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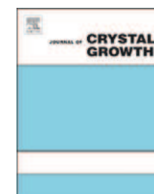

Influence of growth temperature and V/III ratio on the optical characteristics of narrow band gap (0.77 eV) InN grown on GaN/sapphire using pulsed MOVPE

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ABSTRACT

In this study, we report on the pulsed metalorganic vapor phase epitaxy (MOVPE) of InN as well as the optical and electronic properties of the films as a function of V/III ratio and growth temperatures. The growth of InN films was conducted utilizing a vertical reactor with TMIn and NH_3 as the In- and N-precursors, respectively. Metallic droplet-free InN films were achieved on GaN/sapphire template in a pulsed MOVPE mode with low V/III ratio condition. In the pulsed growth mode, NH_3 was constantly flowing while the TMIn was sent into the reactor chamber for a 36-s pulse and then it bypassed the reactor chamber for an 18-s pulse for a total cycle time of 54 s. At a growth pressure of 200 Torr, the effects of growth temperature (510–575 °C) and V/III ratio (12,460–17,100) on the photoluminescence (PL) transitions were investigated. Morphological evolution as well as the electrical quality of the overgrown films have also been studied for the given growth conditions.

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1. Introduction

The InN compound has attracted great attention due to its recently published narrow band gap value (~0.7 eV) [1,2] which makes it very interesting material for applications in solar cells [3], THz optoelectronics [4,5], and high-speed electronic devices [5,6]. However, due to the required low growth temperature and lack of suitable lattice-matched substrates, the growth procedure of high-quality single crystalline InN films is still challenging, in particular by metalorganic vapor phase epitaxy (MOVPE). Different methods [7–19] have been developed to grow InN films and the quality of InN films has significantly improved [7–19]. Commonly, high V/III ratios of input precursors are employed to achieve the droplet-free InN films [13–15]. In order to increase the growth rate as well as to avoid large consumption of group V source, efforts have been made, and growths under comparatively low V/III ratios have also been reported [16–18]. However, the droplet-free growth of InN under low V/III ratios is not common to all MOVPE reactor geometries. Johnson et al. [19] has applied a promising pulsing technique, but the droplet-free InN films were achieved only in a high V/III ratio regime of input precursors.

In this study, we employed a pulsed MOVPE technique to grow narrow band gap (0.77 eV) InN without the requirement of high V/III ratios of input precursors. Specifically, we investigated the effect of growth temperature (510–575 °C) and V/III ratio (10,000–17,000) on the optical properties (photoluminescence (PL) intensities, transition energies) and electronic properties (electron mobilities, and background carrier concentration) of the InN films. Similar pulsing technique had previously been employed [19], however, with a reported condition of high V/III ratios of the input precursors (V/III $\sim 5.2\times10^5$–2×10^6). Particularly, the study of the PL transitions at low temperature ($T = 77$ K) as well as at room temperature ($T = 300$ K) has been carried out to shed more light on the growth conditions dependency of the band gap of InN. It is found that the growth conditions, specifically the growth temperature of film has direct impact on the position of PL transitions which could potentially explain the reported disparity in the band gap values of the MOVPE-grown InN films.

2. Growths of InN with no-pulsing

All the growths of InN on GaN/sapphire templates were performed by using the VEECO P-75 MOCVD reactor, and TMIn and NH_3 were used as the group III and V precursors, respectively with N_2 as the ambient and carrier gases. In our reactor conditions as reported previously [15] and as shown in Fig. 1(a), a high V/III ratio ($>2.7\times10^5$) of input precursors is required to achieve droplet-free InN films when using continuous supply of indium

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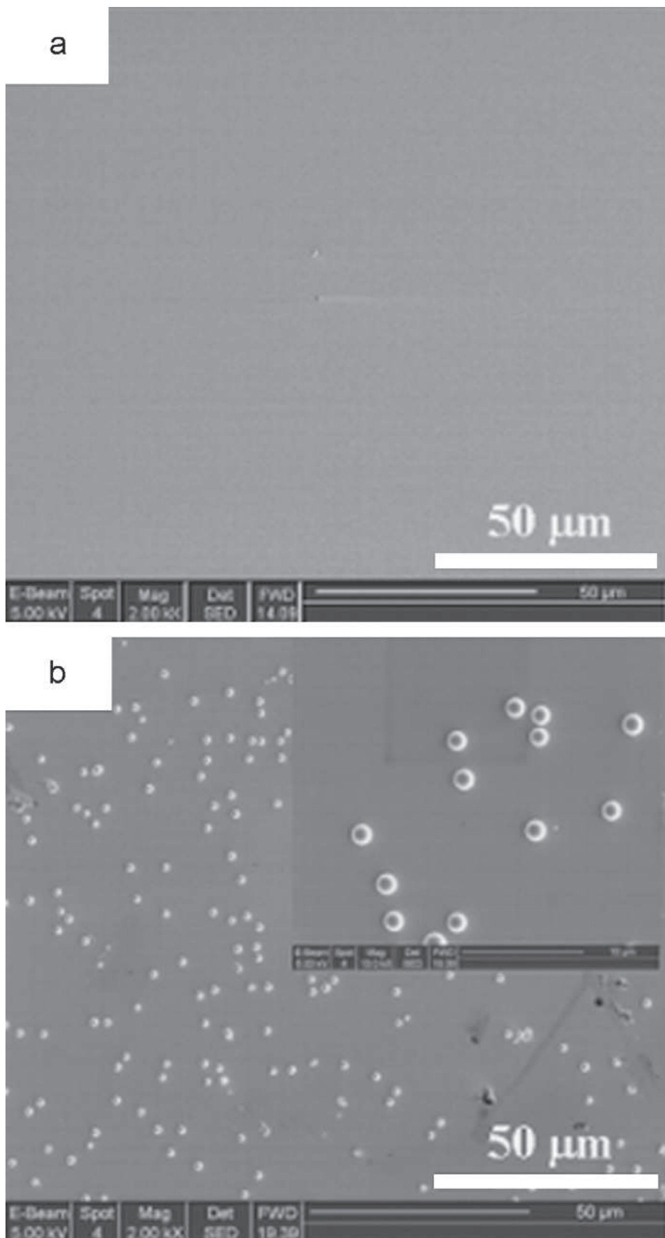

