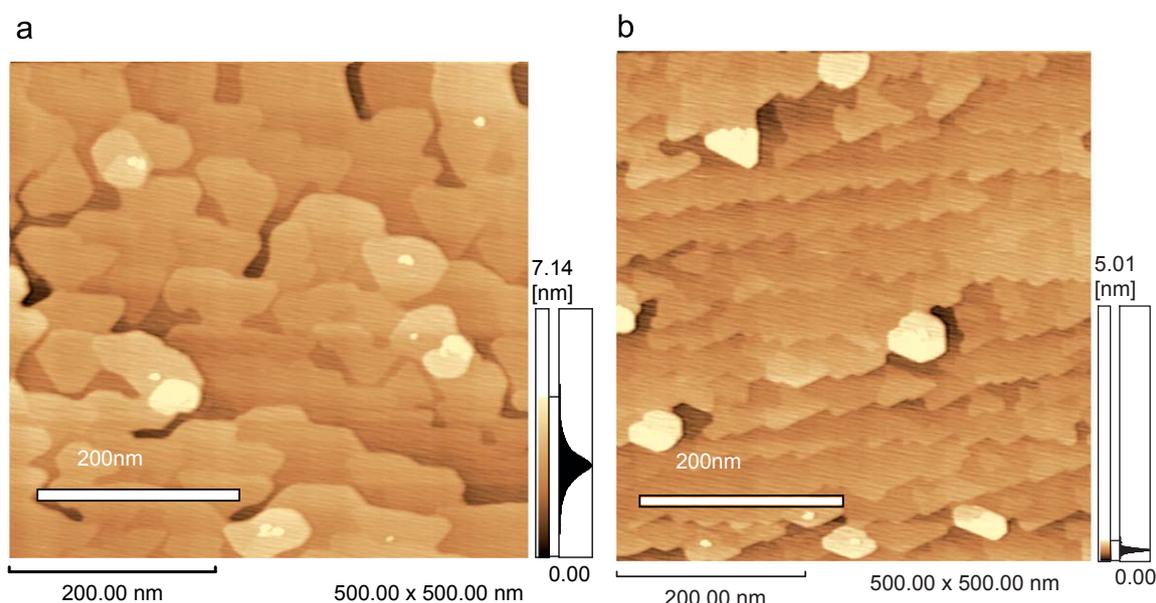
a

b

Fig. 4. Nitridation performed by using the leaked active nitrogen atoms of the strong HB mode with a closed shutter without sample rotation as shown in Fig. 2(a): (a) for center of 3 in Si wafer, (b) for edge.
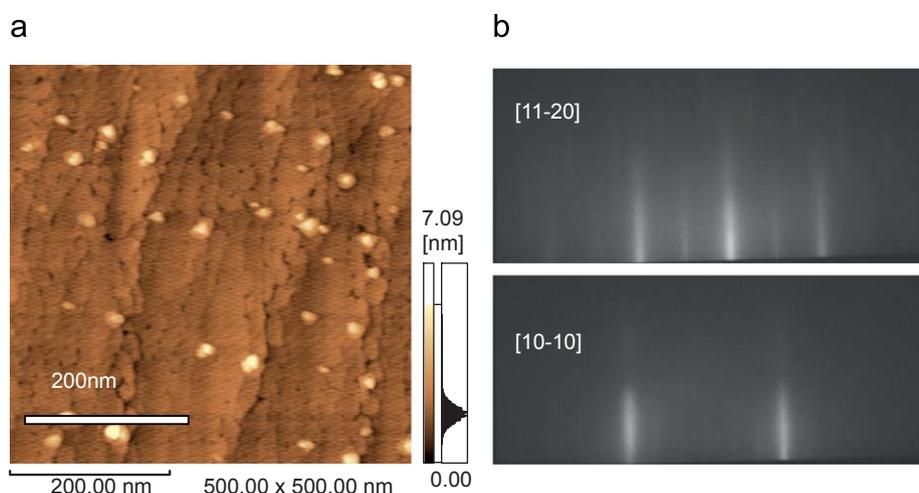
a

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Fig. 5. Nitridation by direct exposure of N and N* flux for 30 s as shown in Fig. 2(b): (a) Surface morphology of β-Si₃N₄ observed by AFM and (b) RHEED patterns of successive AlN.

nitrogen source, the number of atoms was reduced by about 9% compared with opened shutter. When nitridation was performed by using the leaked active nitrogen atoms of the HB mode with a closed shutter, RHEED pattern showed 8×8 pattern of β-Si_3N_4 for 9 min under 500 W RF power and 75 Pa (1.38 sccm) inner pressure as shown in Fig. 3. The calculated thickness of β-Si_3N_4 in this experiment is 35 nA for 540 s i.e. $35 \times 540 \times 5.5 \times 10^{-4}$=10.5 ML. In order to investigate the uniformity of nitridation of 3 in Si(111) substrate the nitridation was performed without rotation of the substrate. The surfaces at center and edge were observed by AFM. Fig. 4 showed small islands, which coalesced with neighbor island, were observed and RMS value over $500 \times 500\,nm^2$ became 0.83 nm. Structure of small island was rarely changed. It was indicated that uniform nitridation could be achieved by using the leaked (N+N*).

