Reactor pressure - growth temperature relation for InN epilayers grown by high-pressure CVD

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Abstract

Results on the achievable growth temperature as a function of the reactor pressure for the growth of InN by high-pressure CVD are presented. As the reactor pressure was increased from 1 bar to 19 bar, the optimal growth temperature raised from 759°C to 876°C, an increase of 6.6 °C/bar. The InN layers were grown in a horizontal flow channel reactor, using a pulsed precursor injection scheme. The structural and optical properties of the epilayers have been investigated by Raman spectroscopy, X-ray diffraction, and IR reflectance spectroscopy.

Keywords: high-pressure CVD, HPCVD, InN, epitaxy, In-rich, MOCVD, growth temperature

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1. Introduction

The growth of indium rich materials as well as InN and its integration into heterostructures will allow the tuning of the band gap in the III-nitrides from UV all the way through the visible spectrum into the IR range. A whole variety of applications from monolithic multi tandem solar cells to color changing light emitters as well as high power high temperature electrical transistors have been proposed.

In recent years a significant progress has been made in the field of synthesizing group III-nitride compound semiconductor alloys. The wide band gap portion of group III-nitrides - especially that of GaN (3.4eV) and its ternaries with aluminum (3.4 - 6.1eV) as well as InGaN with low indium fractions (~2.3 - 3.4eV) - are already being utilized in commercial devices such as light emitting diodes, laser diodes and photo detectors. It has been shown that the growth of

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high quality crystal films can be accomplished by various techniques such as molecular beam epitaxy (MBE), metal organic vapor phase epitaxy (MOVPE) also known as metal organic chemical vapor phase deposition (MOCVD), and high-pressure chemical vapor deposition (HPCVD). Thicker epilayers can be deposited, for instance by hydride vapor phase epitaxy (HVPE), which allows significantly higher growth rates at the cost of slightly reduced crystalline quality [1]. As the indium content in InGaN increases the growth temperature has to be significantly reduced due to lowered decomposition temperature of the InN portion in the material caused by an increase of the nitrogen decomposition rate in the hot reaction layer. On the other hand there is an increasing interest and demand for indium rich materials due to the low band gap of 0.7eV in InN. The growth of high quality InN has been demonstrated by MBE and MOCVD under low-pressure conditions and growth temperatures below 600°C[2, 3]. Such a growth temperature is significantly lower compared to other group III-nitrides like GaN (1080°C, [4]) and InGaN (750°C-1000°C, depending on the growth technique and materials composition [5]). The lower growth temperature for indium rich materials is explained by a significantly increased vapor pressure of nitrogen above the hot growth surface of the film due to decomposition and outgassing of the nitrogen. This makes the incorporation of such films into heterostructures difficult since ramping up the growth temperature for the growth of wider band gap material in order to reach an electrical confinement leads to the decomposition of the already grown indium rich material.

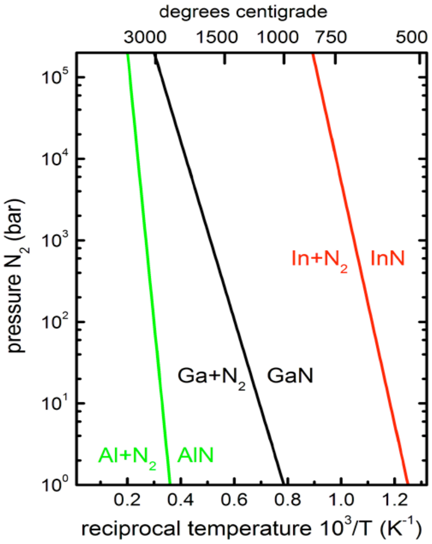

Figure 1: Thermal decomposition pressure vs. reciprocal temperature for III-nitride binaries under thermodynamically equilibrium conditions.(after MacChesney et al. [6])

The stabilization of InN and indium-rich group III-nitride alloys at higher growth temperatures has several advantages. First, a higher growth temperature alters the point defect chemistry, leading to potential improved crystallinity of the layer. A second reason is the integration of indium-rich ternary and quaternary group III-nitride heterostructures at a common processing temperature. The approach taken in our research group at Georgia State University is to explore the growth in indium-rich group III-nitrides by high-pressure Chemical Vapor Deposition (HPCVD). The approach follows theoretical predictions by MacChesney et al. [6], whose thermodynamic equilibrium calculations suggest that the utilization of high pressure nitrogen can stabilize InN at significant higher growth temperatures as shown in Fig. 1.

