MRS Internet Journal of Nitride Semiconductor Research

Volume 2, Article 39

Physical Properties of Bulk GaN Crystals Grown by HVPE

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This article was received on June 11, 1997 and accepted on September 17, 1997.

Abstract

Free standing GaN platelets were fabricated by hydride vapor phase epitaxy (HVPE). The platelets having a current maximum size of 7x6x0.1 mm^3 were obtained by HVPE growth of ~100 µm thick GaN layers on SiC substrates and subsequent removal of the substrates by reactive ion etching (RIE). Surface of the GaN platelets was characterized by reflectance high energy election diffraction (RHEED), and Auger electron spectroscopy (AES). Crystal structure and optical properties of the platelets were studied by x-ray diffraction and photoluminescence (PL), respectively. Raman spectroscopy was also applied for material characterization. Residual strain was detected in the crystals. The stress was eliminated by high temperature anneal.

1. Introduction

The Group III-V nitrides (GaN, AlN, InN) are the prominent materials for blue-green and UV light emitting diodes (LEDs), laser diodes (LDs), and high frequency, high power transistors. High brightness blue and green III-V nitride LEDs have been commercialized [1], and prototype LDs have been demonstrated [2]. Despite a rapid progress in the field, a number of basic scientific and technological issues remain to be unsolved. One of the most severe problem is the lack of a suitable substrate material on which lattice-matched nitride films may be grown.

The most widely used substrates for III-V nitride epitaxy are sapphire [3] and silicon carbide [4]. However, a poor lattice match and difference of thermal expansion coefficients for these substrates usually lead to the formation of threading defects, high dislocation density, and residual strains in the epitaxial layers. These defects may affect both electrical and optical properties of the material and devices. If available, bulk GaN substrates would be a better choice.

Previously, GaN free standing platelets have been fabricated by hydride vapor phase epitaxy (HVPE) using sapphire substrates [5]. We believe that SiC is a better substrate for GaN because of smaller lattice and thermal mismatch. It has been shown that HVPE method insures high quality GaN deposition on SiC substrates providing material with dislocation density in a low 10^8 cm^{-2} range. Thin (~1 µm) GaN layers grown by HVPE on SiC have been used as substrates for Molecular Beam Epitaxy of GaN [6]. In this paper, we report the fabrication of free standing GaN platelets by HVPE of ~100 µm thick GaN layers on SiC substrates and subsequent removal of the substrates by reactive ion etching (RIE).

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2. Sample Preparation

GaN epitaxial layers up to 100 μm in thickness were grown using the HVPE technique. The layers were deposited directly on SiC substrates without any buffer layers [7]. GaN was grown in a horizontal open flow reactor. HCl interacted with liquid Ga in the source zone to form GaCl gas which was transported to the growth zone and reacted with NH_3 resulting in GaN deposition on SiC substrate. The growth temperature was usually kept between 1220 and 1320 K. Ar was used as an ambient gas. GaN growth rate was about 0.06 mm/hr. 6H-SiC and 4H-SiC wafers 30 and/or 35 mm in diameter were used as substrates [a]. SiC substrates with 300, 200 and 40 μm thickness were used at the initial stage of this study. The substrate thinning was done by RIE.

After GaN growth, SiC substrates were removed by RIE in SF_6 containing gas mixture [8]. As a result, GaN layers were released from the substrates and free-standing bulk GaN crystals with a maximum size of 7x6x0.1 mm^3 were obtained (Figure 1). To prove the absence of cracks in these crystals, we etched some of them in CCl_2F_2 containing plasma. As reported earlier, the RIE process decorates the cracks [9]. No cracks were observed on most of the crystals.

The fracture of thick GaN layer was the main factor limiting the size of our bulk crystal. The residual strains which cause the fracture are due to the lattice mismatch and by the difference in thermal expansion coefficient between GaN and SiC. The stresses caused by the lattice mismatch may be significant. We observed the effect of these stresses at growth temperature. Thin (40 μm) SiC substrates were bending during the deposition process. To avoid bending, thick SiC substrates were used for later GaN crystal fabrication.

