Chapter 3

GaN Epitaxy Growth on Sapphire (0 0 0 1) Substrates

3.1 Introduction

Nitridation of sapphire substrates have been reported by many authors as one of the critical steps affecting the quality of GaN and AlN epitaxial layers grown by both MBE and MOCVD system. High temperature is typically used for nitridation with NH_3 in MBE and MOCVD. Because NH_3 is a very stable molecule, high temperature is required to crack the NH_3 and supply active nitrogen during MBE and MOCVD growth. However, a wide range of temperatures can be exploited for nitridation using RF nitrogen plasma or ECR sources due to availability of efficient atomic nitrogen [19, 20]. Moreover, to reduce treading threading dislocations (TDs) in GaN, single and multiple AlN interlayer (AlN-IL) were inserted in GaN [21]. The strain associated with the presence of such interlayer results in bending of dislocations, which propagate from the underlying GaN epitaxial layer. This increases the probability of interactions between dislocations and leads to their reduction in the subsequently-grown GaN epitaxial layers. GaN epitaxial layer grown on vicinal sapphire substrates shows better crystal quality due to that vicinal plane has micro-step [22]. Since strain field situation at the macro-step position is different from that at the flat region due to the structural irregularity. The TDs at the macro-step position were bended and terminated on the surface. So that, the vicinal substrate can reduces TD density in GaN epitaxial layer.

In this chapter, we investigate the crystal quality of GaN epitaxial layer with different nitridation temperatures which from 200 to 800℃ and characteristics of GaN on nitrided or non-nitrided sapphire. Then, we use AlN-IL to reduce TDs and optimize the deposition time of AlN-IL to obtain high quality of GaN epitaxial layer. Final, we study the influence of GaN epitaxial layer on vicinal sapphire substrate.

3.2 Growth procedure of the GaN epitaxial layer on sapphire

The growth procedure of GaN grown on c-sapphire substrate by the RF plasma assisted molecular beam epitaxy system could be separated into four steps, substrate preparation, nitridation, buffer layer growth, and GaN epitaxial layer growth.

- **Substrate preparation：**

Before initiation of growth, the sapphire was first degassed at 850℃ for 1 hr for thermal cleaning. After 1 hr, the clear sapphire RHEED pattern appealed.

- **Nitridation：**

Preconditioning of c-sapphire for GaN growth can improve the crystalline quality of the epitaxial layer. Nitridation process also can convert the upper most monolayer of Al_2O_3 (0 0 0 1) substrate to AlN by exchange of surface oxygen with nitrogen. Therefore, different nitridation temperatures were carried out.

After 1 hr degassed, the substrate temperature was decreased to the nitridation temperature. We adjust the RF power and nitrogen flow rate of two plasma generators to 500W, 4.0 sccm and 500W, 1.5 sccm, respectively. Then, the sapphire substrate was nitrided.

- **High Temperature (HT) -AlN Buffer layer：**

High temperature means that the substrate temperature of the AlN buffer layer growth was equal or higher than the growth temperature of the GaN epitaxial layer. The polarity of GaN epitaxial layer grown by MBE with the HT-AlN buffer layer is the Ga-polarity. In other way, the GaN epitaxial layer with the other kinds of buffer layer, i.e., LT/HT GaN and LT AlN buffer layer, processes N-polarity [23, 24]. Adjusting beam equivalent pressure (BEP) of gallium and the nitrogen flow rate and RF input power of the two plasma generators, the HT-AlN buffer layer was grown at 800℃.

- **GaN epitaxial layer growth：**

After growing the HT-AlN buffer layer, adjust the BEP of gallium, the nitrogen flow rate and RF input power of the two plasma generators and substrate temperature to the parameter of GaN epitaxial layer. We grew GaN epilayer at Ga-rich condition to obtain flat surface of GaN epitaxial layer.

In this chapter, we design the systematicness of samples to study the effect of nitridation, GaN epilayer inserted by AlN-IL and vicinal sapphire substrate. The detail experiment procedure is described as follow.

The sapphire was first degassed at 850℃ for thermal cleaning. Then, the sapphire was nitrided. The AlN buffer layer on nitrided sapphire was subsequently deposited at 800℃. Finally, 2μm thick GaN epitaxial layer was grew. The detail parameters are scribed in the Table 3-1.

The effect of AlN-IL on GaN epitaxial layer was investigated. The growth process as follows. The substrate preparation, 500℃ nitridation, HT-AlN buffer layer and GaN epitaxial layer were implemented by the same process as Table 3-1. The various deposition time of AlN-IL were then deposited on a nominally 250 nm thick GaN epitaxial layer without any growth interruption. Finally, total 1 μm thick GaN was grew with AlN-IL. Following this procedure, a series of four samples has been grown.

3.3 Characteristics of the GaN epitaxial layer on sapphire

The surface morphology of the GaN epitaxial layer on non-nitrided sapphire is very different from the GaN epitaxial layer on nitrided sapphire. The GaN epitaxial layer on non-nitrided sapphire presents several circle-like cavities on the flat surface, which are typical three-dimensional (3-D) island growth with rough surface, as shown in Fig. 3-1 (a). However, the GaN epitaxial layer on nitrided sapphire presents smooth surface, as shown in Fig. 3-1 (b).

