

# Study on nitridation processes of $\beta$ -Ga<sub>2</sub>O<sub>3</sub> single crystal

Xing Li (李 星)<sup>1</sup>, Changtai Xia (夏长泰)<sup>1</sup>, Xiaoli He (何肖丽)<sup>2</sup>,  
Guangqing Pei (裴广庆)<sup>1</sup>, Jungang Zhang (张俊刚)<sup>3</sup>, and Jun Xu (徐 军)<sup>1</sup>

<sup>1</sup>Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800

<sup>2</sup>Key Laboratory of Materials Physics, and Anhui Key Laboratory of Nanomaterials and Nanostructures,  
Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031

<sup>3</sup>GE (China) Research and Development Center Company Limited, Shanghai 201203

Received October 10, 2007

Nitridated  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> (100) substrate was investigated as the substrate for GaN epitaxial growth. The effects of nitridation temperature and surface roughness of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> wafers on the formation of GaN were studied. It was found that the most optimized nitridation temperature was 900 °C, and hexagonal GaN with preferred orientation was produced on the well-polished wafer. The nitridation mechanism was also discussed.

OCIS codes: 350.3850, 240.6700, 250.0250, 290.5860, 250.5230.

GaN based nitrides semiconductors have been widely applied in the high-brightness blue and green light-emitting diodes (LEDs), laser diodes (LDs), ultraviolet (UV) photo-detectors, as well as high power or high temperature microelectronic devices<sup>[1–3]</sup>. However, there exist several problems in the epitaxial growth of nitrides, which originate from the non-availability of high quality single crystalline GaN substrates or other single crystalline substrates with the same lattice parameters as GaN. Recently, most of the epitaxial growth of nitrides is performed on sapphire or SiC substrates. Nevertheless, it is inevitable to introduce large amount of defects and there exist some critical disadvantages of epitaxial nitrides on these two types of substrates<sup>[4]</sup>. Although it is ideal that GaN substrates could be used in epitaxial growth of nitrides thin films and researchers have developed several technologies for growth of bulk GaN single crystal, such as hydride vapor phase epitaxy (HVPE)<sup>[5]</sup>, it is still hard to make it applicable due to its small crystal size and high fabrication cost.

$\beta$ -Ga<sub>2</sub>O<sub>3</sub> belongs to the monoclinic system with space group  $C_{2/m}$ . The lattice parameters are  $a = 1.223$  nm,  $b = 0.304$  nm,  $c = 0.580$  nm and  $\beta = 130.7^\circ$ . It has the widest band gap ( $E_g \sim 4.8$  eV) among transparent conducting oxides (TCOs), and is transparent from visible to UV regions<sup>[6]</sup>. The mismatch between the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> substrate and GaN film is relatively small ( $b$ -axis:  $-4.49\%$ ;  $c$ -axis:  $5.27\%$ ) under the epitaxial relationship being  $(100)_{\text{Ga}_2\text{O}_3} \parallel (001)_{\text{GaN}}$ . Besides, the as-grown  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> single crystal produced by floating zone method is electrically conductive. Ueda *et al.* reported that the Hall mobility was  $46 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$  along  $b$  direction in the (100) plane<sup>[7]</sup>. After that the first blue LED on  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> with vertical current injection was demonstrated by Shimamura *et al.*<sup>[8]</sup>. By combining these advantages,  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> has great potential utility in GaN epitaxial growth. Furthermore, in order to acquire high quality GaN epitaxial films without using a buffer layer, several researchers have tried to nitride the surface of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub><sup>[4,9,10]</sup>. Ohira *et al.*<sup>[9]</sup> reported that approximately 50-nm-thick nitride layer with preferred in-plane orienta-

tion was produced on the surface of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> at 850 °C for 5 h in NH<sub>3</sub> atmosphere. Almost at the same period, Villora *et al.* obtained high quality  $c$ -plane wurtzite GaN on nitridated  $a$ -plane  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> using molecular beam epitaxy (MBE) method<sup>[10]</sup>. However, there is no study focusing on the effects of nitridation temperature and surface roughness on the nitridated layers.

