

Properties of InN grown by High-Pressure CVD

Mustafa Alevli¹, Goksel Durkaya¹, Vincent Woods¹, Ute Haboeck³, Hun Kang², Jayantha Senawiratne¹, Martin Strassburg^{1,2}, Ian T. Ferguson², Axel Hoffmann³, Nikolaus Dietz^{1,*}

¹Georgia State University, Department of Physics and Astronomy, Atlanta, GA 30303, U.S.A.

²Georgia Institute of Technology, School of ECE, Atlanta, GA 30332, U.S.A.

³ Technische Universität Berlin, Institut für Festkörperphysik, D - 10623 Berlin, Germany

ABSTRACT

Group III-nitride compound semiconductors (e.g. AlN-GaN-InN) have generated considerable interest for use in advanced optoelectronic device structures. The fabrication of multi-tandem solar cells, high-speed optoelectronics and solid state lasers operating at higher energy wavelengths will be made possible using $(\text{Ga}_{1-y-x}\text{Al}_y\text{In}_x)\text{N}$ heterostructures due to their robustness against radiation and the wide spectral application range. To date, the growth of indium rich $(\text{In}_{1-x}\text{Ga}_x)\text{N}$ films and heterostructures remains a challenge, primarily due to the large thermal decomposition pressures in indium rich group III-nitride alloys at the optimum growth temperatures. In order to control the partial pressures during the growth process of InN and related alloys, a unique *high-pressure chemical vapor deposition* (HPCVD) system with integrated real-time optical monitoring capabilities has been developed. We report initial results on InN layers grown at temperatures as high as $\sim 850^\circ\text{C}$ with reactor pressures around 15 bar. Such process conditions are a major step towards the fabrication of indium rich group III-nitride heterostructures that are embedded in wide band gap group III-nitrides. Real-time optical characterization techniques are applied in order to study the gas phase kinetics and surface chemistry processes during the growth process.

For an ammonia to TMI precursor flow ratio below 500, multiple phases with sharp XRD features are observed. Structural analysis performed by Raman scattering techniques indicates that the E_2 high mode improves as NH_3 :TMI ratio is decreased to below 500. Optical characterization of these InN layers indicates that the absorption edge shifts from down from 1.85 eV to 0.7 eV. This shift seems to be caused by a series of localized absorption centers that appear as the indium to nitrogen stoichiometry varies. This contribution will correlate the process parameters to results obtained by XRD, Raman spectroscopy and optical spectroscopy, in order to assess the InN film properties.

INTRODUCTION

Indium rich group III-nitride compound semiconductor heterostructures in conjunction with wide bandgap $\text{Ga}_x\text{Al}_{1-x}\text{N}$ layers have many potential applications for novel devices that are of significant importance due to their large spectral tunability. Device structures based on $(\text{Ga}_{1-y-x}\text{Al}_y\text{In}_x)\text{N}$ heterostructures and related alloys will enable the fabrication of high efficiency, monolithic integrated energy conversion systems and high speed optoelectronic devices for optical communications. Presently, the growth of group III nitrides is dominated by low-

* Corresponding author: ndietz@gsu.edu

pressure deposition techniques such as organometallic chemical vapor deposition (OMCVD)[1] and molecular beam epitaxy (MBE) [2,3], relying on off-equilibrium growth conditions to stabilize and the control the growth process. This narrows the process parameter window and limits the temperature regime and the control of gas constituents, which is a challenge for the growth of high quality indium rich group III-Nitride alloys such as InGaN. At present, many of the fundamental properties of the InN compound itself are still in debate[4,5] such as band gap, lattice constants, effective electron mass and the influence of the intrinsic materials point defect chemistry on the optical and electrical properties[6]. The effects of extrinsic impurities such oxygen on the band gap [7,8] is currently being discussed as the origin of the wide variations in the measured physical properties of InN.

