

Chemical Vapor Deposition at High Pressure in a Microgravity Environment

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In this paper we present an evaluation of critical requirements of organometallic chemical vapor deposition (OMCVD) at elevated pressure for a channel flow reactor in a microgravity environment. The objective of using high pressure is to maintain single-phase surface composition for materials that have high thermal decomposition pressure at their optimum growth temperature. Access to microgravity is needed to maintain conditions of laminar flow, which is essential for process analysis. Based on ground based observations we present an optimized reactor design for OMCVD at high pressure and reduced gravity. Also, we discuss non-intrusive real-time optical monitoring of flow dynamics coupled to homogeneous gas phase reactions, transport and surface processes. While suborbital flights may suffice for studies of initial stages of heteroepitaxy experiments in space are essential for a complete evaluation of steady-state growth.

1. Objectives and Approach

The overall objective of the work described in this paper is to extend chemical vapor deposition to super-atmospheric pressure. The specific objective of the experiment in space is to provide conditions of laminar flow for the evaluation of the validity of selected process models and input parameter sets that are needed for analysis and control of chemical vapor deposition at elevated pressure. The motivation for extending chemical vapor deposition to high pressure is to maintain stoichiometric single phase surface composition of materials that are characterized by large decomposition pressures at their optimum elevated processing temperatures. An example is indiumnitride, which under conditions of conventional OMCVD at subatmospheric pressure, is limited to processing temperatures $< 823 \text{ K}^1$). This restriction limits the control of formation and propagation of extended defects in this material, and is one of the reasons why at present, confined $\text{Ga}_x\text{In}_{1-x}\text{N}$ heterostructure devices (e.g., diode lasers²) do not include indium-rich compositions. This in turn restricts quantum well depth and thereby the accessible color range. Here we focus onto deposition temperatures $\geq 900 \text{ K}$, requiring nitrogen pressure $\geq 100 \text{ atm}$ to suppress surface decomposition³). Since at $p \geq 100 \text{ atm}$ the mean free path becomes comparable to molecular dimensions interactions between reactive gas phase constituents are inevitable. For growth of InN we select trimethylindium (TMI) and ammonia as source compounds, which decompose in the hot vapor atmosphere in the vicinity of the heated substrate. Therefore, without special preventive measures, interactions of reactive decomposition products of source materials in the vapor phase are likely to occur. Thus homogeneous gas phase nucleation of InN particles above the hot substrate becomes possible, competing and interfering with nucleation and well defined growth of InN epitaxial films on the substrate surface. In order to avoid this problem separately controlled flows of TMI and ammonia or hydrazine are injected into the reactor in a timing sequence that assures maintenance of their separation by plugs of pure nitrogen carrier gas, as illustrated in Fig. 1. Thus indium and nitrogen precursors to growth never exist simultaneously in the vapor volume above the substrate. A special problem of group III-nitride epitaxy is the absence of lattice matching substrates, resulting in strained layer overgrowth. Thus far SiC and sapphire are the most widely used substrate materials for group III nitride growth to which we add for InN heteroepitaxy GaP coated silicon as a possible alternative.

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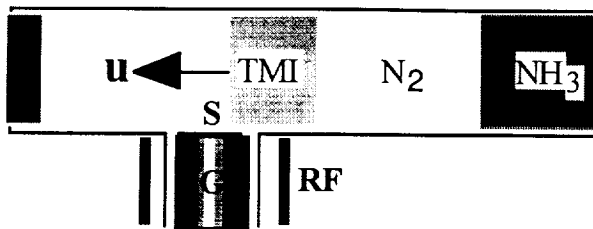


Figure 1. Schematic representation of channel flow at center line velocity u_0 across heated substrate S , employing plugs of source vapor (TMI and NH_3 or N_2H_4) separated by plugs of pure N_2 gas; RF rf coil, G SiC coated graphite susceptor.

