Effect of nucleation period on the physical properties of InN epilayers

S. Gamage[1], M.K.I. Senevirathna[1], R. Atalay[1], A.G.U. Perera[1], A.G. Melton[2], I.T. Ferguson[2] and N. Dietz[1]

[1]Department of Physics and Astronomy, Georgia State University, Atlanta, GA 30303
[2]Dept. of Electrical & Computer Engineering, University of North Carolina Charlotte, Charlotte, NC 28223

ABSTRACT

The influence of structural and optoelectronic properties of InN epilayers on the duration of initial nucleation has been studied. High pressure chemical vapor deposition (HPCVD) has been utilized to deposit InN epilayers on GaN/sapphire (0001) templates at a reactor pressure of 15 bar. The initial nucleation period was varied between 10 s and 60 s, leaving all other growth parameters constant. The structural properties of the grown samples have been investigated by X-ray diffraction (XRD) spectroscopy and Raman spectroscopy. The optoelectronic properties were analyzed by Fourier transform infra-red (FTIR) spectroscopy. The layer thickness, free carrier concentration and void fraction were obtained by simulating IR spectra, using multi-layer stack model for epilayers and Lorentz-Drude model for dielectric function. Raman, X-ray diffraction (XRD) and void fraction calculation results suggest that the optimum nucleation time is between 10 - 20 s. However, simulation results revealed that the free carrier concentration of the bulk layer does not show any significant dependency on the duration of initial nucleation.

Keywords: Indium Nitride (InN), nucleation layer, high pressure chemical vapor deposition (HPCVD), Raman spectroscopy, pulsed precursor injection

*gamage@phy-astr.gsu.edu; phone (404) 413 6038; fax 404 413 6025; http://www.phy-astr.gsu.edu/dietz

1. INTRODUCTION

Due to the possession of the smallest electron effective mass, and the highest mobility among the group III nitride family, InN has become one of the materials under extensive exploration in the semiconductor research community, with the intention of improving the quality of InN and In rich III-nitride materials to fabricate optoelectronic devices such as terahertz emitters and detectors[1], high speed switching devices[2,3], high efficiency energy converters[4], and high performance chemical sensors[5]. InN structures of reasonably good physical quality for device fabrication grown by various low pressure growth techniques such as OMCVD and MBE with or without modifications have been reported[6-9] in recent literature. However, low dissociation temperature of InN at low pressures and the larger difference in partial pressures of nitrogen and group III species restrict the low pressure growth techniques to a very limited growth regime. In addition, the unavailability of lattice matching native substrate materials makes the growth of InN and all III-nitride structures more complicated.

In the HPCVD approach[10,11], super-atmospheric nitrogen (N_2) gas is utilized to mitigate the dissociation of InN at elevated growth temperatures. This enables to increase the growth temperature up to ~ 870 °C by increasing the reactor pressure up to ~20 bar[12]. In this higher growth temperature range, the surface migration of the precursor species and decomposition rate of ammonia precursor[10] are also enhanced. In order to avoid the gas phase reactions of precursors above the growth surface at these higher pressures, precursors are injected alternatively into the growth chamber[11,13]. The real time monitoring tools coupled with the HPCVD system enable to observe the sub-monolayer level changes in the growth surface and the decomposition processes of the precursors during the growth process by means of scattering and principle angle reflection of laser, and UV absorption[11].

Several studies of the initial nucleation of InN at low growth pressure conditions have been reported in literature, particularly using MOCVD and MBE techniques. However, to authors' knowledge, there were no studies reported on the initial nucleation process under super-atmospheric growth conditions. In this study, the dependence of structural and optical properties of InN epilayers grown at 15 bar on GaN/sapphire templates by HPCVD has been investigated. All samples were characterized by Raman spectroscopy, x-ray diffraction (XRD) spectroscopy and infra-red reflection spectroscopy.

