

## Effect of nitridation on the orientation of GaN layer grown on m-sapphire substrates using hydride vapor phase epitaxy

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This study reports the effect of nitridation on the orientation of GaN layers grown on m-plane sapphire ( $\text{Al}_2\text{O}_3$ ) substrates by hydride vapor phase epitaxy (HVPE). Non-polar (10-10) GaN layers were grown on m-sapphire without nitridation. With increasing nitridation time, the crystallographic phases of the GaN layer changed from non-polar to semi-polar (11-22) through mixed phases of (10-1-3) and (11-22). The phase change with nitridation was attributed to the formation of the nanosized AlN protrusions with slanted facets. This was confirmed by X-ray photoelectron spectroscopy and atomic force microscopy.

**Key words:** HVPE, Semi-polar, Non-polar, GaN, Nitridation.

### Introduction

Semiconductors based on III-nitride materials have been widely used in optoelectronic devices such as light-emitting diodes (LEDs) and laser diodes (LDs) [1]. Currently, GaN devices are predominantly grown in the (0001) c-plane orientation on a polar sapphire substrate. However, when using polar substrates, a critical physical problem encountered with nitride semiconductors having a wurtzite crystal structure is their spontaneous and piezoelectric polarization [2-3]. This in turn causes spatial separation of the electron and hole wavefunctions, which degrades the performance of III-nitride optoelectronic devices. Hence, non-polar and semi-polar GaN materials have attracted increasing attention because they reduce the effects of the internal electric polarization fields on the performance of III-nitride optoelectronic devices [4-8]. There are several reports on heteroepitaxially grown (10-10) non-polar GaN and (11-22) semi-polar GaN on foreign substrates [9-11]. M-plane sapphire substrates were used for the growth of (10-10) non-polar and (11-22) semi-polar GaN by hydride vapor phase epitaxy (HVPE) [12-14]. In this study, we investigated the effect of nitridation on the growth of GaN layers/m-plane sapphire substrates by HVPE.


### Experimental Procedure

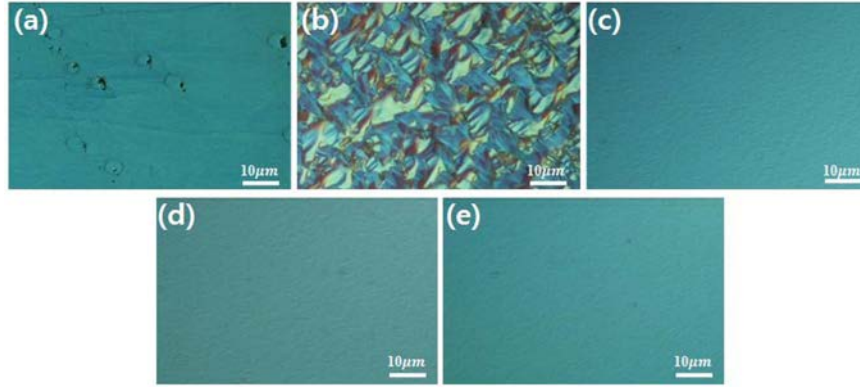
In this study, we used a vertical HVPE system to grow GaN layers. The process zone consisted of two parts, the source zone and the growth zone. Ammonia ( $\text{NH}_3$ ) and hydrochloric acid (HCl) were introduced as the active gases, and the Ga metal was used as the group III precursor. The group III precursor for Ga was located in a separated tube at 800 °C. GaCl gas was generated by the reaction with HCl at the source zone and transported toward the heated substrate at 1040 °C. Prior to the process, the sapphire substrates were heated for 5 min in order to ensure thermal stabilization and then nitridated at different process times ranging from 0 to 16 min. After the nitridation, GaN epilayers were grown in the growth zone, under atmospheric pressure with a V/III ratio of  $\sim 10$  for 15 min. The grown GaN layers were characterized by optical microscopy (OM) and high-resolution X-ray diffraction (HR-XRD). X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) were performed to analyze the surface modification of the m-plane sapphire substrate by nitridation. Al  $K\alpha$  line (1253.6 eV) was used as the X-ray source in the XPS measurements.

