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Epitaxial growth of β-Si_3N_4 by the nitridation of Si with adsorbed N atoms for interface reaction epitaxy of double buffer AlN(0001)/ β-Si_3N_4/Si(111)

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A fabrication process of an interface reaction epitaxy (IRE) β-Si_3N_4 and an IRE AlN were investigated to produce a double buffer layer (DBL) of AlN(0001)/β-Si_3N_4/Si(111) for the growth of group III nitrides films on Si. The β-Si_3N_4 was formed by using adsorbed (ADS) nitrogen atoms irradiated indirectly from a rf-plasma cell. Two surface structures of the β-Si_3N_4, which were "8 x 8" and "8/3 x 8/3" reconstructions, were fabricated by changing the nitrogen irradiation conditions; complete and incomplete nitridation of Si surface and successive heat treatment up to 875 °C formed the "8 x 8" and "8/3 x 8/3" structures, respectively. IRE AlN was grown by 1 monolayer of Al deposition on the β-Si_3N_4 and successive annealing at 875 °C. Al and N polarity DBLs were grown on the "8 x 8" and "8/3 x 8/3" structures, respectively. These results indicated that the polarity of DBL could be controlled by the surface reconstruction of β-Si_3N_4.

1 Introduction Growth of group III-Nitride on Si substrate is very important for mass production of a high electron mobility transistor (HEMT) because of low cost, large surface area and high thermal conductivity of Si substrates. The improvement of AlN/Si(111) interface is expected to grow high quality group III-Nitrides because the interface affects the successive grown crystal quality of AlN [1-5]. Wu *et al.* proposed an coincident-interface AlN/β-Si_3N_4(0001)/Si(111) double-buffer layer (DBL) [6]. The coincident site lattice (CSL)-interface are the 1 : 2 and 5 : 2 lattices formed at the β-Si_3N_4(0001)/Si(111) and AlN(0001)/ β-Si_3N_4(0001) interfaces, respectively, to grow GaN on Si(111). This is related to a nearly perfect lattice matching between Si(111) and β-Si_3N_4(0001); the 2 x 2 cell of the Si(111) surface ($2a_{Si}$ = 0.768 nm) is only 1.1% bigger than the unit cell of β-Si_3N_4 (0001) ($a_{β\text{-}Si3N4}$ = 0.761 nm) [8]. Si_3N_4 films formed on Si are usually amorphous SiN_x. However, a coherent epitaxial β-Si_3N_4/ Si(111) interface can be formed by solid state reaction of thin SiN_x amorphous films by annealing at higher substrate temperatures [7]. Two structural models of "8 x 8" and "8/3 x 8/3" were reported by the several groups [8-15]. The recent structural models of the "8 x 8" and "8/3 x 8/3" were reported as follows; the 3.07 nm superstructure measured by scanning tunneling microscope STM is the 4 x 4 reconstruction of the β-Si_3N_4(0001), which is corresponding to "8 x 8" based on Si(111) unit cell, while the 1.02 nm periodic structure of "8/3 x 8/3" reconstruction is an incomplete nitridation phase on Si(111) surface [9].

For the nitridation of Si by plasma assisted molecular beam epitaxy (PA-MBE), which can lower the nitridation temperature than NH_3-MBE, the control of nitrogen flux is an important issue because the nitridation area and rate is affected by the amount of nitrogen atom flux [18, 19]. For uniform and slow nitridation adsorbed (ADS) nitrogen adatoms by indirect exposure of N+N* was used, because the life time of nitrogen atoms is long enough to reach substrate after reflection from walls of the growth chamber or shutter. *In situ* monitoring of the ADS nitrogen flux was made by the self-ionization of nitrogen atoms on a negatively biased electrode [18].

In this study, in order to grow high quality DBL AlN/β-Si_3N_4(0001)/ Si(111) the fabrication method of β-Si_3N_4, of which surface reconstruction are "8 x 8", "8/3 x

8/3", and IRE-AlN using ADS nitrogen atoms are investigated. Polarity of successively grown buffer AlN by AM-MEE on the DBLs is also studied.

