Computational Fluid Dynamics-Aided Analysis of a Hydride Vapor Phase Epitaxy Reactor

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Abstract

We report the development of a computational fluid dynamics (CFD) model of a dual chamber hydride vapor phase epitaxial (HVPE) growth reactor. Uniformity of reactant concentrations in the growth stream, transient reactor flows, and cross doping between the two growth chambers, all factors critical to the deposition of uniform, low defect semiconductor layers, were modeled. Simulation results were generated by solving the fundamental continuity, momentum and energy equations over a discretized reactor volume by a finite volume analysis with the aid of CFD-ACE+ commercial software. We demonstrated uniformity of the vapor composition within $\pm 1\%$ across the substrate, achieved due to specific features of the reactor design. Small compositional non-uniformity ($\pm 2\%$ absolute) in $\text{In}_{1-x}\text{Ga}_x\text{P}$ layers grown in our reactor was correlated with calculated temperature non-uniformity across the substrate. Gas switching was modeled and the transient time predicted by the model was confirmed by measurement of doping transients in a sample grown in the reactor. Lastly the gas curtains that chemically isolate the reactor chambers were modeled and the results were compared to experimental data for cross doping between the chambers. As an example, we demonstrate, based on insight from the model, that our HVPE reactor is suitable for the deposition of GaAs PV devices. CFD modeling is a critical tool for the scale up of laboratory level processes to industrial levels.

I. Introduction

Metalorganic vapor phase epitaxy (MOVPE) and molecular beam epitaxy (MBE) are the industry standard techniques for the deposition of III-V materials and devices. While regarded for their flexible materials palettes, sub-nanometer control of layer thickness, high purity and low-defect materials, these processes are expensive due to high input costs and low throughput. Hydride vapor phase epitaxy (HVPE) is a III-V semiconductor growth process recognized for its high growth rates, up to $300 \mu\text{m/hr}$ [1], which are obtained without sacrificing material quality [2, 3]. These rates are 1-2 orders of magnitude greater than typical MOVPE and MBE growth rates. Higher growth rates increase throughput and decrease time on tool, significantly decreasing capital intensity, as fewer deposition tools are required to

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output the same quantity of material. HVPE does not require the use of ultra high vacuum equipment as in MBE. Furthermore, HVPE uses elemental metals as starting materials, which are significantly cheaper than the metalorganic reagents used in MOVPE. In the HVPE growth of III-Vs, pure Ga metal reacts *in situ* with anhydrous HCl to form volatile GaCl that is transported into the deposition zone. Elemental Ga currently costs \$0.24–0.29/g vs. \$2.50–4.00/g for trimethylgallium (which equates to \$4.11–6.60/g on an atomic Ga basis) [4]. HVPE also uses low V/III ratios, 2–4 vs. 60–80 for MOVPE, leading to higher hydride utilization efficiency, minimization of waste, and lower costs. HVPE has produced device quality III-V materials for industrial applications such as LEDs [5], telecommunications [6], and GaN substrates [7].

HVPE offers the potential for significant material cost reductions without sacrificing material quality, but is not without challenges. The high growth rate of HVPE (typically 1 $\mu\text{m}/\text{min}$ in our reactor), while a benefit in terms of throughput, makes the growth of multi-layer devices with abrupt interfaces a challenge. For example, the time required to switch dopant flows, e.g. from p-type to n-type, cannot occur quickly enough to achieve the sharp doping profiles required in many devices. Growth interruptions at this critical interface lead to contamination and a decrease in device performance [8]. The HVPE process operates near thermodynamic equilibrium, at relatively low gas phase supersaturation, meaning that relatively small fluctuations in gas phase composition or temperature can create large variations in growth rate and/or solid composition of the growing film. In contrast, MOVPE is typically limited by diffusive transport, making it relatively simple to control layer composition under a wide process window. For an alloy such as $\text{In}_{1-x}\text{Ga}_x\text{P}$, the composition of the film is predominantly controlled via MOVPE by the In/Ga ratio in the vapor, and the effect of temperature on growth rate and solid composition is generally small. In HVPE, the near equilibrium nature of the process means that incorporation in the film is strongly controlled by growth temperature, and widely varying temperature windows are utilized for the growth of specific materials. For example, GaAs is typically grown at 700–750 °C while $\text{In}_{0.48}\text{Ga}_{0.52}\text{P}$, a lattice-matched wide band-gap material used in many III-V devices, is typically grown at 600–650 °C. Growth of both materials in the same HVPE-grown device is problematic, as either the temperature must be changed during the run, requiring a lengthy growth interruption due to the hot wall reactor, or a temperature that is suboptimal for one or both materials must be chosen.