Fig. 1. Scanning electron microscopy images of InN on GaN/sapphire at a growth temperature of 575 °C with input V/III ratio of (a) 2.7×10^5 and (b) 1.8×10^5 (growth pressure = 500 Torr).

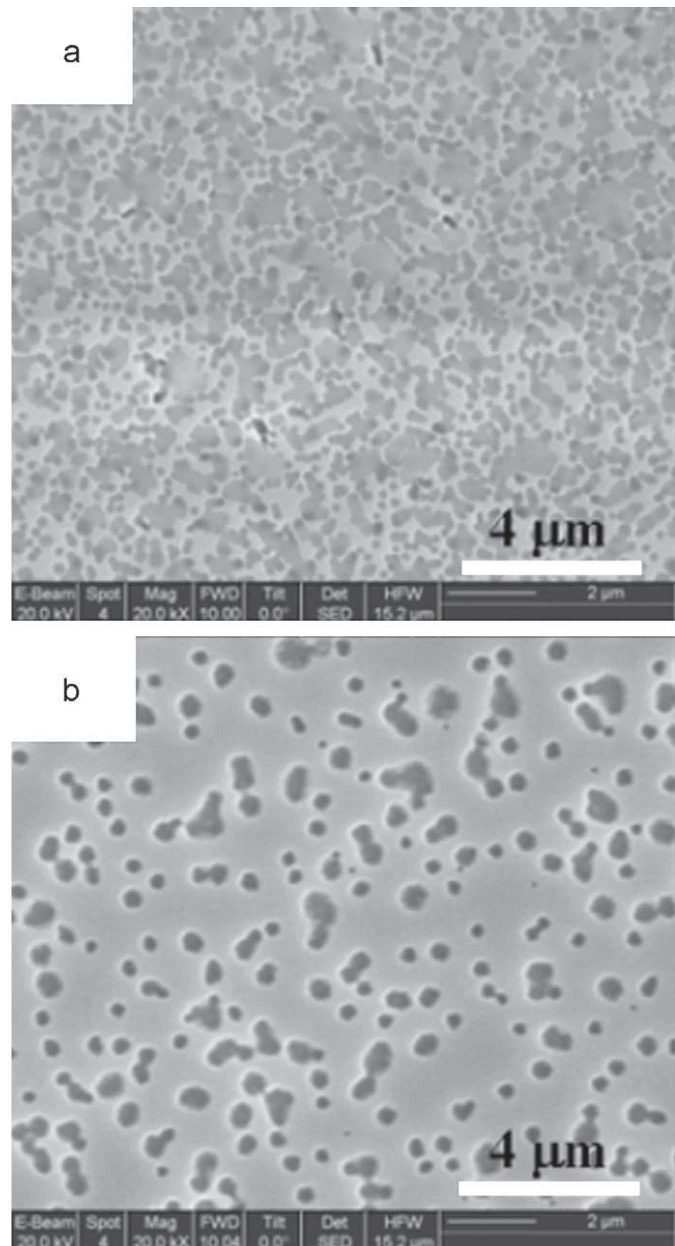

Fig. 2. Scanning electron microscopy images of InN film on GaN/sapphire at a growth temperature of 510 °C with an input V/III ratio of 12,460, (a) as-grown film, (b) upon HCl etching (growth pressure = 200 Torr).

and nitrogen precursors into the reactor chamber. All the growths performed at 500 Torr and for a V/III ratio of 2×10^5 or below resulted in In droplets on the surface. Fig. 1(b) shows a typical SEM image of the metallic In droplets on the surface of the film (with diameter of ~2 μm), grown at 575 °C, for a V/III ratio of ~1.8×10^5. Although the InN films grown at high V/III ratios were smooth in surface morphology and had good crystal quality, the growth rates of the films were found to be very low (0.86 nm/min) due to the need to maintain a very high V/III ratio [15]. It is important to note that the film grown under very high V/III ratio indicated narrow FWHM of X-ray diffraction (XRD) omega rocking curve (281 arcsec) and specular 2-D film with low RMS roughness (~0.27 nm) [15], however, no PL emission was observed from those films. It is unclear at this stage on the reasons behind no PL observed from the InN film grown under high V/III ratio [15]. However, several possible reasons include (1) very small thickness of the layer (~130 nm), and (2) poor optical quality of the InN films grown under high V/III ratio.

