Numerical study of the influence of reactor design on MOCVD with a comparison to experimental data

Andrew N. Jansen *, Mark E. Orazem *

Department of Chemical Engineering, University of Virginia, Charlottesville, Virginia 22901, USA

Bradley A. Fox and William A. Jesser

Department of Materials Science, University of Virginia, Charlottesville, Virginia 22901, USA

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Comparisons were made between experimental data and a two-dimensional model for the MOCVD of GaAs from trimethylgallium and arsine in two horizontal air cooled reactor geometries. A unique feature of this work was that comparison was made, not only on the wafer, but over the entire deposition regime. Excellent agreement was achieved for growth at low system pressures. Experimental deposition profiles under atmospheric pressure were much less uniform than those predicted by the model. This difference could not be attributed to a pressure dependence of heterogeneous reactions. Inclusion of thermal diffusion had little effect on the uniformity of the calculated deposition profile but decreased the magnitude of the growth rate by up to 12%. Through model calculations and experiments, it was determined that a channel with a tilted upper wall and a horizontal susceptor has the same growth rate profile as does a standard horizontal upper wall channel with a tilted susceptor. Substrate rotation was predicted to cause growth rate uniformity within less than 4.3% in horizontal channel flow and 3.8% in a channel with tilted walls.

1. Introduction

Metalorganic chemical vapor deposition (MOCVD) differs from other chemical vapor deposition processes in the type of phenomena that limits the growth rate. In silicon deposition from silane, for example, it has been determined that the growth rate is limited by the rates of gas phase reactions. Models based on this with appropriate chemical reactions and rate constants are able to predict the results of various experimental conditions [1,2]. In contrast, MOCVD processes are usually assumed to be mass transport limited under conventional operating conditions [3–13]. In the case of GaAs grown from arsine and trimethylgallium, the limiting species is assumed to contain gallium. Typical models are based on a LeVêque development in which the governing equations are those for fluid mechanics coupled with convective heat and mass transfer. In these models, gas phase and surface reactions are usually neglected (see ref. [1] for a review). Typical boundary conditions for the convective mass transfer are that concentrations of reactants upstream of the substrate are the same as the inlet concentrations and that the concentration of the limiting reactant on the substrate surface is zero. Deposition is assumed to occur only on the substrate, and the resulting flux of the limiting reactant is infinite at the leading edge of the substrate.

The object of this work was to develop a mathematical model that could be used as a predictive tool for the design of MOCVD reactors. One of the first numerical models developed explicitly for MOCVD was the three-dimensional
model of Moffat and Jensen [4]. A unique feature of this model was that it predicted the formation of axial roll cells that are observed during growth under atmospheric pressures. These roll cells cannot be predicted by two-dimensional models. Their numerical method required that diffusion of momentum, energy, and mass in the direction of flow be neglected. Thermal diffusion was not included, and the heterogeneous reaction was assumed to be first order with a rate constant chosen to be sufficiently large that the deposition was mass transfer limited. Ouazzani and coworkers [5] developed a two-dimensional model that included axial diffusion of momentum, energy, and mass with thermal diffusion. The model also included an entrance region. Chinoy and coworkers [6] modeled the effect of susceptor tilt with a model that was similar to the above but neglected thermal diffusion. Holstein and coworkers [7] analyzed the effect of a tilted susceptor through a two-dimensional model that included axial diffusion of momentum, energy, and mass and thermal diffusion.

Deposition of GaAs has been observed experimentally on regions before and after the substrate. In order to model this effect, a surface reaction expression must be applied to the entrance and exit regions. The usual models do not address these regions. As a result, when most model calculations are compared to experimental data, only data from the middle portion of the substrate can be used. Comparison to data in the leading and trailing regions of the substrate may provide valuable information since it is in these regions that the transport mechanisms undergo the most abrupt changes. The presence of large temperature gradients and the modest Peclet numbers obtained for these flows suggest that thermal diffusion and axial diffusion terms should be retained. Bulsari et al. [8] treated deposition in leading and trailing regions of a tilted susceptor through a two-dimensional model that included the effects of axial diffusion. This work extended the model developed by Bulsari et al. [8] through incorporation of thermal diffusion and treatment of the influence of a tilted upper wall and of substrate rotation.

The work presented here addressed a horizontal reactor through the incorporation of a surface reaction mechanism applied over the entire deposition region. The two-dimensional analysis treated the reactor channel and flow conditions in MOCVD of gallium arsenide (GaAs) from trimethylgallium (TMG) and arsine (AsH3) in a carrier gas of hydrogen (H2). The model predictions were compared to experimental data that encompassed the entire deposition region. The two-dimensional formulation was valid for low pressures where axial roll cells were not expected to develop.

### 2. Reaction kinetics

Models for the growth of III–V materials by MOCVD seem to fall into two classes. Two- or three-dimensional models that account for complicated flow and mass transfer patterns typically assume that the deposition can be described in terms of a simple surface reaction, e.g.,

$$\text{Ga(CH}_3)_3 + \text{AsH}_3 \rightarrow \text{GaAs} + \text{CH}_4. \quad (1)$$

Models for one-dimensional systems have been developed that account for the large number of homogeneous and heterogeneous reactions that are predicted by thermodynamic considerations. Tirtowidjiojo and Pollard [9] have presented a model for the reaction of trimethylgallium and arsine in an impinging jet reactor that included 60 species and 232 reactions in the gas phase and another 19 species and 115 processes at the substrate. Their work explored the operating conditions under which different reactions can control the deposition process.