3. Characterization

3.1. Surface

After substrate removal, both sides of the GaN crystal were investigated. One side was the former GaN/SiC interface. Because of high selectivity of the RIE process, the GaN material would not be etched during SiC substrate removal. The opposite surface is the growth surface of the GaN layer. According to Ref. [10], we assume that the growth surface of GaN layer grown on (0001)Si face of SiC substrate is nitrogen terminated (we did not determine the surface polarity by ourselves). Thus, we name the growth surface of the GaN crystals as a N-face and the opposite side, the former SiC/GaN interface, as a Ga-face.

The Ga-face of the grown crystals is smooth and mirror like. Although this side of the crystal was exposed under low energy ion bombardment during the substrate removal, RHEED data indicated that the surface is monocrystalline (Figure 2). Auger electron spectroscopy showed that the surface has residual contamination as a result of RIE treatment. This contamination can be easily removed by cleaning of the crystals in chloride acid at room temperature (Figure 3). Because the GaN material was not etched during SiC substrate removal, thin (<0.4 μm) surface layer on Ga-face of obtained crystals is highly defective (it was shown that for GaN deposited on SiC, the defect density in 0.2 - 0.4 μm thick GaN interface layer is 2 - 3 orders higher than that in a top portion of the GaN material [7]).

The opposite, N-face is a former as-grown surface of thick GaN film. On this surface, etch pits were observed. We believe that the pits appeared because the surface was etched during the last stage of the growth process. The etch pit density (EPD) ranged for grown GaN crystals from $1.5x10^5 cm^{-2}$ to $5x10^6 cm^{-2}$. Figure 4 shows the scanning electron microscope (SEM) image of N-face of GaN bulk crystal with EPD of about $1.5x10^5 cm^{-2}$. The edge of the crystal cleaved through an etch pit is shown in Figure 5. It should be noted that the pit has the defined shape and that the cleaved edge of the crystal is very smooth.

It is important to note that according to Ref. [11], [12], GaN crystals grown by HVPE on sapphire and separated from the substrates required mechanical polishing to obtain a smooth surface. The GaN crystals fabricated in this study by HVPE growth on SiC and subsequent RIE removal of the substrate demonstrated flat monocrystalline surfaces without any mechanical treatment.

3.2. Crystal quality

The crystal quality of GaN bulk crystals was examined by x-ray diffraction. Rocking curves (RC) at (ω) and (ω,2θ) scanning modes were measured from both sides of bulk crystals. For best crystals, the full width at a half maximum (FWHM) of RC(ω) were measured about 150 arc sec for the N-face and about 170 arc sec for the Ga-face. The smallest FWHM of RC(ω,2θ) were about 19 arc sec and 21 arc sec for N-face and Ga-face, respectively. For all measured samples, the FWHM of RC is smaller for the N-face of the crystal, than that for Ga-face.

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The lattice constants of a grown crystal were measured using triple crystal modification of Bond method [13], [14] for (0004) and ($11\bar{2}4$) reflections. The measurement accuracy was 0.00005 Å for a lattice constant and 0.00002 Å for c lattice constant. High quality 6H-SiC crystals were used as monochromator and analyzer in the x-ray diffractometer. We obtained the following results for the GaN bulk crystal with dimensions of 2x3x0.1 mm^3:

- *for the N - face:* c= 5.18534 Å, a= 3.1879 Å, FWHM of RC(ω) = 180 arc sec;
- *for the Ga - face:* c= 5.18560 Å, a= 3.1893 Å, FWHM of RC(ω) = 340 arc sec.

These results show that GaN crystals had residual strains, since the lattice parameters for Ga-face differ from those for N-face. To reduce these residual strains, we annealed one GaN crystal at 1100 K for 40 min in N_2 ambient. As a result, the lattice parameters measured from both faces of the crystal become the same:

- *for the N-face:* c= 5.18500 Å, a= 3.1890 Å, FWHM of RC(ω) = 130 arc sec;
- *for the Ga-face:* c= 5.18500 Å, a= 3.1890 Å, FWHM of RC(ω) = 390 arc sec.

