Journal of Ceramic Processing Research. Vol. 19, No. 5, pp. 439~443 (2018)

J O U R N A L O F
Ceramic Processing Research

Controlling of the heterogeniously growing GaN polycrystals using a quartz ring in the edge during the HVPE-GaN bulk growth

Jae Hwa Park[a,b], Hee Ae Lee[a], Cheol Woo Park[a,b], Hyo Sang Kang[a,b], Joo Hyung Lee[a], Jun-Hyeong In[a], Seong Kuk Lee[c], and Kwang Bo Shim[a,*]

[a]*Division of Advanced Materials Science and Engineering, Hanyang University, Seoul 04763, Korea*
[b]*AMES Micron Co. LTD, 2, Singok-ro, Gochon-eup, Gimpo-si, Gyeonggi-do, 10124, Korea*
[c]*UNIMO Photron, Seocho-gu, Bangbae-dong, Seoul 479-12, Korea*

The outstanding characteristics of high quality GaN single crystal substrates make it possible to apply the manufacture of high brightness light emitting diodes and power devices. However, it is very difficult to obtain high quality GaN substrate because the process conditions are hard to control. In order to effectively control the formation of GaN polycrystals during the bulk GaN single crystal growth by the HVPE (hydride vapor phase epitaxy) method, a quartz ring was introduced in the edge of substrate. A variety of evaluating method such as high resolution X-ray diffraction, Raman spectroscopy and photoluminescence was used in order to measure the effectiveness of the quartz ring. A secondary ion mass spectroscopy was also used for evaluating the variations of impurity concentration in the resulting GaN single crystal. Through the detailed investigations, we could confirm that the introduction of a quartz ring during the GaN single crystal growth process using HVPE is a very effective strategy to obtain a high quality GaN single crystal.

Key words: HVPE, GaN, Quartz ring.

Introduction

Gallium nitride (GaN) has a wurtzite structure based on a hexagonal lattice and has excellent properties such as a wide band gap, high breakdown voltage, high electron mobility, and high stability at high temperatures. It is therefore a promising material that can be applied to not only power semiconductor devices that require high power and operate at high temperatures but also to optical devices [1-4]. High quality GaN substrates are required for various applications, such as ultra-high brightness light emitting diodes, laser diodes, and high-power devices. In order to obtain these substrates, it is necessary to have a technique capable of growing thick GaN single crystals or other growing technique of GaN single crystals to obtain high quality [5, 6].

The growth of bulk single crystal GaN is mainly performed by the vertical hydride vapor phase epitaxy (HVPE) method, and sapphire single crystal substrates are used mainly for economic reasons[7]. However, the sapphire substrate inevitably contains internal defects and causes residual stress in the GaN single crystal due to the lattice constant mismatch and difference in thermal expansion coefficient during cooling. Such defects and residual stress has been reported to have a serious effect on the efficiency, lifetime, and performance of the manufactured devices [8-11].

Besides the residual stress existing in the GaN single crystal, the polycrystalline GaN generated at the edge of the substrate during growth of the GaN single crystal also becomes a factor which increases the difficulty of manufacturing GaN wafers. Polycrystalline GaN is generated because crystal growth nuclei are formed heterogeneously at the edges and side faces of the substrate where the crystallographic orientation is not constant, allowing polycrystalline GaN to grow in various orientations. The amount of polycrystalline GaN increases as the growth time increases. The polycrystalline GaN hinders the absorption of strain between the sapphire substrate and the GaN single crystal, and it induces new strains. In particular, it acts as bumpy surface that concentrates stress during the process of removing the polycrystalline GaN [12]. In the GaN wafer manufacturing process, this can directly induce cracks in the GaN single crystal, thus significantly reducing the manufacturing yield of GaN wafers.

In this study, based on that a carbon trap to remove carbon contamination generated by long time use of oil-based vacuum pumps has been used to maintain the high vacuum atmosphere of electron microscopes [13, 14], a quartz ring is introduced at the edge of the substrate during the growth process of the bulk GaN single crystal using HVPE to control the formation of polycrystalline GaN at the edge. We analyzed the

*Corresponding author:
Tel : +82-2-2220-0501
Fax: +82-2-2291-7395
E-mail: kbshim@hanyang.ac.kr

characteristics of the as-grown bulk GaN single crystals to understand the effectiveness of quartz ring.

