

MOVPE and photoluminescence of narrow band gap (0.77 eV) InN on GaN/sapphire by pulsed growth mode

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This paper reports the metalorganic vapor phase epitaxy (MOVPE) of InN on GaN/sapphire templates by pulsed growth mode. Photoluminescence analysis of the films has been performed both at room temperature ($T = 300$ K) and low temperature ($T = 77$ K). At room temperature, the band gap of InN is measured as 0.77 eV which is observed to have strong dependence on the growth temperature of the film. The appearance of otherwise less dominant transitions is associ-

ated to defects related luminescence from the films grown at relatively low growth temperatures. The electron mobility of $681 \text{ cm}^2/(\text{V s})$ is obtained for InN alloy grown under optimal condition. The X-ray diffraction (XRD) analysis, structural quality and the evolution of the surface morphology of thin InN films have also been studied in the context of the given growth conditions.

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1 Introduction The recently-revised energy band gap of InN semiconductor ~ 0.7 eV [1, 2] has largely extended the spectral range covered by III-nitrides, from the near infrared for InN (0.7 eV) to the ultraviolet for AlN (6.2 eV) which offers a great advantage of nitrides over other semiconductors for applications in solar cells [3] and terahertz (THz) optoelectronics [4, 5]. In addition, the excellent transport properties of InN make it very attractive alloy for applications in high speed electronic devices [5, 6]. However, the growth of high-quality narrow-bandgap InN films is challenging due to the low dissociation temperature and high equilibrium N_2 vapor pressure over InN film [7, 8]. Due to the low growth temperature required and lack of suitable lattice-matched substrates, the growth procedure of high-quality single crystalline InN films is yet to be established, especially in metalorganic vapor phase epitaxy (MOVPE). Different methods have been developed to grow InN films [9–16] and the quality of InN films has been markedly improved. The band gap of InN, although revised, the origin of the photoluminescence (PL) transitions commonly observed from 0.6 eV to 0.8 eV is still

controversially discussed. Various research groups who position the fundamental band gap of InN around 0.7 eV, suggest the 0.7–0.8 eV PL peak to be the band-edge transition [1, 2, 17]. Others attribute this low-energy transition to an extrinsic recombination process analogous to the process that gives a yellow band in gallium nitride, exciton emissions in the In-rich interfaces and In clustering in the InN epilayers and defect related luminescence [18–20]. A recent report even suggested the 0.76 eV PL transition as the Mg acceptor level in InN [21].

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 (V/III ~ 12460 – 17100). The pulsed growth mode technique had previously been employed [10], however, with a reported condition of high V/III ratios of the input precursors (V/III $\sim 5.2 \times 10^5$ – 2×10^6). We have studied particularly the PL transitions both at room temperature ($T = 300$ K) and low temperature ($T = 77$ K), in an attempt to discern the inherent band gap of InN. It is found that the growth temperature of film has direct impact on the position of PL transi-

tions. The appearance of rather less dominant transitions (0.81 eV, 0.87 eV, 1.15 eV) and the structural and electrical quality of the InN films have been discussed.

2 Experiments The epitaxy of InN on GaN/sapphire templates was performed by using the Veeco P-75 MOCVD reactor. TMIn (12.5 $\mu\text{mol}/\text{min}$) and NH_3 (3.5 slm) were used as the group III and V precursors, respectively, and N_2 was used as the ambient and carrier gas. All the growths of InN layers were conducted at a growth pressure of 200 Torr. The investigated input ratio (V/III ratio) of group V and III precursors was 12460, and the growth temperatures were varied from 510 $^\circ\text{C}$ up to 575 $^\circ\text{C}$. 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 [10], where NH_3 was constantly flowing, while the TMIn was sent into the reactor chamber for a 36-seconds pulse and then it bypassed the reactor chamber for an 18 s pulse for a total cycle time of 54-seconds. The schematic of the pulsed growth mode is shown in Fig. 1. This pulsing cycle was repeated for 80 times resulting in a film thickness of ~ 220 nm.