In this letter, we successfully fabricated GaN layer on  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> (100) surface by nitridation under NH<sub>3</sub> atmosphere. The effects of nitridation temperatures and surface roughness on the nitridated layers were investigated in order to better understand the nitridation process. The characterizations of the surface structure, morphology, photoluminescence, and cathode-luminescence of the nitridated  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> single crystal wafers were performed using various techniques.

The single crystal  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> used in this paper was grown by floating zone method.  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> powder with a commercial grade of 5N (99.999%) purity was used as starting material.  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> powder was pressed into rods by a cold isostatic press under a pressure of 70 MPa, and subsequently sintered at 1500 °C for 10 h in the air. The sintered rod was 70 – 80 mm long and 6 – 7 mm in diameter. Crystal growth was carried out by floating zone technique using four-halogen lamps (FZ-T-10000-H-VI-VP, Japan Crystal Growth System Co., Ltd.). The previously grown single crystal was set as a seed with the (100) plane in the growth direction. The sintered rods rotated at 15 rpm and the crystals were grown with a speed of 5 – 10 mm/h under dry air flow with a rate of 0.2 m<sup>3</sup>/h.

The as-grown single crystal was cut along the plane (100) and the wafers were divided into two groups. The wafers in group one were mechanically polished and the others in group two remained unpolished. Nitridation was carried out in a conventional chemical vapor deposition (CVD) resistively heated furnace with a horizontal alumina oxides reaction tube.  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> (100) substrates were placed in the hot zone inside the reaction tube and kept at 500, 800, 900, 950 and 1000 °C for 5 h, respectively. NH<sub>3</sub> was introduced into the tube with a

constant flow of 40 – 45 sccm. At the temperature of 900 °C, we nitridated two wafers: one was well polished and the other was unpolished. The wafers nitridated at other temperatures were all well polished. The phases and crystal structures of samples were analyzed by X-ray diffraction (XRD) technique using Ni-filtered Cu  $K\alpha$  radiation (Rigaku Corp.; 40 kV, 300 mA). X-ray in-plane diffraction with a grazing incident angle of 0.4° was also employed to analyze the lateral structure of nitridated layers. Raman-scattering experiments were performed using a micro-Raman system at room temperature. The 514-nm lines of an Ar<sup>+</sup> laser with an exposure time of 10 s were used for excitation. The room temperature photoluminescence (PL) spectrum was obtained using a He-Cd laser under excitation of 325 nm and the cathodoluminescence (CL) measurement was conducted by a MonoCL3 cathodoluminescentmeter with the excitation voltage of 10 kV. The surface morphology was observed by field emission scanning electron microscope (SEM) (JEOL JSM-6500F), under an acceleration voltage of 15 kV.

The nitridated samples are classified into four different groups A, B, C, D, respectively. The sample in group A is nitridated at the temperature of 500 °C. Observed from the related SEM images (not listed) and the in-plane XRD results, no GaN related products are found on the surface. The sample in group B is nitridated at the temperature of 800 °C, and its SEM image is shown in Fig. 1(a). We can see that a good many disordered crystal grains form on the substrate. Nitrogen is detected on the grains by the energy dispersive X-ray (EDS) analysis. However, the proportion of nitrogen in the whole nitridated surface is uneven. We select several spots for EDS detection and find a relatively large amount of nitrogen (12.23 at.-%) in some spots such as the spot “a”. The content of nitrogen in other spots is beyond EDS sensitivity. We can conclude that at 800 °C

