Low temperature growth of GaN on sapphire using remote plasma enhanced-ultrahigh vacuum chemical vapor deposition

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A ultrahigh vacuum chemical vapor deposition(UHVCVD)/metalorganic chemical vapor deposition(MOMBE) system equipped with a radio frequency(RF)-plasma cell was employed to grow GaN layer on the sapphire at a low temperature. The x-ray photoelectron spectroscopy analysis of nitrogen composition on the nitridated sapphire surface indicated that a nitridation process is mostly affected by the RF power at low temperature. Atomic force microscope images of nitridated surface showed the protrusion density on the nitridated sapphire is dependent on the nitridation temperature. The crystallinity of GaN grown at 450 ℃ was found to be much improved when the sapphire was nitridated at low temperature prior to the GaN layer growth. Moreover, a strong photoluminescence spectrum of GaN grown by UHVCVD/MOMBE with a rf-nitrogen plasma was observed for the first time at room temperature.

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1. Introduction

Recently the interest for GaN and related materials has increased because those are recognized as promising materials for blue-violet light emitting diodes (LED) and laser diodes (LD). A GaN epitaxial layer has been grown by heteroepitaxy which causes some problems due to the difference in lattice parameters, thermal expansion coefficients, and crystal structures between the sapphire substrate and the GaN epitaxial layer. The quality of the GaN epitaxial layer was greatly improved with the two-step growth method. More improvements in the electrical, optical properties and surface morphology of the GaN epitaxial layer were realized with the nitridation of the sapphire surface prior to the nucleation layer growth[1-3]. But those properties were degraded probably due to the protrusions formed on the sapphire surface when the nitridation time was too long[1-3]. Therefore it is important to find out a way to nitridate the sapphire surface without those protrusions even when the nitridation time is fairly long.

GaN epitaxial layer has been grown by MOCVD at a temperature as high as 1000 ℃, where many problems have been still remained unsolved. At high temperature, equilibrium vapor pressure of nitrogen is so high that the desorption of nitrogen atoms on the growing GaN surface results in the high concentration of nitrogen vacancies which is reduced mostly by supplying an excessive nitrogen precursors. It was also found that the In incorporation in InGaN active layer is decreased with the increase of growing temperature due to the temperature dependence of In desorption rate[4,5]. Moreover, a degradation of interfaces in quantum well structures is a problem when these structures are grown at high temperature. Therefore it is necessary to decrease the growth temperature to avoid those problems caused by the high temperature process. Recently, ultrahigh vacuum chemical vapor deposition(UHVCVD)/metalorganic molecular beam epitaxy (MOMBE) has been employed in the growth of GaN due to its superiority to MOCVD such as low impurity concentration, the precise control of interfacial structure and the low-temperature growth. Despite these advantages, the growth and characteristics of GaN by UHVCVD/MOMBE is not fully understood, since only a few studies have been reported [6-9].

In this study, we have attempted to achieve a nitridation of the sapphire surface without protrusions by decreasing the nitridation temperature. It was found that the GaN overlayer grown on this nitridated surface at a temperature as low as 450 ℃ had a wurtzite structure and its crystallinity was improved as the nitridation time increased. It was also found that the lateral growth of GaN overlayer was promoted by the nitridation of sapphire substrate. We present results of UHVCVD/MOMBE growth of wurtzite GaN thin films at relatively lower temperature and a photoluminescence spectrum which was measured for the first time at room temperature in this study.

2. Experimental

A remote plasma enhanced UHVCVD/MOMBE system used in this experiment was built to investigate the growth of a high quality GaN epitaxial layer at low temperatures. Reactor and loadlock chambers were evacuated by two turbo molecular pumps to obtain an ultrahigh vacuum pressure of 10^{-10} torr. Reactive nitrogen species were produced by cracking the nitrogen gas in a radio frequency-inductively coupled plasma(RF-ICP) cracking cell attached to the top of the reactor. Triethylgallium(TEGa) was carried to the substrate by nitrogen carrier gas. The distance between the plasma source and the substrate could be varied by a sample manipulator.

The sapphire (0001) substrate was cleaned using organic solvents (trichloroethylene, acetone and methanol) in an ultrasonic cleaner, etched with acid (phosphoric acid:sulfuric acid=1:3), rinsed with DI water, dried with 6-nine purity nitrogen gas, and loaded into the reactor. To investigate the nitridation of sapphire surface, a sapphire (0001) was exposed to the activated nitrogen species under various conditions such as RF power, substrate temperature, N_2 flow rate, process pressure, nitridation time, and distance of plasma source-to-substrate. During the cooling process after nitridation, the reactor was maintained under a high pressure of nitrogen to reduce the dissociation of nitrogen on the nitridated surface. The nitridated sapphire surface was then investigated with x-ray photoelectron spectroscopy(XPS), atomic force microscope(AFM), and x-ray specular reflectivity.

A GaN overlayer was grown on the bare and nitridated sapphire (0001) substrates to understand the effect of nitridation on the GaN growth. The crystal structure of GaN and the in-plane epitaxial relationship between GaN and the substrate were investigated by an x-ray in-plane momentum transfer study.

A high quality GaN epilayer was grown to investigate the crystallinity and optical properties. Prior to deposition, the substrate was heated at about 665℃ and exposed to 400 W nitrogen plasma for 15 min in order to clean the surface and produce a thin nitridated layer which acts as a nucleation layer. An optimum growth condition was determined by varying the rf power and the TEGa flux at a nitrogen flux of 1 sccm. The growth of GaN thin film proceeded at 650℃ with a growth rate of 0.17㎛/h. The crystallinity of the GaN overlayer was measured by taking an x-ray $\theta/2\theta$ scan and a θ-rocking curve. The surface morphology of the GaN overlayer was investigated by AFM. The optical property of GaN thin films was studied by photoluminescence (PL) at room temperature.