The optical quality and band gap of InN were determined from the photoluminescence 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 atomic force microscopy (AFM) measurements in tapping mode were used to monitor the surface morphology of the films. The X-ray diffraction (XRD) measurements, using a PANalytical MRD instrument with parallel beam geometry and $\text{CuK}\alpha$ radiation, were performed to evaluate the presence of secondary phases and crystallinity of the InN films.

3 Results and discussion In an earlier publication, we reported the results of the experimental investigation of a wide range of temperature and V/III ratio of input precursors [22]. It was found that a high V/III ratio ($>3 \times 10^5$)

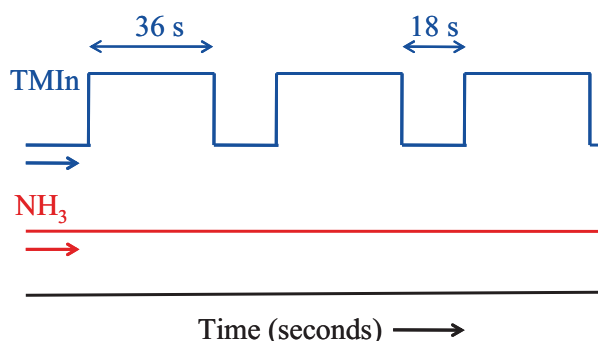


Figure 1 (online colour at: www.pss-a.com) Schematic of the pulsed MOVPE growth of InN alloy.

of input precursors is required to achieve droplet-free InN film. Similar findings have also been reported by others [8, 23]. Although, the successful InN growths under comparatively low V/III ratios have also been reported [11, 12, 24], the droplet-free growth of InN under low V/III ratios is not common to all MOVPE reactor geometries. The use of pulsed growth mode, however, allowed the growth of metallic droplet free InN films without requiring high V/III ratio of input precursors. On the other hand, continuous supply of indium and nitrogen precursors into the reactor chamber resulted in the In droplets on the surface for the same temperature range and V/III ratio of input precursors. In a pulse mode, and for an optimum V/III ratio of 12460, the effects of growth temperature (510–575 $^\circ\text{C}$) on the PL transitions have been investigated.

The PL analysis performed both at room temperature and at 77 K show that the observed luminescence spectra have strong dependence on the growth temperature of the films. Figure 2(a), (b), and (c) show low temperature (77 K) PL spectra of the films grown at 575 $^\circ\text{C}$, 550 $^\circ\text{C}$, and 510 $^\circ\text{C}$, respectively. It is observed that the appearance and intensity of different transition change with temperature. The InN films grown at 575 $^\circ\text{C}$ have higher luminescence intensity and narrower FWHM values than the ones grown at 510 $^\circ\text{C}$. The appearance of otherwise less dominant transitions are more pronounced at the room temperature PL spectra of the films as shown in Fig. 3(a)–(c).

The room temperature PL spectrum of the film grown at 510 $^\circ\text{C}$ exhibits dominant peak transition at ~ 0.81 eV (Fig. 3c). Also, the films grown at relatively low growth temperature are observed to have luminescence features at ~ 1.15 eV. It is important to note that this transition at 1.15 eV and the weak shoulder appearing at 0.87 eV become almost diminished and weak when the film is grown at higher temperature (Fig. 3a). Particularly, the PL spectra for InN films grown at higher temperatures (550–575 $^\circ\text{C}$) exhibited dominant peak luminescence at 0.77–0.78 eV. Recently, the PL transition at 0.76 eV has been associated to Mg related acceptor level [21]. Figure 2(c), and Fig. 3(b) and (c) also show luminescence shoulders at ~ 0.75 –0.76 eV to the low energy side of the dominant transitions, despite the fact no intentional Mg doping of InN films was carried out in this study. This finding indicates that the appearance of these less dominant transitions might have their origin in defects which are incorporated in the films grown at relatively low temperatures. Further study will be required to fully understand the nature of optically active defects and their correlation with the observed less dominant luminescence features.

