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FINAL REPORT

to

NASA GRADUATE STUDENT RESEARCHERS
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entitled

CHARACTERIZATION OF METALORGANIC CHEMICAL VAPOR DEPOSITION

covering the period

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Prepared by

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for

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BACKGROUND

This report addresses a stage of research of chemical vapor deposition CVD that has been a topic of research at UVA for about one decade. The UVA research complements one of the research thrusts at LaRC by a group of researchers involved in the laser velocimetry based modeling of chemical vapor deposition processes. The modeling work at LaRC provides physical data on model systems that can be compared to growths in a production system using precursors and nutrients suitable for growth of such compound semiconductors as InP. Numerical modeling of the process using a commercial heat and mass transfer code known as FLUENT is suitable for comparison with experimental measurements from the laser velocimeter and from the CVD reactor at UVA. In addition there is characterization equipment at UVA suitable for measurement of the deposition profile and chemical composition of the deposited layers. The combining of these two research thrusts into a single thrust provides important information regarding the fundamental understanding of chemical vapor deposition generally and metalorganic chemical vapor deposition MOCVD in particular.

A series of experiments was conducted to enhance the basic scientific knowledge of CVD especially as it is affected by gravity. Generally, the CVD process involves the use of a gas to transport reactive chemical source materials to the locations where the deposition of solid layers is desired. The nature and quality of the layers formed are dependent on mass and energy transport as well as homogeneous and heterogeneous chemical reactions and nucleation. CVD is an extremely important industrial process. It is widely used not only for the production of semiconductor and insulating materials, but also for optical coatings, wear and corrosion-resistant coatings, and the production of drawing stock for optical fibers. In addition to the economic importance of these application areas for terrestrial research and manufacturing, they also represent key manufacturing capabilities for future extraterrestrial development. Each of these CVD applications takes place in reactors which have been developed through decades of empirical trial and error. Engineering design capabilities have been limited due to the extreme difficulty, under Earth-thermal convection, buoyant solutal convection, internally forced convection due to volume changes arising from both thermal and reactive chemistry effects and Soret (thermal) and Fickian (solutal) diffusion. It is the aim of the present research to include these effects in a modeling effort compared to experimentally obtained data so that the effect of gravity on CVD can be used to improve our fundamental knowledge of the CVD process both terrestrially and extraterrestrially.

OVERVIEW

A series of experimental and numerical investigations to develop a more complete understanding of the reactive fluid dynamics of chemical vapor deposition were conducted. In the experimental phases of the effort, a horizontal CVD reactor configuration was used for the growth of InP at UVA and for laser velocimetry measurements of the flow fields in the reactor at LaRC. This horizontal reactor configuration was developed for the growth of III-V semiconductors and has been used by our research group in the past to study the deposition of both GaAs and InP. While the ultimate resolution of many of the heat and mass transport issues will require access to a reduced-gravity environment, the series of groundbased research makes direct contributions to this area while attempting to answer the design questions for future experiments of how low must gravity be reduced and for how long must this gravity level be maintained to make the necessary measurements. It is hoped that the terrestrial experiments will be useful for the design of future microgravity experiments which likely will be designed to employ a core set of measurements for applications in the microgravity environment such as HOLOC, the Fluid Physics/Dynamics Facility, or the Schlieren photography, the Laser Imaging Velocimetry and the Laser Doppler Velocimetry instruments under development for the Advanced Fluids Experiment Module.

A. Chemical Vapor Deposition

With the inclusion of chemical reactions in fluid dynamic models, a number of the fundamental a priori assumptions usually made in fluid dynamics begin to break down. The divergence of molecular density can no longer be set to zero and mass conservation equations must be calculated at the atomic level. With the introduction of condensation or deposition of non-dilute species, the velocity at a wall can no longer be assumed to be zero. Even conceptually simple systems such as the deposition of silicon from SiH_4 are found to have multi-step chemical reactions which result in multiple species being formed and depleted in different thermal and kinetic conditions. Each of these species can lead to solutal convection. In addition, each reaction can lead to a forced convection term due to the change in numbers of molecules present before and after the reaction.