Surface morphology of GaN epitaxial layer on non-nitrided sapphire after 2M KOH chemical wet etching for 30min at room temperature is shown in Fig. 3-1 (c). Original circle-like cavities was etched to hexagonal cavities, but the flat surface did not change after etching. It is believed that the Ga-polarity of GaN is chemically more stable than the N-polarity. KOH solution will etch the N-polarity but not the Ga-polarity [25]. It is determined that the lattice polarity of the smooth surface is Ga-polarity and polarity of cavities is N-polarity. Consisting of regions of GaN with opposite polarity to primary matrix, resulting in different surface morphologies is considered as inversion domains (IDs) [26, 27], which could be due to the step in the sapphire surface and the defects in the substrate surface itself from remnant polishing damage. The IDs are common and more stable during growth of GaN by MBE and the formation of ID is not an intrinsic property of MBE growth of GaN, but is apparently related to nucleation conditions. In order to eliminate the IDs, the nitridation treatment was applied before the AlN growth. It is believed that this thin AlN nucleation layer formed by nitridation process, acting as a superior template to prevent from the presence of IDs and also enhance the lateral growth of following HT AlN buffer and GaN epitaxial layer. The crystal quality of GaN on nitrided and non-nitrided sapphire were characterized by high resolution x-ray diffraction (HRXRD) x-ray rocking curve of symmetric (0 0 0 2) and asymmetric (1 0 $\bar{1}$ 2) diffraction, as shown in Fig. 3-2. The narrower full widths at half-maximum (FWHM) around (0 0 0 2) archived with a lower density of screw and/or mixed threading dislocations in the films, and asymmetric (1 0 $\bar{1}$ 2) reflections are related to overall dislocation (included edge, screw and mixed dislocations) in the films [28]. The GaN on non-nitrided sapphire shows poor crystal quality due to the lack of superior thin AlN nucleation layer formed by nitridation treatment.

The crystal quality of GaN epilayer depends on nitridation temperature. The sapphire surface exposed to active nitrogen at different nitridation temperature was monitored *in situ* by RHEED, as shown in Fig. 3-3. Before exposure active nitrogen on the sapphire substrate, the sapphire RHEED pattern was observed. After 40 min of nitrogen plasma exposure, the, AlN streak pattern all appear for the each nitridation temperature. After 60 min, the RHEED pattern of the 800℃ nitridation shows dimmer sapphire pattern than low temperature nitridation, which is due to high reaction rate at high temperature. Further nitridation leads to an increase in the intensity of AlN streak pattern, and the intensity of sapphire pattern is dim. Finally, streak AlN pattern appears without sapphire pattern after 90 min nitridation treatment. Some spotty pattern was observed in the RHEED pattern of 800℃ nitridation, which is due to the formation of 3D islands.

The crystal quality of GaN on different nitridation temperature sapphire was characterized by HRXRD x-ray rocking curve of symmetric (0 0 0 2) and asymmetric (1 0 $\bar{1}$ 2) diffraction. Fig. 3-4 shows the FWHM value of the x-ray rocking curve as a function of the nitridation temperature. The symmetric (0 0 0 2) FWHM value reduces with decrease of nitridation temperature, but the asymmetric (1 0 $\bar{1}$ 2) FWHM value shows inverse trend. Consequently, the GaN epitaxial layer on 800℃ nitrided sapphire shows a little higher screw dislocation density, but lower overall dislocation density, which the (0 0 0 2) and (1 0 $\bar{1}$ 2) FWHM value is 440 and 1980 arcsec, respectively.

In order to understand the mechanism of the crystal quality vs. nitridation temperature, the AlN buffer layer on the 200℃ and 800℃ nitrided sapphire was survey by atomic force microscope (AFM), as shown in Fig. 3-5. The 3D islands of AlN on 800℃ nitrided sapphire is larger than 200℃ nitrided sapphire. The 800℃ nitrided sapphire promotes the initial 3D growth with low nucleation densities. This leads to the formation of isolated GaN islands on the AlN buffer layer surface, which is latter expanding and coalesce through the lateral overgrowth. This lateral overgrowth in regions between islands prevents propagation of threading dislocations.

To improve the crystal quality of GaN epitaxial layer further, the AlN-IL was inserted in GaN epitaxial layer and vicinal sapphire substrates was applied. The sample structure of

AlN-IL inserted in GaN is shown in Fig. 3-6.

Fig. 3-7 shows the HRXRD x-ray rocking curve of FWHM value of symmetric (0 0 0 2) and asymmetric (1 0 $\bar{1}$ 2) diffraction for the GaN with various deposition time of AlN-IL. It clearly shows that the GaN inserted by 16min AlN-IL has minimum the FWHM value of the asymmetric (1 0 $\bar{1}$ 2) diffraction (1363 arcsec). It means 16min AlN-IL inserted in GaN can reduce the overall dislocation density in the GaN epitaxial layer. The strain associated with the presence of such AlN-IL results in bending of dislocations, which propagate from the underlying GaN layer. This strain field increases the probability of interactions between dislocations and leads to their reduction in the subsequently-grown GaN layers. However, when using thicker HT-AlN intermediate layer, the ability of reducing dislocation was worse than 16min HT-AlN-IL. Because the thickness of AlN-IL exceeded critical thickness, new dislocation was generated in the interface of AlN-IL and GaN layer.

Fig. 3-8 shows the scanning electron microscope (SEM) surface morphology of the GaN with various deposition time of AlN-IL. The surface of the GaN was rougher and the surface roughness increases with increasing deposition time of AlN-IL. The coalescence thickness of GaN epitaxial layer increases with increasing the thickness of AlN-IL.