We conclude that residual strains in the sample were eliminated by the anneal. Broadening of x-ray rocking curve measured for Ga-face of the crystal was observed after the anneal in comparison to unannealed sample. Measured values of lattice constants together with other published data [15], [16] are shown in Table 1. For comparison, we also presented the lattice constants for thin GaN layers grown by HVPE on silicon carbide substrates. The nature of the difference in crystal lattice parameters measured for GaN crystals grown by different methods require further investigations.

3.3. Optical properties

Raman scattering measurements were carried out at room temperature using an Ar^+ laser (λ=488 nm) as a source of excitation. The scattered radiation was analyzed by a double grating monochromator connected to a computer-controlled systems for scanning and data acquisition. A backscattering geometry with the z direction parallel to the optical axis of the crystal was employed. The strains in GaN samples were estimated from the frequency shifts of first-order $E_2^{(2)}$ phonon line (~568 cm^{-1}) in the Raman spectra. The spectral resolution was 0.5 cm^{-1} and the scanning step was 0.1 cm^{-1}. A Ne lamp was used to precisely calibrate the monochromator.

The results of the Raman scattering measurements are shown in Figure 6 and Figure 7. Figure 6 shows a typical Raman spectrum of Ga-face of an annealed bulk GaN crystal. The $E_2^{(2)}$ phonon and A_1(LO) modes, as well as phonon-plasmon coupled LPP^- and LPP^+ modes, are observed. A simultaneous appearance of the A_1(LO) phonon near 740 cm^{-1} and a coupled phonon-plasmon LPP^+ mode near 1700 cm^{-1} in the spectrum is evidence of a nonuniform distribution of free carriers in the sample. The presence of an intense A_1(LO) mode near 740 cm^{-1} points to the existence of regions with the free carrier concentration in the order of $10^{17}cm^{-3}$, while the position of the LPP^+ mode is indicative of the presence of regions with the carrier concentration in the order of $10^{19}cm^{-3}$ [17]. This Figure also presents, on an enlarger scale, the spectra indicating a transformation of the LPP^+ mode depending on sample annealing. Figure 7 demonstrates an effect of the anneal on the coupled LPP^- mode and A_1(LO) phonon in the Raman spectrum. It is evident from the spectra shown in Figure 6 and Figure 7 that free electron concentration in the GaN crystal decreased after the anneal.

The inset in Figure 7 shows the position of the most strain-sensitive phonon line $E_2^{(2)}$ obtained for GaN crystal prior to annealing (curve 2) and after it (curve 3). For comparison, the Figure also shows the position of this line detected in the spectrum of a 2 μm thick GaN layer grown on a SiC substrate (curve 1). The $E_2^{(2)}$ peak positions for an unannealed GaN crystal (567 cm^{-1}) and thin GaN epitaxial layer grown by the same HVPE technique on a SiC substrate (565 cm^{-1}) point to the presence of in-plain tensile strains in unannealed sample and thin GaN epitaxial layer. For annealed sample, the frequency position of the $E_2^{(2)}$ mode (567.4 cm^{-1}) corresponds to the residual-deformation-free GaN crystal [18]. This is in good agreement with the results of x-ray measurements.

The photoluminescence (PL) spectra of the samples were obtained under excitation provided by HeCd-laser (λ= 325 nm) focused in the spot with power density of about 2 W/cm^2. Figure 8 shows a PL spectrum taken at 14 K from the N-face of unannealed GaN crystal. The dominant peak observed at 3.474 eV may be associated with donor bounded exciton. The FWHM of this peak equals to 3.5 meV. A ratio of its intensity to the signal in yellow region of the spectrum is higher than 400. Detail optical study of grown GaN crystals are under way.

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4. Conclusions

The free standing GaN platelets with current maximum size of 7x6x0.1 mm^3 were fabricated by HVPE growth on SiC substrate and subsequent removal of the substrate by RIE, for the first time. The GaN crystals had monocrystalline surfaces and good planarity obtained without mechanical treatment. For best grown crystals, the FWHM of x-ray ω-scan rocking curves was about 150 arc sec. Residual stress has been detected in these crystals by x-ray analysis and Raman spectroscopy. High temperature anneal (830°C for 40 min in nitrogen gas ambient) was used to eliminate residual strains in the crystal. Annealed crystal was strain-free and had the lattice parameters c = 5.18500 Å, and a = 3.1890 Å. The PL measurements performed at 14 K revealed the dominant peak at 3.474 eV having the FWHM of 3.5 meV. Further optimization of growth techniques should lead to increasing of size of these bulk GaN crystals.