In order to understand and optimize the properties of InN and indium-rich alloys, new approaches for gaining insights and controlling the vastly different partial pressures in indium rich group III-alloys are required[6]. High-pressure chemical vapor deposition (HPCVD)[9] is unique technique, specifically development to stabilize compounds with large differences in the partial pressures as encountered in the growth of InN and related materials. HPCVD utilizes reactor pressures up to 100 bar in order to counteract the decomposition of constituents and thereby stabilizes the surface at optimum growth temperatures. This is essential for controlling the point defect chemistry in indium-rich group III-nitride alloys. We have previously demonstrated a successful suppression of InN decomposition for growth temperatures at around 850K-1100K[9,10], which is a major step toward the growth of indium-rich group III-nitride heterostructures. The main advantages of this method are

- (a) *the extended parameter space (e.g. precise control of precursor ratio, partial pressures, temporal separation of constituents, reactor pressure, or temperature) allows to explore and optimize the growth of InN in a process regime not accessible before,*
- (b) *the implemented real-time optical diagnostics in the HPCVD provide crucial insight and understanding in to the gas phase and surface chemistry processes that govern the growth of InN and indium-rich group III nitrides alloys;*
- (c) *the implemented precursor injection scheme enable the precise control and optimization of the gas phase reactions.*

In this contribution, initial results on the structural and optical properties of InN layers grown by HPCVD are reported.

EXPERIMENT

A high-pressure flow channel reactor with incorporated real time optical characterization capabilities is utilized to study and optimize InN nucleation and growth. Ammonia (NH₃) and trimethylindium (TMI) are employed in a pulsed injection scheme, utilizing pulse width, precursor pulse separation, and cycle sequence time as growth control parameters. The pulsed precursors are embedded in a high-pressure carrier stream (ultra-pure nitrogen) and injected in the reactor utilizing a temporally controlled gas injection system. The total gas flow through the reactor as well as the reactor pressure are kept constant at all times during the growth. Ultraviolet absorption spectroscopy (UVAS) is applied in order to monitor the group-V and organometallic group-III precursors in the gas phase perpendicular to the gas flow at the center axis of the substrates [12,13]. The nucleation and growth process is monitored through the backside of the substrate, utilizing the principle angle reflectance spectroscopy (PARS)[14] and laser light scattering (LLS). The InN layers discussed here were grown at a reactor pressure of

15 bar with total gas flows between 9 and 12 slm. The precursor flow ratio was evaluated for molar ratio of ammonia to TMI between 300 to 8000 and growth temperatures between 800 to 900 °C. All temperature settings refer to the calibrated correlation of the analyzed blackbody radiation as a function of the power setting of the substrate heater. The temperature is not corrected for the change in surface emissivity during the growth.

Results and Discussion

The structural properties of epitaxially InN films have been investigated using X-ray diffraction, Raman spectroscopy, and transmission spectroscopy. Figure 1 shows the variations of XRD patterns in a logarithmic scale for InN layers grown with ammonia to TMI flow ratios of 8000, 500, 330, respectively. The XRD peak centered at $2\theta = 31.28$ deg corresponds to the diffraction of hexagonal phase InN(0002) plane. As the ammonia to TMI flow ratio is decreased to 500, the InN(0002) peak slightly broadens and a second peak in close proximity to the InN(0002) peak appears at the lower angle side. A further decrease of the ammonia to TMI flow ratio down to ~ 300 leads to two sharp InN(0002) XRD peaks, as well as the an increase in the InN(101) and InN(100) peaks centered at 32.38 deg and 29.15 deg, respectively. The splitting of InN(0002) peak is observed in InN layers grown on both GaN/sapphire and sapphire substrates. The InN(101) diffraction peak positioned at 32.38 deg increases as the ammonia to TMI precursor ratio is lowered below 500, indication the formation of indium rich phases.

