Effects of the Group V/III Ratio and a GaN Inter-layer on the Crystal Quality of InN Grown by Using the Hydride Vapor-phase Epitaxy Method

Ju-Hyung Ha, Juan Wang and Won-Jae Lee[∗]

Department of Materials and Component Engineering, Electronic Ceramics Center, Dong-Eui University, Busan 614-714, Korea

Young-Jun Choi and Hae-Yong LEE

LumiGNtech Co., Ltd., Seoul 153-801, Korea

Jung-Gon Kim and Hiroshi Harima

Department of Electronics, Kyoto Institute of Technology, Matusgasaki, Kyoto 606-8585, Japan

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The hydride vapor-phase epitaxy (HVPE) method was used to deposit high-quality InN layers on GaN inter-layer/sapphire (0001) structures that had been fabricated by using either the HVPE method or the metal-organic chemical-phase deposition (MOCVD) method. The effects of the group V/III ratio and different GaN inter-layers on the crystal quality of the InN layers were systemically investigated. The InN layer grown at a low Group V/III ratio revealed a high crystal quality with a two-dimensional (2D) growth mode. Also, the 110.7-nm-thick InN layer grown by using HVPE on a GaN inter-layer/sapphire (0001) substrate structure that had been fabricated by using MOCVD had a high crystal quality, with the full width at half maximum (FWHM) of the InN X-ray diffraction (XRD) peak being about 844 arcsec, and a smooth surface with an atomic force microscopy (AFM) roughness of about 0.07 nm. On the other hand, the 145.7-nm-thick InN layer grown by using HVPE on a GaN inter-layer/sapphire (0001) substrate structure that had been fabricated by using the HVPE method had a lower crystal quality, a FWHM value for the InN (0002) peak of about 2772 arcsec, and a surface roughness of about 3.73 nm. In addition, the peak of the E_2 (high) phonon mode for the 110.7-nm-thick InN layer grown by using HVPE on a GaN inter-layer/sapphire (0001) structure that had been fabricated by using MOCVD was detected at 491 cm⁻¹ and had a FWHM of 9.9 cm⁻¹. As a result, InN layers grown by using HVPE on GaN inter-layer/sapphire (0001) substrate structures fabricated by using MOCVD have a high crystal quality and a reduced Raman value, which agrees well with the results of the XRD analysis.

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I. INTRODUCTION

In recent years, InN has attracted considerable attention for promising electronic device applications such as infrared light-emitting diodes and high-speed, highperformance electronic devices [1]. Its narrow band gap of about 0.7 eV [2, 3] enables the emission range of III-nitride-based light-emitting diodes (LEDs) to be extended to cover wavelengths from ultraviolet (UV) to near infrared. In addition, InN has the lowest effective mass of electrons in the III-nitride group, which leads to a higher saturation velocity and a higher mobility [4]. During the last decades, however, InN has not drawn too much attention and the characterization of its physical properties has lagged compared with characterizations of the physical properties of the well-known GaN and AlN semiconductors. This is probably due to the difficulty in growing high-quality InN layers. Nowadays, high-quality InN layers have been mainly obtained by using molecular beam epitaxy (MBE) [5] and metal-organic vapor-phase epitaxy (MOVPE) [6]. The sapphire substrate has become the most common substrate for epitaxial growth of group-III nitrides due to its relatively low cost, good transparency, and stability at high temperatures. However, the large lattice mismatch between InN and sapphire leads to a large residual stress and strain and a three dimensional (3D) growth of InN. The hydride vapor-phase epitaxy (HVPE) method has

[∗]E-mail: leewj@deu.ac.kr; Fax: +82-2-3282-7746

Table 1. Roughnesses (Ra) and FWHMs of the GaN (0002) and (10-12) planes of two different GaN inter-layers on sapphire (0001) substrates.