Experiment

Bulk GaN single crystals were grown on 2 inch (0001) sapphire substrates using vertical HVPE grower. Ga metal (6 N) and NH_3 gas were used as the Ga and N sources, respectively, and nitrogen gas vaporized from liquid nitrogen was used as a carrier gas after purification by an N_2 purifier (PIONICS, UIA-5-A, Korea). The growth thickness was about 3 mm, and the growth parameters were the same as previously reported [11, 15]. One sample used only a sapphire substrate on the sample holder (specimen A). Another sample used a sapphire substrate and quartz ring that was fabricated with a diameter of 52 mm, 2 mm larger than the diameter of the sapphire substrate, and fixed on the sample holder (specimen B), as shown in Fig. 1 [16].

Both samples were characterized and the bulk GaN single crystal grown without the quartz ring was compared to the bulk GaN single crystal grown with the quartz ring. The crystallinity of the GaN single crystals was determined from the full width at half maximum (FWHM) of the X-ray rocking curve (XRC) obtained using a high-resolution X-ray diffractometer (HR-XRD; Rigaku, ATX-G, Japan). A Raman spectrometer (JASCO, NRS-3100, England) was used to observe the stress variations in the grown GaN single crystal. The excitation laser source had a 534 nm wavelength and the power was 2.5 mW. Photoluminescence (PL) measurements (Dongwoo optron, MonoRa 750i, Korea) were carried out to observe variations in the optical properties, using a 325 nm He-Cd laser excitation source. Analysis of the impurities present in the bulk GaN single crystals was carried out using secondary impact mass spectroscopy (SIMS; (ION-TOF), TOF.SIMS 5, Germany).

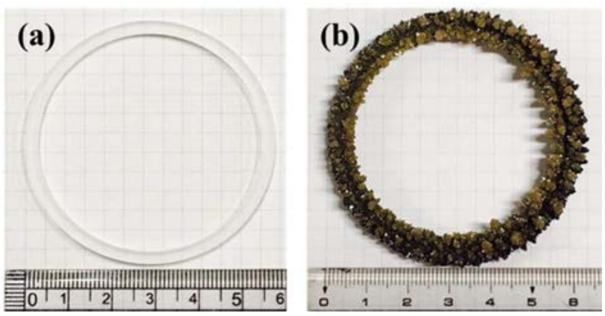

Fig. 1. Quartz ring introduced in growth process : (a) before growth process, (b) after growth process.

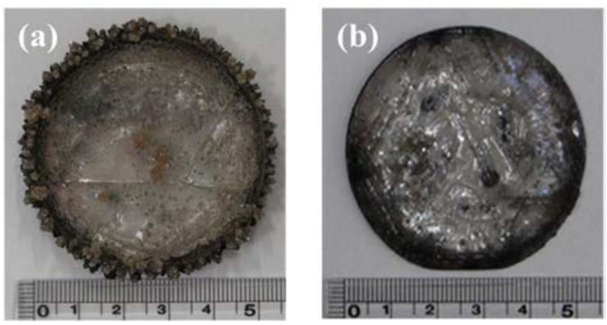

Fig. 2. Bulk GaN single crystal grown by HVPE: (a) without using the quartz ring(specimen A) and (b) with the using the quartz ring (specimen B).

Result and Discussion

Fig. 2(a) shows a bulk GaN single crystal grown via HVPE without using the quartz ring, and Fig. 2(b) shows a bulk GaN single crystal grown using the quartz ring. As shown in Fig. 2, by using the quartz ring during bulk GaN single crystal growth, the polycrystalline GaN at the edge of GaN single crystal could be effectively removed. As shown in Fig. 3(a), this induced initial nucleation of polycrystalline GaN at the edge of the sapphire substrate resulted in a thicker layer on the quartz ring surface than on the sapphire substrate (Fig. 3(b)), and it is considered that the quartz ring acts as a trap for the formation of initial nuclei, thus making it possible to effectively remove the polycrystalline GaN that is generated.

Fig. 4 shows the XRC measured using the HR-XRD in order to observe variations in the crystallinity with or without the quartz ring. The FWHM value of the XRC for the GaN single crystal grown without the quartz ring was calculated at 189 arcsec, and the FWHM value for the GaN single crystal grown using the quartz ring was 113.04 arcsec, showing a decrease of about 76 arcsec. The GaN single crystal grown using the quartz ring showed a sharper peak because defects transmitted from the polycrystalline GaN at the edge of the GaN single crystal were effectively controlled by using the quartz ring, which confirms that GaN of improved quality can be grown [17, 18].