Comparison of experimental data to model calculations seems to indicate that the growth rate is diffusion limited under typical operating conditions for flow-by reactors [3,9–13]. Thus, TMG was assumed to be the limiting reactant for a heterogeneous deposition of GaAs. The kinetic rate expression used was either first order in concentration ($R = k_\omega \text{TMG}$) or expressions based on Langmuir–Rideal or Langmuir–Hinshelwood mechanisms [13]. With the assumptions of strong arsine adsorption [13–15], constant concentration
of arsine, and a relatively small partial pressure of TMG, the Langmuir expressions reduce to

\[ R_{LR} = k_{LR} \omega_{TMG} P, \]

(2)

and

\[ R_{LH} = k_{LH} \omega_{TMG} P^2, \]

(3)

where \( R_{LR} \) and \( R_{LH} \) are the rate of reaction for the Langmuir–Rideal and the Langmuir–Hinshelwood mechanisms, respectively, and \( k_{LR} \) and \( k_{LH} \) are pseudo rate constants that follow an Arrhenius relation. These expressions are referred to as surface reaction mechanisms that are first order and second order in total pressure (first order in concentration of TMG) since these expressions represent asymptotic limits of the complete Langmuir expressions.

3. Procedure

The conditions and properties used in the model, including Fickian and thermal diffusion coefficients, viscosities, densities, and flow rates, were chosen to match those of the experiment. The only adjustable parameter involved in the model was that of the heterogeneous reaction rate constant, \( k \).

3.1. Experimental

The experimental system was a Crystal Specialties Model 425 horizontal air-cooled MOCVD epitaxial reactor. Two different quartz channels were used in the experiments. The first was a standard horizontal channel with a height of 4 cm and an angle of inclination of 9.0° for the susceptor. The second channel was a custom design fabricated for this research which had a horizontal susceptor on the lower surface wall and a tilted upper wall. The height of this channel was 3 cm and the angle of declination was 7.4°. Both reactor channels were of a length of 19.3 cm from the inlet manifold to the exit manifold and a width of 9 cm (see figs. 1a and 2a).

The carrier gas was hydrogen at pressures of 0.1 or 1.0 atm. Two mass flow rates were used at both pressures for each channel (the high mass

![Fig. 1. The horizontal tilted susceptor reactor: (a) geometry; (b) finite element mesh.](image)
The horizontal tilted upper wall reactor: (a) geometry; (b) finite element mesh.

3.2. Numerical

The two-dimensional steady state model of the horizontal CVD reactor incorporated the simultaneous solution of the equation of continuity,

$$\frac{\partial \rho u}{\partial x} + \frac{\partial \rho v}{\partial y} = 0, \quad (4)$$

the equations of motion,

$$\rho u \frac{\partial u}{\partial x} + \rho v \frac{\partial u}{\partial y} = - \frac{\partial P}{\partial x} + \mu \left( \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right), \quad (5)$$

and

$$\rho u \frac{\partial v}{\partial x} + \rho v \frac{\partial v}{\partial y} = - \frac{\partial P}{\partial y} + \mu \left( \frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} \right) - \rho g, \quad (6)$$

the equation of energy,

$$\rho C_p u \frac{\partial T}{\partial x} + \rho C_p v \frac{\partial T}{\partial y} = k \left( \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right), \quad (7)$$

and the equation of convective diffusion for the limiting reactant,

$$\rho u \frac{\partial \omega}{\partial x} + \rho v \frac{\partial \omega}{\partial y}$$

$$= \frac{\partial}{\partial x} \left( \rho D \frac{\partial \omega}{\partial x} \right) + \frac{\partial}{\partial y} \left( \rho D \frac{\partial \omega}{\partial y} \right) + \frac{\partial}{\partial x} \left( \rho \frac{\partial \ln T}{\partial x} \right) + \frac{\partial}{\partial y} \left( \rho \frac{\partial \ln T}{\partial y} \right), \quad (8)$$
where the variables are defined in the list of symbols.

These equations were solved under the assumptions:

1. The aspect ratio (defined as the ratio of reactor width to reactor height) was assumed to be large. In other words, the reactor side walls were assumed to have no effect on the flow conditions inside the reactor. This allowed a two-dimensional model to be used.

2. The composition of the inlet gas was assumed to be 99% hydrogen and 1% TMG (mass fraction) with physical properties that correspond to hydrogen.

3. The gas was assumed to be a Newtonian ideal gas.

4. The heat capacity and thermal conductivity were assumed to be constant.

5. The shear stress terms were evaluated under the assumption that the contribution of the term \( \nabla \cdot u \) was negligible, where \( u \) is the velocity vector.

6. Viscous heating was assumed to be negligible due to the low Brinkman number present (\( Br < 10^{-6} \)). This assumption is generally valid when the Brinkman number is less than 2 [16].

7. The heat of reaction was neglected in the calculation of the temperature field.

8. Pressure and velocity fields were assumed to be unaffected by the molar change in reactant concentration.

9. Transport of energy via concentration gradients was neglected (i.e., no Dufour effect).

10. The rate of deposition on the wafer was assumed to be mass transport limited based on the observed increase in growth rate as the mass flow rate is increased. Hence, no homogeneous reactions were included.

The Fickian diffusivity of TMG was assumed to be independent of concentration and given by [4]:

\[
D = 2.23 \times 10^{-5} T^{1.73} / P, \tag{9}
\]

where \( D \) is in \( \text{cm}^2/\text{s} \), \( T \) is in kelvin, and \( P \) is in atm. The thermal diffusivity was based on the higher order Kihara approximation [17]. Upon linearization, it can be represented by

\[
D^T = C^T \omega, \tag{10}
\]

where \( C^T \) is a function of temperature, molecular weight and the Lennard-Jones parameters, \( \sigma \) and \( \epsilon / k \). The Lennard-Jones parameters were obtained from ref. [18]. This linearization was valid for small concentrations of TMG. The order of magnitude of the thermal diffusivity can be appreciated by noting that \( C^T \) can be approximated to be \( 6.18 \times 10^{-7} T^{0.73} \) g/cm·s. At a temperature of 800 K, this correspond to a thermal diffusion factor, \( \alpha = 1.13 \). This was comparable to that reported in ref. [18] of \( \alpha = 1.22 \).

