



# Nucleation and growth of InN thin films using conventional and pulsed MOVPE

M.C. Johnson<sup>a</sup>, S.L. Konsek<sup>a,b</sup>, A. Zettl<sup>a,b</sup>, E.D. Bourret-Courchesne<sup>a,\*</sup>

<sup>a</sup>*Lawrence Berkeley National Laboratory, Materials Science Division, Center for Advanced Materials, 1 Cyclotron Road, Mailstop 2R0200, Berkeley, CA 94720, USA*

<sup>b</sup>*Department of Physics, University of California, Berkeley, CA 94720, USA*

## Abstract

InN was deposited on c-sapphire and GaN substrates using conventional and pulsed metalorganic vapor-phase epitaxy. The nucleation and evolution of thin film growth was investigated. Growth temperature, V/III molar ratio, and substrate material were varied for the two different growth modes (conventional vs. pulsed MOCVD). It was found that InN deposition was sensitive to V/III molar ratio and growth temperature. Photoluminescence results show a peak emission at 0.83 eV. Results are presented that show the highest quality InN was deposited using pulsed metalorganic vapor-phase Epitaxy on GaN substrates.

© 2004 Published by Elsevier B.V.

PACS: 81.15.Gh; 81.05.Ea; 68.37.Hk; 78.55Cr

Keywords: A1. Nucleation; A1. Photoluminescence; A1. Scanning Electron Microscopy; A3. Metalorganic chemical vapor deposition; B1. Indium Nitride (InN); B1. Nitrides

## 1. Introduction

Over the past several years, InN has become attractive due to recent discoveries of its inherent optical and electrical properties. Early absorption studies reported a bandgap transition to be

$E_g = 1.8\text{--}2.0\text{ eV}$  [1–3]. But these samples showed no corresponding band-edge photoluminescence (PL) and, therefore, there was no conclusive evidence of a bandgap transition to be  $\sim 1.9\text{ eV}$ . Recently, a more accepted band-edge emission was found to be  $\sim 0.8\text{ eV}$  [4–6]. This new discovery has generated a large interest in potential applications for some very practical optoelectronic devices. Because of its direct bandgap alloying with GaN, materials can be produced with bandgaps ranging from the near infrared (IR) to the ultraviolet (UV)

\*Corresponding author. Tel.: +1-510-486-5553; fax: +1-510-486-5530.

E-mail address: [EDBourret@lbl.gov](mailto:EDBourret@lbl.gov)  
(E.D. Bourret-Courchesne).

which covers a lot of the solar spectrum. As a result, InN and its alloy  $\text{In}_x\text{Ga}_{1-x}\text{N}$  ( $0 < x < 1$ ) are very promising for visible and near IR optoelectronics and high-efficiency solar cells. Additionally, InN was predicted to have the lowest effective mass for electrons in all the Group III-Nitride semiconductors which leads to high mobility and high saturation velocity [7]. It was also found to exhibit extremely high peak drift velocity at room temperature and the transport characteristics were insensitive to variations in temperature and doping concentration [8–10]. Therefore, InN is a promising material and has distinct advantages for use in electronic devices such as high-frequency mm and cm wave devices and high-speed, high-performance heterojunction FETs.

Unfortunately, research efforts have been hindered by difficulties in growing high-quality InN epitaxial thin films. Various methods have been used for deposition of InN including molecular beam epitaxy (MBE) [11], magnetron sputtering [12], halogen vapor-phase epitaxy (HVPE) [13], laser-assisted CVD [14], and variations on metalorganic chemical vapor deposition (MOCVD) [15–19]. MBE has grown some very high-quality films while progress in MOVPE is slow. However, MOVPE is a technique of choice for commercial device fabrication due to its high throughput and large growth rates. Device quality InN films have not been achieved using MOCVD mainly due to high quantity of defects. These large defect densities are attributed to the lack of a lattice-matched substrate material and restricted growth conditions owing to the low dissociation temperature of InN itself ( $\sim 600^\circ\text{C}$ ) [20]. Normally, the growth temperature should be kept relatively low ( $450\text{--}600^\circ\text{C}$ ) when compared to the deposition of the other nitrides which occur at growth temperatures in excess of  $1000^\circ\text{C}$ . This low growth temperature prevents InN dissociation but also limits the cracking efficiency of  $\text{N}_2$  or  $\text{NH}_3$ . To overcome these limitations, variations of MOCVD using various substrate materials have been attempted, including atomic layer epitaxy [15], two-step growth techniques [16], and double-zone MOCVD [17]. But a lack of fundamental understanding of deposition of InN has prevented the establishment of a consistent growth strategy.

