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Wing-cheong Gilbert Lai
Louisiana State University and Agricultural & Mechanical College

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Reactor analysis of chemical vapor deposition of TiO$_2$ and Cu thin films

Lai, Wing-Cheong Gilbert, Ph.D.

The Louisiana State University and Agricultural and Mechanical Col., 1994
REACTOR ANALYSIS OF
CHEMICAL VAPOR DEPOSITION OF TiO₂ AND Cu THIN FILMS

A Dissertation
Submitted to Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in Partial Fulfillment of the
Requirements for the Degree of
Doctor of Philosophy

in

The Department of Chemical Engineering

by
Wing-Cheong Gilbert Lai
B.Ch.E., University of Minnesota, 1988
M.S., Louisiana State University, 1991
August 1994
To my mother.
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ABSTRACT

A set of reactor models for chemical vapor deposition (CVD) of titanium dioxide films from titanium tetraisopropoxide (TTIP) in a vertical cold-wall CVD reactor has been developed. The effects of the carrier gas on the deposition of TiO$_2$ films were examined. The reaction mechanism proposed by the earlier workers in our group was used for the reactor modeling (Siefering and Griffin, 1990a; 1990b). The kinetic parameters were estimated from the reactor models at three levels of approximation; i.e., a lumped parameter (LP) model, a one-dimensional stagnation point flow reactor (1-D SPFR) model, and a full 2-D SPFR model. The 2-D SPFR modeling equations were solved using a control volume based finite difference method (SIMPLE). Based on the 2-D SPFR model, a more accurate activation energy for gas phase reaction was estimated to be 55 kJ/mole. It showed that 1-D SPFR model provided a good agreement with the 2-D SPFR model with our reactor geometry. The relationship between the carrier gas and pure TTIP experiments was explained by the collision theory.

Copper films with low resistivity have been deposited from copper(II) hexafluoroacetylacetonate [Cu(hfac)$_2$] diluted by H$_2$ in a horizontal warm-wall CVD reactor. The effects of substrate temperature and hydrogen pressure on the growth rate of Cu film were examined. A transport controlled regime was observed at substrate temperature of 350°C and H$_2$ pressures above 300 Torr. On the other hand, a reaction controlled regime was observed at the substrate temperature of 250°C and low H$_2$ pressure. A 2-D horizontal flow reactor model was developed to describe the temperature and
concentration gradients. First, I calculated the surface concentration profiles by matching the measured growth rates with a power rate expression. Using the predicted surface concentration profiles, I proposed a non-competitive adsorption reaction mechanism to give a more physically realistic rate expression. Kinetic parameters were estimated based on both theory and measured results.
CHAPTER 1
INTRODUCTION

Chemical vapor deposition (CVD) is an important process employed in microelectronics manufacturing for the deposition of thin solid films. High purity solid films with well-controlled properties can be deposited by CVD, in large part due to advances in the synthesis of organometallic precursors. Using chemically reactive precursors in CVD process is the major distinction from other conventional physical deposition methods.

One of the advantages of the CVD method is excellent conformal coverage. It is able to fill high aspect ratio gaps and to provide high uniformity across the wafer. Thus, the leading edge microprocessors can be fabricated with submicron feature size. For example, the Intel’s Pentium 60 MHz chip and IBM’s Power PC601 50 MHz chip have minimum gate length of 0.65 and 0.5 μm, respectively (Denboer, 1994).

CVD reactors are considered to be one of the unit operations in the semiconductor manufacturing. However, a trial and error approach is frequently used to obtain the optimal operating conditions for a specific reactor configuration. Recently, several groups have shown that numerical simulations can play a vital role in the design of good reactors (Geller, 1993; Werner, 1993; McInerney et al., 1993; Cale et al., 1993; and Studiner et al., 1993).

The single-wafer CVD reactor is becoming an increasingly important configuration. The advantages are low particle contamination, efficient removal of
reaction by-products, excellent uniformity on large wafers, and easy wafer handling. A detailed reactor analysis will be beneficial to optimize the reactor geometry and the operating conditions.

New dielectric and metal films are being sought for advanced semiconductor devices. High dielectric constant film is important in memory integrated circuit (IC) technology such as the 64 Megabit DRAM (dynamic random access memory) chips. Low resistivity metal film is significant in microprocessor technology. For example, there are five levels of metal interconnection in IBM’s Power PC601 chips (Denboer, 1994).

In the first part of this dissertation (cf., Chapter 2, 3, and 4), I will examine the CVD of a promising dielectric material, TiO₂. In Chapter 2, the applications and precursors from the literature for TiO₂ film will be reviewed. The previous kinetic studies by Siefering and Griffin (1990a; 1990b) will be presented in detail. Modeling of vertical CVD reactors will be summarized.

In Chapter 3, I discuss experiments where the TiO₂ film is deposited on copper substrates from titanium tetraisopropoxide (TTIP) diluted with nitrogen carrier gas. The reaction mechanism proposed by Siefering and Griffin (1990b) is employed for the reactor models. I analyze the vertical cold-wall CVD reactor using a series of reactor models: a lumped parameter (LP) model, and one-dimensional (1-D) and two-dimensional (2-D) stagnation point flow reactor (SPFR) models. The assumptions for each model will be discussed individually. The velocity, temperature, concentration profiles will be presented. Finally, I will examine and compare the kinetic parameters estimated using each model.
In Chapter 4, I discuss TiO₂ films deposited on copper substrates from pure TTIP without carrier gas at four substrate temperatures. The reaction mechanism proposed by Siefering and Griffin (1990a) is employed for the reactor models. I also analyze the measured results using the LP, 1-D and 2-D SPFR models. Because of different substrate temperature, the activation energy based on each model is obtained and compared. I also obtain the pre-exponential factor corresponding to each model. Finally, the carrier gas and pure TTIP experiments are compared.

In the second part of this dissertation (cf., Chapter 5, 6, and 7), I will examine the CVD of a promising metal, Cu. In Chapter 5, the applications and precursors from the literature for Cu films will be reviewed. The previous mechanistic studies can be divided into adsorption studies under ultra-high vacuum and kinetic studies under normal CVD conditions. Modeling of horizontal CVD reactors will be summarized.

In Chapter 6, I describe the apparatus and procedure for the CVD experiments using copper(II) hexafluoroacetylacetonate [Cu(hfac)_2] as the precursor and H₂ as the carrier gas. The vapor phase of the precursor feed is monitored for each experiment to ensure a known constant concentration at the inlet of the CVD reactor. The Cu films are deposited inside a horizontal warm-wall CVD reactor with a vacuum system. I will discuss the substrate preparation and the thickness measurement for the Cu film deposited on the substrate. Three sets of previously obtained experimental results from our group will be presented.

In Chapter 7, I describe the kinetic analysis of the experimental results in Chapter 6. A two-dimensional horizontal flow reactor model is used to study the growth kinetics
of Cu films. An empirical rate expression is utilized to obtain the surface concentration profiles. The velocity and temperature profiles inside the warm-wall reactor will also be presented. I will propose a new mechanism for the experimental results to explain the effects of pressure and temperature, after I review the mechanisms proposed by Lai et al. (1991) and Kim et al. (1993). The kinetic parameters for the new mechanism will be estimated and compared with the available literature values.
CHAPTER 2
LITERATURE REVIEW OF TITANIUM DIOXIDE FILMS

2.1 Applications of TiO₂ Films

Titanium dioxide film is a promising material for high performance microelectronic and optoelectronic devices due to its superior electrical and optical properties. In microelectronic areas, there are two major applications.

First, it can be used for the next generation of dynamic random access memory (DRAM) memory cells such as 64 Megabit DRAM memory storage capacitors. DRAM manufacturers have done everything possible to reduce the dielectric’s thickness and increase the capacitor area to maintain the required cell capacitance, so the only option left available is to increase the dielectric constant (Treichel et al., 1993). A dielectric constant as high as 86 was reported by Fuyuki and Matsunami (1986).

Second, it can also be used for the new packaging methods, such as high density multichip modules (MCMs). MCMs are being developed to improve the density and speed of integrated circuits (ICs). The TiO₂ thin films with titanium metal core are deposited on gold MCM interconnections, to provide electrical isolation between the individual metal lines (Kohl, 1993).

In optoelectronic area, transparent TiO₂ films are often use in solar cells, energy-efficient window coatings, and electro-optical displays due to the high refractive index (Gordon, 1993). Other applications can be found in both Zhang (1993) and Siefering (1988).
2.2 Precursors for TiO$_2$ Films

There are two major precursors used to prepare TiO$_2$ thin films by chemical vapor deposition (CVD). The first is titanium tetrachloride (TiCl$_4$), originally reported by Banning (1941) and later studied by Cheng et al. (1987). However, this reactant has several disadvantages. For example, it requires a high operating temperatures (400 to 1000 °C) to give a reasonable growth rate. Either oxygen or water vapor is required, as a co-reactant and the HCl product is corrosive.

Titanium tetraisopropoxide (TTIP) is the other precursor used to grow TiO$_2$ thin films. It is a better and more popular precursor for the CVD processes due to its low operating temperature and lack of corrosive products. Yokozawa et al. (1968) started to study the film growth with presence of O$_2$. Recently, Gokoglu et al. (1993) studied the reactor performance for TiO$_2$ film with presence of O$_2$ in N$_2$ as a carrier gas.

Siefering (1988) studied the deposition of TiO$_2$ films from decomposition of TTIP at low pressure without the presence of O$_2$ and N$_2$. Siefering and Griffin (1990a) reported the pure TTIP experiments. They showed that the film growth rate was second order in TTIP pressure at low pressure, and zero order at high pressures. The experiments will be described more completely in the next section.

To compare the results with Takahashi et al. (1985), Siefering and Griffin (1990b) also reported experiments using N$_2$ carrier gas. They showed that the film growth rate was first order in TTIP pressure at all pressures. Zhang (1993) reported similar results with different reactors.
2.3 Previous Kinetics Studies

In our reactor analysis of CVD TiO₂ thin film growth, I will use the experimental results obtained from Siefering and Griffin (1990a; 1990b) in a cold wall low pressure vertical CVD reactor. The reactor configuration is the same for both pure TTIP and carrier gas experiments. The reactor consists of a standard six-way cross with inside diameter of 3.2 cm, as shown in Figure 2.1 (Siefering, 1988).

One end of the cross is mounted on the surface analysis chamber, so that in-situ surface analysis can be performed. A gate valve is used to separate the reactor and the chamber. On the same axis, a polished sample transfer rod with the substrate is inserted from the opposite end of the cross. A pyrex window located on the horizontal level and another window located on the top flange are used to check the substrate position.