### Results and Discussion

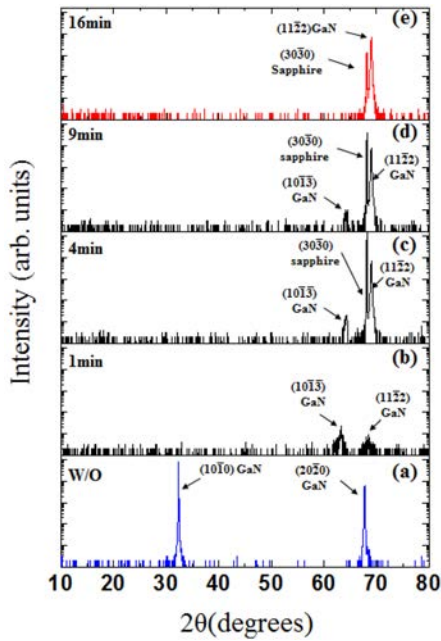
From previous works, it was established that nitridation plays a critical role to determine crystal orientation of GaN layers on the m-sapphire substrate [12, 15]. Besides, Vennéguès *et al.* reported the existence of aluminum nitride (AlN) layers between the semi-polar GaN layer and the sapphire substrate [16].

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**Fig. 1.** Optical microscopy images of GaN on sapphire substrates (a) without and (b) with nitridation for 1 min, (c) 4 min, (d) 9 min and (e) 16 min, respectively.



**Fig. 2.** XRD 2θ-ω scans of GaN layers grown on m-sapphire (a) without and with nitridation for (b) 1 min, (c) 4 min, (d) 9 min and (e) 16 min.

Fig. 1 shows the OM images of GaN layers grown on m-plane sapphire substrates without and with nitridation for nitridation times varying between 0 and 16 min under the same temperature conditions. The surfaces of the GaN layers were mostly smooth and flat except in the case of nitridation for 1 min, where the surface was very rough, as shown in Fig. 1(b).

HR-XRD 2θ-ω scans revealed the crystal orientation of the GaN layers grown on m-sapphire in all samples. As shown in Fig. 2, GaN layers grown on m-sapphire without nitridation show two diffraction peaks of (10-10) GaN and (20-20) GaN, which indicates that the non-polar (10-10) single-phase layer grows dominantly on the non-nitridated m-sapphire. In contrast, after nitridation for 1 min, a mixed phase of semi-polar (10-1-3) and (11-22) GaN layers were grown, probably because of the very rough surface morphology. With

**Table 1.** Ratio of XRD integrated intensities of GaN without and with nitridation.

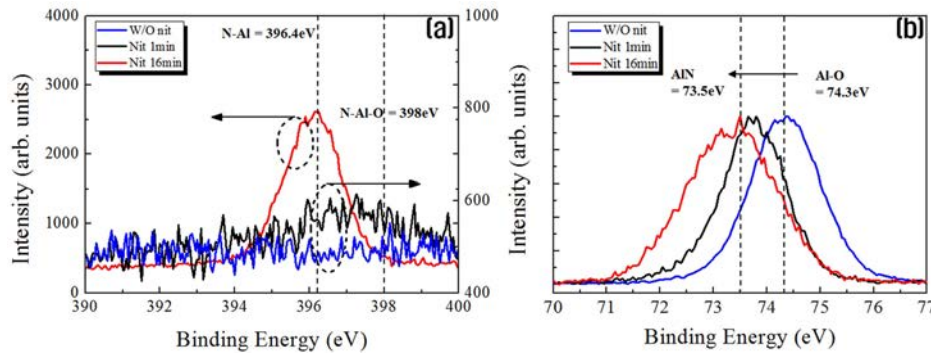
Nitridation Time	$I_{(10-10)}/I_{\text{total}}$	$I_{(10-1-3)}/I_{\text{total}}$	$I_{(11-22)}/I_{\text{total}}$
W/O	100%	0%	0%
1 min	0%	84.6%	15.4%
4 min	0%	0.3%	99.7%
9 min	0%	0.1%	99.9%
16 min	0%	0%	100%

$$(I_{\text{total}} = I_{(10-10)} + I_{(10-1-3)} + I_{(11-22)}).$$

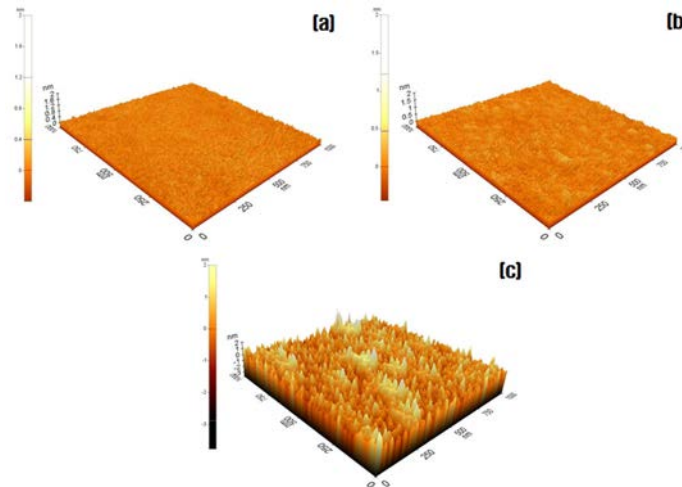
increasing nitridation time, the semi-polar (11-22) GaN peak became dominant in the GaN layers, while the peak intensity related to the semi-polar (10-1-3) GaN decreased. Consequently, only one peak related to the semi-polar (11-22) GaN was observed after nitridation for 16 min.