In this paper, a systematic study on the deposition of InN on sapphire and GaN substrate materials using conventional and pulsed MOCVD is reported. The nucleation and evolution of thin film growth was investigated. Growth temperature, V/III molar ratio, and substrate material were varied for the two different growth modes (conventional vs. pulsed MOCVD). The surface morphology and optical properties of the resulting films were studied.

## 2. Experimental procedure

InN was deposited at atmospheric pressure using a vertical flow, Emcore 125 Turbodisc MOCVD reactor. Epichem Solution Trimethylindium (TMI) and ammonia were used as the In and N sources, respectively.  $\text{N}_2$  was used as the carrier and dilution gases. Sapphire (0001) and previously MOVPE grown high-quality  $2\text{ }\mu\text{m}$  thick GaN(0001) were used as substrate materials. The sapphire substrates were thermally cleaned at  $1000^\circ\text{C}$  for 10 min before being nitridated at  $1000^\circ\text{C}$  for 15 min in ammonia. The GaN substrates were used as-grown and the InN was deposited directly on top at the desired growth conditions. For conventional MOCVD, the TMI and ammonia were simultaneously flowed to the substrate surface for pyrolysis and deposition. In the pulsed MOCVD mode, the ammonia was constantly flowing while the TMI reactant was sent into the reactor chamber for a 6-s pulse and then it bypassed the reactor chamber for a 10-s pulse for a total cycle time of 16-s. This pulsing cycle was repeated for as many times as the growth period demanded. The films were cooled down under a  $\text{N}_2$  ambient. Nucleation studies were performed using growth times of 10, 20, and 30 min on both substrates at different conditions.

Post-growth characterization was used to investigate surface morphology and optical properties. Surface morphology was studied using scanning electron microscopy (SEM). An FEI Sirion 200 ultra-high-resolution SEM was used for SEM imaging operated at 2 kV. Low temperature (14 K) and room temperature photoluminescence (PL) were used to obtain optical properties. The

photoluminescence signals were generated in the backscattering geometry by excitation with the 515 nm line of an argon laser. The signals were then dispersed by a 1-m double-grating monochromator and detected by a LN2 cooled Ge photodiode detector.

### 3. Results and discussion

All samples presented were confirmed to be hexagonal InN with X-ray diffraction analysis. Compositional confirmation was verified using both Rutherford Backscattering Spectroscopy and Electron Diffraction Spectroscopy which showed samples to be InN with no detection of impurities above the detection limits.

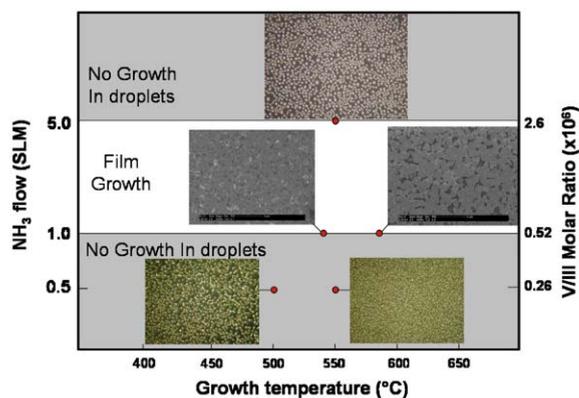


Fig. 1.  $\text{NH}_3$  vs.  $T_g$  growth parameter space for InN deposition using TMI and  $\text{NH}_3$  as reactant species.

#### 3.1. V/III molar ratio

We found that the deposition of InN is very sensitive to the V/III molar ratio. Groups of samples were grown at various growth temperatures (460–600 °C) and various V/III molar ratios. Fig. 1 shows the growth parameter space determined for our reactor and the SEM images of a representative group of samples at different growth conditions. There is a specific growth parameter space which allows deposition of InN shown in the white block, between  $V/III = 1.0 \times 10^5$ – $2.6 \times 10^6$ . If V/III is greater than  $2.6 \times 10^6$ , large amounts of  $\text{H}_2$  are produced from the pyrolysis of  $\text{NH}_3$ , thus, preventing InN deposition. This results in In droplet formation as shown in the top picture of Fig. 1. This increase in  $\text{H}_2$  production at high V/III decreases the Gibbs free energy for InN formation and results in InN decomposition. Koukitsu et al. reports and discusses the thermodynamic limitations of InN deposition in the presence of  $\text{H}_2$  [21]. On the other hand, if V/III is below  $5.2 \times 10^5$ , the reaction rate of InN formation is too slow, limited by the amount of N radicals from the pyrolysis of  $\text{NH}_3$ , and also results in In droplet formation. This is seen in the bottom pictures in Fig. 1.