3. Results and discussion

The sapphire surface exposed to the activated nitrogen species was analyzed by XPS to investigate compositional changes under the various nitridation conditions. Fig. 1 shows that the main peak of the N_{1s} photoemission is located at 397.2 eV which is a binding energy of the AlN[10,11]. This indicates that a AlN layer is mostly formed on the sapphire surface. Two peaks at the higher binding energy side suggest that aluminum oxide species are also formed in the nitridated layer. Fig. 2 shows the intensity oscillations of the x-ray specular reflectivity obtained from the nitridated layer on the sapphire surface. The data were obtained in q_z direction while $q_{\parallel}$ was kept at zero, where q_z and $q_{\parallel}$ are the out-of-plane and the in-plane wave vector transfer respectively. The thickness of the nitridated layer was calculated using the equation $2\pi/\delta q_z$[12,13], where δq_z is the period of the intensity oscillations. The thickness of the nitridated layer was calculated to be less than 6 nm and the thickness was increased with nitridation time. The thickness of the AlN layer formed on the sapphire surface was also reported to be less than 10 nm by TEM[3] and XPS depth profile[14].

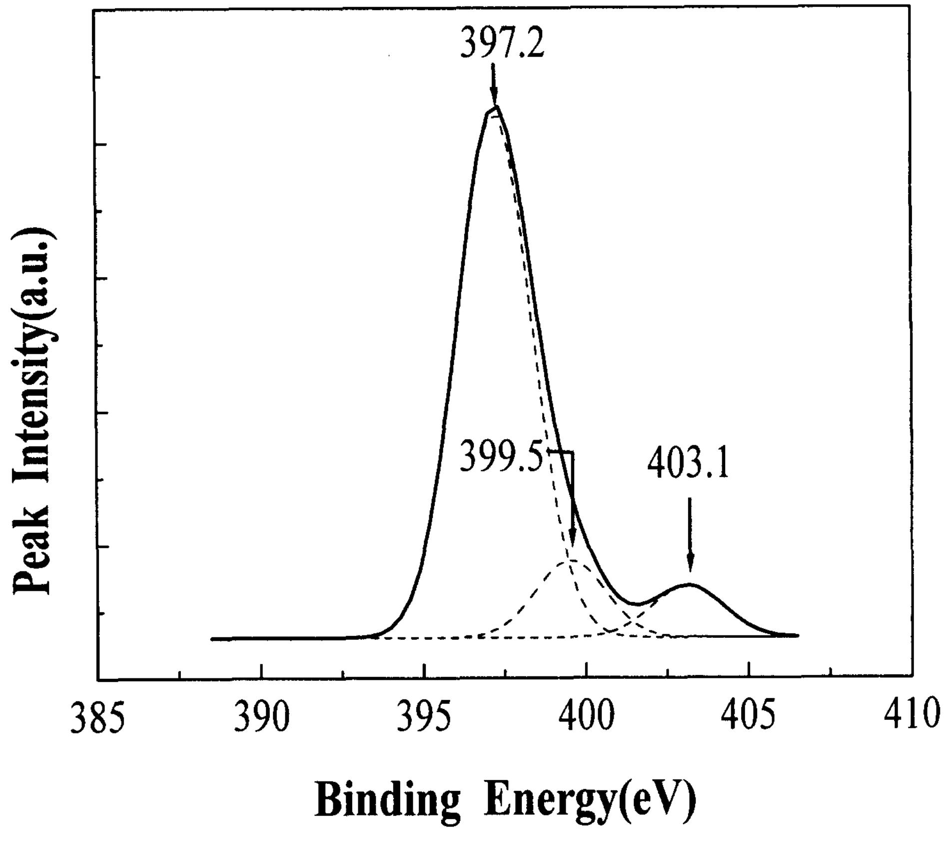


Fig. 1. N_{1s} XPS spectrum from a nitridated sapphire surface.