For GaP heteroepitaxy on silicon substrates we have developed pulsed chemical beam epitaxy (CBE) using p-polarized reflectance (PRS) for real-time optical process monitoring and triethylgallium (TEG) and tertiary-butylphosphine (TBP) as source vapors⁴⁾⁻⁷⁾. Here we focus onto recent results concerning initial stages of heteroepitaxy that, in conjunction with theoretical predictions of gas phase kinetics, help in estimating the time requirements for the envisioned experiments. Figure 2 shows PRS intensity as a function of time for three experiments employing continuous flow of TBP and pulsed flow of TEG at 0.3 s pulse width at 0.2 Hz repetition rate. Three distinct stages - verified by atomic force microscopy and high resolution cross sectional transmission electron microscopy studies⁸⁾ - are observed:

(i) In the initial incubation period of length $t \leq \tau_i$ surface reactions result in gradual build-up of products of source vapor decomposition on the surface of the silicon substrate. During this stage no structure coinciding with the arrival of the TEG pulses exists in the PR signal.

(ii) Once the critical supersaturation for nucleation of GaP islands is reached steps in the PR signal are observed, coinciding in time with the arrival of TEG pulses, and indicating GaP nucleation and island growth on the silicon surface^{5), 8)}.

(iii) At $t = \tau_h$ the contributions to the PRS signal-associated with the early stages of nucleation and overgrowth that are described by effective medium theory-join smoothly into the slow oscillations in reflectivity-associated with interference of partial waves reflected at the ambient/film and film/substrate interfaces⁴⁾ for steady-state growth of a contiguous GaP film.

In view of efficient heat transfer from the hot susceptor and substrate surfaces to the vapor phase at high pressure, homogeneous gas phase reactions replace pyrolysis of source vapor molecules on the substrate surface under conditions of CBE.

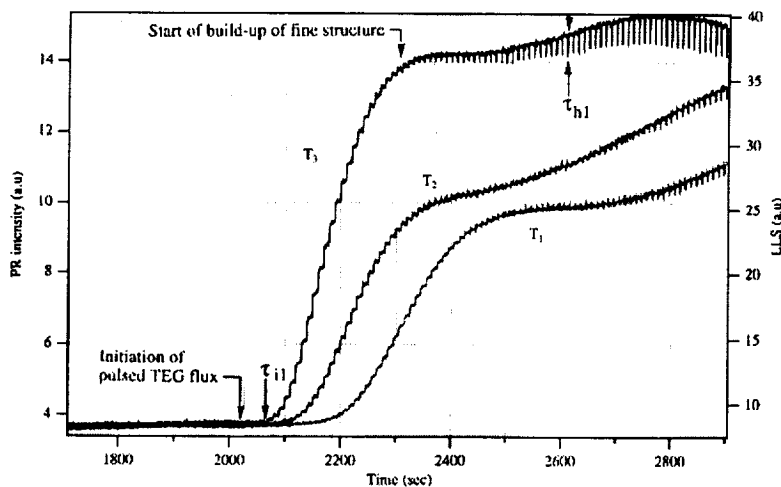


Figure 2. P-polarized reflectance as function of time for growth of GaP on Si(100): $T_1=350^\circ C$, $T_2=420^\circ C$, $T_3=490^\circ C$; $\tau_{i1} = 160$ s, $\tau_{i2} = 95$ s, $\tau_{i3} = 50$ s. $\tau_{h1} \approx 10$ min, $\tau_{h2} \approx 13.5$ min s, $\tau_{h3} \approx 16$ min.

Calculations of the fall-off curves for unimolecular rate constants on the basis of Rice-Ramsperger-Kassel-Marcus theory⁹⁾ predict at ~ 100 atm pressure and $T \approx 900$ K faster group III alkyl decomposition rates than observed under the conditions of CBE⁵⁾. Also, the flux reactive molecular fragments instead of intact source vapor molecules to the surface at higher temperature than accessible under conditions of low pressure growth can be expected to result in faster kinetics of surface reactions, surface transport and incorporation of constituent atoms into the lattice of the

nuclei and, in later stages, of the growing epitaxial film. Of course, diffusivities decrease with increasing pressure. However this is compensated, in part, by access to higher temperature, which increases transport rate, and, in part, by the possibility to sustain at high pressure steeper concentration gradients. Therefore, we expect that short periods of time will suffice for studies of incubation and nucleation, which thus can be addressed on suborbital flights. Such studies are important since both type and distribution of defects in the epitaxial film are determined during initial stages of island growth prior to coalescence⁸⁾. However, a complete investigation, including steady-state growth, takes substantially longer uninterrupted experiment time than accessible with suborbital flights, that is, requires access to an experiment in space.