2 Experimental The nitiridation and AlN growth were performed in the growth chamber of MBE (VG-80H). The nitridation was performed by N+N* generated by a plasma cell IRFS-501 radio frequency inductively coupled plasma (rf-ICP) cell made by Arios Inc. The evolution of the surface reconstruction was monitored by reflection high energy diffraction (RHEED) observed from azimuth [11-20] during the growth. Polarity was confirmed by KOH etching of the surface and reconstruction patterns of RHEED. Temperature of a thermo couple of VG80H system was calibrated by the temperature of the phase transition of surface reconstruction 7x7 to 1x1 of 856 ^{o}C [20] by using the formula of $T_{sub} = (T_{TC} - 300)$ x [(975-856)/(975-300)] + 300 [^{o}C], where T_{TC} is temperature of a thermo couple and T_{sub} calibrated surface temperature; T_{TC} = 975 ^{o}C for T_{sub} = 856 ^{o}C the transition temperature of 7 x 7 to 1 x 1; $T_{TC} = T_{sub}$ = 300 ^{o}C. Surface morphology was measured by atomic force microscopy (AFM).

Following procedures were used:

(i) Cleaning and flattening of a Si(111) surface by using SiO_2 film as a sacrifice layer on Si(111) formed by wet processing with HCl and H_2O_2. As a Si clean surface 7x7 structure, the oxidized film was removed by thermal decomposition by 865 ^{o}C. Before Si temperature reached at Si 1x1 reconstruction (*i.e.* 856 ^{o}C) bare Si surface was appeared and small protrusions of SiC were formed and appeared in AFM image as white dots;

(ii) The nitridation of Si with ADS nitrogen atoms to form β-Si_3N_4, 80 Pa (1.38 sccm of N_2 flow) at 200 W or 500 W rf power changing nitridation temperature from 300 ^{o}C to 818 ^{o}C at 7 x 7 Si surface reconstruction;

(iii) Pre-deposition of 1 ML(mono layer) Al adatoms on a β-Si_3N_4 layer to form an IRE-AlN template: One ML of Al is 22.7 s irradiation at 1050 ^{o}C of Al K-cell temperature and the amount of deposited Al on β-Si_3N_4 was controlled by the opening time of mechanical shutter and Al temperature;

(iv) A 30nm buffer AlN on the DBL buffer layer were grown by activity modulation migration enhanced epitaxy (AM-MEE) for PA-MBE [21].

3 Results and discussion

3.1 Nitridation of Si and formation of β-Si_3N_4

(1) Formation of β-Si_3N_4 by solid state reaction at higher temperature: N+N* atoms were generated by a rf-ICP plasma cell. From at about 200 ^{o}C to 580 ^{o}C for irradiation of N+N* atoms the surface reconstruction of β-Si_3N_4 was not appeared and Si 7x7 pattern was faded away gradually to reach 1x1 reconstruction depending on percentage of surface nitridation. RHEED patterns with elevating temperature after the nitridation at 300 ^{o}C for 1 min were shown in Fig. 1. With elevating the nitridation temperature, Si 7x7 pattern was disappeared around 818^{o}C (Fig. 1(b)). In additional increasing temperature up to 875 ^{o}C, the "8/3 x 8/3" structure was appeared showing by white arrows (Fig. 1(c)). When the substrate was cooled down to 300 ^{o}C, Si 7x7 pattern was appeared again as shown in Fig. 1(d). These results indicated that the nitradation took place partially. This fact is consistent of the result of [9]. Figure 2 shows an evolution of RHEED pattern after the nitridation at 300 ^{o}C for 4 min. All Si 7x7 patterns were converted to 1x1 pattern, which comes from the coverage of Si surface completely by amorphous SiN_x as shown in Fig. 2(a). After annealing at 875 ^{o}C for 4 min and cooling to 300 ^{o}C, the"8 x 8" reconstruction pattern was appeared and Si 7x7 structure did not appear as shown in Fig. 2(b). White arrows

