Real-time optical monitoring of gas phase dynamics for the growth of InN at elevated pressures

N. Dietz[*] , H. Born, M. Strassburg and V. Woods
Department of Physics & Astronomy, Georgia State University, Atlanta GA 30303
[*]ndietz@gsu.edu

ABSTRACT

The request for increased performance in high-power / high-frequency optoelectronic devices requires new methods for the fabrication of high quality III nitride alloys that exhibit large thermal decomposition pressure such as InN and related materials. To extend the process and growth window towards elevated pressures, a high-pressure CVD system with integrated real time optical characterization techniques has been constructed. The built-in real-time monitoring techniques allow the characterization of gas flow dynamics, precursor decomposition kinetics, as well as the monitoring of the crucial steps of nucleation and film formation. The gas flow dynamics has been characterized and the process parameter are obtained under which the thin film growth process can be maintained under laminar flow condition. Laser light scattering (LLS) has been proven as the most robust optical tool to characterize the onset of turbulence.

INTRODUCTION

InN is a semiconductor material that is intensively considered for applications in optical devices based on AlN-GaN-InN alloys and heterostructures, since this material system may provide active optoelectronic devices in the blue and ultraviolet spectral regions capable of operating at high power levels, high temperatures and in harsh environments. High quality Ga-rich epilayers of $Ga_xIn_{1-x}N$ can be fabricated successfully[1-3] by traditional low pressure chemical vapor deposition (CVD) methods where the influence of flow dynamics on growth conditions are minimal. However, low-pressure deposition processes are limited to a regime where the partial pressures of the constituents do not differ vastly and the decomposition process can be countered by off-equilibrium process conditions. Off-equilibrium conditions such as employed in MBE and organometallic CVD growth of InN require low growth temperature to overcome the thermal decomposition pressures, which limits the quality of InN and In rich $Ga_xIn_{1-x}N$ epilayers[4-6]. Due to the low growth temperatures, extremely high V-III ratios have to be applied to prevent the formation of metal droplets on the surface. New approaches for the growth of In-rich $Ga_xIn_{1-x}N$ have to be explored, in order to obtain more accurate structural and optical properties of InN[7] and related alloys. The approach taken here is to utilize a CVD growth process at elevated pressure in order to stabilize the surface of InN at optimal processing temperatures. A high background pressure of nitrogen has been shown to stabilize the surface of InN at elevated temperatures[8] but has not yet been incorporated into a CVD growth scheme. Expanding the processing window for the growth of InN towards higher pressures (1 - 100 bar) may allow the growth at higher temperatures, leading to an improved crystalline quality and providing a closer match to the optimal processing temperature of InN.

However, the growth in an elevated pressure regime requires an assessment of the thermodynamic driving force and kinetic limitations of growth for understanding and optimization of high-pressure organometallic chemical vapor deposition (HPCVD) processes. The maintenance of laminar flow conditions during CVD growth is also crucial in order to provide homogeneous growth conditions.

In order to gain insights in the growth dynamics under elevated pressures, we designed and constructed a high-pressure flow channel reactor system for the growth of group III-nitrides that incorporates real time optical characterization capabilities[9-12]. At higher pressures, only optical diagnostic techniques can provide real time information pertaining to gas flow dynamics, allowing the characterization of laminar and turbulent flow regimes. Optical diagnostics will also be utilized to obtain relevant information on the precursor decomposition kinetics. In the following we describe the high-pressure reactor system and the real time optical technique proven to be most robust and valuable in the characterization of the gas flow conditions in the flow channel reactor. The characterization of the gas flow dynamic in the reactor is presented and analyzed with respect of flow and pressure in order to determine the process parameter under which laminar flow can be maintained.

