REAL-TIME OPTICAL MONITORING OF FLOW KINETICS AND GAS PHASE REACTIONS UNDER HIGH-PRESSURE OMCVD CONDITIONS

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Abstract:
This contribution addresses the real-time optical characterization of gas flow and gas phase reactions as they play a crucial role for chemical vapor phase depositions utilizing elevated and high pressure chemical vapor deposition (HPCVD) conditions. The objectives of these experiments are to validate on the basis of results on real-time optical diagnostics process models simulation codes, and provide input parameter sets needed for analysis and control of chemical vapor deposition at elevated pressures. Access to microgravity is required to retain high pressure conditions of laminar flow, which is essential for successful acquisition and interpretation of the optical data. In this contribution, we describe the design and construction of the HPCVD system, which include access ports for various optical methods of real-time process monitoring and to analyze the initial stages of heteroepitaxy and steady-state growth in the different pressure ranges. To analyze the onset of turbulence, provisions are made for implementation of experimental methods for in-situ characterization of the nature of flow. This knowledge will be the basis for the design definition of experiments under microgravity, where gas flow conditions, gas phase and surface chemistry, might be analyzed by remote controlled real-time diagnostics tools, developed in this research project.

Introduction:
In this paper we describe our process in work on the real-time optical monitoring of high-pressure chemical vapor deposition, building on previous research presented elsewhere[1,2]. The objective is to study the kinetics of nucleation and coalescence of heteroepitaxial thin films, which is an important step of chemical vapor deposition since it defines the perfection of the heteroepitaxial film both in terms of extended defect formation and chemical integrity of the interface. It also defines the film quality during the later stages of film growth. Present growth efforts focus on low pressure processing to minimize the influence of flow dynamics on process uniformity and favors for III-V compounds organometallic chemical vapor deposition (OMCVD). However, the extension to above atmospheric pressures is necessary for retaining stoichiometric single phase surface composition for materials that are characterized by large thermal decomposition pressures at optimum processing temperatures. For example, $Ga_xIn_{1-x}N$ heterostructures have been identified as an important basis for manufacturing of optoelectronic

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and microelectronic devices, such as, light sources, detectors and high power microwave devices for which large potential markets can be identified. Due to the high thermal decomposition pressure of InN, these devices are at present limited to gallium-rich compositions. High nitrogen pressure has been demonstrated to suppress thermal decomposition of InN, but has not been applied yet in chemical vapor deposition or etching experiments. Because of the difficulty with maintaining stochiometry at elevated temperature, current knowledge regarding thermodynamic data for InN, e.g., its melting point, temperature-dependent heat capacity, heat and entropy of formation are known with far less accuracy than for InP, InAs and InSb. Gaining access to these data will require the development of new real-time optical diagnostics, capable to obtain sufficient accurate data on flow conditions, gas phase reactions as well as on the surface reaction kinetic to support modeling and simulations of thin film growth under laminar and/or turbulent flow conditions at sup-atmospheric pressure. The present focus is on the heteroepitaxial growth of group III-nitrides/phosphides.

Properties of group III nitrides and methods of heteroepitaxy:

Group III nitride films have been grown on a variety of compound substrates by several vapor growth methods, such as, halide transport[3] plasma-assisted OMCVD[3] and gas source molecular beam epitaxy of GaN on 6H-SiC on (11.0) and (00.1) misoriented by 4° off the singular surface toward [112][4,5], and conventional OMCVD on AlN coated sapphire using ammonia as nitrogen source[6,7]. A two-step OMCVD process[8,9], growing first a buffer layer at low temperature (1073 K) followed by high temperature (1273K) GaN growth, allows to suppress three-dimensional growth. A trade-off is made in this method between promoting continuous film growth and preserving surface stoichiometry, favoring growth at relatively high pressure[10].

The p - T - x relations in the indium - nitrogen system are not known at present, but studies of the nitrogen pressure needed to prevent thermal decomposition of bulk InN according to

$$InN(s) \rightarrow In(l) + \frac{1}{2} N_2(g) \tag{1}$$

results in the $p - T^{-1}$ relation shown in Fig. 1[11]. We note that since reversibility has not been shown by McChesney et al., the interpretation of the linear relation between p and T according to the equation

$$p(N_2) \rightarrow p_0 \exp\left[-\frac{\Delta H_r}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{2}$$

obtained by integration of van t'Hoff's reaction isobar is not reliable. However, for the purpose of our study this is not important since it suffices to know that in the range $p_{N_2} \leq 10^2$ atm at substrate temperature ≤ 900 K surface decomposition of InN will be effectively suppressed. In view of the higher melting temperature of InN (~1200°C) as compared to InP (1062°C) this appears to be a minimum requirement for the growth of high quality epitaxial InN heterostructures. Most low pressure OMCVD studies of InN employ substrate temperatures of ~ 773K, which in the case of ALE has been extended to 823K, where difficulties with loss of indium from the surface and formation of indium droplets in the epilayer becomes severe [12].