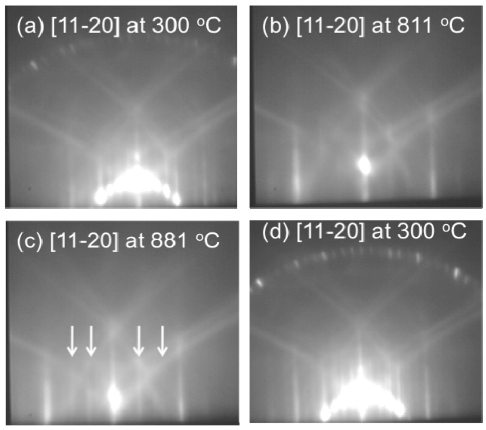

Figure 1 The evolution of RHEED pattern as a function of substrate temperature for incomplete nitridation at 300 ^{o}C for 1min nitridation: (a) after nitridation at 300^{o}C for 1min nitridation, (b) heating up to 818 ^{o}C, (c) annealed at 875 ^{o}C. White arrows show clear "8/3 x 8/3" pattern at 875 ^{o}C, and (d) cooled down to 300 ^{o}C.

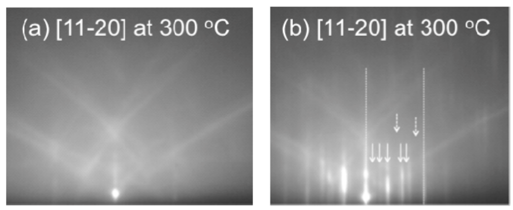

Figure 2 The evolution of RHEED pattern as a function of substrate temperature for complete nitridation at 300 ^{o}C for 4 min nitradation: (a) after nitridation at 300^{o}C for 4 min nitradation, (b) after heating up to 875^{o}C and cool down to 300 ^{o}C. White arrows show clear "8 x 8" reconstruction pattern at 300 ^{o}C. The lines of 4/8 and 7/8 were missing.

show "8 x 8" reconstruction. Figure 3 shows surface morphology of β-Si_3N_4 formed by N+N* AFM image of the surface of β-Si_3N_4 after the annealing at 875 ^{o}C; nitirdation time is 1 min at 300 ^{o}C corresponding Fig. 1(d). From the AFM image the mixed surface of Si 7 x 7 and "8 x 8" are difficult to distinguish the difference.

(2) Formation of β-Si_3N_4 by IRE at higher temperature: When nitridation temperatures were higher than about 600 ^{o}C IRE of nitridation was occurred directly at the sur-

face of Si by the reaction between Si adatoms and ADS N atoms without conversion from amorphous to single crystal. Figure 4 shows RHEED patterns at 300 °C after heat treatment for nitridation temperatures at 464 and 628 °C and successive annealing at 875 °C. Tabe et al. pointed out the activity of Si adatoms on the surface above 500 °C on 7 x 7 [22, 23]. Figure 4 shows the results of IRE reaction at 818 °C. Si 7 x 7 pattern changed to “8 x 8” directly. Figure 5 shows RHEED patterns after the annealing and cooling down. When the nitridation time was completed initially

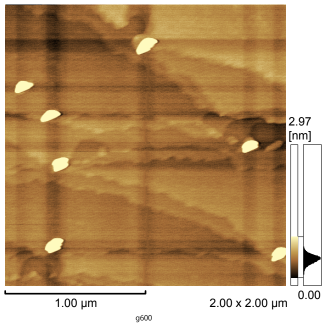

Figure 3 An AFM image of the surface of mixture of Si 7x7 and “8/3 x 8/3” β-Si_3N_4 after the annealing; nitridation time is 1 min at 300 °C corresponding Fig. 1(d).