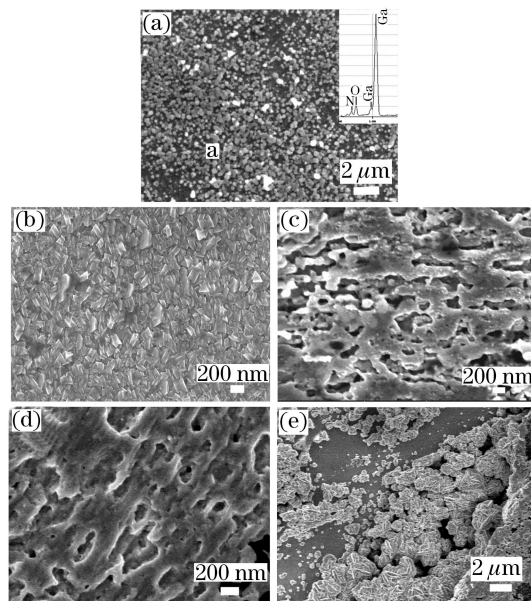
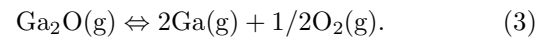
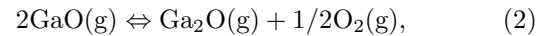
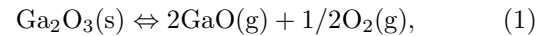


Fig. 1. Field emission SEM images of surface morphology of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> (100) after nitridation at different temperatures of (a) 800 °C, the inset is the EDS result corresponding to the spot “a”; (b) 900 °C (the well-polished sample); (c) 900 °C (the unpolished sample); (d) 950 °C; (e) 1000 °C.

crystal grains form as GaN<sub>x</sub>O<sub>y</sub> particles, a mixed phase of GaN and  $\beta$ -Ga<sub>2</sub>O<sub>3</sub><sup>[9]</sup>. The samples in group C that were nitridated at the temperature of 900 °C are of yellowish coloration. As displayed in Fig. 1(b), the grain size is about 100 – 500 nm, far larger than that reported in Ref. [9]. And the nitridated layer is compact and appears as a form of layer. The corresponding XRD results (see C<sub>0</sub> and C<sub>1</sub> in Fig. 2) indicate that these crystal grains are not simple aggregation of GaN particles but exist as a layer preferably oriented in the direction of GaN [001]. Besides, on the surface of the sample without polishing treatment before nitridation, many cavities along with discontinuous nitridated layers can be observed, as seen from Fig. 1(c). In order to obtain the most optimized nitridation condition we also performed nitridation treatment at the temperatures of 950 and 1000 °C. The samples in group D under these nitridation temperatures appear dark-yellowish. The morphologies of these samples are given in Figs. 1(d) and (e). Apparently when the temperature increases over 950 °C the surfaces of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> substrates are nitridated heavily. Poor quality with porous nitridated layers and low adhesiveness are obtained. Especially at the temperature of 1000 °C the nitridated layer falls off, which can be explained as: the evaporation of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> at high temperature results in the porous layer following the reactions<sup>[11]</sup>



And it can be stimulated in the reducing atmosphere since the NH<sub>3</sub> will be decomposed into the reactive nitrogen and hydrogen.

The XRD patterns of the samples nitridated at temperatures of 900 (C<sub>0</sub>—unpolished, C<sub>1</sub>—polished), 950 (D<sub>0</sub>), and 1000 °C (D<sub>1</sub>) are exhibited in Fig. 2. The patterns of all the samples contain a strong diffraction peak corresponding to  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> (400) in addition to several GaN peaks, indicating that the surface of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> substrates has changed structurally to GaN at these nitridation temperatures. The reflection peaks at  $2\theta = 32.3^\circ$ ,  $34.48^\circ$  and  $36.72^\circ$  correspond to hexagonal GaN (100), (002) and (101), respectively, which are well matched with the JCPDS card 50-0792. Another peak located at  $37.4^\circ$