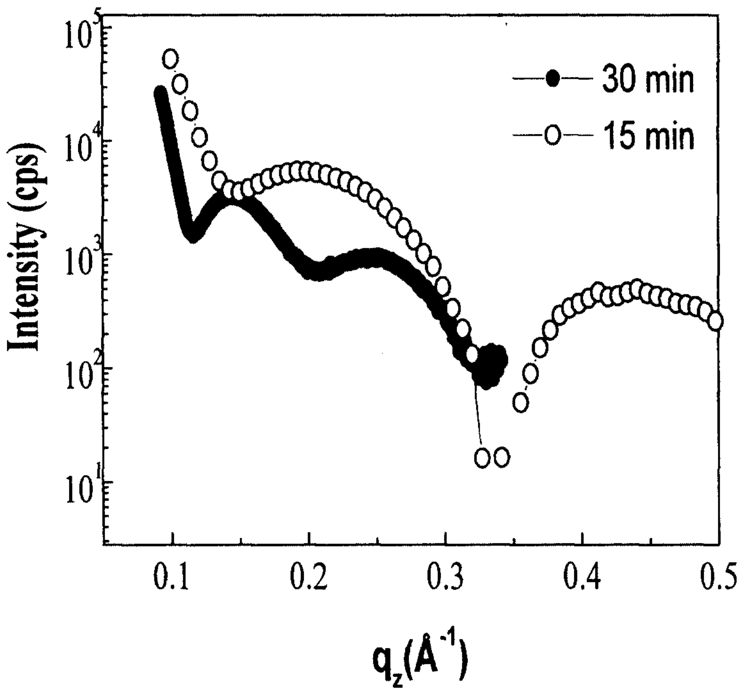
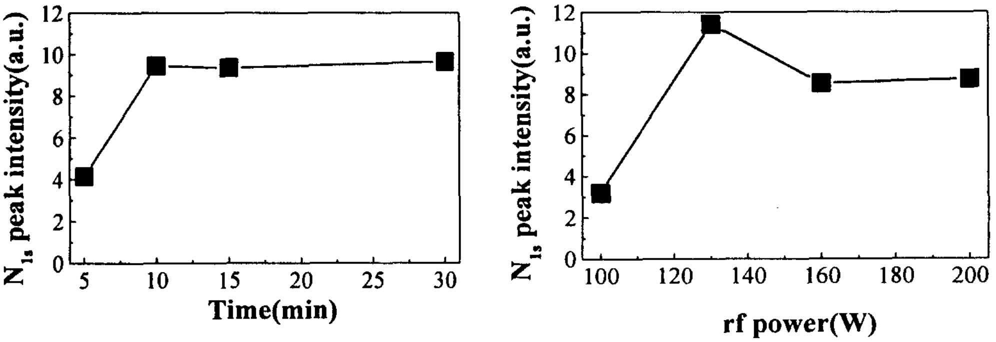


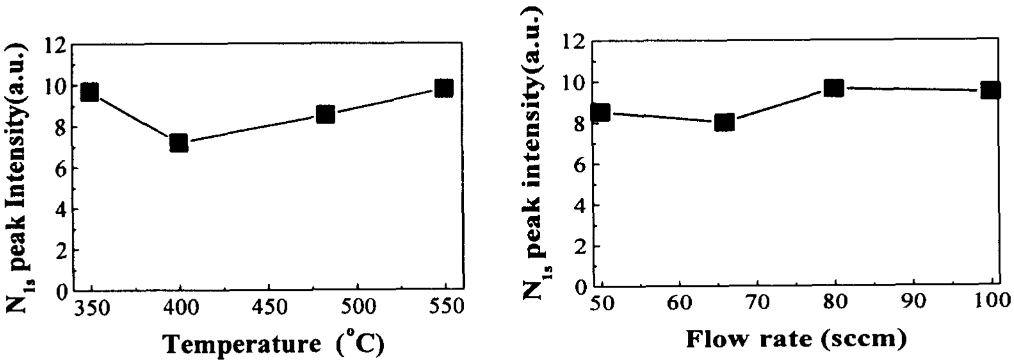
Fig. 2. X-ray specular reflectivity as a function of q_z.

Fig. 3 shows the changes in N_{1s} peak intensity as a function of various nitridation conditions, where the intensity represents the nitrogen concentration on the surface of substrate. Fig. 3(a) shows that N_{1s} peak intensity increases with nitridation time and then it is saturated at a certain value, which was also reported by other group[3,10]. N_{1s} peak intensity is also dependent on the RF power and the highest intensity of N_{1s} peak was obtained at a RF power of 130 W as shown in Fig. 3(b). This indicates that the generation of reactive nitrogen species in the plasma cell is greatly dependent on the RF power, producing the maximum amount of reactive nitrogen species at a RF power of 130 W. Furthermore it was observed that nitrogen composition of the nitridated substrate surface was not significantly affected by N_2 flow rate and substrate temperature as shown in Figs. 3 (c) and (d) respectively. The results shown in Fig. 3(d) suggest that the effective flux of reactive nitrogen species at the growth front increases with increasing the N_2 flow rate in the plasma cell but it will be decreased due to the scattering of reactive nitrogen species in the growth chamber. In fact, the mean free path of reactive species is decreased with the pressure in reactor because the pressure increases with increasing the flow rate of nitrogen gas. This was evidenced by the fact that the N_{1s} peak intensity was markedly decreased with increasing the reactor pressure when the N_2 flow rate was maintained constant. Therefore the N_2 flow rate will not change the nitrogen composition of the nitridated surface since the amount of activated nitrogen species arriving on the surface is affected by the reactor pressure as well as the amount of nitrogen gas which flows into the plasma cell and reactor. It was also oberved that the N_{1s} peak intensity is decreased by a factor of 6 with an increase in source-to-substrate distance by a factor of 2. This suggests that the amount of activated nitrogen species arriving on the surface of sapphire substrate is critically affected by the distance of plasma source-to-substrate since the activated nitrogen species may be deactivated by many collisions with other neutral nitrogen molecules. Fig. 3(c) shows that the nitridation is not significantly affected by the substrate temperature because the bonding energy of nitrogen molecule is too large for nitrogen molecules to be thermally dissociated on the surface. Taferner et al.[15] have studied the nitridation process by exposing the sapphire surface to ECR plasma of nitrogen at various temperatures. At the range of 200-600 ℃, the surface was nitridated irrespective of the substrate temperature but nitridation was not observed at temperatures above 600 ℃. This was contrary to the nitridation process performed by MOCVD, where nitridation of sapphire surface occured only at a temperature higher than 800 ℃[16]. These results can be expected since the activated nitrogen species are supplied from the plasma in the plasma-based nitridation process but ammonia is thermally decomposed on the surface in the MOCVD process. Therefore it was possible to nitridate the sapphire surface even at low temperatures in this study.