2. EXPERIMENTAL DETAILS

In order to study the effect of initial nucleation period, a set of four samples grown with initial nucleation durations of 10, 20, 40 and 60 s were analyzed. The growth profile for each sample with temperature and precursor variations is shown in Fig. 1(a); the initial nucleation period is denoted by t_n.

Trimethylindium (TMI) and ammonia (NH_3) have been used as the group III and V precursors, respectively. All the InN epilayer samples analyzed in this study have been grown at 15 bar by HPCVD on GaN/sapphire substrates. In order to avoid gas phase reactions in the reactor chamber, TMI and NH_3 are embedded into a nitrogen carrier gas stream and they are injected alternately by pulsed injection scheme, maintaining a constant reactor pressure throughout the entire growth process. As shown in Fig. 1(b), in the pulsing sequence used for the injection of precursors into the reactor chamber, TMI and NH_3 pulse durations were set to 800 and 2000 ms, respectively. Pulse separation between TMI and NH_3 , s_1 was 1650 ms and a separation of 350 ms, s_2 was kept between NH_3 and TMI. The gas flow velocity above the sample surface was kept constant. All samples were grown at a temperature of ~850 °C. Total gas flow through the reactor during the growth was kept constant at 12 slm. At steady state growth, TMI flow was 1000 sccm and NH_3 flow was 1200 sccm leaving the V/III molar ratio at 2400.
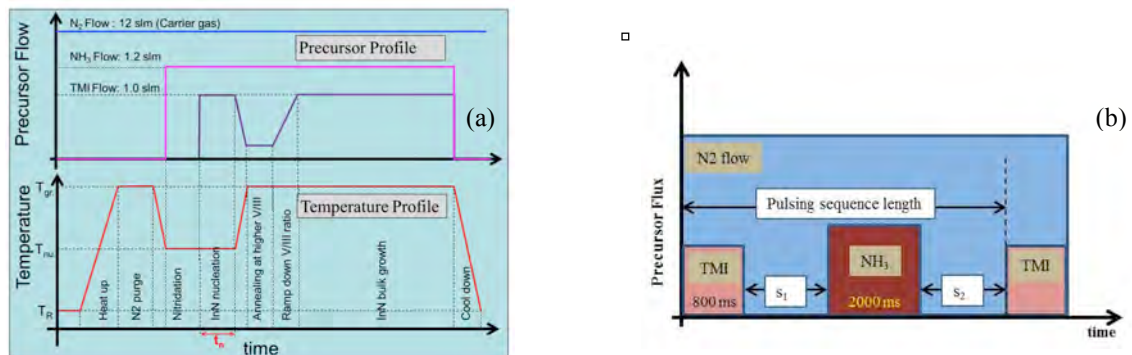

Fig. 1. Schematic diagrams for temperature and precursor profile for the growth process (a) and precursor pulse timing (b).

The GaN/sapphire substrate loaded in the reactor chamber was first thermally cleaned in a N_2 flow at growth temperature. Then, before the growth of low temperature nucleation layer of InN for time t_n, as depicted in Fig.1 (a), the substrate surface was nitridized for two minutes at low nucleation temperature. (For the four samples analyzed in this study, t_n = 10, 20, 40 and 60 s). Next, temperature was gradually raised to the steady state growth temperature while increasing the V/III ratio to ~12000 by lowering the TMI flow and kept for 2 minutes to anneal the nucleation layer. Then, the TMI flow was gradually increased so that the V/III ratio was dropped down to ~2400 for the steady state growth. The optimization study of the V/III ratio for InN growth will be published elsewhere[14]. Finally, the reactor chamber was cooled down to room temperature.

The structural properties of the epilayers were probed using Raman and XRD spectroscopy and the FTIR spectroscopy was utilized to investigate the optical and electrical properties. In order to extract the dielectric function, layer thickness, and free carrier concentration, the IR spectra were simulated using the multilayer stack model and Lorentz-Drude model. Void fraction was calculated using the dielectric function obtained from the simulation results.