The photoluminescence (PL) measurement was performed at 13K to investigate the optical properties of the GaN epitaxial layer with various deposition time of AlN-IL as shown in Fig. 3-9. The 13K-PL spectrum shows a dominant emission peak at 3.49eV, which is attributed to the neutral-donor-bound exciton (D^{o}X) of the wurtzite GaN epitaxial layer. The defect level emission (DLE) centered at about 2.2eV is very weak in GaN epilayer with suitable thickness of the AlN IL, but the DLE is stronger in GaN epitaxial layer without AlN IL. Consequently, from the XRD and PL analysis the defect density of GaN epilayer can be reduced by using AlN-IL.

Fig. 3-10 shows the HRXRD ω-scan profile of symmetric (0 0 0 2) and asymmetric (1 0 $\bar{1}$ 2) diffraction for the GaN epitaxial layer on off-axis sapphire and vicinal sapphire (0001).

The GaN epitaxial layer on 1.0^{o}-off cut sapphire shows the FWHM value of 85 arcsec (0 0 0 2) and 1796 arcsec (1 0 $\bar{1}$ 2), which is better than the GaN epitaxial layer on off-axis sapphire (153 arcsec in (0 0 0 2) plane and 2178 arcsec in (1 0 $\bar{1}$ 2) plane). This is due to the many macro-steps on the surface of vicinal sapphire. The treading dislocation on the macro-step was inclined. Then, this inclined treading dislocations combined with vertical treading dislocation on the macro-steps. Consequently, some of treading dislocations was eliminated.

The FWHM of asymmetric (1 0 $\bar{1}$ 2) diffraction reduces with the c-axis lattice constant of GaN approaching to theoretical value (5.185 Å) [29], as shown in Fig. 3-11. The overall dislocation density decreases together with the smaller residue strain. As a consequently, the high quality GaN epilayer could be obtained by reducing the residue strain. The study of reducing residue strain method has been under the way.

3.4 Summary

The crystal quality of GaN epitaxial layer on nitrided and non-nitrided sapphire has been studied. GaN epitaxial layer on nitrided sapphire shows no IDs and better crystal quality due to superior thin AlN nucleation layer formed by nitridation treatment. The GaN epitaxial layer of symmetric (0 0 0 2) FWHM value reduces with decrease of nitridation temperature, but the GaN epitaxial layer of asymmetric (1 0 $\bar{1}$ 2) FWHM value shows inverse trend. The GaN epitaxial layer on 800℃ nitridation shows lowest overall dislocation density even the screw dislocation increase a little. For improving crystal quality of GaN epitaxial layer further, AlN-IL was introduced in GaN epitaxial layer. The AlN-IL can reduce the dislocation density of GaN epitaxial layer, which has been confirmed by above experiment. The GaN epitaxial layer on vicinal sapphire substrate (1.0^{o}-off cut) shows lower overall dislocation density due to macro-step.

Table 3-1 The growth parameters of GaN epitaxial layer with various nitridation temperatures

	Nitridation	**HT-AlN Buffer layer**	**GaN epitaxial layer**
Growth Time	90 min	60 min	300 min
Sub. Temp.	200, 500, 800℃	800℃	740℃
Beam Equivalent Pressure		$Al_{BEP}=2.5\times10^{-8}$ torr	$Ga_{BEP}=3.6\times10^{-7}$ torr
N* Plasma	500W/1.5sccm 500W/4.0sccm	300W/1.5sccm	500W/1.5sccm 500W/4.0sccm