2. Need for Processing at Reduced Gravity

A necessary condition for realizing pulsed high pressure OMCVD is the absence of contamination of the flow by buoyancy-driven recirculation, which would result in mixing of the separately injected plugs of source vapors. Based on results of simulations of flow for a variety of reactor geometries we conclude that channel flow at high center-line velocity indeed eliminates residual buoyancy driven recirculation for Richardson number $Ri \equiv Gr/Re^2 \gg 1$ ¹⁰⁾. Gr and Re stand for the Grasshof and Reynolds numbers, respectively. This sets a lower limit for flow velocity, $|\mathbf{u}| \gg (z_0 g \beta \Delta T)^{1/2}$ and consequently a lower limit for $Re = \rho |\mathbf{u}| z_0 / \eta$, where z_0 , g , ρ , β , η and ΔT refer to the characteristic channel dimension, length of the gravity vector, gas density, volume expansion coefficient, dynamic viscosity and temperature difference across the channel, respectively. At $p \geq 100$ atm for a conventional reactor design (see section 3) $Re > 10^4$ on the ground, which makes onset of turbulence likely. Turbulent flow involves interactions between many degrees of freedom over wide ranges of spatial and temporal scales and thus cannot be adequately simulated with present computer technology. Attempts have been made at reducing complexity by eliminating inessential degrees of freedom, e.g., on the basis of observations of organized structures (eddies) in turbulent flows at low Re ¹¹⁾. Proper orthogonal decomposition (POD)¹²⁾, in particular, represents the fluctuating velocity field $\mathbf{u}(\mathbf{r}, t)$ by the sum over a denumerably infinite set of POD modes $\{\Phi_j^{(m)}(\mathbf{r})\}$ that are functions of position $\mathbf{r} = c_j \mathbf{r}_j + c_k \mathbf{r}_k$ and are weighted by random coefficients $\alpha_m(t)$ that depend on time t . The POD modes are mutually orthogonal eigenfunctions of two-point correlation tensor $R_{ij}(\mathbf{r}, \mathbf{r}') = \langle u_i(\mathbf{r}) u_j^*(\mathbf{r}') \rangle$, where subscripts refer to components parallel to basis vectors \mathbf{r}_i , \mathbf{r}_j and $\langle \rangle$ represents an averaging operation. The set $\{\lambda^{(m)}\}$ of eigenvalues associated with $\{\Phi_j^{(m)}\}$ is ordered so that $\lambda^{(p)} > \lambda^{(q)}$ for any pair of integers $p < q$. For specific cases of low Re channel flow it has been shown¹³⁾ that major parts of kinetic energy and turbulence generation can be captured by a limited set of low order modes $\Phi^{(m)}$. However, the same set may not represent other properties of the flow, that is, a substantial number of POD modes may be required for adequate representation. Although significant progress has been made during the past decade with regard to direct numerical simulations of turbulent flow¹⁴⁾, their viability for simulations of heteroepitaxy presently is not assured, since local variations in reaction rates, associated variations in composition, and localized generation/consumption of heat result in a strong interdependence of the evolutions of turbulent flow and heteroepitaxial growth. For these reasons, it appears prudent to address this problem as far as possible experimentally, so that future progress in computational methods can be tested against experimental results. Reliable results can be obtained by experimentation at reduced gravity, where the flow velocity needed for suppression of buoyancy driven recirculation and thereby Re are reduced. Thus laminar flow conditions can be realized for high pressure OMCVD processes. In this case, the coupling to chemical reactions and transport can be simulated reliably

on the basis of known physico-chemical models with proven mathematical methods and validated by experiment.