For reacting flows, groundbased experiments must deal with thermophysical properties which are temperature and concentration dependent; external forced convection; forced convection due to Soret and solutal diffusive effects, thermal expansion, and solutal expansion; and buoyant convection due to thermal expansion and solutal convection for each of the species present. The groundbased experiments serve as a base line for similar experiments in a reduced-gravity field where the buoyancy terms become negligible. Such a comparison will help to resolve the importance of the effects arising from solutal expansion and diffusive effects. One of the goals of the numerical modeling portion of this research is to determine the gravitational levels at which these buoyancy effects might reasonably be expected to be negligible. For the very coarse, non-reactive model discussed previously, this level is of the order of 10^{-3}g. It seems likely that a reacting flow experiment with multiple species would require a lower gravitational level in order to neglect buoyancy effects.

B. InP Growth

The ultimate test of any materials research effort is whether, at the end of the research, one has a better understanding of the material an whether one can make that material better. To ensure this end, the growth of semiconductor layers is part of the research for direct validation of both the numerical and experimental modeling efforts.

The initial InP growth efforts concentrated on obtaining a full mapping of the growth rate in the reactor. For this purpose, large-area substrates were used which extend past the edges of the susceptor in both the upstream and downstream directions. This is essential to obtain the critical growth rate information at the leading and trailing edges of the susceptor. This data is largely unavailable in the literature but is critically important for complete testing of the modeling efforts. Because of the reactor geometry, these extended parts of the substrate do not protrude into the gas flow. The primary experimental data used in these experiments is the amount of deposition as a function of position in the reactor. Such data are also generated by simulation through numerical modeling for comparison.

C. Numerical Modeling

A commercially available finite difference computational fluid dynamic code knows as FLUENT was used to model the flow fields and deposition patterns in this research. The FLUENT finite difference code has been enhanced under the NASA SBIR program to include Soret diffusion effects, thermal- and solutal-dependent thermophysical properties, and multiple homogeneous and heterogeneous chemical reactions with deposition. In addition, the FLUENT code includes Lagrangian particle tracking capabilities incorporating thermophoretic effects. With these enhancements, FLUENT is especially well suited for the present modeling effort. The numerical modeling effort predicts the thermal, solutal, and flow fields and the deposition patterns in the reactors as a function of gas flow velocity and pressure in the reactor. In addition FLUENT models the transport of tracer particles used for laser velocimetry measurements and flow visualization at NASA LaRC. The numerical predictions for unigravity were tested experimentally. Reduced-gravity predictions form the basis for determining the requirements for the follow-on reduced-gravity experiments to be proposed.

APPROACH

This study focuses on flow measurements during CVD deposition and investigating the effects of transients which occur at the introduction and removal of growth source materials and during the heating and cooling of the susceptor. The effects of these two classes of transients and the time for the flow and deposition rate to stabilize after these perturbations are critical to determining the minimum time required to make accurate measurements in reduced gravity experiments. These transients will be examined both numerically and experimentally.

PROJECT DETAILS

Experimental Methods

A Crystal Specialties Model 425 horizontal reactor was employed for InP deposition. The reactor vessel was constructed of fused quartz and consisted of a rectangular flow channel surrounded by a concentric cylindrical channel where forced convection of the carrier gas was also used to cool reactor walls. Within the rectangular channel a SiC coated graphite susceptor was tilted at an angle of approximately 9 degrees with a length of 10 cm. The flow channel width was 9.1 cm, and the corresponding height represented by $h(y) = h_o - y\tan(\theta)$, where h_o is the entrance region height and is equal to 4 cm and y is relative height in the vertical direction. A cross-section of the rectangular channel can be seen in Figure 1 .

Deposition took place at a pressure of 0.1 atm on a fused quartz substrate which spanned the entire length of the graphite suceptor as well as extending at least 2.5 cm beyond the leading and trailing suceptor edges. A total gas flow rate of 7.72 l/min was used in all experiments and hydrogen was employed as a carrier gas. Trimethylindium (TMI) and phosphine (PH_3) were used as the primary reactants with mole fractions of 6.5×10^{-4} % and 0.39% respectively. A two steps process was employed to promote continuous and uniform growth by first allowing a low temperate nucleation layer to be deposited at 623 K for 20 minutes. Heating of the graphite susceptor was achieved by radio frequency induction and temperature measurements were made by a quartz encapsulated type-R thermocouple held adjacent to the susceptor backside. The temperature was then raised to a growth temperature of 873 K and annealed in a phosphine atmosphere for 10 minutes. TMI was then reintroduced for the 2 hour primary growth step.