The substrate is mounted on a susceptor using screws with washers which slightly overlap its edges. The susceptor is a 3.2 cm diameter hemi-cylindrical stainless steel block welded to the end of the transfer rod. It is heated by a 250 Watt cartridge heater. A pair of chromel alumel thermocouples are used to measure the temperature. The temperature can be controlled within 1 °C by adjusting a Variac power supply and an Omega digital temperature controller. The reactor wall is heated to 100 °C with heating tapes and wrapped with aluminum foil to avoid condensation of TTIP.

A liquid nitrogen-cooled sorption pump is connected to the top flange of the cross through a quarter-inch tubing. The reactor pressure, measured by a Granville-Phillips convectron gauge, can be reduced to a minimum of $1.0 \times 10^{-3}$ Torr with a needle value. The bottom flange of the cross is connected to a turbomolecular pump, which creates a
Figure 2.1  Cold Wall Low Pressure Vertical CVD Reactor Designed by Siefering (1988)
base pressure of $1.0 \times 10^{-3}$ Torr. The volumetric flow rate of 22 sccm is measured, based on the chamber evacuation rate. This value is used for both pure TTIP and carrier gas experiments.

The difference between the pure TTIP and the carrier gas experiments is the configuration of the reactant source. For pure TTIP experiments, the TTIP (Aldrich Chemical), which is liquid at room temperature (melting point 20 °C), is contained in a glass bottle shown in Figure 2.2 (Siefering, 1988), wrapped with heating tape and aluminum foil for insulation. It is kept at a constant temperature between 65 and 110 °C during deposition, depending on the required deposition pressure. The TTIP vapor is allowed into the reactor from the bottom and controlled via a bellows sealed metering value to adjust the reactant pressure.

For the carrier gas experiments, a glass bubbler is used as shown in Figure 2.3 (Siefering, 1988), with one end connected to the N$_2$ cylinder and the another end connected to the reactor. The total pressure in the bubbler is maintained at 500 Torr by setting a metering valve upstream from the bubbler on the carrier gas supply line at a constant position and adjusting the pressure upstream of the metering value with the gas pressure regulator on the N$_2$ cylinder.

The mixture of TTIP and N$_2$ is delivered directly into the reactor from the bottom flange. A needle valve between the reactor and bubbler is used to reduce the bubbler pressure to the reactor pressure of 5 Torr. The inlet partial pressure of TTIP is varied by changing the bubbler temperature from 40 to 90 °C. The calibration curve between the inlet TTIP partial pressure and bubbler temperature is described by Siefering (1988).
Figure 2.2  Glass Bottle for the Pure TTIP Experiments (Siefering, 1988)
Figure 2.3  Glass Bubbler for the Carrier Gas Experiments (Siefering, 1988)
Siefering and Griffin (1990a) reported the TiO₂ growth rates from pure TTIP experiments at substrate temperatures from 220 to 300 °C and TTIP inlet pressures from 0.04 to 2.0 Torr. The reaction order plot for the pure TTIP experiments is shown in Figure 2.4. The average film growth rates were measured from the weight change and the deposition area and they ranged from 0.005 to 30 μm/h. From the results, these authors proposed three elementary steps involving gas phase decomposition, adsorption of intermediate species, and surface reaction.

The activation energy, \( E_3 \) and pre-exponential factor, \( k_3^* \) of rate constant \( k_3 \) for surface reaction was obtained in the saturation region. The value for \( E_3 \) was similar to the result obtained from a separate temperature programmed desorption study. They reported that \( E_3 = 154 \text{ kJ/mole} \) and \( k_3^* = 8.6 \times 10^6 \text{ mole/cm}^2/\text{s} \). On the other hand, only a composite parameter value was estimated for the gas phase reaction from the second-order region. The composite parameter was composed of residence time, \( \tau \), desorption rate, \( k_2 \), and rate constant, \( k_{\text{TTIP/TTIP}} \). The activation energy of \( k_{\text{TTIP/TTIP}} \), \( E_4 \) was 35.2 kJ/mole, and the combined parameter, \( \tau k_2 k_{\text{TTIP/TTIP}}^* \) was \( 4.7 \times 10^{10} \text{ cm}^3/\text{mole/s}^2 \).

Siefering and Griffin (1990b) reported the TiO₂ growth rates from carrier gas experiments at a substrate temperature of 300 °C and TTIP inlet partial pressures from 0.004 to 0.109 Torr. The reaction order plot for the carrier gas experiments is shown in Figure 2.5. The average film growth rate ranged from 0.16 to 5.9 μm/h. For these experiments, the \( E_4 \) was assumed the same as the pure TTIP experiments. A collision efficiency for N₂ relative to TTIP, \( \phi_{\text{N}_2} \), was defined from the first-order region. Therefore, the pre-exponential factor for the gas phase reaction between TTIP and N₂.
Figure 2.4  Reaction Order Plot of TiO₂ Films from the Pure TTIP Experiments (Siefering and Griffin, 1990a)
Figure 2.5  
Reaction Order Plot of TiO$_2$ Films from the Carrier Gas Experiments 
(Siefering and Griffin, 1990b)
$k_{\text{TIP/N}_2}$ can be expressed as $k_{\text{TIP/N}_2} = \phi_{\text{N}_2} k_{\text{TIP/TIP}}$. The experimentally determined value of $\phi_{\text{N}_2}$ was 0.43.

2.4 Reactor Modeling

A good understanding of coupled transport and chemical processes is required for the future chemical vapor deposition (CVD) applications. CVD can produce sophisticated materials with superior properties. With a good reactor model, we can relate the film growth rate and quality with the operating conditions and reactor geometry (Jensen, 1987). A comprehensive review by Jensen (1989) gives a basic introduction to the principles of transport phenomena and reaction kinetics for the CVD research.

The reactor configuration used by Siefering and Griffin (1990a; 1990b) resembled the stagnation point flow reactor (SPFR). The SPFR is a vertical, axisymmetric reactor with the susceptor perpendicular to the incoming gas flow. The substrate or wafer is held on the susceptor which is heated to deposition temperature, most commonly by resistive heating. It is also normally operated below atmospheric pressure with standard vacuum systems.

The initial interest in the SPFR geometry was primarily as an experimental system. However, it is becoming an important type of single-wafer reactor for thin film deposition in the semiconductor industry. This is because the SPFR gives large uniform areas and high film qualities. With the advance of larger wafer diameters (greater than 150 mm), the SPFR has become more applicable as a single wafer production reactor.
Another advantage of the SPFR is for reactor designs calculations. Because of the axial symmetry, the momentum, mass, energy, species balance equations can be reduced to two-dimensional (2-D) equations. While these 2-D equations must be solved numerically, this is still much faster than corresponding three-dimensional (3-D) equations.

Near the centerline where wall effects can be neglected, it is possible to transform the transport equations still further to yield a one-dimensional (1-D) system. This will further reduce the computational time and greatly simplify the analysis of heat and mass transfer. It is beneficial to first use a well-defined 1-D flow model to estimate the kinetic parameters. This is because the estimation of kinetic parameters from the 2-D model requires greater computational time. A 1-D model may also be preferred to develop a fast response reactor control system.

Schlichting (1968) presented the exact solutions of the Navier-Stokes equations for isothermal stagnation flow with no chemical reactions. He also presented the 1-D similarity transformation analysis for the two-dimensional (2-D) balance equations in plane flow (Hiemenz flow). He compared the isothermal velocity profiles for both 1-D and 2-D models, and showed that the axial velocity was very similar. The stagnation region in a plane flow is shown in Figure 2.6.

Wahl (1977) presented the full solutions for 2-D axisymmetric Navier-Stokes equations with varying physical properties. He used finite difference techniques to solve the partial differential balance equations for momentum, mass, energy, and species. The importance of this paper is that he showed the comparison between the calculated flow
Figure 2.6  Stagnation in a Plane Flow (Schlichting, 1968)
lines and visualization experiments with satisfactory agreement. However, he used arbitrary gas-phase and surface reaction kinetics to study the effects of growth uniformity and thermal diffusion.

Houtman et al. (1986) studied the SPFR with well known reaction kinetics. Their work deserves special attention, since it is directly related to our 1-D analysis. They compared the classical 1-D treatment with the 2-D modeling results for the SPFR. They give an overview of the parameter ranges for which the 1-D treatment will give reasonably accurate results.

In this work, we will compare 1-D and 2-D models. We will also compare a lumped parameter model, which requires still less computational time. Our 2-D reactor analysis is based on the methods developed by Patankar (1980). The numerical method used to solve the partial differential balance equations is a control volume-based finite difference method. The continuity equation was coupled to the momentum equation through a pressure correction method [SIMPLE].

The SIMPLE methods have been used by several recent authors. For example, Kleijn’s group at Delft University of Technology (The Netherlands) have used these methods to compare their model with the experiment results obtained from a single-wafer CVD reactor for CVD tungsten (Kleijn et al., 1989; ibid, 1991; and Oosterlaken et al., 1993).
CHAPTER 3

TiO₂ FILMS FROM CARRIER GAS EXPERIMENTS

The TiO₂ thin film growth rates obtained by Siefering and Griffin (1990b) from titanium tetraisopropoxide (TTIP) and diluted by nitrogen carrier gas were reviewed in Chapter 2. In those experiments, the TTIP vapor was transferred from the constant temperature bubbler to the chemical vapor deposition (CVD) reactor using nitrogen. Changing the bubbler temperature gave different TTIP partial pressures, and different thicknesses of TiO₂ films were formed on a heated substrate inside the CVD reactor. The results were reported in the form of a reaction order plot.

In this chapter I will develop an improved kinetic parameter analysis based on these results. I begin by reviewing the reaction mechanism proposed by Siefering and Griffin (1990b). The mechanism involves chemical reactions both in the gas phase and on the surface, which will be incorporated in the species balance equations and boundary conditions. In the gas phase, a bimolecular collision between TTIP and N₂ to form a reactive intermediate is proposed. At the surface, the intermediate is adsorbed and reacts to form a thin TiO₂ film.

I will examine a series of models for the cold wall vertical CVD reactor used by Siefering and Griffin (1990b) in order to estimate the kinetic parameters for their proposed mechanism. The first model will be based on a lumped parameter (LP) model. The CVD reactor is operated at low pressure (5 Torr) where diffusion will be fast and concentration gradients will be small. Therefore, a LP model may be reasonably accurate. It is also a useful model for obtaining a preliminary estimate of the kinetic parameters.
The second model is based on the stagnation point flow reactor (SPFR). It is formulated as a one-dimensional (1-D) model using a similarity transformation. This model should give a better description than the LP model for the velocity, temperature, and concentration profiles in the cold wall vertical CVD reactor, while requiring less computational time than a two-dimensional (2-D) model. Therefore, we should obtain a reasonable solution with modest computational time.

The final model will be the full 2-D SPFR model. This model can represent the three-dimensional (3-D) behavior of a CVD reactor with axisymmetric geometry. This model provides all the information about the flow, temperature, and concentration fields, without solving the full set of 3-D balance equations.