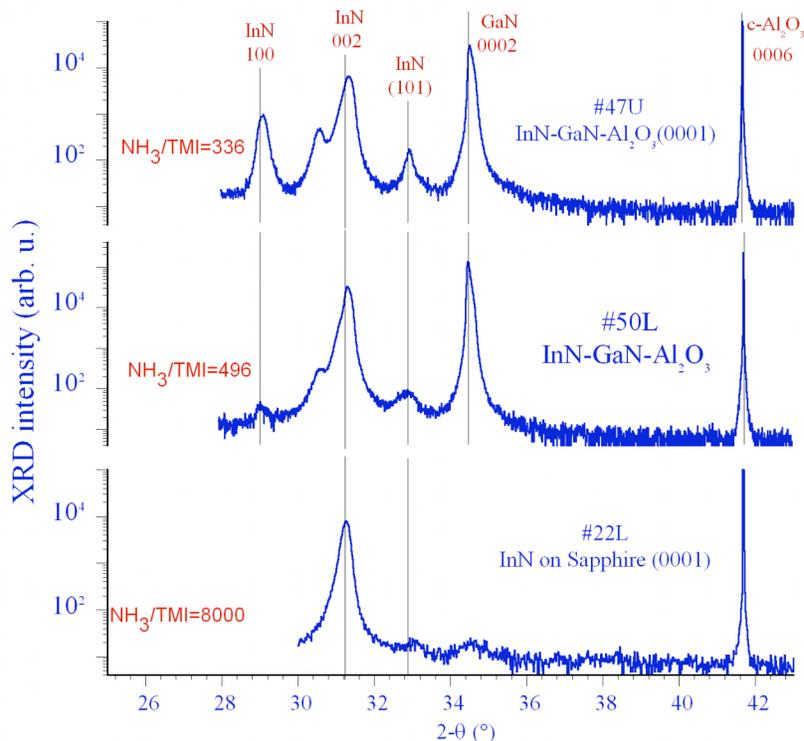


Figure 1

XRD spectra for InN layers grown on sapphire and GaN/sapphire with the various NH_3/TMI ratio

Figure 2 shows Raman spectra of InN samples grown on sapphire (22U, 39U) and GaN/sapphire substrates (47U, 50L), which were analyzed using an excitation energy of 2.33 eV. The Raman spectra are observed in backscattering configuration. All spectra are normalized to the peak

intensity of the E_2 (high) phonon feature. The three optical phonon modes of hexagonal InN at 300 K analyzed in Raman spectra are E_2 (high), $A_1(\text{LO})$, and $B_1(\text{high})$. The peak centered at wave numbers in range $489\text{-}492\text{ cm}^{-1}$ is attributed to the scattering of light from E_2 (high)-phonon modes which is most sensitive to strain [16]; whereas, the peak at 587 cm^{-1} is assigned to $A_1(\text{LO})$ phonons in InN. As depicted in Fig. 2, the $A_1(\text{LO})$ is suppressed in the spectra as the precursor flow ratio is increased. The observed peak positions are in good agreement with those found in InN layers grown by MBE and OMCVD[17]. Based on the allowed phonon mode peak positions for E_2 (high) and $A_1(\text{LO})$, our experimental peak positions are similar to the calculated value of 483 cm^{-1} and 588 cm^{-1} in Rfs.[17].

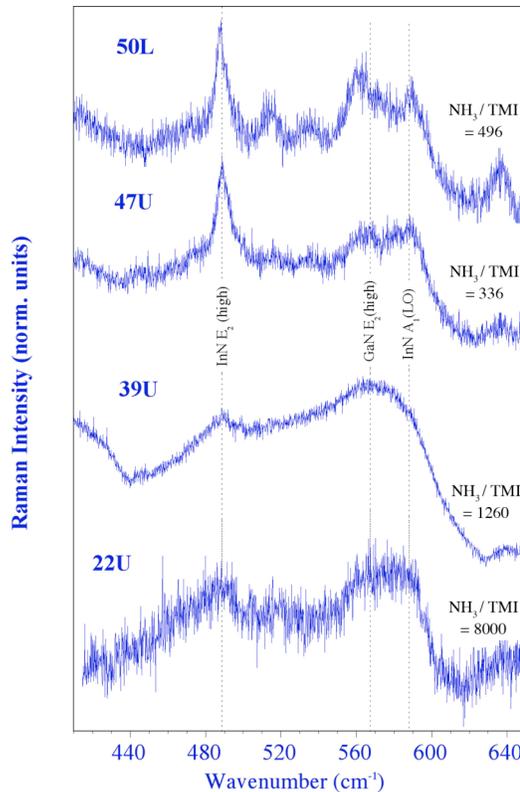


Figure 2

Raman spectra for InN layers grown on sapphire and GaN/ sapphire with the various NH_3/TMI ratio.

Figure 3 depicts the ‘full width half maximum’ (FWHM) of the E_2 (high) mode together with the FWHM of the InN(0002) XRD peak plotted as a function of the precursor flow ratio. As the flow ratio decreases to 500, the FWHM of the E_2 (high) decreases. A sharp Lorentzian shaped E_2 (high) mode along with $A_1(\text{LO})$ and $E_1(\text{LO})$ mode indicates high quality hexagonal InN. Comparison with the XRD spectra shows, however, that with decreasing ammonia to TMI flow ratio the FWHM of InN(0002) XRD peak splits in two well defined structures. At the same time the InN(101) and InN(100) phases become stronger.