The problem of turbulence in high pressure vapor deposition of thin film heterostructures for large Reynolds number flows is an impediment to the successful processing of advanced materials for microelectronics and optoelectronics applications, such as InN and its solid

solutions, which are characterized by thermal decomposition pressures exceeding atmospheric pressure at their optimum processing temperature. Control of defect formation mandates operating temperatures in excess of 600°C, and requires a nitrogen pressure of $\geq$ 100 atm to avoid surface decomposition. In order to address the problem of materials processing at super-atmospheric pressure by high pressure organometallic chemical vapor deposition (HPOMCVD) additional insights can be provided by real-time process monitoring using optical real-time diagnostics.
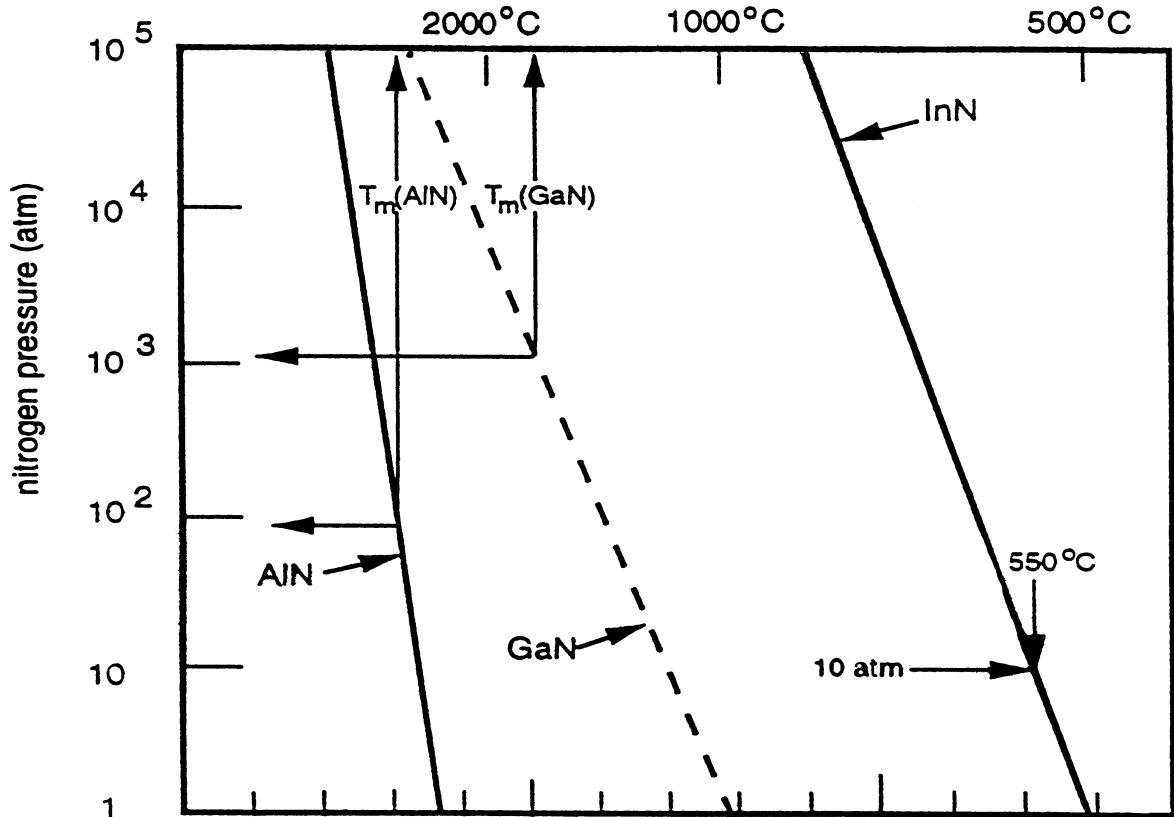
Figure 1: Thermal decomposition pressure vs. reciprocal temperature for AlN, GaN and InN. After McChesney et al.[11].