(a) nitridation time

(b) RF power



(c) nitridation temperature

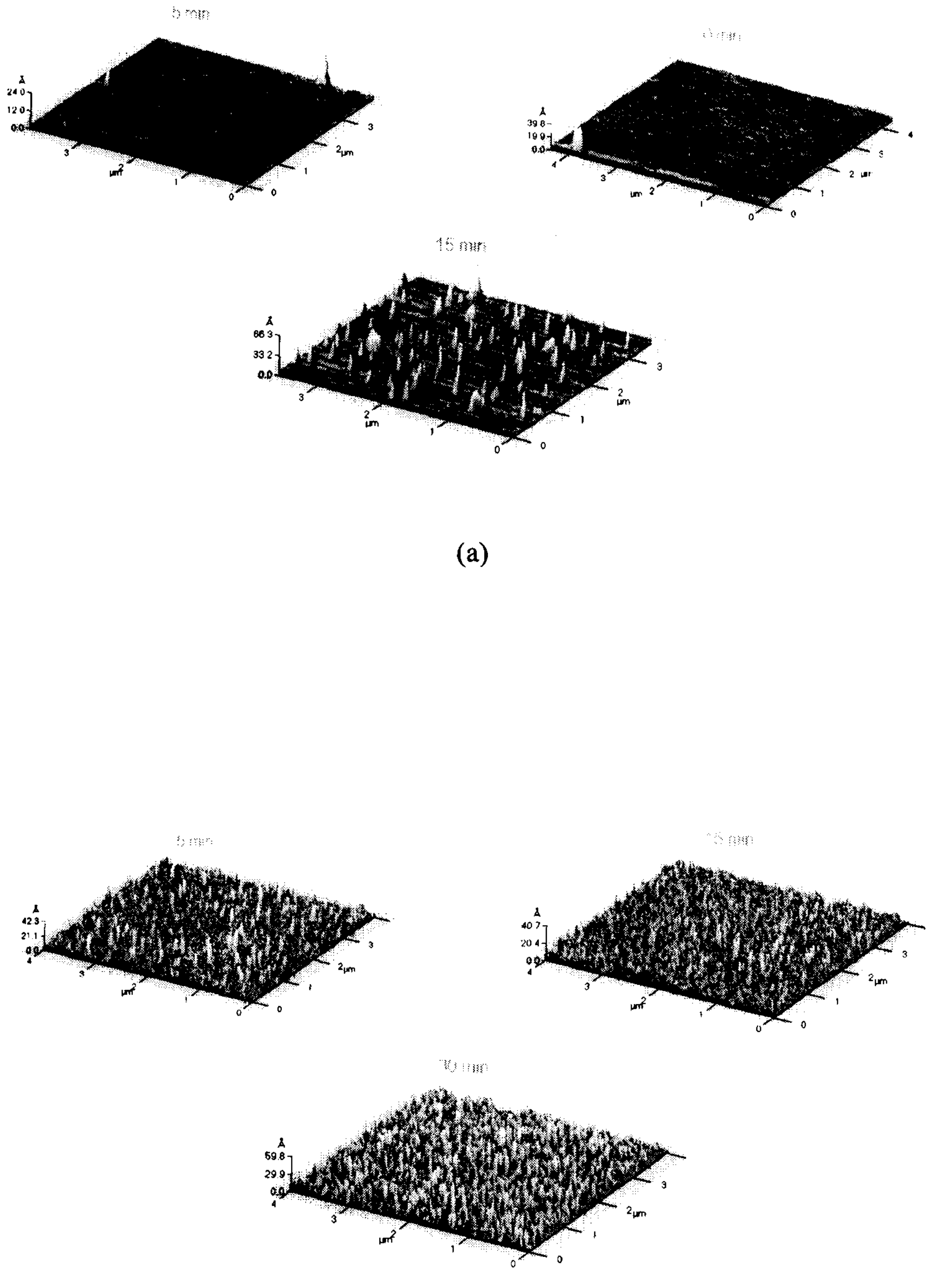
(d) N_2 flow rate

Fig. 3. N_{1s} peak intensity as a function of nitridation conditions;

Figure 4 shows that the protrusion density on the nitridated sapphire surface was sensitively dependent on the substrate temperature. As shown in Fig. 4(a), the surface of sapphire nitridated at 400 ℃ for the first 10 min was smooth and then the density of protrusion increased with the nitridation time longer than 10 min. At 450 ℃, a relatively high density of protrusion was observed even when the nitridation time was only 5 min as shown in Fig. 4(b). However protrusions were not observed at 300 ℃ when the nitridation time was increased up to 30 min. Uchida et al.[3] suggested that the protrusions are formed to relax the elastic strain energy stored in the nitridated layer due to the lattice mismatch between the nitridated layer and the sapphire substrate. However, the effect of the substrate temperature on the protrusion density was not mentioned in their work. But this study shows that the protrusion density is critically dependent on the substrate temperature as shown in Fig. 4. The formation of such protrusions could be explained by the stress-enhanced migration[3] which can also be greatly enhanced by thermal energy since the atomic migration is a thermally activated process. Therefore a nitridated surface without protrusions can be obtained when the nitridation temperature is as low as 300 ℃ since a supply of thermal energy for atomic migration on the nitridated surface is too small to assist the formation of such protrusions at this low temperature.