Finally, the kinetic parameters obtained using all three models will be compared and discussed. I will discuss the sensitivity of the calculated growth rate with respect to the assigned values of the kinetic parameters, operating conditions, and reactor geometry. I will also compare the overall accuracy of the three models. For example, I will examine the velocity, and temperature profiles predicted by both 1-D and 2-D SPFR models. The concentration profiles for TTIP and intermediate will also be examined for all three models.

3.1 Reaction Mechanism

To develop an accurate kinetic model for the CVD process, it is necessary to propose a reaction mechanism in terms of elementary steps. Siefering and Griffin (1990b)
proposed a simple mechanism for their results, which I will review here. In the following sections, we will apply this mechanism using each of our reactor models.

The three proposed elementary steps for the reaction taking place in the presence of a carrier gas are:

\begin{align*}
\text{Reaction (3.1)} & : \quad \text{TTIP} + \text{N}_2 \rightarrow I + P \\
\text{Reaction (3.2)} & : \quad I + \theta_{v} \rightarrow \theta_{i} \\
\text{Reaction (3.3)} & : \quad \theta_{i} \rightarrow \text{TiO}_2 + R
\end{align*}

Here \( P \) and \( R \) represent additional products from the gas phase and surface reactions, and \( \theta_{v} \) and \( \theta_{i} \) represent the fraction of the substrate that is vacant or occupied by absorbed intermediate.

The rate of the bimolecular collision between \( \text{TTIP} \) and \( \text{N}_2 \) to form the intermediate species \( I \) in Reaction (3.1) is assumed to have the form:

\[ r_1 = k_1 [\text{N}_2] [\text{TTIP}] \] (3.4)

where \([\text{TTIP}]\) and \([\text{N}_2]\) are the concentration of \( \text{TTIP} \) and carrier gas \( \text{N}_2 \) in mole/cm\(^3\).

In all of the carrier gas experiments performed by Siefering and Griffin (1990b), the pressure of \( \text{N}_2 \) was fixed at 5.0 Torr. This corresponds to a concentration of \( 1.4 \times 10^7 \) mole/cm\(^3\).
Because the carrier gas is present in great excess, Equation (3.4) can be rewritten:

\[ r_1 = k_1[TTIP] \]  \hspace{1cm} (3.5)

where \( k_1 = k_1[N_2] \) is the pseudo first-order rate constant for the gas phase activation of TTIP. Based on previous results, we assume an Arrhenius dependence:

\[ k_1' = k_1^0 \exp\left(\frac{-E_1}{RT}\right) \]  \hspace{1cm} (3.6)

where \( k_1^0 \) is the pre-exponential factor in s\(^{-1}\), and \( E_1 \) is the activation energy. A value of \( E_1 = 35.2 \text{ kJ/mole} \) was determined by Siefering and Griffin (1990a). We will obtain revised estimates for this value in our calculations below.

Reaction (3.2) represents the adsorption of intermediate species \( I \) at vacant sites on the reactive surface. Its rate can be expressed as:

\[ r_2 = k_2[I] \theta_v \]  \hspace{1cm} (3.7)

A value of \( k_2 \) can be estimated, based on gas kinetic theory:

\[ k_2 = \frac{1}{4} \langle V \rangle = \frac{1}{4} \left( \frac{8RT}{\pi M} \right)^{\frac{3}{2}} \]  \hspace{1cm} (3.8)

where \( \langle V \rangle \) is the average molecular speed. The gas constant is \( R = 8.314 \times 10^7 \) ergs/mole/K and the molecular weight of TTIP is \( M = 284 \) g/mole. This leads to an estimated value of \( k_2 = 5.2 \times 10^3 \text{ cm/s} \) at \( T = 573 \text{ K} \).
Reaction (3.3) describes the decomposition of the adsorbed intermediate to produce TiO$_2$. Its rate can be expressed as:

$$r_3 = k_3 \theta_j$$

(3.9)

The rate constant $k_3$ is assumed to obey an Arrhenius dependence:

$$k_3 = k_3^0 \exp \left( \frac{-E_3}{RT} \right)$$

(3.10)

where $k_3^0$ is the pre-exponential factor and $E_3$ is the activation energy. Siefering and Griffin (1990a) determined values of $k_3^0 = 8.59 \times 10^9$ mole/cm$^2$/s and $E_3 = 154$ kJ/mole. We will also retain these values in our calculations below.

The fractional coverage variables, $\theta_\chi$ and $\theta_\delta$, can be eliminated by combining Equations (3.7) and (3.9). At steady state, $r_2 = r_3$. We also assume $\theta_\chi + \theta_\delta = 1$. Then, the overall rate of reaction at the surface becomes:

$$r_2 = r_3 = \frac{k_2k_3[I]}{k_3 + k_2[I]}$$

(3.11)

All of the carrier gas experiments were performed at 573 K. At this temperature, $k_3 = 10^{-9}$ mole/cm$^2$/s and $k_2[I] = 10^{-11}$ mole/cm$^2$/s, based on the highest concentration of intermediate expected (see below). Thus, the surface decomposition reaction is much faster than the adsorption step, and $r_2$ can be simplified as:

$$r_2 = k_2[I]$$

(3.12)
3.2 Lumped Parameter Model

In this section I derive the species balance equations for the lumped parameter (LP) model. The essential feature of the LP model is that the shape of the concentration and temperature profiles are assumed. The magnitude of each profile is thus characterized by a single undetermined coefficient. These coefficients are obtained by solving a set of coupled algebraic balance equations. The pre-exponential factor in the proposed mechanism for the gas-phase reaction will be estimated by comparing with the average growth rates measured by Siefering and Griffin (1990b). The sensitivity to the model assumptions will be discussed.

3.2.1 Governing Equations

The species balance equation for TTIP (species A) is:

\[ Q(C_A - C_{A_0}) = -V k_1^{LP} C_A \]  \hspace{1cm} (3.13)

where \( Q \) and \( V \) are the volumetric flow rate and active reactor volume, respectively. \( C_A \) and \( C_{A_0} \) are the exit and inlet TTIP concentrations. The new parameter \( k_1^{LP} \) represents the spatially averaged value of \( k_i \) and is defined to include the effect of a non-uniform 1-D temperature profile (see below).

The species balance equation for the intermediate (species B) is:

\[ Q C_B = V k_1^{LP} C_A - A k_2^{LP} C_B \]  \hspace{1cm} (3.14)
where $A$ is the active substrate area. The new parameter $k_{2}^{LP}$ describes the arrival rate of the intermediate at the substrate under diffusion limited conditions (see below).

Finally, the TiO$_2$ film growth rate is given by:

\[
G = r_2 = k_2^{LP} C_B
\]  

(3.15)

where $G$ is in flux units (i.e., mole/cm$^2$/s). This can be converted to thickness units using the TiO$_2$ molar density (1 mole/cm$^2$/s = 6.75 x 10$^8$ pm/h).

The value of $k_{1}^{LP}$ determined using the LP model represents a spatially averaged value over the non-uniform temperature profile of the cold-wall reactor:

\[
k_{1}^{LP} = \frac{1}{V_1^{o}} \int_{V_1} \exp\left(\frac{-E}{RT}\right) dV
\]  

(3.16)

I can evaluate the volume integral numerically using the temperature profile from the 1-D SPFR model and the activation energy determined in Chapter 4. For example, the value of $k_{1}^{LP}$ predicted by Equation (3.16) as the average value for the present cold-wall reactor geometry is about 30 percent of the value based on the substrate temperature (i.e., the hottest point in the reactor).

We estimate a value for $k_{2}^{LP}$ as follows. We assume that the intermediate is generated at a spatially uniform rate in front of the substrate, and diffuses to the substrate where it is immediately adsorbed. With these assumptions, the 1-D concentration profile of the intermediate is parabolic, varying from zero at the substrate to a maximum at the inlet.
The flux at the substrate than becomes:

\[ j_B = \frac{3D}{L} C_B \]  (3.17)

where \( D \) is the diffusion coefficient at the operating conditions (i.e., \( T_s = 300 \, ^\circ\text{C} \) and \( P = 5.0 \, \text{Torr} \)). \( L \) is the distance between the inlet plane and the substrate plane. \( C_B \) is the volume-averaged concentration of the intermediate.

Equation (3.17) allows us to define an effective value of \( k_2^{LP} \) by replacing the second term on the right hand side of Equation (3.14):

\[ k_2^{LP} = \frac{3D}{L} \]  (3.18)

For the present conditions, \( D = 16 \, \text{cm}^2/\text{s} \) and \( L = 1.6 \, \text{cm} \). Then, \( k_2^{LP} \approx 30 \, \text{cm/s} \).

### 3.2.2 Parameter Estimation

Siefering and Griffin (1990a) have determined values for the kinetic parameters in terms of \( \tau k_1 k_2 \). Because of the simple reactor model used for their analysis, they were unable to determined a values for \( k_1^* \). In this section I will determine a value for \( k_1^* \), using the more accurate LP model. I will use the activation energy, \( E_1 \), determined in Chapter 4, \( E_1 = 45 \, \text{kJ/mole} \).

We proceed by solving Equations (3.13) and (3.14) for the TTIP and intermediate concentrations using the Newton-Raphson method (subroutine NLSYST) with a trial value of \( k_1^{LP} \) and assumed values for the remaining parameters (cf. Table 3.1). Then the TiO\textsubscript{2}
of \( k_{r,1p} \) and assumed values for the remaining parameters (cf. Table 3.1). Then the TiO\(_2\) film growth rate is determined by Equation (3.14). The process is repeated using different values of \( k_{r,1p} \), and the optimum value is obtained using non-linear regression (subroutine NLRGR) to fit all the experimental data.

This procedure yields an optimized value of \( k_{r,1p} = 1.4 \text{ s}^{-1} \). The coefficient of determination is 0.855. Finally, the exponential factor is calculated using Equation (3.16): \( k_{r,e} = 5.9 \times 10^4 \text{ s}^{-1} \). The results are summarized in Table 3.2. The calculated growth rate is compared to the measured values in Figure 3.1.

### 3.2.3 Discussion

The uncertainty associated with the optimized value of \( k_{r,e} \) can be estimated qualitatively using the sensitivity information listed in Table 3.3. The second column, \( S_{GIX} \), lists the dependence of the calculated growth rate (\( G \)) on an individual model parameter (\( X \)), defined as follows:

\[
S_{GIX} = \frac{d \ln(G)}{d \ln(X)}
\]  

(3.19)

The derivation is calculated by a finite difference approximation, using growth rates calculated with a pair of different values for each parameter of interest.

