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MOVPE of InN films on GaN templates grown on sapphire and silicon(111) substrates

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This paper reports the study of MOVPE of InN on GaN templates grown on sapphire and silicon(111) substrates. Thermodynamic analysis of MOVPE of InN performed using NH_3 as nitrogen source and the experimental findings support the droplet-free epitaxial growth of InN under high V/III ratios of input precursors. At a growth pressure of 500 Torr, the optimum growth temperature and V/III ratio of the InN film are 575–650 °C and $>3 \times 10^5$, respectively. The surface RMS roughness of InN film grown GaN/sapphire template is ~0.3 nm on 2 µm × 2 µm area, while the RMS roughness of the InN film grown on GaN/Si (111) templates is found as ~0.7 nm. The X-ray diffraction (XRD) measurement reveals the (0002) texture of the InN film on GaN/sapphire template with a FWHM of 281 arcsec of the InN (0002) ω rocking curve. For the film grown on GaN/Si template under identical growth conditions, the XRD measurements show the presence of metallic In, in addition to the (0002) orientation of InN layer.

1 Introduction InN has attracted great attention due to its recently published low band gap value, ~0.7 eV, which makes it very interesting material for applications in solar cells [1], optoelectronics [2], and high frequency devices [3]. Despite these potential applications, InN remains the least understood material of the group III-nitride compounds because of the challenges in growing high-quality epitaxial films, due to the low dissociation temperature (~550 °C) and the extremely high vapor pressure of N for the epitaxy of InN layers [4, 5]. Ammonia is commonly used as the nitrogen source for the growth of nitrides in metalorganic vapor phase epitaxy and the pyrolysis efficiency of NH_3 is very low for temperatures lower than 650 °C. In order to prevent etching of InN or the formation of In droplets, a high input V/III ratio is required [5, 6].

The growth of monocrystalline InN has been studied on different substrates and underlying layers over a wide range of growth conditions [7–10]. In contrast to the more mature development of InN material systems by MBE, the epitaxy of InN materials with metalorganic vapor phase epitaxy (MOVPE) still requires further improvement in material quality. Up to date, the highest mobility and lowest background carrier concentration are 1100 $cm^2/(Vs)$ and 3.9×10^{18} cm^{-3}, respectively, in MOVPE-grown InN [11, 12]. MOVPE growth of InN on *c*-plane sapphire using a close-coupled showerhead reactor also yields promising results [13]. The thermodynamic analysis of InN growth by MOVPE using NH_3 and other nitrogen sources has been performed before [5, 14] and has been very useful in furthering the understanding of this material system. However, experimental findings do not always follow the thermodynamically predicted high V/III ratio growth regimes of InN. Besides the high V/III ratios [15, 16], growths under comparatively low V/III ratios have also been reported [13, 17, 18]. In this study, in addition to the experimental investigation of growth regimes under low and high V/III ratios of input precursors, the thermodynamic analysis of InN by MOVPE was also performed. The thermodynamic analyses