#### 3.2. Growth temperature

Fig. 2 shows SEM images for the three growth temperatures indicated at a  $V/III = 5.2 \times 10^5$ . These images show that as the growth temperature

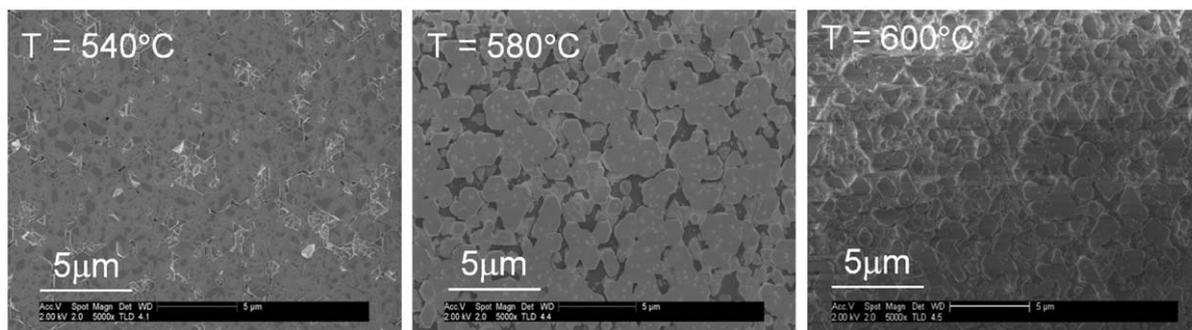


Fig. 2. SEM images of InN grown using conventional MOVPE at the indicated growth temperatures.



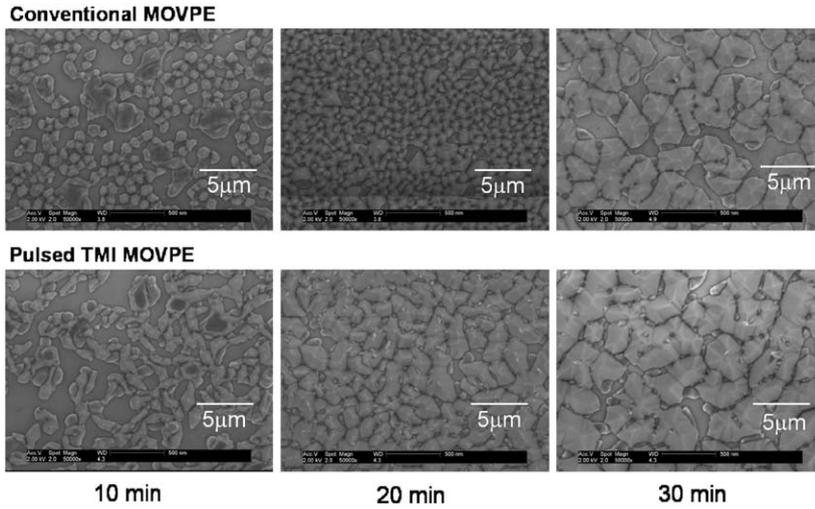


Fig. 4. Comparison of SEM images for the nucleation of InN grown on GaN using conventional and pulsed MOVPE for 10, 20, 30 min. The growth temperature was 540 °C with a V/III of  $5.2 \times 10^5$ .

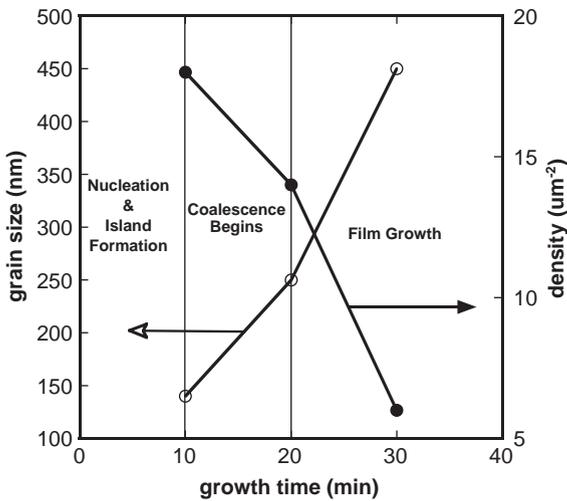


Fig. 5. Nucleation properties and growth schematic for InN grown on GaN substrate using pulsed MOVPE. The growth temperature was 540 °C with a V/III of  $5.2 \times 10^5$ .

3.3.2. Nucleation on GaN

Fig. 4 shows the comparison of SEM images for InN deposited on GaN substrates using conventional and pulsed MOVPE. Both growth modes seem to have similar nucleation and evolution mechanisms. The first 10 min initiate nucleation and island formation. These islands increase in size and start coalescing during the next 10 min.