In the HPCVD growth reactor, the group III and group V precursors are injected temporally controlled in the reaction zone to prevent gas phase reactions and to control the growth surface chemistry. The precursors are embedded into a high-pressure carrier gas stream, which maintains the pressure in the reactor zone at all times. The pulsed injection scheme implemented in the HPCVD growth system introduces new growth parameters such as the duration of each precursor's injection and separation times between the precursor pulses, which provide additional flexibilities to optimize the growth process.

2. Experimental Details

The samples analyzed and discussed here have been grown by HPCVD in the pressure range of 1 to 19 bar. The HPCVD system is equipped with optical access ports for real-time Laser Light Scattering (LLS), Principle Angle Reflection spectroscopy (PARS) and UV Absorption Spectroscopy (UVAS) analysis to investigate the surface roughness, growth rate and the precursor decomposition kinetics, respectively. Two substrates can be placed in the reactor zone at the upper and the lower side of the flow channel, both of which are heated independently. Further details on the HPCVD growth system are given elsewhere [7-10].

All samples discussed here were grown on GaN templates on sapphire except the sample at 19 bar which was grown directly on sapphire. The reactor pressure was varied from 1 to 19 bar and the substrate temperatures were 759°C to 876°C. The opposite heater - on the top side of the reactor zone - was varied between 478°C and 751°C and was utilized to adjust the gas phase temperature independently. This arrangement allows the control of the decomposition of the precursors in the reactor zone and thus control of the diffusion process of the active precursor fragments to the growth surface. The V/III molar flow ratio of the precursors was kept constant at 7500 for all the samples, except for the samples grown at 15 bar and 19 bar for which a V/III-ratio of 3000 was used. The reduction of the V/III ratio at higher pressures is due to improved cracking efficiency of the ammonia precursor [10] and an assumed reduced loss rate of nitrogen out of the growing film. The carrier gas flow was adjusted according to the growth pressure such that the overall flow velocity within the reactor zone is kept constant.

The grown epilayers have been characterized by X-ray diffraction (XRD). The IR reflection measurements were performed at room temperature on a Perkin-Elmer Fourier-transform infrared spectrometer with an HgCdTe (MCT) detector and KBr beamsplitter for the range of 400-7000cm^{-1} under the near-normal incidence geometry (less than 8° incidence angle). The Raman spectra of the InN layers were obtained unpolarized in backscattering geometry along the [0001] crystal orientation of the film using excitation energy of 2.33 eV at room temperature.

3. Results and Discussion

As depicted in Fig. 2, the 2Θ-ω XRD analysis of the layers grown on GaN templates showed one (0002) XRD Bragg reflex related to the single InN phase, while layers directly grown on sapphire show an additional weak Bragg reflex at 33° which has been assigned to a nucleation related (01-11) InN phase [11] along the InN-sapphire interface. The FWHM of the InN (0002) reflexes of all samples but the one grown at 5 bar are in the range of 390 to 680 arcsec. The one grown at 5 bar showed a slightly higher value of 790 arcsec (Fig.3). As shown for InN epilayers grown at 15bar [12], the crystalline quality for the present InN epilayers can be improved.

The epilayers grown on GaN/sapphire templates show for the particular geometry expected Raman modes at 488cm^{-1} and 593cm^{-1}, which are assigned to E_2(high) and A_1(LO) Raman modes respectively. InN layers directly grown on sapphire show in addition very weak signals assigned to the A_1(TO) and E_1(TO) Raman modes at 449cm^{-1} and 472cm^{-1} respectively. These modes are forbidden in the used Raman geometry and are most likely due to the tilted facets in the nucleation layer along the interface to the sapphire substrate. The FWHM of the E_2(high) modes observed varied between 8.6cm^{-1} and 14.5cm^{-1}. For a further increase of crystalline quality, growth parameters such as the precursor pulse injection timing [13] for each pressure as well as usage of particular substrate templates [14] with controlled surface polarity have to be explored.

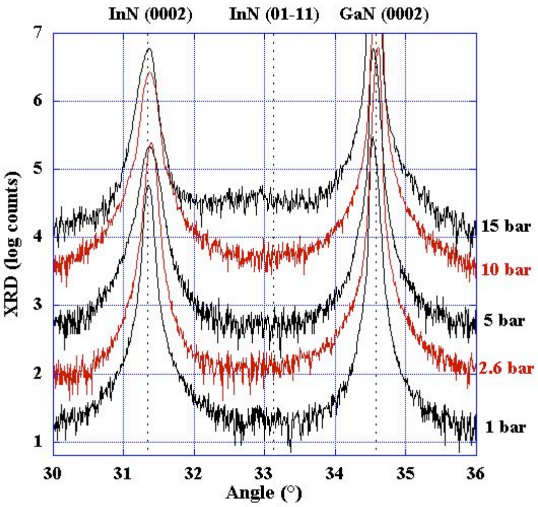

Figure 2: 2Θ-ω XRD spectra of InN films grown on GaN templates at 1 to 15 bar pressure at growth temperatures between 766°C to 854°C, respectively