Figure 4 shows the absorption spectra observed for a set of characteristic samples; #22U, #32L, #38L, and #47L. As depicted in Fig. 4, all samples show a dominant absorption structure centered at 0.63 eV. For the estimated ammonia to TMI precursor flow ratios (#22U / #32L → #38U → 47U) the absorption edge shifts downwards from an estimated 1.5 eV to approximate 0.7 eV, with absorption peaks / shoulders around 1.1 eV and 1.3 eV. The appearance and strength of these absorption centers coincide with the reduction of the ammonia to TMI precursor flow ratio, suggesting a close correlation between precursor ratio and the stoichiometry of the

deposited InN layers. The absorption peak centered at 0.63 remains constant in strength and position. This feature has recently been assigned to plasmon excitations in the conduction band[18] due to large free carrier concentrations. If this theory proves correct, it would suggest that the absorption edge shift towards lower energies is not directly related to the free carrier concentration, but rather to stoichiometry variations in InN.

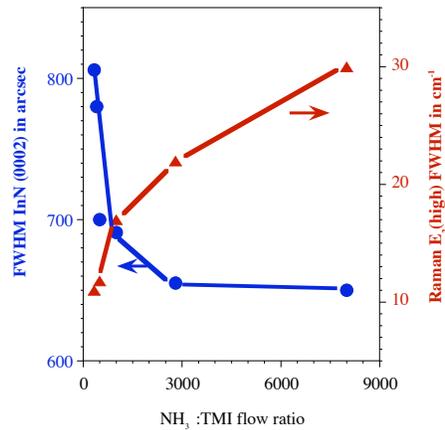


Figure 3

Correlation of Full width half maximum (FWHM) of Raman E₂(high) and of InN(0002) XRD-peak intensity as function of molar ammonia to TMI flow ratio.

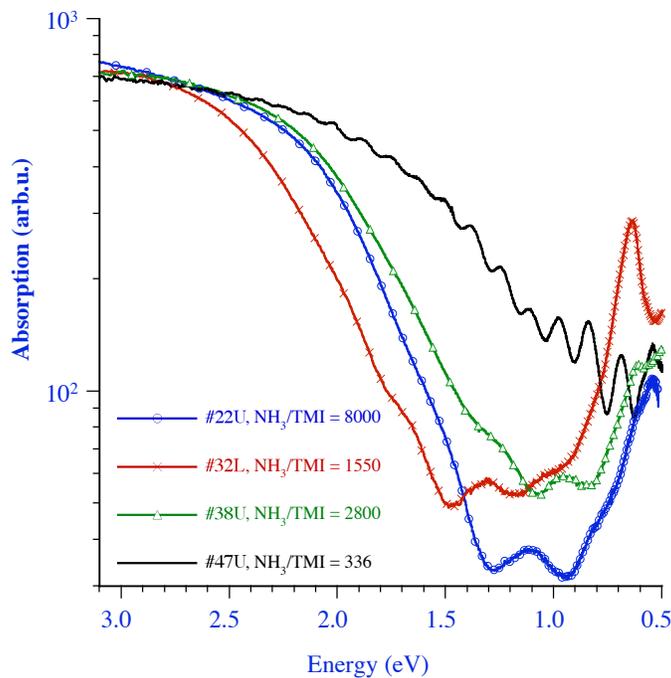


Figure 4:

Shift of absorption edge for characteristic InN samples grown with different ammonia to TMI ratio.

Summary Conclusion

XRD, Raman, and absorption spectroscopy have been used to characterize InN epilayers grown under high-pressure CVD conditions on GaN/sapphire and sapphire substrates. HPCVD has been demonstrated to be a viable technique for the growth InN and related materials that exhibit high thermal decomposition pressures. Sharp E_2 (high) and A_1 (LO) at 488 cm⁻¹, 590 cm⁻¹ phonon modes are observed with decreasing ammonia to TMI flow ratio. The XRD results show that InN grown with higher NH₃:TMI flow ratios have smaller FWHM and are single phase in structure, while for decreasing NH₃:TMI ratio multiple phases in XRD pattern are observed.

