Activity modulation MEE growth of 2H-AlN on Si(111) using double buffer layer grown by PA-MBE

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As a demonstration of the activity modulation migration enhanced epitaxy (AM-MEE) heteroepitaxial 2H-AlN thin films of 53.8 nm and 171.3 nm thickness on Si(111) on a double buffer layer (DBL) have been grown by the AM-MEE of plasma assisted molecular beam epitaxy (PA-MBE) method. It is a droplet free growth and an atomic layer epitaxy (ALE). The influence of the DBL, which was formed in a MBE chamber before the AM-MEE growth of 2H-AlN thin films on Si(111), was studied to improve the crystallinity of AlN films. For the growth of high quality 2H-AlN on Si(111), the optimization of growth of the DBL. The interface roughness of the DBL as a layer between two layers of AlN and Si,

AlN/DBL/Si was characterized by grazing incidence X-ray reflectivity (GIXR) and the surfaces were observed by AFM. Full width at half maximum (FWHM) of $\omega/2\theta$ for 53.8 nm and 171.3 nm thickness AlN (0002) films were 12.1 arcmin and 7.1 arcmin, respectively. AFM images showed droplet free growth after the AM-MEE and importance of the preparation of initial clean Si surface. Unifrom formation of DBL on a large size wafer of Si was available to use indirect exposure of N radical atoms. By increasing the thickness of the AlN the crystallinity was improved but the surface roughness of AlN did not depend on the thickness of the AlN films obtained by fitting results of GIXR curves.

1 Introduction

Mass production of the group III nitrides and their alloys on a large size Si wafer such as 150 or 200 mm diameter is current interest for clean energy world and energy saving society [1]. Charming points of Si substrate are easy preparation of large area wafer, inexpensive, having higher thermal conductivity than sapphire.

Plasma-assisted molecular beam epitaxy (PA-MBE) growth is a promising mass production method because of a cleaner method without using poisonous gases, lower growth temperature for device applications, and less materials consumption. MBE method is able to apply migration enhanced epitaxy (MEE) growth [2,3] using periodical supply of metal atoms and nitrogen atom flux. PA-MBE with rf nitrogen discharge, therefore, is the best way for Si substrates because it is a single and continuous MBE

growth system from a Si wafer to electronic or optical devices of group III nitrides.

Although hetero epitaxial growth for a Si substrate faces to a large lattice mismatch with the group III nitrides as highly lattice mismatched (HM^2) hetero-epitaxy [4], a concept of the coincidence site lattice (CSL) interface [5-7] could overcome the HM^2 problems. The concept of the CSL is an atomic site which is common to both lattices. In a CSL interface the two crystals "match", as an atom there is a lattice site in both crystals [5]. The ratios of the lattice parameters for β-Si$_3$N$_4$ ($a_{\beta\text{-Si3N4(0001)}} = 0.7586$ nm), 2H-AlN ($a_{\text{AlN(0001)}} = 0.3112$ nm) and 2H-GaN ($a_{\text{GaN(0001)}} = 0.3186$ nm) against Si ($a_{\text{Si(111)}} = 0.3840$ nm) are 2, 4/5 and 5/6, respectively. Interface between β-Si$_3$N$_4$(0001) and Si(111) coinsides with $a_{\beta\text{-Si3N4(0001)}} = 2a_{\text{Si(111)}}$. Interface between AlN(0001) and β-Si$_3$N$_4$(0001) coincides with $2a_{\beta\text{-Si3N4(0001)}} = 5\ a_{\text{AlN(0001)}}$. The CSL between AlN(0001), β-Si$_3$N$_4$(0001)

and Si(111) is an advantage of AlN growth from a Si sub-strate under a PA-MEB chamber. Double buffer layer (DBL) AlN(0001)/β-Si$_3$N$_4$(0001)/Si(111) was proposed by Wu etal. [8,9]. The DBL of AlN(0001)/β-Si$_3$N$_4$ /Si(111) is also proposed by the group of the present authors [10-13] using indirect exposure of N radical atoms.

Understanding of radio frequency inductively coupled plasma (rf-ICP) discharge, the present authors proposed an activity migration enhanced epitaxy (AM-MEE) growth method [13, 14]. The AM-MEE growth method supplies periodically the group III metal atoms, chemically active radical nitrogen atoms (N+N*), where N is the ground state atom and N* is the excited state atoms, and physically active excited nitrogen atom N$_2$* following Horikoshi et.al who proposed a MEE method by enhancing Ga surface migration under less As condition [2,3] by supplying a Ga and/or Al beam and an As beam alternately. The MEE or AM-MEE is one of atomic layer epitaxy (ALE) [15-20]. ALE is a method for producing high quality thin layers of single crystals and has been invented by Suntola [15] and studied extensively after 1984 [16].