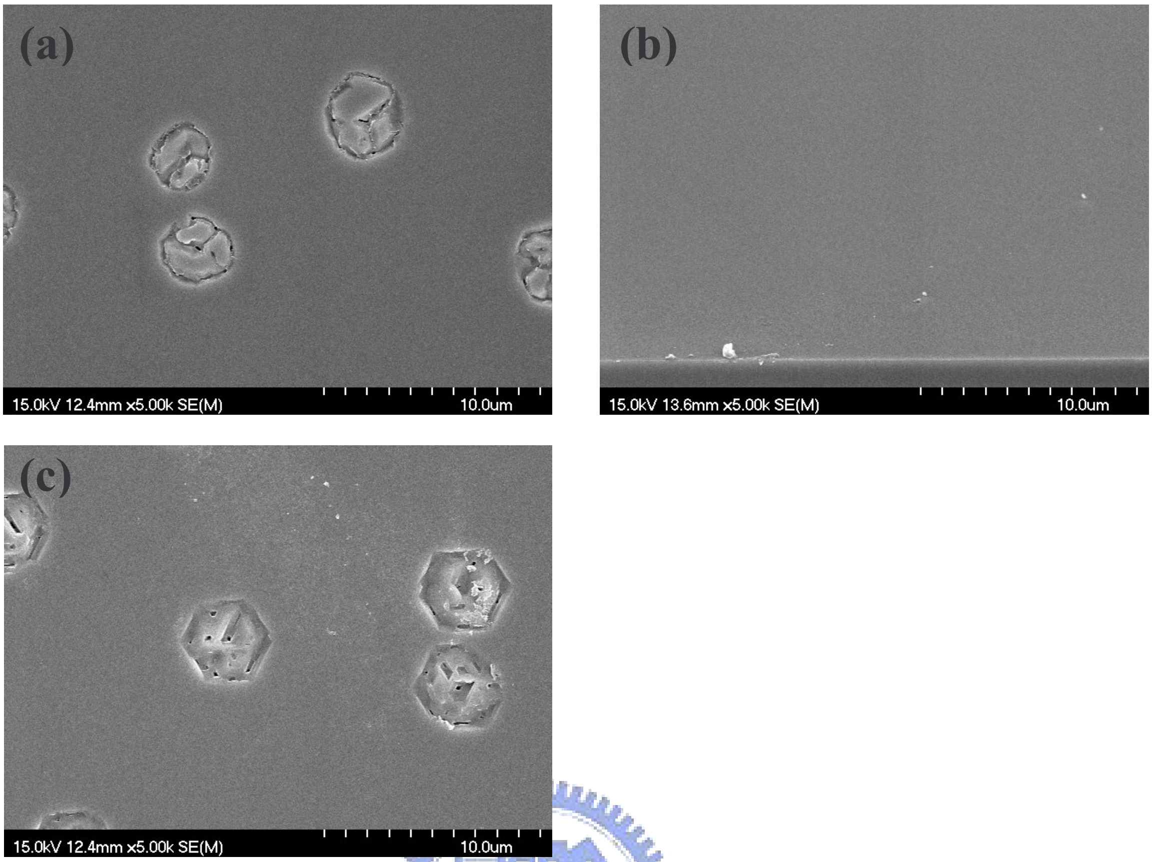


Fig. 3-1 SEM surface morphologies of GaN on (a) non-nitrided sapphire, (b) nitrided sapphire and (c) after 2M KOH etching for 30min.

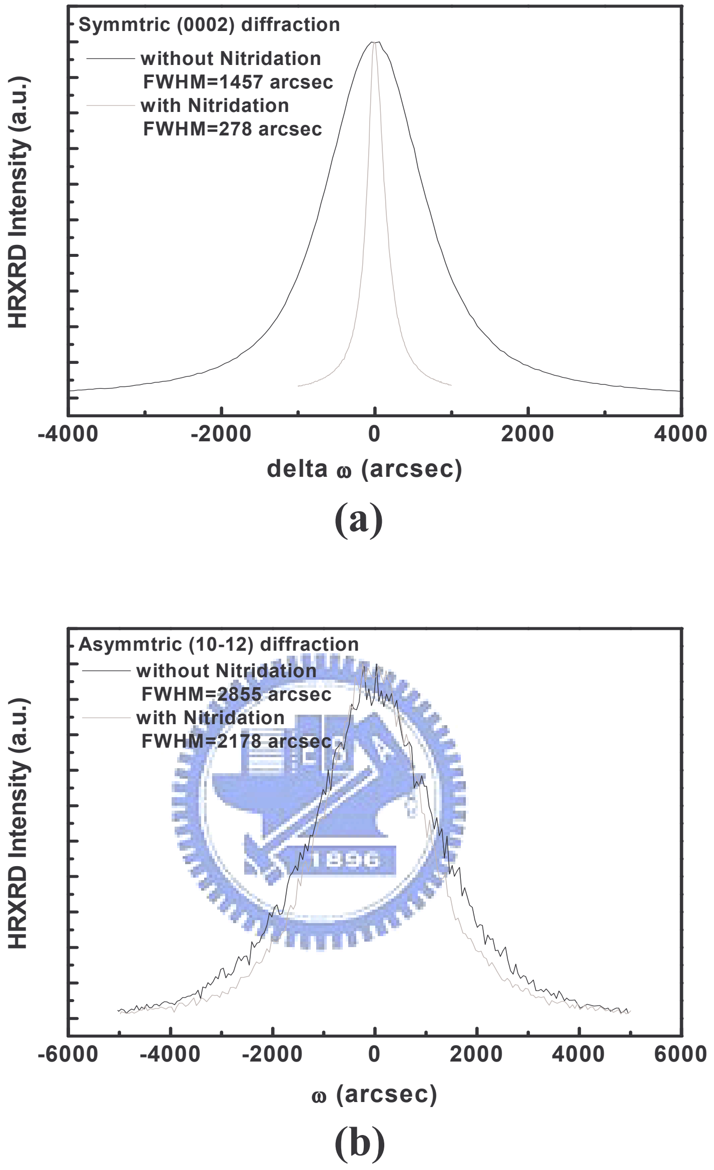


Fig. 3-2 (a) symmetric (0 0 0 2) and (b) asymmetric (1 0 ī 2) rocking curve of GaN epitaxial layer on nitrided and non-nitrided sapphire.