Since the Reynolds number was of the order of 50, the flow was assumed to be laminar throughout the reactor with an inlet parabolic velocity profile, i.e.,

\[
u = 4 U_0 \left[ \frac{y}{h} - \left( \frac{y}{h} \right)^2 \right] \quad \text{and} \quad v = 0 \quad \text{at} \quad x = 0. \tag{11}\]

A schematic of the tilted upper wall channels is given in figs. 1 and 2, respectively, along with the finite element mesh used for each. These meshes were generated with the PATRAN-G software.

<table>
<thead>
<tr>
<th>Table 1</th>
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<tbody>
<tr>
<td>Property values and conditions</td>
</tr>
<tr>
<td>( \mu ) Viscosity</td>
</tr>
<tr>
<td>( k ) Thermal conductivity</td>
</tr>
<tr>
<td>( C_p ) Specific heat</td>
</tr>
<tr>
<td>( D ) Fickian diffusivity</td>
</tr>
<tr>
<td>( D^T ) Thermal diffusivity</td>
</tr>
<tr>
<td>( g ) Gravitational constant</td>
</tr>
<tr>
<td>( U_o ) Maximum inlet velocity</td>
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<tr>
<td>( T_o ) Susceptor temperature</td>
</tr>
<tr>
<td>( T_{sur} ) Temperature around susceptor</td>
</tr>
<tr>
<td>( T_i ) Inlet temperature</td>
</tr>
<tr>
<td>( T_w ) Upper wall temperature</td>
</tr>
<tr>
<td>( h ) Channel entrance height</td>
</tr>
<tr>
<td>( l ) Total channel length</td>
</tr>
<tr>
<td>( l_i ) Location of insulator</td>
</tr>
<tr>
<td>( l_s ) Beginning of tilt</td>
</tr>
<tr>
<td>( l_{is} ) Beginning of susceptor</td>
</tr>
<tr>
<td>( l_e ) Ending of susceptor</td>
</tr>
<tr>
<td>( \Theta ) Angle of inclination</td>
</tr>
<tr>
<td>( \psi ) Angular of declination</td>
</tr>
</tbody>
</table>
The dimensions of the reactor channels, the fluid properties, and the temperature boundary conditions are given in Table 1.

The boundary conditions used for the fluid mechanics equation were: a parabolic velocity profile (eq. (11)) at the inlet, a zero normal velocity gradient at the exit, and zero velocity components at the upper and lower surface walls. The pressure was specified at the exit of the reactor as

\[ P = P_0 + \rho g y, \]

where \( P_0 \) is the reference pressure.

For the energy equation, an inlet temperature was specified up to a boundary line where the temperature increases abruptly to account for an inlet manifold. A zero normal temperature gradient was specified at the exit. The temperature for the upper surface wall was assumed to be constant at 675 K. The upper wall temperature was below the detection limit by optical pyrometry; therefore this value was chosen based on the observation of the onset of deposition on the upper wall which can be considered to be negligible at temperatures below 650 K [13]. The susceptor was assumed to be held at a constant temperature (973 K). This temperature was measured with a thermocouple built into the susceptor.

The lower surface wall temperature around the substrate was determined via an energy balance on the quartz wall that surrounds the substrate. It was assumed that the quartz wall conducts the heat in an axial direction with heat loss due to radiation to the upper wall. This can be expressed as

\[ k \frac{d^2 T}{dx^2} = \sigma (T^4 - T_a^4)/L, \]

where \( k \) is the thermal conductivity of quartz taken as 0.0138 W/cm \cdot K, \( \sigma \) is the Stefan constant taken as \( 5.67 \times 10^{-12} \text{ W/cm}^2 \cdot \text{K}^4 \), \( T_0 \) is the temperature of the upper wall (675 K), and \( L \) is the quartz thickness (0.5 cm). The boundary conditions were

\[ T = T_0 \quad \text{at} \quad x = 0, \]

and

\[ \frac{dT}{dx} = 0 \quad \text{at} \quad T = T_a. \]

This differential equation was solved by the forward difference method, and the result is shown in Fig. 3. This temperature profile was used as the boundary condition on the quartz wall that surrounds the substrate. The above boundary conditions were then used in the simultaneous solution of eqs. (4) to (7).

The boundary conditions for eq. (8) were: the mass fraction of TMG was set to 0.01 at the inlet, and the normal flux of TMG was set equal to zero on the upper wall surface, at the exit, and on the lower surface wall of the entrance region, \( I_2 \). The flux of TMG normal to the bottom wall was set equal to a kinetic rate expression on the susceptor.
and the region before and after it. This expression can be represented as

\[ R = k_\alpha \omega_{\text{TMG}} P^n, \]  

(18)

where \( P \) is total pressure, \( n = 0, 1, \) or \( 2, \) and \( k_\alpha \) follows an Arrhenius relation:

\[ k_\alpha = A e^{-E/RT}, \]  

(19)

with \( E = 270 \text{ kJ/mol} \) and \( A P^n = 0.6 \times 10^{14} \text{ g/cm}^2 \cdot \text{s} \) [8].

3.2.1. Solution of fluid mechanics and energy equations

A significant simplification was made when the equations of fluid mechanics and energy (eqs. (4) to (7)) were decoupled from the equation for convective diffusion (eq. (8)). This can be done with the assumption that the heat of reactions and molar changes between reactants and products had negligible effect on the fluid mechanics and energy equation (the mass fraction of TMG was less than 1.0% of the total gas flow). Thus the fluid mechanics and energy equations could be solved separately to determine the velocity components and temperature throughout the reactor. These results were then used in the mass balance equation to solve for the concentration profile throughout the reactor.

Eqs. (4) through (7) were solved with the use of a finite element software package developed by Rice and Schnipke [20,21]. A unique feature of this software was its use of an equal-order velocity-pressure formulation which eliminated spurious pressure modes. This method was incorporated in program TURBO2D, a tailored version of the commercial program package FLOTRAN which is distributed by COMPUFLO Inc. [22]. This program used an iterative method that could be monitored by the error residuals for the velocity components, temperature, and pressure at each iteration. The program was terminated after the error residual leveled off at typically \( 10^{-7} \). In most cases this required 300 to 400 iterations. This program was executed on a PRIME 4150 in typically 6 h of CPU time in an interactive mode.

