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Polarity of freestanding GaN grown by hydride vapor phase epitaxy

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Abstract The freestanding GaN substrates were grown by hydride vapor phase epitaxy (HVPE) on (0001) sapphire substrate and prepared by using laser induced lift-off. After a mechanical polishing on both Ga and N-surfaces of GaN films with 100 μm thick, their polaritis have been investigated by using chemical etching in phosphoric acid solution, 3 dimensional surface profiler and Auger electron spectroscopy (AES). The composition of the GaN film measured by AES indicated that Ga and N terminated surfaces have the different N/Ga peak ratio of 0.74 and 0.97, respectively. Ga-face and N-face of GaN revealed quite different chemical properties: the Ga polar surfaces corresponding to (0001) plane are resistant to a phosphoric acid etching whereas N-polar surfaces corresponding to $(000\bar{1})$ are chemically active.

1. Introduction

Semiconductor nitrides such as aluminum nitride (AlN), gallium nitride (GaN), and indium nitride (InN) are very promising materials for opto-electronic devices (both emitters and detectors) and high power/temperature electronic devices [1, 2]. Nitride semiconductors have been deposited by hydride vapor phase epitaxy (HVPE) [3-5], organometallic vapor phase epitaxy (OMVPE) [6], and by molecular beam epitaxy (MBE) [7]. However, these devices are grown on foreign substrates such as sapphire and SiC due to the lack of GaN substrates [8]. Consequently, the difference of the lattice constants and the thermal expansion coefficients between GaN and foreign substrates cause GaN layers exhibiting a high density of dislocations and cracking and bending of the GaN layer.

GaN has a polar wurtzite structure and this epitaxial film typically has been grown along the polar axis. The most common growth direction is normal to the (0001) basal plane and a basal plane surface may be either Ga or N terminated. Ga-terminated means that Ga is located on the top position of the basal plane. Since the polarity of GaN has a great effect on the growth and the device performance, determination of the polarity is one of the important factors to consider. That is, one of the key parameters for obtaining smooth and low defect density films is the polarity of the GaN epilayer [9]. The attempts to study the polarity of GaN epilayers were reported by Sasaki *et al.* and using X-ray photoemission spectroscopy (XPS) and by Khan *et al.* using Auger electron spectroscopy (AES) techniques [10, 11]. More recently, convergent beam electron diffraction (CBED) and a simple method using chemical solution such as H_3PO_4 and KOH have been used to determine the polarity of the sample [12]. The GaN film by HVPE system also is mainly grown along a polar axis, which results in the polar orientation of GaN materials.

This paper reports on the polarity determinations in GaN film grown on (0001) sapphire substrates by HVPE. After growing the crack free GaN thick films with two inches size and preparing the freestanding GaN by laser induced lift-off, we used a mechanical polishing, a chemical etching, and AES analysis to probe the polarity of two surfaces of film.

2. Experimental Procedure

Undoped GaN thick films with a thickness of 300 μm were grown by hydride vapor phase epitaxy on (0001) sapphire substrates [5]. C-plane sapphire substrate with two inches in diameter is placed on a 1030°C horizontal susceptor in a hot-wall HVPE reactor. Ga metal and HCl are pre-reacted to form GaCl gas, which is transported by nitrogen as a carrier gas to the hot growth-zone where it reacts with NH_3 and

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deposits GaN on the (0001) sapphire substrate. In order to investigate the polarity on both sides of the GaN crystals, the freestanding GaN was prepared by separation from the sapphire substrates using laser induced lift-off. Both sides of them, Ga- and N-face, then were polished by diamond paste to a thickness of 100 µm. Double-crystal x-ray diffraction (DXRD) was employed to evaluate the crystalline structure and quality of both sides of the freestanding layer. The polished surfaces of Ga-face and N-face were observed by optical 3-dimensional surface profiling system (3-D surface profiler), and the polarity of the sample was determined by AES. For the chemical etching of GaN films, the samples were placed in H_3PO_4 with a 85 % concentration at 220°C. The morphology of surfaces after etching was examined using optical microscope and 3-D surface profiler.

3. Results and Discussion

GaN epitaxial films are almost grown with either [0001] or [$000\bar{1}$] normal to the surface of the substrates. Generally, the most common growth direction is norml to the (0001) basal plane, and the [0001] orientation grown by HVPE on sapphire substrate is known as Ga-face, while the [$000\bar{1}$] orientation is as N-face. The polarity is a bulk property, not a surface property. Figures 1 and 2 illustrate the crystal structure of GaN and the freestanding GaN, with 2 inches size and crack free, grown by HVPE on sapphire substrates. The freestanding GaN films are rough growth surfaces with large number of hillocks and have some bowing resulted from the difference of the thermal expansion coefficient and the lattice parameter of GaN/sapphire. Also, to compare the polar properties, Ga- and N-polar, in a condition of a similar status, we did the mechanical polishing by 100 µm thick so that the flat and smooth surfaces were obtained. Figure 3