NREL recently constructed a custom, dual-chamber HVPE reactor that mitigates many of these issues. The reactor allows the ability to separate the growth of materials of differing chemistries, such as arsenides and phosphides, and to form abrupt interfaces by rapid translation of the substrate between deposition chambers with unique steady state flows and temperatures. Optimization of growth temperature and reactant inputs in each chamber is required for the deposition of high-quality devices. Empirical optimization of the HVPE process for device growth is expensive and time consuming due to the large parameter space available and the interdependencies of each of the parameters. Additionally, the hot wall nature of the

process requires envelopment of the reactor in a closed, insulated resistance heated furnace. This limits the use of traditional *in situ* measurement techniques and limits the acquisition of real time growth data from inside the reactor. Computational fluid dynamics (CFD) simulations provide a valuable way to model growth phenomena inside the reactor, including gas velocities, gas concentration profiles, and temperature profiles at any point in the reactor for any set of growth conditions. The geometry of the growth system can be varied easily as well, enabling evaluation of hardware modifications without the need for experimental verification. With suitable kinetic data, chemical reactions (the subject of future development) can also be modeled. In the future, coupling the flow and energy modeling with kinetic growth models will allow for the optimization of not only the reactor geometry, but of the entire growth process for desirable outcomes such as high throughput, high yield and spatial uniformity. This is valuable both during the reactor design phase as well as for the understanding and optimization of an existing system.

In this study, we report on the use of CFD modeling software (CFD-ACE+, ESI North America, Santa Clara) to model key factors affecting epitaxial layer growth by HVPE. We model the fluid flow and perform mass and energy balances leading to spatial determination of flow profiles and gas concentrations for the specific geometry of our reactor under real process conditions. We examine factors that influence the deposition of high quality epitaxial layers, such as uniformity of the reactant stream, temperature variations, transient flows, and cross doping between the two chambers in the reactor. Where possible, we verify these model predictions experimentally. Application of our system to low-cost, one-sun III-V photovoltaic device production is discussed. We demonstrate that CFD modeling is a critical tool for the conception of new industrial-size HVPE arsenide- and phosphide-based systems that do not currently exist in industry.

II. HVPE Process and Reactor Design

The distinguishing feature of HVPE is the transport of the Group III element as a gaseous metal chloride. The process occurs in a hot wall reactor, through the *in situ* generation of metal chlorides (MCl , where $M = Ga$ or In , for example) through the reaction of anhydrous HCl gas with pure liquid Ga and/or In elemental sources. The metal sources exist inside the reactor in separate quartz vessels, or “boats”, shown in Figs. 1 and 2, which serve to isolate the sources from the reactor environment and ensure intimate contact between the HCl gas and the liquid metal surface. The reaction requires sufficient residence time to drive complete conversion of HCl to MCl . The boats were sized with residence time in mind to ensure a reproducible process.

Group V atoms are transported by the hydrides of As and P, AsH_3 and PH_3 . These gases inject downstream of the metal chloride sources to prevent premature deposition on the reactor walls, which can occur if thermodynamic supersaturation levels in the vapor are too high. These hydrides are unstable at typical reactor temperatures, 600–750°C, and rapidly decompose to V_4 and V_2 species. Small

amounts of unreacted HCl are added to the gas mixture through the top of each growth chamber to moderate and control the gas-phase supersaturation [9]. The reactant gases are mixed with a hydrogen carrier gas whose flow can be varied to control the gas velocity and reactant partial pressures in the deposition zone. Typical reactant partial pressures are on the order of 10^{-3} atm when the process is conducted at atmospheric pressure. Deposition occurs by the adsorption and reaction of MCl and Group V compounds on the surface of a single crystal substrate. The growth rate is a strong function of the supersaturation in the vapor, which is a function of the partial pressures of the input gases and the deposition temperature, with surface kinetics also playing a role. An in-depth treatment of the thermodynamics and kinetics that govern HVPE growth is found in ref. [10].

Figure 1 shows the specific HVPE reactor geometry considered in this study [11]. This design is envisioned as a proof-of-concept towards a continuous, in-line reactor, in which the substrate is shuttled through a series of growth tubes that deposit the desired layer chemistries in succession. The vertically oriented reactor features two separate chambers that spatially separate the growth of two different layers or alloys. The substrate is mechanically shuttled between the two growth chambers for the formation of heterointerfaces by means of a quartz transfer arm. There are four independent temperature zones in the reactor, delineated by the black dotted lines in Fig. 1: one for each metal source boat, and one for each of the lower temperature deposition zones. Heating in these zones is provided by rectangular resistive heating elements, and the temperature in each zone is monitored by a thermocouple that contacts the surface of the quartz in the center of each zone. A temperature controller maintains the desired temperature using feedback from these thermocouples. We note that the temperature at the substrate is likely higher than the thermocouple temperature, potentially due to convective heat transfer from gas coming down from the hotter source zone. This design allows for the independent choice of temperature for each source and deposition zone in each reaction chamber. The lower left zone in Fig. 1 also serves as the “heat-up zone” where the substrate resides as oxides are desorbed from its surface while it heats up to the growth temperature.

The chambers are wider at the top to accommodate large surface areas of the metals in the boats, which promote conversion of HCl to MCl, but narrower in the growth zone to promote higher velocities and reduced residence time. The deposition zones are 3” in diameter at their narrowest point, able to accommodate 2” wafers. Each source boat has two chambers that are physically separated from each other. The large boat is 3x larger than the small one, as shown in Fig. 2. Ga is typically placed in the small boat and In in the large one, because the conversion of HCl to GaCl is more efficient. The H_2 /HCl mixture flows through each boat inlet tube, and the resultant metal chlorides flow out through an outlet in the top of the boat (see the arrows in Fig. 1). H_2 , the dopant gases, and Group V sources flow through a center tube that passes through the center of the boat directly toward the deposition zone. The unreacted HCl that helps control the gas-phase supersaturation flows through the top of each main chamber along with additional H_2 carrier gas.

