# Investigation on buffer layer for InN growth by molecular beam epitaxy

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The effects of various buffer layers on the InN growth were studied by using atomic force microscopy (AFM), X-ray diffraction (XRD), KOH wet etching and photoluminescence (PL). GaN or InN buffers with various temperatures and conditions were prepared for the InN growth by using plasma-assisted molecular beam epitaxy (PAMBE). For GaN buffers, the InN polarity was controlled by the GaN polarity. Namely, high temperature buffers (HT, 765°C–880°C) led to -c polar InN with better quality, while intermediate-temperature buffers (IT, 500°C–650°C) to +c polar InN with lower quality. When InN buffer was used, the quality of main InN was lower than that on GaN buffer. This reason is attributed to the twist misorientation (rotation of InN unit cell along *c*-axis) in InN/InN-buffer/sapphire structure. This drawback has been effectively suppressed by a longer substrate nitridation, or by inserting a GaN buffer between sapphire and InN buffer. By comparing the InN grown on GaN, InN or (GaN + InN) buffer, we concluded that GaN grown at about 800°C was the optimal buffer because it had atomically flat surface and led to -c polar InN with small misorientation.

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### 1. Introduction

InN has attracted much attention in the past decade for various electrical and optical applications owing to its remarkable physical properties.<sup>1)</sup> However, the high-quality InN crystal growth is very difficult because of its low dissociation temperature, stoichiometric instability and extremely high equilibrium vapor pressure of nitrogen over InN.<sup>2)</sup> Consequently, many physical properties of InN have not been fully understood yet due to the lack of high-quality InN crystal. A well-known example is the controversy on the fundamental bandgap of InN.<sup>2)-6)</sup> Recently, the quality of InN grown by plasma-assisted molecular beam epitaxy (PAMBE) on c-plane sapphire has been improved significantly<sup>7)–9)</sup> by carefully controlling the growth condition as well as by using appropriate buffer layers. For III-nitrides growth, due to the typically large lattice mismatch between nitrides and commonly used substrates (e.g., sapphire, 6H-SiC), buffer layers are being used extensively. For InN growth, the main functions of buffer layers involve (1) reducing the effective lattice mismatch; (2) providing high density of nucleation site; (3) blocking the diffusion of oxygen from substrate if sapphire is used. The most commonly used buffer layers for InN growth are GaN and InN grown at relatively low temperature. However, to our best knowledge, the systematic comparison of different types of buffer layers is still scarce and little attention has been paid to the influence of the buffer growth temperature on the polarity of the InN film. In this work, we employed a variety of buffer preparation to grow InN epifilms on c-plane sapphire substrates by PAMBE. These buffer layers can be divided into three categories, i.e., (1) GaN buffer layer; (2) InN buffer layer and (3) the combination of GaN and InN buffer layers denoted as (GaN + InN). For convenience, we also define three growth temperature ranges: (1) high-temperature (HT, 765°C–880°C); (2) intermediate-temperature (IT, 500°C–650°C) and (3) lowtemperature (LT, 350°C). The InN films grown on these buffer layers were evaluated by atomic force microscopy (AFM), X-ray diffraction (XRD), photoluminescence (PL). The polarity of GaN and InN was examined by KOH wet etching technique. By comparing the subsequent InN films, the influences of the buffer layers were discussed.

#### Experimental details

The samples studied in this work and their growth conditions are compiled in **Table 1**. They are denoted according to the buffer layer under the InN main layer (HG = HT–GaN, IG = IT–GaN, LI = LT–InN, and LGI = LT–(GaN + InN)). The growth

Table 1.	Sample Description
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Samples	Nitridation duration (h)	Buffer layer	InN growth temperature
HG1	2.5	GaN (880°C)	500°C
HG2	2.5	GaN (800°C)	500°C
HG3	2.5	GaN (765°C)	500°C
IG1	2.5	GaN (650°C)	500°C
IG2	2.5	GaN (500°C)	500°C
IG3	2.5	GaN (500°C)	400°C
LI1	5	InN (350°C)	500°C
LI2	2.5	InN (350°C)	500°C
LGI	2.5	GaN(350°C) /InN (350°C)	500°C

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procedure was conducted by a PAMBE (ULVAC, Inc) using a radio frequency (RF) plasma generator (SVT Associates, Inc) to activate the nitrogen source and conventional Knudsen effusion cells for the Ga and In source. The nitrogen flow rate was 0.5 sccm for all samples causing a nitrogen partial pressure in the growth chamber stabilized at approximately  $2.5 \times 10^{-6}$  Torr. The power of RF generator was set at optimized value of 300 W. An ion-trapper was used to deflect the high energetic ion species that induce defects into the epitaxial layer.<sup>1)</sup>