The use of higher growth temperature also improves the electrical quality of the InN films, as shown in Fig. 4. The background n-type carrier concentrations of InN films range from $1.39 \times 10^{19} \text{ cm}^{-3}$ ($n_{2D} = 2.78 \times 10^{14} \text{ cm}^{-2}$) up to $3.9 \times 10^{19} \text{ cm}^{-3}$ ($n_{2D} = 7.8 \times 10^{14} \text{ cm}^{-2}$), with the lowest background doping materials obtained at growth temperature of 575 $^\circ\text{C}$. The electron mobility values for the

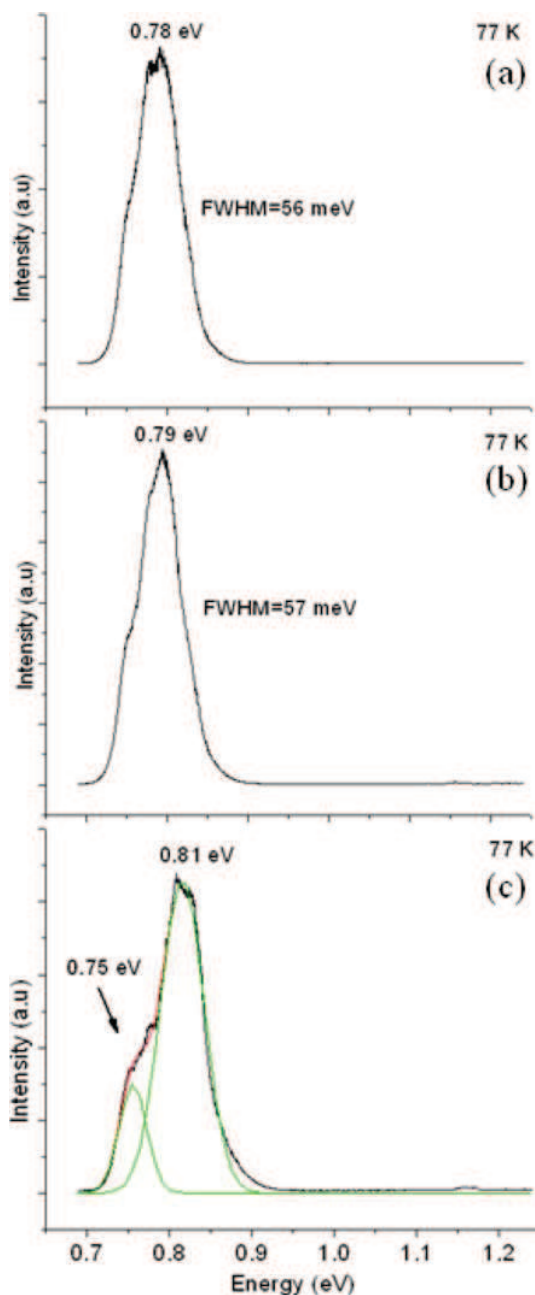


Figure 2 (online colour at: www.pss-a.com) Low temperature (77 K) photoluminescence spectra of InN films grown on GaN/sapphire templates at (a) 575 °C, (b) 550 °C, and (c) 510 °C.

above growth conditions ranged from $325 \text{ cm}^2/(\text{V s})$ up to $681 \text{ cm}^2/(\text{V s})$. The electron mobility increases significantly with the increase in growth temperature which is partially caused by the decrease in background sheet concentration. It is interesting to note that the films grown at 550 °C and 575 °C have roughly similar background carrier concentration whereas the mobility is still higher for