Protective H_2 gas flows through a gas “curtain” located between the growth chambers, providing resistance to the cross-flow and diffusion of gases between the adjacent reactor tubes. An additional curtain is located between the heat-up zone and the first growth chamber. Before growth begins, the sample undergoes native oxide desorption at the desired growth temperature under a H_2/AsH_3 mixture (in the case of GaAs) in the heat-up zone. Meanwhile, the desired reactant concentrations are established in each of the growth chambers, allowing these gases to equilibrate and reach steady-state while the oxide desorption occurs. After oxide desorption, the sample moves into one of the growth chambers, initiating growth by providing a nucleation site for the supersaturated gas. When growth of one layer is complete, for example, GaAs in the chamber on the left, the sample can be mechanically translated into the other chamber by the transfer tool, initiating growth of an $In_{1-x}Ga_xP$ layer, for example. Rapid transfer of the substrate ensures the formation of abrupt compositional interfaces because the mechanical transfer takes ~ 1 s, compared to gas switching, which occurs over 10's of seconds. The substrate surface is not affected by this transfer, because arsenide materials can withstand periods of at least 12 s at similar temperatures under H_2 without degradation of the growth surface [12, 13].

As an example of the transfer procedure described in the previous paragraph, secondary ion mass spectrometry (SIMS) data for a Zn-doped GaAs layer are presented in Fig. 3. The sample was mechanically transferred back and forth between the two growth chambers (GC1 and GC2), with 4 layers grown in each chamber. A distinct diethylzinc (DEZn) flow was set for each layer, and decreased in each subsequent layer. While the first layer in GC2 was growing, the next desired DEZn flow was set in GC1 and allowed to equilibrate. Upon completion of the layer in GC2, the substrate was rapidly transferred to GC1, where GaAs growth with a new Zn doping level was initiated. The DEZn flow in GC2 was then set to a new value and allowed to equilibrate, and then the sample was transferred back to GC2 initiating growth, and so on. In this manner, a layer with multiple distinct, abrupt doping levels was deposited, all at $1 \mu m/min$ without growth interruption. The doping level of the transition nearest the surface (depth $\sim 0.5 \mu m$) falls at a rate of 15 nm/decade. The complete transition occurs over ~ 20 nm, which equates to a transit time of ~ 1.2 s at a growth rate of $1 \mu m/min$. The actual transition width is expected to be narrower, as sputter roughness and knock-on effects tend to broaden SIMS data at this scale.

III. CFD Modeling

The modeling detailed in this work was carried out using a commercially available computational fluid dynamics package, CFD-ACE+. The software package contains multiple modules which assist the user in developing a discretized 3D reactor geometry (as in Fig. 1, right), defining initial boundary conditions, numerically solving the mass and energy balances throughout the volume and then visually and

numerically analyzing the output of the model. The solver module evaluates the fundamental governing equations for flow, continuity, momentum and energy (detailed in refs. [14, 15]) using a finite volume approach. The solution domain is a discretized volume containing a number of cells known as control volumes. In the finite volume approach of CFD-ACE+, the governing equations are numerically integrated over each of these control volumes.

For multi-species problems, CFD-ACE+ solves these equations for each species in order to compute species mass fractions in the computational domain. This approach requires the solution of the transport equations for every species in the system. A multi-component diffusion approach is employed in this model, in which the individual species diffuse at different rates. A result of this approach is that the species mass fractions do not automatically add up to unity, and a correction must be applied to guarantee species conservation. Employing the Stefan-Maxwell equations enforces species conservation. This is the most rigorous of all the approaches, but is computationally more expensive.

The modeling conducted in this study considered fluid and heat transport. Chemical reactions will be the focus of future development and are not considered in this study. At the boundaries of the various inlets, a fixed volumetric flow with a user-defined composition was set. Pressure is the only parameter defined at the outlet and was set to a value of 1 atm. The pressure at the inlet is automatically calculated based on the outlet pressure plus the pressure drop between the inlet and the outlet, which is a function of the flow rate. The reactor temperature was set using an isothermal boundary condition at the reactor walls, which were assumed to be infinitely thin. Each wafer surface was treated as a wall, and given an adiabatic thermal boundary condition.

IV. Results and Discussion

A. Spatial reactant uniformity at the substrate surface

The development of uniform gas concentration profiles in the vapor stream above the substrate surface is the first step towards ensuring uniformity of growth rate and solid composition, vital factors for the growth of high quality devices. A key parameter, then, becomes the distance from the boats to the substrate. This must be large enough for complete mixing of the gas species, but small enough to keep the physical growth system manageable. The gas concentration profile is nearly impossible to measure experimentally, but can be simulated by CFD using the same geometry and flow rates employed in the physical reactor and then compared to epilayer uniformity data.