Finally, the islands converge and start film growth. This growth evolution is described in the schematic in Fig. 5. The major difference between conventional and pulsed MOVPE manifests itself when thicker films (~0.5 μm) are grown as discussed below.

3.4. Pulsed MOVPE growth of GaN

Fig. 6 shows the SEM images for thick (~0.5 μm) InN grown using pulsed MOVPE on c-Al<sub>2</sub>O<sub>3</sub> and GaN substrates. The film grown on GaN is much smoother and has much better uniformity. The film grown on Al<sub>2</sub>O<sub>3</sub> exhibits some rough features which is due to a stress induced 3D-growth mechanism caused by a large lattice mismatch. Fig. 7 shows the PL spectra of the two samples. Both show an emission peak at 0.83 eV which is in agreement with reported values of MBE and MOVPE grown material [4–6], which report a PL range of 0.77–0.90 eV, but in disagreement with values reported for sputtered films [3,22]. The 0.83 eV peak intensity of the InN grown on GaN is much greater than that of the film grown on sapphire. The film grown on sapphire has an increased defect density that act as non-radiative traps. The PL emission for InN deposited on GaN by conventional MOVPE also

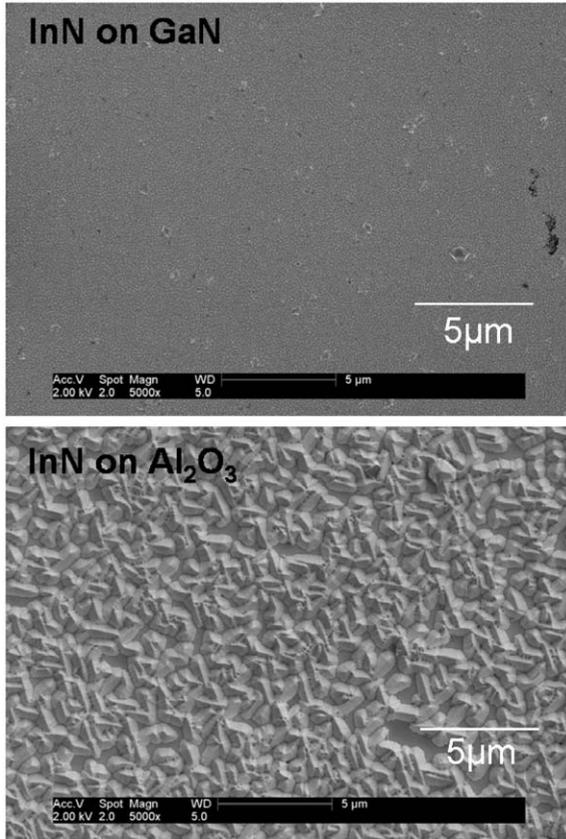


Fig. 6. Plan view SEM images of InN grown on GaN and  $\text{Al}_2\text{O}_3$  substrates. The films were grown using pulsed MOVPE at a growth temperature of  $540^\circ\text{C}$  with a  $V/\text{III} = 5.2 \times 10^5$ .

exhibited a much lower emission intensity than the material grown using pulsed MOVPE. We must note that the PL emission peak has a FWHM of  $0.12\text{ eV}$  and that further optimization of the growth process is needed to further reduce the total defect density.

#### 4. Conclusion

Pulsed MOVPE gives much better film quality for both GaN and  $\text{Al}_2\text{O}_3$  substrates than conventional MOVPE. This is due to the increased surface mobility of the In adatoms. This results in better uniformity and increased surface coverage which is shown to give a stronger PL emission at  $0.83\text{ eV}$ . Using GaN substrates result in higher

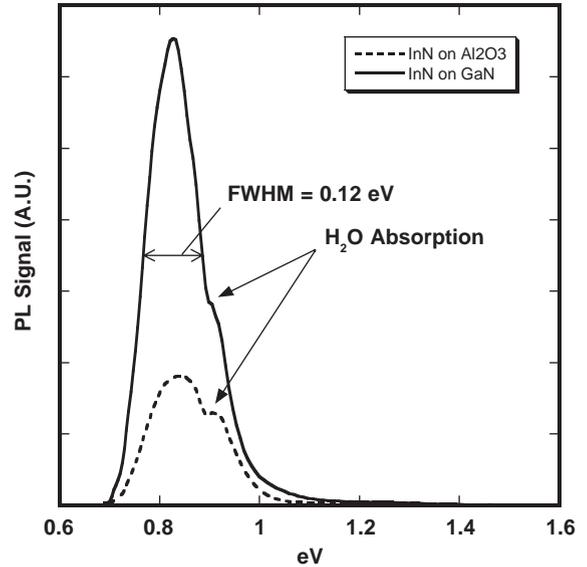


Fig. 7. Comparison of low temperature (14 K) PL of InN grown on GaN and  $\text{Al}_2\text{O}_3$  substrates using pulsed MOVPE. The growth temperature was  $540^\circ\text{C}$  with a  $V/\text{III}$  of  $5.2 \times 10^5$ .

quality films than using c- $\text{Al}_2\text{O}_3$  substrates due to a decreased mismatch of the lattice constants and of the thermal expansion coefficients.