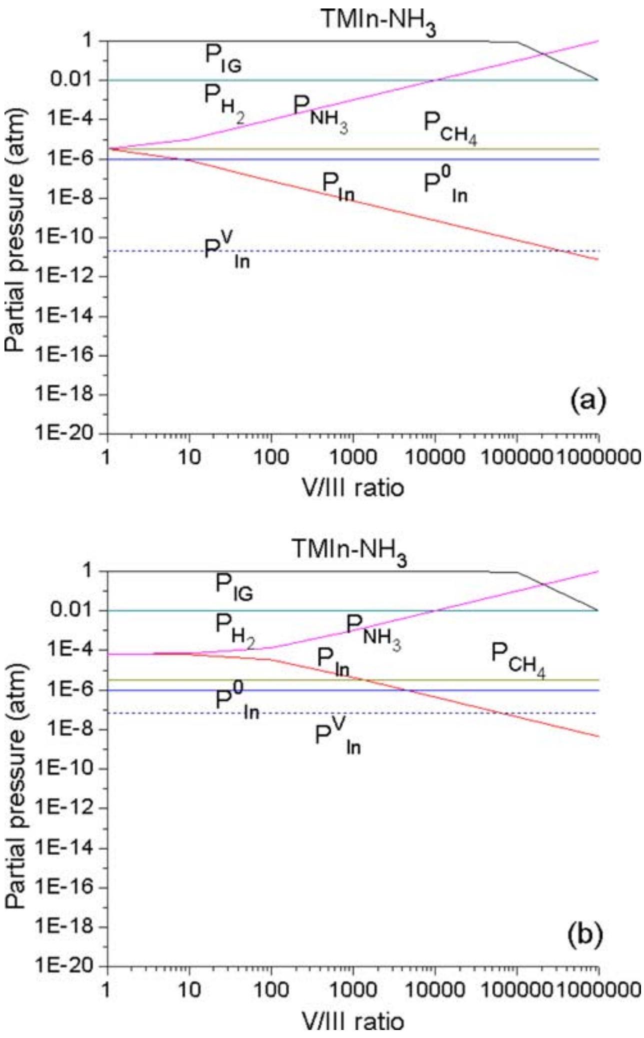

Figure 1 (online colour at: www.pss-a.com) Equilibrium partial pressures of gaseous species as a function of the input V/III ratio using NH_3 as nitrogen source, for the growth temperatures of (a) 500 °C, and (b) 700 °C.

as well as our experimental findings do not support the growth of droplet-free InN under reported low V/III ratios. An effort has been made to investigate the origin of these conflicting growth regimes as well as the effect of high V/III ratio on the epitaxial growth rate of InN. Also, as opposed to the direct growth of InN on Si(111) substrate which is generally of poor quality, the epitaxy of InN films on thick GaN templates both on sapphire and Si(111) substrates has been studied. Under identical growth conditions, the comparison of the overgrown InN films shows that the film grows differently and has better quality on GaN/sapphire template than when grown on GaN/Si(111) template.

2 Thermodynamic analysis of MOVPE of InN

Thermodynamic analysis of InN growth by MOVPE was performed using NH_3 and TMIn as nitrogen and In precursors respectively and N_2 as the carrier gas. The calculation procedure is similar to that presented by others [5, 14] and the thermo-chemical data used here were obtained from Refs. [5, 14, 19]. Figure 1(a) and (b) show the comparison of the equilibrium partial pressures of gaseous species over InN as a function of input V/III ratio at growth temperatures of 500 °C and 700 °C. Note that P^0_{In} denotes the input partial pressures of group III species (TMIn, in this case), dotted lines show the vapor pressures of pure In metal (P^V_{In}) and P_i is the equilibrium partial pressures of gaseous species, In, NH_3, CH_4, H_2 and inert gas (IG) (N_2) over the InN surface. As shown in Fig. 1, the equilibrium partial pressures of In (P_{In}) change significantly with the input V/III ratios. There exist three deposition modes: ($P_{In} < P^0_{In}$), ($P_{In} > P^V_{In}$) and ($P_{In} > P^0_{In}$) [5]. The region where P_{In} is higher than P^V_{In} gives rise to In droplets on the growing surface. Similarly, etching can occur, when P_{In} is higher than P^0_{In}. The growth of InN occurs in the region where $P_{In} < P^0_{In}$.