HIGH-PRESSURE FLOW CHANNEL REACTOR SYSTEM

Utilizing elevated pressures for the growth of group III-nitrides, requires a complete new reactor system design. Based on the result of flow simulations[9-11] a flow channel reactor geometry as depicted in **Fig. 1a** has been utilized. The inner reactor cylinder consists of two halves that form a squared flow channel. Symmetrically arranged, each half has a substrate embedded in a ceramic plate (α-Al_2O_3) that is heated from the back side. Utilizing such an arrangement, a deposition on the opposite reactor wall and be avoided and heat induced turbulence above the substrate surface can be reduced. The reactor channel height is 1 mm, accounting for the reduced precursor diffusion length at elevated pressures and optimized use of the gases. In order to minimize flow induced turbulence in the reactor, a constant cross section is maintained from gas inlet (circular cross section), throughout the reactor (squared cross section: 50 mm x 1mm), and the reactor exit (circular cross section). The inner reactor cylinder slides in a second, outer cylinder (dia. 6”, length=12”) that can be pressurized up to 100 bar. This outer cylinder has inserted double o-ring seals (corrosive resistant) for each of the openings that hold the reactor pressure against atmospheric pressure.

Along the centerlines of the two substrates, perpendicular to the flow direction, optical access ports are integrated in the flow channel reactor as schematically depicted in **Fig. 1b**. The optical ports allow the probing of the gas phase dynamics and chemistry, while the three ports entering through the back side of the substrate allow the monitoring of growth surface, film growth, and scattering processes from the gas phase.

Gaining a detailed insight in the growth kinetics at elevated pressure has to analyze each step critical to the growth process. Maintaining laminar flow is crucial in order to provide a consistent supply of precursor constituents that allows the correlation of gas phase constituent concentrations to the diffusion process and to the surface chemistry processes which drive the thin film growth. Therefore, the first task that has to be addressed is to establish the process conditions under which laminar flow can be maintained. To characterize the gas flow dynamics, two real time optical characterization techniques were utilized simultaneously; laser beam profile analysis and laser light scattering (LLS). As schematically illustrated in F**ig. 2a**, laser light was focus through an optical access port at the center of the flow channel. The transmitted beam passes through an exit rod and its beam profile was analyzed via a CCD array. Simultaneously, a photo-multiplier tube was employed to monitor the forward component of LLS. The picture in F**ig. 2b** shows the laser light focused on the optical entrance port of the HPCVD reactor.

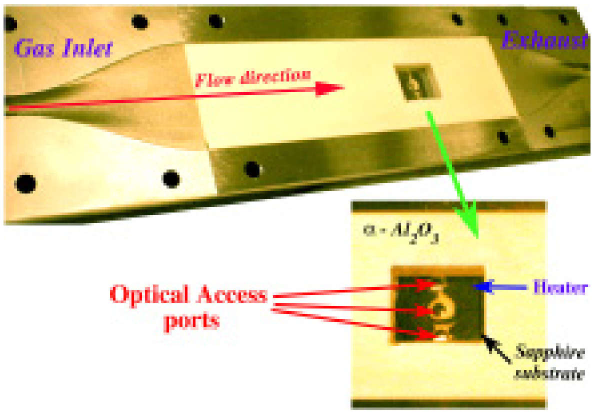

Figure 1a: Half of the reactor flow channel assembly showing flow direction. The flow channel is designed with a constant cross sectional area for the maintenance of laminar flow. The sapphire substrate is seen along center axis of flow and is held in two α-Al_2O_3 plates.

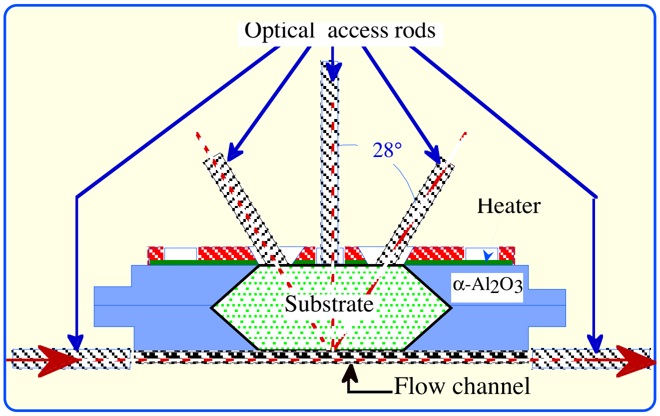

Figure 1b: Schematic cross section of the inner flow channel reactor containing the optical access ports and the center of the substrates. Two optical ports provide access to the flow channel and three ports in each of the two half sections of the reactor provide access to the growth surface.