Similar growths of InN with no-pulsing conducted at low pressure (200 Torr) also resulted in In droplets on the surface, as shown in Fig. 2(a) and (b). Fig. 2(a) shows the as-grown InN film grown at 510 °C for a V/III ratio of 12,460, and the SEM image of the same film after HCl etching is shown in Fig. 2(b). The comparison of InN film before and after HCl etching shows that InN film growth also takes place concurrently. It is noted that the In droplets formed under such conditions have diameters in the range of ~100 nm up to ~1 μm. However, droplet-free films were not realizable for the investigated V/III ratio regime (12,460–17,088) and growth pressures (200–500 Torr) under continuous flow conditions using our reactor geometry.

3. Pulsed MOVPE experiments and characterizations of InN

The pulsed MOVPE process of InN growths were conducted by controlling the pulsing of the In precursor in the chamber, while maintaining a constant flow of NH_3. All the pulsed growths of InN layers were conducted at a growth pressure of 200 Torr. The input ratio (V/III ratio) of group V and III precursors was investigated from 12,460 to 17,088 and the growth temperatures were varied from 510 °C to 575 °C. The GaN templates (2.5 μm thick) on sapphire were grown using standard low temperature GaN buffer layer followed by annealing and high temperature GaN film. Thin InN films were grown on GaN templates in a pulse growth mode, where NH_3 was constantly flowing, while the TMIn was sent into the reactor chamber for a 36-s pulse and then it bypassed the reactor chamber for an 18-s pulse for a total cycle time of 54 s. This pulsing cycle was repeated for 80 times resulting in a film thickness of ~220 nm.

The optical quality of InN was determined from the PL studies carried out at room temperature ($T = 300$ K) and low temperature ($T = 77$ K). The electrical properties of the grown films were obtained from Hall measurements in a Van Der Pauw method. The surface morphology of the overgrown films was characterized by atomic force microscopy (AFM). The XRD measurements, using a PANalytical MRD instrument with parallel beam geometry and CuK_α radiation, were performed to evaluate the crystallinity of the InN films.

4. Results and discussions from pulsed MOVPE InN alloys

The use of pulsed growth mode allowed the growth of metallic droplet-free InN films without requiring high V/III ratio of input precursors. For the same V/III ratio (V/III = 12,460) and growth temperature ($T_g = 510$ °C) as those of from Fig. 2(a), the growth with the pulsing of In precursor results in the droplet-free InN film as shown in Fig. 3. In a pulse mode, the effects of growth temperature (510–575 °C) and V/III ratio (12,460–17,088) on the PL transitions have been investigated. Fig. 4 shows low temperature (77 K) PL spectra of the films grown at 575 °C, 550 °C, and 510 °C, respectively. It is observed that both the luminescence intensity and emission wavelength change significantly with temperature. The peak emission from InN films grown at 575 °C lie to the lower energy side of the spectrum and have higher intensity and narrower FWHM values than the ones grown at 510 °C. On the other hand, the study of the effect of V/III ratio at a given growth temperature, shows moderate increase in intensity with V/III ratio, and no clear shift is noted in the emission wavelength, as shown in Fig. 5.

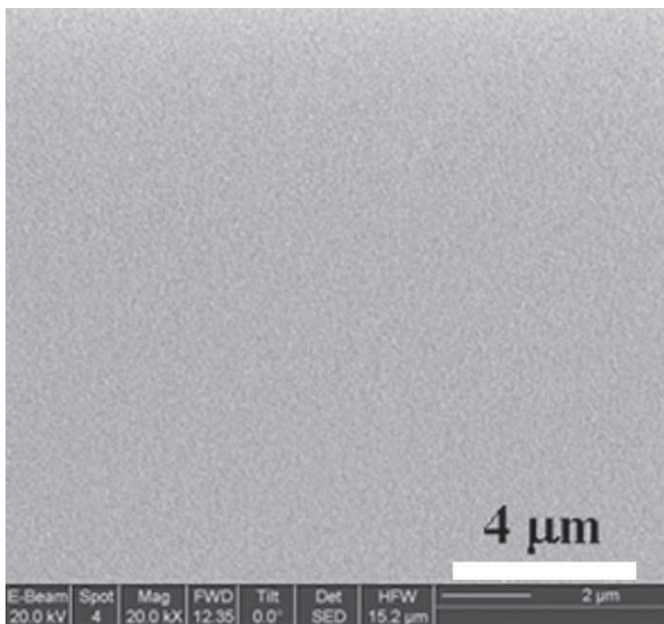

Fig. 3. Scanning electron microscopy image of InN film on GaN/sapphire at a growth temperature of 510 °C with an input V/III ratio of 12,460 for film grown with TMIn pulsing (growth pressure = 200 Torr).