The third column, \( S_{GIX/k_{r,e}} \), shows the sensitivity of \( k_{r,e} \) to uncertainties in the parameters of interest, defined as follows:

\[
S_{k_{r,e}/X} = \frac{S_{GIX}}{S_{GIX/k_{r,e}}}
\]  

(3.20)
Table 3.1 Parameters of the Carrier Gas Experiments using LP Model

<table>
<thead>
<tr>
<th>Type</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Assumed Reactor Geometry</td>
<td>Reactive Area</td>
<td>$A = 8.04 \text{ cm}^2$</td>
</tr>
<tr>
<td></td>
<td>Reactive Volume</td>
<td>$V = 12.9 \text{ cm}^3$</td>
</tr>
<tr>
<td>Operating Conditions</td>
<td>Inlet Volumetric Flow Rate</td>
<td>$Q = 55.6 \text{ cm}^3/\text{s}$</td>
</tr>
<tr>
<td></td>
<td>Inlet Temperature</td>
<td>$T_o = 100 \degree \text{C}$</td>
</tr>
<tr>
<td></td>
<td>Substrate Temperature</td>
<td>$T_s = 300 \degree \text{C}$</td>
</tr>
<tr>
<td></td>
<td>Reactor or N$_2$ Pressure</td>
<td>$P = 5.0 \text{ Torr}$</td>
</tr>
<tr>
<td>Kinetic Parameter</td>
<td>Mass Transfer Coefficient for Intermediate</td>
<td>$k_{2^{'}}^m = 30 \text{ cm/s}$</td>
</tr>
</tbody>
</table>

Table 3.2 Summary of Calculated Results for the Carrier Gas Experiments using LP Model

<table>
<thead>
<tr>
<th>Type</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>TTIP Gas Phase Decomposition</td>
<td>Rate Constant</td>
<td>$k_{r LP} = 1.4 \text{ s}^{-1}$</td>
</tr>
<tr>
<td></td>
<td>Pre-exponential Factor$^1$</td>
<td>$k_{r^m} = 5.9 \times 10^4 \text{ s}^{-1}$</td>
</tr>
<tr>
<td>Dimensionless Exit Concentration</td>
<td>TTIP</td>
<td>$C_A/C_{An} = 0.755$</td>
</tr>
<tr>
<td></td>
<td>Intermediate</td>
<td>$C_{R}/C_{An} = 0.0459$</td>
</tr>
</tbody>
</table>

$^1$Assume $E_t = 45 \text{ kJ/mole}$, from Chapter 4.
Figure 3.1  Order Plot for TiO₂ Films from the Carrier Gas Experiments using LP Model
Table 3.3 Summary of Sensitivity Studies for the Carrier Gas Experiments using LP Model

<table>
<thead>
<tr>
<th>Parameter (X)</th>
<th>$S_{GNX}$</th>
<th>$S_{AVX}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{1p}$</td>
<td>0.75</td>
<td>---</td>
</tr>
<tr>
<td>$k_{2LP}$</td>
<td>0.20</td>
<td>-0.26</td>
</tr>
<tr>
<td>$Q$</td>
<td>0.06</td>
<td>-0.08</td>
</tr>
<tr>
<td>$V$</td>
<td>0.75</td>
<td>-1.0</td>
</tr>
<tr>
<td>$A$</td>
<td>-0.80</td>
<td>1.07</td>
</tr>
</tbody>
</table>
We note that the sensitivity of the calculated rate with respect to the rate constant, $S_{G/k_r} = 0.75$, is less than unity. This reflects the fact that the calculated fractional conversion of TTIP is 24 percent at these conditions. This means that the growth rate is conversion limited, and is only partially dependent on the rate constant associated with the intrinsic kinetics.

Finally, the greatest uncertainty in the estimated rate constant is associated with the substrate surface area (cf., $S_{s/k_A} = 1.07$).

### 3.3 1-D SPFR Model

The LP model examined in the last section is an algebraic reactor model. In contrast, the cold wall CVD reactor used by Siefering and Griffin (1990b) is expected to have temperature and concentration gradients which will require differential equations to obtain an accurate description. As a first step toward describing these gradients, I choose to examine a one-dimensional stagnation point flow reactor (1-D SPFR) model. This model will incorporate the temperature and concentration gradients in the axial direction.

First, I will discuss the general balance equations in vector form. Based on the general balance equations, I formulate the 1-D SPFR model by applying a similarity transformation to the 2-D balance equations in cylindrical coordinates. The reaction mechanism described in section 3.1 is incorporated into the species balance equations. The boundary conditions for the flow, temperature, and concentration will be defined. Dimensionless variables and groups are used to simplify the balance equations.
Finally, I will show the axial and radial velocities, temperature, and concentration profiles predicted by the 1-D SPFR model. The gas-phase rate constant in the proposed mechanism will be estimated by comparing with the average growth rates measured by Siefering and Griffin (1990b), and its sensitivity to the model assumptions will be discussed.

3.3.1 General Conservation Equations

The general balance equations in vector form can be found in Bird, Stewart, and Lightfoot (1960). These equations govern the velocity, temperature, concentration, and pressure distributions. The continuity equation at steady state can be expressed as:

$$\nabla \cdot \rho \mathbf{V} = 0$$

(3.21)

where $\rho \mathbf{V}$ is the mass flux, and its divergence is the net rate of mass efflux per unit volume. The momentum balance equation at steady state and neglecting gravitational force can be expressed as:

$$\rho (\mathbf{V} \cdot \nabla \mathbf{V}) = \nabla \cdot \tau$$

(3.22)

where the term on the left hand side is due to convection. The term on the right hand side is due to viscous transfer, where $\tau$ is the viscous stress tensor:

$$\tau = \mu [\nabla \mathbf{V} + (\nabla \mathbf{V})^T] - \left[ \frac{2}{3} \mu (\nabla \cdot \mathbf{V}) + P \right] \mathbf{I}$$

(3.23)
The energy balance equation is simplified by neglecting Dufour effects, viscous dissipation, and radiation. The heat generation by reactions is normally small by using carrier gas. It can be expressed as:

\[ \rho C_p (V \cdot \nabla T) = \nabla \cdot (k \nabla T) \]  

(3.24)

where the terms on the left hand side and right hand side are due to convection and conduction, respectively.

The species balance equation of species \( i \) in a binary mixture can also simplified by neglecting Soret diffusion (i.e., the thermal diffusion effect), and assuming Fick’s law. It can be expressed as:

\[ \nabla \cdot V C_i = \nabla \cdot (D \nabla C_i) + R_i^p \]  

(3.25)

where \( R_i^p \) the rate of production or consumption of species \( i \), as discussed for the reaction mechanism described in section 3.1.

### 3.3.2 Similarity Transformation

A 1-D similarity transformation is used to reduce the 2-D partial differential equations into ordinary differential equations. Due to the axisymmetric geometry, we are able to apply this transformation. The active geometry of the 1-D SPFR model is chosen to be the region between the face of the susceptor and the end of the inlet tube (cf. Figure 3.2). The inlet tube radius is 1.6 cm, and the distance from the end of the inlet tube to the face of susceptor is also 1.6 cm.
Figure 3.2 Reactor Geometry for 1-D SPFR Model
I will follow the 1-D analysis presented by Houtman and Jensen (1986). First, they introduced a stream function $\Psi(r,z)$ in cylindrical coordinates which satisfies the continuity equation.

$$\frac{\partial \psi}{\partial z} = \rho r v_r$$  \hspace{1cm} (3.26)

$$\frac{\partial \psi}{\partial r} = -\rho r v_z$$  \hspace{1cm} (3.27)

They assumed that the radial dependence of the stream function is given by $\Psi(r,z) = r^2 f(z)$. Thus, $v_r$ and $v_z$ can be expressed as:

$$v_r = \frac{r}{\rho} \frac{df}{dz}$$  \hspace{1cm} (3.28)

$$v_z = -\frac{2}{\rho} f$$  \hspace{1cm} (3.29)

The transformed momentum equation is formulated by substituting Equations (3.28) and (3.29) into the 2-D axisymmetric momentum balance equation to yield:

$$\frac{1}{\rho} \frac{d}{dz} \left[ \mu \frac{d}{dz} \left( \frac{1}{\rho} \frac{df}{dz} \right) \right] - \left( \frac{1}{\rho} \frac{df}{dz} \right)^2 + \frac{2f}{\rho} \frac{d}{dz} \left( \frac{1}{\rho} \frac{df}{dz} \right) = \Gamma$$  \hspace{1cm} (3.30)

where $\Gamma$ is an unknown constant related to the pressure gradient.
The transformed energy equation is formulated by substituting Equations (3.28) and (3.29) into the 2-D axisymmetric energy balance equation to yield:

\[ \frac{d}{dz} \left( k \frac{dT}{dz} \right) + 2\phi \frac{d^2T}{dz^2} = 0 \]  (3.31)

The transformed species equation for species A is formulated by substituting Equations (3.28) and (3.29) into the 2-D axisymmetric species balance equation to yield:

\[ \frac{d}{dz} \left( D \frac{dC_A}{dz} \right) + \frac{2f}{\rho} \frac{dC_A}{dz} - k_A C_A = 0 \]  (3.32)

The transformed species equation for species B is formulated by substituting Equations (3.28) and (3.29) into the 2-D axisymmetric species balance equation to yield:

\[ \frac{d}{dz} \left( D \frac{dC_B}{dz} \right) + \frac{2f}{\rho} \frac{dC_B}{dz} + k_A C_A = 0 \]  (3.33)

The TiO\textsubscript{2} film growth rate is determined from:

\[ G = -D \frac{dC_B}{dz} \]  (3.34)

where \( G \) is in terms of flux units (1 mole/cm\textsuperscript{2}/s = 6.75 x 10\textsuperscript{8} \textmu m/h).
3.3.3 Boundary Conditions

Boundary conditions are required to solve the above transformed balance equations. At the inlet plane \((z = 0)\), the radial and axial velocities are governed by:

\[
\nu_r = 0 \iff \frac{df}{dz} = 0 \tag{3.35}
\]

\[
\nu_z = u_o \iff f = -\frac{\rho u_o}{2} \tag{3.36}
\]

I assume that radial velocity is zero and the axial velocity is uniform at the inlet plane. The temperature is governed by:

\[
T = T_o \tag{3.37}
\]

I assume that the inlet temperature is same as the wall temperature. The TTIP (species A) and intermediate (species B) concentrations are governed by:

\[
u_o(C_{Ao} - C_A) = -D \frac{dC_A}{dz} \tag{3.38}
\]

\[
-u_o C_B = -D \frac{dC_B}{dz} \tag{3.39}
\]

These are the Danckwerts' boundary conditions for species A and B, which account for both diffusion and convection of species across the inlet plane.
At the face of the susceptor \((z = L)\), no-slip velocity conditions are assumed at the susceptor plane. The radial and axial velocities are governed by:

\[
v_r = 0 \iff \frac{df}{dz} = 0 \quad (3.40)
\]

\[
v_z = 0 \iff f = 0 \quad (3.41)
\]

The temperature is governed by:

\[
T = T_s \quad (3.42)
\]

(i.e., \(T_s = \) substrate temperature). The TTIP (species A) and intermediate (species B) concentrations are governed by:

\[
-D \frac{dC_A}{dz} = 0 \quad (3.43)
\]

\[
C_B = 0 \quad (3.44)
\]

Equation (3.43) assures that species A does not react on the susceptor, but species B reacts on the susceptor very fast so that its concentration is zero (cf. Equation 3.44).

