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To cite this article: T. Sekiguchi et al 2002 Sci. Technol. Adv. Mater. 3 91

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Cathodoluminescence study of h- and c-GaN single crystals grown by a Na or K flux

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Received 14 November 2001; revised 3 December 2001; accepted 3 December 2001

Abstract

Luminescence properties of hexagonal (h-) and cubic (c-) GaN freestanding single crystals were studied by means of cathodoluminescence spectroscopy. The h-GaN crystals of about 0.2–2 mm in dimension were synthesized at 750 °C by the reaction of Ga and N\textsubscript{2} in a Na flux, while c-GaN crystals of about 0.3 mm or less in a K flux. The h-GaN showed rather strong band edge emission at room temperature compared with the crystal grown by using NaN\textsubscript{3} as a nitrogen source. At 20 K, the band edge emission of h-GaN was split into four peaks. The main energy peak position was 3.478 eV, which was assigned as the A-free exciton emission. The energy position of the main peak of c-GaN was 3.268 eV. Assuming the binding energies of excitons in h- and c-GaN as 25 and 26 meV, respectively, the energy difference of bandgap between h- and c-GaN is estimated to be 29 meV. Since these crystals are free from strain from the substrates, the peak energies are reliable for the intrinsic GaN crystals. The full widths at half maximum of the emission of c-GaN were much broader than those of h-GaN, suggesting that the cubic phase is much defective compared with the hexagonal one. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Cubic-GaN; Hexagonal-GaN; Flux growth; Cathodoluminescence; Exciton

1. Introduction

Great progress has been made in the science and technology of GaN and related III-nitrides for the use of blue-light emitters [1–3]. For the laser application, high quality GaN wafer is necessary to achieve the long life performance. Since most of the GaN wafers are grown on sapphire substrates, it is difficult to get strain-free and dislocation-free wafers. Many efforts were carried out to reduce the strain due to lattice mismatch from the substrate, such as Ga + HCl treatment [4], ZnO buffer [5] or low temperature growth of GaN buffer layer [6]. Epitaxial lateral overgrowth (ELO) [7] is an outstanding technique to reduce the dislocation density of GaN layer. However, it introduces rather high and nonuniform residual strain [8], which may accelerate the degradation of lasers. On the other hand, several techniques have been developed to grow freestanding GaN ingot. Such freestanding GaN ingots are desirable because they are free from the strain due to lattice mismatch. Porowski grew GaN single crystal of hexagonal platelet with 1 cm in dimension by solution growth at high-temperature and high-pressure [9,10]. He synthesized GaN at 1500 °C and under high N\textsubscript{2} pressure of 1 GPa. Yamane et al. [11] succeeded to grow single crystals using Na flux under rather low temperature and low pressure. First, they used NaN\textsubscript{3} for the nitrogen supplier. They put Ga and NaN\textsubscript{3} into a stainless steel container and heated them up to 750 °C. However, the nitrogen pressure decreased in accordance with GaN growth. They improved this technique to realize steady state growth under constant nitrogen pressure [12,13]. In this paper, we have characterized the bulk GaN crystals of hexagonal (h-) and cubic (c-) phase synthesized with improved alkali flux method.

2. Experimental

GaN single crystals were grown by an alkali flux method. For h-GaN, Ga (99.9999%) and Na (99%) metals were put in a BN crucible and capped in a BN plate. The crucible was set in a stainless steel container, which was connected to a N\textsubscript{2} gas-feed line. The container was heated up to 750 °C and N\textsubscript{2} gas was fed into it up to a pressure of 5 MPa. Keeping this condition for 200 h, the agglomerate of single crystals was grown in the crucible. The details of the crystal growth condition are shown in Ref. [13]. For c-GaN, Ga and K (99.5%) were put in a BN crucible and treated in the same
manner [12]. The differences from the h-GaN case were the 
N$_2$ pressure of 7 MPa and the growth duration of 96 h.
The grown crystals were characterized by scanning
electron microscope (SEM), X-ray diffraction, and cathodo-
luminescence (CL). CL measurement was performed with a
CL system attached with a SEM [14]. Charge coupled
device (CCD, Jobin Yvon; Spectra View 2D) was used for
the parallel detection of luminescence spectra [15]. A
grating of 100 grooves/mm with a blaze wavelength of
450 nm was used for the wide range observation. The slit
width was 0.1 mm, which corresponds to the wavelength
resolution of 2.9 nm. A grating of 1200 grooves/mm with
a blaze wavelength of 300 nm was used for the high-
resolution measurement. The slit width was 50 μm
corresponding to 0.12 nm resolution. Most of the CL
measurement was carried out with an electron beam of
5 kV and 1 nA.