In this analysis it is assumed that the mole fraction of decomposed NH_3 decomposing prior to InN growth is zero which is difficult to determine exactly as it has a strong dependence on the growth conditions (particularly temperature) and reactor chamber design. Thus, the model presented here will slightly underestimate the generation of atomic hydrogen produced from the thermal decomposition of NH_3. The results of the above analysis indicate that for NH_3 as the nitrogen source, a high V/III ratio is required to obtain deposition of InN film and prevent In-droplet formation. As shown in Fig. 1(a) and (b), the MOVPE growth mode of InN film (without droplets) is only possible with a very large V/III ratio of $> \sim 4 \times 10^5$ for the growth temperature of 500 °C. By increasing the growth temperature from $T_g = 500$ °C to $T_g = 700$ °C, the overall growth region shifts to higher V/III ratio and etching of the film becomes dominant. The large equilibrium partial pressures of In (P_{In}) (in comparison to those of Ga or Al for AlGaN growth) leads to the need for a very large V/III ratio in excess of $\sim 4 \times 10^5$ for achieving the film growth mode, which is fairly in agreement with our experimental results (given below).

3 Experiments

The epitaxy of InN was conducted in a vertical flow rotating disc Veeco P-75 MOCVD reactor utilizing TMIn as the group-III precursor and NH_3 as the group V precursor. Sapphire substrates were first annealed at 1080 °C in H_2. The temperature was then ramped down and InN films were grown at 500 Torr for different V/III ratios in the temperature range of (525 – 650 °C). The investigation of this wide range of V/III ratios and temperatures was carried out to verify the thermodynamically predicted growth regimes of InN as well as to achieve the In-droplets free growth condition. Nitridation of sapphire substrates at higher temperature (1000 °C) was also carried out prior to InN growth in order to examine the effect on the nucleation density. N_2 was used as a carrier gas as well as the ambient for InN growths in all our experiments.

The GaN template on sapphire was prepared using standard low temperature GaN buffer layer followed by annealing and high temperature GaN film. The growth of GaN template on Si(111) substrate was carried out using 90 nm AlN buffer layer and 3 pairs of thin 135 nm GaN/50 nm AlN interlayers to suppress the cracking in the overgrown GaN film. Prior to the growth of AlN buffer layer, Si substrates were chemically etched for 30 seconds in 7% HF to remove the oxide layer and were further in-situ annealed in H_2 ambient for 10 min at a temperature of 1100 °C.

Thickness of the GaN templates both on sapphire and Si(111) substrates was kept at 2 µm and the growth of InN (growth time = 2.5 hours) on both templates was performed at 650 °C with input V/III ratio of $\sim 2.2 \times 10^5$ (NH_3 = 5000 sccm, TMIn = 18 sccm). Temperature of the susceptor was then ramped down to room temperature in NH_3 and N_2 ambient. Films were characterized with scanning electron microscopy (SEM) and atomic force microscopy (AFM) for metallic droplets and for surface morphology of InN. X-Ray diffraction analysis was performed to evaluate the presence of secondary phases and crystallinity of the InN films grown on GaN/sapphire and GaN/Si(111) templates. Note that all the temperatures quoted here for our experiments refer to the susceptor temperatures.

4 Results and discussion

4.1 InN on sapphire The SEM images of Fig. 2(a)–(c) for InN grown on sapphire show the change in density of metallic In droplets with growth temperature. For the same V/III ratio (1.3×10^5), the droplet density decreases with the increase in temperature indicating higher cracking efficiency of NH_3 at higher temperature. Similarly, the increase in V/III ratio reduces the droplet formation at a constant temperature as shown in Fig. 3(a)–(c). The droplet-free growth is achieved at 575 °C for V/III ratio $>2.7 \times 10^5$ as shown in Fig. 3(c). All the growths conducted at V/III ratio of $\leq 2.7 \times 10^5$ for growth temperatures ranging from 525 °C till 600 °C resulted in In droplets on the surface.