The substrate was  $10 \times 10 \times 0.5 \text{ mm}^3$  c-plane sapphire with 100-nm-thick titanium on the backside. Having been loaded into the growth chamber, the substrate was first thermally cleaned for 1 h at 800°C and was nitrided by exposing to the nitrogen plasma for 2.5 h (or 5 h) at 300°C. Then the buffer layer was grown for 1 h at the desired temperature. Due to the different growth rate, the resultant thicknesses of the buffers were typically 150 nm for HT-GaN, 100 nm for IT-GaN, and 60 nm for LT-InN. An In layer with the nominal coverage of about 1.8 monolayers was deposited before the growth of InN main layer. This In monolayer deposition has been proved to significantly improve the quality of the subsequent InN main layer in our previous experiment.10),11) Then the InN main layer was grown at 500°C (or 400°C for +c polarity). The In/N ratio was close to the stoichiometry and slightly N-rich. When the InN growth finished, the substrate was immediately cooled down to room temperature without any treatment.

The film thickness was determined by stylus profilometry and the morphology of sample surface was revealed by an AFM operated in the tapping mode. High-resolution XRD (Philips, X'Pert–MRD) using Cu  $K_{\alpha l}$  radiation was carried out to evaluate the structural properties, while the temperature-dependent (5 K– 295 K) PL measurements were performed to evaluate the optical properties. The excitation source of PL is the 514.5 nm line of an Ar<sup>+</sup> laser and the luminescence was detected by a PbS detector. The KOH (10 wt%) wet etching at room temperature was used to examine the polarity of GaN and InN.<sup>12),13)</sup>

## 3. Results and discussion

## 3.1 GaN buffers

We first discuss the effect of growth temperature of GaN buffer on the InN main layer. The growth temperature range can be divided into two regimes according to the polarity of the subsequent InN, which will be explained in detail later. The first regime is 765°C–880°C represented by the sample HG1, HG2 and HG3, and the second regime is 500°C–650°C represented by the sample IG1, IG2 and IG3.

**Figure 1** shows the XRD  $\theta$ -2 $\theta$  profiles of the InN grown on HT–GaN buffers (HG1, HG2 and HG3). The insets are the X-ray  $\omega$  rocking curves (XRC) for InN (0002) and GaN (0002),

respectively. In the  $\theta$ -2 $\theta$  profiles, the strong diffraction peaks for InN (0002) at 31.3° and for GaN (0002) at 34.5° were observed in all three samples implying the high structural quality of InN film and GaN buffer. Comparing the diffraction intensities of GaN (0002) peaks and InN (0002) peaks in the  $\theta$ -2 $\theta$  profiles and their full-width at half maximum (FWHM) in the XRCs, the structural quality of InN main layers and GaN buffers are rated as InN(HG2) > InN(HG1) > InN(HG3) and GaN(HG1) >GaN(HG2) > GaN(HG3), respectively. Note that GaN buffers in the three samples did not differ very much from the structural quality point of view, but the resultant InN main layers did. This suggests that the structural quality of InN did not strongly depend on that of the GaN buffer layer. Figure 2(a)-(c) shows the surface morphologies of the GaN buffer layers grown at 880°C, 800°C and 765°C, respectively. Among the three samples, GaN grown at 800°C showed the flattest surface, while GaN grown at 880°C had many hexagonal pits presumably due to the intense re-evaporation of GaN at high temperature, and GaN grown at 765°C on the other hand showed deep valleys which is generally attributed to the insufficient surface migration of Ga and N adatoms at low temperature.<sup>1)</sup> Due to the presence of these pits or valleys, the root-mean-square (RMS) roughness of the GaN grown at 880°C or 765°C was much larger than that of GaN grown at 800°C, which was in the order of RMS(GaN800) < RMS(GaN880) < RMS(GaN765). This order is consistent with the structural quality of InN revealed by XRD, i.e., InN(HG2) > InN(HG1) > InN(HG3), indicating the buffer surface flatness is the most important factor which determines the InN quality. If InN is grown on a rough surface, the migration length of In adatoms will be greatly suppressed because of the presence of high density of chemical potential wells. In contrast, if InN is grown on a very flat surface, the migration length of In adatoms is large. In adatoms will have enough time to diffuse



Fig. 1. XRD  $\theta$ -2 $\theta$  profile for the InN epifilms grown on high-temperature GaN buffers. (Sample: HG1, HG2 and HG3). Insets: XRCs along InN (0002) and along GaN (0002), respectively.



Fig. 2. AFM surface morphologies of the high-temperature GaN buffers grown at (a) 880°C, (b) 800°C and (c) 765°C. Note that the height scales are different.

freely on the surface, with a greater probability of exploring the possible incorporation site,<sup>14)</sup> thus improving the structural quality of InN film.