3. Results and discussion

The GaN crystals grown under the Na flux were wurtzite
type (hexagonal). The morphology varied from prism to
platelet according to Na/(Na + Ga) ratio [11]. Fig. 1(a)
shows the secondary electron (SE) image of the agglomerate
of h-GaN crystals. It was an ensemble of small prismatic
crystals whose size was about 200 μm. The color of the
crystal varied from colorless transparent to dark brown
according not only to the batch of the crystal growth but
also to the position in the crucible. Sometimes, the bigger
prisms of about 2 mm in length were grown in the crucible
as shown in Fig. 1(b). This crystal was transparent and the
surface was rather smooth.

Fig. 2 shows the CL spectra of various prismatic h-GaN
crystals taken at room temperature. The spectra are
displayed in the order of transparency. The spectra (a)–(c)
in Fig. 2 were taken from the colorless transparent prism,
faint orange crystal, and pale brown one, respectively. The
transparent prisms had a strong band edge emission at
3.4 eV, which is more than two times stronger than those
in the colored crystals. No significant emission was
observed in the visible region. In the colored crystals, on
the other hand, a broad emission at 2.4 eV was observed as
well as the band edge emission. The darker the color of the
crystal is, the stronger the visible emission becomes. The
typical CL spectrum of the crystal grown from Ga and NaN$_3$
is also shown in Fig. 2(d). The peak position of the visible
emission in this case was 2.8–3.0 eV, indicating that the
species of impurity or defect were different from those in
the present growth method. It also indicated that, although
there exists the variation of CL spectra among the crystals in

Fig. 1. Secondary electron images of h-GaN crystals. (a) Agglomeration
and (b) bigger prism.

Fig. 2. CL spectra taken from h-GaN grown by the present method.
(a) Transparent, (b) faint orange, and (c) pale brown crystals and (d) the
brown crystal grown by Ga and NaN$_3$. Electron beam of 5 kV and 1 nA,
temperature 295 K.

Fig. 3. Secondary electron image of c-GaN crystals.
one growth batch, the visible emission in the crystals grown by the new method became weaker compared to that in the former ones [16]. The band edge emission, in turn, became stronger in the present crystals.

Contrary to the growth in Na flux, most of the crystals grown in K flux were zinc-blende type (cubic). The crystal structure and lattice parameters were determined by X-ray diffraction [12]. Fig. 3 shows the SE image of the cubic crystals. The square facets or the existence of fourfold and threefold-axes reflects the cubic symmetry. The crystals were about 30 µm or less in size. The largest one we have grown was 0.1 mm or less in size. Many steps were observed in the facets, indicating that the c-GaN crystals have lots of planar defects such as stacking faults or twins. The color of the crystal also varied from transparent to black. Fig. 4 shows the CL spectra taken from (a) fairly transparent, (b) pale orange and (c) brown c-GaN crystals. In all the spectra, a sharp peak was observed at 3.2 eV and a broad band was observed in the range from 2.4 to 2.8 eV. The former corresponds to the band edge emission while the latter to the impurity or defect related emission. Similar to the h-GaN case, the colored crystals have the smaller band edge emission and the stronger visible emission than the transparent one. In the brown crystal, the CL intensities of UV and visible emission have been suppressed, suggesting that this crystal contains a large amount of impurities and/or defects acting as nonradiative centers. Although the origin of this visible emission is not clear at all, this may come from the contamination of surroundings. Thus, the transparency of the crystal can roughly tell us the purity of the crystal.