In this report as a demonstration of the AM-MEE hetero-epitaxial hexagonal 2H-AlN growth on Si(111) has been perfoemed and grown films were characterized by X-ray diffraction (XRD), grazing incidence X-ray reflectivity (GIXR) and atomic fore micrscopy(AFM).

2 Experimental

2.1 PA-MBE system and characterization

A rf-ICP discharge of nitrogen gas is the most suitable way to produce chemically active nitrogen atoms to grow group III nitride semiconductors using PA-MBE. A VG80H MBE system, which was used to grow GaAs layers, was converted to a group III nitrides system by installing a rf - ICP (IRFS-501, Arios Co.) cell, which has an automaching box and a time sequence periodic power supply [10-14]. The rf -ICP discharge has two modes of discharge, one is high brightness (HB) discharge mode and the other is low brightness (LB) one. As (N+N*) atoms have long life time and are still active as adsorbed (ADS) atoms during the HB discharge, indirect irradiation of (N+N*) at behind of the shutter or a remote plasma position in a growth chamber was effective.

Substrates were mirror polished 2 or 3 inch wafers of n-type Si(111) with 0.02 Ωcm. Prior to growth, the surface of a 2- or 3-in Si(111) on-axis wafer was oxidized in HCl : H$_2$O : H$_2$O$_2$; 3 : 1 : 1 solution to form a thin SiO$_2$ layer on the Si(111) surface [21]. Temperature of a thermo couple of VG80H system was calibrated by the temperature of the phase transition of surface reconstruction od Si(111) 7x7 to 1x1 at 856 ^{o}C [22].

The surfaces were observed by AFM of SPM-9500 (Shimazu) and SPA400 (SI NannoTec.). Measurement of rocking curve of ω /2θ FWHM for AlN (0002) XRD peak was also performed by PANalytical MRD. The interface roughness of DBL as a layer between two layers of AlN

and Si was characterized by GIXR by reflectivity software of PANalytical.

2.2 Preparation of DBL
Using indirect irradiation of (N+N*) atoms, nitridation of Si(111) for DBL AlN(0001)/β-Si$_3$N$_4$(0001)/Si(111) growth was performed under at 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. Pre-deposition of 2 ML (mono layer) Al adatoms on a β -Si$_3$N$_4$ layer to form an DBL (1 ML of Al is 22.7 s irradiation of Al flux at 1050 ^{o}C of Al K-cell temperature).

2.3 AM-MEE
Using direct irradiation of chemically active (N+N*) atoms, physically active N$_2$*, and the group III metal atoms periodically AM-MEE was performed controlling time sequences of metal K-cells and nitrogen source shutters as shown in Fig. 1 and Fig. 2. Time sequence of the duration of the Al or Ga cells shutter and N source shutter operation, the duration of the HB mode and the LB mode are shown in Fig. 1. Within one period T one ML was grown as ALE. Using mode change of rf discharge and shutter operation AM-MEE was possible. Controlling exposure times of chemically active N radical
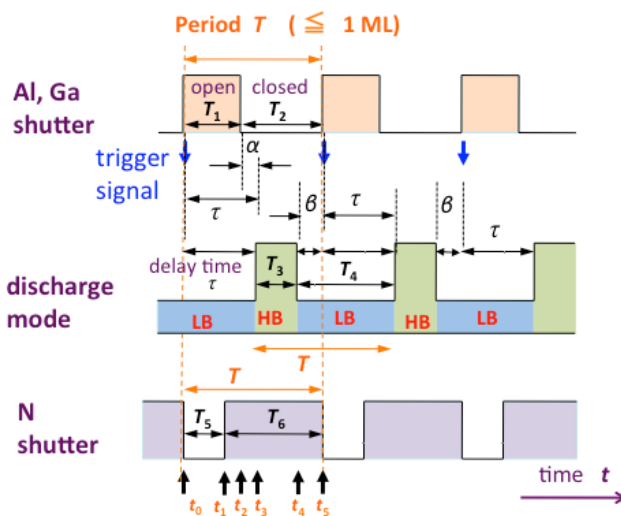