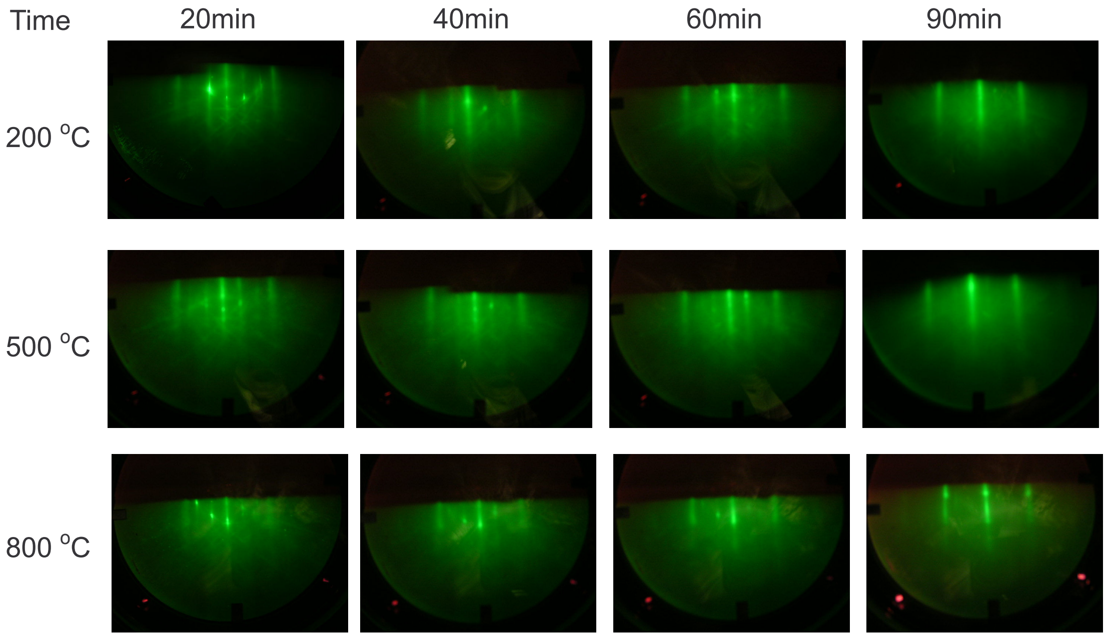


Fig. 3-3 Real time RHEED pattern for nitridation on sapphire at 200℃, 500℃ and 800℃ along the $<1\ 1\ \bar{1}\ 0>$ azimuth.

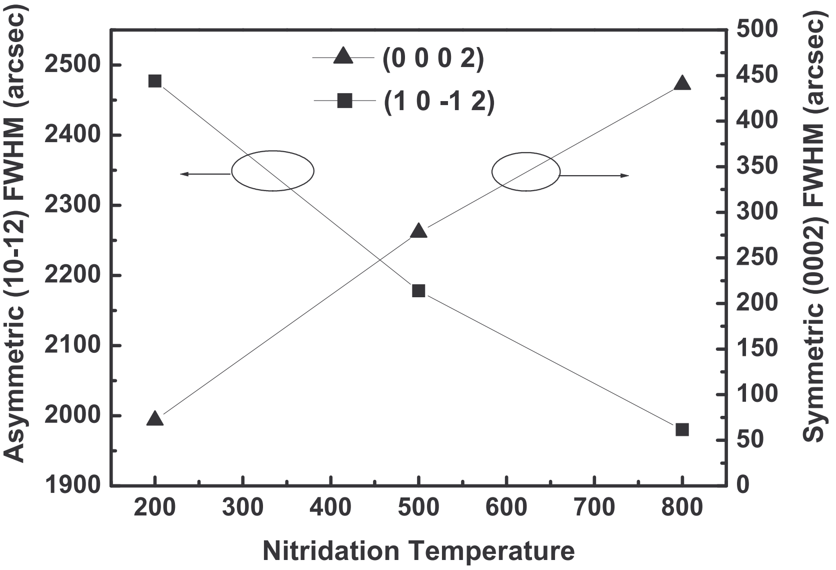


Fig. 3-4 FWHM of the x-ray rocking curve for the symmetric (0 0 0 2) and asymmetric (1 0 ī 2) diffraction of GaN on different nitridation temperature sapphire.