Inter-layer	Growth	Thickness	Roughness (Ra)	FWHM (0002)	FWHM (10-12)
	Method	μ m	nm)	(arcsec)	(arcsec)
$_{\rm GaN}$	MOCVD	2.0	$0.30\,$	305	358
GaN	HVPE	5.5	0.29	621	666

Table 2. Conditions for the growth of InN inter-layers at a group V/III ratio of 400:40 $(= 10)$ on MOCVD and HVPE-GaN/sapphire (0001) substrates.

attracted some attention as a favorable approach to fabricating low-cost InN layers at a high growth rate. In addition, the lattice mismatch of the InN layer can be reduced somewhat by employing HVPE and commercial high-quality GaN substrates. However, previous reports of InN layers prepared by using the HVPE technique are scarce. Most reports deal with a thermodynamic analysis of the HVPE system [7, 8], the effects of growth conditions such as the growth temperature [9] and the Group V/III ratios [10], and the effects of various In source materials, such as $InCl₃$ powder and $Cl₂$ gas [11, 12]. At the same time, in order to reduce the lattice mismatch and improve the quality of InN layers, researchers have employed GaN inter-layers [13–18].

In this study, we prepared InN layers by using HVPE on two types of GaN inter-layer/sapphire (0001) structures grown by using the HVPE and the MOCVD methods, respectively. The effects of the Group V/III ratios and the GaN inter-layers on the crystal quality of the InN layers were systematically investigated. The surface morphologies were characterized by using scanning electron microscopy (SEM) and atomic force microscopy (AFM). In addition, the crystal quality of the InN layers was characterized by using X-ray diffraction and Raman scattering measurements.

II. EXPERIMENTS AND DISCUSSION

In this work, the InN layers were deposited on GaN/sapphire (0001) substrates by using a homemade, horizontal, HVPE system with a ∼1.5-m-long two-zone reactor (source and growth zone). The $InCl_x$ (InCl and $InCl₃$) gases used as the Group-III source were synthesized by using a reaction of In metal and HCl gas in the source zone at 550 ◦C. InN layers were deposited on

GaN/sapphire (0001) substrates by using a reaction of $NH₃$ gas as the Group-V source with the N₂ carrier gas in the growth zone at 550 ◦C. These processes were the same as those used for the growth of GaN layers. The flows of the input gas precursors were $20 \sim 40$ sccm for HCl, which was used as the Group-III source gas (we assumed that InCl was synthesized ideally with a 100% conversion by using the supplements of HCl gas) and 400 sccm for NH_3 , which was used as the Group-V source gas. For all processes, the total gas flow, including the carrier gas, was fixed at 800 sccm at atmosphere pressure.

Prior to the deposition of the InN layers, we prepared two types of GaN inter-layer/sapphire (0001) structures: one by using the HVPE method and the other by using the MOCVD method (Table 1). The surface roughnesses of the 2.0- μ m-thick and the 5.5- μ m-thick GaN/sapphire (0001) structure grown by using HVPE and MOCVD, respectively, were measured as 0.30 and 0.29 nm. From the X-ray diffraction (XRD) analysis, the value of the full width at half-maximum (FWHM) for the GaN (0002) plane structures grown by using MOCVD (hereafter referred to as MOCVD-GaN/sapphire (0001) substrates or structures) and by using HVPE (hereafter referred to as HVPE-GaN/sapphire (0001) substrates or structures), respectively, were 305 and 621 arcsec. Also, for the GaN (10-12) plane, the values of the FWHM were 358 and 666 arcsec, respectively. In order to study the effect of the Group V/III ratio on the properties of the InN layers, we grew InN on HVPE-GaN/sapphire (0001) for 1 h with different Group-V/III ratios $(400:50 \ (= 8), 400:40)$ $(=1 0)$, 400:30 $(= 13.3)$ and 400:20 $(= 20)$). Then, InN layers were grown on sapphire with different GaN interlayers. Table 2 shows the growth conditions: the types of inter-layers, the growth temperature, the Group V/III ratio, the growth time, and the total gas flow.

The surface morphologies of the InN layers were ana-

(b) Cross-sectional view

Fig. 1. SEM (a) surface and (b) cross-sectional images of InN layers on HVPE-GaN/sapphire (0001) substrates for different Group V/III ratios.

lyzed by using scanning electron microscopy (SEM, FEI, Quanta 200 FEG FE-SEM, Japan) at a magnification of 30,000 and atomic force microscopy (AFM, Seiko, SPA-400, Japan) for a scan area of $5 \times 5 \ \mu \text{m}^2$. The structural crystal qualities of the InN layers were characterized by using high-resolution X-ray diffraction (HR-XRD, PANalytical, X'Pert-PRO MPD and MRD, Holland) and Raman scattering measurements (SPEX 1403, 0.85-m double spectrometer, Industries, USA). Raman scattering was conducted at room temperature by using an optical microscope and an Ar^+ ion laser with a 488-nm wavelength for excitation. The growth-plane backscattering geometry was employed.