The source boats were designed to maximize uniformity at the substrate. Small outlets in the top of the boats force the exiting metal chlorides to take a long path to the substrate, thereby increasing the path length without physically extending the length of the reactor. Figure 4 shows the velocity magnitude of the gas exiting the In

boat. The gas exits at just over 2 m/s at a H₂ carrier flow of 425 sccm, and takes a circuitous path before it reaches the substrate, flowing up and then around the boat through the small gap between the boat and the reactor tube wall. The GaCl exits with even higher velocity due to the higher H₂ carrier flow rate in that inlet. The extended flow path allows the GaCl and InCl sufficient time to diffuse such that a uniform concentration profile is established before the gas reaches the substrate.

A steady-state CFD model was prepared with flow conditions representing a standard growth recipe for GaAs in GC1 and In_{0.48}Ga_{0.52}P in the GC2. The specific flow rates of each gas are listed in Table 1. The temperatures were set at 800 °C in zones 1 and 2 (defined in Fig. 1), and 650 °C in zones 3 and 4. Figure 5 plots the GaCl and InCl gas concentration (x_{InCl} and x_{GaCl}) profiles in the reactor at steady state. Figure 6 plots the GaCl and InCl concentrations as a function of horizontal position at multiple locations in the reactor from $y = 0$ –16" above the substrate, as labeled in the InCl profile in Fig. 5. The center of the growth chamber is defined as $x = 0$.

Above the source boats at $y = 16$ ", the horizontal GaCl and InCl profiles are asymmetric, which can be attributed to the fact that the boat outlets are not centrally located. As the gas flows downstream, these concentration variations smooth out, becoming nearly uniform at $y = 8$ " where the reactor tube starts to narrow. The concentration profiles do not change much between 8" and the substrate, and the concentrations of GaCl and InCl at $y = 0$ " between $x = -1$ " and 1" (the diameter of a 2" substrate) vary less than 1%. This high degree of uniformity is achieved due to the design of the source boats and the length and shape of the deposition chambers.

The prediction of the CFD model was tested by the experimental growth of an In_{1-x}Ga_xP layer using the exact same flow rates as in the model. In_{1-x}Ga_xP is a useful wide band gap semiconductor that is lattice matched to GaAs. Device performance is highly dependent on the growth of a spatially uniform In_{1-x}Ga_xP layer at the lattice-matched composition ($x = 0.52$) in order to prevent the strain induced nucleation of dislocations which can degrade device performance. The solid composition of an HVPE In_{1-x}Ga_xP layer is particularly sensitive to the InCl:GaCl ratio in the gas phase above the substrate and also substrate temperature [16, 17], making In_{1-x}Ga_xP an effective test platform of the modeled spatial uniformity.

The Ga composition of a nominally lattice matched ($x = 0.52$) In_{1-x}Ga_xP layer was measured as a function of position on a 2" wafer using symmetric (004) x-ray diffraction (XRD) scans. Figure 7 (top) shows the Ga composition determined from Vegard's law, assuming pseudomorphically-strained InGaP on a GaAs substrate. The composition varies within $\pm 2\%$ (absolute) across the wafer. There is some non-uniformity, with a gallium rich maximum centered near $x = 5$ mm, $y = 3$ mm. The film is indium rich at the left edge. This non-uniformity is not expected from the uniform spatial MCl concentration profiles calculated using the CFD model. Possibly other factors are affecting the compositional uniformity.

In addition to In/Ga ratio in the gas phase, substrate temperature also strongly affects the composition of HVPE-grown $\text{In}_{1-x}\text{Ga}_x\text{P}$. Indium incorporation in the film decreases with temperature [16] due to the fact that the formation energy for GaP is lower (more negative) than for InP [18]. Under typical growth conditions, the GaP incorporation reaction is always driven to near completion while temperature variation alters the extent of the InP reaction, decreasing it with increasing temperature because the reaction is exothermic. An examination of the temperature calculated at the wafer surface, plotted in Fig. 7 (bottom), indicates that there is some non-uniformity in the temperature, with a maximum near the center of the wafer. The localized heating of the substrate is caused by the heated gas flowing down from the source zone where the temperature is 150 °C hotter. The center of the gas stream is hotter than the edges due to cooling from the reactor walls in the deposition zone. A local maximum in temperature across the substrate would explain the experimentally observed gallium rich region in the epilayer. While the two maxima do not correlate exactly spatially, the difference in position could be explained by a slight misalignment of the position of the wafer in the tube. The similarities in the shapes of the maxima support the argument that temperature variation is the cause of the compositional non-uniformity, rather than In/Ga variation in the gas phase.

In addition to providing insight into the compositional variation measured across the substrate, the model can be used to predict conditions which optimize uniformity. A logical conclusion from the model is that the temperature uniformity can be improved by optimizing the gas flow over the substrate. Additional modeling (not shown) demonstrates that the temperature variation over the substrate can be reduced to $\sim 1^\circ$ if the H_2 carrier gas flow is cut in half. This growth condition should decrease compositional non-uniformity in the deposited layer, and will be explored in future experimental work.