Figure 5 shows that a GaN overlayer with wurtzite structure was successfully grown even at a low temperature of 450 ℃. Three peaks shown in Fig. 5(a) were identified as peaks from the GaN (0002) plane, sapphire (0006) plane, and GaN (0004) plane. Lattice spacing of the GaN basal plane was calculated to be 5.18 Å, which agrees well with the result in other study[17]. Peaks from GaN asymmetry plane were observed at every 60° as shown in Fig. 5(b), indicating that the GaN overlayer has a wurtzite structure which has a six-fold symmetry. It also shows that the peaks from GaN and sapphire substrate are alternately observed at intervals of 30 °, indicating that the GaN lattice is rotated by 30 °(in-plane) with respect to the sapphire substrate. This result also agrees well with other results[18-20]. The full width at half maximum of the θ-rocking curve decreased with the nitridation time, indicating that the alignment of c-axis in the GaN overlayer is improved with the nitridation time. The AFM image of GaN overlayer showed that a GaN layer grown on nitridated sapphire has large facet-shaped islands on the surface while small GaN islands are formed on bare sapphire surface, suggesting that the lateral motion of adatoms is enhanced by the nitridation process. It is generally believed that the atomic mobility on the surface can be increased by supplying enough thermal energy to overcome the activation energy for surface migration. But in this study, it is suggested that the activation energy for adatom migration is decreased on the surface by nitridation process, as a result surface migration of adatom is enhanced even at low GaN growth temperature.

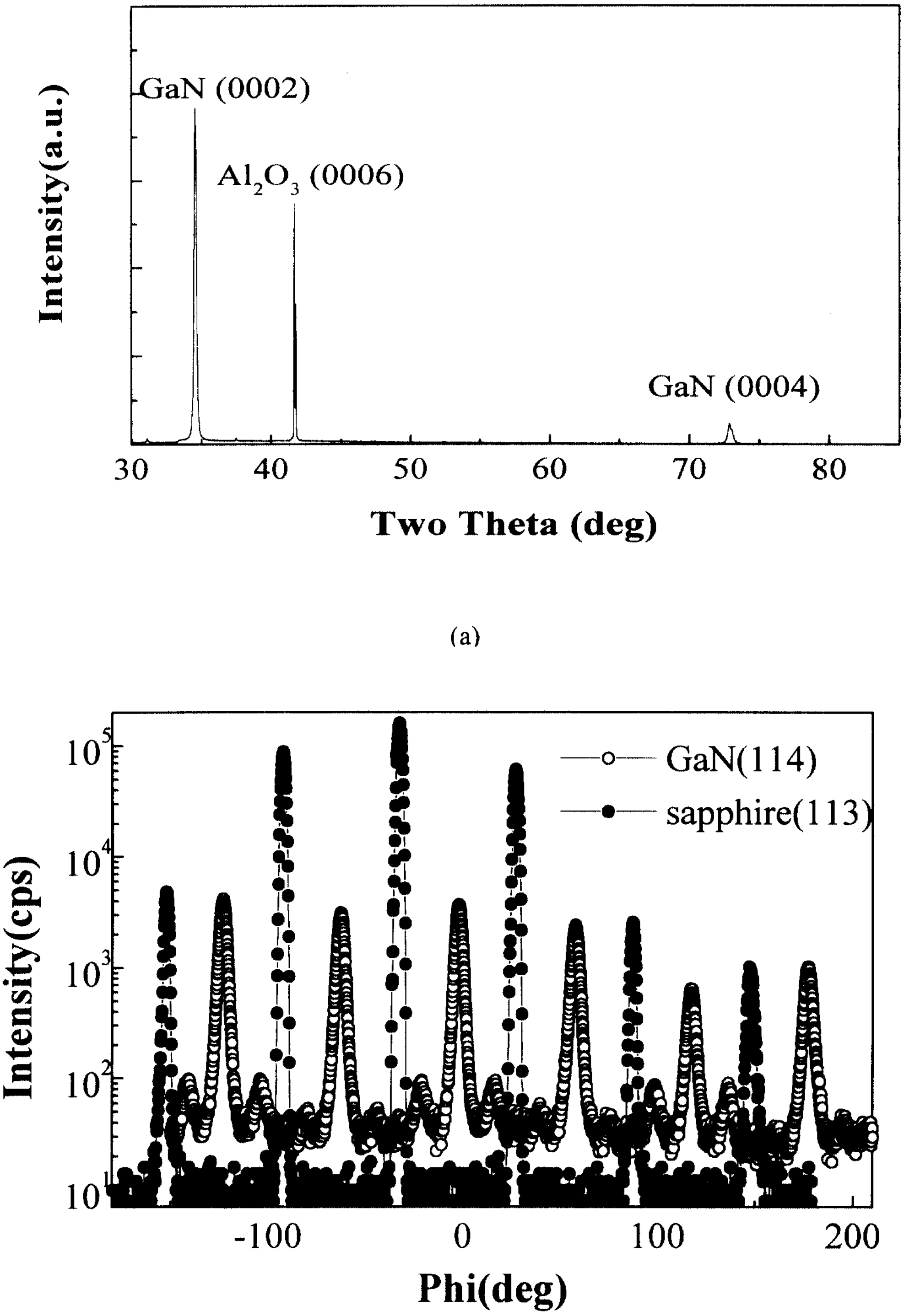
The nitrogen rf-plasma was characterized by an optical emission spectroscopy to optimize the atomic nitrogen concentration in the plasma source. All of the optical emission



(a)

(b)

Fig. 4. AFM images of sapphire surfaces which were nitridated at (a) 400 ℃ and (b) 450 ℃.



(a)

(b)

Fig. 5. (a) X-ray θ/2θ scan, (b) X-ray in-plane momentum transfer of the GaN and sapphire substrate.

spectra revealed that a significant amount of atomic nitrogen, which emits near 740, 820, and 860 nm, is present in the plasma with a very small amount of ionic species. A measurement of atomic nitrogen emission intensity as a function of N_2 flow rate showed that the emission intensity of atomic nitrogen decreases as a nitrogen flow increases. As power was raised from 300 W to 500 W for a given nitrogen flow of 1 sccm, the atomic nitrogen intensity increased by a factor of two.