Raman spectroscopy was used to examine the influence of the use of the quartz ring on the stress in the GaN single crystal, and Fig. 5 shows the E_2(high) mode peak with and without the use of the quartz ring. The E_2 (high) vibration mode from the III-nitride single crystal having the hexagonal structure of the (C63mc) group is caused by the vibration of atoms parallel to the c-plane, which is the growth surface, and many studies of residual stress inside the material have been carried out using this measurement [10, 11]. In this study, biaxial compressive stress exists inside the GaN single crystal due to the use of sapphire as the substrate, and when compressive stress exists in the GaN single crystal, the E_2 (high) peak is blue shifted from its original position, while red shift is caused by relaxation of compressive stress [10, 11, 19]. Fig. 5 shows that the E_2 (high) peak exhibited a red shift after using the quartz ring. It can be seen that using a quartz ring

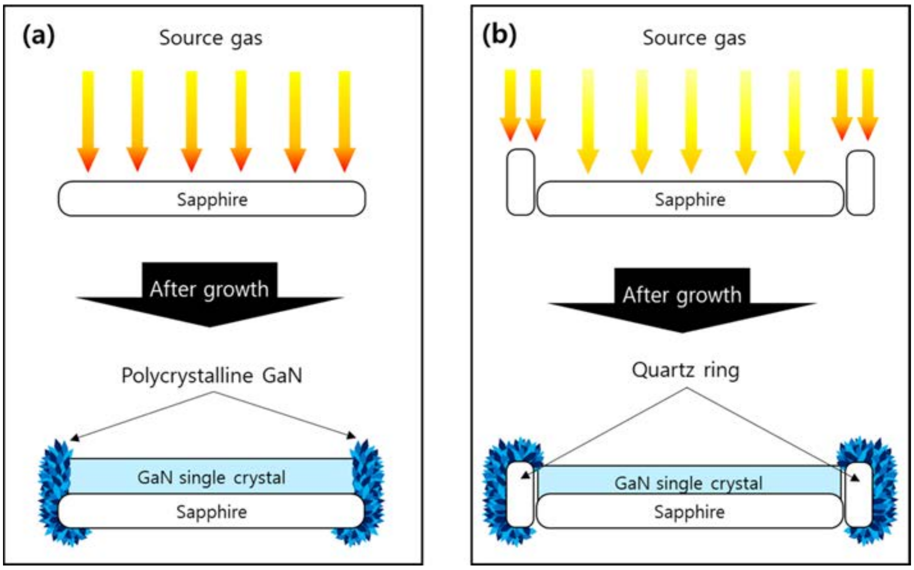

Fig. 3. Schematic diagram of growth position variation of polycrystalline GaN: (a) without using the quartz ring, (b) using the quartz ring.

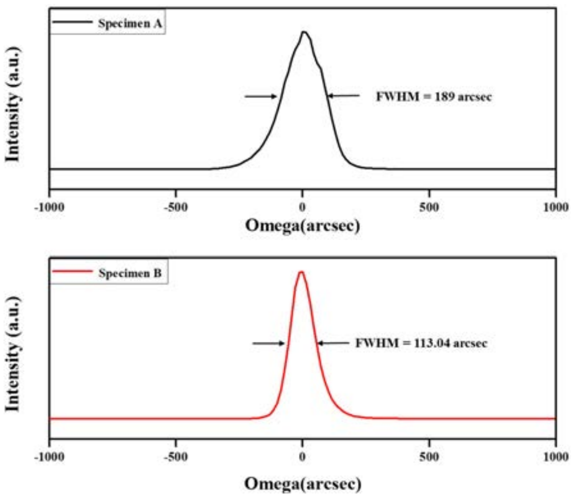

Fig. 4. FWHM variation of XRC with and without using the quartz ring.

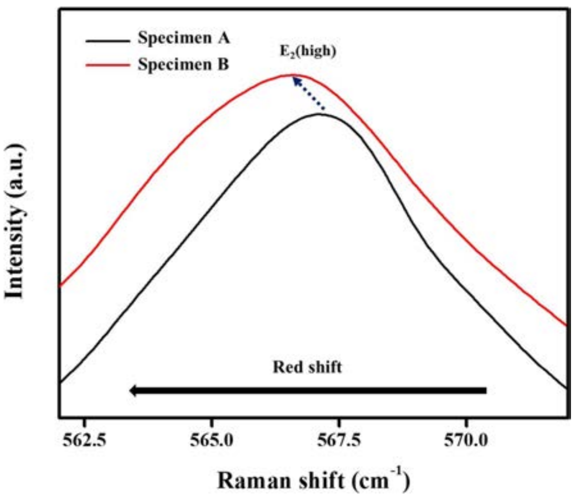

Fig. 5. E_2(high) peaks variation of Raman spectrum with and without using the quartz ring.

during the growth of a GaN single crystal can easily remove the edge polycrystalline GaN and can relax the residual stress inside GaN single crystal.