Figure 3 shows the XRD  $\theta$ -2 $\theta$  profiles of the samples using IT-GaN buffers (IG1, IG2 and IG3). We first tried to grow InN film at 500°C on the IT-GaN buffer. However, as shown in Fig. 3, the XRD measurement on the IG1 and IG2 showed no InN (0002) peak at all. Instead, the metallic In (101) peak appeared. This suggests that the InN film has not been successfully grown in sample IG1 and IG2. Considering the presence of metallic In, we speculated that the InN grown on the IT-GaN buffer might have +c polarity. The +c polar InN easily decomposed and left metallic In on the sample surface, because it has a decomposition temperature about 100°C lower than its -c polar counterpart.<sup>15)</sup> To clarify this speculation, we decreased the growth temperature for InN film to 400°C. As expected, in sample IG3, InN film was successfully grown on the IT-GaN buffer as indicated by the presence of InN (0002) peak. It is worth noting that the crystal quality of +c polar InN is inferior to -c polar InN due to the relatively low growth temperature.

To confirm the polarity, we used KOH wet etching to check the sample IG3, as well as sample HG2 and the GaN buffer grown at 800°C for comparison. The etching time for all samples was 5 min. As well known, -c polar InN or GaN can be easily removed by KOH etching, in contrast +c polarity is resistant to KOH. As shown in Table 2, we first examined the change of band-edge luminescence of GaN and InN after etching. As expected, the luminescence vanished for HG2 and GaN/800°C after etching due to the complete removal of the -c polar films; however, the band-edge luminescence for IG3 did not show any significant decrease after 5 min etching, implying that IG3 was +c polarity. This result is in agreement with the AFM results shown in Fig. 4. Figure 4(a)-(c) are the surface morphologies of IG3, HG2 and GaN/800°C, before (above) and after (below) etching, respectively. It is clear that after 5 min etching, IG3 and HG2 showed completely different morphologies indicating their different resistance to the KOH solution. For IG3, the etching did not dramatically change the morphology and only some hexagonal holes appeared at the position of threading dislocations. The etching rate was very small and the change of the film thickness after etching was not detectable by surface stylus profilometry. On the other hand, for HG2, the InN film was completely removed, together with the underlying GaN buffer and left some dome-shape GaN with facets. The morphology of GaN/ $800^{\circ}$ C also dramatically changed after etching and its -c polarity was confirmed.

In our study, it was found that the InN films always followed the same polarity of GaN buffer layer. Therefore, to achieve a better controlling of the polarity, we systematically examined the polarity of GaN buffers grown at different temperatures. For 100nm-thick GaN film, the etched thicknesses in KOH solution for 60 sec are shown in **Fig. 5**. We concluded that GaN had +c polarity if grown at a temperature between 500°C and 650°C, and it had -c polarity if grown at a temperature higher than 765°C. The temperature range for polarity transition from +c polar to -c polar was 650°C-765°C. To grow -c polar InN, HT–GaN must be used.

#### 3.2 InN buffer and (GaN + InN) buffer

When LT–InN buffer was used, an important finding was that the crystal quality of InN main layer was not only affected by the growth condition of LT–InN, but also by the duration of nitridation before buffer growth. **Figure 6** shows the XRD  $\varphi$  scan along asymmetric InN (11–22) (solid lines). The  $\varphi$  angles correspond-



Fig. 3. XRD  $\theta$ -2 $\theta$  profile for the InN epifilms grown on intermediate-temperature GaN buffers (Sample: IG1, IG2 and IG3).

Table 2. Change of Band-Edge Luminescence after KOH Etching

	IG3	HG2	GaN/800°C
before	Yes(0.78eV)	Yes(0.69eV)	Yes(3.44eV)
after	Yes(0.78eV)	No Luminescence	No Luminescence



Fig. 4. AFM surface morphologies of (a) IG3, (b) HG2 and (c) GaN buffer grown at 800°C, before (above) and after (below) 5 min wet etching by 10 wt% KOH solution. Note that the height scales are different.

ing to sapphire (11-23) peaks are indicated by the dotted lines. It is clear that the relationship of [10-10]<sub>InN</sub>//[11-20]<sub>sap</sub> held very well in LI1 with 5 h nitridation. In contrast, two orientations, which are [10-10]<sub>InN</sub>//[11-20]<sub>sap</sub> and [10-10]<sub>InN</sub>//[10-10]<sub>sap</sub>, were found in LI2 with 2.5 h nitridation. The presence of two orientations with 30° difference is attributed to the incomplete AIN coverage on sapphire substrate after the nitridation process.<sup>2)</sup> Table 3 lists the lattice mismatch between nitrides and sapphire in the case of 30° rotation,<sup>16),17)</sup> and no rotation nucleation. If LT– InN buffer is directly grown on the sapphire area that is not covered by AlN during nitridation, two orientations of nucleation have the similar magnitude of lattice mismatch, thus neither of them is dominantly favored. Consequently, the InN main layer has also two orientations following the LT-InN buffer. However, if the nitridation duration is sufficient (like 5 h in LI1), a complete coverage of AlN forms, thus there will be only one orientation relationship is favored, which is [10-10]<sub>InN</sub>//[10-10]<sub>AIN</sub>// [11-20]<sub>sap</sub>. By contrast, if HT-GaN buffer was used, only one orientation relationship was found: [10-10]<sub>InN</sub>//[10-10]<sub>GaN</sub>//[11-20]<sub>sap</sub>, and it was not sensitive to the nitridation duration.