B. System Transients

While growths are designed to occur under steady state conditions inside the reactor, there are many transient processes that are also of interest to the crystal grower. It is necessary to determine the time required to reach a steady state condition at the substrate from the time at which changes to gas inputs are made. In a transient CFD model, an initial reactor condition is established at $t = 0$ s and the model is solved for a given time step using the given boundary conditions. The process iterates forward in time, using the solution of the previous step as the initial condition for the new step, arriving at a new solution for the new time-step. The CFD-ACE+ software is equipped with transient modeling capability that automates this process.

To determine the flow transient in the CFD model, a transient CFD model was prepared using an initial condition of a reactor filled with static H_2 . At $t = 0$ s, the gas flows listed in Table 2, with the addition of 50 sccm of 100 ppm H_2Se in H_2 ($x_{\text{Se}} = 5 \times 10^{-7}$), were turned on, and the gas-phase concentrations of the reactants at a

monitoring point centered just above the substrate in GC1 were calculated as a function of time. Figure 8 plots the normalized H_2Se concentration at the substrate as a function of time. The concentration at a given time is normalized to the steady state concentration at $t = \infty$. The concentration of H_2Se became non-zero at the substrate almost immediately and increased steadily until leveling off at about 30 s. The steady-state concentration was reached after about 45 s.

In order to test the accuracy of the model, the gas switching transient time was measured experimentally in the HVPE reactor by a dopant switching experiment. First, an undoped GaAs layer was grown for 1 minute, at which time DEZn flow was turned on and p-type GaAs:Zn (using DEZn as the dopant) was grown. After 1 min of p-GaAs growth the DEZn dopant flow was abruptly shut off and a H_2Se dopant flow was initiated to begin the growth of n-type GaAs:Se, which lasted for the remainder of the growth. The growth rate was $1.3 \mu\text{m}/\text{min}$. The sample was analyzed by SIMS to measure the thickness over which the doping transition took place.

Figure 9 shows the SIMS Zn and Se concentrations as a function of depth for the GaAs sample described above. At the start of the dopant transient, the Zn concentration started in the low 10^{18} cm^{-3} and then rapidly decreased as the Se signal began to increase. Both transients approached their steady state values after $\sim 1 \mu\text{m}$ of growth. At the measured growth rate of $1.3 \mu\text{m}/\text{min}$, this thickness corresponds to a transient of 46 s. This value agrees quite well with the modeling result, which predicted that steady state in the reactor would be reached by ~ 45 s, and provides confirmation of the accuracy of the transient CFD flow model.

C. Gas Curtain Efficacy

The key feature of our HVPE reactor is the dual growth chamber design. In this design, the reaction chambers are connected by a horizontal tube that allows transfer of the substrate between chambers. This tube enables the formation of abrupt interfaces, but also presents a path by which the gases in the two chambers can mix. It is preferred to keep the reaction chemistries in each tube separate to avoid cross doping of material in one growth chamber by reactants in the other, for example, avoiding the incorporation of P into GaAs. Gas curtains were incorporated into the reactor design to provide a barrier to the cross flow of material between the two chambers. It is possible to both model and experimentally verify the level of cross contamination by, for example, determining the concentration of PH_3 originating from GC2 that reaches the substrate in GC1, which results in unintentional P incorporation. Figure 10 shows the concentration of PH_3 at each position in the reactor determined from CFD calculations under steady-state conditions using the flows shown in Table 2 with 2500 sccm of H_2 flowing in each curtain. This model was repeated for gas curtain flows in the range 0 – 2500 sccm. Figure 11 plots the resulting PH_3 concentration, x_{PH_3} , immediately above the

substrate in the arsenide chamber, showing a decrease in cross doping for increasing curtain flow, as expected.

The reactor design and the spatial separation of the two growth chambers provides much of the reduction in cross contamination, with x_{PH_3} decreasing from 5×10^{-3} in GC2 to $\sim 2 \times 10^{-7}$ at the location of the substrate in GC1 even with no hydrogen flow in the curtains. The model shows that the curtains provide additional protection between the two chambers, with over an order of magnitude further reduction in the level of PH_3 for a curtain flow of 2500 sccm.

To compare the cross doping model with experimental data, a GaAs layer was grown at 650 °C (measured surface of the quartz) in GC1 while PH_3 was flowing in GC2. Flow rates identical to those modeled in the simulation were employed during growth. During the growth, the flow in the curtain between GC1 and GC2 was decreased sequentially from 2500 to 0 sccm and then increased back to 2500 sccm to evaluate the effect of curtain flow rate on cross doping. Figure 12 plots a SIMS measurement of the concentration of phosphorus, [P], as a function of depth in the GaAs layer. No curtain flow resulted in $[\text{P}] \sim 8.0 \times 10^{19} \text{ cm}^{-3}$ in the GaAs layer while the highest curtain flow reduced [P] to $4.0 \times 10^{19} \text{ cm}^{-3}$. The atomic density of As in GaAs is $2.2 \times 10^{22} \text{ cm}^{-3}$, so the P mole fraction in the layer with the highest curtain flow, or x_{GaP} , is 0.0018. [P] decreased by half when increasing the curtain flow from 0 to 2500 sccm, which is less than the order of magnitude decrease in PH_3 concentration predicted by the model.