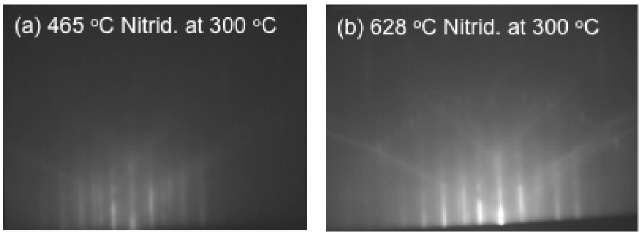

Figure 4 RHEED patterns obtained at nitridation temperature of 465 °C for 4 min (a) and 628 °C or 3 min (b) after heating up to anneal at 875°C and cool down to 300°C.

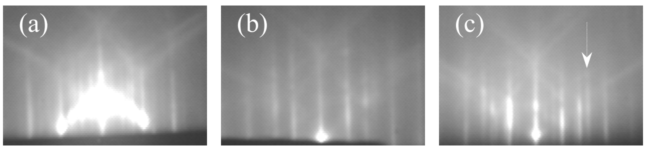

Figure 5 RHEED patterns cooled down to 300°C for nitridation times (a) 1 min, (b) 2 min, (c) 4 min. (a) Mixture of Si 7 x 7 and “8/3 x 8/3” The white arrow indicates the mixture of “8 x 8” pattern in “8/3 x 8/3” pattern.

for 1 min, Si 7 x 7 pattern was remained and observed together with “8/3 x 8/3” pattern. With increasing the nitridation time at 300 °C, the “8 x 8” patterns, which was shown by a white arrow, appeared in “8/3 x 8/3” pattern as shown in Fig. 5(c). These results showed that increasing of nitridation time leads to transform of surface reconstruction of β-Si_3N_4 from “8/3 x 8/3” structure to “8 x 8” structure.

3.2 Interface reaction epitaxy (IRE) AlN Interface reaction was occurred by the reaction between Al irradiated atoms and N atoms in the β-Si_3N_4 layer to form AlN layer. Because the melting point of Al is 660 °C, irradiation of Al to the surface of β-Si_3N_4 forms Al deposited film. Figure 6 shows RHEED patterns before and after 1 ML Al deposition on to the “8 x 8” surface reconstruction β-Si_3N_4 surface. Al was deposited at 464°C, and afterward substrate was heated up to 875°C. After the 1 ML Al deposition, the RHEED pattern of β-Si_3N_4 as shown in Fig. 6(a) became weak because of the Al metal deposition on the β-Si_3N_4 surface without reaction as shown in Fig. 6(b). With elevating the substrate temperature IRE took place and streak pattern of AlN was observed at 818°C because Al atoms reacted with N atoms in β-Si_3N_4 layer when substrate temperature exceeded the melting point of Al. Inside peak was Si substrate or β-Si_3N_4 whereas outside peak was AlN peaks (Fig. 6(c)). Finally, inside peak was disappeared during annealing at 875 °C, which meant only AlN was formed on the surface.

On the other hand, when Al was deposited on “8/3 x 8/3”, which is an incomplete nitridation phase and is a mixture of Si surface and β-Si_3N_4 formed at nitridation power of 500 W, the outside intensity of AlN RHEED pattern was weaker than that of inside peak and was dot pattern, which indicated 3D islands, as shown in Fig. 7(a). This result indicated that Al atoms reacted with Si atoms