As shown in Table 1, the ratio of the integrated intensities of GaN indicates that perfect non-polar (10-10) GaN was grown without nitridation, and perfect semi-polar (11-22) GaN was grown with nitridation for 16 min. Poly crystalline GaN layers were grown after nitridation for varying times between 1 min and 9 min. These results demonstrate that single-phase GaN layers having various orientations, such as non-polar (10-10) GaN and semi-polar (11-22) GaN, can be grown on m-sapphire by controlling the nitridation conditions.

The XPS spectra (Fig. 3) show the effect of nitridation on m-sapphire without and with nitridation for 1 min and 16 min. Fig. 3(a) shows the N 1s photoelectron peaks from the surface of the sapphire substrates without and with nitridation. The binding energy of 396.4 eV is attributed to N-Al binding [17]. The N 1s shape of peak changed with nitridation time. No peak between 390 eV and 400 eV was observed from the sapphire without nitridation. The sapphire, after a nitridation time of 1 min, showed weak and broad N-Al and N-Al-O peaks between 396.4 eV and 398 eV. In the case of nitridation for 16 min, the intensity of the peak at 396.4 eV increased,



**Fig. 3.** XPS spectra of sapphires without and with nitridation for 1 min and 16 min: (a) N 1s (b) normalized Al 2p, respectively.



**Fig. 4.** AFM images of m-sapphire surfaces (a) without and with nitridation for (b) 1 min and (c) 16 min, respectively.

which indicates very strong N-Al bonding on the sapphire surface.

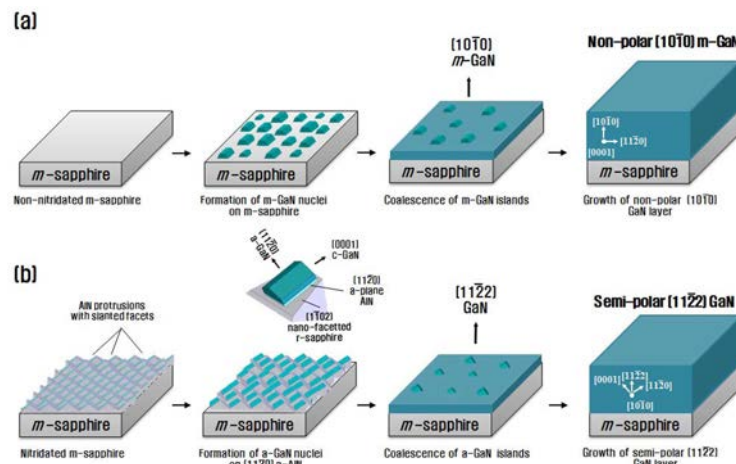
Fig. 3(b) shows the normalized intensities for the Al 2p photoelectron peak from the sapphire surface without and with nitridation. The binding energies of 73.5 eV and 74.3 eV were attributed to Al-N bonding and Al-O bonding, respectively [17-18]. The peaks shifted from 74.3 eV to 73.5 eV with increasing nitridation time, which is evidence for AlN formation on the surface of the sapphire substrate.

Fig. 4 shows the AFM images (area:  $1\ \mu\text{m} \times 1\ \mu\text{m}$ ) of the sapphire surface without and with nitridation for 1 min and 16 min. As shown in Fig. 4(a), the sapphire surface without nitridation had a flat surface ( $R_{\text{rms}} = 0.074\ \text{nm}$ ). The sapphire surface after nitridation for 1 min became slightly rough, as shown in Fig. 4(b) ( $R_{\text{rms}} = 0.088\ \text{nm}$ ), because of AlN formation. After nitridation for 16 min, many protrusions shaped like slanted facets (width  $\sim 50\ \text{nm}$ ) were observed on the sapphire surface, as shown in Fig. 4(c) ( $R_{\text{rms}} = 0.604\ \text{nm}$ ). These results suggest that the nitridation process induces the formation of AlN layers composed of nanosized protrusions with slanted facets on the surface of the sapphire substrate and thereby facilitates the growth of the semi-polar (11-22) GaN layer.