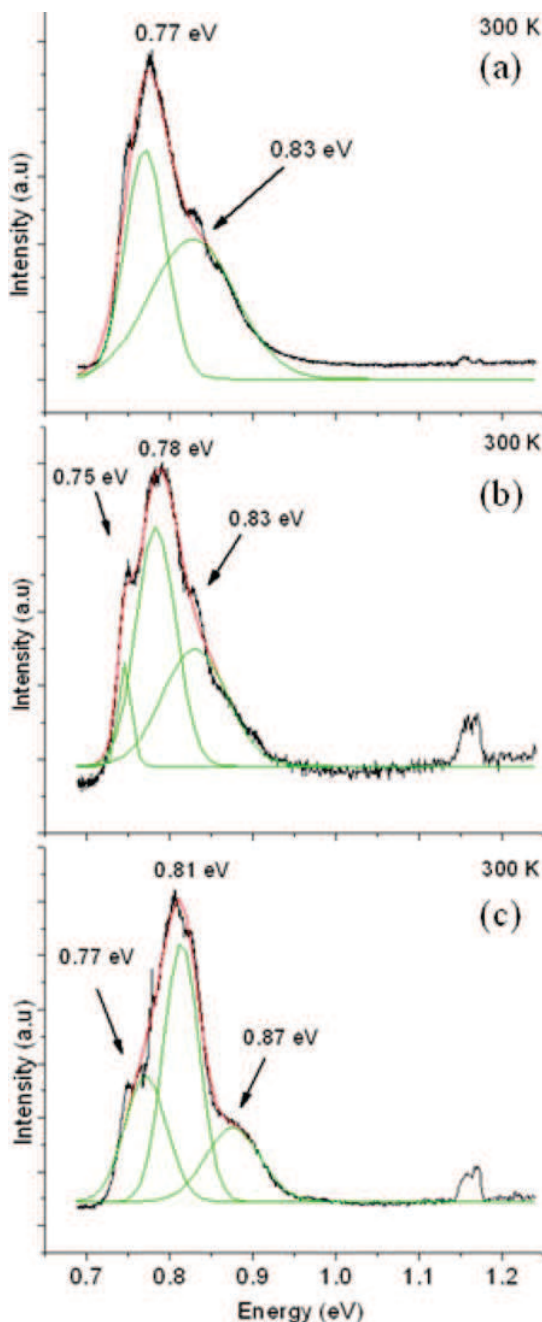


Figure 3 (online colour at: www.pss-a.com) Room temperature photoluminescence spectra of InN films grown on GaN/sapphire templates at (a) 575 °C, (b) 550 °C, and (c) 510 °C.

the film grown at 575 °C. This could be explained by reductions in scattering centers and grain boundaries with increase in growth temperature, which leads to increase of the carrier mobility. Under the optimum ($T_g = 575 \text{ °C}$) InN growth conditions with pressure of 200 Torr and V/III of 12460, the carrier mobility and n-type carrier concentration

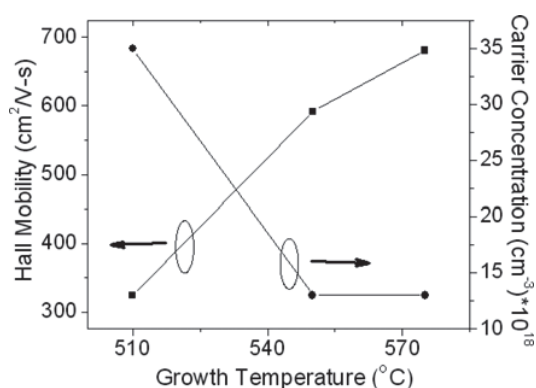


Figure 4 Plot of Hall carrier mobility and sheet concentration as a function of growth temperature of the films.

were measured as $681 \text{ cm}^2/(\text{V s})$ and $1.5 \times 10^{19} \text{ cm}^{-3}$, respectively.

Figure 5(a)–(c) show the surface morphology of InN films. The surface RMS roughness values of the films grown at 510°C , 550°C and 575°C are $\sim 9 \text{ nm}$, 15 nm , and 31 nm , respectively, for a scan size of $1 \mu\text{m} \times \mu\text{m}$, as given in the Table 1. All the films investigated in this study result in 3D morphology and film growth temperature is observed to govern the size of InN islands. At lower temperature, the island density is higher with smaller island size. The growth at higher temperature leads to lower island density, while the size of individual island/grain increases. We believe that the relatively high growth temperature is the factor that leads to the increased island size at the beginning of InN growth. As there exists a 10% lattice mismatch between InN and underlying GaN layers, this induces a significant compressive strain in the overgrown thin films leading to the preferred growth mode with 3D morphology. At lower growth temperatures, however, the diffusion of the reactant species is relatively small leading to the poor film quality but high nuclei/island density on the surface. Comparatively higher growth temperature, on the other hand, enhances the diffusion of reactant species resulting in the increase in the size of islands formed at the beginning of growth.