Figure 1 Time sequence of shutter operation of AM-MEE, where T_1, T_2, T_3, T_4, T_5, T_6, α, β, and τ are the duration of the Al or Ga shutter opening, the duration of the Al or Ga shutter closing, the duration of the HB mode, the duration of the LB mode, the duration of the N shutter closing, the duration of the N shutter opening, the duration of migration of Al or Ga atoms when the N shutter is open, the duration of cleaning of Al or Ga atoms when the N shutter is open, the delay time of starting the HB mode after the start of Al of Ga irradiation, respectively. One period $T = T_1 + T_2 = T_3 + T_4 = T_5 + T_6$ is controlled by group III cells and $T_3 + T_4$ is controlled by a rf-ICP discharge system. The migration time of Al or Ga atoms and the duration of removal excess Al or Ga atoms are μ and β, respectively [13].
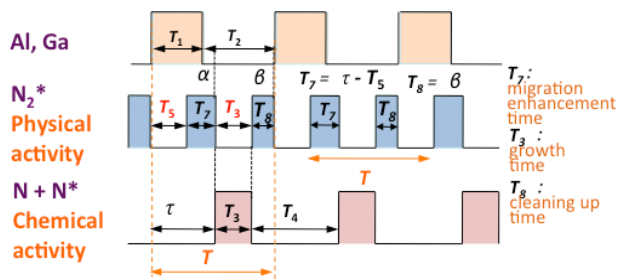
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Figure 2 Time sequence of irradiation flux of AM-MEE, where T_1, T_2, T_3, T_4, T_5, T_6, α, β, and τ are the same as in Fig. 1. Chemical activity modulation: T_3, T_4 are the duration of irradiating (N+N*), the duration of no (N+N*) flux. Physical activity modulation: T_7, T_8 are the duration of irradiating N_2*, the duration of no N_2* irradiation.

atoms (N+N*) and physically active excited nitrogen molecules N_2* , the migration time of Al or Ga atoms and the duration of removal time of excess Al or Ga atoms are μ and β, respectively are shown in Fig. 2.

Under conditions of T_1, T_2, T_3, T_4, T_5, T_6, T_7, T_8 , α, β, τ with 1, 2, 1, 2, 0, 3, 1, 1, 0, 1, 1 s respectively the growth of 60 nm and 200 nm desinged thickness of AlN, were performed by repeating 600 and 2000 cycles of a 3 s period using the above mentioned experimental conditions.

3 Results and discussion

3.1 AFM observation Initial substrate, Si surface is very important for epitaxial growth. Heating up Si substrate to 870 ^{o}C of the 1x1 surface reconstruction of Si(111) and keeping at this temperature for about 5 min to remove the SiO_2 layer completely in a high-vacuum MBE chamber the Si surface became clean. An AFM image at room temperature as shown in Fig. 3 shows that white dots were observed at corners of step bunching of Si(111) surface. White dots in the circles may be SiC particles. Forming mechanism of bunching step edges of Si surface and white dots, which were observed in Fig. 3, is not clear in this stage. White dots free Si surface is necessary to realize for high quality AlN films on Si.
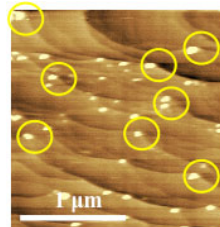

Figure 3 AFM image of Si surface. White dots were observed at corners of bunching steps. White dots in the circles may be SiC particles.

Surfaces of AlN film of 53.8 nm and 171.3 nm grown by AM-MEE on the DBL are shown in Fig. 4(a) and (b), respectively. Black dots in circles correspond to white dots at the corners of bunching steps as shown in Fig. 3. Even Al

rich condition of PA-MBE growth was performed no Al droplets were observed as shown in Fig. 4. A droplet free growth was proved for AM-MEE growth. It is a superior point of AM-MEE to grow high quality films under metal rich condition. In order to improve the crystal quality white dots free Si surface preparation before nitridation in one of issue should be solved.
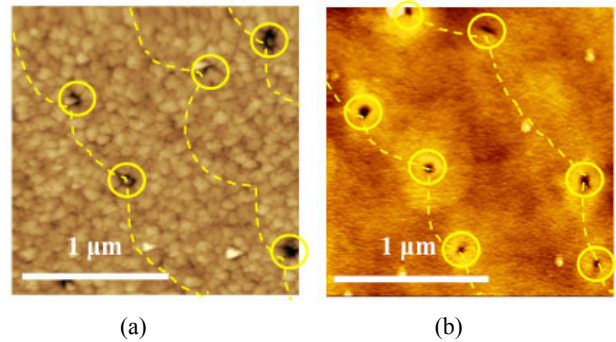

(a)   (b)

Figure 4 AFM images of AlN surface. Black dots in circles are formed on the white dots at the corners of bunching steps as shown in Fig. 3. The thickness of AlN for (a) and (b) are 53.8 and 171.3 nm, respectively.