### 3.3.4 Transport Properties

Since the concentration of \(N_2\) carrier gas is much larger than the precursor, the transport properties of the gas mixture are based on the 5.0 Torr of \(N_2\). First, the
temperature dependence of density is assumed to follow the ideal gas law:

\[ \rho = \left( \frac{MP_o}{RT_o} \right) \frac{T_o}{T} \quad \Leftrightarrow \quad \rho = 7.49 \times 10^{-6} \left( \frac{T_o}{T} \right) \]  

(3.45)

where \( M \) is molecular weight of \( \text{N}_2 \) and \( R \) is universal gas constant. \( P_o \) is the reference pressure of 5 Torr and \( T_o \) is the reference temperature of 300K.

The temperature dependence of the absolute viscosity, \( \mu \), and thermal conductivity, \( k \), are based on the Chapman-Enskog formula (Bird et al., 1960):

\[ \mu = \mu_o \left( \frac{T}{T_o} \right)^{1/2} \quad \Leftrightarrow \quad \mu = 2.01 \times 10^{-4} \left( \frac{T}{T_o} \right)^{0.5} \frac{g}{\text{cm sec}} \]  

(3.46)

\[ k = k_o \left( \frac{T}{T_o} \right)^{1/2} \quad \Leftrightarrow \quad k = 6.86 \times 10^{-5} \left( \frac{T}{T_o} \right)^{0.5} \frac{\text{cal}}{\text{cm sec K}} \]  

(3.47)

where both \( \mu_o \) and \( k_o \) are calculated from the Chapman-Enskog method at the reference temperature. The required parameters are listed in Table 3.4. The heat capacity of \( \text{N}_2 \), \( c_p \), varies only slightly between the inlet and substrate temperatures. Thus, an average value of \( c_p \) is estimated to be 0.253 cal/g/K (Kreith and Bohn, 1986).

Finally, the diffusion coefficient for the gas mixture TTIP-N\(_2\) and I-N\(_2\) are assumed to be the same and they are based on the method by Fuller, Schettler, and Giddings (Perry’s Handbook, Page 3-285). The required parameters are listed in Table 3.5.
### Table 3.4  Physical Parameters of $N_2$

<table>
<thead>
<tr>
<th>Gas</th>
<th>$N_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight, $M$ (g/gmole)</td>
<td>28.02</td>
</tr>
<tr>
<td>$\varepsilon/\kappa$ (K)</td>
<td>91.5</td>
</tr>
<tr>
<td>$\sigma$ ($\text{Å}$)</td>
<td>3.681</td>
</tr>
<tr>
<td>$\Omega_p$ (600K)</td>
<td>0.9</td>
</tr>
<tr>
<td>Diffusion Volume, $\Sigma V$ ($\text{Å}^3$)</td>
<td>17.9</td>
</tr>
</tbody>
</table>

### Table 3.5  Physical Parameters of TTIP

<table>
<thead>
<tr>
<th>Gas</th>
<th>TTIP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight, $M$ (g/gmole)</td>
<td>284.26</td>
</tr>
<tr>
<td>Diffusion Volume, $\Sigma V$ ($\text{Å}^3$)</td>
<td>276</td>
</tr>
</tbody>
</table>
The temperature and pressure dependence is expressed as:

\[
D = D_o \left( \frac{P_o}{P} \right) \left( \frac{T}{T_o} \right)^{1.75} \quad \Rightarrow \quad D = 7.8 \left( \frac{P_o}{P} \right) \left( \frac{T}{T_o} \right)^{1.75} \frac{cm^2}{sec}
\]

(3.48)

where \(D_o\) is calculated at the reference temperature of 300K, and the reference pressure of 5 Torr.

3.3.5 Dimensionless Groups

I will introduce a few dimensionless groups to simplify the numerical analysis of the balance equations. First, the dimensionless vertical distance is defined as:

\[
\zeta = \frac{z}{L}
\]

(3.49)

where \(L\) is the distance between the inlet and susceptor planes.

The dimensionless axial and radial velocities are defined as:

\[
\phi = -\frac{2}{\rho u_o} f \quad \Rightarrow \quad \phi = \frac{v_z}{u_o}
\]

(3.50)

\[
\frac{d\phi}{d\zeta} = -\frac{2L}{\rho u_o} \frac{df}{dz} \quad \Rightarrow \quad \frac{d\phi}{d\zeta} = -\frac{2L}{r} \frac{v_r}{u_o}
\]

(3.51)

where \(r\) is the distance from the center of the susceptor.
The dimensionless temperature is defined as:

\[ \theta = \frac{T}{T_o} \]  

(3.52)

The dimensionless concentration for TTIP (species A) and intermediate (species B) are defined as:

\[ \gamma_A = \frac{C_A}{C_{Ao}} \]  

(3.53)

\[ \gamma_B = \frac{C_B}{C_{Ao}} \]  

(3.54)

where \( C_{Ao} \) is the inlet TTIP concentration calculated from the inlet TTIP pressure at the inlet temperature of 100 °C using the ideal gas law.

After substituting the dimensionless variables from Equations (3.49) to (3.54) and the temperature dependence of the transport properties from Equations (3.45) to (3.48), a few dimensionless groups arise from the balance equations. The first one is the Reynolds number \( (Re) \) for the momentum equation:

\[ Re = \frac{L u_o \rho_o}{\nu_o} \]  

(3.55)

which represents the ratio of momentum flux by convection and momentum flux by diffusion.
The second one is the thermal Peclet number ($Pe_h$) for the energy equation:

$$Pe_h = \frac{L u_0 \rho_o c_p}{k_o}$$

(3.56)

which represents the ratio of thermal flux by convection and thermal flux by diffusion.

The third one is the mass Peclet number ($Pe_m$) for the species equation:

$$Pe_m = \frac{L u_0}{D_o}$$

(3.57)

which represents the ratio of mass flux by convection and mass flux by diffusion.

Finally, the dimensionless activation energy and Dämkoehler number for the gas phase reaction are:

$$\Sigma_1 = \frac{E_1}{R T_o}$$

(3.58)

$$Da_{g1} = \frac{L k^1_o}{u_o}$$

(3.59)

where $R$ is the gas constant. $Da_{g1}$ represents the ratio of the characteristic time for flow and the characteristic time for gas-phase reaction.

I rewrite the equations of change in terms of these dimensionless variables and groups, and substitute the temperature dependence of the transport properties such as viscosity, thermal conductivity, and diffusivity. Due to the power-law dependence of the
transport properties on temperature, this creates an additional temperature dependent term in each equation.

The momentum equation becomes:

$$\frac{2}{Re} \theta^2 \phi'' - \left(2 \phi - \frac{1}{Re} \theta^2 \theta' \right) \phi'' + (\phi')^2 = \Gamma$$  \hspace{1cm} (3.60)

The energy equation becomes:

$$\frac{1}{Pe_h} \theta^3 \theta'' + \left( \frac{1}{2 Pe_h} \theta^2 \theta' - \phi \right) \theta' = 0$$  \hspace{1cm} (3.61)

The species balance equations for species A becomes:

$$\frac{1}{Pe_m} \theta^2 \gamma_A'' + \left( \frac{7 Pe_m}{4} \theta^2 \theta' - \phi \right) \gamma_A' - D_{gL} \exp\left(-\frac{\Sigma_1}{\theta} \right) \gamma_A = 0$$  \hspace{1cm} (3.62)

The species balance equations for species B becomes:

$$\frac{1}{Pe_m} \theta^2 \gamma_B'' + \left( \frac{7 Pe_m}{4} \theta^2 \theta' - \phi \right) \gamma_B' + D_{gL} \exp\left(-\frac{\Sigma_1}{\theta} \right) \gamma_A = 0$$  \hspace{1cm} (3.63)

At the end of the inlet tube ($\zeta = 0$), the velocities, temperature, and concentration are governed by:

$$\phi' = 0 \hspace{0.5cm} \phi = 1 \hspace{0.5cm} T = 1$$  \hspace{1cm} (3.64)
\[- \frac{1}{P_{e_m}} \frac{d\gamma_A}{d\zeta} + \gamma_A = 1 \quad (3.65)\]

\[- \frac{1}{P_{e_m}} \frac{d\gamma_B}{d\zeta} + \gamma_B = 0 \quad (3.66)\]

At the face of the susceptor ($\zeta = 1$), the velocities, temperature, and concentration are governed by:

\[
\phi' = 0; \quad \phi = 0; \quad \theta = \theta_s; \quad \frac{d\gamma_A}{d\zeta} = 0; \quad \gamma_B = 0 \quad (3.67)
\]

### 3.3.6 Parameter Estimation

In this section we will determine the optimized value for $k_i^n$ using the 1-D SPFR model. The assumed parameters for the 1-D SPFR model are listed in Table 3.6. First, we use the shooting method with the Runge-Kutta integrator (subroutine RKSYST) to solve the velocity and temperature profiles from the momentum and energy equations (subroutine MEBAL). In Equations (3.60), there are one unknown constant and one unknown initial condition. In Equation (3.62), there is one unknown initial condition. Initial guesses are made for the unknowns, and converged values are obtained using the Newton-Raphson method (subroutine NLSYST).

On the other hand, a more general finite difference method (subroutine FDSYST) is developed to solve the species balance equations for both TTIP and intermediate concentration profiles from species equations (subroutines SABAL and SBBAL). This is because the species equations are stiffer than the momentum and energy equations.
Table 3.6 Parameters of the Carrier Gas Experiments using 1-D SPFR Model

<table>
<thead>
<tr>
<th>Type</th>
<th>Parameter</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor Geometry</td>
<td>Inlet Radius</td>
<td>$R_0 = 1.6$ cm</td>
</tr>
<tr>
<td></td>
<td>End of Inlet to Face of Susceptor</td>
<td>$L = 1.6$ cm</td>
</tr>
<tr>
<td>Operating Conditions</td>
<td>Inlet Axial Velocity</td>
<td>$u_i = 6.91$ cm/s</td>
</tr>
<tr>
<td></td>
<td>Inlet Temperature</td>
<td>$T_i = 100$ °C</td>
</tr>
<tr>
<td></td>
<td>Substrate Temperature</td>
<td>$T_s = 300$ °C</td>
</tr>
<tr>
<td></td>
<td>Reactor or N$_2$ Pressure</td>
<td>$P = 5.0$ Torr</td>
</tr>
<tr>
<td>Kinetic Parameter</td>
<td>Rate Constant of Adsorption of Intermediate on Reactive Surface</td>
<td>$k_2 = 5.2 \times 10^3$ cm/s</td>
</tr>
</tbody>
</table>
Using a trial value of $k_{r,0}$, we obtain the intermediate concentration profile (see next section). The TiO$_2$ film growth rate is determined using Equation (3.34), and compared with the measured rates obtained by Siefering and Griffin (1990b). The process is repeated using different trial values of $k_{r,0}$, and the optimum value is obtained using non-linear regression (subroutine NLREGR) to fit all the experimental data.