The X-ray diffraction (XRD) measurement reveals dominantly the (0002) texture of the InN films (not shown here). The full widths at half maximum (FWHMs) values of the XRD rocking curves of the symmetric (0002) and asymmetric (10–12) reflections are given in Table 1. The FWHMs of the symmetric and asymmetric reflections for the film grown at 510°C are 518 arc sec and 1548 arc sec , respectively, and those for the film grown at 575°C are 1281 arc and 1800 arc sec , respectively. The larger FWHMs of the rocking curves of the asymmetric reflections can be attributed to the relatively greater degree of twist in the crystallites of InN film. The observed difference between the FWHMs of the rocking curves of the film grown at low temperature (510°C) and the ones at higher temperature (575°C) indicates that both the tilt

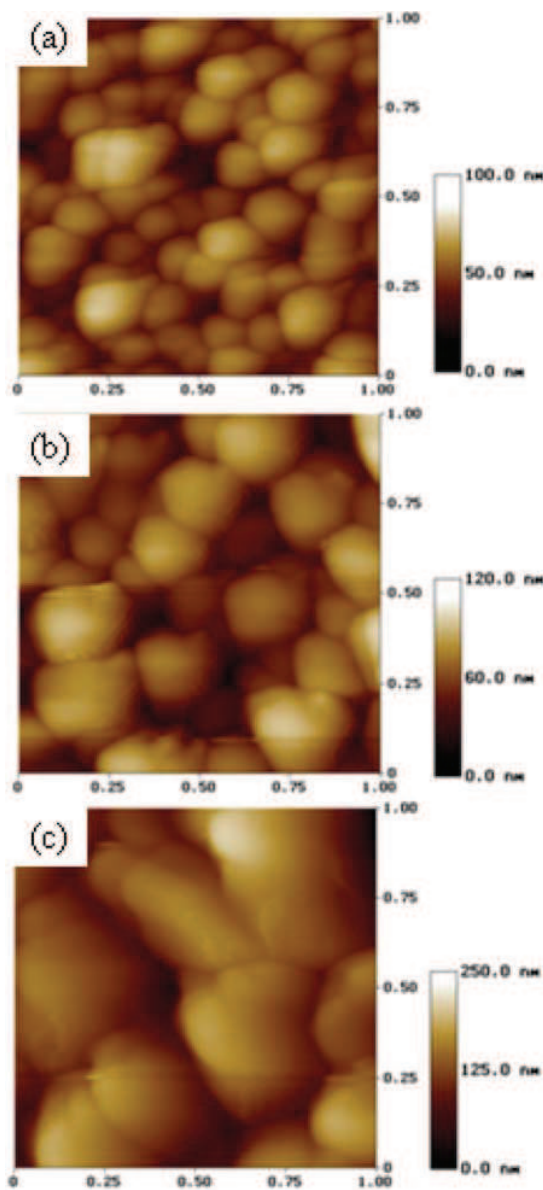


Figure 5 (online colour at: www.pss-a.com) Atomic force microscopy images of the surface morphology of InN films grown at (a) 510°C , (b) 550°C , and (c) 575°C .

(out-of-plane misorientation) and twist (in-plane misorientation) components of the film increase with the increase in growth temperature. These findings are surprising, as the higher growth temperature in general leads to improved crystal quality of the film. There is apparently an inconsistency in the experimental observations as the PL and Hall data also indicate that the optical and electrical quality of the film improves at higher growth temperature.

In general, the broadening of XRD reflections has contributions from the degree of tilt and twists in the crystal-

Table 1 Structural and electrical data of InN films grown on GaN/sapphire templates.