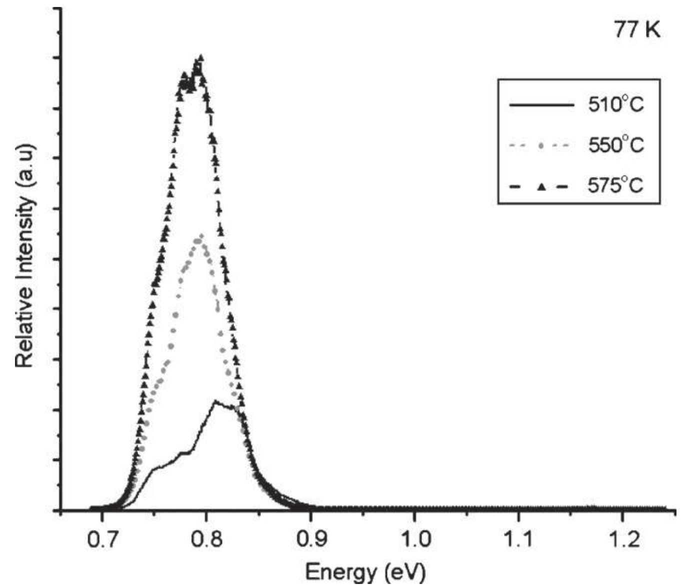

Fig. 4. Low temperature (77 K) PL spectra of InN films grown on GaN/sapphire templates, shown as a function of growth temperature.

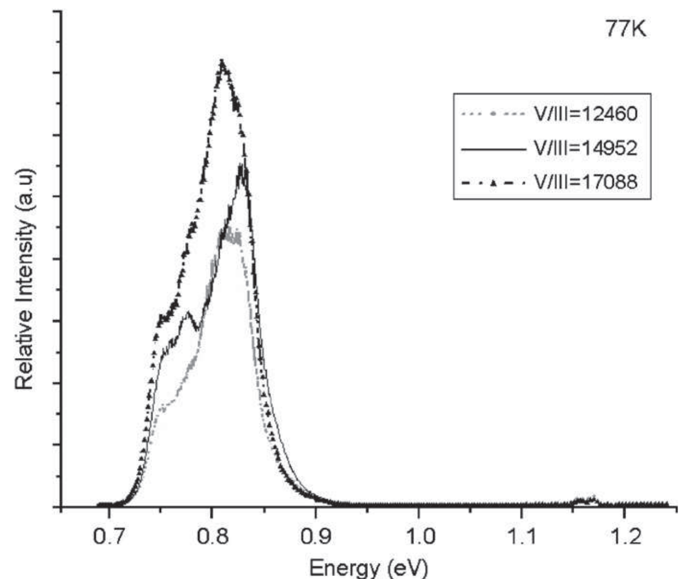

Fig. 5. Low temperature (77 K) PL spectra of InN films grown at 510 °C on GaN/sapphire templates, as a function of V/III ratio of input precusors.

The appearance of otherwise less dominant transitions are more pronounced in the representative room temperature PL spectra of the films as shown in Fig. 6(a)–(c). It is noted that the films grown at relatively low temperatures (510 °C) often exhibit transitions at ~0.81, and 1.15 eV where the transition at 1.15 eV becomes diminished and weak, when the film is grown at high