Fig. 7. Surface morphology observed by AFM of β-Si_3N_4: Nitridation method was by using direct exposure both (a) active atoms (N+N*) for 30 s and (b) active molecules (N_2^*) for 5 min.

3.2. Nitridation by (N+N*) and N_2^* using the weak HB plasma with open shutter

Nitridation of Si which was directly exposed with opened shutter was performed. The amount of (N+N*), which was monitored by Langumuir-like probe, was set to be small enough selecting discharge condition. Figs. 5(a) showed a surface of β-Si_3N_4 irradiated by the HB mode under 120 W RF power and 26 Pa (0.5 sccm) for 30 s. The nitrogen flux in this experiment was 81 nA atom current, i.e. 0.44 ML/s of (N+N*) flux. The surface of β-Si_3N_4, of which nitridation was performed for 30 s whose thickness is about 13 ML as shown in Fig. 5(a) showed small islands and step pattern observed by AFM and RMS value over $500 \times 500\,nm^2$ was 0.65 nm. The several spikes whose height was about 5 nm could be also observed. AlN layer grown on β-Si_3N_4 of 30 s nitridation showed 2×6 RHEED pattern as shown in Fig. 5(b) that indicated Al polarity and became flat surface and RMS value over $500 \times 500\,nm^2$ was 0.88 nm.

3.3. Nitridation by N_2^* using the LB plasma with open shutter

Chemical activity of excited nitrogen molecules N_2^* is small compared with one for (N+N*). Reaction of Si and N_2^* however available. Fig. 6 shows the AFM images for nitridation with LB plasma. The island diameter of 50 nm could be found at the surface of β-Si_3N_4 and RMS value over $500 \times 500\,nm^2$ was 1.27 nm. This surface structure affected the island size of successive AlN layer. In fact, successive AlN layer have about 16 nm island size that was larger than that on β-Si_3N_4 by (N+N*) and RMS value over $500 \times 500\,nm^2$ became 0.83 nm. Step morphology was observed in detail to know the effect by varying the kind of species. Enlarged AFM images of β-Si_3N_4 were shown in Fig. 7. It was found that the islands were detached from upper terrace when (N+N*) flux was used as the nitridation species.
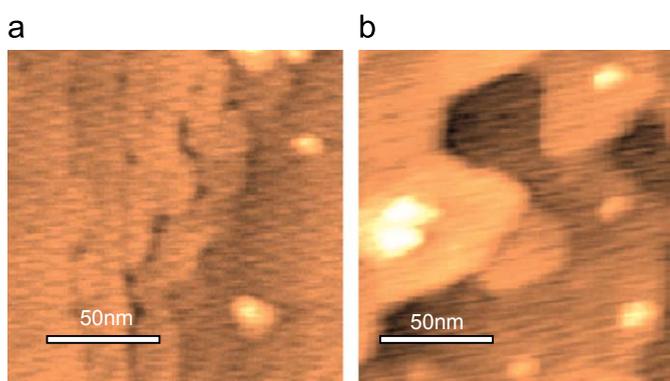

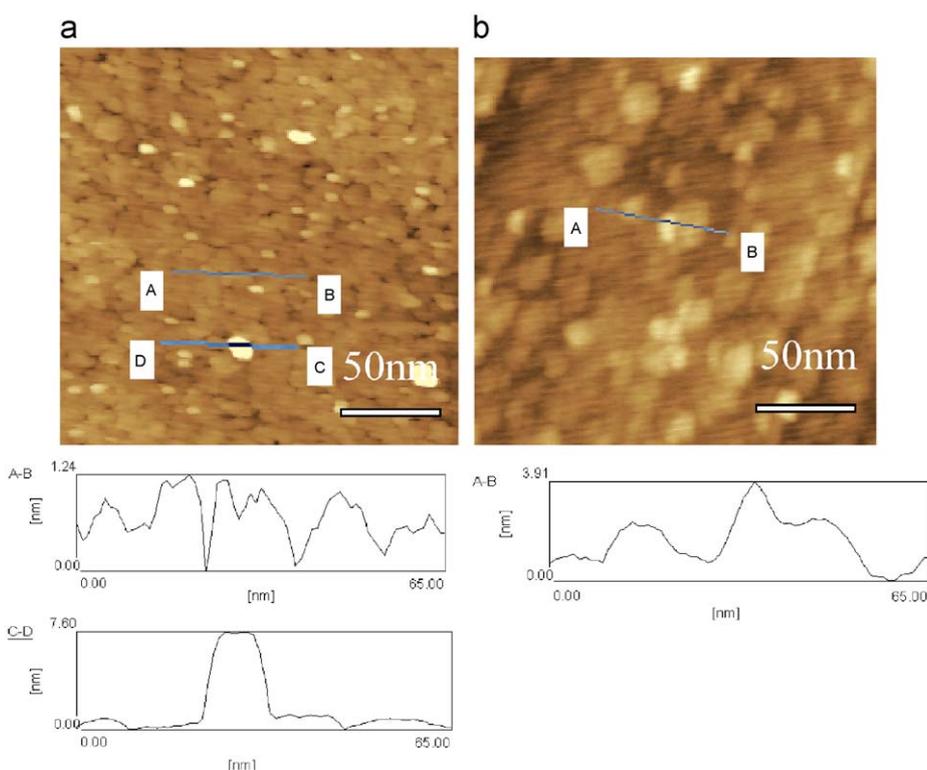**Fig. 8.** Surface morphology of AlN observed by AFM: Nitridation method was by using (a) active atoms (N+N*) for 30 s, (b) active molecules (N_2^*) for 5 min.