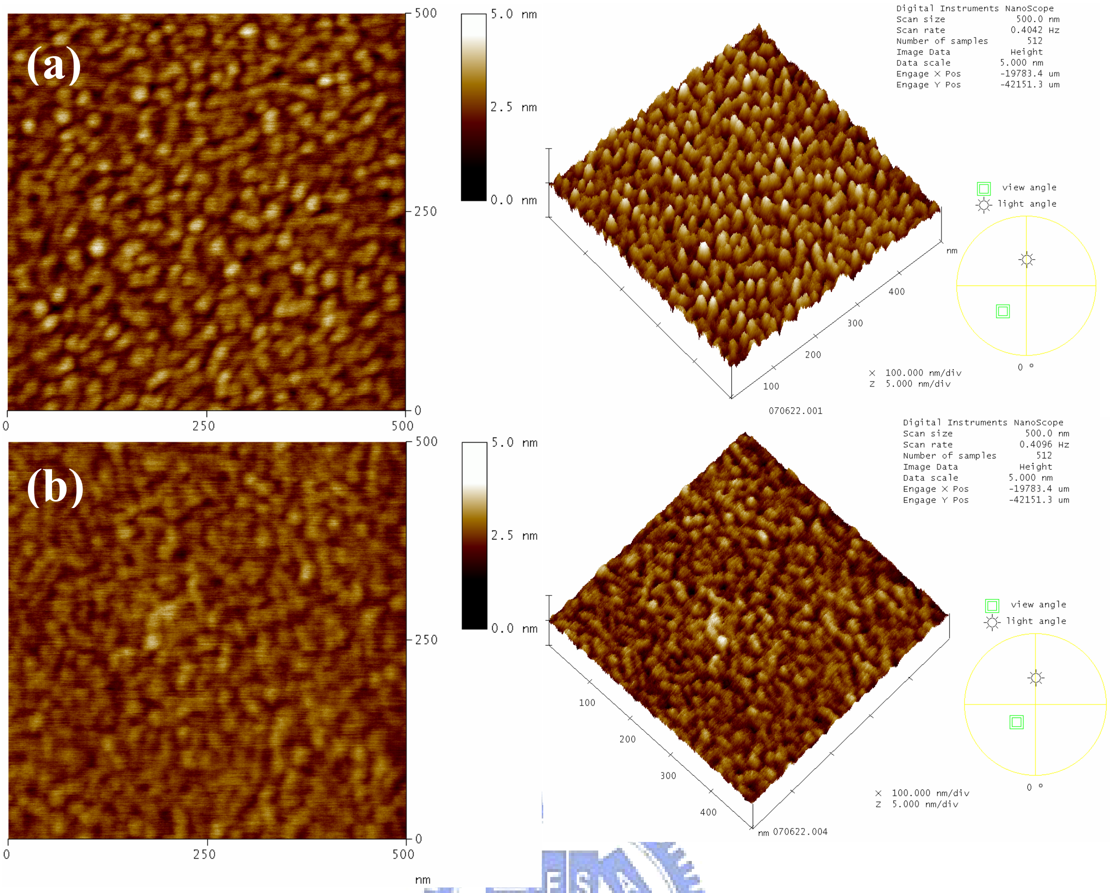


Fig. 3-5 AFM image of AlN buffer layer on the (a) 800℃ and (b) 200℃ nitrided sapphire

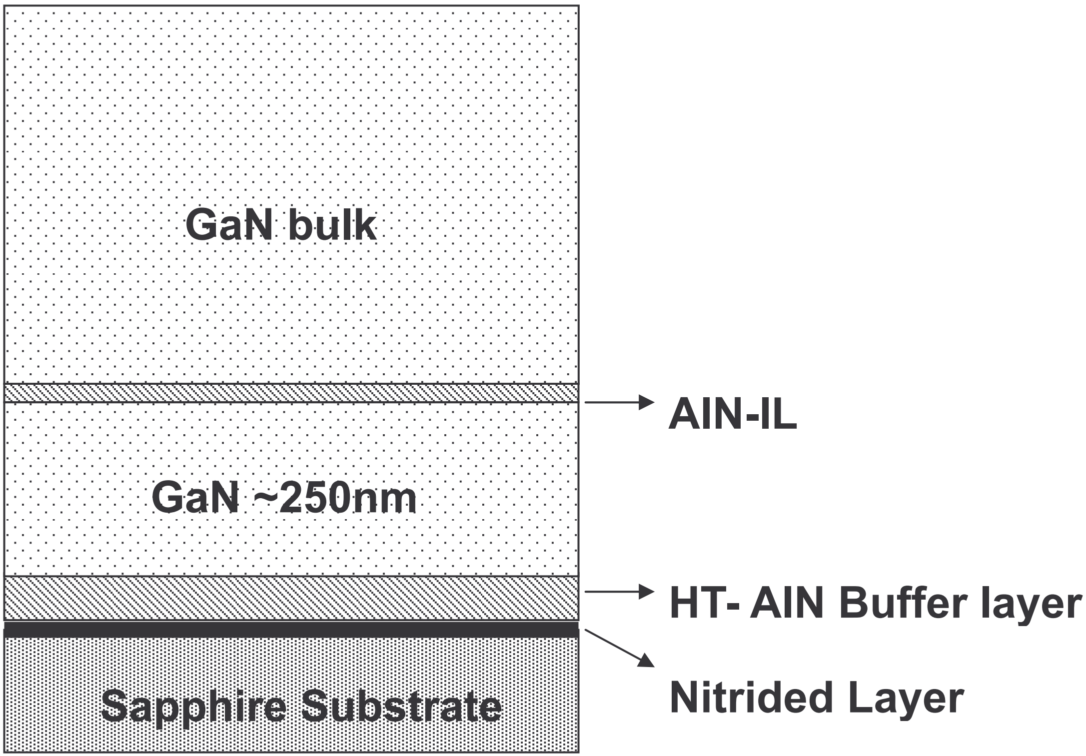


Fig. 3-6 The schematic diagram of AlN-IL inserted in GaN.