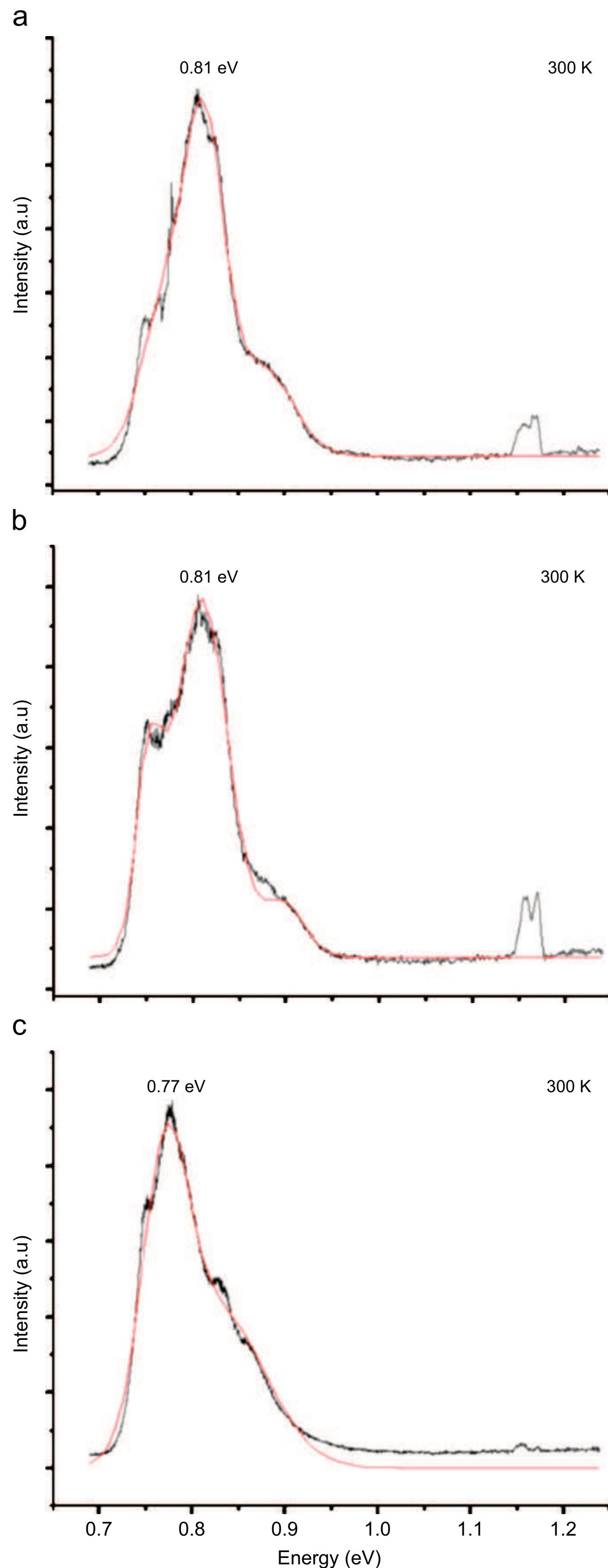

Fig. 6. Room temperature PL spectra of InN films grown on GaN/sapphire templates at, (a) reference sample $T = 510\,^{\circ}\mathrm{C}$, V/III = 12,460, (b) $T = 510\,^{\circ}\mathrm{C}$, V/III = 17,088, and (c) $T = 575\,^{\circ}\mathrm{C}$, V/III = 12,460.

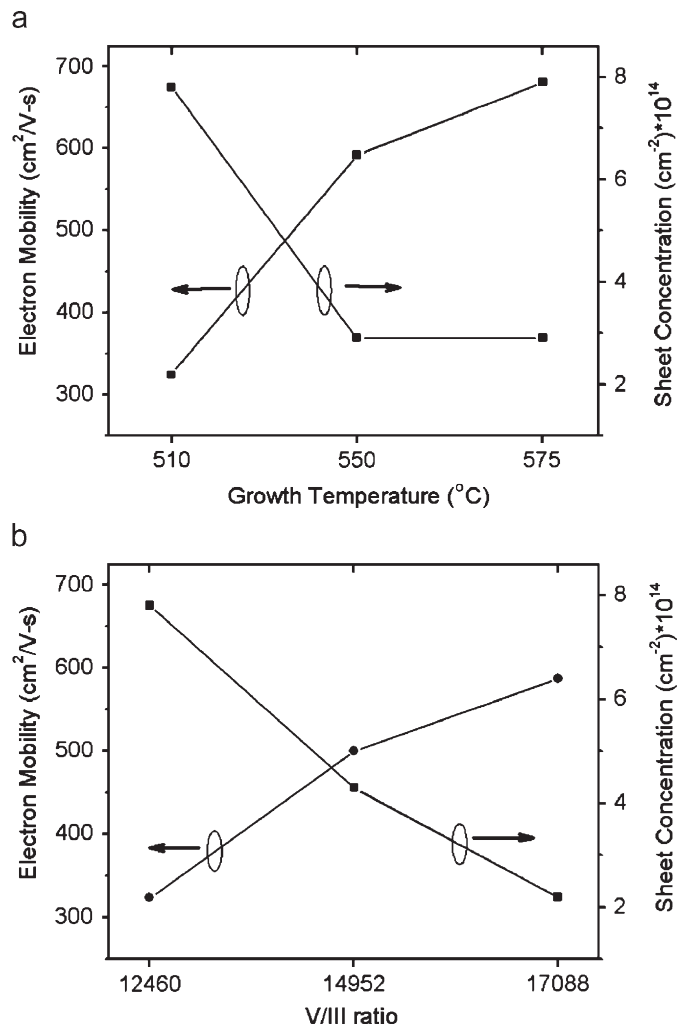

Fig. 7. Plot of Hall carriers mobility and sheet concentration of the films as a function of (a) growth temperature (b) V/III ratio of input precursors.

temperature (575 °C). The PL spectra for InN films grown at higher temperature exhibited dominant peak luminescence at 0.77 eV, as shown in Fig. 6(c). Recently, the PL transition at 0.76 eV has been associated to Mg related acceptor level [20]. As shown in Fig. 6(a) and (b), we also note the luminescence shoulders at ~0.75–0.76 eV to the low energy side of the dominant peak transitions, despite the fact that no intentional Mg doping of InN films was carried out in this study. This finding indicates that the appearance of these less dominant transitions may have their origin in defects which are more stable at low growth temperatures of the films.

The films grown at higher temperature also have the better electrical quality, as shown in Fig. 7(a). The background n-type sheet carrier concentrations of InN films range from $n_{2D} = 2.9 \times 10^{14}$ to $7.8 \times 10^{14}\,\mathrm{cm}^{-2}$, with the lowest background doping materials obtained at growth temperature of 575 °C. The electron mobility value increases from 324 to 681 $\mathrm{cm}^2/(\mathrm{V\,s})$ with the increase in temperature which is partially caused by the decrease in background sheet concentration. Notably, the InN films grown at 550 °C and 575 °C have roughly same background carrier concentration where as the mobility is still higher for the film grown at 575 °C. This could be explained by reductions in scattering centers and grains boundaries with increase in growth temperature, which results in the increase in the mobility of the carriers.

