Time Evolution of a High-temperature GaN Epilayer Grown on a Low-temperature GaN Buffer Layer using a Low-pressure MOCVD

Kyunghwa Chang and Sung Il Cho
Department of Chemical Engineering, University of Seoul,
Jeonnong 3-dong, Dongdaemun-gu, Seoul 130-743, Korea

Myoung Seok Kwon[a]
Department of Materials Science and Engineering, University of Seoul,
Jeonnong 3-dong, Dongdaemun-gu, Seoul 130-743, Korea

[a]E-mail : mskwon@uos.ac.kr

(Received September 8 2005, Accepted December 8 2005)

In this paper, the time evolution of undoped GaN epilayers on a low-temperature GaN buffer layer grown on c-plane sapphire at a low pressure of 300 Torr was studied via a two-step growth condition in a horizontal MOCVD reactor. As a function of the growth time at a high-temperature, the surface morphology, structural quality, and optical and electrical properties were investigated using atomic force microscopy, high-resolution x-ray diffraction, photoluminescence, and Hall effect measurement, respectively. The root-mean-square roughness showed a drastic decrease after a certain period of surface roughening probably due to the initial island growth. The surface morphology also showed the island coalescence and the subsequent suppression of three-dimensional island nucleation. The structural quality of the GaN epilayer was improved with increasing growth time considering the symmetrical (002) and asymmetrical (102) rocking curves. The variations of room-temperature photoluminescence, background carrier concentration, and Hall mobility were measured and discussed.

Keywords : GaN, MOCVD

1. INTRODUCTION

Gallium nitride (GaN) and related nitride compound semiconductors are interesting due to their applications in light-emitting diodes (LEDs), laser diodes (LDs) in the green to the ultraviolet (UV) regions, and in high-temperature electronic devices[1,2]. The GaN epilayer is widely grown through metalorganic chemical vapor deposition (MOCVD) mainly on a c-plane sapphire substrate despite the large mismatch in lattice constants and thermal expansion coefficients because of the lack of other suitable substrates[3-5].

The GaN epilayer on c-plane sapphire is widely grown through the two-step MOCVD growth method using an AlN buffer layer[6] or a low-temperature GaN buffer layer[7]. As regards the structural and morphological evolution of undoped GaN growth on c-plane sapphire using a low-temperature GaN buffer layer through the two-step MOCVD, previous papers have reported nucleation layer evolution[8]; the effects of the reactor pressure and carrier gas for GaN buffer layer growth on the morphological evolution of GaN[9-11]; surface morphology investigations[12,13]; the structural evolution of epitaxial GaN layers, including film coalescence in the initial growth stage[14-17]; and microstructural evolution, focused on threading dislocation generation[18].

The objective of this paper is to present the time evolution of high-temperature GaN epilayer growth on a low-temperature GaN buffer layer to investigate the fundamental aspects of the high-temperature growth of a GaN epilayer during a typical two-step growth method on a c-plane sapphire substrate through MOCVD. To achieve this aim, the growth condition of the low-temperature GaN buffer layer was optimized through low-pressure MOCVD in a horizontal flow reactor, and the growth time of the high-temperature GaN epilayer was changed. The process pressure of the horizontal MOCVD reactor (300 Torr), the growth condition of low-temperature GaN, and other process variables were fixed for each different growth time of high-temperature GaN.

This paper shows the time evolutions of the GaN epilayer, particularly in terms of surface morphology, structural quality, and optical and electrical properties. Atomic force microscopy (AFM), high-resolution x-ray diffractometry (HRXRD), photoluminescence (PL) measurement, and Hall measurement were conducted using the van der Pauw technique.

2. EXPERIMENTAL PROCEDURE

An undoped GaN epilayer was grown on a c-plane sapphire substrate in a horizontal MOCVD reactor at a low pressure of 300 Torr, as described in the authors' previous paper[19]. In all the experiments, a two-step growth method of GaN—consisting of the deposition of the low-temperature GaN buffer layer and the high-temperature GaN epitaxial growth—was employed. The growth time of high-temperature GaN was changed from 1 min to 15 min to study the time evolutions of high-temperature GaN growth during two-step MOCVD growth.