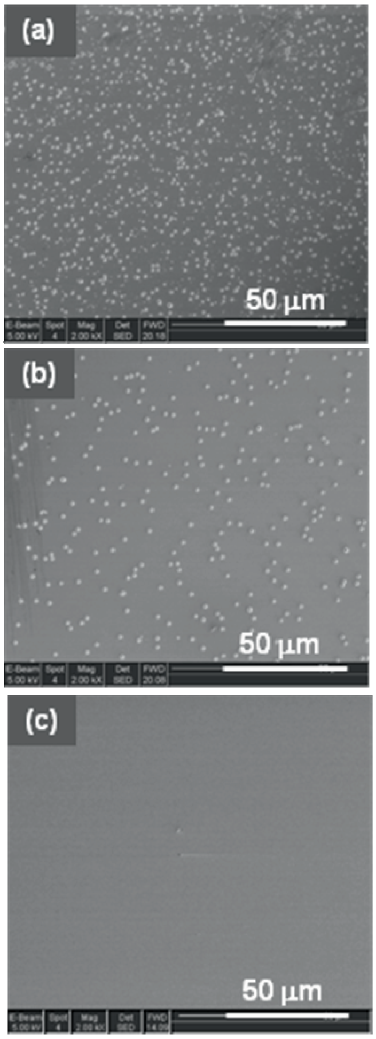

Figure 2 Scanning electron microscopy images of InN layer on sapphire with V/III $\sim 1.3 \times 10^5$ at growth temperature of a) $T_g \sim 525$ °C, b) $T_g \sim 575$ °C and c) $T_g \sim 630$ °C.

The growths of InN with V/III ratio of $\geq 2.7 \times 10^5$ for growth temperatures of 575 °C, 600 °C, and 625 °C resulted in droplet-free films. The In-droplets observed in the MOVPE-grown InN with low V/III ratio are consistent with the prediction from thermodynamic analysis. Growths of InN at fairly low V/III ratios have also been reported [13, 17, 18], however, our experiments conducted in a vertical flow rotating disc MOVPE reactor for the V/III ratios 5000, 8500, 12800, 17000 and 24000 do not show any droplet-free InN films for the given growth conditions (T_g = 550 °C, Growth Pressure = 500 Torr). This implies that the conflict among the reported InN growth regimes is also associated to the effect of different reactor geometries and varying reactor conditions.

Figure 4(a) shows the surface morphology of a sapphire substrate prior to growth (shown for comparison purpose). Before the epitaxial growth, the substrate was annealed at 1080 °C for 3 minutes under H_2 atmosphere and the temperature was then ramped down to InN growth temperature (575 °C) and a nucleation layer of InN was grown (growth time = 60 min) at a V/III ratio of 2.7×10^5. Figure 4(b) shows nucleation and the density of small InN islands on sapphire. In order to study the effect of nitridation, sapphire substrate after annealing was also nitridated under NH_3 at 1000 °C for 5 minutes followed by growth of an InN nucleation layer under the same conditions used for the layer of Fig. 4(b). It is observed as shown in Fig. 4(c) that nitridation of the substrate enhances the nuclei density and helps achieve better surface coverage. A close observation shows clearly that the nuclei density is higher in Fig. 4(c) and the RMS roughness is low whereas the nuclei-density is low and RMS roughness is high in Fig. 4(b). The treatment of sapphire nitridation prior to the growth of InN has been employed before for reducing the lattice mis-

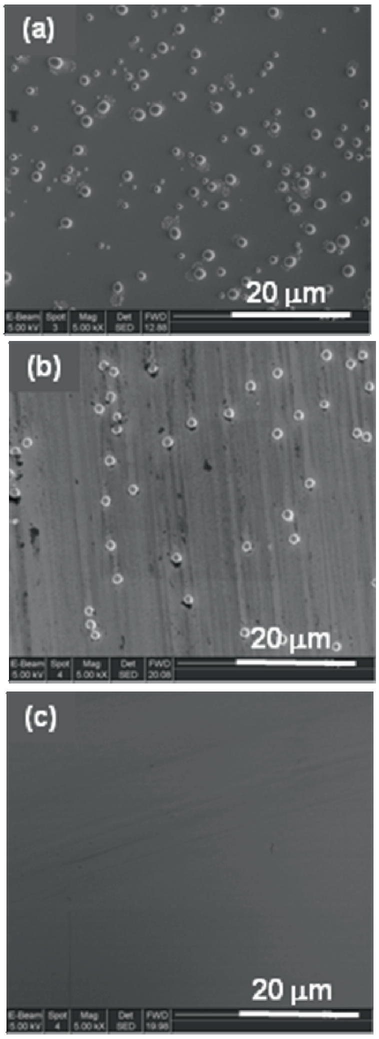

Figure 3 Scanning electron microscopy images of InN on sapphire at growth temperature of 575 °C with input V/III ratio of a) 8.1×10^4, b) 1.3×10^5, and c) 6×10^5.