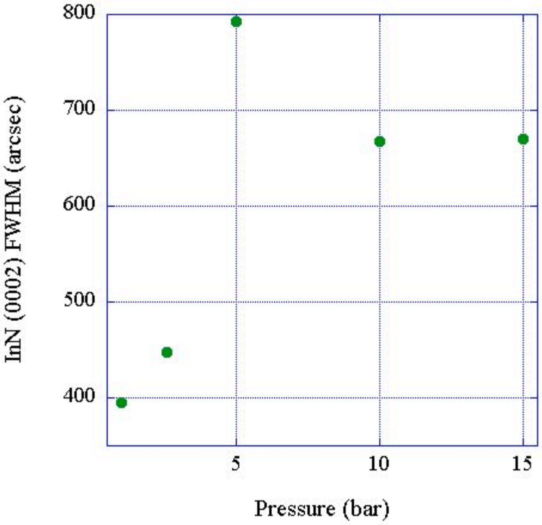

Figure 3: FWHM of InN (0002) Bragg reflexes in 2Θ-ω scans plotted vs. reactor pressure

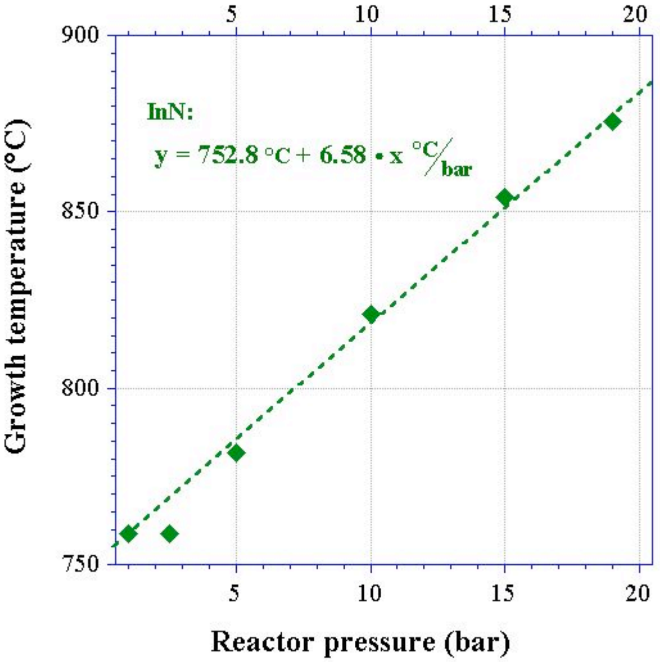

Figure 4: Reactor pressure vs. growth temperature for the growth of InN by HPCVD

Depicted in Fig. 4 are optimum growth temperatures as a function of the reactor pressure. The optimum growth temperature for each reactor pressure was established based on the structural properties of the epilayers as evaluated by Raman and XRD for the evaluated processing parameter stated above. Note that critical process parameters such as V/III molar precursor ratio, precursor pulse exposure times and pulse separation have been kept constant in this study, parameters which remain to be evaluated in further studies and which might lead to a revision of the optimum process conditions. As shown in Fig. 3, the optimum growth temperature increases linearly by about 6.6 °C/bar, enabling an increase on the growth temperature of more than 120°C if the reactor pressure increased from atmospheric pressure to 19 bar.

4. Conclusion

The structural quality of InN epilayers grown at super-atmospheric reactor pressures in the range of 1 bar to 19 bar has been studies as function of growth temperature. It has been shown that the optimum growth temperature increases linearly from 752°C at atmospheric pressure to 833°C at 19 bar reactor pressure. For the evaluated process parameter set, no significant improvement in the crystalline structure of the epilayers was found, however the growth surface can be stabilized at significantly higher growth temperatures. Further studies in an extended process parameter space are needed to improve the crystalline quality of the InN epilayers. We showed that HPCVD enables the growth of high quality InN at significantly increased growth temperatures, which is critical for the integration of InN epilayers into gallium-rich $In_{1-x}Ga_xN$ heterostructures. Utilizing the established reactor pressure growth temperature relationship will allow an estimate on the required reactor pressure to match the growth temperatures of device heterostructures with different group III-Nitride alloy compositions.

5. Acknowledgment

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