Trimethylgallium (TMGa) and ammonia (NH_3) were used as precursors for GaN growth. TMGa was contained in a low-temperature bubbler and was carried by an H_2 carrier for the sccm order of flow with an electronic pressure control, maintaining a constant pressure of 800 Torr. Using H_2 push gas, the NH_3- and H_2-carried TMGa were pushed into the main run line—the injection head of the inner cell—with an order of slm of the flow rate[19]. The substrate was degreased using acetone, methanol, and deionized water overflow. The N_2-dried substrate was chemically etched in a boiling solution of H_2SO_4:H_3PO_4 = 3:1. It was then rinsed in deionized water overflow and methanol, boiled in 2-propanol, and finally dried with N_2 using a blowing gun.

The substrate loaded in the reactor was thermally cleaned in H_2 atmosphere at 1100 °C for 10 min before the two-step growth of the undoped GaN film. The substrate was pre-nitrated with 1 slm of NH_3 flow at 500 °C for 30 sec, and the buffer layer was then grown at 500 °C. The optimum buffer layer thickness at 500 °C was fixed at 40 nm in this paper's typical two-step growth.

The final GaN epilayer was grown at 1080 °C for various growth times. The NH_3 flow rate was fixed at 1 slm during the growth of the GaN layer. The V/Ⅲ ratios were 2740 and 1370 for buffer growth and the main high-temperature growth, respectively. The growth rate was fixed at 0.07 μm/min, so the thickness of that grown for 15 min was estimated at 1.1 μm.

AFM was used to observe the surface morphology and to measure the root-mean-square (rms) roughness of the GaN epilayers. The rms roughness was determined for the areas of 2.0 μm × 2.0 μm using the AFM software. The crystallographic qualities of the GaN layers were evaluated with symmetric (002) and asymmetric (102) rocking curves (ω-scans) of wurtzite GaN through triple-axis high-resolution x-ray diffraction (HRXRD). Photoluminescence (PL) measurement was conducted at room temperature, using the 325-nm line of He-Cd laser. Hall measurements were conducted at room temperature using the van der Pauw technique to measure the background carrier concentration and mobility.

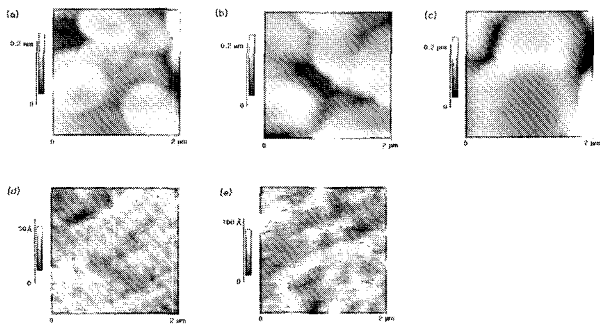

Fig. 1. Two-dimensional AFM images of the surface morphology of the GaN epilayer grown for: (a) 1 min; (b) 2 min; (c) 5 min; (d) 10 min; and (e) 15 min.

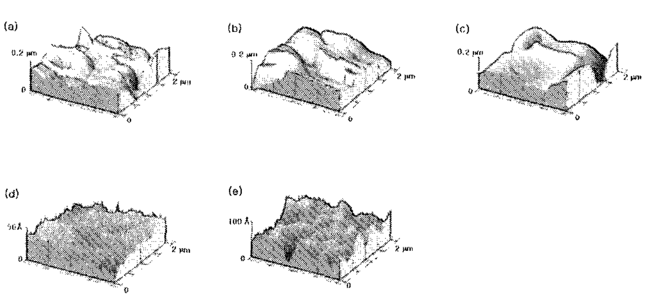

Fig. 2. Three-dimensional AFM images of the surface morphology of the GaN epilayer grown for: (a) 1 min; (b) 2 min; (c) 5 min; (d) 10 min; and (e) 15 min.

3. RESULTS AND DISCUSSION

Figure 1 and Fig. 2 show the two-dimensional and three-dimensional AFM images of surface morphology with increasing growth time of high-temperature GaN, respectively.