The code calculated nodal velocity components, temperature, and pressure. These results can either be used for input into the mass transfer analysis or to view the streamlines, temperature, or pres-

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Fig. 4. Typical profiles in the horizontal tilted susceptor reactor: (a) streamlines; (b) temperature; (c) pressure.
Fig. 5. Typical profiles in the horizontal tilted upper wall reactor: (a) streamlines; (b) temperature; (c) pressure.

Comparison of model calculations to experimental data taken at low pressure (0.1 atm) was complicated by lack of convergence of the fluid mechanics and energy equations for high mass flow rates at pressures below 0.15 atm. This lack of convergence could be explained by use of a too large relaxation parameter, lack of double precision, and too coarse of a mesh in local regions. A correction for these would have greatly increased the computation time. However, at a pressure of 0.15 atm the solution did converge. Therefore, the velocities used in the model were scaled to those of the experiment by equating the mass flow rate used in the model at 0.15 atm to the mass flow rate used in the experiment at 0.1 atm. This decision was based on previous work which demonstrated that mass transport limited deposition profiles at different pressures were identical when the mass flow rate was held constant [8].

3.2.2. Solution of the equation for convective diffusion

The solution of the convective diffusion equation was based on the streamline upwind finite element method developed by Rice and Schnipke [23]. This method was designed for convection

sure profiles. Examples of calculated results are presented in figs. 4 and 5 for the tilted susceptor and the tilted upper wall reactors, respectively. The profiles exhibited in these figures are nearly identical for all the flow conditions studied. The pressure results would appear to indicate a strong pressure gradient; however, the pressure difference between the inlet and exit of the reactor was less than 1 Pa, which was insignificant when compared to the system pressure of 15 kPa.

The meshes used for the tilted susceptor and tilted upper wall geometries are presented in figs. 1b and 2b, respectively. Nodal points were concentrated in regions where flow phenomena were present. Nodal points were concentrated next to the lower surface wall where deposition occurs; near the leading and trailing edges of the susceptor where the temperature gradients were large; near the upper wall, which created a flow restriction for the tilted upper wall geometry; and at the exit where the flow restriction ceased. Initially, a total of 960 nodal points were used for each mesh. This yielded streamline profiles that were nonuniform. Use of 1144 and 1560 nodes gave identical results such as the streamlines given in figs. 4 and 5.
dominated flows such as those that exist in a horizontal CVD reactor. The mesh used was identical to the mesh used in the solution of the fluid mechanics and energy equations. This program was written by this group to incorporate thermal diffusion effects and heterogeneous reaction rates as surface boundary conditions into the convective diffusion equation. This program yielded the flux on the substrate and the concentration profile in the reactor.

This program did not require an iterative method since the fluid mechanics and energy equations were decoupled from the convective diffusion equation. In order to test the accuracy of the results, a check of the mass balance was performed. This consisted of a comparison between the sum of the total flux that left the reactor channel plus the deposition flux against the flux of reactant that entered the reactor. There was typically a 1% to 5% difference between these two quantities. It was found that a further increase in the number of iterations of the TURBO2D program had little effect on this difference. This program was also executed on a PRIME 4150 in usually 30 min of CPU time in an interactive mode.

4. Results and discussion

This discussion is divided into two sections. The first deals with comparisons between experimental data and model predictions while the second section involves only the model predictions. In the second section the tilt angle and channel height of the tilted upper wall channel are identical to that of the tilted susceptor channel. The figures presented in this section are referenced to distance from the leading edge of the substrate.

4.1. Comparison of calculations to experimental data

Comparisons between the experimental growth rate and the model predictions of growth rate are presented in this section. These comparisons are made at both the high and low mass flow rates for each channel geometry. Note that the comparisons between the experimental data and the model predictions cover the entire deposition region and that the model correctly predicted the deposition profile near the leading edge of the substrate.

The maximum inlet velocity was calculated from the assumption of a two-dimensional Poiseuille profile without consideration of the finite aspect ratio. The maximum inlet velocities used for comparison to experimental data, therefore, are approximately 23% lower than that recommended by Ouazzani et al. [5]. An increase in velocity to account for the finite aspect ratio would increase the growth rate comparison by about 8% and this value is in the order of the scatter of the data.

The experimental data are compared to the model predictions in fig. 6 for the high mass flow rate in the tilted susceptor channel. The model predictions are based on a pressure of 0.15 atm and a maximum inlet velocity of 55 cm/s. The experimental data were taken at 0.1 atm and a maximum velocity of 82 cm/s. The low mass flow rate case in the same channel is given in fig. 7. Here the maximum inlet velocity was 27 cm/s at a pressure of 0.15 atm for the model and 41 cm/s at a pressure of 0.1 atm for the experiment. The mass flow rates used in the tilted upper wall channel were the same as those used in the tilted susceptor.
channel. The resultant flow velocities were, however, higher due to the lower channel height. The growth rate comparison for the high mass flow rate in the tilted upper wall channel is illustrated in fig. 8. The maximum inlet velocity for the model was 65 cm/s at 0.15 atm, which corresponded to 92 cm/s for the experiment conducted at 0.1 atm. The results of the low mass flow rate in this channel are given in fig. 9. For this case, the maximum inlet velocity was 30 cm/s at 0.15 atm for the model and 45 cm/s at 0.1 atm for the experiment.

These comparisons demonstrate that the model predictions were well within an order of magnitude of the experimental data and that the model predicted correctly the influence of mass flow rate and channel geometry. The deposition profile was more uniform and the magnitude of deposition was greater at the high mass flow rate (figs. 6 and 8) as compared to the low mass flow rate (figs. 7 and 9). These observations held for both the tilted upper wall channel and the tilted susceptor channel.