This procedure yields an optimized value of $k_{r,0} = 8.5 \times 10^4$ s$^{-1}$. The coefficient of determination is 0.855. The calculated growth rate is compared to the measured values in Figure 3.3. The species concentration profiles will be presented in the next section.

### 3.3.7 1-D Profiles

Calculated 1-D axial and radial velocity profiles are shown in Figure 3.4. The inlet axial velocity is calculated based on the cross sectional area of the inlet tube and the volumetric flow rate. The axial velocity decreases as the carrier gas approaches the susceptor. On the other hand, the radial velocity at the radius of the susceptor increases up to the midway of the reactor, then decays to zero approaching the susceptor. Thus, the carrier gas enters the reactor axially from the inlet plane and exits radially through the projected cylindrical plane defined by the susceptor radius.

The calculated 1-D temperature profile is shown in Figure 3.5. The temperature at the end of the inlet tube is assumed to be 100 °C, since the inlet tube is kept at constant temperature of 100 °C. The substrate temperature is 300 °C. The temperature profile is very close to a straight line, which indicates that heat transfer is conduction dominated.
Figure 3.3  Order Plot for TiO₂ Films from Carrier Gas Experiments using 1-D SPFR Model
Figure 3.4  Axial and Radial Velocity Profiles for 1-D SPFR Model
Figure 3.5  Axial Temperature Profile for 1-D SPFR Model
Figure 3.6 shows the calculated dimensionless TTIP concentration profile. First, the TTIP concentration decreases from the inlet to susceptor, due to the gas phase reaction. At the inlet the dimensionless concentration is less than unity, due to the Danckwerts' boundary condition which allows reactants to diffuse back to the inlet. The TTIP concentration gradient approaches zero at substrate surface because the TTIP does not react on the substrate surface. The overall conversion of TTIP is about 40 percent.

Finally, the dotted line shown in Figure 3.6 is the calculated intermediate dimensionless concentration. The intermediate concentration approaches zero near the susceptor because it reacts very fast at the substrate surface. The unreacted intermediate builds up away from the substrate. The concentration \( \frac{C_{\text{p}}}{C_{\text{a}}} \) increases to the maximum value of 0.025 at 1.0 cm from the substrate. The intermediate dimensionless concentration at the inlet is greater than zero, again due to the Danckwerts' boundary condition.

### 3.3.8 Discussion

The uncertainty associated with the optimized value of \( k_{r}^{o} \) can be estimated qualitatively using the sensitivity information listed in Table 3.7. The second and third columns are defined in Equation (3.19) and (3.20).

I note that the sensitivity of the calculated rate with respect to the rate constant, \( S_{G,kr} = 0.58 \), is less than unity. This reflects the fact that the calculated fractional conversion of TTIP is 40% at these conditions. This means that the growth rate is conversion limited, and is only partially dependent on the rate constant associated with
Figure 3.6 Axial TTIP and Intermediate Dimensionless Concentration Profiles for 1-D SPFR Model
Table 3.7  Summary of Sensitivity Studies for the Carrier Gas Experiments Using 1-D SPFR Model

<table>
<thead>
<tr>
<th>Parameter (X)</th>
<th>$S_{G/X}$</th>
<th>$S_{h/x}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{p}^{0}$ (Pre-exponential Factor)</td>
<td>0.58</td>
<td>---</td>
</tr>
<tr>
<td>$u_o$ (Inlet Velocity)</td>
<td>0.32</td>
<td>-0.56</td>
</tr>
<tr>
<td>$D$ (Diffusivity)</td>
<td>0.06</td>
<td>-0.11</td>
</tr>
<tr>
<td>$L$ (Reactor Height)</td>
<td>0.49</td>
<td>-0.85</td>
</tr>
</tbody>
</table>
the intrinsic kinetics. This is also reflected by the strong sensitivity to the flow rate (cf., $S_{t\Delta u} = 0.32$), because the flow rate determines the rate at which TTIP is supplied to the reactor.

The uncertainty in the estimated rate constant associated with the diffusivity is fairly small (cf., $S_{k\Delta d} = -0.11$). This indicates that the our operating conditions are in the reaction controlled limited region. Instead, an increase in the diffusivity is accompanied by a compensating decrease in the concentration of the intermediate. On the other hand, the greatest effect to the estimated rate constant is associated with the reactor height (cf., $S_{kH/L} = -0.85$). This is because the reactor height increases the reaction volume.

3.4 2-D SPFR Model

The 1-D SPFR model examined in the last section is a reactor model that includes only axial gradients. To fully describe the cold wall CVD reactor used by Siefering and Griffin (1990b), we need to expand our model to include temperature and concentration gradients in both axial and radial directions. Therefore, I choose to examine a two-dimensional stagnation point flow reactor (2-D SPFR) model.

First, I will formulate the 2-D SPFR model by expressing the general balance equations described in section 3.3.1 in cylindrical coordinates. The reaction mechanism described in section 3.1 is incorporated into the species balance equations. The boundary conditions for the velocity, temperature, and concentration will be defined.
Finally, I will show the velocity vectors, and the temperature and concentration contours predicted by the 2-D SPFR model. The gas-phase pre-exponential factor in the proposed mechanism will be estimated by comparing the calculated centerline growth rates with the average growth rates measured by Siefering and Griffin (1990b), and its sensitivity to the model assumptions will be discussed.

3.4.1 Axisymmetric Balance Equations

The reactor is assumed to be axially symmetric, with no angular variation. Therefore, I am able to apply the balance equations in cylindrical coordinates to completely describe the 3-D behavior of the reactor. The active geometry of the 2-D SPFR model is chosen to be the region between the bottom of the inlet tube and the top of the outlet tube (cf. Figure 3.7).

Both inlet and outlet tubes have a radius of 1.6 cm. The length of the inlet and outlet tubes are assumed to be 3.2 cm and 1.6 cm, respectively. The reactor is defined as a cylindrical region with radius of 3.2 cm. The height of the reactor is 3.2 cm. The distance from the inlet of the inlet tube to the face of susceptor is 4.8 cm. The susceptor is assumed to be a 0.8 cm thick circular cylinder with radius of 1.6 cm. The distance from the edge of the susceptor to the reactor wall is 1.6 cm, and the distance from the back of susceptor to the entrance of the outlet tube is 0.8 cm.

The momentum, energy, and species balance equations in cylindrical coordinates are developed in the same manner described by Patankar (1980).
Figure 3.7 Reactor Geometry for 2-D SPFR Model
The continuity equation is:

\[ \frac{\partial}{\partial r} (\rho rv_r) + \frac{\partial}{\partial z} (\rho rv_z) = 0 \]  \hspace{1cm} (3.68)

The \( r \)-momentum balance equation is:

\[ \frac{1}{r} \frac{\partial}{\partial r} (\rho rv_r v_r) + \frac{\partial}{\partial z} (\rho rv_z v_z) = \frac{1}{r} \frac{\partial}{\partial r} \left( \mu r \frac{\partial v_r}{\partial r} \right) + \frac{\partial}{\partial z} \left( \mu \frac{\partial v_z}{\partial z} \right) - \frac{\partial p}{\partial r} \]  \hspace{1cm} (3.69)

The \( z \)-momentum balance equation is:

\[ \frac{1}{r} \frac{\partial}{\partial r} (\rho rv_z v_r) + \frac{\partial}{\partial z} (\rho v_z v_z) = \frac{1}{r} \frac{\partial}{\partial r} \left( \mu r \frac{\partial v_z}{\partial r} \right) + \frac{\partial}{\partial z} \left( \mu \frac{\partial v_z}{\partial z} \right) - \frac{\partial p}{\partial z} \]  \hspace{1cm} (3.70)

The energy balance equation is:

\[ \frac{1}{r} \frac{\partial}{\partial r} (\rho c_p v_r T) + \frac{\partial}{\partial z} (\rho c_p v_z T) = \frac{1}{r} \frac{\partial}{\partial r} \left( k r \frac{\partial T}{\partial r} \right) + \frac{\partial}{\partial z} \left( k \frac{\partial T}{\partial z} \right) \]  \hspace{1cm} (3.71)

The species balance equation for TTIP (species A) is:

\[ \frac{1}{r} \frac{\partial}{\partial r} (r v_r C_A) + \frac{\partial}{\partial z} (v_z C_A) = \frac{1}{r} \frac{\partial}{\partial r} \left( D r \frac{\partial C_A}{\partial r} \right) + \frac{\partial}{\partial z} \left( D \frac{\partial C_A}{\partial z} \right) - k_1 C_A \]  \hspace{1cm} (3.72)
The species balance equation for intermediate (species B) is:

\[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \nu_r C_B \right) + \frac{\partial}{\partial z} \left( \nu_z C_B \right) = \frac{1}{r} \frac{\partial}{\partial r} \left( D \frac{\partial C_B}{\partial r} \right) + \frac{\partial}{\partial z} \left( D \frac{\partial C_B}{\partial z} \right) + k_1 C_A \]  

(3.73)

The TiO₂ film growth rate is determined from:

\[ G = -D \frac{\partial C_B}{\partial n} \]  

(3.74)

where \( G \) is in terms of flux units (1 mole/cm²/s = 6.75 \times 10^8 µm/h). Here \( n \) is the outward normal to the reactive or susceptor surfaces.

### 3.4.2 Boundary Conditions

Boundary conditions are required to solve the above balance equations. The velocity boundary conditions are: no tangential velocity at the walls and susceptor; no normal velocity at the walls and susceptor; uniaxial flow at the inlet; no radial gradient at the centerline; and no axial gradient at the outlet. For the temperature boundary conditions, I have defined constant temperatures for the walls and the susceptor. There is also no radial gradient at the centerline and no axial gradient at the outlet.