Figure 7(a)-(c) show the XRD measurements on the sample LI1, which is the InN film grown on LT-InN buffer under the optimal condition. In order to compare the LT-InN buffer with the HT-GaN buffer, the XRD results of the sample HG2 are also shown. In the  $\theta$ -2 $\theta$  profile of LI1, the strong diffraction peak at 31.3° for the InN (0002) can be observed, implying the highquality InN growth. From the XRCs along the symmetric InN (0002) and asymmetric InN (10-15), it was found that FWHMs of LI1 were much wider than those of HG2, indicating LI1 had lower structural quality with greater tilt and twist misorientation. In our work, InN films with LT-InN buffer were typically inferior compared with those with HT-GaN buffer. We found that using LT-InN buffer led to a very narrow growth window for InN main layer. By contrast, using HT-GaN buffer makes the subsequent InN growth much controllable, which is only sensitive to the growth parameter during the growth of InN layer.

Double buffers consisting of the LT–GaN and the LT–InN were also investigated. **Figure 8** shows the XRD  $\varphi$  scan for the InN grown on double buffers (sample LGI). In this case, there was also only one orientation relationship  $[10-10]_{InN}//[10-10]_{GaN}//[11-20]_{sap}$ . It was obvious that the twist misorientation we found in LI2 was effectively suppressed by adding a LT–GaN layer between sapphire and LT–InN layer. Under the same growth condition for InN main layer, LT–(GaN + InN) buffer typically led to a higher crystal quality of InN than LT–InN buffer; however, it was still not as good as HT–GaN buffers, probably due to the rough buffer surface of LT–(GaN + InN).





Fig. 5. Etched thickness of 100-nm-thick GaN films grown at different temperatures. KOH solution: 10 wt%; 60 sec.



Fig. 6. XRD  $\varphi$  scan for the InN films grown on low-temperature InN buffer, LI1 with 5 h nitridation and LI2 with 2.5 h nitridation. The solid lines show the peaks for the asymmetric InN (11–22) reflections, whereas the dotted line shows the peaks for the asymmetric sapphire (11–23) reflections.

Table 3. Lattice Mismatch between III-Nitrides and Sapphire in the Case of 30° Rotation Nucleation and No Rotation Nucleation. Compressive: "+" and Tensile: "-". (F: Favored Orientation Relationship During Heteroepitaxy)

Effective lattice mismatch	30° rotation	No rotation
AlN and sapphire	+13.3%(F)	-34.6%
GaN and sapphire	+16.1%(F)	-33.0%
InN and sapphire	+28.8%	-25.7%
InN and AlN	N/A	+13.7%(F)
InN and GaN	N/A	+10.9%(F)



Fig. 7. XRD measurements for the InN films grown on low-temperature InN buffer (L11) and on high-temperature GaN buffer (HG2). (a)  $\theta$ -2 $\theta$  profiles, (b) XRC along symmetric InN (0002), and (c) XRC along asymmetric InN (10–15).



Fig. 8. XRD  $\varphi$  scan for the InN films grown on low-temperature (GaN + InN) buffer. The solid lines show the peaks for the asymmetric InN (11–22) reflections (above) and for the asymmetric GaN (11–22) reflections (below), whereas the dotted line shows the peaks for the asymmetric sapphire (11–23) reflections.

## 4. Conclusions

We present the InN growth by PAMBE on a variety of buffers, including GaN buffer, InN buffer and their combination. For GaN buffer, it was found -c polarity of buffer led to -c polarity of InN main layer that could tolerate higher growth temperature. In the case of using HT-GaN buffer, the resultant InN was -c polarity. The surface flatness of the buffer is the key to obtain high-quality InN. In contrast, InN grown on IT-GaN buffer always showed +c polarity, thus having low crystal quality due to the limited growth temperature. For LT-InN buffer, twist misorientation was typically large especially when nitridation was not sufficient. Using LT-(GaN + InN) buffer effectively suppressed the twist misorientation in the InN film. By a comprehensive comparison, we rate the buffers studied in this work as HT-GaN > LT-(GaN + InN) > LT-InN > IT-GaN. We believe that a good buffer layer for InN epi-growth should have the atomically flat surface, -c polarity and small misorientation.

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