Figure 1 shows the surface morphologies and crosssectional views of InN layers grown on HVPE-GaN/sapphire (0001) substrates with different Group

Fig. 2. (Color online) (a) (0002) rocking curves of InN layers grown on HVPE-GaN/sapphire (0001) with different Group V/III ratios and (b) plot of the values of the FWHM as a function of the V/III ratio.

V/III ratios (400:50 (= 8), 400:40 (= 10), 400:30 (= 13.3) and $400:20 (= 20)$ as observed by using SEM. As the Group V/III ratio was increased from $400:50 (= 8)$ to $400:20 (= 20)$, the growth mode tended to change from a 2D growth to a 3D growth, as exhibited in Fig. 1(a). Individual separated islands were observed in the SEM surface images for Group V/III ratios of 400:30 and 400:20. This result indicates that a high NH3 flow rate and a high Group-V/III ratio lead to 3D (column structure) growth of the InN layers, which is similar to the result repeated for GaN growth [20]. Also, the InN islands grown at lower Group V/III ratios were larger. Similar trends in InN grown by using MOVPE and MOCVD were reported by Johnson et al., Singh et al., Jamil et al. and Wang et al. [15–18]. The top surfaces of the samples for Group V/III ratios of $400:50 (= 8)$ and $400:40$ $(= 10)$ appear almost to be coalesced compared to the surfaces of the samples grown at the other two ratios. From the cross-sectional view (Fig. 1(b)), the InN layer for a Group V/III ratio of $400:40 (= 10)$ can be observed to have a relatively high 2D growth rate of about 145.7 nm/h.

The ω scan rocking curves for the (0002) symmetry planes of the InN layers grown on HVPE-GaN/sapphire (0001) substrates with different Group V/III ratios are

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Fig. 3. Plane and cross-sectional SEM images of InN layers grown on MOCVD- and HVPE-GaN/ sapphire (0001) substrates; (a) and (b) are plane views and (c), and (d) are cross-sectional views.

shown in Fig. 2. The FWHMs of the InN (0002) peaks obtained from the rocking curves are 2547, 2775, 3216 and 3374 arcsec for InN layers grown on HVPE- GaN/sapphire (0001) substrates with Group V/III ratios of 400:50 (= 8), 400:40 (= 10), 400:30 (= 13.3) and $400:20 (= 20)$, respectively. These broad values are expected to be due partially to poor coalescence, as shown in Fig. 1(a). Also, they may result from the poor crystal quality of HVPE-GaN/sapphire (0001) substrate, as mentioned in Table 1. This implies that the crystal quality for the InN grown with lower Group V/III ratios needs to be improved.

In this work, among the four samples, the InN layers grown with a Group V/III ratio of 400:40 showed the highest growth rate and a high crystal quality with a 2D growth mode. This growth condition is shown in Table 2 and was selected for investigating different GaN interlayers.

The surface morphologies and the cross-sectional views of InN layers, as obtained by using SEM, are shown in Figs. $3(a)-(d)$. The surface morphology of the InN layer grown on a MOCVD-GaN/sapphire (0001) substrate is smooth and has better uniformity, indicating 2D growth with surface coalescence $(Fig. 3(a))$ while that of the InN layer grown on a HVPE-GaN/sapphire (0001) substrate has a rough surface with not-well-coalesced islands $(Fig. 3(b))$. In addition, Figs. $3(c)$ and (d) show the corresponding cross-sectional SEM images. An interface is clearly observed between the InN layer and the GaN inter-layer. The thicknesses of the InN layers grown on MOCVD- and HVPE-GaN/sapphire (0001) substrates are found to 110.7 nm and 145.7 nm, respectively.