The effect of increasing rf power on the crystal structure and optical property of GaN film is shown in Figs. 6 and 7. These results show that the properties of GaN films are strongly influenced by rf power. A GaN layer grown under very high flux of atomic nitrogen reveals the improved crystallinty, especially, and coherency length in the film. This also shows the increase in the intensity ratio of I_b/I_d between band-edge luminescence I_b and deep level luminescence I_d. Considering the report that a yellow luminescence is closely related with the defects, such as disloction and N vacancy[21], the increase in I_b/I_d can be ascribed to the compression of N vacancy in GaN films due to surplus of N atoms, which also contributes to the crystal quality, as shown in Fig. 6. These results clearly indicate that the growth of GaN is limited by the amount of atomic nitrogen.

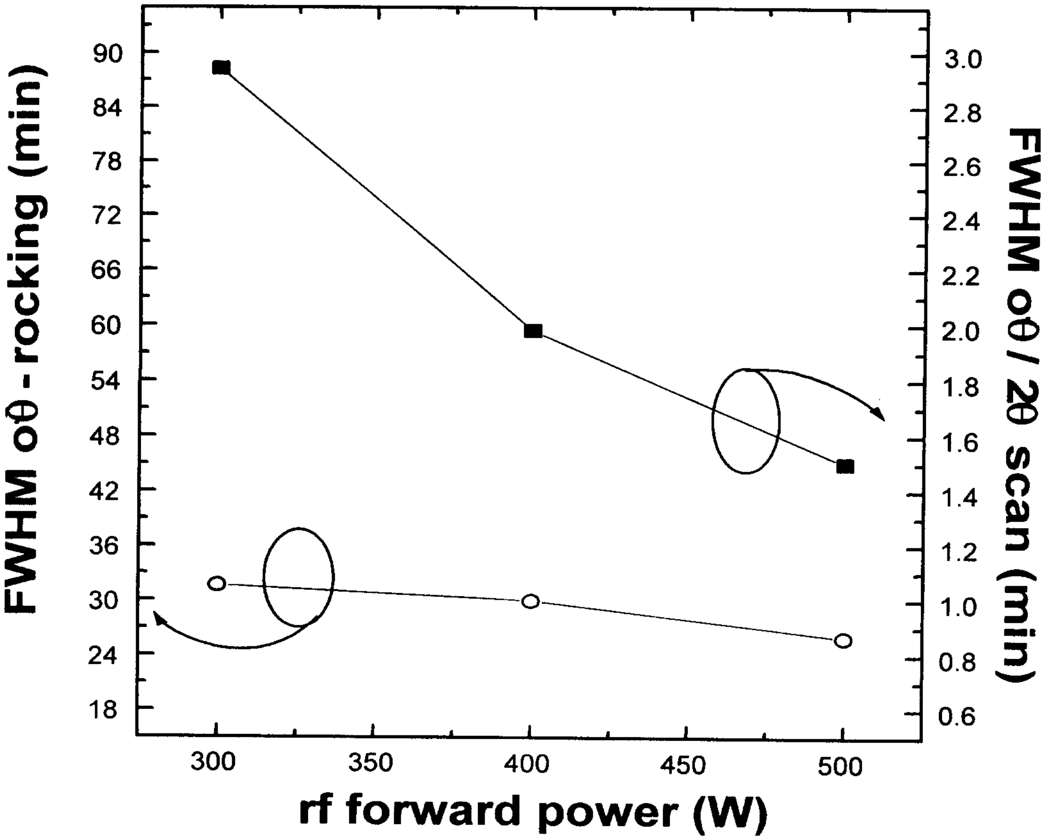


Fig. 6. The variation in FWHM of GaN grown with rf power changes

(a) FWHM of θ -rocking curve (b) FWHM of $\theta/2\theta$ scan.