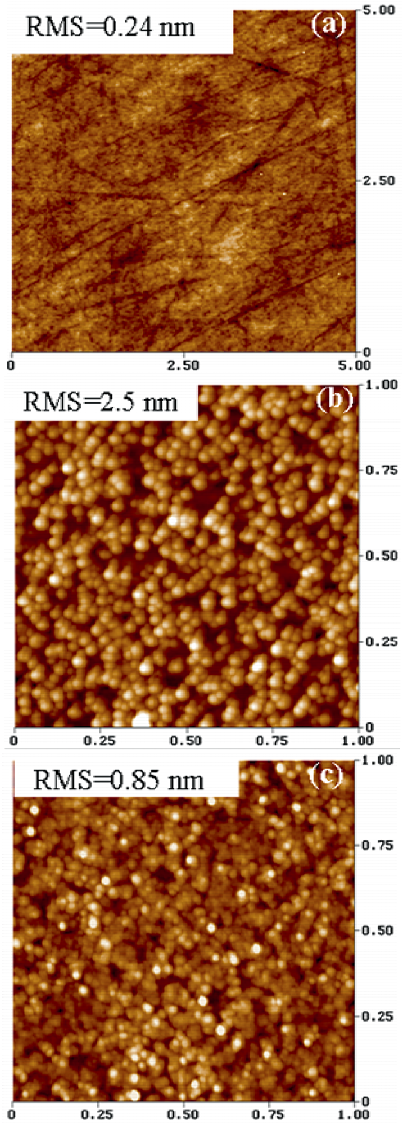

Figure 4 (online colour at: www.pss-a.com) AFM images of (a) sapphire substrate and InN (growth time = 1 hour) on sapphire at growth temperature of 575 °C with input V/III ratio of 2.7×10^5 (b) without nitridation, (c) with nitridation.

match and for selecting one epitaxial relationship [20, 21]. After optimizing the growth conditions for InN buffer layer on sapphire, InN film was grown for 2.5 hours at higher temperature (650 °C) with a V/III ratio of 2.2×10^5. The high temperature InN film continues to grow in 3D mode and the 3D buffer islands get bigger in size but did not coalesce to form 2D layer for the given growth time of 2.5 hours.

4.2 InN on GaN templates on sapphire and Si (111) substrates The surfaces of InN films grown on GaN/sapphire and GaN/Si(111) templates under identical growth conditions are shown in Fig. 5(a) and (b), respectively. The InN film grown on GaN/sapphire grows in layer by layer mode and evolves into a very smooth film having RMS roughness of 0.27 nm, measured on a 2 µm × 2 µm area. However, the roughness of the InN film grown on GaN/Si template is comparatively higher (RMS = 0.7 nm) than on GaN/sapphire template. Note that the RMS roughness values for the GaN/sapphire and GaN/Si templates prior to InN growth are 0.30 nm and 0.76 nm, respectively. In order to increase the growth rate, the TMIn flow rate was increased while maintaining the other growth conditions. However, it was observed that a slight increase in TMIn flow (V/III ~ 1.5×10^5) results in jagged morphology of the InN film on both templates as shown in Fig. 6(a) and (b). The dislocation defect density is distinctly higher on the GaN/Si(111) template as shown in Fig. 6(b). This indicates that the evolution and quality of the overgrown InN film depends strongly on the surface condition of the starting template.