Both XRD and Raman investigations revealed high structural quality of the InN epilayers with hexagonal symmetry. The absorption spectra indicate a shift of the absorption edge below 1 eV as the NH₃:TMI flow ratio decreases. The observed shifts indicate a wide homogeneity range in InN, accommodating excess indium as well as excess nitrogen in the lattice. A precise control of growth process parameter combined with real-time process characterization is required to gain more detailed insights in the growth chemistry and the associated InN material properties.

ACKNOWLEDGMENTS

This work was supported by NASA grant NAG8-1686 and GSU-RPE.

REFERENCES

- [1] T. Schmidling, M. Drago, U. W. Pohl and W. Richter, *J. Cryst. Growth* **248**, 523-527 (2003).
- [2] T. Tsuchiya, M. Ohnishi, A. Wakahara and A. Yoshida, *J. Cryst. Growth* **220**(3) 191-196 (2000).
- [3] V.Yu. Davydov, A.A. Klochikhin, V.V. Emtsev, D.A. Kurdyukov, S.V. Ivanov, V.A. Vekshin, F. Bechstedt, J. Furthmüller, J. Aderhold, J. Graul, A.V. Mudryi, H. Harima, A. Hashimoto, A. Yamamoto, E.E. Haller, *Physica Status Solidi B*, **234**(3) 787-795 (2002).
- [4] T. Inushima, V. V. Mamutin, V. A. Vekshin, S. V. Ivanov, T. Sakon, M. Motokawa, and S. Ohoya, *J. Crystal Growth* **227-228** pp. 481-485 (2001).
- [5] V. Yu. Davydov and A. A. Klochikhin, *Semiconductors* **38**(8), 861-898 (2004).
- [6] A. G. Bhuiyan, A. Hashimoto, and A. Yamamoto, *J. Appl. Phys.* **94**(5), 2779-2808 (2003).
- [7] E. Kurimoto, M. Hangyo, H. Harima, M. Yoshimoto, T. Yamaguchi, T. Araki, Y. Nanishi, K. Kisoda, *Appl. Phys. Lett.* **84**(2), 212-214 (2004).
- [8] K.S.A. Butcher and T.L. Tansley, *Superlattices and Microstructures* **38**(1), 1-37 (2005).
- [9] "*Indium-nitride growth by HPCVD: Real-time and ex-situ characterization*," N. Dietz, book chapter 6 in "*III-Nitrides Semiconductor Materials*", ed. Z.C. Feng, Imperial College Press (ICP) pp. 203-235 (2005).
- [10] N. Dietz, M. Alevli, V. Woods, M. Strassburg, H. Kang, and I. T. Ferguson, *phys. stat. sol. (b)* **242**(15), 2985-2994 (2005).
- [11] N. Dietz, M. Alevli, H. Kang, M. Straßburg, V. Woods, I. T. Ferguson, C. E. Moore and B. H. Cardelino. *Proc. SPIE Vol. 5912*, ISBN 0-8194-5917-8, pp. 78-85 (2005).
- [12] G. A. Hebner, K. P. Killeen and R. M. Biefeld, *J. Crystal Growth*, **98**(3) 293-301 (1989).
- [13] M. C. Johnson, K. Poochinda, N. L. Ricker, J. W. Rogers Jr. and T. P. Pearsall, *J. Crystal Growth* **212**(1-2), 11-20 (2000).
- [14] N. Dietz, V. Woods, S. McCall and K.J. Bachmann, *Proc. Microgravity Conf. 2002*, NASA/CP-2003-212339, 169 -181 (2003).
- [15] N. Dietz, M. Strassburg and V. Woods, *J. Vac. Sci. Technol. A* **23**(4), 1221-1227 (2005).
- [16] V. Y. Davydov, V. V. Emtsev, I. N. Goncharuk, A. N. Smirnov, V. D. Petrikov, V. V. Mamutin, V. A. Vekshin, S. V. Ivanov, M. B. Smirnov and T. Inushima, *Applied Physics Letters* **75**, 3297-3299 (1999).
- [17] V. Yu. Davydov and A. A. Klochikhin, *Semiconductors* **38**(8), 861-898 (2004).
- [18] D.B. Haddad, J.S. Thakur, V.M. Naik, G.W. Auner, R. Naik, and L.E. Wenger, *Mat. Res. Soc. Symp. Proc.* **743**, L11.22 (2003).