3.2 XRD $\omega/2\theta$ measurement
Figure 5 plots the X-ray diffraction from 2θ between 10 to 160°. FWHM of Si and AlN peaks measured for 53.8 nm and 171.3 nm AlN films on Si are listed in Table 1. The values of 53.8 nm and 171.3 nm are obtained by GIXR, which will be shown in the next section after reflectivity analysis. Extinction Si(222) peak is appeared in Fig. 5. FWHM of $\omega/2\theta$ curve of AlN(0002) are 0.117 deg (7.1 arcmin) and 0.202 deg (12.1 arcmin) for 53.8 and 171.3 nm thickness, respectively. Increasing thickness from
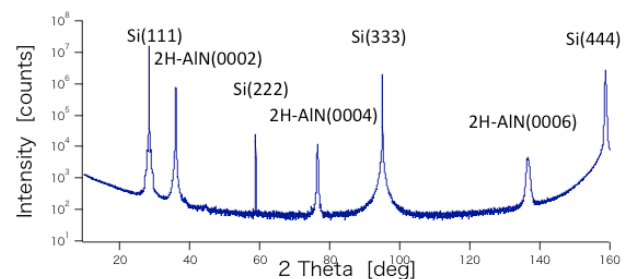

Figure 5 XRD pattern of $\omega/2\theta$ scan of AM-MEE grown AlN.

Table 1 FWHM values of ω /2θ scan in Fig. 5

Peak	FWHM 60 nm [deg]	FWHM 200 nm [deg]
Si(111)	0.06159	0.06035
AlN(0002)	0.20177	0.1166
Si(222)	0.06085	0.0686
AlN(0004)	0.31471	0.27608
Si(333)	0.07311	0.07441
AlN(0006)	0.92242	0.87635
Si(444)	0.20957	0.2176

57.8 to 171.3 nm the FWHM value was decreased. These FWHM values are good value for thin film AlN on Si. FWHM of thicker films will be expected to be smaller than the present samples.

3.3 GIXR observation GIXR reflectivity analysis for heteroepitaxial grown films of AlN/DBL/Si(111) are shown in Fig. 6(a) and (b) for 60 and 200 nm designed thickness, respectively. Using a three layer model of GIXR, which consisted of three layers of AlN, DBL and Si as shown in Fig. 6 fitting results by a software of reflectivity, PANalytical are shown in Fig. 6(a) and (b) too. True thickness are 53.8 and 171.3 nm, respectively. The surface roughness for 53.8 and 171.3 nm samples are 1.4 and 1.5 nm, respectively. The roughness of DBL are 1.4 and 1.3 for for 53.8 and 171.3 nm samples, respectively.
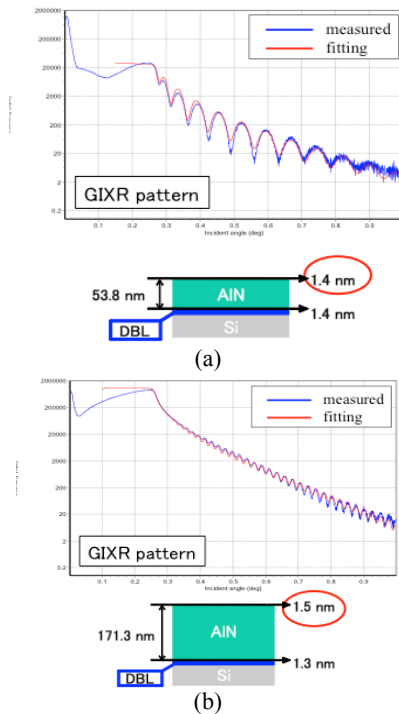

Figure 6 GIXR patterns for (a) 60 nm（53.8 nm by fitting) and (b) 200 nm (171.3 nm by fitting) AlN templates and results of simulation by a PANalytical software of reflectivity.

4 Conclusion

AM-MEE growth method was demonstrated using rf-ICP discharge cell for nitrogen source as an ALE method. DBL prepared by indirect exposure of N radical atoms worked as a good buffer layer between AlN and Si. This AM-MEE PA-MBE growth system, which uses both indirect irradiation and direct irradiation of nitrogen atoms, operates as a droplet free MBE system to realize a growth condition of metal rich condition for high quality epitaxial film growth. It is a single-MBE-growth system to prepare from a Si wafer to group III nitrides devices in a chamber and is expected to use group III nitrides on a large Si wafer.

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