Acknowledgments

The authors would like to thank V. Sizov, A. Nikolaev and M. Sheglov for technical assistance. This work was supported partially by the Arizona State University.

Footnotes

[a] Cree Research Inc., 2810 Meridian Parkway, Suite 176, Durham, NC 27713, USA.

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Table 1

GaN **a** and **c** lattice parameters measured at 300 K (Å).

	a	**c**
Thin (<1.5 μm) GaN layers grown by HVPE on SiC [this work]	3.1937-3.1969	5.1786 -5.1811
Bulk GaN crystal grown by HVPE [this work]	3.1893 (Ga face) 3.1879 (N face)	5.18560 (Ga face) 5.18534 (N face)
Annealed bulk GaN crystal grown by HVPE [this work]	3.1890	5.18500
Thick GaN layers grown by HVPE on sapphire substrate [15]	3.1892±0.0009	5.1850±0.0005
Bulk GaN crystals grown at high pressure [16]	3.1890±0.0003 (Ga face) 3.1881-3.1890 (N face)	5.1864±0.0002 (Ga face) 5.1856-5.1864 (N face)

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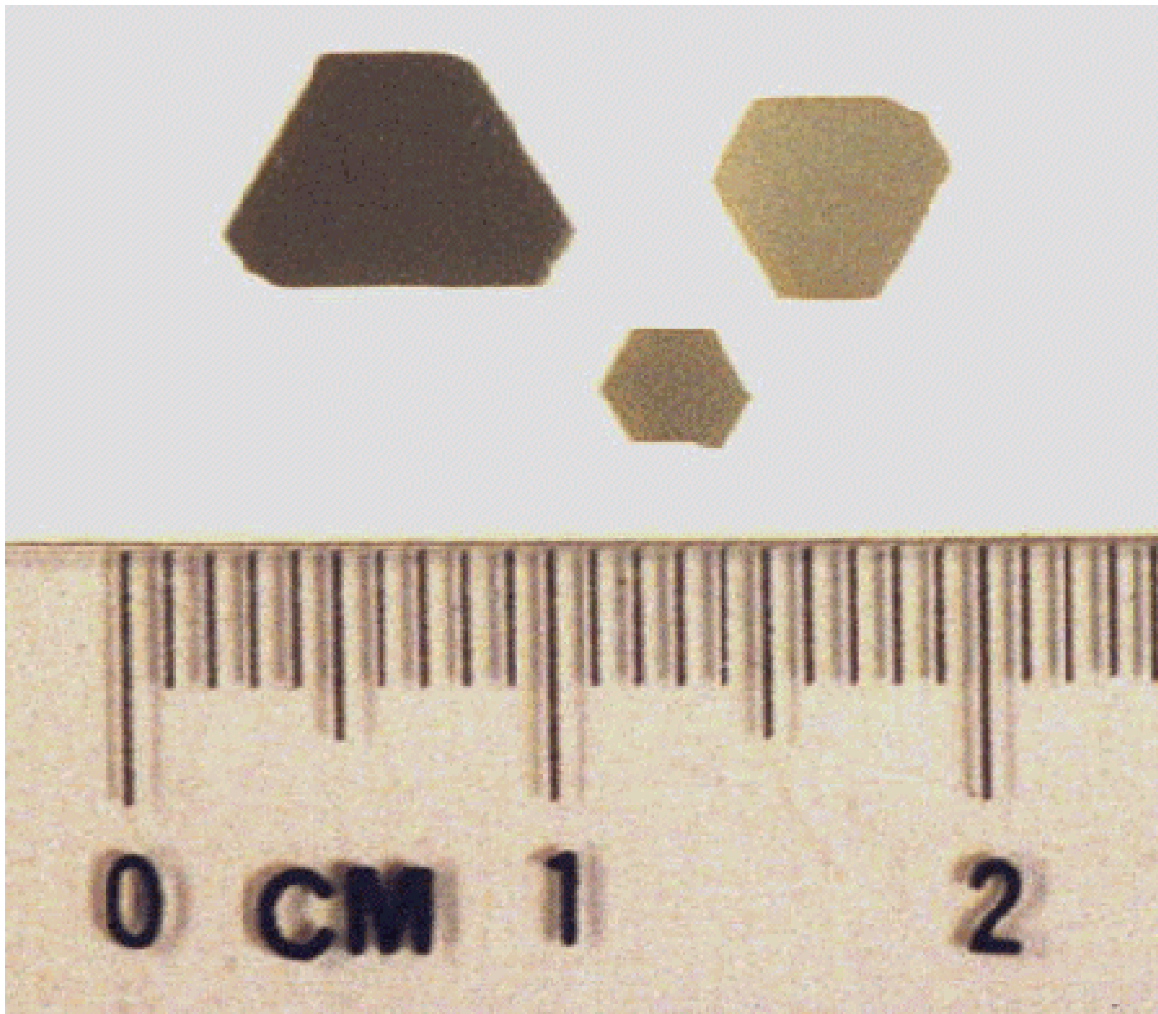