Figure 4 shows the 3D AFM surface morphologies of

Fig. 4. (Color online) 3D AFM images of InN layers grown on MOCVD- and HVPE-GaN/ sapphire (0001) substrates.

the InN layers. The average roughness (Ra) values for a scan area of $5 \times 5 \mu m^2$ are estimated to be 0.87 and 3.73 nm for the InN layers grown on MOCVD- and HVPE-GaN /sapphire (0001) substrates, respectively. The smaller Ra value for the InN layer grown on the MOCVD-GaN/sapphire (0001) substrate demonstrates a better surface morphology, and these results correspond well with the SEM results for the surface morphology. The values of Ra for the MOCVD- and HVPE-GaN/sapphire (0001) were almost the same, 0.30 and 0.29 nm (Table 1), but the values of Ra for the InN layers grown on MOCVD- and HVPE-GaN/sapphire (0001) substrates are found to be very different, 0.87 and 3.73 nm, under the same growth conditions for the HVPE system.

The coalescence of the InN layer grown on the MOCVD-GaN/sapphire (0001) substrate is much more than that of the InN layer grown on the HVPE-GaN/sapphire (0001) substrate, although the thickness of the InN layer grown on the HVPE-GaN/sapphire (0001) substrate is smaller than that of the InN layer grown on the MOCVD-GaN/sapphire (0001) substrate. In the rocking curves (RCs), the FWHM values of the XRD RCs for the MOCVD- and the HVPE-GaN (0002) plane are different, 305 and 621 arcsec, respectively, and the FWHM values of the XRD RCs for the MOCVDand the HVPE-GaN (10-12) plane are 358 and 666 arcsec, respectively. The 2D growth rate of the InN layer grown on the MOCVD-GaN/sapphire (0001) substrate is faster than that of the InN layer grown on the HVPE-GaN/sapphire (0001) substrate due to the different In/N ratios on the GaN surfaces [13–17] and the different crystal qualities of the GaN layers. This implies that the different surface morphologies of the InN layers on MOCVD- and HVPE-GaN/sapphire (0001) substrates may be due to the different mosaic structures of the GaN (0002) plane between the MOCVD- and the HVPE-GaN/sapphire (0001) substrates, as represented by the different FWHMs of the RCs.

The θ -2 θ XRD patterns of the InN layers are exhibited in Fig. $5(a)$. The diffraction peaks detected at $31.4°$ and $65.4°$ correspond to the InN (0002) and (0004) peaks, respectively. The XRD peaks of GaN (0002), sapphire

Fig. 5. (Color online) (a) θ -2 θ XRD patterns and (b) (0002) and (10-12) XRD rocking curves for InN layers grown on MOCVD- and HVPE-GaN/sapphire (0001) substrates.

(0006), and GaN (0004) are also clearly observed. This implies that the c-plane InN layers are obtained as single crystals for both the MOCVD- and HVPE-c-plane GaN/sapphire (0001) substrates and that the growth of m- and a-plane InN does not occur [19].

The XRD rocking curves of the (0002) symmetry and the (10-12) asymmetry planes of the InN layers are shown in Fig. 5(b). Figure 5(b) also shows a comparison of the (0002) and the (10-12) FWHMs of the InN layers grown on MOCVD- and HVPE-GaN/sapphire (0001) substrates. The different FWHM values of the XRD RCs for the InN (0002) plane, which are between 844 and 2652 arcsec, partially result from the different crystal qualities of the GaN layers grown on MOCVD- and HVPE-GaN/sapphire (0001) substrates, as mentioned in the previous section, and are thought to be due partially to the degree of coalescence of the InN layers as shown, Fig. 3. The FWHM value of the XRD RC for InN (10- 12) grown on a MOCVD-GaN/sapphire (0001) substrate cannot be distinguished from that for the InN (10-12) grown on a HVPE-GaN/sapphire (0001) substrate. The large value of the FWHM for InN (10-12) grown on a MOCVD-GaN/sapphire (0001) substrate, 2652 arcsec, is unexpected. This poor value for the asymmetric (10- 12) plane of InN is thought to be related to incomplete coalescence and to small pits, which are shown as black spots in Fig. 3(a). According to previous reports $[14,17,$ 20–22], the rocking curves of the (0002) plane are fairly sensitive to screw and mixed-type threading dislocations (TDs) while those of the (10-12) plane are related to all types of TDs, including pure edge dislocations [17,21,22]. Also, we expect the phenomena of coalescence for the InN layer, which are similar to those for the GaN layer, to be closely related to the formation of pure edge dislocations. This result according to XRD rocking-curve data in this study clearly indicates that the InN layer grown on the MOCVD-GaN/sapphire (0001) substrate has better crystal structural quality and lower dislocation density compared to the InN layer grown on the HVPE-GaN/sapphire (0001) substrate.