Reactor Design and Implementation:

The reactor design is aimed to analyze gas phase and surface kinetic reactions parameter during HPCVD gas flow and film growth under normal and reduced gravity conditions. As depicted in Figure 2, the design employs machined inner walls grading in and out of the entrance and exit ports such that the flow channel formed does not change in cross section from entrance to the exit. The substrate blocks are incorporated symmetrically in the upper and lower channel walls. Thus the bifurcation of nutrient fluxes to the top and bottom channel walls is symmetric to the center-line. Thus well behaved flow and deposition can be expected to prevail at $< 10^{-4}$ g gravity in the targeted pressure range. A fully machined and assembled half-part of this reactor system is shown in Figure 3. Two of these inner parts together form the inner shell of the HPCVD reactor, which will be inserted in a 6-inch diameter pressure confinement shell that withstand pressures up to 100 atm.

Figure 2:

Schematic perspective outline of the inner HPCVD reactor. The design provides optical access ports for real-time gas-phase and surface diagnostics.
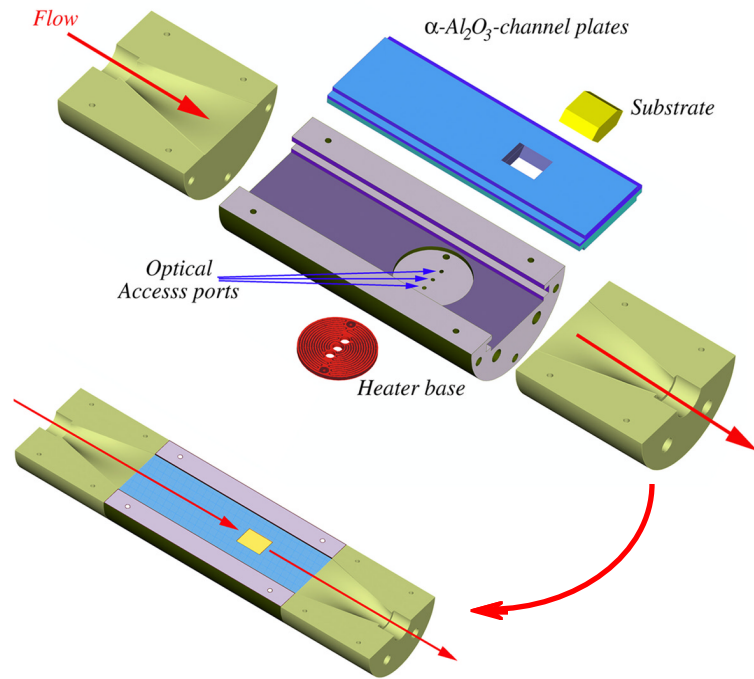

Figure 3:

Perspective view of one of the machined and assembled inner half-parts of the HPCVD reactor.
The transparent Sapphire substrate allows a view on the heater element as well as to the optical ports entering from the back.
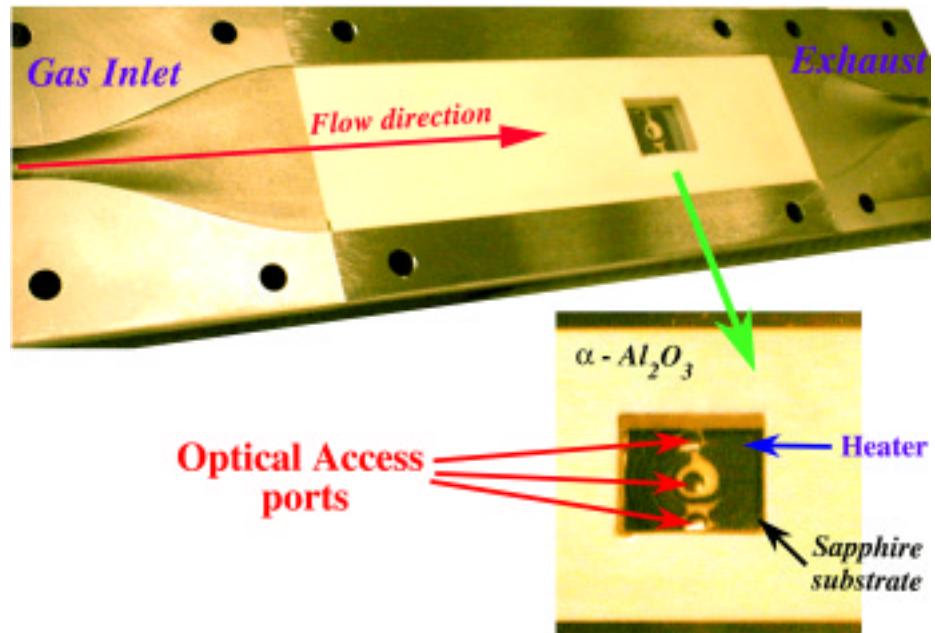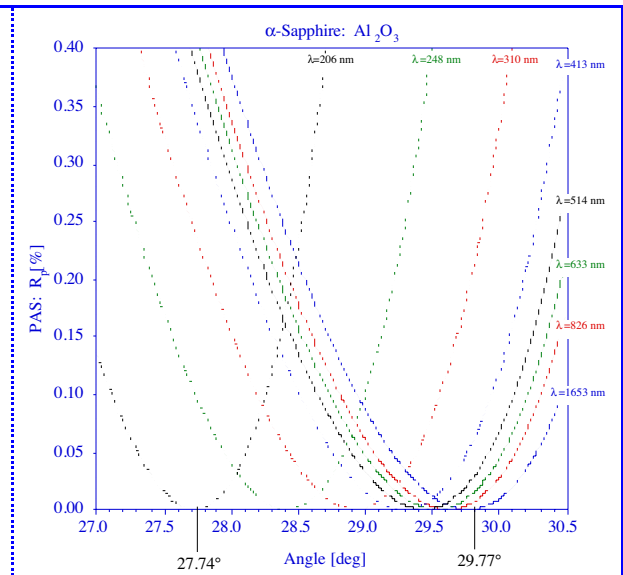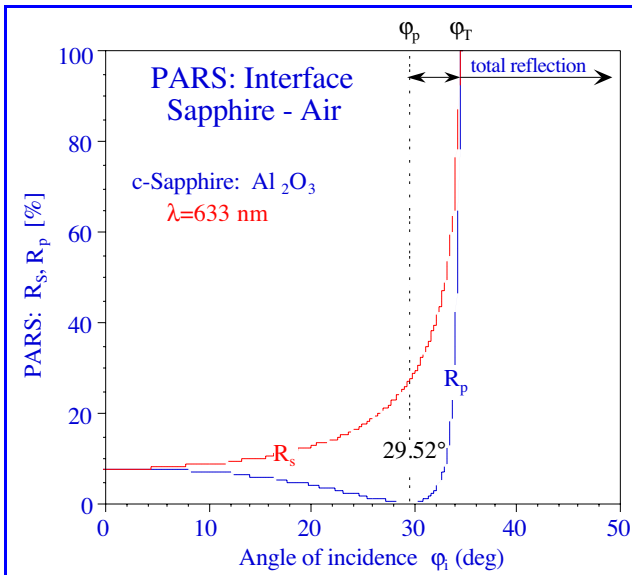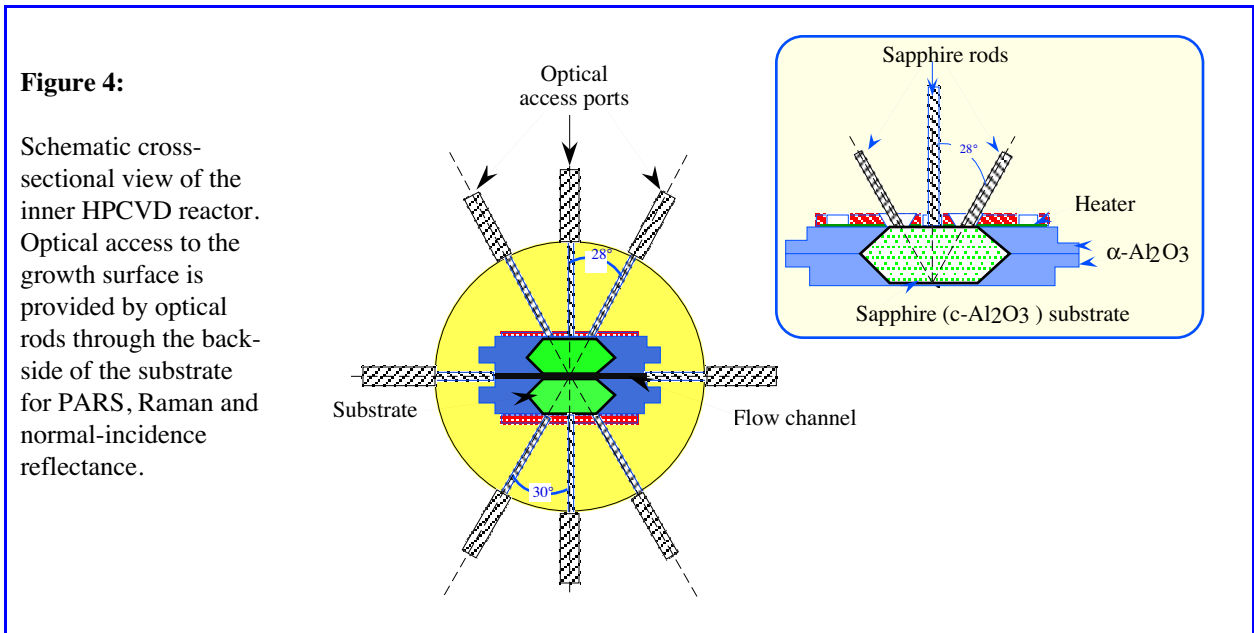
Figure 4 shows schematically a cross-sectional cut – along the optical probe axis and perpendicular to the flow axis - of the inner reactor system, where the two half-parts are put together and the optical Sapphire rods are attached. Because of the symmetry of the lay-out of the top and bottom channel walls with regard to the channel center line and a coupled control of substrate heating, we expect under conditions of laminar flow equivalent nucleation and overgrowth kinetics on both substrate surfaces. Both inner half parts are identical with exemption of the angle of incidence for principal angle reflectance spectroscopy (PARS), which have been chosen