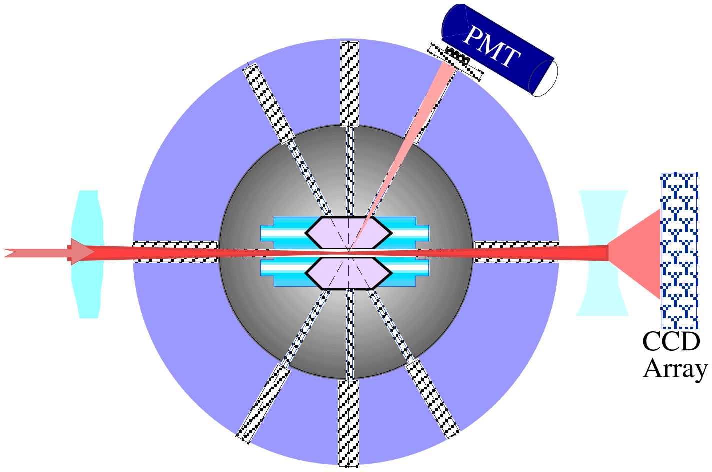

Figure 2a: Schematic cross section showing the optical access ports utilized to characterize the gas flow dynamics. The direct transmitted beam profile and the forward scattered laser light intensity were analyzed using a CCD camera and a photo multiplier tube (PMT), respectively.

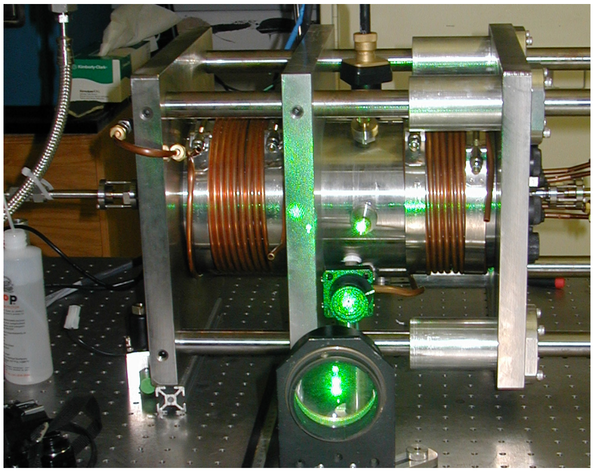

Figure 2b:View at the HPCVD reactor along the optical monitoring axis, perpendicular to the reactor flow channel.

To analyze the gas flow dynamics, the flow rates were varied from 3 slm to 21 slm for a given constant reactor pressure. The experiments were repeated for a series of pressure. The optical monitoring experiments were performed for both increasing and decreasing flows.

RESULTS

Image analysis of the laser beam profile showed variations induced in the laser beam intensity by microscopic imperfections in the fused Silica rods uses as optical access ports. These imperfections introduced an additional broadening in the laser beam profile that are superimposed to the beam broadening expected for turbulent flow conditions. The error bars obtained from the beam profile analysis for different flows and pressures suggest that this technique is not a reliable and robust enough to characterize the gas flow condition. The analysis of the simultaneous monitored LLS intensity as function of flow rates and pressures showed surprisingly good results, allowing to focus solely on LLS analysis for the characterization of the gas flow dynamics. As an example, **Fig. 3** shows the LLS intensities collected under constant pressure (9 bar) conditions and flow rates varied between 3 slm and 21 slm. The LLS intensity remains constant for flow rates below a critical point of approximately 7 slm. For flow rates above the critical point, a monotone increase in the intensity of LLS is observed. The region where the steady LLS intensity begins to increase is denoted as “transition point” and indicates the transition from a laminar to turbulent flow condition. A slight hysteresis in the LLS intensity is observed for increasing and decreasing flow rates in the reactor. However, within the error range the “transition point” remains the same. In the further text the “transition point” is denoted as “onset of turbulent flow”.