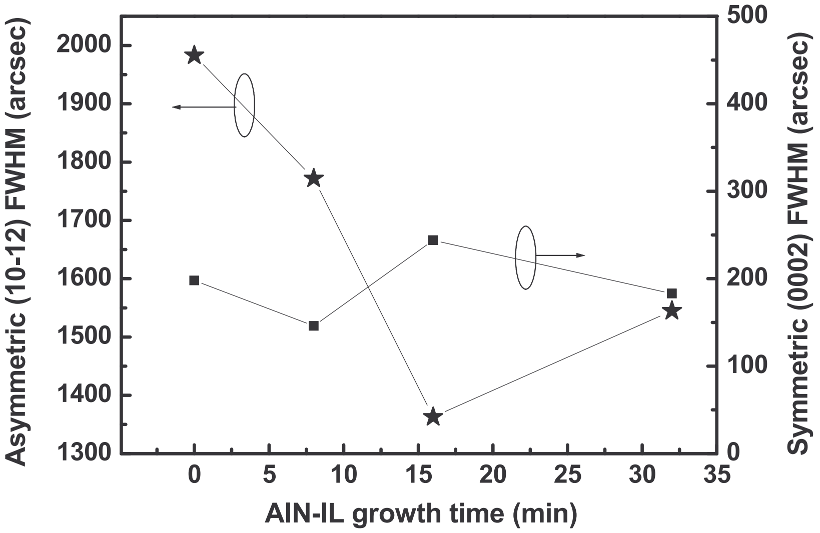
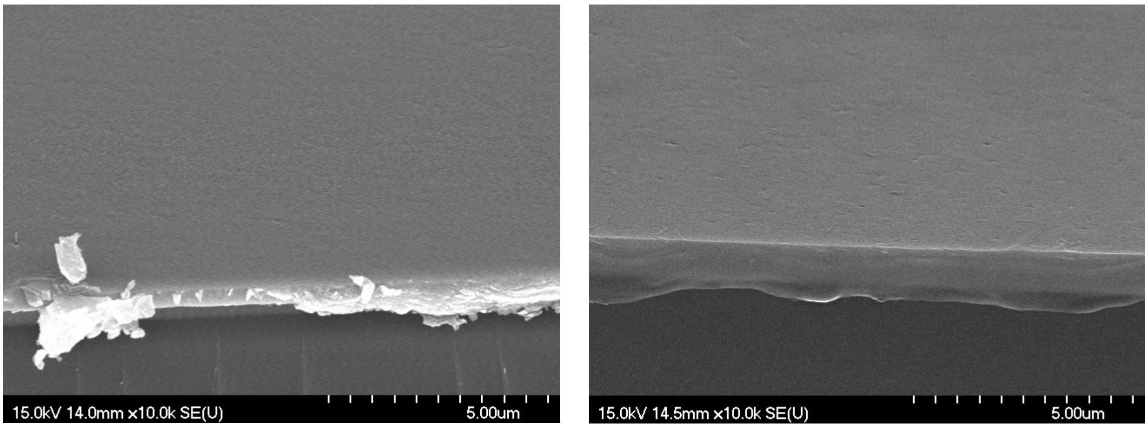
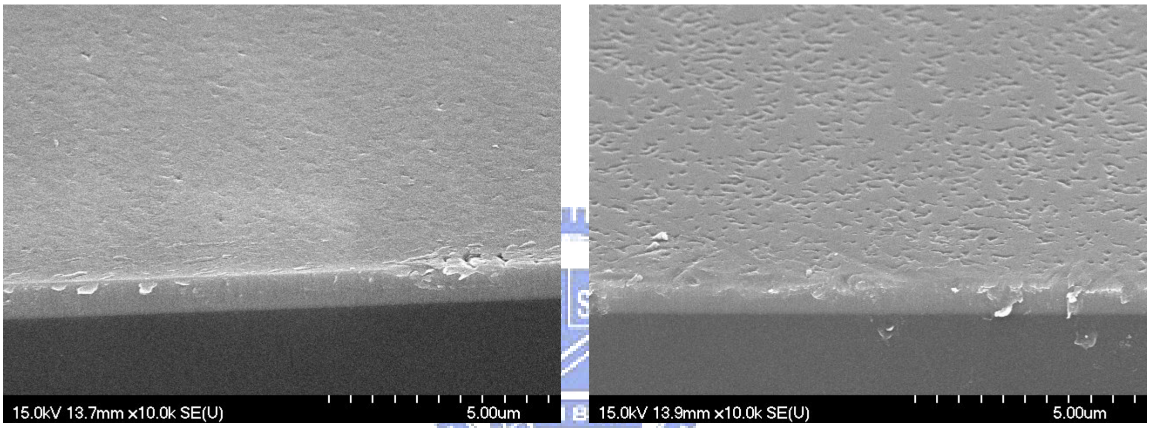


Fig. 3-7 FWHM of the x-ray rocking curve for the symmetric (0 0 0 2) and asymmetric (1 0 $\bar{1}$ 2) diffraction of GaN epilayer with various growth time of AlN-IL.



without AlN-IL

8min AlN-IL



16min AlN-IL

32min AlN-IL

Fig. 3-8 SEM surface morphology of the GaN with various growth time of AlN-IL.

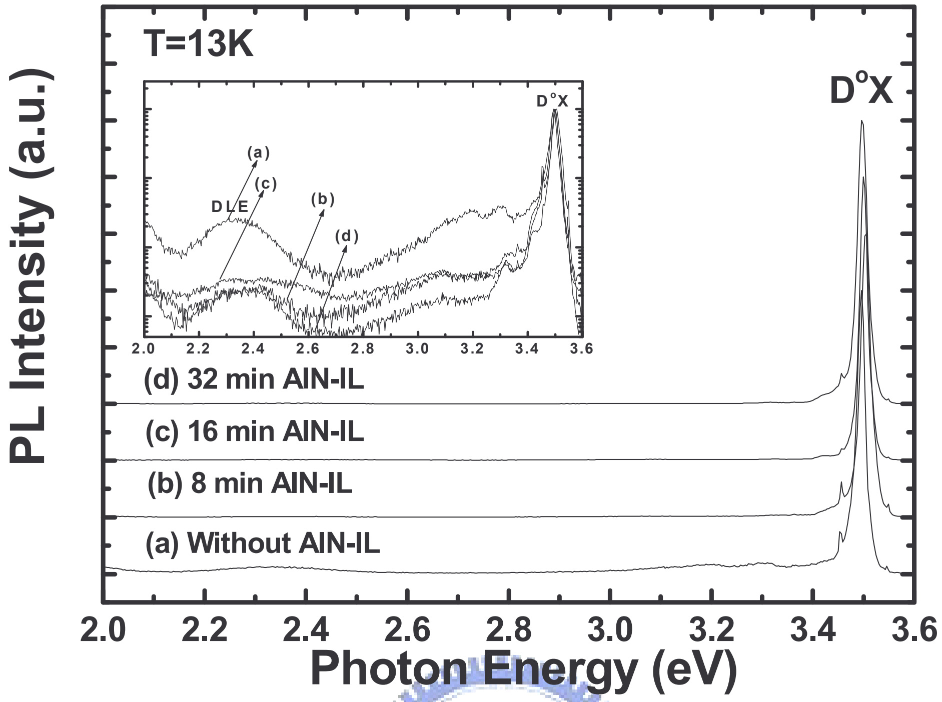


Fig. 3-9 PL spectra (linear scale) of the GaN with various growth time of AlN-IL. The inset is the PL spectra (log scale) of the GaN with various growth time of AlN-IL, which normalize to neutral-donor-bound exciton (D^{o}X) peak.