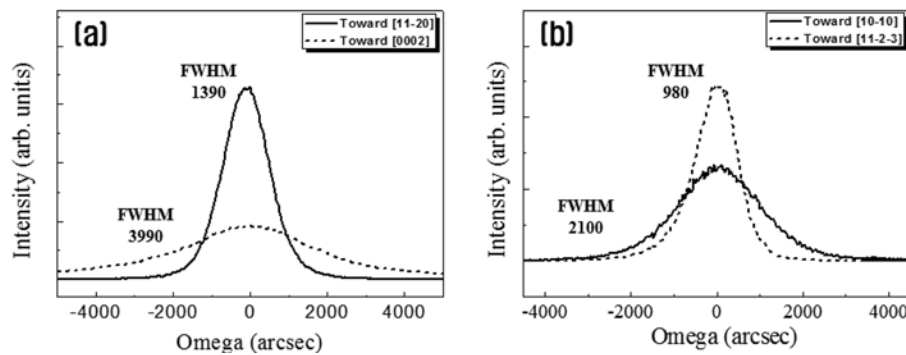
Fig. 5 shows the schematic representation of the

GaN growth mode on the sapphire substrates without and with nitridation. Non-polar (10-10) GaN nuclei were predominantly formed on m-sapphire without nitridation, as shown in Fig. 5(a). This can be explained by the low surface energy of the non-polar (10-10) GaN formation on the m-sapphire (10-10) substrate without nitridation [16]. Thus, non-polar (10-10) GaN layer was finally grown on m-sapphire (10-10). On the other hand, with nitridation, the AlN layers composed of protrusions with slanted facets were formed on the surface of m-sapphire. It has been well known that r-plane  $\{1-102\}$  nanofacets, which intersect m-sapphire at  $32.28^\circ$ , are generated on m-sapphire with nitridation and the III-nitride films grown on r-sapphire have a nonpolar a-planes  $\{11-20\}$  [16, 19]. At initial growth stage, a-GaN nuclei were formed on a-plane  $\{11-20\}$  of AlN layer:  $[1-102]_{\text{Sapphire}} \parallel [11-20]_{\text{AlN}}$  and  $[11-20]_{\text{AlN}} \parallel [11-20]_{\text{GaN}}$ , and then the coalescence of a-GaN islands proceeds during the growth, as shown in Fig 5(b). Finally, the top surface of GaN progresses to the semi-polar (11-22) layer, which is inclined by  $31.6^\circ$  respect to a-GaN [16].

Double-crystal XRD rocking curves of the on-axis planes of the non-polar (10-10) GaN and semi-polar (11-22) GaN layers were measured, as shown in Fig. 6. The full width at half maximums (FWHMs) of the



**Fig. 5.** Schematic representation of GaN growth process on m-sapphire substrates (a) without and (b) with nitridation.



**Fig. 6.** DXRD rocking curves of (a) NP (10-10) GaN and (b) SP (11-22) GaN, respectively.

non-polar (10-10) GaN layers were 3990 arcsec and 1390 arcsec when the rocking direction was parallel to the [0002] and [11-20], respectively. Meanwhile, the FWHMs of semi-polar (11-22) GaN were 2100 arcsec and 980 arcsec toward the [10-10] and [11-2-3] directions, respectively. These FWHM values are relatively high compared to the previous studies [13, 20], which was attributed to non-optimization in the growth condition. Further study is currently underway to improve crystal quality of GaN layers.

## Conclusions

In conclusion, we have demonstrated the effect of nitridation treatment on the orientation of GaN grown on m-sapphire substrates. Non-polar (10-10) GaN was grown on sapphire without nitridation. On the other hand, semi-polar (11-22) GaN was predominantly grown on sapphire with nitridation treatment. The XPS spectra of the N 1s and Al 2p peaks showed the formation of an AlN layer on the nitridated surface of m-sapphire. Further, the nitridation treatment changed the surface morphology of m-sapphire to AlN protrusions with slanted facets. Our study suggests that non-polar and semi-polar GaN layers can be grown under controlled nitridation conditions in the HVPE process.

## Acknowledgments

This work was supported by Industrial Strategic Technology Development program no. 10041188 of the Ministry of Knowledge Economy and the National Research Foundation of Korea (NRF) grant funded by the Korea government (MEST) no. 2012R1A2A2 A01011702.

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