Figure 3 shows the measured rms roughness of the GaN surface as a function of the growth time of the high-temperature GaN epilayer. In the two-dimensional and three-dimensional AFM images, the formation of

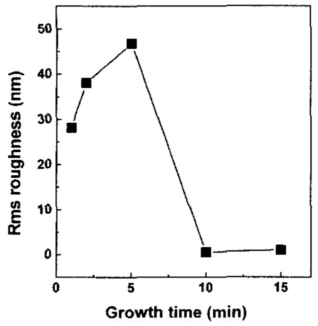

Fig. 3. The measured rms roughness of the GaN epilayer surface as a function of growth time at a high temperature.

three-dimensional islands can be seen on the buffer layer at the initial stage of high-temperature growth. Moreover, the AFM images show the evolution of GaN island growth and coalescence, especially from the images at the initial stages of high-temperature growth (from 1 min to 5 min). In the 1-min and 2-min samples, the three-dimensional islands looked like flat-top-shaped islands rather than hillock-type ones. As the growth time increased from 1 min to 5 min, the rms roughness showed an increasing tendency from 28.2 nm to 46.8 nm. Above 10 min, the island shape could no longer be sharply defined in the AFM images within the scanned area (2 μm × 2 μm), and the measured rms roughness showed a drastic decrease—from 46.8 nm (5 min) to 0.53 nm (10 min)—which may reflect the suppression of the three-dimensional characteristic of GaN epilayer growth at a high temperature after a certain growth time.

Figure 4 shows the symmetric (002) rocking curves (ω-scans) obtained through HRXRD, as well as the measured full widths at half-maximum (FWHM), as a function of growth time. The intensity of the rocking count increased and sharpened as the growth time increased—that is, as the epilayer thickness increased. In addition, the FWHM showed a monotonous decreasing tendency with increasing growth time.

Symmetric rocking curves are known to provide information regarding tilt mosaicity, and may be broadened by screw or mixed threading dislocations, thus being insensitive to pure-edge threading dislocations that are predominant in GaN films grown on c-plane sapphire[20,21]. As such, the asymmetric GaN (102) reflections were measured to investigate the edge-type threading dislocation and the twist mosaicity of the GaN epilayer. Figure 5 shows the asymmetric (102) rocking curves (ω-scans) obtained through HRXRD, as well as the measured FWHM, as functions of growth time. The intensity of the rocking count increased and sharpened with increasing growth time—that is, as the epilayer thickness increased. The FWHM also showed a monotonous decreasing tendency as the growth time increased.

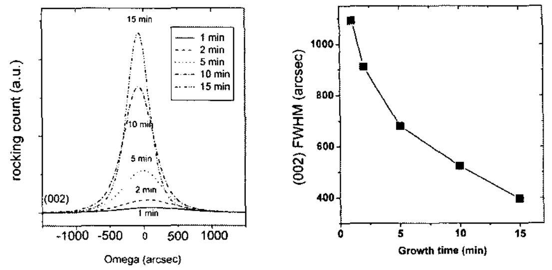

Fig. 4. (a) Symmetric (002) rocking curves (ω-scans) and (b) the measured FWHMs as a function of growth time.

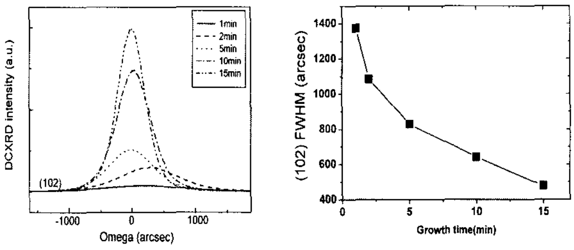

Fig. 5. (a) Asymmetric (102) rocking curves (ω-scans) and (b) the measured FWHMs as a function of growth time.

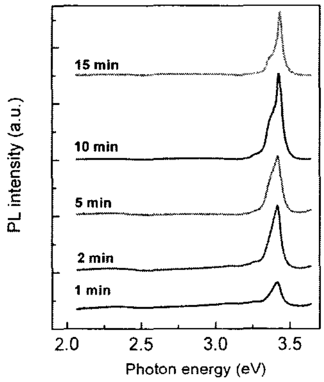

Fig. 6. Room-temperature photoluminescene spectra of the undoped GaN epilayers with increasing growth time.

Figure 6 shows the room-temperature PL spectra with increasing growth time of the GaN epilayer.

The spectra at room temperature were dominated by near-band-edge-related luminescence. The FWHM of band-edge emission for the 15-min sample was 42 meV. All the samples showed either no yellow band and donor-acceptor pair (DAP) transition or only a trace of it,

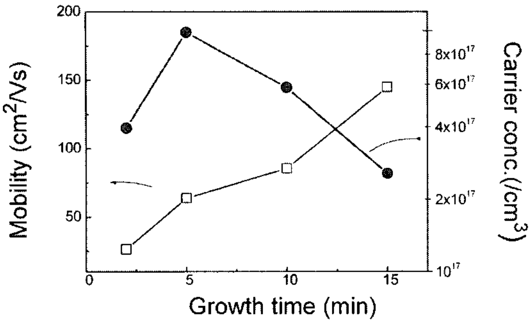

Fig. 7. Hall mobility and background carrier concentration as functions of growth time.