Figure 1. Bulk GaN crystals grown by HVPE (SiC substrate was removed).

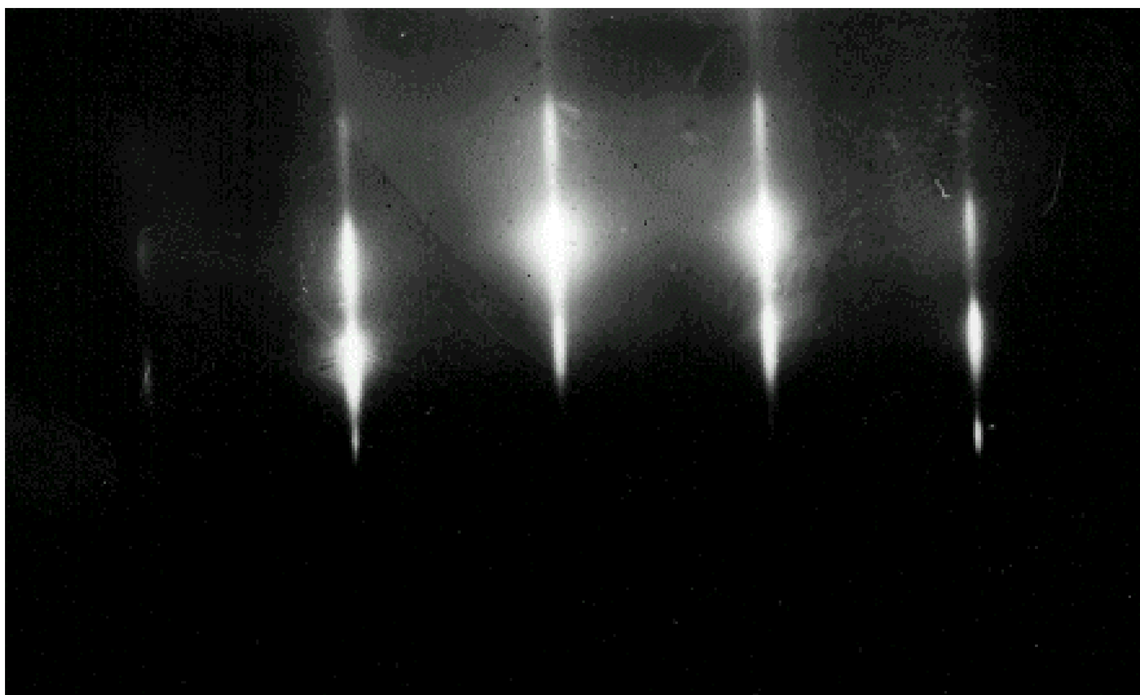

Figure 2. RHEED pattern obtained from the Ga-face of bulk GaN.