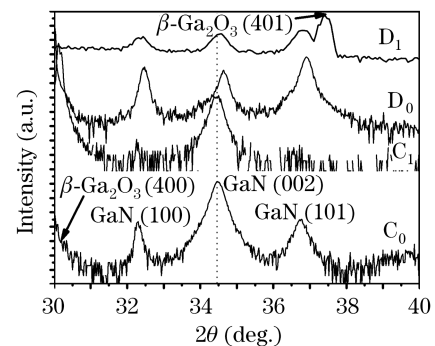


Fig. 2. XRD pattern of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> substrate after nitridation with NH<sub>3</sub> at different temperatures: C<sub>0</sub>—900 °C (no polishing); C<sub>1</sub>—900 °C (well-polished); D<sub>0</sub>—950 °C; D<sub>1</sub>—1000 °C.

of  $D_1$  corresponds to  $\beta$ - $\text{Ga}_2\text{O}_3$  (401), because single-crystal  $\beta$ - $\text{Ga}_2\text{O}_3$  substrates are damaged in the reducing atmosphere at this high temperature. Close examination of the XRD diffraction patterns implies us two important experiment results. First, the hexagonal GaN (002) is preferably detected on the sample  $C_1$  well-polished before nitridation by XRD  $\theta$ - $2\theta$  scan. The lattice parameters determined from the XRD data are  $a = 0.31889$  nm and  $c = 0.51875$  nm, a little smaller than the results reported in Ref. [9]. Second, as the temperature increases from 900 to 950 °C, the diffraction patterns shift to higher angles, and the lattice constants decrease to  $a = 0.31727$  nm and  $c = 0.51727$  nm. The lattice constants of samples nitridated at 950 and 1000 °C are almost equal. As shown in Fig. 1, the nitridated GaN layers on the substrates in group C are compact and those in group D (950 and 1000 °C) are porous layers with low adhesiveness. Consequently, different residual stresses within these different nitridated layers contribute to the changes of lattice constants. We have also tried to monitor the nitridated layers of the samples in group A and B using X-ray in-plane diffraction with a grazing incident angle but no peaks corresponding to GaN were detected.

The measured phonon frequencies at room temperature are demonstrated in Fig. 3 and assignments of the phonon modes are listed in Table 1. Our results can be compared

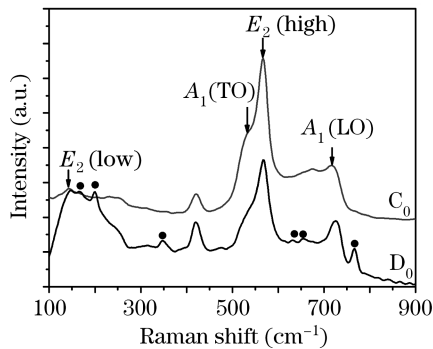


Fig. 3. Room temperature Raman spectra of nitridated samples at different temperatures:  $C_0$ –900 °C;  $D_0$ –1000 °C. The symbol “●” represents the phonon modes of the substrate  $\beta$ - $\text{Ga}_2\text{O}_3$ .

**Table 1. Raman Peaks (Unit:  $\text{cm}^{-1}$ ) Observed in Our Work and the Corresponding Symmetry Assignments (Raman Peaks in Others’ Works Are also Listed for Comparison)**

Bulk GaN	GaN Film <sup>b</sup>	GaN Nanowires <sup>c</sup>	Our Work	Symmetry Assignments
144	145		145	$E_2$ (Low)
			253	Zone-Boundary Phonon
			312	Acoustic Overtone
			421	Acoustic Overtone
533	533	531	531	$A_1$ (TO)
561	561	560	567	$E_2$ (High)
735	735	733	715	$A_1$ (LO)
743	742	745		$E_1$ (LO)

<sup>a</sup>From Ref. [12]; <sup>b</sup>from Ref. [13]; <sup>c</sup>from Ref. [14].