To estimate the amount of P expected to incorporate into the GaAs film, we employ an equilibrium model in which the solid is treated as a regular solution. The reactions leading to deposition of the solid are assumed to have the form:

with the equilibrium constants

$$K_{\text{As}} = \frac{a_{\text{GaAs}} P_{\text{HCl}}}{P_{\text{H}_2} P_{\text{GaCl}} P_{\text{As}_4}} \quad (3)$$

$$K_{\text{P}} = \frac{a_{\text{GaP}} P_{\text{HCl}}}{P_{\text{H}_2} P_{\text{GaCl}} P_{\text{P}_4}} \quad (4)$$

where P_i is the partial pressure of the i^{th} species. The equilibrium constants of the deposition reactions, K_{As} and K_{P} , were calculated at $T = 700 \text{ °C}$ using thermochemical data from Kirwan [19]. The activities of the solid components, a_{GaAs} and a_{GaP} , were

calculated by the regular solution model, where $a_i = \gamma_i x_i$. γ_i is the activity coefficient, evaluated by [20]:

$$\ln \gamma_i = \frac{(1 - x_i)^2 \Omega}{RT} \quad (5)$$

where x_i is the mole fraction of each solid component, Ω is the GaAs-GaP interaction parameter, taken to be 1000 cal/mol [21], R is the gas constant, and T is the reaction temperature. We assume that $P_{P_4} = P_{PH_3}/4$, with the values of P_{PH_3} taken from the model data of Fig. 11. The initial partial pressures of the other species (in atm) were $P_{HCl} = 0.002$, $P_{GaCl} = 0.0012$, $P_{As_4} = P_{AsH_3}/4 = 0.0012$, with the balance of the atmospheric pressure composed of H_2 . The equilibrium compositions of all the species were calculated using Eqs. (3-5). Figure 13 plots both the modeled and experimentally determined values of x_{GaP} as a function of $P_{PH_3}/(P_{PH_3} + P_{AsH_3})$ at the substrate position. The experimental values are averaged P concentration values from Fig. 12 for each flow rate.

The model prediction provides qualitative agreement, underestimating the phosphorus concentration determined by SIMS, although the difference is smaller at higher $P_{PH_3}/(P_{PH_3} + P_{AsH_3})$ ratios. Improvement in the model could come from multiple sources. The model is sensitive to the substrate temperature, which is not known with complete accuracy in our reactor, because only the furnace temperature is controlled. Accurate data regarding the decomposition of PH_3 to P_4 (and P_2) would also improve the model. Given the dilute nature of these species, it is quite unlikely that full conversion to P_4 occurs although it is the more thermodynamically stable species. The presence of a phosphorus background condensed on a cold surface somewhere in the system could also lead to a higher experimentally observed value of $[P]$. Regardless, the CFD model predicts the correct order of magnitude and provides valuable understanding about cross doping in our reactor and our ability to control it.

V. Application to Photovoltaic Device Growth

HVPE belongs to a suite of high purity, vapor phase epitaxial growth technologies, including MOVPE and MBE, which can all grow high quality III-V materials. HVPE, with high throughput and usage of low cost starting materials, offers the potential for significant cost reductions compared to the other two techniques. Photovoltaic devices are an application of III-V materials, among many others, that would greatly benefit from the significant reductions in the cost of materials growth enabled by HVPE. The highest demonstrated photovoltaic (PV) device efficiencies are consistently achieved using III-V semiconductor materials. Despite marked advantages over silicon in efficiency, weight, flexibility, and annual energy harvesting efficiency, III-V photovoltaics have not achieved widespread adoption due to a combination of high substrate and epitaxy costs [4]. These costs must be decreased by at least two orders of magnitude for high-efficiency III-V cells to

achieve terrestrial one-sun market relevance. Cost analysis indicates that this scenario becomes more practical if materials growth by MOVPE or MBE is replaced by HVPE [4].

HVPE can reduce the epitaxy costs of III-V photovoltaics while maintaining high efficiency, but the growth of PV devices by HVPE presents a unique set of challenges. The device structure of interest is a single junction GaAs cell, comprising five separate layers of varying chemical composition, thickness, and doping, as depicted in Fig. 14. Many targets must be achieved to reach an ideal device, including high purity and material quality, interfaces with abruptness of a few monolayers, and $\text{In}_{1-x}\text{Ga}_x\text{P}$ composition controlled within a few percent to prevent the nucleation of dislocations, which can degrade device performance. The high growth rate offered by HVPE can make it difficult to grow layers with precise thickness, and the long reactor transients prevent rapid changes in doping or chemistry that are accomplished easily in MOVPE. Enabled by our unique reactor design, however, we demonstrate that growth of these devices is possible by HVPE.