which, according to previous papers, confirms the high quality of the authors' samples[19,22]. Traces of yellow luminescence were detected in the 1-min to the 5-min samples. The ratio of yellow intensity to the main band-edge emission had a maximum value of 0.09 in the 1-min sample, then decreased until it was almost absent in the 10-min and 15-min samples. The main band-edge emission showed a continuous blue shift (0.03 eV) with increasing growth time in the 1-min to 15-min samples, which may reflect the increased residual compressive stress along the *a* axis as the film thickened.

Figure 7 shows the background carrier concentration and the Hall mobility resulting from the use of the van der Pauw method at room temperature. The electrically active background carrier was n-type, which is typical in the MOCVD growth of undoped GaN epilayers. With increasing growth time, the background concentration showed a decreasing tendency towards $2.6\times10^{17}/\mathrm{cm}^3$ for 15 min. The Hall mobility, on the other hand, showed an increasing tendency of up to 145 cm^2/Vs for 15 min with increasing growth time.

All the above experimental results correspond to the GaN epilayer growth up to the film thickness of about 1.1 ㎛. All the samples showed almost no yellow-band emission, which reflects the relatively high quality of the two-step growth condition of the GaN epilayer on the c-plane sapphire substrate. The two-step growth condition led to the formation of a flat-top-like shape of the GaN island at the initial stage of high-temperature growth rather than a pyramid-like shape, as seen in the AFM images.

The three-dimensional islands then grew with increasing growth time and finally coalesced, which was what happened as well in the studies reported in the previous papers[10,14-17]. Up to that stage, the rms roughness is thought to increase, probably due to surface roughening, as suggested by Han et al.[10]. Figge et al. also suggested that the average roughness of the epilayer increases as long as the grain size stays below the nucleation site spacing from the in-situ reflectance signal [15].

When the coalescence occurred, however, the rms roughness decreased drastically, which may show that quasi two-dimensional growth[10,14] may be dominated or that the additional three-dimensional island nucleation and growth may be suppressed. As a result, when a certain thickness is reached after a commensurate growth time, the surface morphology changes drastically to uniform surface coverage for the subsequent film growth.

Some previous papers reported the opposite tendency of the FWHM of symmetric and asymmetric rocking curves according to some variations of experimental parameters or some specific film microstructures, such as the opposite tendency resulting from the variations of pre-nitridation time before two-step growth[20] and an opposite trend for the (002) and (102) rocking curves as a result of a specific threading dislocation geometry[21].

In this experiment, the FWHM of the (002) and (102) rocking curves showed the same decreasing tendency with increasing growth time. The rocking curve is broadened by various factors. When the layer thickness increases, so does the volume of the layer scattering x-rays coherently. Therefore, the narrowing of the rocking curve with increasing layer thickness may just be an effect of x-ray diffraction. Other important factors may be the fluctuation of the lattice parameters, fluctuations in the crystallite orientation of the mosaic structure, the disruption of the x-ray photon coherence by the extended defects coming from the evolution of the different growth mode, and the resulting different microstructure of the GaN layers. One supporting result is that the (002) FWHM showing the tilt mosaicity decreased up to a certain thickness, and then started to increase. The twist mosaicity, on the other hand, did not change much up to 1.4 ㎛ thickness. It is thus assumed that the evolution of the different growth modes and the resulting microstructures, including the defect structures, may be important factors for the measured behaviors of symmetric and asymmetric rocking curves as a function of growth time. It can therefore be concluded that the sample with a longer growth time shows a reduced threading dislocation density and improved crystallinity (both tilt and twist mosaicity) considering the decreasing tendency of the FWHM of the symmetric and asymmetric rocking curves.

Also, the decrease rate of the FWHM of the symmetric and asymmetric rocking curves was higher during the initial stage of growth—up to 5 min— which corresponds to 0.35 ㎛ of growth. Thus, much of the reduction of threading dislocations is thought to be predominant at the initial stage of high-temperature growth of GaN, which may imply the existence of two different mechanisms concerning the reduction of threading dislocations as a function of growth time (film thickness). Another possibility is that the distribution of dislocations stabilizes after the initial stages, and that beyond that point, the density and distribution of dislocations remain almost constant. Thus, the narrowing of the rocking curve may be merely an effect of x-ray diffraction due solely to the thickness increase effect. Pure-screw or mixed threading dislocations are expected to decrease faster with increasing growth time probably due to the ease of cross slip of screw dislocations, especially prominent in the initial stage of high-temperature GaN epilayer growth.