The experimental data for the tilted upper wall channel exhibited more scatter than the data for the tilted susceptor channel. This might be attributed to irregularities in the tilted upper wall channel such as the supports for the upper wall. Also, there was no orientation to the growth since the substrate was quartz and not a single GaAs
crystal. This resulted in a deposit that was polycrystalline.

The pressure and velocities used in the above cases reflect typical operating conditions for the MOCVD growth of GaAs. At a pressure of 1.0 atm the experimental deposition profile was non-uniform, as is illustrated in fig. 10 for the tilted susceptor channel. This corresponded to the same high mass flow rate as used at a pressure of 0.1 atm. Here the maximum inlet velocity prediction was 8.0 cm/s at 1.0 atm and 7.7 cm/s at 1.0 atm for the experimental data. At this pressure, the model did not adequately predict the profile exhibited by the experimental data. Similar results were obtained for the low mass flow rate in this channel as well as for the high and low mass flow rates in the tilted upper wall channel. There were several possible explanations for this poor correlation. The first was that homogeneous reactions may become important at higher pressures, and these were not treated in the present model. The second was the effect of roll cells which were possible at this pressure [24–27]. Since roll cells are inherently three-dimensional and the model was only two-dimensional, the effect of these roll cells could not be determined by the current model.

A third possibility was pressure dependence of the surface reaction, which could be analyzed by this model.

Initially the model used a simple surface reaction mechanism that was first order in total pressure of TMG, but independent of pressure. This yielded model predictions that were also independent of pressure even though the diffusivity coefficient was pressure dependent. This result was obtained because the mass transport was convection dominated. A surface reaction mechanism that was linearly dependent on total pressure and on concentration of TMG was used. The results are illustrated in fig. 11 where the normalized flux for the high mass flow rate in the tilted susceptor channel is plotted as a function of position at pressures of 1.0 atm and around 0.1 atm. The normalized flux was used to make comparisons between the deposition uniformity rather than the magnitude of the growth. At around 0.1 atm the model prediction agreed with the experimental data. However, at 1.0 atm the model did not predict the abrupt decrease in deposition 4 cm...
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Any great extent. Total pressure did not yield results that deviated to any great extent.

4.2. Analysis of numerical predictions

Three major results are discussed in this section. These are the effects of thermal diffusion, reactor geometry, and substrate rotation. The first subject provides physical insight between the mathematical model and reality. The last two subjects result from the use of the model to predict the effects of reactor conditions. In this section the tilted upper wall channel is a mirror image of the tilted susceptor channel.

4.2.1. Effects of thermal diffusion

The effects of thermal diffusion on the growth rate are demonstrated in figs. 13 and 14 for the tilted upper wall channel. The model calculations of the low mass flow rate case are illustrated in fig. 13 where the two curves represent the model calculations with and without thermal diffusion. Both calculations were at a pressure of 0.15 atm and a maximum inlet velocity of 27 cm/s. The high mass flow rate case is illustrated in fig. 14 for this same reactor channel. Here, the maximum inlet velocity was 55 cm/s at a pressure of 0.15 atm.

An expression that was second order in total pressure and first order in concentration of TMG was also tried. These results are given in fig. 12 and correspond to the conditions used in fig. 11 except that the surface reaction mechanism was different. The model predicted the deposition profile exhibited by the data at pressures around 0.1 atm, but at atmospheric pressures the model did not predict the abrupt decrease in the deposit near the middle of the substrate. This indicated that second order pressure dependent mechanisms alone also cannot account for the pressure dependence exhibited by the experimental data. No other surface mechanisms were investigated based on the conclusion that surface reaction mechanisms that were zeroth, first, and second order in total pressure did not yield results that deviated to any great extent.

![Fig. 12. Experimental and calculated (solid line) normalized flux as a function of position for the tilted susceptor channel. Calculation engaged a surface reaction mechanism that was second order in total pressure. (a) Calculated values for $U_0 = 55$ cm/s at 0.15 atm, (b) calculated values for $U_0 = 8.0$ cm/s at 1.0 atm, (c) experimental data with $U_0 = 82$ cm/s at 0.1 atm, and (D) experimental data with $U_0 = 7.7$ cm/s at 1.0 atm.](image1)

![Fig. 13. Flux as a function of position in the tilted upper wall channel for $U_0 = 27$ cm/s and a pressure of 0.15 atm for (a) thermal diffusion and (b) no thermal diffusion.](image2)
The thermal diffusion effects in the tilted susceptor channel are not illustrated here because, as discussed in the next section, the growth rates were found to be identical to those in the tilted upper wall channel at each mass flow rate.

As is demonstrated by these two figures, thermal diffusion decreased the growth rate by up to 12% for the low mass flow rate case and up to 9% for the high one. Similar results were found in other works [9,11,18]. When the growth rates were normalized against the average rate for each calculation and plotted in the same manner, there was no difference between the calculation with thermal diffusion and the calculation without thermal diffusion. This indicates that thermal diffusion had little effect on the growth uniformity. However, thermal diffusion did affect the magnitude of the growth rate.

This result differs somewhat from that of Ouazzani et al. [5] who indicated that thermal diffusion decreased the growth rate at the leading edge and increased the growth rate at the trailing edge of the susceptor. This may be due to differences in the boundary conditions used. In the work of Ouazzani et al. [5], the concentration on the lower wall was set equal to zero on the susceptor and the flux was set equal to zero on the surface adjacent to the susceptor. In this work, the flux was set equal to an Arrhenius rate expression on the susceptor as well as the surface adjacent to it as mentioned above. Also, the thermal boundary conditions differ. The temperature of the upper wall treated by Ouazzani et al. [5] was 300 K as compared to 675 K in the present work. The temperatures of the susceptors were the same. This implies that the temperature gradient normal to the susceptor in the former case was significantly larger than in this work.