28 deg and 30 deg for the upper and lower part, respectively. As schematically depicted in Figure 5a, PARS utilizes p-polarized light impinging the substrate-ambient interface near the principal angle φ_P. The angle of total reflection, φ_T, is approximately 5 deg above φ_P.

Figure 4:

Schematic cross-sectional view of the inner HPCVD reactor. Optical access to the growth surface is provided by optical rods through the back-side of the substrate for PARS, Raman and normal-incidence reflectance.

Figure 5a: Angle dependency of reflectance for p- and s-polarized light at the interface Sapphire – ambient, Depict are the characteristic angles: principal angle φ_P and total reflection angle φ_T.

Figure 5b: Wavelength dependency of the p-polarized reflectance component and shift in the principal angle φ_P in the wavelength range of 200 nm and 1700 nm, calculated for the Sapphire – ambient interface.

The wavelength dependency of the principal angle is shown in Figure 5b with a calculated shift of more than 2 deg in the wavelength range of 200 nm and 1700 nm. The temperature shift is in the order of 0.2 deg between room temperature (RT) and 1000°C. Utilizing these two angles of incidence, two independent but complementary measurements can be performed at the same time. The entrance- and exit ports for PARS, together with the normal incidence access port, will be also used Raman spectroscopy.

For flow visualization, analysis of flow dynamic, as well as for studies of gas phase reactions, optical access ports are integrated perpendicular to the flow axis. Rayleigh scattering[13] has been utilized widely in detecting turbulent flow (see refs.[14,15] for recent reviews). Operation at high frequency ν is desirable since the Rayleigh scattered intensity $I_R(\nu)$ is proportional to the fourth power of ν. Limits in the useful range of ν are imposed by effects on gas phase chemical kinetics, so that tradeoffs between sensitivity and control of chemical mechanisms must be made. Etalons have been used to advantage in analyses of flow dynamics based on quantitative analyses of contributions of molecular motion to the line shape for Rayleigh-Brillouin scattering[16,17] and for achieving high resolution in Raman line shape analysis. At low pressure and high temperature, where thermal motion is described by the Maxwell-Boltzmann distribution, a Gaussian line shape is observed for the Doppler-shifted intensity. However, at high pressure, the Gaussian line shape is altered by superposition of Lorentzian components associated with collective motions, such as, thermal diffusion and Brillouin scattering from acoustic waves[14]. Because of the relatively small solid angle for collection of incoherently scattered radiation it may be necessary to add absorption spectroscopy at specific energies in resonance with vibrational-rotational signatures for the most important molecular fragments diffusing toward the surface of the growing film. Simultaneous monitoring of Raman scattering, absorption spectroscopy, Rayleigh-Brillouin scattering, and PARS, provides information on temporal and spatial temperature fluctuations, variations in flow velocity components, and variations of concentrations of specific constituents in the vapor phase. In conjunction with the results of process simulations these experimental data provide all necessary experimental input needed for flow simulation and process control.

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