The above conditions can be expressed as:

At the walls,

\[ V_r = 0 ; \quad V_z = 0 ; \quad T = T_w \]  

(3.75)
At the susceptor,

\[ V_r = 0 ; \quad V_z = 0 ; \quad T = T_s \quad (3.76) \]

At the inlet,

\[ V_r = 0 ; \quad V_z = u_o ; \quad T = T_o \quad (3.77) \]

At the centerline,

\[ V_r = 0 ; \quad \frac{\partial V_z}{\partial r} = 0 ; \quad \frac{\partial T}{\partial r} = 0 \quad (3.78) \]

At the outlet,

\[ V_r = 0 ; \quad \frac{\partial V_z}{\partial z} = 0 ; \quad \frac{\partial T}{\partial z} = 0 \quad (3.79) \]

The concentration boundary conditions are based on the reaction mechanism described in Section 3.1. The assumption of no net normal flux is used on all non-reactive boundaries (i.e., walls, centerline, and outlet). At the susceptor surface, TTIP (species A) does not react, but intermediate (species B) reacts very fast so that its concentration is zero. The concentrations across the inlet are assumed to follow the Danckwerts’ boundary conditions.
The above conditions can be expressed as:

At non-reactive surfaces,

$$\frac{\partial C_A}{\partial n} = \frac{\partial C_B}{\partial n} = 0$$ \hspace{1cm} (3.80)

At the susceptor,

$$\frac{\partial C_A}{\partial n} = 0$$ \hspace{1cm} (3.81)

$$C_B = 0$$ \hspace{1cm} (3.82)

At the inlet,

$$u_o (C_{Ao} - C_A) = -D \frac{dC_A}{dz}$$ \hspace{1cm} (3.83)

$$-u_o C_B = -D \frac{dC_B}{dz}$$ \hspace{1cm} (3.84)

### 3.4.3 Parameter Estimation

In this section I will determine the value for $k_{1,0}$ using the 2-D SPFR model. The transport properties have been defined in Section 3.3.4. The assumed parameters for the 2-D SPFR model are listed in Table 3.8.
Table 3.8 Assumed Parameters for 2-D SPFR Model

<table>
<thead>
<tr>
<th>Type</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor Geometry</td>
<td>Inlet Radius</td>
<td>$R_o = 1.6$ cm</td>
</tr>
<tr>
<td></td>
<td>Susceptor Radius</td>
<td>$R_s = 1.6$ cm</td>
</tr>
<tr>
<td></td>
<td>Reactor Wall to Susceptor</td>
<td>$R_{ws} = 1.6$ cm</td>
</tr>
<tr>
<td></td>
<td>Reactor Radius</td>
<td>$R = 3.2$ cm</td>
</tr>
<tr>
<td></td>
<td>Inlet Tube</td>
<td>$L_i = 3.2$ cm</td>
</tr>
<tr>
<td></td>
<td>Inlet Tube to Susceptor</td>
<td>$L_{is} = 1.6$ cm</td>
</tr>
<tr>
<td></td>
<td>Susceptor Thickness</td>
<td>$L_s = 0.8$ cm</td>
</tr>
<tr>
<td></td>
<td>Reactor Height</td>
<td>$L_R = 3.2$ cm</td>
</tr>
<tr>
<td></td>
<td>Inlet to Outlet</td>
<td>$L = 8.0$ cm</td>
</tr>
<tr>
<td>Operating Conditions</td>
<td>Inlet Axial Velocity</td>
<td>$u_o = 6.91$ cm/s</td>
</tr>
<tr>
<td></td>
<td>Wall Temperature</td>
<td>$T_w = 100$ °C</td>
</tr>
<tr>
<td></td>
<td>Substrate Temperature</td>
<td>$T_s = 300$ °C</td>
</tr>
<tr>
<td></td>
<td>Reactor or N$_2$ Pressure</td>
<td>$P = 5.0$ Torr</td>
</tr>
</tbody>
</table>
I use a control volume-based finite volume method (Pantankar 1980) to solve the partial differential balance equations for the velocity vectors, and the temperature and concentration contours. Based on this method, the partial differential balance equations are solved by program SOUR2 obtained from Professor Sumanta Acharya of the Mechanical Engineering Department. This program was examined in the course "Computation of Fluid Flow and Heat Transfer" (ME 7823) during the Fall Semester 1989. It is designed to solve 2-D partial differential balance equations for viscous flow.

For the flow field, the continuity equation is coupled to the momentum equations through a pressure correction method named SIMPLE (Semi-Implicit Method for Pressure-Linked Equations). A power law scheme is used for interpolation between grid points and to calculate the face value of variables. The coupled, nonlinear equations are solved iteratively using a line by line method (TDMA = Tri-Diagonal-Matrix Algorithm) sweeping from top to bottom or vice versa, and then from left to right or vice versa, respectively. The details of the SIMPLE algorithm can be found in Appendix A.

To use the program, I need to modify a subroutine USER for our reactor geometry (entry GRID), transport properties (entry START), and boundary conditions (entries BOUND and GAMSOR). I also need to define grid spacing (entry GRID), initial values (entry START), stopping criteria (entry OUTPUT), and maximum iterations (BLOCK DATA). The main program and the subroutines are listed in Appendix A.

The equations are discretized into a uniform, cylindrical grid with grid spacing of 0.1 cm. This grid spacing gives relative small error compared with grid spacing of 0.05
cm. The grid consists of 80 cells in the axial direction and 32 cells in the radial direction. All calculations were carried out on a IBM 3090 600E supercomputer. To reach a fully converged solution for a typical conditions, it takes about 18 minutes of CPU time and 4000 iterations with the vector processor.

Using a trial value of $k_r^n$, we obtain the concentration contour of the intermediate (see next section). Since Siefering and Griffin (1990b) only measured the average growth rate, I compared the average growth rate with the calculated centerline growth rate using equation (3.74). The process is repeated using different trial values of $k_r^n$, and the optimum value is obtained.

This procedure yields an optimized value of $k_r^n = 8.0 \times 10^5$ s\(^{-1}\). This is based on an activation energy, $E_t = 55$ kJ/mole as determined in Chapter 4. The coefficient of determination is 0.855. The calculated growth rate at the centerline is compared with the average measured values in Figure 3.8.

### 3.4.4 2-D Profiles

A calculated velocity vector plot is shown in Figure 3.9. The velocity vectors are parallel to the z-axis at the inlet, which reflects the assumptions that the inlet axial velocity is uniform and there is no inlet radial velocity. Along the inlet tube, the magnitude of the vector decreases to approach zero near the walls due to the no-slip condition, and increases near the centerline. A parabolic velocity profile develops along the inlet tube.
Figure 3.8 Order Plot for TiO$_2$ Films from the Carrier Gas Experiments using 2-D SPFR Model
Figure 3.9  Velocity Vector Plot for 2-D SPFR Model
The magnitude of the vector in the axial direction starts to decrease near the centerline when the carrier gas approaches the susceptor. On the other hand, the magnitude of the vector in the radial direction increases and moves away from the centerline. The overall magnitude of the velocity decelerates due to the larger cross sectional area in the reactor. As the flow enters the outlet tube, the overall magnitude of the velocity accelerates again due to the narrower cross sectional area. At the end of the outlet tube, the velocity vectors become parallel to the z-axis.

A calculated 2-D temperature contour profile is shown in Figure 3.10. The temperature at the walls is 100 °C, and the substrate temperature is 300 °C. The temperature over most of the inlet region is below 120 °C. The temperature of the end of the inlet tube is about 140 °C due to the conduction from the susceptor. The temperature contour lines are quite uniform near the centerline. However, the temperature gradient is steeper near the edge of the susceptor. On the back of the susceptor, the temperature contour lines are also quite uniform near the centerline.

Figure 3.11 shows the calculated dimensionless TTIP concentration contours ($C_a/C_{a_0}$). The TTIP concentration decreases from the inlet to susceptor due to the gas phase reaction. At the inlet, the $C_a/C_{a_0}$ is less than unity due to the Danckwerts' boundary condition. The contours remain quite uniform near the susceptor and outlet regions. This is because the diffusion is much higher near substrate, where the temperature is higher. On the other hand, most of the TTIP concentration gradient occurs along the inlet tube. The cross-sectional area of inlet tube is much less than the reactor. Thus, it requires a larger gradient to maintain the same diffusive flux of TTIP.
Figure 3.10  Temperature Contour Profile for 2-D SPFR Model
Figure 3.11  Dimensionless TTIP Concentration Contours ($C_A/C_{A_0}$) for 2-D SPFR Model
Figure 3.12 shows the calculated contours for the dimensionless concentration of the intermediate \( \frac{C_Y}{C_A^o} \). The \( \frac{C_Y}{C_A^o} \) at the inlet is greater than zero, again due to the Danckwerts' boundary condition. The intermediate concentration increases from the inlet towards the substrate due to generation by gas phase reaction and it passes through the maximum value of \( \frac{C_Y}{C_A^o} = 0.04 \) near 1.6 cm from the substrate. Then, the intermediate concentration decreases due to the diffusion to the substrate. It approaches zero at the substrate because it reacts very fast at the substrate surface. A finite concentration of the intermediate exists at the outlet (i.e., the gradient approaches zero).

Figure 3.13 shows the calculated growth rate across the substrate surface as a function of the distance from the centerline. This corresponds to the film growth rate profile in the radial direction. This information can be calculated using the 2-D model, because it is the first of our models to include radial concentration gradients. The figure shows the growth rate at each position normalized by the centerline value. Because the carrier gas experiments are performed in the first order kinetic regime, the calculated growth rate profiles are independent of inlet TTIP partial pressure.

The growth rate is uniform over most of the susceptor. It varies by less than 5% up to a distance of 1.2 cm (i.e., 75% of the susceptor radius). In addition, the substrate does not extend to the edge of the susceptor. Over this region of the susceptor, the growth rate occurs by diffusion of the intermediate species from the gas volume immediately above the susceptor. As the edge of the susceptor is approached, the growth rate increases rapidly. This is because growth rate occurs via diffusion of the intermediate from the region immediately outside the susceptor radius, as well as from the region above the susceptor (cf., Figure 3.7).
Figure 3.12  Dimensionless Intermediate Concentration Contours ($C_\text{m}/C_\text{ao}$) for 2-D SPFR Model
Figure 3.13  Thickness Profile for TiO$_2$ Films from the Carrier Gas Experiments using 2-D SPFR Model
3.4.5 Discussion

The uncertainty associated with the optimized value of \( k_{f0} \) can be estimated qualitatively using the sensitivity information listed in Table 3.9. The second and third columns are defined in Equation (3.19) and (3.20).

I note that the sensitivity of the calculated rate with respect to the rate constant, \( S_{G/k_f} = 0.58 \), is less than unity. This reflects the fact that the calculated fractional conversion of TTIP is 55% at these conditions. This means that the growth rate is conversion limited, and is only partially dependent on the rate constant associated with the intrinsic kinetics. This is also reflected by the strong sensitivity to the flow rate (cf., \( S_{G/u_0} = 0.36 \)), because the flow rate determines the rate at which TTIP is supplied to the reactor.