At a given growth temperature of 510 °C, a similar trend in the improvement of the electrical quality is also observed for an increase in V/III ratio of input precursors, as shown in Fig. 7(b). Background sheet concentration decreases from $n_{2D} = 7.8 \times 10^{14}$ to $2.2 \times 10^{14}\,cm^{-2}$ with an increase in V/III ratio. The mobility of the carriers also increases with V/III ratio, however, the effect of V/III ratio on the mobility is found to be modest compared to the effect of growth temperature. The PL and Hall data show that both the increase in growth temperature and the increase in V/III ratio result in the decrease in background sheet concentration. Previously, Sugita et al. [21] observed blue shift in the peak energy at lower growth temperatures, which was attributed to the increase in carrier concentration in the films. In our studies, the decrease in carrier concentration and shift in peak energy position are linked only when change in temperature is involved. This finding indicates that the observed shift in peak energy position (Figs. 4 and 5) may be due to the better optical quality of the films resulting from the higher growth temperature, rather than from the decrease in carrier concentration.

Although the origin of PL peak energy shift in our InN sample is not fully clear at present, the current data provides important information on the strong temperature dependency of the PL peak energy transition. It is also important to point out that the different growth conditions (ours versus Sugita and co-workers et al. [21]) can lead to different types and level of defects incorporation in the films which will affect the luminescence features as well as the observed shift in peak energy transition. Further studies are required to weigh the balance between the impacts of the growth temperature and the carrier concentration on the peak energy shift of the film, and to investigate the incorporation of optically active defects and their correlation with the luminescence features from pulsed MOVPE InN films.

Fig. 8(a)–(c) show the surface morphology of InN films grown at 510 °C, 550 °C and 575 °C. The surface RMS roughness values of the films are ~9, 16, and 45 nm, respectively, for a scan size of 2 μm × 2 μm. All the thin films investigated in this study have 3D morphology and film growth temperature is observed to govern the size of InN islands. At lower growth temperatures, the diffusion of the reactant species is relatively small leading to the poor optical and electrical quality of the film but high nuclei/island density on the surface. The growth at higher temperature leads to lower island density, while the size of individual islands increases. Since higher growth temperature enhances the diffusion of reactant species, it results in the increase in the size of islands formed at the beginning of growth, leading to undesired rough surface morphology.

The effect of V/III ratio on the surface morphology is again found to be small as illustrated in Fig. 9(a)–(c). At the given temperature, the increase in V/III ratio does not seem to affect noticeably the islands density or lateral size of the islands. Surface RMS roughness increases primarily due to increased aspect ratio of the islands. This finding is little surprising because in the literature on hetero-epitaxial growth such as for GaN [22,23], it has been found that the increase in V/III ratio enhances the nuclei density and/or increase the lateral growth of the islands. This phenomenon was not observed here, as the V/III ratio of the InN growth had no clear effect on the island density or lateral size of the islands in the studied range. Unfortunately, the investigation of a wider range of V/III ratios is not possible in this case, since the droplet-free InN films are realized only in a narrow V/III ratio regime of input precursors.

The results of the XRD measurements, reported elsewhere [24] reveal the (0 0 0 2) texture of the InN films. The FWHM values of the (0 0 0 2) omega XRD rocking curves were measured as 518, 662, and 1281 arcs for InN films (V/III ratio = 12,460) grown at 510 °C, 550 °C, and 575 °C, respectively. The higher FWHM value in