Figure 6 shows typical Raman spectra of hexagonal InN layers grown on MOCVD- and HVPE-GaN/sapphire (0001) substrates. According to group theory for hexagonal crystals, two phonon modes, E_2 (high), and A_1 (LO), are Raman active in the present scattering geometry (c-plane backscattering). The phonon E_2 (high) mode is observed at 491.0 cm⁻¹ and 490.6 cm⁻¹ for InN layers grown on MOCVD- and HVPE-GaN/sapphire (0001) substrates, respectively, as expected [23]. Also, the phonon A_1 (LO) mode is observed at about 590

Fig. 6. (Color online) Raman spectra of InN layers grown on (top) MOCVD-GaN sapphire (0001) and (bottom) HVPE-GaN/sapphire (0001) substrates.

cm−¹ for the InN layers grown on both MOCVD- and HVPE-GaN/sapphire (0001) substrates. In addition, the phonon modes of the GaN inter-layer are observed at about 568 and 734 cm⁻¹ for the E_2 (high) and the A_1 (LO) mode, respectively. A sapphire signal also appears at 418 cm−¹ for the InN layer grown on the MOCVD-GaN/sapphire (0001) substrate. It probably has a dense surface even though the thickness is smaller. The discussion of the LO phonon-plasmon-coupled (LOPC) mode, which appears at 450 cm⁻¹, is beyond the scope of this work [24].

In order to characterize the crystal quality, we focus here on the spectral line shape of the E_2 (high) phonon mode at 490 cm⁻¹ [25,26]. Because the E_2 (high) phonon mode has the strongest signal and its peak width and frequency are sensitive to the crystal quality and the stress/strain field, a discussion of the crystal quality is possible. The FWHM values of the E_2 (high) mode peak are measured as 9.9 cm^{-1} and 14.9 cm^{-1} for the InN layers grown on MOCVD- and HVPE-GaN/sapphire (0001) substrates, respectively. Compared to the value of 4.2 cm⁻¹ for a 3-µm-thick freestanding InN layer [26], these values of about 0.1 μ m for the thickness of the InN layers for our samples indicate good crystal quality and good lattice coherence. Also, because of the peak shifts from 490 cm^{-1} to higher wavenumber, we suppose that the InN layers of our samples have compressive strains [23, 26]. As a result, the InN layers grown on MOCVD-GaN/sapphire (0001) substrates show high crystal quality, which agrees well with the result of the XRD analyses.

III. CONCLUSION

InN layers were successfully grown by using HVPE at an appropriate group V/III ratio on GaN interlayer/sapphire (0001) substrates that had been fabricated by using MOCVD. The effects of the Group V/III ratio indicate that a low ratio results in 2D growth and improved InN crystal quality. In addition the influences of the two types of GaN inter-layer/sapphire (0001) substrates, one fabricated by using MOCVD and the other fabricated by using HVPE, on the structural properties of the InN layers were investigated, and the results were discussed. The surface morphologies were characterized by using SEM and AFM analyses, and the crystal qualities were cross-checked by using XRD and Raman analyses. The surface morphology and the crystal quality of the InN layer deposited by using HVPE on the GaN Inter-layer/sapphire (0001) structure that had been fabricated by using MOCVD were remarkably improved compared to those of the InN layer deposited by using HVPE on the GaN inter-layer/sapphire (0001) structure that had been fabricated by using HVPE. This work clearly demonstrates the feasibility of fabricating high-quality InN layers by using HVPE under the appropriate conditions, *i.e.*, the proper Group V/III ratio and the proper inter-layer/substrate structure.

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