with previous works for bulk GaN<sup>[12]</sup>, GaN thin film<sup>[13]</sup> and GaN nanowires<sup>[14]</sup>. According to the factor group, eight sets of optical phonons can be found in GaN single crystal near the zone center<sup>[15]</sup>. In our study, four Raman-active phonon bands at 145, 531, 567 and 715  $\text{cm}^{-1}$  are observed, which correspond to  $E_2$  (low),  $A_1$  (TO),  $E_2$  (high) and  $A_1$  (LO), respectively. The strong  $E_2$  (high) phonon line in these two samples reflects the wurtzite phase of nitridated GaN layer. Besides these four bands, additional four peaks positioning at 253, 312, 421 and 672  $\text{cm}^{-1}$  are also observed, which are not permitted by the  $C_{6v}^4$  space group in the first order Raman scattering at the zone center. We can attribute the modes of 312 and 421  $\text{cm}^{-1}$  with  $A_1$  symmetry to the overtone of transverse-acoustic phonons<sup>[16]</sup>. An extra mode at 254  $\text{cm}^{-1}$  could possibly be ascribed to the zone-boundary phonons activated by the surface disorder<sup>[17]</sup>. In addition, the broad and weak band at 672  $\text{cm}^{-1}$  is probably associated to a defect level below the minimum of GaN conduction band<sup>[15]</sup>. We note that there are several phonon bands corresponding to  $\beta$ - $\text{Ga}_2\text{O}_3$  substrate (marked by the symbol “●” in Fig. 3) in the sample nitridated at 1000 °C, which can be due to the emerging surface of the substrate by nitridation. We have also measured the Raman spectra of the sample nitridated at 800 °C but no band corresponding to wurtzite GaN can be observed except the bands of  $\beta$ - $\text{Ga}_2\text{O}_3$ .

PL spectra of the samples nitridated at temperatures 900, 950, and 1000 °C are given in Fig. 4. Each PL spectrum shows a near band-edge peak at about 362 nm and a broad “yellow” peak at approximately 560 nm. We have tried to measure the PL spectrum of the sample nitridated at 800 °C, but we cannot observe the emission from GaN due to the strong emission of  $\beta$ - $\text{Ga}_2\text{O}_3$  substrates. Because CL has some advantages compared with PL, such as higher energy and stronger focusing capability, we investigated CL of the sample nitridated at 800 °C, as shown in the inset of Fig. 4. When the spectrum is extracted by Gauss fitting, two separate peaks corresponding to 385 and 416 nm are observed. The 385-nm peak probably originates from the emission of  $\text{GaN}_x\text{O}_y$  particles on the  $\beta$ - $\text{Ga}_2\text{O}_3$  substrate. And the appearance of the 416-nm peak can be due to the emission of  $\beta$ - $\text{Ga}_2\text{O}_3$  substrate induced by the penetration of the high energy electrons<sup>[18]</sup>.

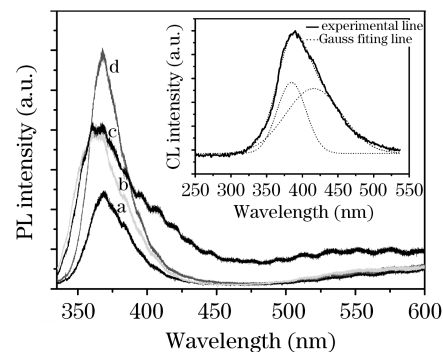


Fig. 4. Room temperature PL spectra of the nitridated samples: a–900 °C (well-polished); b–950 °C; c–1000 °C; d–900 °C (no polishing). Inset: CL spectrum of the sample nitridated at 800 °C.

In conclusion, hexagonal GaN layer was successfully produced on the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> (100) surface in NH<sub>3</sub> atmosphere in the conventional CVD reactor. This method could be served as a new way to fabricate suitable substrates for GaN related nitrides epitaxial growth. The XRD and SEM results reveal that the formed GaN layer greatly depends on nitridation temperatures and surface conditions. A dense and highly oriented GaN layer was fabricated on the well-polished wafer at 900 °C, which is crucial for the epitaxial growth of GaN thin film. A strong near band emission of GaN is also observed in the samples nitridated at 900, 950, and 1000 °C.