#### Acknowledgement

This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Materials Science and Engineering, of the US Department of Energy under Contract no. DE-AC03-76SF00098.

#### References

- [1] K. Osamura, S. Naka, Y. Murakami, J. Appl. Phys. 46 (1975) 3432.
- [2] N. Puycherier, M. Menoret, Thin Solid Films 36 (1976) 141.
- [3] T.L. Tansley, C.P. Foley, J. Appl. Phys. 59 (1986) 3241.
- [4] J. Wu, W. Walukiewicz, K.M. Yu, J.W. Ager III, E.E. Haller, H. Lu, W.J. Schaff, Y. Saito, Y. Nanishi, Appl. Phys. Lett. 80 (2002) 3967.
- [5] T. Inushima, V.V. Mamutin, V.A. Vekshinb, S.V. Ivanov, T. Sakon, M. Motokawa, S. Ohoya, J. Crystal Growth 227–228 (2001) 481.

- [6] V. Yu. Davydov, A.A. Klochikhin, R.P. Seisyan, V.V. Emtsev, S.V. Ivanov, F. Bechstedt, J. Furthmuller, H. Harima, A.V. Mudryi, J. Aderhold, O. Semchinova, J. Graul, *Phys. Stat. Sol. B* 229 (2002) R1.
- [7] S.N. Mohammad, H. Morkoc, *Prog. Quant. Electron.* 20 (1996) 361.
- [8] S.K. O'Leary, B.E. Foutz, M.S. Shur, U.V. Bhapkar, L.F. Eastman, *J. Appl. Phys.* 83 (1997) 826.
- [9] E. Bellotti, B.K. Doshi, K.F. Brennan, J.D. Albrecht, P.P. Ruden, *J. Appl. Phys.* 85 (1999) 916.
- [10] B.E. Foutz, S.K. O'Leary, M.S. Shur, L.F. Eastman, *J. Appl. Phys.* 85 (1999) 7727.
- [11] T. Yodo, H. Yona, H. Ando, D. Nosei, Y. Harada, *Appl. Phys. Lett.* 80 (2002) 968.
- [12] Q. Guo, A. Okada, H. Kidera, T. Tanaka, M. Nishio, H. Ogawa, *J. Crystal Growth* 237–239 (2002) 1032.
- [13] O. Igarashi, *Jpn. J. Appl. Phys.* 31 (1992) 2665.
- [14] Y. Bu, L. Ma, M.C. Lin, *J. Vac. Sci. Tech. A* 11 (1993) 2931.
- [15] R.S.Q. Fareed, R. Jain, R. Gaska, M.S. Shur, J. Wu, W. Walukiewicz, M.A. Khan, *Appl. Phys. Lett.* 84 (2004) 1892.
- [16] F.H. Yang, J.S. Hwang, K.H. Chen, Y.J. Yang, T.H. Lee, L.G. Hwa, L.C. Chen, *Thin Solid Films* 405 (2002) 194.
- [17] A. Yamamoto, M. Adachi, A. Hashimoto, *J. Crystal Growth* 230 (2001) 351.
- [18] A.G. Bhuiyan, A. Yamamoto, A. Hashimoto, Y. Ito, *J. Crystal Growth* 236 (2002) 59.
- [19] S. Keller, I.B. Yaacov, S.P. Denbaars, U.K. Mishra, *Proc. Int. Workshop on Nitride Semiconductors., IPAP Conf. Ser. I* (2000) 233.
- [20] O. Ambacher, M.S. Brandt, R. Dimitrov, T. Metzger, M. Stutzmann, R.A. Fischer, A. Miehr, A. Bergmaier, G. Dollinger, *J. Vac. Sci. Tech. B* 14 (1996) 3532.
- [21] A. Koukitu, Y. Kumagai, N. Kubota, H. Seki, *Phys. Stat. Sol. B* 216 (1999) 707.
- [22] S. Inoue, T. Namazu, T. Suda, K. Koterazawa, *Vacuum* 74 (2004) 443.