Under the previously stated conditions, two primary experiments were performed which included deposition over the entire quartz substrate and selective deposition over the leading half of the substrate. The quality and quantity of the InP deposit depended greatly upon the preparation of the fused quartz surfaces. In some instances substrates would undergo the entire experimental process and yield virtually no deposit and in others, irregular deposit would occur characterized primarily by a blotchy appearance and growth rate variation of 50% or more in a localized area. Therefore before loading into the reactor, substrate surfaces had to be carefully prepared. First, degreasing took place in a trichloroethylene solution followed by an acetone bath. The substrate was then etched for a brief period of time in a solution of buffered HF and then extensively rinsed by filtered deionized water followed by a heated 2-proponal solution. Finally, nitrogen was used to blow dry the substrate. For some experiments, it was necessary to remove the substrate from the reactor during the deposition process and chemically remove portions of the surface deposit. This was accomplished by applying a aqua regia solution to etch away selected InP deposits, rinsing with filtered deionized water and using nitrogen to blow dry

the surfaces. Subsequently the substrate was reloaded into the reactor. After deposition, InP thickness measurements were taken with a Tencor Alpha Step 200 profiler having a vertical resolution of 5nm.

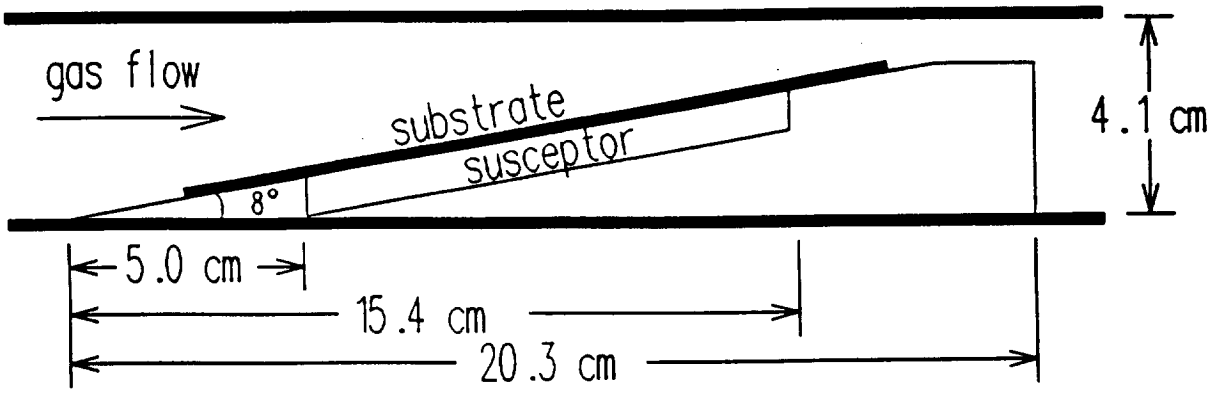

Figure 1. Schematic of the MOCVD reactor growth region. The width of the flow channel is 9.2 cm.

Numerical Model

A complete model of the MOCVD process involves solving the coupled nonlinear transport equations of mass, momentum (Navier-Stokes), energy, and species given the appropriate physical properties and boundary conditions. The commercially developed CFD package, Fluent 4.3.1, which utilizes a control volume based finite difference method to numerically solve the transport equations for two and three dimensional grid domains, was made available to us through a license to LaRC.

Transport properties

The solution process for the governing conservation equations began by tailoring the allowed Fluent model inputs to represent experimental conditions. Laminar flow and time independence was presumed of the reactor gas as well as Newtonian ideal fluid behavior resulting in a density, ρ, calculated from the ideal gas equation of state. Other physical property inputs included the operating pressure and molecular weights and formation enthalpies for each species. The presence of reactant species in an extreme excess of carrier gas (reactant mole fractions $< 0.4\%$) allowed for simplifying approximations of some physical properties. As a result, heat capacity, C_p, dynamic viscosity, μ, and thermal conductivity, κ, were input as temperature dependent polynomial equations interpolated from the carrier gas. In addition, the binary Fickian diffusivity, D, and binary thermal diffusivity, D^T, were substituted for multicomponent mass diffusion. The values for these diffusion coefficients were calculated by Fluent from the kinetic theory

of gasses which in addition to molecular weights required the input of the size parameter σ and the potential factor ε/κ for each species.