To clarify the difference of band gap energy in h- and c-GaN, the CL spectra were taken at 20 K. Fig. 5 shows the CL spectra of transparent crystals at the band edge region in a high resolution mode. Four peaks were observed in h-GaN, while two in c-GaN. These spectra were fitted using Lorentzian and the fitted peak positions, intensities and full widths at half maximum are listed in Table 1. In h-GaN, CL lines are composed of one intense peak at 3.478 eV and three weak lines at 3.447, 3.393, and 3.299 eV. The main peak at 3.478 eV was assigned as A-free exciton involving holes in Γv valence band (abbreviated as A-FE). The small peak at 3.447 eV was attributed as neutral acceptor bound excitonic transition (A′X). Other two peaks are one and two longitudinal-optical (1-LO and 2-LO) phonon replicas of A-FE, since the energy of LO phonon in h-GaN is 91 meV. Because the A-exciton binding energy is 25 meV [17], the bandgap energy of h-GaN is 3.503 eV. The two peak positions of c-GaN were determined as 3.268 and 3.202 eV. We assigned the former to the exciton recombination (X). Since the latter peak is not so clear, we tentatively attribute it to donor–acceptor pair recombination (DA), according to the literature [18,19]. As et al. [19] reported that the binding energy of exciton in c-GaN is 26 meV. If we assume this value, the bandgap energy of c-GaN is 3.294 eV. Ramírez-Flores et al. [20] reported this value as 3.302 eV. Menninger et al. [18] estimated it to be 3.297–3.300 eV. Our value is a few meV smaller than these reported values. Since the former study used the GaN crystals grown on the substrate other

Table 1
The parameters of CL peaks in h-GaN and c-GaN

| Number | Peak position (eV) | Peak intensity (cps) | FWHM (meV) |
|--------|-------------------|---------------------|-------------|
| h-GaN  |                   |                     |             |
| 1      | 3.4784            | 4471                | 9.6         |
| 2      | 3.4472            | 316                 | 6.8         |
| 3      | 3.3931            | 399                 | 12          |
| 4      | 3.2989            | 199                 | 16          |
| c-GaN-1|                   |                     |             |
| 1      | 3.2683            | 5028                | 44          |
| 2      | 3.2072            | 1340                | 118         |
| c-GaN-2|                   |                     |             |
| 1      | 3.2666            | 2130                | 32          |
| 2      | 3.1970            | 469                 | 95          |

Fig. 4. CL spectra taken from c-GaN grown by the present method. (a) Transparent, (b) pale orange, and (c) brown crystals. Electron beam of 5 kV and 1 nA, temperature 295 K.

Fig. 5. CL spectra taken from one h-GaN and two c-GaN crystals at 20 K. High-resolution, electron beam of 5 kV and 1 nA.
than GaN, they were not free from the residual strain. In our case, however, we are free from such a constraint. Thus, our data seem more reliable to represent the intrinsic band gap of c-GaN. It is also noted that, if we adopt these data, the difference of bandgap energy between h-GaN and c-GaN is estimated to be 209 meV.

The A-FE line in h-GaN is rather narrow having a full width at half maximum (FWHM) of 9.6 meV. Contrary to this, the X line in c-GaN is broad with FWHM of about 40 meV. Menninger et al. [18] have grown h- and c-GaN crystals of 1 μm in size by molecular beam epitaxy on GaAs substrate and observed their CL spectra. They reported 10 meV as FWHM of A-FE line in h-GaN and 8 or 11 meV for X line in c-GaN. Since our FWHM of A-FE is same as their value, our freestanding h-GaN crystals have similar crystallinity like MBE grown one. On the other hand, the large FWHM value suggests that our c-GaN is rather defective. The existence of surface steps in SE image is consistent with this large FWHM. These observations show that the growth condition of c-GaN is rather critical. If we use these freestanding crystals for the seed of bulk GaN growth, h-GaN crystals are suitable for this purpose. However, some improvement is necessary to obtain the defect free c-GaN crystals.

4. Summary

We have grown hexagonal and cubic GaN freestanding crystals by alkali flux method using Na and K, respectively. The transparent crystals have stronger band edge emission and weaker visible emission than colored ones. The c-GaN crystals were rather defective containing planar defects. CL spectra showed that the A-free exciton emission peak in h-GaN is 3.478 eV while the excitonic emission in c-GaN is 3.268 eV. These values are reliable because the crystals are free from the effect of strain from substrates. Assuming the binding energies of exciton in h- and c-GaN as 25 and 26 meV, respectively, the difference of bandgap energy between h- and c-GaN is estimated as 209 meV.