Within the thickness range of this experiment (up to 1.1 μm), the PL results showed a decreasing tendency of the FWHM of the band-edge emission and the disappearance of the yellow band and the DAP with increasing growth time, which may have resulted from the improved crystal quality. As the growth time increased, the band-edge emission showed a blue shift, implying the increased compressive residual stress or the relaxation of tensile stress, as indicated in previous papers.

The background carrier concentration decreased and the Hall mobility increased as the growth time increased. The decrease of the residual electron concentration may be related to the narrowing of the PL band-emission lines. The background electron was considered to have come from oxygen incorporation, and the measured concentration was the net concentration after compensation with p-type impurities like carbon. Oxygen and carbon are known to be the most frequently occurring inherent impurities in MOCVD. The improved crystalline quality and the increased compressive residual stress or the relaxation of tensile stress with increasing growth time is thought to reduce the efficiency of oxygen incorporation into the GaN epilayer. If this is indeed the case, the background electron concentration could decrease. The carbon incorporation efficiency is also thought to decrease with increasing growth time, which may result from the improved crystal quality, the increased compressive stress, or the relaxation of tensile stress. Thus, the improved crystal quality and the reduced threading dislocations, as well as the reduced impurity incorporation efficiency resulting in a lower compensation level, could be important factors for the improvement of the Hall mobility with increasing growth time. Wu et al. attributed the difference in mobilities to the higher threading dislocation density in the epilayer, and assumed that the charged dislocations due to the trap states—which give rise to Coulomb scattering—could become dominant scattering centers when threading dislocation densities are in excess of 10^9 cm^{-2}[18]. Interestingly, the decrease of oxygen incorporation is thought to be more prominent than that of carbon incorporation with increasing growth time, considering the net decrease of the residual electron concentration, including the possible compensation between the oxygen and carbon impurities.

4. CONCLUSION

The time evolution of a high-temperature GaN epilayer during two-step GaN growth on c-plane sapphire was investigated in a horizontal MOCVD reactor at a low- pressure (300 Torr). The surface morphology of the GaN epilayer showed a drastic decrease after initial surface roughening and the suppression of the three-dimensional growth of the GaN islands only after a certain initial growth time. With increasing growth time, the structural quality was improved and the threading dislocation density was reduced judging from the symmetric and asymmetric rocking curves obtained through HRXRD. The room-temperature PL results confirm the relatively high quality of the two-step growth condition proposed in this study. The background carrier concentration showed a decreasing tendency while the Hall mobility showed an increasing trend with increasing growth time. All the results may be attributed to the structural quality, particularly that related to the threading dislocation density, residual stress, and the incorporation efficiency of the oxygen and carbon impurities as the GaN epilayer thickens.

REFERENCES

[1] M. O. Manasreh and I. T. Ferguson, "Ⅲ-Nitride Semiconductor Materials: Growth", Taylor & Francis, p. 159, 2003.

[2] H. S. Nalwa and L. S. Rohwer, "Handbook of Luminescence, Display Materials, and Devices, Vol. 2", American Scientific Publishers, p. 46, 2003.

[3] J. I. Pankove and T. D. Moustakas, "Gallium Nitride (GaN) I ", Academic Press, p. 20, 1998,

[4] B. Gil, "Group Ⅲ Nitride Semiconductor Compounds", Oxford University Press Inc., p. 87, 1998.

[5] J. H. Edgar, S. Strite, I. Akasaki, H. Amano, and C. Wetzel, "Properties, Processing and Applications of Gallium Nitride and Related Semiconductors", INSPEC, p. 416, 1999.

[6] H. Amano, N. Sawaki, I. Akasaki, and Y. Toyoda, "Metalorganic vapor phase epitaxial growth of a high quality GaN film using an AlN buffer layer", Appl. Phys. Lett., Vol. 48, No. 5, p. 353, 1986.

[7] S. Nakamura, "GaN growth using GaN buffer layer", Jpn. J. Appl. Phys., Vol. 30, No. 10A, p. L1705, 1991.