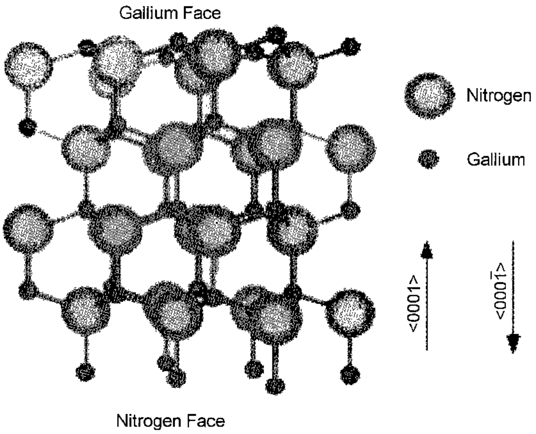


Fig. 1. The wurtzite crystal structure of GaN.

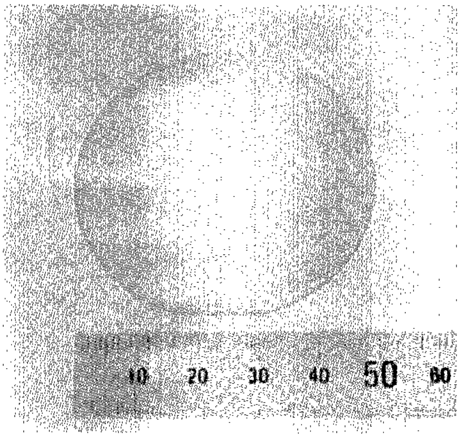


Fig. 2. Freestanding GaN substrate grown by HVPE.

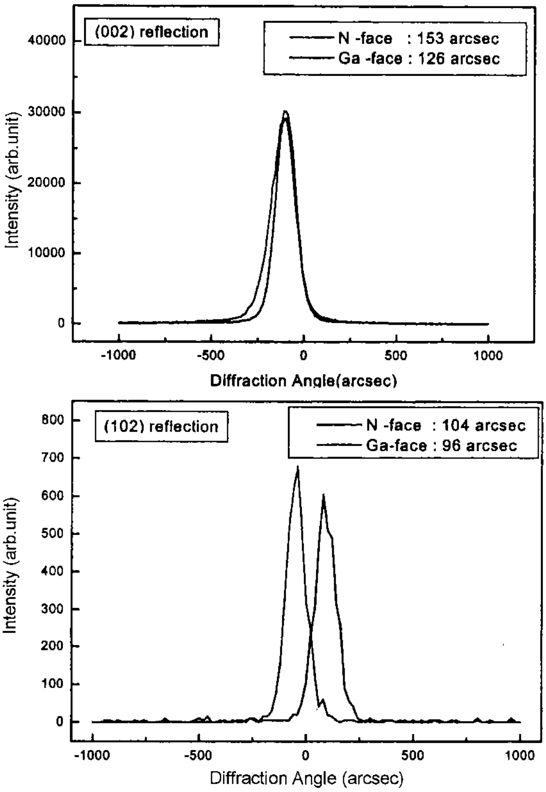
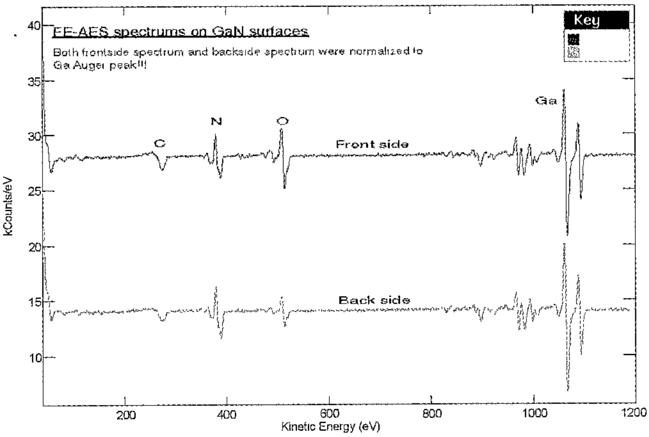


Fig. 3. X-ray diffraction rocking curves of GaN.