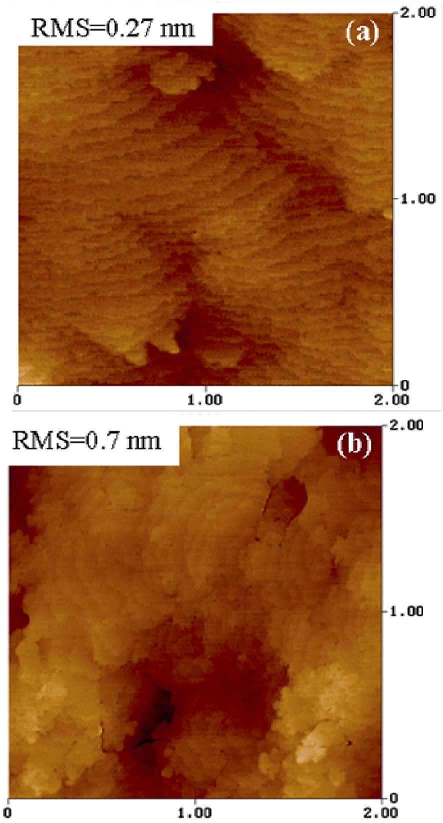

Figure 5 (online colour at: www.pss-a.com) AFM images of InN film (V/III ratio = 2.2 × 10^5) at growth temperature of 650 °C (a) on GaN/sapphire template, Z scale = 5 nm, (b) GaN/Si(111) template, Z scale = 7 nm.

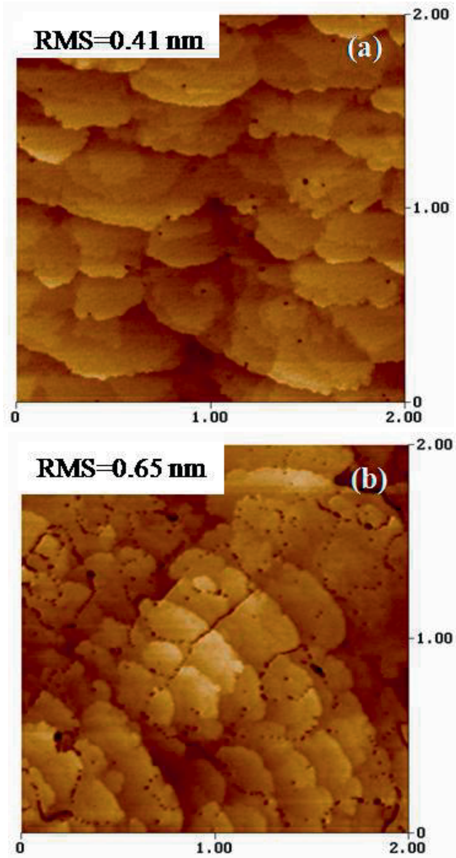

Figure 6 (online colour at: www.pss-a.com) AFM images of InN film (V/III ratio = 1.5 × 10^5) at growth temperature of 650 °C (a) on GaN/sapphire template, Z scale = 5 nm, (b) GaN/Si(111) template, Z scale = 7 nm.

It is worth noting here that the growth rate of InN film shown in Fig. 5 as well as for the film given in Fig. 7 is very slow under given conditions (~0.86 nm/min) and the InN film thickness is ~130 nm. The growth rate of InN film shown in Fig. 6(a) and (b) is 1.26 nm/min and thickness of the film is measured as 190 nm. The observed very low growth rate is due to the small amount of reactive indium available (which is low in our case by the V/III ratio constraint) as well as the etching of the film which is believed to be competing the growth at the given temperature of 650 °C.