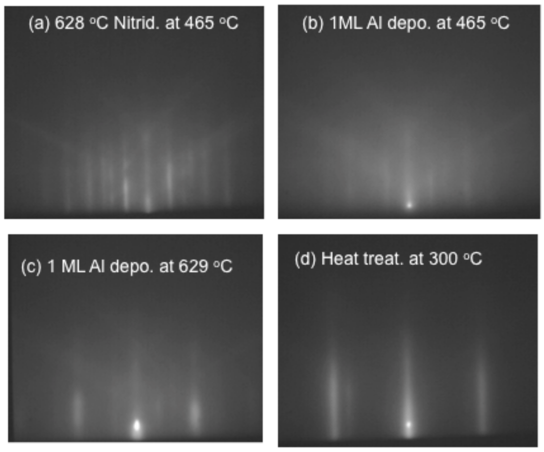

Figure 6 The evolution of RHEED pattern with elevating the substrate temperature after 1 ML Al deposition; (a) 0 ML (β-Si_3N_4) at 465 °C, (b) after 1ML Al deposition at 465 °C, (c) on heating to 875 °C observed at 628 °C and (d) after cooling down to 300 °C.

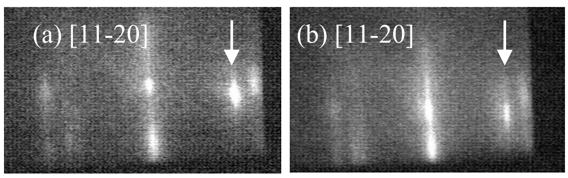

Figure 7 RHEED patterns of IRE-AlN on “8/3 x 8/3” structure as a function of the nitridation time at 300 °C and 500 W rf power; (a) 30 s and (b) 1 min. White arrow indicate inside peak.

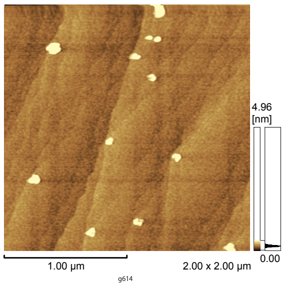

Figure 8

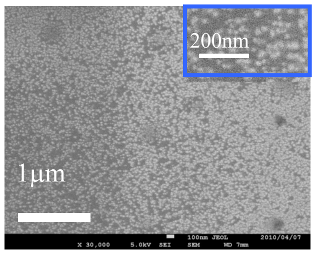

Figure 9

Figure 8 An AFM image of the surface of DBL corresponding to Fig. 6(d).

Figure 9 A SEM image of N polarity AlN film after KOH etching. Inside blue square is enlarged picture.

and Si islands were formed. When the nitridation time was increased to 1 min from 30 s (Fig. 7(b)), inside peak became streak pattern which indicate flat surface was formed, brighter than outside AlN peak.

3.3 Polarity of buffer AlN A 30nm buffer AlN on DBL structure was grown on Si(111) to evaluate the surface polarity of AlN film. As polarity of DBL film was affected by the surface reconstruction of β-Si_3N_4, the polarity of the grown 30 nm AlN buffer layer was the same one of DBL. When KOH etching of AlN grown on N-DBL AlN surface was conducted, many hexagonal islands were observed by SEM measurement as shown in Fig. 9. As a result, N polarity AlN film was grown on "8/3 x 8/3" structure. Al polarity AlN film was shown in Ref. [21] grown on Al polarity DBL grown on "8 x 8" structure. Comparing with IRE-AlN on "8 x 8" structure, from previous RHEED patterns, Al-Si bond is dominant rather than IRE-AlN on "8/3 x 8/3" and Al metal layer was assumed to form on the surface. As a result, Al deposition on the mixture of Si and "8/3 x 8/3" structure caused polarity inversion from Al to N one because this is equivalent of the case of AlN film was grown on Si using Al pre-deposition invented by Nikishin *et al.* [3].

4 Conclusions Polarity of AlN grown on β-Si_3N_4 was controlled by the selection of two surface structures of β-Si_3N_4, which is "8 x 8" and "8/3 x 8/3" structure formed by N+N* generated in rf-plasma cell. The "8 x 8" was fabricated at 830 ^{o}C whereas the "8/3 x 8/3" structure was fabricated by annealing of SiN_x formed at 300 ^{o}C. After the growth of AlN, N polarity AlN was grown on "8/3 x 8/3" structure whereas Al polarity AlN was grown on "8 x 8" structure.

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