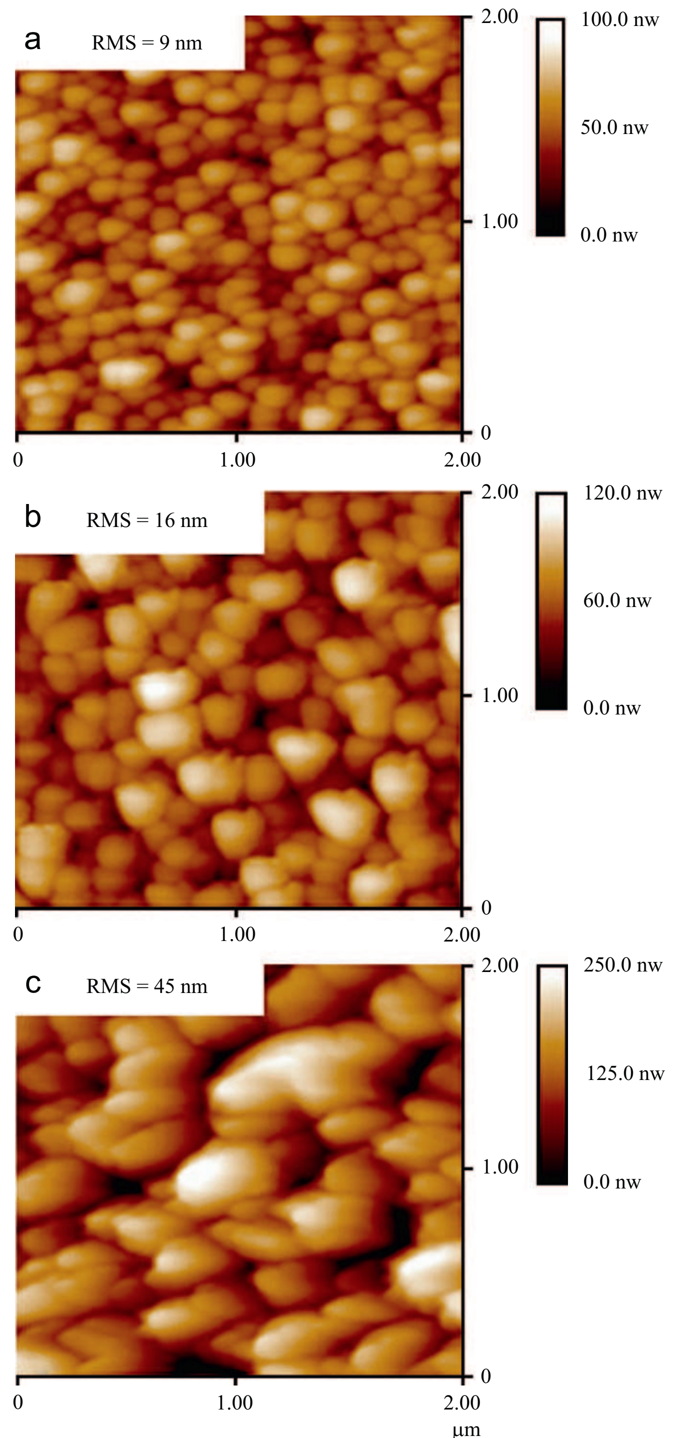

Fig. 8. AFM images of the surface morphology of InN films grown at (a) 510 °C, (b) 550 °C, and (c) 575 °C.

XRD data is observed for the film grown at 575 °C [24], and we believe that the larger out-of-plane mis-orientation amongst various InN islands/grains grown at higher temperature leads to the larger broadening of the (0 0 0 2) rocking curves (similar to finding by Suihkonen and co-workers [18]). The AFM images (Fig. 8) show that the higher growth temperature leads to the larger InN islands on the surface. It is also evident from the PL and electrical measurements data that the optical and electrical properties of the InN film improve at higher growth temperature. However, we found that the change in V/III ratio (12,460–17,100)

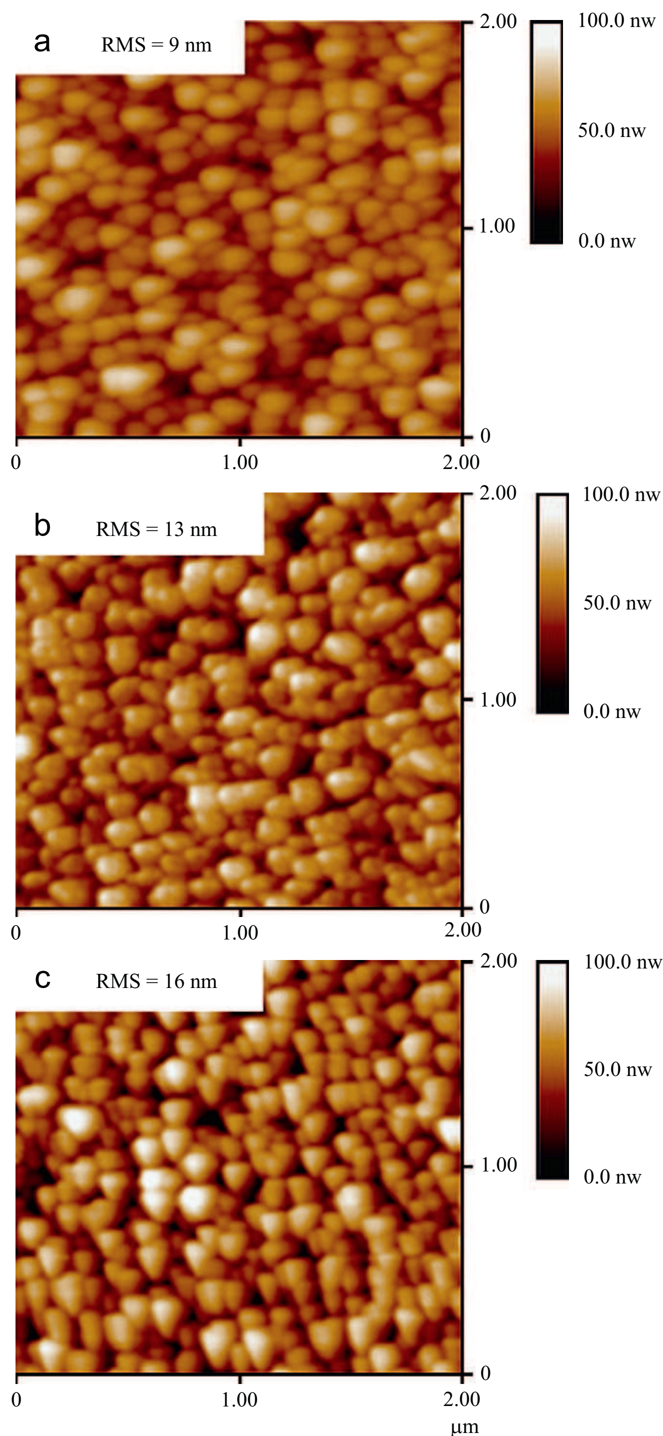

Fig. 9. AFM images of the surface morphology of InN films grown at 510 °C, for a V/III ratio of input precursors (a) 12,460, (b) 14,952, and (C) 17,088.

of input precursors in the given range has smaller effect on the island size, luminescence intensity as well as on the emission wavelength of the InN films grown by the pulsed MOVPE technique. Based on these observations, it is believed that the quality of the individual larger InN islands grown at relatively higher temperature is better.