3. RESULTS AND DISCUSSION

Figure 2 shows a nonlinear behavior of the FWHM of both Raman E_2(high) vibration mode and XRD Bragg reflexes with the nucleation time. However, Fig. 2(a) and (b) suggest that the local and long range crystalline quality show an inverse correlation. When the duration of low temperature nucleation increases, three dimensional growth becomes dominant over epitaxial growth. This results in creating a higher point defect density causing extended defects degrading the long range ordering of the structure as depicted in Fig. 3. However, local ordering of the structure remains

less affected by this phenomenon. The set temperatures for gas phase and the substrate may cause this tendency. A detailed study on the effect of the temperature distribution of the gas phase and the substrate is yet to be performed for HPCVD growth technique.
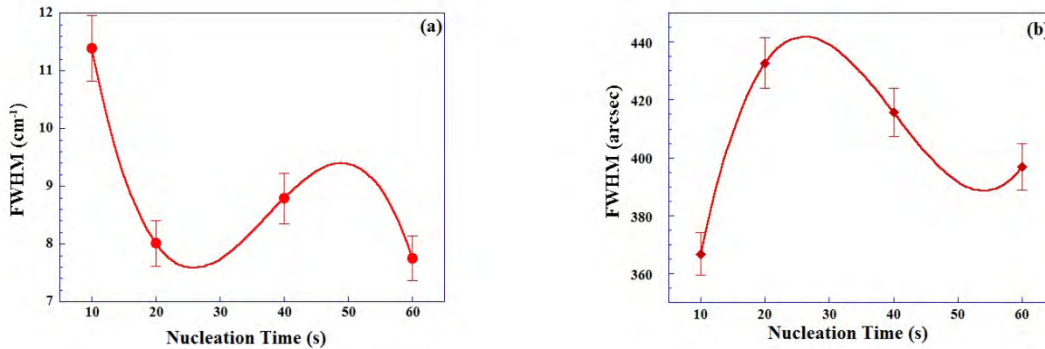

Fig. 2. Dependence of the local and long range ordering on the duration of initial nucleation. FWHM values of Raman E_2(high) mode (a) and XRD Bragg reflexes (b).

The initial stage of the nucleation is very crucial to obtain epitaxial growth of a high quality film. The layer thickness, effective dielectric constant, free carrier concentration and void fraction, the IR spectra obtained in near normal incidence (~8°) configuration at room temperature using a Perkin-Elmer FTIR spectrophotometer, in the spectral range of 450-7000 cm^{-1} were simulated using the multilayer stack model and Lorentz-Drude model.
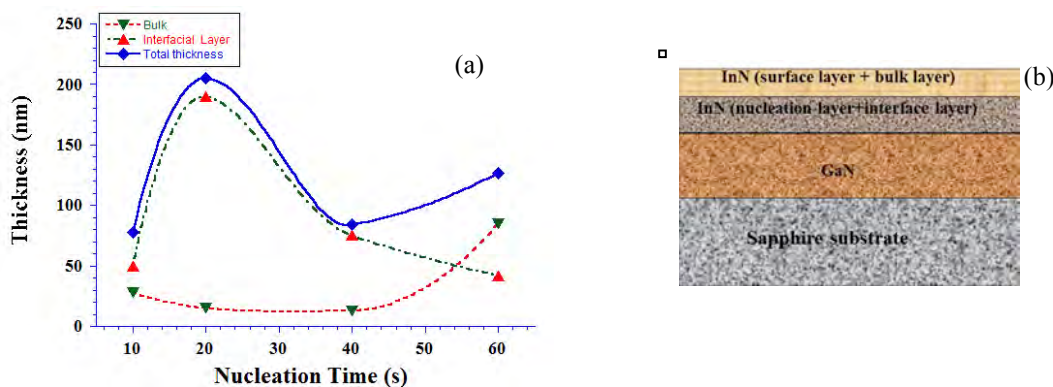

Fig. 3. Variation of the layer thickness with nucleation time (a) and a schematic of the multi-layer stack model used in simulation of IR spectra (b).