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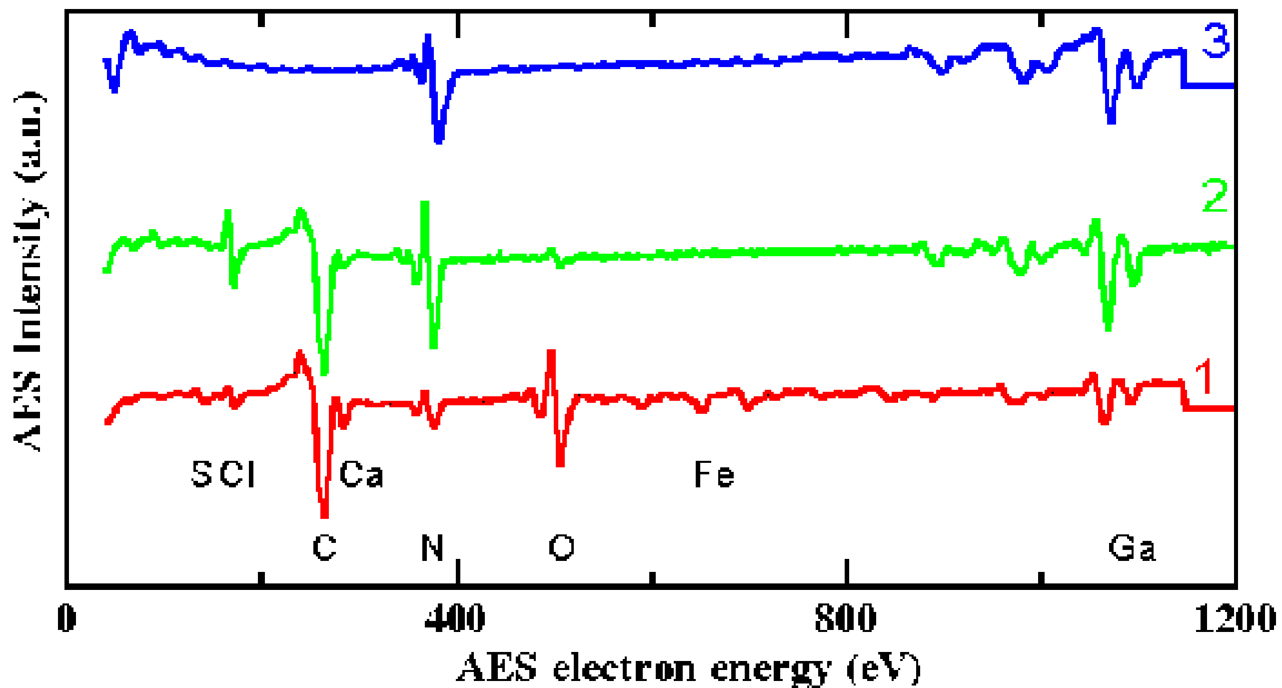

Figure 3. AES data taken from Ga-face of bulk GaN crystal: (1) after SiC substrate removal, (2) after chemical cleaning for 4 min in HCl at room temperature, and (3) after Ar sputtering for 260 sec (thickness of the sputtered material is about ~260 Å).