	Sample A $T_g = 510\text{ }^\circ\text{C}$	Sample B $T_g = 550\text{ }^\circ\text{C}$	Sample C $T_g = 575\text{ }^\circ\text{C}$
AFM: RMS roughness (nm) (scan = $1\text{ }\mu\text{m} \times 1\text{ }\mu\text{m}$)	8.9	14.8	31.1
XRD: ω -RC (002) FWHM (arc sec)	518	662	1281
ω -RC (102) FWHM (arc sec)	1548	1440	1800
Hall: Mobility ($\text{cm}^2/\text{V s}$)	324	592	681
Sheet cc $\times 10^{14}$ (cm^{-2})	-7.8	-2.9	-2.9

lites, heterogeneous strain, small correlations lengths and impurities in the film. In our InN materials, film grows in 3D morphology instead of layer by layer mode. At lower growth temperatures, the InN film has higher island density (Fig. 5a) and low RMS roughness. However, the growth conducted at higher temperature leads to larger InN islands and lower island density on the surface, as shown in Fig. 5(c). One possible explanation of the above contrasting results is that the higher growth temperature results in larger InN domains that are more tilted and twisted with respect to each other, resulting in the larger broadening of XRD rocking curves. Similar findings by Suihkonen and co-workers [24] also reported broadening of the XRD rocking curve for (0002) orientation for the InN film grown at higher temperature.

On the other hand, it is important to note that the observed improvement in the optical and electrical quality of the film at higher growth temperature suggests better quality of the individual larger islands. The larger InN islands with lower density will have comparatively lesser coalescence boundaries and likewise the less scattering centers which may partially explain the results of observed higher electron mobility values for the films grown at higher temperature. Suihkonen and co-workers [24] also reported improvement in the carriers' mobility of InN film grown at higher temperature, despite the broadening of the XRD rocking curve.

As shown above, good optical quality droplet-free InN films have been achieved using pulse mode of deposition. However, it is not fully understood why pulsing of In source is efficient in removing In droplets, since In vapor pressure is extremely low, and that In droplets, once formed will not necessarily be re-evaporated. We speculate that the pause in the supply of In source helps in consuming the droplets (by reactive nitrogen species coming from cracked ammonia) at the initial stage of formation. A similar finding by Petit and co-workers [25] have also indicated the possibility of metallic In droplets being consumed by reactive nitrogen species. However, further studies are still required to fully understand the mechanism of droplets removal by pulse mode as well as the effect of pulse duty cycle on the quality of heteroepitaxial InN films.

The pause in In supply during the pulsed MOVPE growth of InN can also lead to a loss of material by etching (due to the change in the balance of growth versus etching). This could affect the overall growth rate while being ad-

vantageous for the quality of the films since etching will preferably happen to the defects sites and low quality material of the layers. The more precise determination of the effect of pulsing on layer quality would have been possible if the droplet free growth of InN without pulsing was also realizable under same growth conditions. However, it is important to note that the epitaxy of InN under identical growth condition in our reactor without pulsing resulted in InN film with In droplets (diameter $\sim 100\text{ nm}$ up to $1\text{ }\mu\text{m}$). For comparison purpose, Suihkonen and co-workers [24] reported growth rate of $\sim 200\text{--}250\text{ nm/hr}$ for InN growth in closed coupled shower (CCS) reactor (for TMIn flow rate of $12.5\text{ }\mu\text{mol/min}$), which is comparable to the growth rate (185 nm/hr for TMIn flow rate = $12.5\text{ }\mu\text{mol/min}$) obtained from our pulsed epitaxy of InN in our reactor geometry.

4 Conclusion In summary, high quality InN films have been grown on GaN/sapphire using pulsed MOVPE technique. Narrow band gap InN films were achieved without utilizing a high V/III ratio of input precursors. The band gap of InN film at $T = 300\text{ K}$ is measured as 0.77 eV from photoluminescence studies, 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 ($T_g = 575\text{ }^\circ\text{C}$, pressure = 200 Torr , and $V/\text{III} = 12460$) also result in higher electron mobility [$\mu_e = 681\text{ cm}^2/(\text{V s})$] and lower background concentration ($n = 1.5 \times 10^{19}\text{ cm}^{-3}$). The surface RMS roughness of the films, however, increases with the increase in growth temperature. It is found that the degree of tilt and twist in the components of the film also increases with temperature which in turn increases the broadening of XRD omega rocking curves for both symmetric and asymmetric reflections.

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