This work was supported by the National Natural Science Foundation of China under Grant No. 50672105, and the Hundred Talents Program of Chinese Academy of Sciences. C. Xia is the author to whom the correspondence should be addressed, his e-mail address is xia\_ct@siom.ac.cn.

## References

1. N. S. Yu, L. W. Guo, H. Chen, Z. G. Xing, B. H. Ge, J. Wang, X. L. Zhu, M. Z. Deng, J. F. Yan, H. Q. Jia, and J. M. Zhou, *J. Alloys and Compounds* **428**, 312 (2007).
2. S. Nakamura, M. Senoh, S.-I. Nagahama, N. Iwasa, T. Tamada, T. Matsushita, H. Kiyoku, Y. Sugimoto, T. Kozaki, H. Omemoto, M. Sano, and K. Chocho, *Jpn. J. Appl. Phys.* **36**, L1568 (1997).
3. J. Lang, B. Gu, Y. Xu, and F. Qin, *Laser Technol. (in Chinese)* **27**, 321 (2003).
4. E. G. Villora, K. Shimamura, K. Aoki, and N. Ichinose, *J. Crystal Growth* **270**, 462 (2004).
5. Z. Yin, F. Zhong, K. Qiu, X. Li, and Y. Wang, *Chin. J. Semiconductors (in Chinese)* **28**, 909 (2007).
6. J. Zhang, C. Xia, F. Wu, G. Pei, and J. Xu, *J. Synthetic Crystals (in Chinese)* **34**, 676 (2005).
7. N. Ueda, H. Hosono, R. Waseda, and H. Kawazoe, *Appl. Phys. Lett.* **70**, 3561 (1997).
8. K. Shimamura, E. G. Villora, K. Domen, K. Yui, K. Aoki, and N. Ichinose, *Jpn. J. Appl. Phys.* **44**, L7 (2005).
9. S. Ohira, M. Yoshioka, T. Sugawara, K. Nakajima, and T. Shishido, *Thin Solid Films* **496**, 53 (2006).
10. E. G. Villora, K. Shimamura, K. Aoki, and K. Kitamura, *Thin Solid Films* **500**, 209 (2006).
11. Y. Tomm, P. Reiche, D. Klimm, and T. Fukuda, *J. Crystal Growth* **220**, 510 (2000).
12. P. Perlin, J. Camassel, W. Knap, T. Taliercio, J. C. Chervin, T. Suski, I. Grzegory, and S. Porowski, *Appl. Phys. Lett.* **67**, 2524 (1995).
13. H. M. Chen, Y. F. Chen, M. C. Lee, and M. S. Feng, *Phys. Rev. B* **56**, 6942 (1997).
14. G. S. Cheng, L. D. Zhang, Y. Zhu, G. T. Fei, L. Li, C. M. Mo, and Y. Q. Mao, *Appl. Phys. Lett.* **75**, 2455 (1999).
15. M. Ramsteiner, O. Brandt, and K. H. Ploog, *Phys. Rev. B* **58**, 1118 (1998).
16. H. Siegle, G. Kaczmarczyk, L. Filppidis, A. P. Litvinchuk, A. Hoffmann, and C. Thomsen, *Phys. Rev. B* **55**, 7000 (1997).
17. H.-L. Liu, C.-C. Chen, C.-T. Chia, C.-C. Yeh, C.-H. Chen, M.-Y. Yu, S. Keller, and S.-P. Denbaars, *Chem. Phys. Lett.* **345**, 245 (2001).
18. L. Binet and D. Gourier, *J. Phys. Chem. Solid* **59**, 1241 (1998).