While the dual chamber design is beneficial for the formation of abrupt chemical interfaces, cross doping by the diffusion of reactants between the two growth chambers could pose an issue due to the open connection between them. In the SIMS measurement of Fig. 12, 10^{19} cm^{-3} levels of P in were observed in a GaAs layer grown in GC1 with phosphide growth conditions flowing in GC2. This level of cross doping is low enough that it will not appreciably alter the band gap or lattice constant of the GaAs layer, and is sufficient for the deposition of a GaAs PV device. Furthermore, unintentional dopant incorporation will be at least four orders of magnitude lower, far below the doping levels required for the targeted device. High purity material has already been demonstrated in HVPE [2], and we show that our reactor design does not alter this purity.

Regarding abrupt interfaces, we have also demonstrated the ability to deposit layers with abrupt doping transitions (see, for example, Fig. 2). We note that a doping transition created by gas switching without a growth interruption (Fig. 9) is too wide, and not suitable for the formation of an abrupt pn -junction interface. Guided by preliminary CFD modeling, we chose a dual chamber design in part for its ability to form abrupt interfaces through rapid transfer of the substrate between two chambers containing different gas chemistries. Mechanical transfer of the substrate enables the deposition of materials of varying chemical composition and doping while obviating the need for growth pauses which may lead to interfacial contamination [8]. Abrupt interfaces are enabled by the dual chamber design.

The final question becomes whether the observed compositional non-uniformity in the $\text{In}_{1-x}\text{Ga}_x\text{P}$ layer is sufficient for the deposition of PV devices. $\pm 2\%$ (absolute) compositional variation was observed in the XRD map of Fig. 7. The equilibrium critical thickness for this level of compositional variation, before the generation of extended crystal defects, is $\sim 100 \text{ nm}$ [22], significantly thicker than the 40 nm of surface passivation layers required in a high-efficiency GaAs cell. This range

includes the variation at the edges, while the majority of the epilayer falls within an even tighter range than $\pm 2\%$. This result provides confirmation that our HVPE reactor can deposit sufficiently uniform $\text{In}_{1-x}\text{Ga}_x\text{P}$ for PV applications. Modeling indicates that further improvement can be gained by smoothing out temperature non-uniformities at the substrate by balancing the gas flow.

Using our HVPE reactor, we have demonstrated the growth of unpassivated GaAs *pn*-junction devices with open-circuit voltage (V_{oc}) greater than 0.96 V grown at rates in excess of 1 $\mu\text{m}/\text{min}$ [23]. This V_{oc} is comparable to that observed in a similar device structure grown by MBE [3] indicative of the deposition of high quality material by HVPE. The addition of an $\text{In}_{1-x}\text{Ga}_x\text{P}$ cladding layer to the front surface of our PV devices led to improved blue response and an increase of 26% in short circuit current density (J_{sc}) [23]. The on-going development of the back surface cladding layer is expected to lead to further improvement. These results were enabled by CFD modeling, which guided the design and operation of two generations of HVPE reactors [3, 8], and will continue to guide cell development in the future.

V. SUMMARY AND CONCLUSION

A custom HVPE reactor designed for the deposition of III-V electronic devices was modeled by CFD-ACE+ simulation software. Various aspects of reactor operation were modeled and related to specific features of the reactor design and to experimental data. Modeling of the gas concentration under typical flow conditions indicated that the gas stream achieved a high degree of spatial uniformity before reaching the substrate. The uniformity was attributed to the boat design, which directs the gas stream away from the substrate initially at high velocity. A long flow path to the substrate allows sufficient time for the reactants to spread evenly across the reaction chamber. The gas concentration uniformity was evaluated experimentally by the growth of a 2" $\text{In}_{1-x}\text{Ga}_x\text{P}$ layer with an absolute compositional variation of $\pm 2\%$ across the wafer. The variation that was observed was correlated with temperature variation at the substrate caused by heating from the gas flows. Transient modeling determined the time required for transient gas flows in the reactor to reach steady state. This value was ~ 45 s for a flow of 10 slm in each growth chamber. SIMS data from an epitaxial GaAs layer in which the doping was switched mid-run from zinc to selenium indicated that the doping transition was completed in ~ 46 s, in agreement with the model. Lastly, the cross doping between the chambers was modeled as a function of the curtain gas flow. The CFD model predicted that the concentration of PH_3 (originating in GC2) at the substrate in GC1 would decrease by an order of magnitude as the curtain flow rate was increased from 0 to 2500 sccm. SIMS measurements on a GaAs sample grown in GC1 with PH_3 flowing in the opposite chamber showed that the P concentration in the layer decreased about 2x. The CFD simulation accurately modeled multiple features of a complex HVPE reactor design and confirmed its utility as a vital tool for process development and reactor design. Application of this reactor toward the growth of photovoltaic devices was demonstrated.

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VII. References

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Fig. 1 –Left: schematic of our custom HVPE reactor. The reactor consists of two separate growth chambers connected by a central horizontal tube, allowing mechanical transfer of the substrate between chambers. Gas curtains between GC1 and GC2 provide resistance to cross-flow between the chambers. Ga and In source metals are stored in the upper part of each chamber inside quartz vessels called “boats”. Extra H_2 and unreacted HCl can be added through the top of each chamber as an additional control on gas phase supersaturation. A resistance furnace with rectangular heating elements whose bounds are delineated by the dotted lines provides independent temperature control for each zone. Right: Discretized 3D model of the reactor HVPE reactor utilized in the CFD simulations.