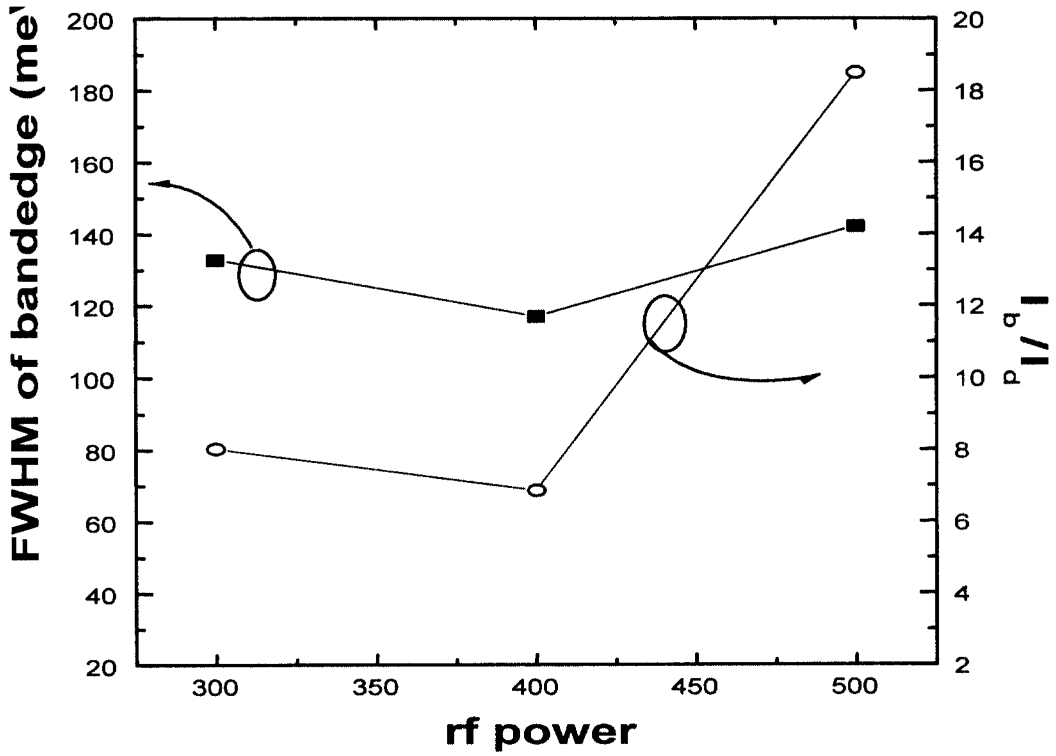


Fig. 7. The variation in optical properties of GaN grown with rf power changes.

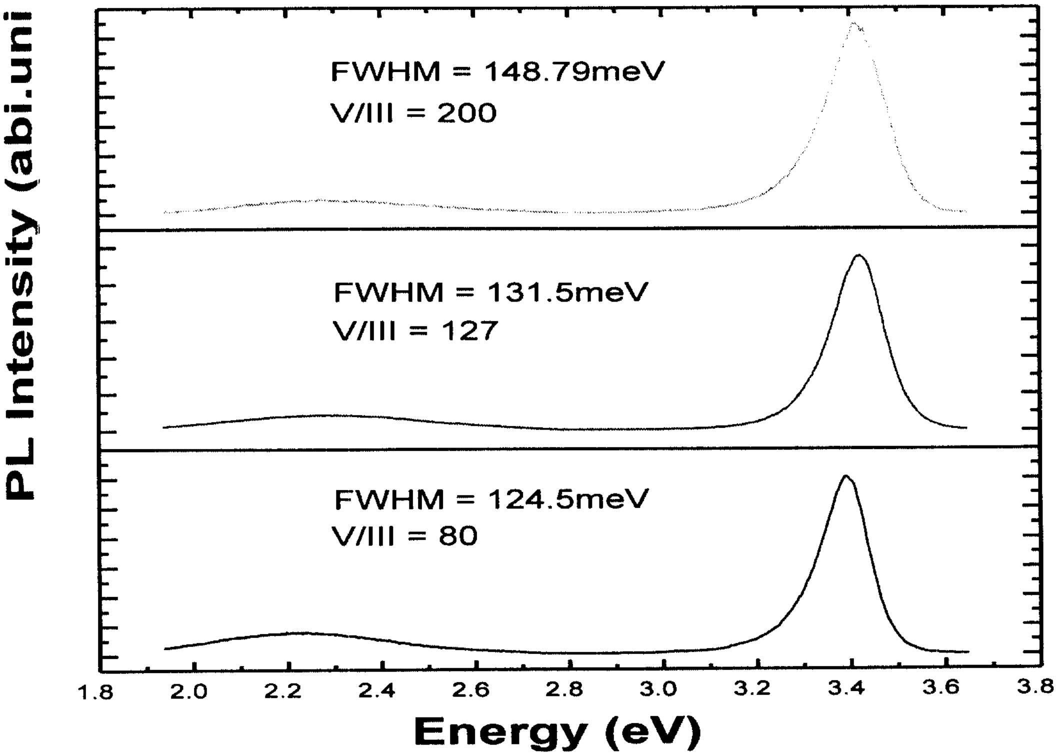


Fig. 8. The variation in optical properties of GaN grown with V/III ratio changes.

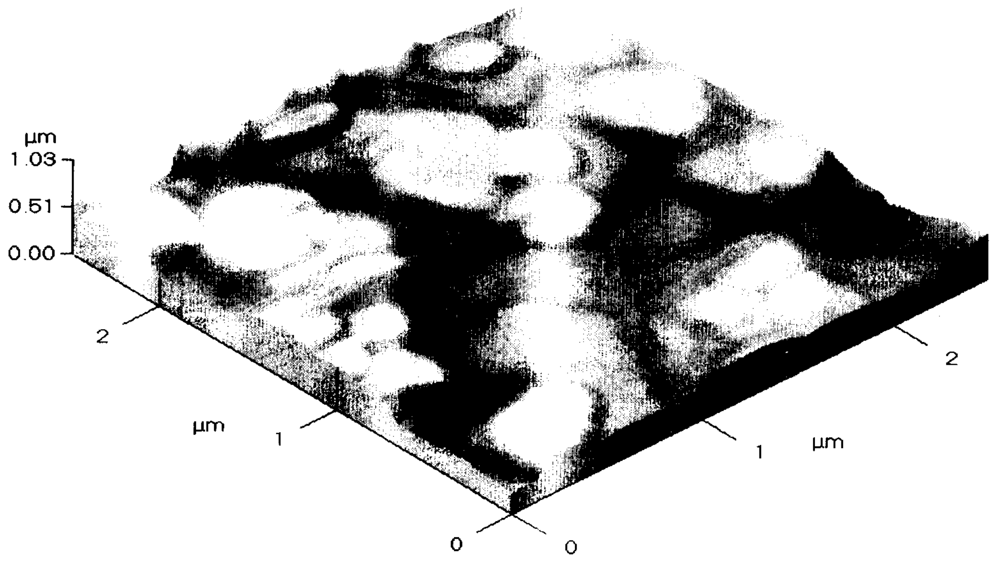


Fig. 9. A representative AFM image of GaN layers grown at 650℃ on sapphire substrate nitridated for 15 min.