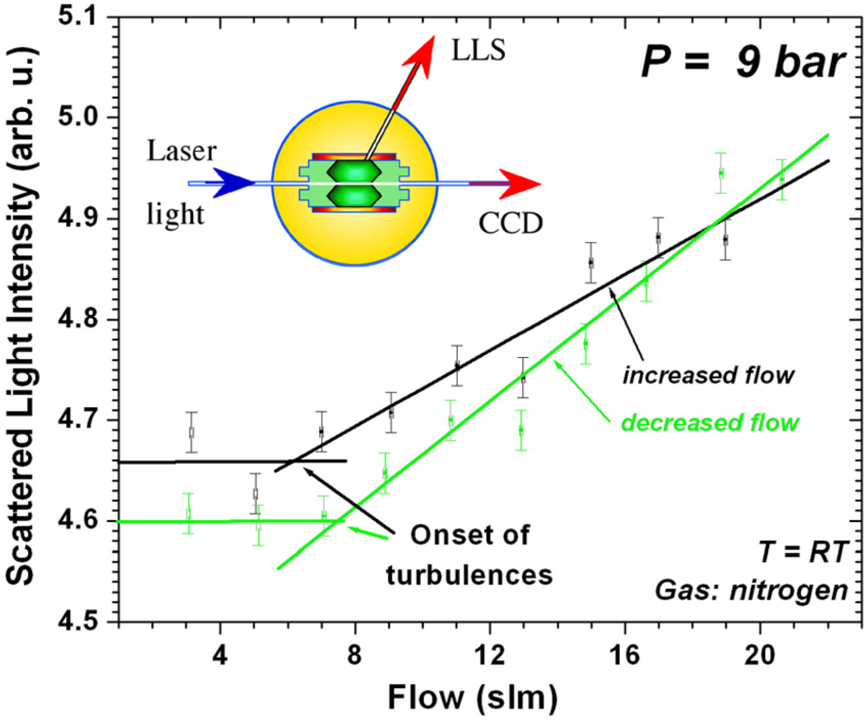

Figure 3: Characterization of flow behavior in the HPCVD reactor by laser light scattering (LLS). The data were collected at 9 bar for flows of 3 slm to 21 slm. The onset of the increase in intensity corresponds to the transition from laminar to turbulent flow and occurs at approximately 7 slm.

In order to map the onset of turbulent flow in the HPCVD flow channel reactor, the LLS intensities were measured and analyzed for pressures between 5 bar and 15 bar and flow rates from 3 to 21 slm. For each set of low rates at constant pressure, the transition point in the LLS intensity determined. The summary of this analysis is shown in **Fig. 4** as a function of pressure and flow rate. The inset in **Fig. 4** shows the change in the LLS intensity as function of pressure. The observed slope is always positive. As depicted in **Fig. 4**, the transition towards turbulent flow occurs at lower flow rates for increased pressures, following an inverse relationship. This behavior is expected from the definition of the Reynolds number [13],

$$Re = \frac{\rho\, u\, l}{\eta},$$

where ρ is the density and η is the viscosity of the gas, l is a characteristic length determined by the geometry of the flow channel and u is the flow velocity. Assuming ideal gas law, the gas density ρ is proportional to the pressure of the gas. The viscosity should be independent of gas pressure and should vary with temperature as $T^{1/2}$ [13]. With a constant geometric reactor characteristic, an inverse relationship between flow rate and pressure in laminar/turbulent flow transitions is expected.