Fig. 6 shows PL measurement results which confirm the optical properties of GaN grown with and without using the quartz ring. It can be seen that a relatively high yellow luminescence (YL) was observed from the GaN single crystal grown using a quartz ring, as compared with the GaN single crystal grown without using a quartz ring. YL observed near 2.2 eV in the PL spectrum of a GaN single crystal acts as an indicator of the characteristics of the final optical devices manufactured using the GaN substrate [20]. There are various factors reported to cause YL, such as C-O and associated impurities and Si impurities contained in dislocations, among others [21, 22]. Therefore, the main reason for the large difference in YL depending on whether or not the quartz ring is used during growth is that Si and O from the quartz ring used in the high temperature growth atmosphere can diffuse into the GaN single crystal; we therefore conclude that they can act as impurities in the GaN single crystal to form a new energy band [23].

During the growth of GaN single crystals, SIMS measurements were carried out to elucidate the influence of impurities introduced by the quartz ring, and the impurities present inside the GaN single crystal were analyzed. Fig. 7 shows the results of SIMS analysis, showing the impurity contents of Si and O present in the GaN single crystals grown with and without a quartz ring. It can be confirmed that the GaN single crystal grown using the quartz ring showed an oxygen intensity about two times higher than that of the GaN single crystal grown without using the quartz ring. In the case of Si, a trace amount was detected. However, it was confirmed that more Si impurities exist inside the GaN single crystal grown using the

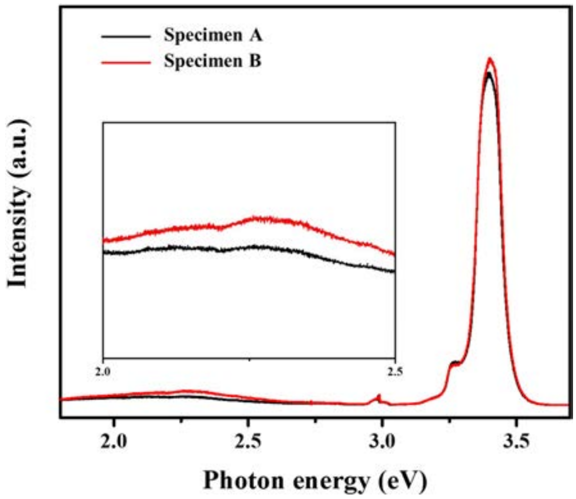

Fig. 6. PL spectrum of bulk GaN single cystal with and without using the quartz ring.

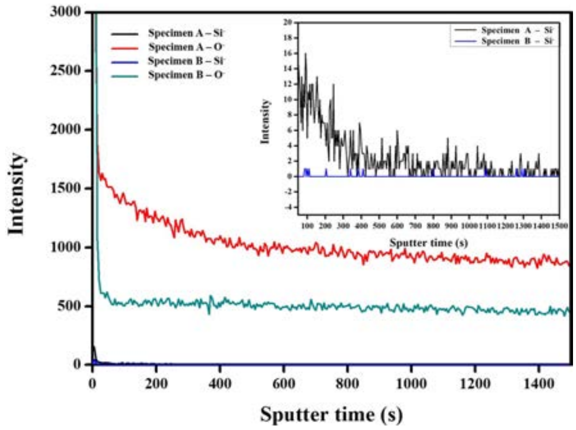

Fig. 7. Impurities of silicone and oxygen in bulk GaN single crystals with and without using the quartz ring.

quartz ring compared to that grown without using the quartz ring. We conclude that when using a quartz ring, the long-term and high temperature growth process allows Si and O to diffuse into the growing GaN single crystal. This conclusion is supported by the observation of increased YL in the PL results shown in Fig. 6.

Conclusions

Bulk GaN single crystals were grown using a vertical HVPE system and were able to eliminate the formation of polycrystalline GaN at the edge of the substrate by using a quartz ring. The FWHM of the XRC obtained utilizing HR-XRD was about 113 arcsec for the GaN grown with a quartz ring, which was narrower than that obtained for the GaN grown without a quartz ring. It was therefore confirmed that the crystallinity of the GaN single crystal can be improved. After using the quartz ring in the HVPE process, we used Raman spectroscopy to confirm the relaxation of residual compressive stress in the bulk GaN single crystal, which typically results from heteroepitaxy. YL was observed relatively strongly in the GaN single crystal grown using the quartz ring, but SIMS analysis confirmed that Si and O, which are the main components of the quartz ring, acted as impurities in the GaN single crystal.