Figure 2 - Schematic of the boat assembly. Each boat has a large chamber and a small chamber that are physically separated from each other and can hold two different metals. HCl is flowed into each boat

chamber to generate GaCl and InCl, while Group V hydrides and dopants can be flown through the tube passing through the center of each boat.

Fig. 3 – SIMS data of a sample that was mechanically transferred between the two growth chambers (GC1 and GC2) with the growth of GaAs with varying zinc doping occurring in each chamber. Four layers were grown in each chamber, and the DEZn dopant flows in each chamber were decreased for each subsequent layer.

Fig. 4 – Velocity magnitude of the reactant gases near the InCl boat outlet in GC2. The position of the boat is indicated in Fig. 1.

Table 1 – Flow rates (in sccm) of gases in the CFD simulation described section IV.A.

	Growth Chamber 1 (GC1)				Growth Chamber 2 (GC2)			
	Small Boat	Large Boat	Center Tube	Top Flange	Small Boat	Large Boat	Center Tube	Top Flange
H ₂	2500	2500	2500	2500	2500	425	2500	2500
GaCl	6	18	0	0	1.5	0	0	0
InCl	0	0	0	0	0	35	0	0
AsH ₃	0	0	50	0	0	0	0	0
PH ₃	0	0	0	0	0	0	50	0
HCl	0	0	0	20	0	0	50	0

Fig. 5 – InCl and GaCl mole fraction (X_{InCl} and X_{GaCl}) in GC2 for the standard In_{0.48}Ga_{0.52}P growth case. The white areas in the illustration possess a mole fraction higher than the maximum on the scale. The InCl and GaCl compositions at the positions marked by the dotted lines in the left figure are plotted as a function of horizontal position in Fig. 6.

Fig. 6 - InCl (top) and GaCl (bottom) vapor phase mole fractions as a function of horizontal position in the reactor tube. The concentration profiles are plotted at five different vertical heights above the substrate, as depicted by the black lines in Fig. 5. Note that the concentration is zero inside the center tube for $y = 16''$ and $y = 12''$.

Fig. 7 – (top) Experimental Ga composition as a function of position in an $\text{In}_{1-x}\text{Ga}_x\text{P}$ epilayer grown on a 2" GaAs substrate as determined by XRD. (bottom) Cross section depicting the spatial temperature profile inside GC2 at wafer level calculated by the model. The black circle represents the boundary of a centered wafer.

Table 2 - Flows (in sccm) employed in the model presented in section IV.B.

	Growth Chamber 1				Growth Chamber 2			
	Small Boat	Large Boat	Center Tube	Top Flange	Small Boat	Large Boat	Center Tube	Top Flange
H ₂	2500	2500	2500	2500	2500	2500	2500	2500
GaCl	3	9	0	0	0	0	0	0
InCl	0	0	0	0	0	0	0	0
AsH ₃	0	0	50	0	0	0	0	0
PH ₃	0	0	0	0	0	0	50	0
HCl	0	0	0	20	0	0	0	0

Fig. 8 - Modeled H₂Se concentration at the substrate as a function of time for the transient simulation described in IV.B. The concentration is normalized to its steady state value.

Fig. 9 – SIMS measurements of a doped GaAs layer first doped with Zn, then Se as the DEZn is turned off and H₂Se turned on mid-growth.

Fig. 10 – Log₁₀ of PH₃ concentration in the reactor for the case where PH₃ is flowing in GC2 with flows simulating growth of a GaAs layer in GC1. 2500 sccm of H₂ is flowing through each gas curtain.

Fig. 11 – Mole fraction of PH₃ at the center of a substrate in GC1 as a function of curtain H₂ flow rate for the case in which PH₃ is flowing in GC2.

Fig. 12– SIMS measurement of the solid phosphorous concentration, [P], in a GaAs layer grown under the conditions in Table 2 in GC1 with 50 sccm of phosphine flowing in GC2. The flow in the H₂ gas curtain was gradually decreased throughout the growth, leading to increases in the phosphorus concentration in the layer. The curtain flow rate is listed above each corresponding concentration step.

Fig. 13 – GaP solid fraction, x_{GaP} , in $\text{GaAs}_{1-x}\text{P}_x$ for a GaAs layer grown in GC1 with 50 sccm of PH_3 simultaneously flowing in GC2. The marker values were determined from SIMS data while the curve was calculated by the thermodynamic model described in the text using PH_3 concentrations calculated by the CFD model.

	<u>Layer</u>	<u>Thickness</u>	<u>Doping</u>
	Contact	300 nm	$1 \times 10^{19} \text{ n}$
	Window	20 nm	$1 \times 10^{19} \text{ n}$
	Emitter	100 nm	$1 \times 10^{18} \text{ n}$
	Base	$2.5 \mu\text{m}$	$5 \times 10^{16} \text{ p}$
	Back Surface Field	20 nm	$1 \times 10^{19} \text{ p}$
	Substrate	$350 \mu\text{m}$	$1 \times 10^{19} \text{ p}$

Figure 14 – GaAs single junction solar cell that is the target of this study.