A schematic diagram of the multilayer stack model is shown in Fig. 3(b). A defect rich InN interfacial nucleation layer is grown on GaN/sapphire substrate prior to the growth of InN bulk layer. This interfacial layer relaxes the strain caused by lattice mismatch between GaN substrate and InN bulk layer. The structural strain and defect formation of the bulk layer depend on the thickness and quality of the this interfacial layer; as presented in Fig. 3(a), the samples with nucleation times in the range of 10 to 40 s show a thinner interfacial layer of less than 30 nm in contrast to the thicker interfacial layer of 75 nm obtained from the nucleation for 60 s. This correlates with FWHM values of XRD Bragg reflexes; long range ordering of the bulk layer is negatively affected by thinner interfacial layers.

The free carrier concentration, n obtained from the simulation for bulk and interfacial layers is presented in Fig. 4(a). The n value of the interfacial layer in the sample with 40 s of nucleation time is $\sim10^{21}$ cm^{-3} due to the presence of higher number of defects. This higher point defect density in the interfacial layer decreases the effective dielectric function calculated by the simulation. However, this defect rich interfacial layer enables to grow a strain relaxed bulk layer on top of it with lower free carrier concentration.
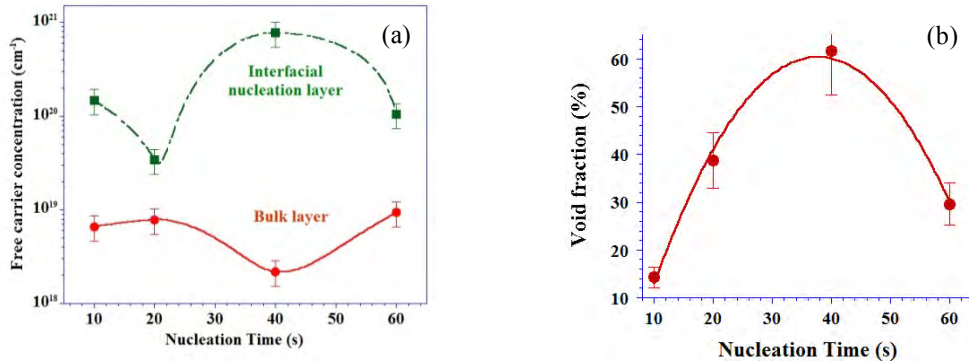

Fig. 4. Dependence of the free carrier concentration of bulk and interfacial layers (a) and void fraction on the duration of initial nucleation. FWHM values of Raman E_2(high) mode (a) and XRD Bragg reflexes (b).

The free carrier concentration of bulk region is not significantly improved by the nucleation, as shown in Fig. 4(a). The void fraction of each sample is calculated according to the ref. [15]. Higher void fraction can be seen at 40 s nucleation time sample. Calculated void fraction is presented as a function of nucleation time in Fig. 4(b). Figures 2(b) and 4(b) reveal that there is a direct correlation between the long range ordering and void fraction. .

4. Summary

A series of InN layers was grown by HPCVD with various nucleation times from 10 to 60 s. The nucleation layers where afterwards overgrown for 3 hours under identical conditions in order to evaluate the influence of the nucleation growth. The epilayers were characterized using Raman spectroscopy, XRD and FTIR spectroscopy. The physical properties such as layer thickness and interfacial layer properties were obtained by simulating the IR spectra using a multi-layer stack model. XRD results show the best crystalline quality is obtained with thinner nucleation layer corresponding to shorter nucleation time of 10 s. The estimated void fraction shows a compact overgrowth with a fairly large defect-rich nucleation layer. For a nucleation time of 20 s, the growth process improves with higher growth rate, better local ordering and smaller interfacial nucleation layer. However, the increase in the void fraction and FWHM of the InN Bragg reflex indicate a more 3-D growth mode behavior. For even longer nucleation times - larger than 20 s - no significant improvement in the InN bulk layer properties was observed.

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