3. Description of a Ground-Based Reactor

Figure 3 shows a photograph of the reactor section of a high pressure OMCVD system for ground-based studies at relatively low pressure ($p \leq 7$ atm) constructed at North Carolina State University. The innermost reactor shell R is made from fused silica, and is mounted on base plate B. Under operating conditions R is sealed in pressure bearing stainless steel second confinement shell C (raised in Fig. 3 for installation of R). Active controls are provided for a selected small pressure differential between inside and outside of R and for the absolute pressure inside C. The design provides for flexibility in the evaluation of variations in reactor geometry by exchange of fused silica reactors without need for changes in pressure bearing parts of the system. For real-time monitoring of growth rate, and of changes in surface composition due to sequential pulsed exposure of the hot surface to TMI and NH_3 or N_2H_4 we have made provisions for p-polarized reflectance spectroscopy (PRS), that is, admission of a chopped p-polarized laser beam through a window on the perimeter of C and tube 1 and recovery of the reflected beam through tube 2 for phase sensitive detection by a photodiode outside C. In order to establish pulsed exposure of the substrate surface to precursors to growth at high pressure, flows of source vapor/carrier gas mixtures are either directed into the run line connected to entrance tube 3 on R or into a vent line bypassing R. When a source vapor is added to the run line flow a matching flow of nitrogen carrier

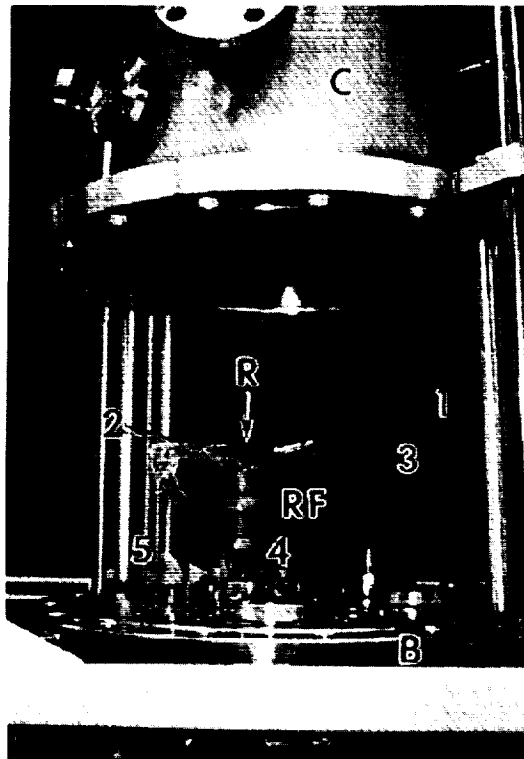


Figure 3. Photograph of the reactor section of a high pressure OMCVD system.

gas is subtracted from the run line flow and redirected into the vent line. Thus the total flow through the reactor remains unchanged. The gas flow is passed over the substrate wafer mounted on a susceptor in vertical fused silica tube 4 attached to R, so that the wafer surface is flush with the bottom channel wall and the susceptor is located inside single-turn rf-coil RF. Waste products are exhausted through tube 5. Errors in positioning S, resulting in a step in the bottom of the channel at the location of the substrate wafer, or irregularities in the channel side walls, can trip

eddies in the flow even at low Re. This is demonstrated in Fig. 4 by flow visualization using injection of smoke.

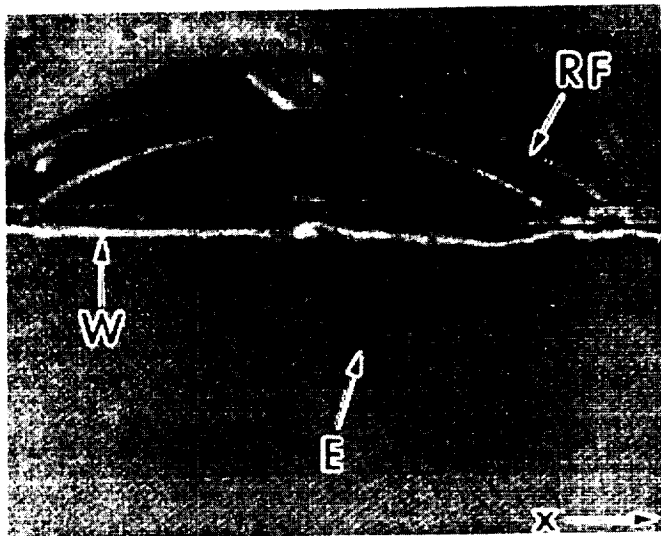


Figure 4. Visualization by smoke injection of an eddy marked E in a flow of nitrogen through R in x-direction for $Re = 300$ near a large irregularity in channel sidewall W.