The observation that thermal diffusion acts to reduce growth rates can be attributed to the positive thermal diffusion coefficient throughout the reactor channel. A positive coefficient for a species enhances the flux from a hot region to a cooler one.
region [16]. In the reactor channel this caused the TMG to diffuse away from the hot susceptor and towards the cooler upper wall. This was in opposition to the Fickian diffusion which caused the TMG to diffuse towards the susceptor. Fig. 15 depicts the concentration profile with and without thermal diffusion for the tilted upper wall channel for a typical flow condition. Likewise, fig. 16 depicts these same profiles in a tilted susceptor channel. The uppermost isoconcentration line above the susceptor for the profiles that include thermal diffusion was around 1.1 (the inlet was 1.0). This demonstrates that thermal diffusion enhanced the concentration of TMG near the cooler upper wall.

Since thermal diffusion drove TMG toward the cooler upper wall over the susceptor, this suggests that it might be possible to hinder or enhance the flux of TMG with an imposed temperature profile on the upper wall. Growth uniformity may be enhanced by an imposed temperature profile on the upper wall such that it would be cooler over the leading edge of the susceptor and hotter over the trailing edge of the susceptor. This approach would be limited, however, by the requirement that the temperature of the upper wall not exceed the temperature at which deposition occurs.

4.2.2. Effects of reactor geometry

A direct comparison is made in this section between the model calculations based on a tilted upper wall and the model calculations based on a tilted susceptor. The normalized flux distributions for each reactor channel under several flow conditions are compared in figs. 17 to 19. In fig. 17, the normalized flux is plotted as a function of position along the susceptor for both geometries at a pressure of 0.15 atm and a maximum inlet velocity of 55 cm/s in each reactor channel. This was the high mass flow rate case. Likewise, fig. 18 illustrates the normalized flux versus position for both channels at the low mass flow rate case. For this case, the maximum inlet velocity was 27 cm/s.

![Fig. 16. Typical concentration profile in the tilted susceptor channel (a) with thermal diffusion and (b) without thermal diffusion.](image)

![Fig. 17. Normalized flux as a function of position with \( U_0 = 55 \) cm/s at 0.15 atm for the tilted upper wall channel and the tilted susceptor channel.](image)
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The high and low mass flow rates used in this channel were the same as in the tilted wall channels. Comparison of figs. 17 and 18 to fig. 19 shows that use of a tilted wall significantly improved the growth uniformity. Plots of the growth rate versus position are not included since this simply involves a change of scales. The results of figs. 17 and 18 demonstrate that the tilted upper wall model predicted the same results as the tilted susceptor model if the tilt angle and the height were the same for each. In other words, the deposition profiles were identical if the two geometries were mirror images. The remainder of this section is devoted to an explanation of this phenomenon.

The dominant transport mechanism in MOCVD differs from the Knudsen diffusion observed in low pressure epitaxial processes such as molecular beam epitaxy (MBE) and sputtering [1]. Under usual operating conditions the mean free path is on the order of 9000 cm for MBE and 1 cm for sputtering deposition. Typical MOCVD reactors operate at comparatively high pressures. Even under low pressure operation (10 kPa), the mean free path is estimated to be 0.0002 cm. Since the dimensions of each of these reactor systems are of the order of centimeters, the increase of the growth rate uniformity must be due to some change in the bulk fluid flow.

A first approximation would be to characterize the flow over the susceptor as if it were an isothermal flow over a smooth semi-infinite flat plate [16]. This is a well-known boundary layer flow which yields an analytic expression for the flux into the plate:

$$\mathcal{N} = Cx^{-1/2}u_\infty^{1/2}y_\infty,$$  \hspace{1cm} (20)

where $\mathcal{N}$ is the species flux, $C$ is a constant, $u_\infty$ is the approach velocity outside the boundary layer, $x$ is the distance from the leading edge of the plate measured tangent to the plate, and $y_\infty$ is the species concentration outside the boundary layer. Note that eq. (20) implies that the flux can never be uniform due to its $x$ dependence ($u_\infty$ and $y_\infty$ are constant for each flow condition). The flux predicted by this expression would be infinite at the leading edge and decrease in accordance to

![Fig. 18. Normalized flux as a function of position with $U_0 = 27$ cm/s at 0.15 atm for the tilted upper wall channel and the tilted susceptor channel.](image)

![Fig. 19. Normalized flux as a function of position with (a) $U_0 = 27$ cm/s and (b) $U_0 = 55$ cm/s at 0.15 atm for the channel with two horizontal walls.](image)
1\sqrt{x}$ along the flat plate. This would also be true for a tilted plate although the power dependence on $x$ would be a function of the tilt angle. This expression cannot adequately explain the uniform growth region that was observed experimentally.

The reason this expression does not apply to the reactor channels used is that the upper wall prevents the formation of a true boundary layer. A concentration boundary layer develops on the susceptor in the entrance region, but intersects the upper wall a short distance down the reactor. Depletion changes the effective reactant concentration, and reduction of the cross-section normal to the direction of flow (as with a tilted susceptor) increases the effective flow velocity. Thus, upstream velocities and concentrations, $u_\infty$ and $y_{avg}$, respectively, are not relevant to this problem. It is desirable to define some velocity and concentration that would show some insight to the benefit of a tilted wall. It is proposed that $u_{avg}$ be the normalized $x$ velocity averaged in a vertical cross-section along the susceptor and $y_{avg}$ be the normalized concentration averaged in the same vertical cross-section along the susceptor. In order to study the effects of the velocity distribution and not its magnitude, $u_{avg}$ was normalized to its value at the exit.

To gain a physical understanding of why either a tilted upper wall or a tilted susceptor increased the growth uniformity, both $u_{avg}^{1/2}$ and $y_{avg}$ are plotted as a function of position for all three flow channels in figs. 20 and 21. In these plots, curve (a) is the square root of the average velocity, curve (b) is the average concentration for the high mass flow rate case, and curve (c) is the average concentration for the low mass flow rate case. Fig. 20 corresponds to a channel with two horizontal walls, fig. 21 corresponds to either the tilted upper wall channel or the tilted susceptor channel.