The default transport equations incorporated in Fluent were also modified to reflect experimental conditions. For the relatively low fluid velocities common to CVD inertial forces tend to be small allowing for compressible flows to be modeled as incompressible, i.e., $\nabla \cdot \mathbf{u} = 0$ where $\mathbf{u}$ is the fluid velocity vector. As a result of this assumption, a reduced form of the Navier-Stokes equation was employed requiring less computational effort. Furthermore the energy equation was employed without contributions from the Defour effect and mechanical energy, (pressure effects and viscous dissipation), because any contributions were expected to be minor, however, changes due to radiation and chemical reactions were included.

Solution method

Finite difference methods were utilized to solve the necessary transport equations over nonuniform grid domains. The solution grids were numerically generated with the software package and imported to Fluent. For both 2-D and 3-D domains, two Cartesian nonuniform grids were utilized, one for deposition over the entire quartz substrate and another for deposition in selected portions of the substrate. The corresponding 3-D nodal point distributions are 217 x 56 x 56 (x x y x z) and 256 x 56 x 56 respectively. The 2-D grid geometry's are represented by the x x z values. To arrive at a solution over the grid domains, the SIMPLE pressure correction method was implemented for the coupled momentum and continuity equations and the Power Law Differencing Scheme was employed for equation discretization. The resultant equations were solved iteratively using a line-by-line method which incorporated multi-grid acceleration techniques to reduce non-localized errors and hasten solution convergence. Convergence is determined by monitoring how closely each finite difference equation is balanced. Fluent reports this in the form of residuals. A solution was considered to be well converged when normalized residuals were below 10^{-3} (10^{-6} for enthalpy and radiation) and subsequent iterations produced monotonically decreasing residuals and an invariant flow field.

Physical model

The form of the InP deposited on heated substrates consists of columnar grains that result in a rough surface caused by the facetting of each grain joined along their length normal to the substrate. When the film is thick, there is only a small variance in the thickness measurement, however, when the film thickness is comparable to the grain diameter, then the thickness measurement contains substantial variance in its values. Accordingly, when measurements occur in regions of the substrate where the deposit is small, one should regard the data as semi-quantitative rather than as quantitative. The measurement of deposit thickness on the fused quartz reactor is qualitative and determined from the darkness of the deposit rather than from a direct measurement of the thickness itself. Nevertheless, estimates can be made from the degree of opacity which are useful in assessing the need to incorporate loss of material from the gas stream by depletion to the reactor walls. It is the measurement of deposit thickness as a function of position on the substrate that represents the physical phenomenon to be modeled by the Fluent calculations.

Reaction Kinetics

InP reaction chemistry was included in the numerical model through implementation of the species equation. Based on work of Black and Buchan et al , one homogeneous reaction,

$In(CH_3)_3 \rightarrow InCH_3 + 2CH_3$ Reaction (1)

and two heterogeneous reactions,

$In(CH_3)_3 + PH_3 \rightarrow InP(s) + 3CH_4$ Reaction (2)
$InCH_3 + PH_3 \rightarrow InP(s) + CH_4 + H_2$ Reaction (3)

were chosen for InP deposition. Buchan suggested that reaction mechanisms for TMI and Ph_3 decomposition below 673 K differs from those at higher temperatures. At low temperatures, reactant species depletion was expected to occur equally, resulting in Reaction (3). However, above 673 K, TMI decomposes homogeneously and secondary surface reactions are expected to occur, represented here by reactions (1) and (2).

Boundary conditions

For the 2-D model, the inlet region was assigned a parabolic velocity profile characteristic of fully developed Poiseuille flow and gas flow tangential and normal to boundary wall surfaces was considered to have velocities of zero. In addition, with aspect ratios (the ratio of the reactor width to reactor height) varying from 2.3 to 8.3, reactor side walls were considered sufficiently far away for experimental center line data to be modeled in 2-D.