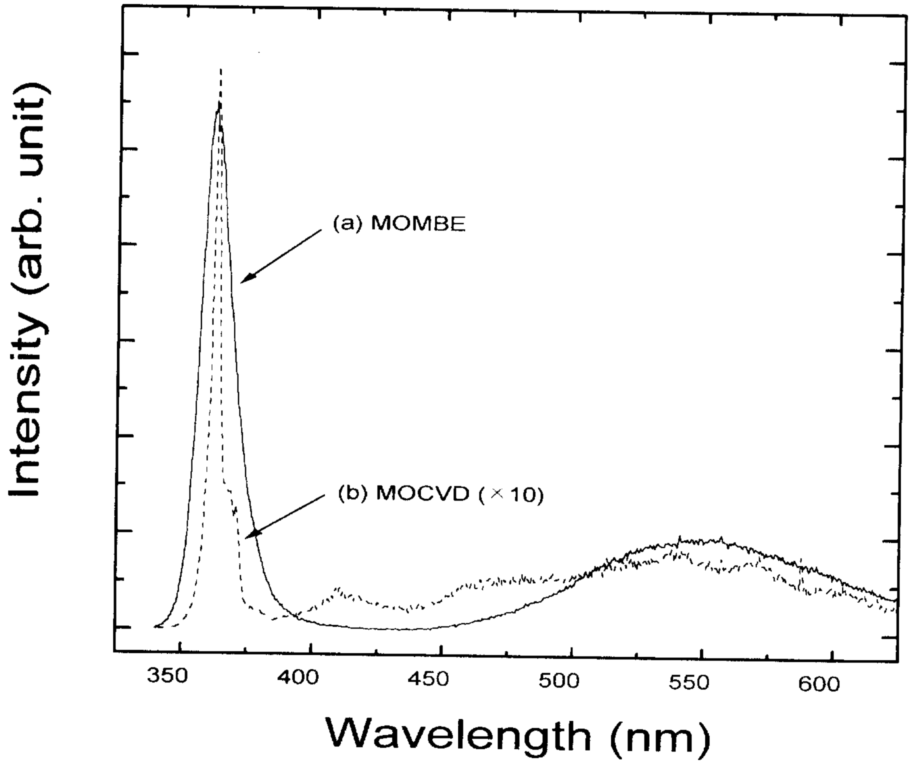


Fig. 10. Room-temperature photoluminescence spectra of GaN samples (a) a UHVCVD/MOMBE-grown GaN epilayer at 650℃ (b) a MOCVD-grown GaN epilayer at 1050℃.

The relation of optical property with V/III ratio is shown in Fig. 8. The V/III ratio was changed from 80 to 200 by varying the TEGa flow. When GaN film was grown with a low V/III flux ratio of 80, I_b/I_d increased, resulting in a poor crystal quality. This may be attributed to the low diffusion rate of Ga at a low growth temperature under high TEGa flux and also to a poor stoichiometry between Ga and N causing Ga and N vacancies. Such a kinetic limitation of Ga or N atoms on the substrate can also be ascertained with hexagonal structures on the surface shown in Fig. 7. The creation of vacancy is also supported by the shift of peak toward higher energy, indicating that the GaN film is relatively stress-relaxed when V/III ratio is increased. It has been explained that such a lower strain film was affected by the point defects [22]. On the basis of these results, it is found that rf power of 500 W and V/III ratio larger than 80 are suitable for the growth of GaN thin film which shows the superior crystal and optical qualities.

A room-temperature photoluminescence spectrum from a GaN epilayer grown with a V/III ratio of 65 is compared with that of MOCVD-grown sample as shown in Fig. 10. To the best of our knowledge, this is the first reported PL spectrum from GaN grown by UHVCVD/MOMBE using TEGa and nitrogen plasma. The band-edge emission exhibits a strong transition at 362 nm corresponding to a donor bound exciton recombination with a FWHM of 133 meV. The yellow-band emission, which is a defect-related luminescence, appears at 550 nm with weak intensity. In Fig. 10, PL spectra (a) and (b) were measured under the same measurement condition. It should be noted that the intensity of band-gap luminescence in Fig. 10 (a) is much stronger by a factor of 10 compared to that of MOCVD-grown GaN shown in Fig. 10 (b), while the ratio I_b/I_d is about the same. These XRD and PL results suggest that a high quality GaN can be grown on the sapphire substrate by UHVCVD/MOMBE.

4. Conclusions

A protrusion-free surface which was fully nitridated was successfully obtained at low temperatures using the UHVCVD/MOMBE method. The thickness of the nitridated layer was measured less than 6 nm. The surface nitrogen composition was not affected by substrate temperature and N_2 flow rate but mostly affected by RF power, process pressure, and the distance of source-to-substrate. However, the protrusion density on the nitridated sapphire surface was greatly dependent on the substrate temperature and a nitridated sapphire surface without protruions could be obtained at low substrate temperature. The GaN epitaxial layer grown at 450 ℃ had a hexagonal wurtzite structure and an in-plane epitaxial relationship with the sapphire substrate. The nitridation of the sapphire at low temperatures was found to improve the crystallinity in GaN layer and enhance the lateral growth of GaN. A room temperature PL clearly showed that a high quality GaN epitaxial layer can be realized by UHVCVD/MOMBE method by optimizing the low temperature nitridation and growth processes.

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