In fig. 20, $u_{avg}^{1/2}$ is nearly constant except over the susceptor where large temperature gradients exist. These large temperature changes caused the density of the gas to decrease, and, by the equation of continuity, the velocity of the gas must increase. Once past the susceptor, the gas cooled, which increased the density and, thus, decreased the velocity. In fig. 21, $u_{avg}^{1/2}$ increased steadily due to the flow constrictions created by the tilted walls. Here too, the slight increase and decrease in $u_{avg}^{1/2}$ was due to the density changes as the gas passed over the hot susceptor. Notice that the $u_{avg}^{1/2}$ curve is identical for both the high and low mass flow rate cases in both figures. This demonstrates that the velocity profile was determined solely by the channel geometry so long as buoyancy effects or turbulence were not present.
In both figures, the average concentration was larger for the case of the high mass flow rate. This was due to the dependence of the inlet flux on $u$. If the reaction was kinetically controlled, an increase in mass flow rate would have no effect on the deposition rate and the exit composition would become a stronger function of velocity.

The reason that a tilted wall increased the growth uniformity along the susceptor is explained with the aid of figs. 20 and 21. In both figures, the average concentration decreased along the susceptor. The velocity can be considered independent of position in the channel with two horizontal walls, it increased for both the tilted upper wall and the tilted susceptor channels. This increase in velocity compensated for the decrease in concentration due to deposition of the reactant species. The net effect was a more uniform growth profile. An optimum uniformity in growth is obtained when the rate of reactant replenishment (due to the increase in velocity) matches the rate of reactant consumption. This optimum was reached in the high mass flow rate case as depicted in fig. 17. Note that this explanation does not depend on how the velocity is increased. Thus, it is expected that either a tilted upper wall or a tilted susceptor channel will have the same effect so long as the channel height and tilt angle are the same for each.

4.2.3. Effects of substrate rotation

There is a growing trend in the semiconductor industry to incorporate substrate rotation in horizontal reactors to improve uniformity [28–30]. The rotation averages the deposition over the substrate. The object of this study was to investigate the effect of geometry and operating conditions on the degree of uniformity achieved by rotation of the substrate.

Since the present model was only two-dimensional, it was not possible to incorporate the radial motion of the substrate into the model. Thus, it was assumed that the flux of TMG to the rotating substrate was the same as the flux of TMG to a stationary substrate. In other words, the rotation speed of the substrate was assumed to be sufficiently slow that the gas phase velocity profile above the substrate was not affected by the rotation. This allowed the calculation of the radial growth distribution from the stationary model predictions via trigonometric relations.

It is stressed that this analysis is valid only at low rotation speeds. The upper limit of the rotation speed considered here can be estimated by the ratio of the kinematic viscosity and a characteristic length (reactor height in this case). The kinematic viscosity was 38.1 cm$^2$/s at 800 K and 0.15 atm. With a reactor height of 4 cm, this yielded a characteristic velocity of 10 cm/s which corresponds to a rotation rate of 23 revolutions per minute for a susceptor radius of 4 cm. In order for the axial velocity profile to be unaffected by the susceptor rotation, the rotation rate must be at least one or two orders of magnitude below 23 RPM. This analysis may therefore apply to rotation rates that are less than 2 RPM. Analysis for rotation rates larger than this will require a three-dimensional model.

Consider a rotating disk of radius $r$ inscribed in a square plane with an $x, z$ origin at the left most intersection of the plane and the disk, where $x$ is in the direction of the flow field over the plane (see fig. 22). The disk rotates clockwise with an angular velocity $\Omega$. Only the motion in the $x$ direction of a particle on this disk is of importance, since deposition is only a function of $x$. The

Fig. 22. A schematic representation of the method used to calculate the growth rate on a rotating substrate.
position $x$ of this particle is represented by this trigonometric relation,

$$x = r - r \cos \Theta,$$  \hspace{1cm} (21)

where $\Theta$ is the angle formed by the radial position of the particle and the $x$ axis, with $\Theta$ equal to zero when the particle is at the $x$, $z$ origin. The plane was divided into narrow strips of width $\Delta x$ parallel to the $z$ axis. The length of time that the particle resides in this narrow strip determines the amount of growth due to the flux at this axial position. The calculation of this residence time was done with the relation $\Theta = \Omega t$, where $t$ is time. With this relation, it is understood that $\Theta$ is zero when $t$ is zero. The residence time $\Delta t$ of a particle in each narrow strip can be represented as

$$\Delta t = \frac{1}{\Omega} \left[ \arccos \left( \frac{r - x - \Delta x}{r} \right) - \arccos \left( \frac{r - x}{r} \right) \right].$$  \hspace{1cm} (22)

The amount of growth on the disk in this time span is

$$\Delta G = g \Delta t,$$  \hspace{1cm} (23)

where $\Delta G$ is the incremental amount of growth on the disk and $g$ is the growth rate that exists on the plane which was obtained from the model calculations of the previous sections. $\Delta G$ was summed as the particle entered each narrow strip to obtain a total growth amount $G$ at radius $r$. To determine $G$ at various radial positions, the same procedure was done with the new disk of radius $r$ and its corresponding square.

A three inch (8 cm) disk size was used to correspond to a disk slot designed into a typical susceptor. The center of this disk was 5 cm from the leading edge of the susceptor, which eliminates a majority of the peak exhibited in the previous flux profiles. In order to compare the uniformity at various flow conditions, $G$ is normalized with respect to the value of $G$ at the center of the disk. The normalized growth is given in fig. 23 as a function of position for the tilted susceptor channel at high and low mass flow rates. These mass flow rates were consistent with previous mass flow rates. Similar results are presented in fig. 24 for the channel with two horizontal walls. In these figures, the normalized growth is plotted for cases with rotation and without rotation. The normal-
ized growth curves for the cases without rotation differ from the figures previously presented because for these cases the normalization was with respect to the lowest value of the growth rate over the 8 cm section of interest and not the average value over the whole deposition area.