FRONT

Peak	Centre	SF	[AT]%
C KL1	264.00	0.60	**19.837**
N KL1	381.75	0.30	**27.799**
O KL1	510.50	0.96	**14.737**
Ga LM2	1064.00	0.70	**37.627**

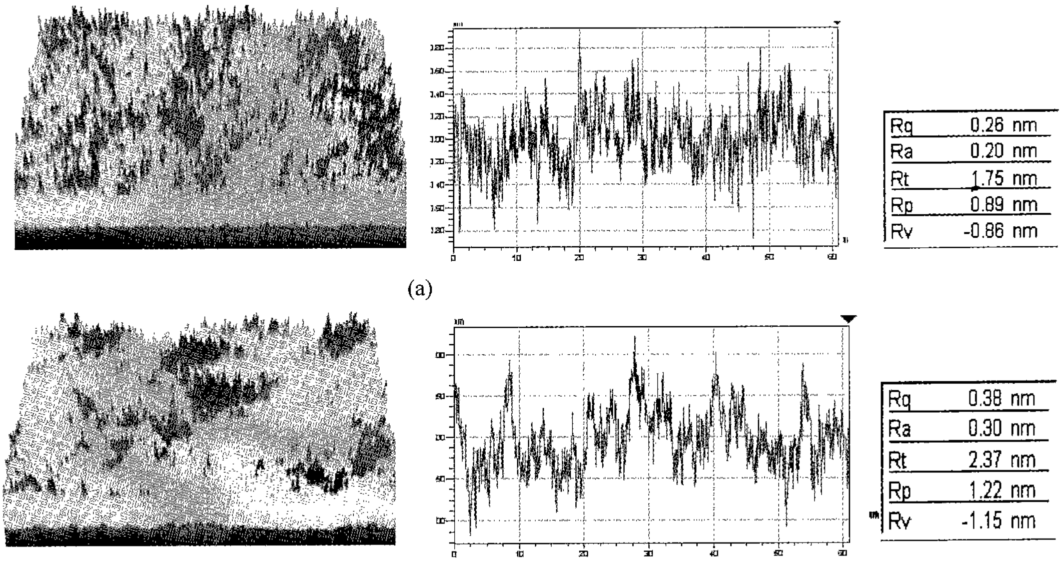
BACK

Peak	Centre	SF	[AT]%
C KL1	264.00	0.60	**15.085**
N KL1	381.75	0.30	**38.106**
O KL1	510.50	0.96	**7.487**
Ga LM2	1064.00	0.70	**39.322**

Fig. 4. Auger electron spectroscopy (AES) of GaN substrate after polishing to reveal the Ga/N ratio between Ga- and N-face.

shows the X-ray rocking curves of both surfaces of 100 μm thick GaN films, symmetric (002) reflection and asymmetric (102) reflection. The full width at half maximum (FWHM) of the (002) peak for the Ga-face and the N-face were 126 and 153 arcsec, respectively. Their asymmetric (102) peaks that are sensitive to the structure of the pure edge threading dislocations [13] also were 96 and 104 arcsec. It is believed that the small difference in the (002) and the (102) XRD measurement of the two faces results from the improvement in crystal quality with increasing layer thickness. That is, from the XRD analysis, the FWHM of GaN film may be independent on the surface and orientation of the GaN templates.

Figure 4 shows Auger spectra of the polished GaN templates to reveal the N/Ga ratio between Ga- and N-face. We measured the composition of the top 10 Å of the film weighted by the escape probabilities of the Auger electrons. In spite of the difference between this experiment and other researchers, the N/Ga ratio



Rq	0.26 nm
Ra	0.20 nm
Rt	1.75 nm
Rp	0.89 nm
Rv	-0.86 nm

(a)

Rq	0.38 nm
Ra	0.30 nm
Rt	2.37 nm
Rp	1.22 nm
Rv	-1.15 nm

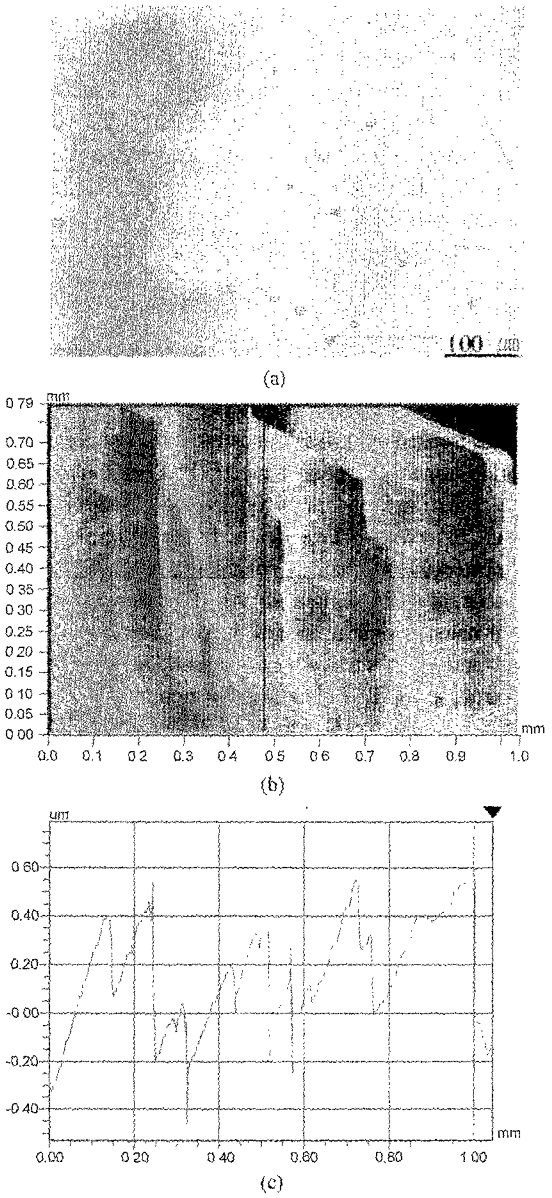
(b)