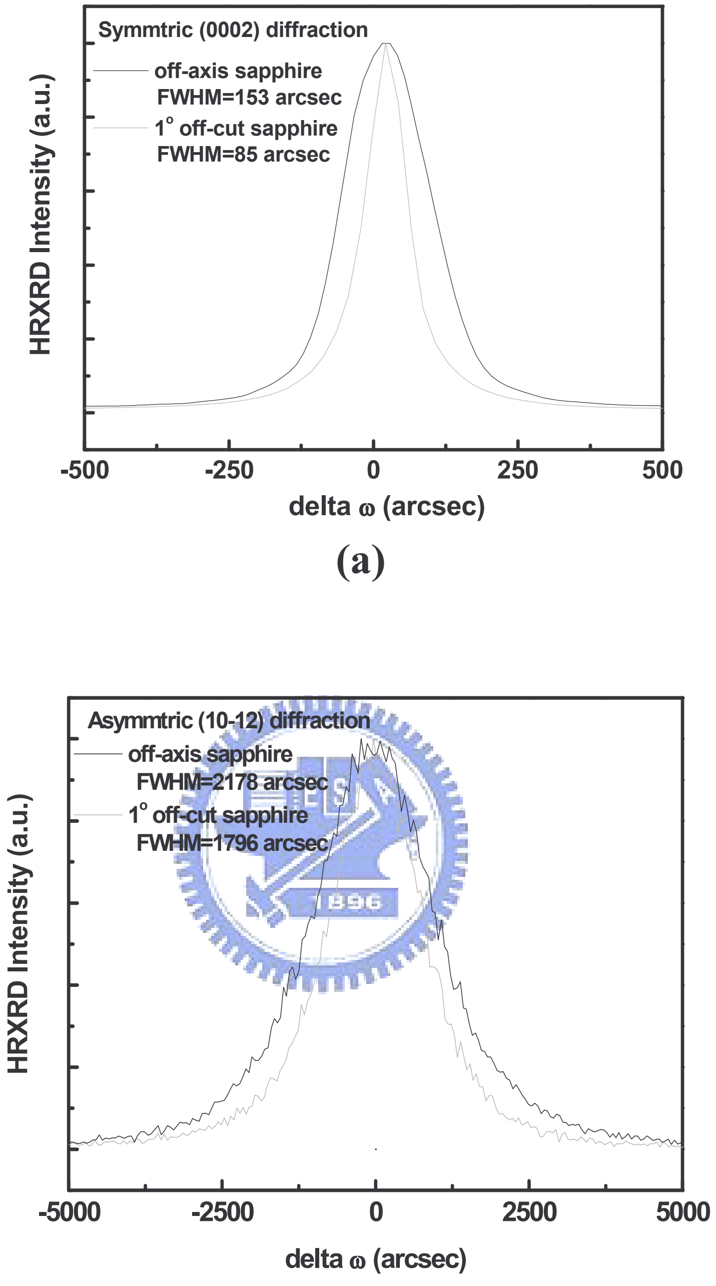


Fig. 3-10 (a) Symmetric (0 0 0 2) and (b) asymmetric $(10\ \bar{1}\ 2)$ (bottom figure) rocking curve of GaN epitaxial layer on 1.0°-off cut and no-off cut sapphire.

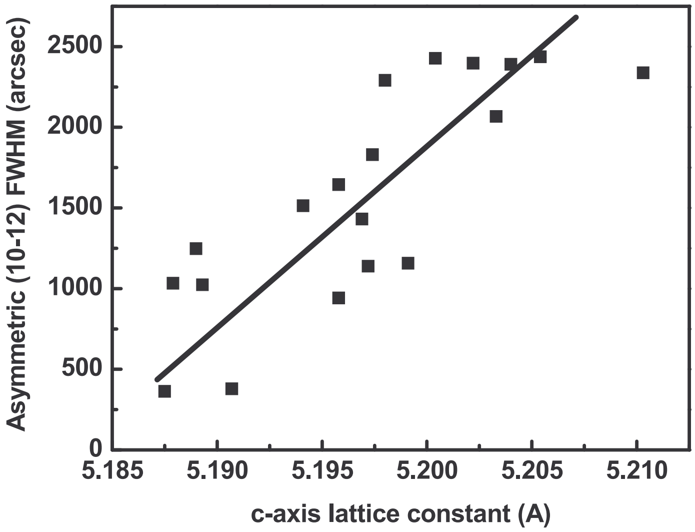


Fig. 3-11 FWHM of the x-ray rocking curve for asymmetric $(1\ 0\ \bar{1}\ 2)$ diffraction as function of c-axis lattice constant of GaN.