For the so far optimal growth conditions (V/III ~2.2 × 10^5, T = 650 °C), the X-ray diffraction (XRD) (θ–2θ scan) reveals dominantly the (002) texture of the InN film on GaN/sapphire template as shown in Fig. 7(a). The (002) omega rocking curve of InN film (not shown here) gives a FWHM value of 281 arcsec which is among the best reported values for MOVPE-grown InN. This indicates a good crystal quality of the film on GaN/sapphire template. For the film grown on GaN/Si(111) template under identical growth conditions, the XRD measurements (θ–2θ scan) show the presence of metallic In, in addition to the (002) orientation of InN layer as shown in Fig. 7(b), although no In droplets were found on the surface of the film. A small diffraction peak at 33° is seen to be present in both samples and since the d-spacing (2.69 Å) of InN (101) is very close to the d-spacing (2.72 Å) of metallic In (101), it is generally difficult to assign the peak observed at 33° to either case especially in the absence of additional evidence. For the film grown on GaN/Si (111) template however, another diffracted peak at 2θ = 36.24° (d-spacing = 2.47 Å) is also observed as shown in Fig. 7(b) which is from In (002), hence confirming the presence of metallic In. Although both samples were grown under identical conditions, the presence of metallic In on GaN/Si(111) template is believed to be linked to the higher thermal conductivity of the Si substrate which leads to the difference in real surface temperatures on the two templates.

5 Conclusion Thermodynamic analysis and the experimental findings in our reactor conditions show that a high V/III ratio of input precursors is required to obtain the epitaxy of droplet-free InN films. Experimental results show that at a growth pressure of 500 Torr, the optimum growth temperature and V/III ratio of the InN film are 575–650 °C and >3 × 10^5, respectively. A comparison of

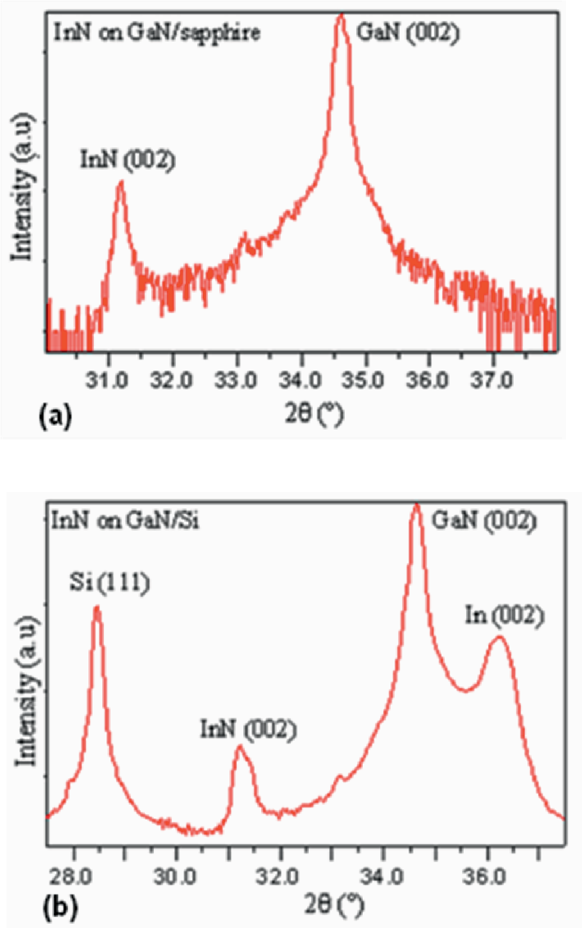

Figure 7 (online colour at: www.pss-a.com) XRD θ–2θ scans (log scale) of InN film grown on (a) GaN/sapphire and (b) GaN/Si(111).

the morphological evolution of InN film under identical growth conditions shows better film quality on GaN/sapphire than on GaN/Si(111) template. The X-ray diffraction (XRD) measurements reveal the (0002) texture of the InN film on GaN/sapphire template. The FWHM of 281 arcsec of InN (002) ω rocking curve indicates good crystal quality of the film. For the film grown on GaN/Si template under identical growth conditions, the XRD measurements show the presence of metallic In, in addition to the (0002) orientation of InN layer.

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