References

[1] S. Nakamura, M. Senoh, N. Iwasa, S.-i. Nagahama, High-brightness in InGaN blue, green and yellow light-emitting diodes with quantum well structures, Jpn. J. Appl. Phys. 34 (1995) L797–L799.
[2] S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, H. Kiyoku, Y. Sugimoto, InGaN-based multi-quantum-well-structure laser diodes, Jpn. J. Appl. Phys. 35 (1996) L74–L76.
[3] J.W. Orton, C.T. Foxon, Group III nitride semiconductors for short wavelength light-emitting devices, Rep. Prog. Phys. 61 (1998) 1–75.
[4] K. Naniwae, S. Itoh, H. Amano, K. Itoh, K. Hiramatsu, I. Akasaki, Growth of single crystal GaN substrate using hydride vapor phase epitaxy, J. Cryst. Growth 99 (1990) 381–384.
[5] T. Detchprohm, K. Hiramatsu, H. Amano, I. Akasaki, Hydride vapor phase epitaxial growth of a high quality GaN film using a ZnO buffer layer, Appl. Phys. Lett. 61 (1992) 2688–2690.
[6] H. Tsujiya, K. Sunaba, T. Saemasu, F. Hasegawa, Growth condition dependence of GaN crystal structure on (001) GaAs by hydride vapor-phase epitaxy, J. Cryst. Growth 189/190 (1998) 395–400.
[7] A. Usui, H. Sunakawa, A. Sakai, A.A. Yamaguchi, Thick GaN epitaxial growth with low dislocation density by hydride vapor phase epitaxy, Jpn. J. Appl. Phys. 36 (1997) L899–L902.
[8] F. Bertram, T. Riemann, J. Christen, A. Kaschner, A. Hoffmann, C. Thomsen, K. Hiramatsu, T. Shibata, N. Sawaki, Strain relaxation and strong impurity incorporation in epitaxial laterally overgrown GaN: direct imaging of different growth domains by cathodoluminescence microscopy and micro-Raman spectroscopy, Appl. Phys. Lett. 74 (1999) 359–361.
[9] S.Porowski, High pressure growth of GaN—new prospects for blue lasers, J. Cryst. Growth 166 (1996) 583–589.
[10] S. Porowski, Bulk and homoepitaxial GaN-growth and characterisation, J. Cryst. Growth 189/190 (1998) 153–158.
[11] H. Yamane, M. Shimada, T. Sekiguchi, F.J. DiSalvo, Morphology and characterization of GaN single crystals grown in a Na flux, J. Cryst. Growth 186 (1998) 8–12.
[12] H. Yamane, T. Kajiwara, T. Sekiguchi, M. Shimada, Zinc-blende-type cubic GaN single crystals prepared in a potassium flux, Jpn. J. Appl. Phys. 39 (2000) L146–L148.
[13] M. Aoki, H. Yamane, M. Shimada, T. Sekiguchi, T. Hanada, T. Yoo, S. Sarayama, F.J. DiSalvo, Growth of GaN single crystals from a Na–Ga melt at 750 °C and 5 MPa of N2, J. Cryst. Growth 218 (2000) 7–12.
[14] T. Sekiguchi, K. Sumino, Quantitative electron-beam tester for defects in semiconductors (CL/EBIC/SDLTS system), Rev. Sci. Instrum. 66 (1995) 4277–4282.
[15] T. Sekiguchi, H.S. Leipner, Damage-induced luminescence in InP, Appl. Phys. Lett. 67 (1995) 3777–3779.
[16] T. Sekiguchi, N. Ohashi, H. Yamane, Cathodoluminescence study on ZnO and GaN, Diffus. Defect Data B (Solid State Phenom.) 63–64 (1998) 171–181.
[17] A. Shikanai, T. Azuhata, T. Sota, S. Chichibu, A. Kuramata, K. Horino, S. Nakamura, Biaxial strain dependence of exciton resonance energies in wurtzite GaN, J. Appl. Phys. 81 (1997) 417–424.
[18] J. Menninger, U. Jahn, O. Brandt, H. Yang, K. Ploog, Identification of optical transitions in cubic and hexagonal GaN by spatially resolved cathodoluminescence, Phys. Rev. B 53 (1996) 1881–1885.
[19] D.J. As, F. Schmitgus, C. Wang, B. Schottker, D. Schikora, K. Lischka, The near band edge photoluminescence of cubic GaN epilayers, Appl. Phys. Lett. 70 (1997) 1311–1313.
[20] G. Ramirez-Flores, H. Navarro-Contreras, A. Lasstras-Martinez, R.C. Powell, J.E. Greene, Temperature-dependent optical band gap of the metastable zinc-blende structure [beta]-GaN, Phys. Rev. B 50 (1994) 8433–8438.