In conclusion, polycrystalline GaN at the edge of the GaN single crystal could be effectively removed, which is expected to improve the manufacturing yield of GaN single crystal wafers. It is expected that high-quality GaN wafers can be manufactured at low cost by combining technologies capable of effectively controlling impurities present in GaN single crystals in the future.

Acknowledgements

This work was supported by Industrial Strategic Technology Development Program of the Ministry of Trade, Industry, and Energy (No. 10080599).

References

1. H. Amano, N. Sawaki, I. Akasaki, and Y. Toyoda, Appl. Phys. Lett. 48 (1986) 353.
2. S. Nakamura, T. Mukai, and M. Senoh, Jpn. J. Appl. Phys. 32 (1993) L16.
3. S. Nishida, and N. Kobayashi, Phys. Status Soldi (a) 188 (2001) 113.
4. P. Von Dollen, S. Pimputkar, and J.S. Speck, Angew. Chem. Int. Ed. 53 (2014) 13975.
5. K. Fujito, S. Kubo, H. Nagaoka, T. Mochizuki, H. Namita, and S. Nagao, J. Cry. Growth 311 (2009) 3011-3014.
6. H.M. Foronda, A.E. Romanov, E.C. Young, C.A. Robertson, G.E. Beltz, and J.S. Speck, J. Appl. Phys. 120 (2016) 035104.
7. X. Liu, D. Li, X. Sun, Z. Li, Z. Li, H. Song, H. Jiang, and Y. Chen, Cryst. Eng. Comm. 16 (2014) 8058-8063.
8. A.P. Zhang, L.B. Rowland, E.B. Kaminsky, V. Tilak, J.C. Grande, J. Teetosv, A. Vertiatchikh, and L.F. Eastman, J. Electron. Mater. 32[5] (2003) 388-394.
9. S. Choi, E. Heller, D. Dorsey, R. Vetury, and S. Graham, J. Appl. Phys. 133 (2013) 093510.
10. F.C. Wang, C.L. Cheng, Y.F. Chen, C.F. Huang, and C.C. Yang, Semicon. Sci. Technol. 22 (2007) 896-899.
11. J.H. Park, H.E. Lee, J.H. Lee, C.W. Park, J.H. Lee, H.S. Kang, H.M. Kim, S.H. Kang, S.Y. Bang, S.K. Lee, and K.B. Shim, J. Ceram. Proc. Res. 18[2] (2017) 93-97.
12. Z.J. Pei, S.R. Billingsley, and S. Miura, Int. J. Mach. Tool. Manufact. 39 (1999) 1103-1116.
13. M.T. Postek, Scanning 18 (1996) 269-274.
14. L. Holland, Vacuum 20[5] (1970) 175-192.
15. D.K. Oh, S.Y. Bang, B.G. Choi, P. Maneeratanasam, S.K. Lee, J.H. Chung, J.A. Freitas Jr., and K.B. Shim, J. Cryst. Growth 356 (2012) 22-25.
16. S.K. Lee and K.B. Shim, KR Patent No. 1015453940000, (2015).
17. B. Heying, X.H. Wu, S. Keller, Y. Li, D. Kapolnek, B.P. Keller, S.P. DenBaars, and J.S. Speck, Appl. Phys. Lett. 68[5] (1996) 643-645.
18. S.S. Kushvaha, M. Senthil Kumar, K.K. Maurya, M.K. Dalai, and N.D. Sharma, AIP Advances 3 (2013) 092109.
19. A.G. Kontos, Y.S. Raptis, N.T. Pelekanos, A. Georgakilas, E. Bellet-Amalric, and D. Jalabert, Phys. Rev. B 72 (2005) 155336.

20. W. Grieshaber, E.F. Schubert, and I.D. Goepfert, J. Appl. Phys. 80[8] (1996) 4615-4620.
21. H. Gu, G. Ren, T. Zhou, F. Tian, Y. Xu, Y. Zhang, M. Wang, Z. Zhang, D. Cai, J. Wang, and K. Xu, J. Alloys Compd. 674 (2016) 218.
22. L. Li, J. Yu, Z. Hao, L. Wang, J. Wang, Y. Han, H. Li, B. Xiong, C. Sun, and Y. Luo, Comput. Mater. Sci. 129 (2017) 49.
23. S.R. Xu, Y. Hao, J.C. Zhang, Y.R. Cao, X.W. Zhou, L.A. Yang, X.X. Ou, K. Chen, and W. Mao, J. Cryst. Growth 312 (2010) 3521-3524.