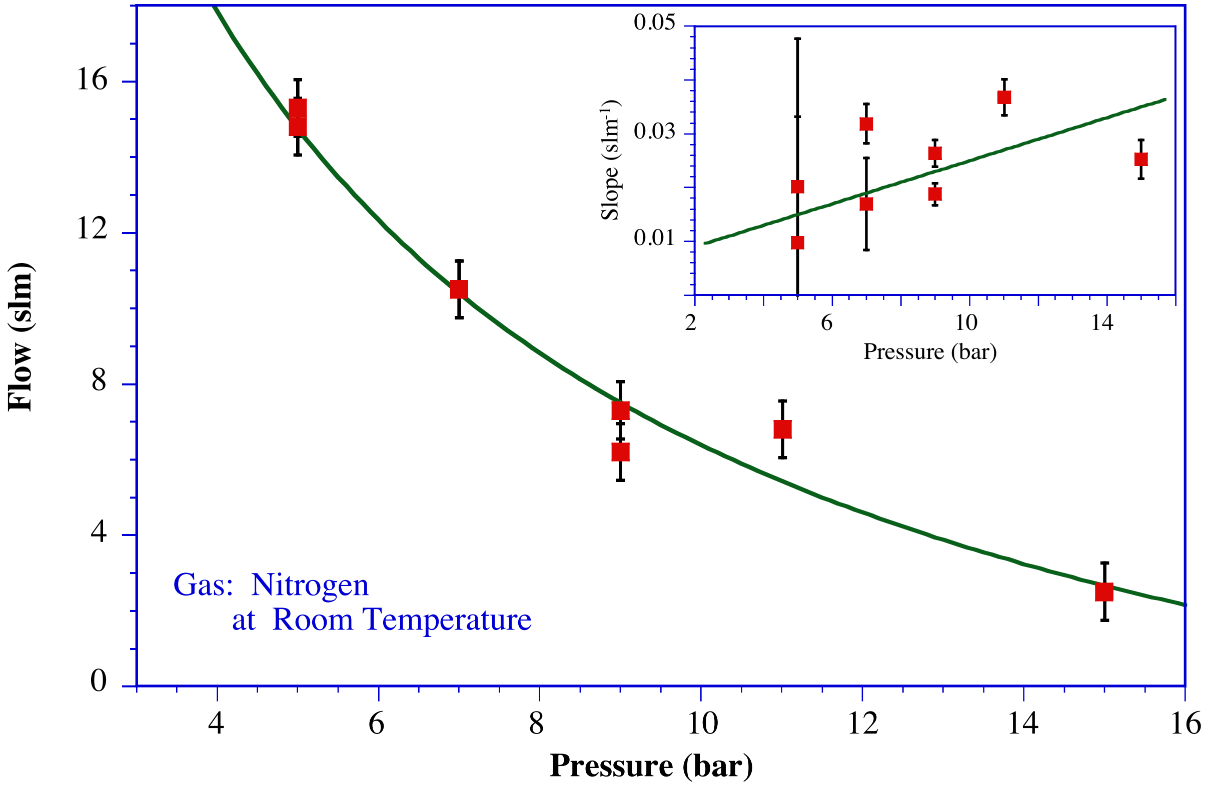

Figure 4: Characterization of *"onset of turbulent flow"*: Summary analysis of the transition from laminar to turbulent flow conditions as determined by LLS intensity measurements. Laminar gas flow conditions are expected for pressures and flow rates settings beneath the line connecting the onset points.

Since the Reynolds number as well as the characteristic reactor length l are two unknowns, further experimental results are required to uncouple and determine both values. The application of laser light scattering to evaluate the onset of turbulence is not restricted to a HPCVD reactor but can also be applied to other types of CVD reactor geometries.

CONCLUSIONS

Utilizing integrated real time optical characterization capabilities, the gas flow dynamics in the HPCVD flow channel reactor has been analyzed. The process window for laminar growth conditions of InN and related compounds has been established by analyzing the laser light scattering (LLS) intensity as a function of gas flow rate and pressure. The analysis determined the onset of turbulent flow as the transition point where the LLS intensity monotone increases. Laminar gas flow conditions can be maintained in a processing window where the pressure varies from 1 bar to 15 bar and flow rates from 3 slm to 21 slm. LLS has been demonstrated as a simple and robust tool to characterize the gas flow dynamics at elevated pressures.

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