For thermal boundary conditions, the model has been divided into six temperature regions. The inlet region is represented as T_1, the horizontal bottom wall adjacent to the inlet and the tilted susceptor leading edge, and the entire top wall section are designated as T_2, the susceptor leading edge as T_3, the susceptor as T_4, and the susceptor trailing edge as T_5,. A temperature of 300 K was assumed for the inlet gas of region T_1. Boundary temperature T_4 is determined by the corresponding experimental conditions. For the growth conditions being considered, this temperature was 873 K. The thermal transition temperatures, T_3 and T_5, were supplied temperature profiles based on a cooling fin approximation tailored to fit the onset of

reactor walls. It is the measurement of deposit thickness as a function of position on the substrate that represents the physical phenomenon to be modeled by the Fluent calculations. deposition observed in experimental growth. The outlet thermal boundary condition was not specified.

Results and Discussion

The upstream end of the substrate is at ambient temperature and as distance from this end increases, the temperature of the substrate increases to a steady state value suitable for deposition of the material of interest. In the earlier work involving deposition of GaAs, conducted by Brad Fox and Jianming Kui, measurement of thickness resulted in a peak in this region of the substrate where temperature increased to the steady state. After that region, the deposition was reasonably uniform with position along the centerline of the substrate. This peak was ascribed to the increase in reaction rate with temperature occurring at a position where depletion of the gas species had not yet occurred and the concentrations were high. Once depletion of the reacting species occurred the reaction kinetics settled into a steady state condition.

When the identical experiment is conducted but this time with InP as the deposition species, two peaks are found in the region of the substrate where temperature is increasing. These two peaks are ascribed to two heterogeneous reactions rather than the one heterogeneous reaction ascribed to the GaAs deposition. In order to test this hypothesis, experiments were conducted in the region of the substrate where temperature was constant with position. This was accomplished by suppressing deposition in the initial region of the substrate and allowing deposition to start in the mid-stream position of the substrate where the rise in temperature was absent and the steady-state temperature had been established. The results of the measurement of InP thickness with position showed one peak rather than two. This confirms the idea that the rising temperature is responsible for one of the peaks. and that the appearance of two peaks is not inconsistent with the presence of two heterogeneous reactions. This is the first time such a result has been demonstrated.

PROFESSIONAL AND PROGRAMMATIC TRAVEL

Mr. William H. Clements traveled to NASA Langley Research Center several times during the course of this program. In addition Dr. Ivan O. Clark make trips to the University of Virginia to discuss research results. The dates of these visits were not recorded, however there was a group meeting at UVA with Dr. Samuel A. Lowry from CFD Research Corp. in Huntsville Alabama on September 19, 1997 to exchange results of the experiments and modeling efforts conducted under this program. Dr. Lowry is working with NASA Marshall Space Flight Center on a similar modeling effort directed toward reacting gas flow over a substrate leading to deposition on the substrate. Since that meeting several e-mail exchanges of information have taken place in order to incorporate the experimental results from UVA into the modeling efforts of CFD.

Mr. Clements has not delivered lectures on his work, however he did make a presentation at NASA LaRC of the results of his modeling and experimental results. There has been no directed teaching experience of Mr. Clements as the opportunity for such an experience is limited in our Department of Materials Science and Engineering which has no undergraduate degree program.

Mr. Clements has finished all of his course work for the Masters of Science degree and has started to write up his thesis as well as a paper. Hopefully these two writings will be finished sometime in 1998. No publications nor patent applications have resulted from this research at this time. It is not expected that a patent application will be made.

The best address to use for Mr. Clements is the
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Charlottesville VA 22903-2442

APPRAISAL OF THE GSRP

The Graduate Student Researchers Program generally is a very useful program which stimulates students to work in areas of research of interest to NASA, but I would like to speak to the specific experience it provided for Mr. Clements, an African American whose home is located in the peninsula area of Virginia. Mr. Clements is a very bright young man who was given an opportunity to pursue his graduate education through the NASA GSRP. Without it that opportunity would have been much more difficult for him.

The level of funds is adequate and even competitive at the Masters level. I highly recommend keeping the program as a service primarily to students who need the funding and secondarily to stimulate interest in research of relevance to the goals of NASA.

Faculty Adviser Signature: W a Jesser Date: 2/23/98