a

b

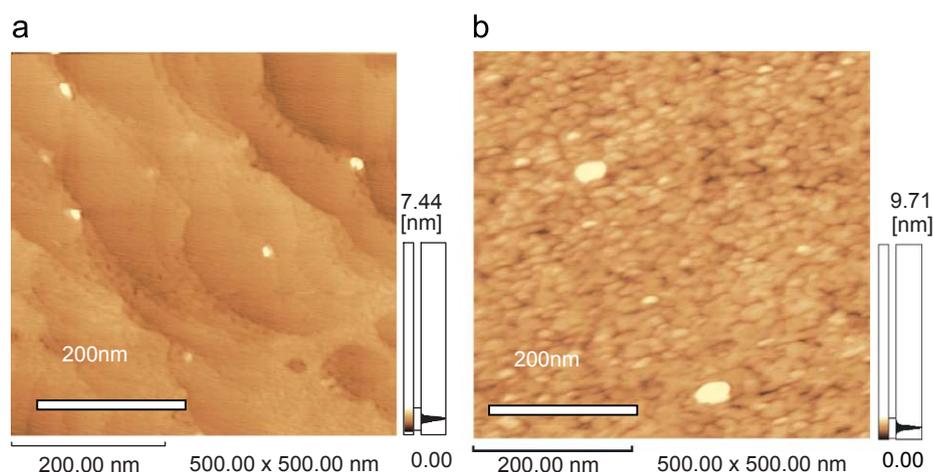**Fig. 9.** Effect of N_2^+ ions exposure as shown in Fig. 2(d): Surface morphology observed by AFM of (a) β-Si$_3$N$_4$ and (b) successive AlN: Nitridation method was by using active atoms (N+N*) and ions (N_2^+) for 30 s.

Similar results were showed in Ref. [12]. On the other hand, the size of islands became larger without detachment of island from terrace when N_2^* was used as shown in Fig. 7(b). Fig. 8 showed AFM images of successive AlN layer grown on β-Si$_3$N$_4$ by using (N+N*) atoms and N_2^* to compare the effect on the AlN surface morphology. RMS value when N_2^* was used was almost uniform in every place. When (N+N*) was used, RMS value with and without spikes was different. RMS value excluding spikes became 0.5 nm, which was better value than by using N_2^*.

3.4. The effect of N_2^+ for nitridation

Nitrogen ions (N_2^+) have high energy compared with nitrogen molecules N_2^* and active nitrogen atoms (N+N*). Fig. 9(a) shows the nitridation by (N+N*) and N_2^* for 30 s using HB discharge with 120 W, 26 Pa and (b) shows nitridation using HB without eliminator potential i.e. with ions (N_2^+) for 30 s. When Si surface was exposed by (N+N*) and N_2^* for 30 s, many steps and many 10 nm height spikes were observed. Compared to previous method, when we use N_2^+ for nitridation, the number of spikes was little. Therefore, there were few spikes on the successive AlN layer. However, because N_2^+ has very high energy compared to other species, steps of β-Si$_3$N$_4$ were broken and showed rounded shape. RMS of successive grown AlN was 1.08 nm that was worse value than that without N_2^*.

4. Conclusion

RF plasma source generated various nitrogen species, active nitrogen molecules (N_2^*), active atoms (N+N*), nitrogen ions (N_2^+). Surface morphology of β-Si$_3$N$_4$ formed by various active nitrogen species was observed. Active atoms (N+N*) is a key element for nitridation of Si substrate because RMS value of β-Si$_3$N$_4$ formed by (N+N*) was better than that formed by other species. When only (N+N*) were used for nitridation in the condition of flux 0.02 ML/s, it was found that several island structures which were detached from upper terrace were formed. The growth of 2H-AlN(0 0 0 1)/ β-Si$_3$N$_4$ /Si(1 1 1) structure was also performed. RMS value of AlN grown on β-Si$_3$N$_4$ which was formed by (N+N*) became 0.88 nm.

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