Fig. 5. 3-D Surface Profiling Images of Ga- and N-face after polishing (R_q: root mean squares, R_t: total height between peak to valley).

which was calculated from the atomic percent of Ga and N peaks for the (0001) GaN grown on the sapphire was 0.74, while that for (000$\bar{1}$) GaN was 0.97. Also, other peaks such as carbon and oxygen were appeared. Oxygen peak is more intensive at the front surface compared to back surface. It is considered that much oxygen owing to a thin galliumoxide layer by mechanical polishing exist at Ga terminated surface in comparison with N terminated surface. This fact that also indicates the polar property of GaN film. Carbon peak would be a result of contamination during analysis. Based on the measured N/Ga ratios, it is suggested that the top surface of the GaN film, which is grown on the (0001) sapphire substrate, reveal the Ga terminated property.

To investigate the polishing properties of Ga-face and N-face of GaN films, we analyzed the polished surfaces by using 3-D surface profiler. The subsequent polishing for both sides yielded mirror-like surfaces. Although some scratch lines and wave are remained as appeared in Fig. 5, the morphology of the polished Ga-face is more uniform than N-face. Also, the roughness of the Ga-face such as R_q (root mean squares: rms) and R_t (the value of peak to valley) reveals lower values than the N-face. This result suggests that the N-face surface of GaN templates is mechanically weaker than the Ga-face.

It is well known that Ga-face and N-face of GaN have quite different chemical properties. The details of the etching mechanism are obscure but an increase in etching temperature normally increases the etch rate of a GaN crystal. The Ga-face of GaN is chemically more stable than the N-face. It has been reported that hot phosphoric acid and KOH aqueous solution strongly etches the N-face of GaN but not the Ga-face [14]. The only defect sites on the Ga-face of GaN are attacked by these chemical etchants, producing the etch pits that reveal the location of point defects that form in GaN. Etching experiments using the mask-patterned GaN samples were carried out in 85 % H_3PO_4 solution at 220°C and 3-D surface profiler was used for the etching rate measurements. The etching of GaN template revealed that only one side, N-face, of the two polar surfaces was attacked by solution. The measured etching rates were close to zero for Ga-face and about 1 μm/min for N-face, respectively. Still the scratch lines that resulted from the mechanical polishing process are visible on the Ga-face in Fig. 6(a), indicating that Ga-face has not etched by hot H_3PO_4 acid. However, on the contrary, the N-face is quickly dissolved. This fact can be proved from the photoluminescence spectra analysis that is one of the indirect methods to confirm the existence of the damage layer occurred by a mechanical polishing. The PL intensity of N-face after the etching process was entirely recovered but not for the Ga-face. In order to observe the etching property of N-face of GaN, we performed the over-etching test at 220°C for 10 min. Figure 6 shows



(a)

(b)

(c)

Fig. 6. Images of the etched N-face of GaN substrate by phosphoric acid (a) Optical microscope, (b) and (c) 3-D surface profiler.

the etched morphology of N-face, indicating that the N-face was preferentially etched toward the special planes. From the etched images, it is shown that the etching of N-face of GaN films appeared the stepped morphology. In order to observe the step appearance, we used 3-D surface profiler. As shown in Fig. 6(b) and (c), the inclination of the stepped plane, the ratio of c-axis to a-axis, by etching was approximately estimated 2, as will be discussed in detail elsewhere.

4. Conclusions

The freestanding GaN substrates were grown by hydride vapor phase epitaxy (HVPE) on (0001) sapphire substrates and prepared by using laser induced lift-off. In order to investigate the polar property, we performed the mechanical polishing on both Ga and N-surfaces of GaN films and the polarity was investigated using chemical etching in phosphoric acid solution, and 3-D surface profiler and Auger electron spectroscopy (AES). The composition of the film by AES indicated that Ga- and N-face have the different N/Ga peak ratio of 0.74 and 0.97, respectively. Ga-face and N-face of GaN revealed quite different chemical properties: the Ga polar surface, (0001) plane, was resistant to a phosphoric acid etching whereas N-polar surface corresponding to $(000\bar{1})$ was chemically active.

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