[8] X. H. Wu, D. Kapolnek, E. J. Tarsa, B. Heying, S. Keller, B. P. Keller, U. K. Mishra, S. P. DenBaars,

and J. S. Speck, "Nucleation layer evolution in metal-organic chemical vapor deposition grown GaN", Appl. Phys. Lett., Vol. 68, No. 10, p. 1371, 1996.

[9] J. Chen, S. M. Zhang, B. S. Zhang, J. J. Zhu, X. M. Shen, G. Feng, J. P. Liu, Y. T. Wang, H. Yang, and W. C. Zheng, "Influences of reacor pressure of GaN buffer layrs on morphological evolution of GaN grown by MOCVD", J. Cryst. Growth, Vol. 256, p. 248, 2003.

[10] J. Han, T.-B. Ng, R. M. Biefeld, M. H. Crawford, and D. M. Follstaedt, "The effect of H_2 on morphological evolution during GaN metalorganic chemical vapor deposition", Appl. Phys. Lett., Vol. 71, No. 21, p. 3114, 1997.

[11] A. P. Grzegorczyk, L. Macht, P. R. Hageman, J. L. Weyher, and P. K. Larsen, "Influences of the nucleation layer morphology and epilayer structure on the resistivity of GaN films grown on c-plane sapphire by MOCVD", J. Cryst. Growth, Vol. 273, p. 424, 2005.

[12] E. M. Goldys, M. Godlewski, R. Langer, and A. Barski, "Surface morphology of cubic and wurtzite GaN films", Appl. Surf. Sci., Vol. 153, p. 143, 2000.

[13] J. Zhou, J. E. Reddic, M. Sinha, W. S. Ricker, J. Karlinsey, J.-W. Yang, M. A. Khan, and D. A. Chen, "Surface morphologies of MOCVD-grown GaN films on sapphire studied by scanning tunneling microscopy", Appl. Surf. Sci., Vol. 202, p. 131, 2002.

[14] D. Kapolnek, X. H. Wu, B. Heying, S. Keller, B. P. Keller, U. K. Mishra, S. P. DenBaars, and J. S. Speck, "Structural evolution in epitaxial metalorganic chemical vapor deposition grown GaN films on sapphire", Appl. Phys. Lett., Vol. 67, No. 11, p. 1541, 1995.

[15] S. Figge, T. Böttcher, S. Einfeldt, and D. Hommel, "In situ and ex situ evaluation of the film coalescence for GaN growth on GaN nucleation layers", J. Cryst. Growth, Vol. 221, p. 262, 2000.

[16] H. Yuan, D.-C. Lu, X. Liu, Z. Chen, P. Han, X. Wang, and Du Wang, "Statistical investigation on morphology development of gallium nitride in initial growth stage", J. Cryst. Growth, Vol. 234, p. 77, 2002.

[17] H. Yuan, Z. Chen , D.-C. Lu, X. Liu, P. Han, and X. Wang, "A geometrical model of GaN morphology in initial growth stage", J. Cryst. Growth, Vol. 234, p. 115, 2002.

[18] X. H. Wu, P. Fini, E. J. Tarsa, B. Heying, S. Keller, U. K. Mishra, S. P. DenBaars, and J. S. Speck, "Dislocation generation in GaN heteroepitaxy", J. Cryst. Growth, Vol. 189/190, p. 231, 1998.

[19] M. S. Kwon and S. I. Cho, "Effects of total gas velocity during growth of undoped GaN epitaxial layer on sapphire (0001) substrate by horizontal MOCVD", J. Cryst. Growth, Vol. 266, p. 435, 2004

[20] S. Keller, B. P. Keller, Y.-F. Wu, B. Heying, D. Kapolnek, J. S. Speck, U. K. Mishra, and S. P. DenBaars, "Influence of sapphire nitridation on properties of gallium nitride grown by metalorganic chemical vapor deposition", Appl. Phys. Lett., Vol. 68, p. 1525, 1996.

[21] B. Heying, X. H. Wu, S. Keller, Y. Li, D. Kapolnek, B. P. Keller, S. P. DenBaars, and J. S. Speck, "Role of threading dislocation structure on the x-ray diffraction peak widths in epitaxial GaN films", Appl. Phys. Lett., Vo. 68, No. 5, p. 643, 1996.

[22] A. K. Viswanath, J. I. Lee, S. Yu, D. Kim, Y. Choi, and C.-H. Hong, "Photoluminescence studies of excitonic transitions in GaN epitaxial layers", J. Appl. Phys., Vol. 84, No. 7, p. 3848, 1998.