In order to address the issue of undesired rough surface morphology of the films, we have investigated the use of InN-based buffer layer employing silane burst during the growth. The silane burst was inserted into the layers through a silane flow of 0.178 μm/min for 36 s during periodic growth interruption with ammonia on, during the growth of the buffer layer. We employed three successive silane bursts sandwiched between ~8 nm InN layers during the start of growth followed by the InN pulsed growth at the same conditions as that of the one given in Fig. 8(c). It is found, as shown in Fig. 10, that the insertion of short pulses of silane significantly improves the surface morphology of the overgrown InN film. We anticipate that silane flow might be leading to Si_xN_y formation causing compressive strain on the overgrown InN film which results in the comparatively smoother surface morphology. However, these are very preliminary results and further studies are still required to fully investigate and understand the mechanism of surface morphology improvement as a result of this technique.

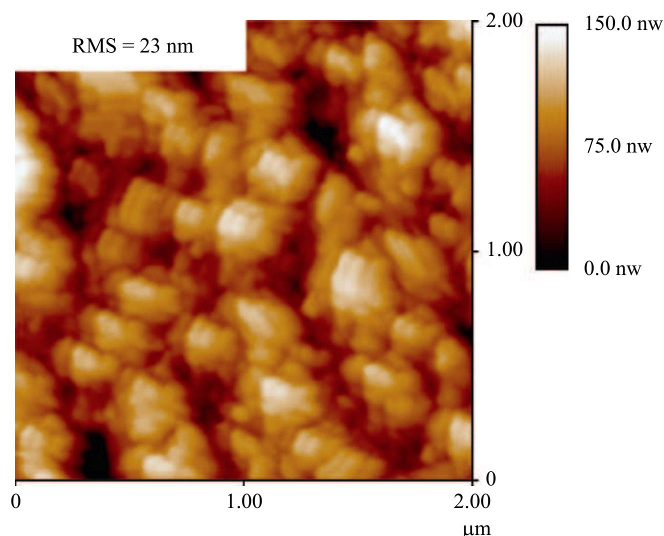

Fig. 10. AFM image of the surface morphology of InN film grown at 575 °C (V/III = 12,460), with the insertion of silane bursts during the start of InN film growth.

Table 1 represents the comparison data for the PL and Hall measurements of MOVPE-grown InN films as reported by various groups [7,11,12,16–19,21]. Our results show good agreement with the comparison data in Table 1, which indicate the band gap of MOVPE-grown InN is ~0.7–0.8 eV. The band gap of InN, although revised, there is still a range of reported values (0.7–0.9 eV) and the origin of the PL transitions is still controversially discussed. Further research works are still required to further investigate and understand the potential contributions of extrinsic defects related luminescence and origin of disparity in PL transitions among various reports.

5. Conclusion

In summary, high quality InN films have been grown on GaN/sapphire using pulsed MOVPE technique realizing metallic droplet-free films in a low V/III ratio of input precursors. Under the optimal growth conditions, the PL measurements on InN film conducted at room temperature ($T = 300$ K) indicated transition at 0.77 eV, and the quality of the film is observed to have strong dependence on the growth temperature of the films. The InN films grown at relatively high growth temperature ($T_g = 575$ °C, pressure = 200 Torr, and V/III = 12,460) also result in higher electron mobility [$\mu_e = 681\ cm^2/(V\,s)$] and lower background concentration ($n = 1.5 \times 10^{19}\ cm^{-3}$). Our experimental results also show that increase in V/III ratio in a given range (12,460–17,088) has minimal effect on the transition energy and on the luminescence intensity. The surface RMS roughness of the films

Table 1
Photoluminescence and Hall data of InN films (under optimal growth conditions), and comparison with the published results on MOVPE grown InN

	PL at 300 K (eV)	PL at 77 K (eV)	Mobility (cm^2/V-s)	Bulk doping (cm^{-3})
Sugita et al. [21]	0.7–0.9		730	5.8×10^{18}
Matsouka et al. [7]	0.7–0.8			
Maleyre et al. [16]	0.77–0.78		800	3×10^{19}
Johnson et al. [19]		0.83 (14 K)		
Suihkonen et al. [18]	0.78–0.85		200	1×10^{20}
Xie et al. [11]	0.74		939	3.9×10^{18}
Kadir et al. [17]	0.82–1.1		200	2×10^{19}
Khan et al. [12]	0.76–0.87		1400	7×10^{18}
Present work	0.77	0.78	681	1.5×10^{19}

increases significantly with the increase in growth temperature whereas the change in V/III ratio for a given temperature is observed to have small effect on the surface RMS roughness or the lateral sizes of InN islands.

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