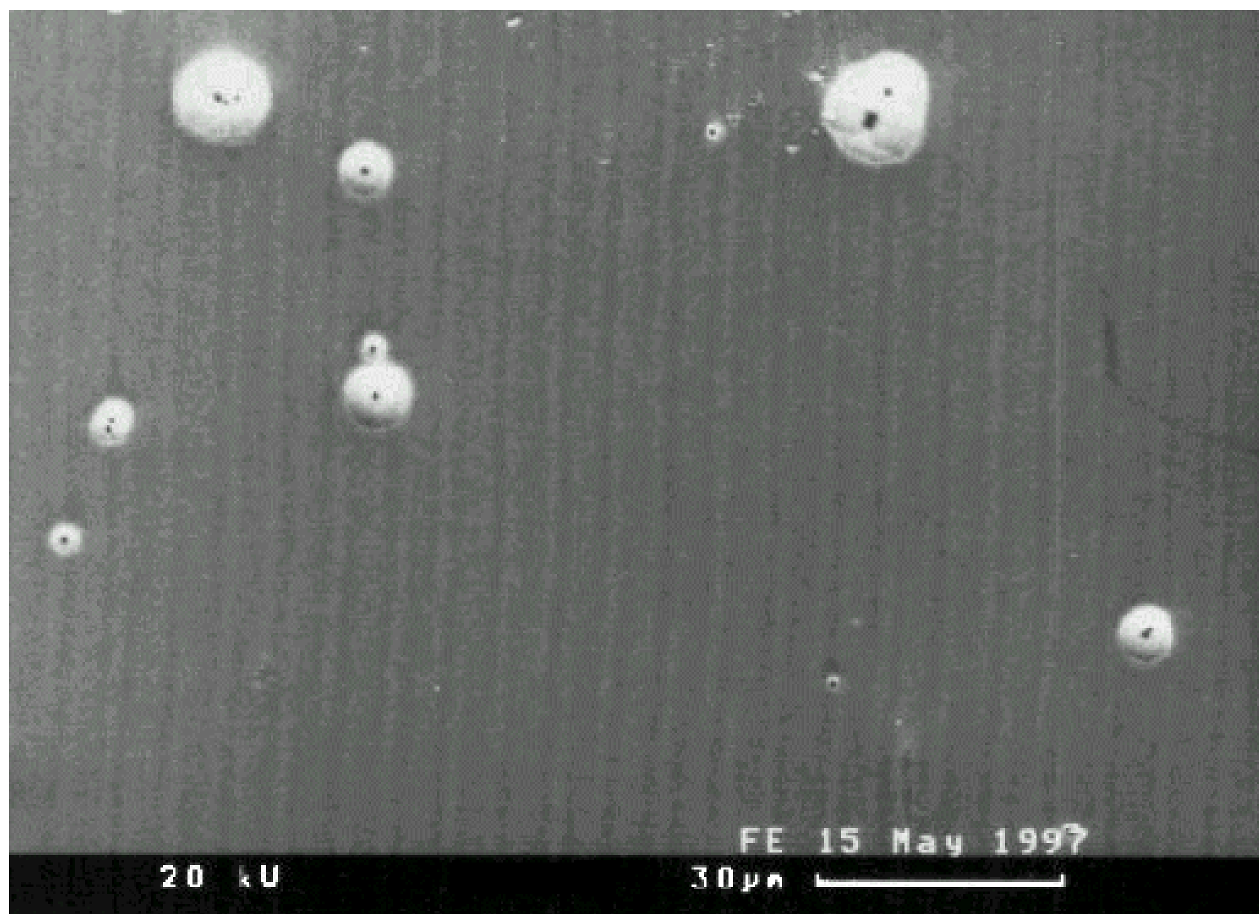

Figure 4. The SEM image of N-face of GaN bulk crystal with EPD $1.5x10^5$ cm^{-2}.

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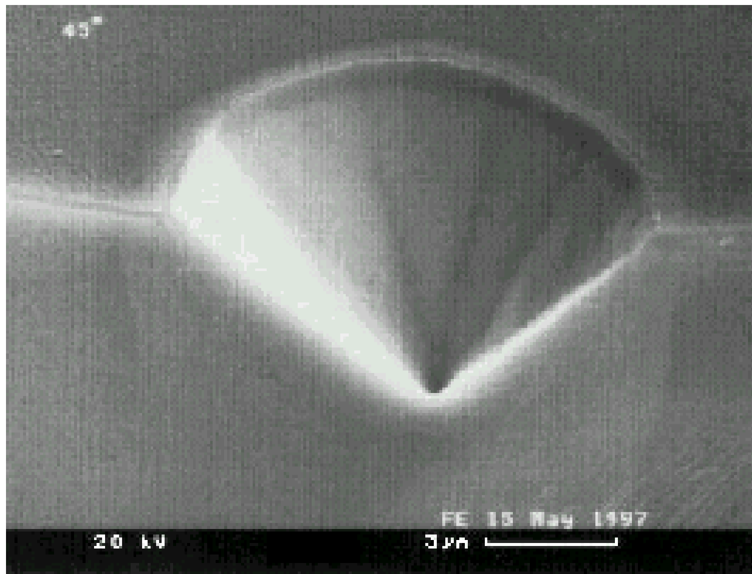

Figure 5. The SEM image of the edge of GaN bulk crystal cleaved through the etch pit.