Figs. 23 and 24 demonstrate that rotation increased the deposition uniformity over the section of interest. The deposition uniformity was nearly identical for all four conditions analyzed, with the largest deviation less than 4.3% for the channel with two horizontal walls and less than 3.8% for the tilted wall channel. These results were close to the experimental results obtained by Okamoto and coworkers [29,30], who tested the effects of rotation on the growth uniformity in a channel with two horizontal walls. They obtained uniformities of ±2.6% in growth rate and ±3.5% in doping concentration over a 8 cm section of the substrate in a geometry almost identical to the one studied in this work. It should be noted that this agreement was obtained in spite of the fact that the rotation rate used in their experiments (12 RPM) was larger than the rotation rates for which this analysis can be expected to apply. These results will be sensitive to variations in growth rate in the direction transverse to the flow and to the location of the substrate to be rotated.

The results presented in this section have a number of (perhaps) surprising features. The first is that, upon rotation of the substrate, the deposition uniformity became insensitive to flow rate. This was in contrast to the case with a stationary substrate where an optimal flow rate existed for a given angle of inclination. The second is that the tilted susceptor under near optimal flow rates improves the uniformity of growth on a rotating substrate by only 0.5% as compared to the untilted case. These results show that uniformity can be achieved by rotation if the growth rate is a linear function of position. The extent of uniformity was not influenced by the magnitude of the linear decrease of growth rate with position. Once again, the reader is cautioned that these results apply in the limit of slow rotation speeds and that prediction of the influence of larger rotation speeds will require development of an appropriate three-dimensional model.

5. Conclusions

This work illustrates the value of comparison of model calculations to the complete deposition profile. The model correctly predicted the deposition near the leading edge of the substrate through the use of an Arrhenius rate constant applied over the whole susceptor region. The model agreed well with the experimental data at typical operating pressures around 0.1 atm but not as well for atmospheric pressures. It was also found that pressure dependent surface reaction mechanisms that were first order and second order in total pressure (first order in concentration of TMG) alone could not account for the pressure dependence exhibited by the experimental data. Based on this result, it is suggested that either homogeneous reactions, the inclusion of the third dimension, or both may be required to predict the deposition profile under atmospheric conditions.

Thermal diffusion had little effect on the growth rate uniformity under the conditions studied but decreased the magnitude of the growth rate by up to 9% to 12%, depending on the mass flow rate. Thermal diffusion drove the TMG away from the hot susceptor and towards the cooler regions of the reactor such as the upper wall. Due to this effect, the concentration of TMG at the upper wall was greater than the inlet concentration.

Through experiments and model calculations, a channel with a tilted upper wall and a horizontal susceptor was found to behave in the same manner as a tilted susceptor channel. The results of each were identical if the height of each channel and the tilt angle were the same. This was due to the identical averaged velocity and concentration profiles that were created in each of these flow channels. In this manner, the growth rate profile was independent of the method used to create a desired velocity profile (i.e. the tilted upper wall channel created the same flow constriction as did the tilted susceptor).

Substrate rotation increased the growth uniformity with deviations less than 4.3% for the channel with two horizontal walls and less than 3.8% for the tilted wall channels. In this case, a tilted wall improved the uniformity by only 0.5%. This reduces the incentive to design a tilted chan-
nel if a rotating substrate is also incorporated into the design. The deposition uniformity was also shown to be insensitive to flow rate if the substrate is rotated.

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List of symbols

\[
\begin{align*}
A & \quad \text{Arrhenius rate parameter, g/cm}^2 \cdot \text{s} \\
C_p & \quad \text{Heat capacity, J/g \cdot K} \\
D & \quad \text{Fickian diffusivity, cm}^2/\text{s} \\
D^T & \quad \text{Thermal diffusivity, g/cm} \cdot \text{s} \\
G & \quad \text{Growth amount, } \mu \text{m} \\
g & \quad \text{Gravitational constant, cm/s}^2 \\
\mathcal{g} & \quad \text{Gravitational acceleration, m/s}^2 \\
h & \quad \text{Reactor channel height, cm} \\
k & \quad \text{Thermal conductivity, W/cm \cdot K} \\
k_r & \quad \text{Reaction rate constant, g/cm}^2 \cdot \text{s} \\
l & \quad \text{Reactor channel length, cm} \\
l_1 & \quad \text{Distance to manifold insulation, cm} \\
l_2 & \quad \text{Distance to start of tilt, cm} \\
l_3 & \quad \text{Distance to leading edge of susceptor, cm} \\
l_4 & \quad \text{Distance to trailing edge of susceptor, cm} \\
\mathcal{A} & \quad \text{Species flux, g/cm} \cdot \text{s} \\
P & \quad \text{Pressure, atm} \\
R & \quad \text{Surface reaction rate, g/cm}^2 \cdot \text{s} \\
r & \quad \text{Radius of susceptor disk, cm} \\
T & \quad \text{Temperature, K} \\
T_0 & \quad \text{Temperature of susceptor, K} \\
T_i & \quad \text{Inlet temperature, K} \\
T_{\text{var}} & \quad \text{Temperature around susceptor, K} \\
T_w & \quad \text{Temperature of upper wall, K} \\
TMG & \quad \text{Trimethylgallium} \\
U_0 & \quad \text{Maximum velocity in parabolic profile, cm/s} \\
\mathcal{U} & \quad \text{Velocity in } x \text{ direction, cm/s} \\
\mathcal{V} & \quad \text{Velocity in } y \text{ direction, cm/s} \\
x & \quad \text{Horizontal coordinate} \\
y & \quad \text{Vertical coordinate} \\
\Theta & \quad \text{Polar angle of disk, rad} \\
\theta & \quad \text{Angle of inclination, deg} \\
\mu & \quad \text{Viscosity, g/cm} \cdot \text{s} \\
\rho & \quad \text{Density, g/cm}^3 \\
\psi & \quad \text{Angle of declination, deg} \\
\Omega & \quad \text{Rotation rate of disk, rad/min} \\
\omega & \quad \text{Normalized mass fraction of TMG}
\end{align*}
\]

References