Therefore, even under the conditions of low Re flow localized flow instabilities can exist that are likely to affect process uniformity. In order to prevent this problem and to verify laminar flow conditions, improvements of reactor design and characterization of the flow dynamics as part of the experiment are necessary requirements.

Figure 5 shows the design of a prototype high pressure reactor for work at reduced gravity and has

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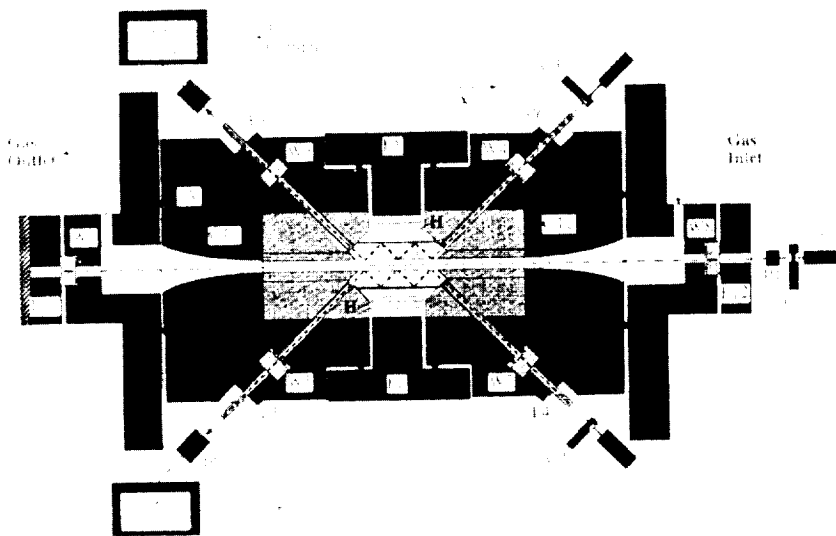
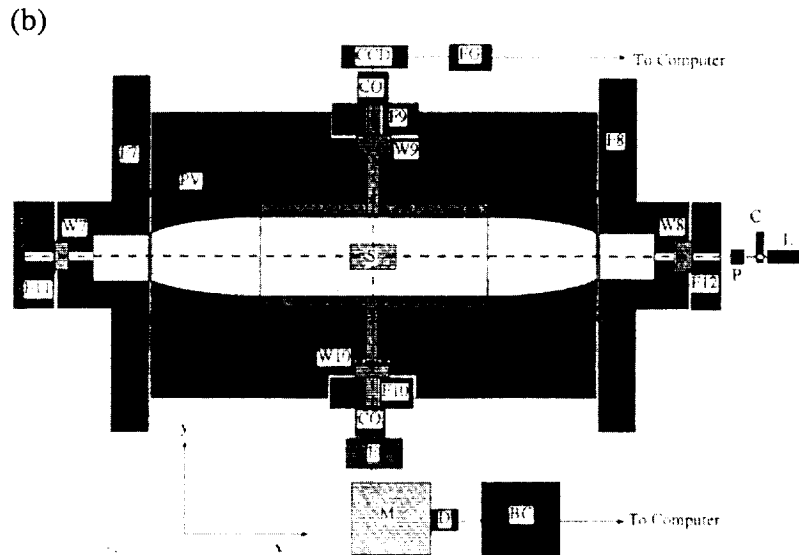


Figure 5. Schematic representation of a reactor for high pressure OMCVD at μg : W1-W8 fused silica windows, H heater ribbons, S substrate prisms, PV pressure vessel, F1-F12 flanges. CO collecting optics, E Fabry-Perrot etallon, M monochromator, D detector, BA boxcar averager, CCD camera, FG frame grabber, P polarizer, C1-C3 choppers, L1-L3 lasers.



the following improved features: absence of purge flows perturbing the channel flow and composition of the nutrient phase in the vicinity of the substrates, pairing of heated substrate prisms that are incorporated into the top and bottom channel walls achieving high symmetry, and continuous cross section of the channel from entrance to exit ports of the reactor.

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