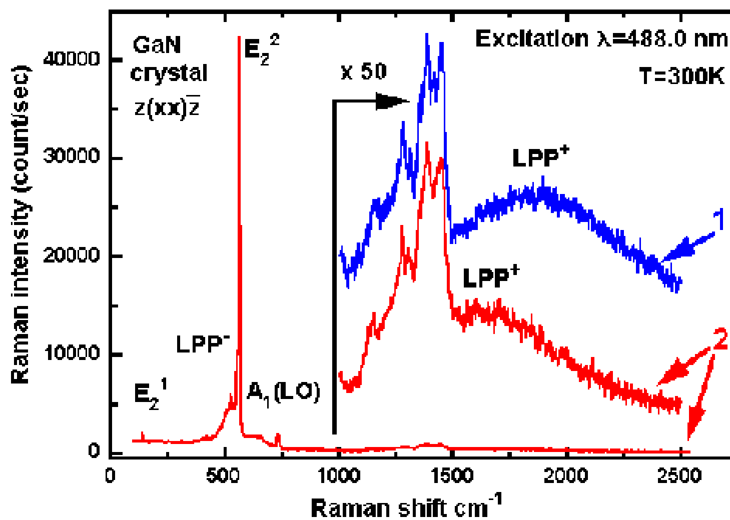

Figure 6. Raman spectra for (1) unannealed and (2) annealed bulk GaN crystal.

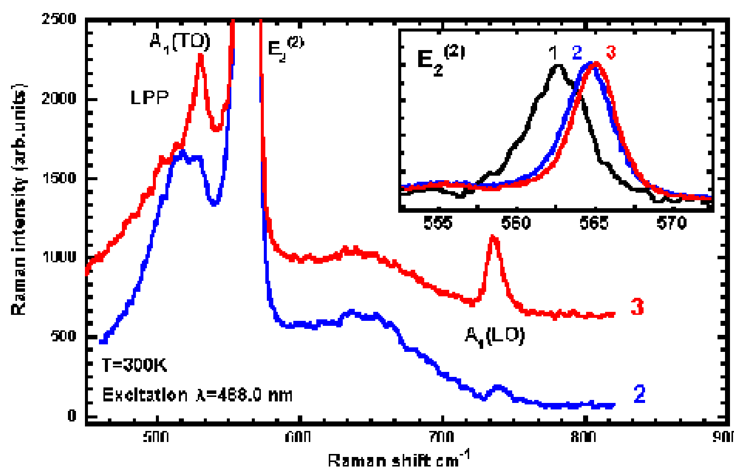

Figure 7. Raman spectra for (1) thin GaN epitaxial layer grown by HVPE on SiC, (2) unannealed and (3) annealed bulk GaN crystal.

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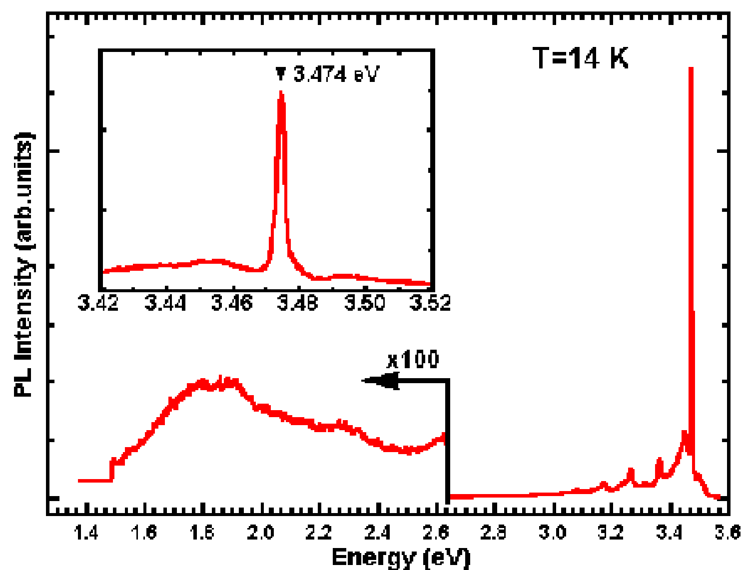

Figure 8. Photoluminescence spectrum taken from the N-face of unannealed GaN crystal measured at 14 K.

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