There is very little uncertainty in the estimated rate constant associated with both the diffusivity (cf., \( S_{k_f/D} = -0.11 \)) and susceptor thickness (cf., \( S_{k_f/l_s} = 0.13 \)). The calculated concentration profiles indicate that increasing the diffusivity is accompanied by a compensating decrease in the concentration of the intermediate. As a result, the flux of intermediate to the surface remains relatively unchanged. On the other hand, the greatest effect on the estimated rate constant is associated with the susceptor radius (cf., \( S_{k_f/r_s} = 0.77 \)). This is because the susceptor radius can increase the reaction area.

Finally, there is more uncertainty in the estimated rate constant associated with the distance from the inlet tube to susceptor (cf., \( S_{k_f/l_{in}} = -0.65 \)) than with the length of the inlet tube (cf., \( S_{k_f/l_{in}} = -0.28 \)). It is because there is more intermediate generated in the volume closer to susceptor.
Table 3.9 Summary of Sensitivity Studies for 2-D SPFR Model

<table>
<thead>
<tr>
<th>Parameter (X)</th>
<th>( S_{G/X} )</th>
<th>( S_{K/F/X} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_{Y,0} ) (Pre-exponential Factor)</td>
<td>0.58</td>
<td>---</td>
</tr>
<tr>
<td>( u_0 ) (Inlet Velocity)</td>
<td>0.36</td>
<td>-0.61</td>
</tr>
<tr>
<td>( D ) (Diffusivity)</td>
<td>0.06</td>
<td>-0.11</td>
</tr>
<tr>
<td>( L_i ) (Length of Inlet Tube)</td>
<td>0.16</td>
<td>-0.28</td>
</tr>
<tr>
<td>( L_{ns} ) (Distance from Inlet Tube to Susceptor)</td>
<td>0.38</td>
<td>-0.65</td>
</tr>
<tr>
<td>( R_{ws} ) (Distance from Reactor Wall to Susceptor)</td>
<td>-0.20</td>
<td>0.34</td>
</tr>
<tr>
<td>( R_s ) (Susceptor Radius)</td>
<td>-0.45</td>
<td>0.77</td>
</tr>
<tr>
<td>( L_s ) (Susceptor Thickness)</td>
<td>-0.08</td>
<td>0.13</td>
</tr>
</tbody>
</table>
3.5 Comparison of Different Reactor Models

I have examined three reactor models in the last three sections (i.e., the LP, 1-D SPFR, and 2-D SPFR models). The assumptions involved for each model can be found in Sections 3.2, 3.2, and 3.4, respectively. Here I compare the axial and radial velocity profiles and the temperature profile predicted by the 1-D and 2-D SPFR models using a fixed set of operating conditions. The concentration profiles of TTIP and the intermediate species are compared for all three models. Finally, I compare the optimized pre-exponential factor obtained using each model based on the activation energy obtained from Chapter 4.

3.5.1 Axial and Radial Velocity, and Temperature Profiles

In order to understand the behavior of the different models, I will compare the velocity, temperature, and concentration profiles calculated using each model.

Axial Velocity. Figure 3.14 shows the axial velocity profiles near the centerline calculated using the 1-D and 2-D models. The axial velocities near the substrate are similar and approach zero. The axial velocity near the inlet plane is higher for the 2-D model than the 1-D model. This reflects the difference in boundary conditions assumed for the two models. The inlet velocity for the 1-D model is a single value, reflecting the assumption of radial uniformity. In contrast, a parabolic inlet velocity is assumed for the 2-D case. The average velocity is the same for the two models, but the centerline velocity is higher for the 2-D model.
Figure 3.14  1-D and 2-D Axial Velocity Profiles near the Centerline
Radial Velocity. The radial velocity profiles at \( r = R_s \) (i.e., the radius of the susceptor) are shown in Figure 3.15. The radial velocities are zero at the inlet plane, because the inlet velocity is assumed to have no radial component. The radial velocities at the substrate (i.e., \( z = 1.6 \text{ cm} \)) are zero for both models because of the no slip condition. Both models show a maximum in the radial velocity about midway between the inlet plane and susceptor. The position of the maximum is somewhat closer to the inlet plane for 2-D model, and the maximum velocity is somewhat lower. The radial velocity decreases earlier as it approaches the susceptor for the 2-D model because gas near the susceptor is forced to flow axially as it enters the region between the susceptor wall and the outer wall. This is shown more clearly in the streamline profile (Figure 3.9). The integrated area under both radial velocity profiles (i.e, the momentum fluxes across the boundary at \( r = R_s \)) is the same for both models. This confirms that both models satisfy the macroscopic continuity equation.

Temperature. Figure 3.16 shows the 1-D and 2-D temperature profiles near the centerline. There is good agreement near the substrate, which suggests that the 1-D model works well near the stagnation point. The 2-D model predicts a higher temperature near the inlet plane than the 1-D model. This reflects a difference in the boundary conditions assumed at the inlet. The inlet temperature for the 1-D model is assumed to be the same as the wall temperature (i.e., 100 °C), and is assumed to be radially uniform. In contrast, a radial gradient is allowed for the 2-D case, and the temperature near the inlet plane is determined by the wall and substrate temperature. The calculated temperature contours can be found in Figure 3.10.
Figure 3.15  1-D and 2-D Radial Velocity Profiles at r = R_s
Figure 3.16  1-D and 2-D Temperature Profiles near the Centerline
3.5.2 Concentration Profiles of TTIP and Intermediate

The concentration profiles for all three models are obtained based on equal growth rates. This requires different optimized pre-exponential factor values of $k_1$. The details of the parameter estimation can be found in Section 3.2.2, 3.3.5, and 3.4.3 for the LP, 1-D and 2-D SPFR models, respectively.

**Concentration of TTIP.** The concentration profiles of TTIP (species A) near the centerline are compared in Figure 3.17 for all three models. The concentration profiles obtained by 1-D and 2-D models are similar, and both are lower than the LP model. The average concentration profile obtained by the 1-D model is higher than the 2-D model. This is because some of the TTIP has already reacted in the inlet tube region for the 2-D model (i.e., some reaction occurs before the gas passes the inlet plane).

Both 1-D and 2-D models predict a modest axial concentration gradient, with a variation of 40%. For example, the TTIP varies from 0.7 to 0.5 between the inlet plane and the substrate. The modest gradients reflects a high value of diffusivity.

**Concentration of Intermediate.** Figure 3.18 shows the concentration profiles of intermediate (species B) near the centerline for all three models. The curve for the LP model reflects the assumption of a transport-limited boundary layer (cf. Section 3.2.1).

The concentration for all three models reaches zero at the substrate surface, due to the assumption of a fast surface reaction. The concentrations near the inlet plane differ significantly, decreasing in the order of LP > 2-D > 1-D. For 2-D model, this reflects the fact that intermediate forms in the outer region of the reactor volume ($r > R_s$) and diffuses back into the volume above the susceptor.
Figure 3.17  TTIP (Species A) Concentration Profiles near the Centerline
Figure 3.18  Concentration Profiles of Intermediate (Species B) near the Centerline
3.5.3 Kinetic Parameters

The comparison of pre-exponential factor and activation energy for the three reactor models is listed in Table 3.10. The first two columns list the optimized values of $k_r^0$ and $E_r$ for each model. As discussed above, I used the value of the activation energy determined in 1-D SPFR model for the LP model. The values for the 1-D and 2-D SPFR models are determined separately (cf., Chapter 4). This accounts for most of the difference in the values of $k_r^0$ for the 1-D and 2-D models.

The last two columns show the rate constant $k_r$, evaluated at 220 and 300 °C, based on the parameter values for each model. The values for each temperature are fairly consistent. The LP model differs by 15 to 22% from the 2-D model for 220 to 300 °C. On the other hand, the 1-D model differs by 40 to 13% from the 2-D model for 220 to 300 °C. However, these variations are well within the limit of uncertainty for each model. For example, the uncertainty associated with the area of the susceptor (ca. 50 %) gives rise to an uncertainty of 40% in the value of $k_r$ (cf., Table 3.9).
Table 3.10  Comparison of Pre-exponential Factor and Activation Energy for Different Reactor Models

<table>
<thead>
<tr>
<th>Reactor Model</th>
<th>Pre-exponential Factor, $k_r^n$ (s$^{-1}$)</th>
<th>Activation Energy, $E_t$ (kJ/mole)</th>
<th>Rate Constant at 220°C, $k_r$ (220°C) (s$^{-1}$)</th>
<th>Rate Constant at 300°C, $k_r$ (300°C) (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LP</td>
<td>$5.9 \times 10^4$</td>
<td>45</td>
<td>1.01</td>
<td>4.67</td>
</tr>
<tr>
<td>1-D SPFR</td>
<td>$8.5 \times 10^4$</td>
<td>45</td>
<td>1.45</td>
<td>6.72</td>
</tr>
<tr>
<td>2-D SPFR</td>
<td>$8.0 \times 10^3$</td>
<td>55</td>
<td>1.19</td>
<td>7.75</td>
</tr>
</tbody>
</table>
CHAPTER 4

**TiO$_2$ FILMS FROM PURE TTIP EXPERIMENTS**

In this chapter I analyze the experiments performed by Siefering and Griffin without the use of carrier gas. The TiO$_2$ thin film growth rates obtained by Siefering and Griffin (1990a) from pure TTIP were reviewed in Chapter 2. In those experiments, the TTIP vapor was transferred from the constant temperature glass bottle to the CVD reactor by means of its own vapor pressure, instead of using a carrier gas as in the previous experiments. Different thicknesses of TiO$_2$ films were formed on a heated substrate using different TTIP vapor pressures, as controlled by the temperature of the glass bottle. The results were reported in the form of a reaction order plot for four different substrate temperatures.

The reaction mechanism proposed by Siefering and Griffin (1990a) for pure TTIP experiments is similar to the mechanism proposed for the carrier gas experiments. The only difference is in the gas phase activation step, which is proposed to occur via a bimolecular collision between TTIP and TTIP to form a reactive intermediate. I will examine the series of models described in the last chapter for the CVD reactor used by Siefering and Griffin (1990a) in order to estimate the kinetic parameters for the proposed mechanism. I will also discuss the sensitivity of the calculated growth rate with respect to the assigned values of the kinetic parameters and operating conditions. Finally, the kinetic parameters obtained using all three models will be compared and discussed.
4.1 Reaction Mechanism

The elementary steps proposed in the carrier gas experiments can be applied to the pure TTIP experiments, except for the gas phase activation step (cf. Reaction 3.1). For pure TTIP experiments, Siefering and Griffin (1990a) proposed that activation occurred by a collision between two TTIP molecules. In the following sections, I will apply this mechanism using each of the reactor models.

The proposed elementary step for the reaction taking place in the pure TTIP is:

$$r_1$$

$$TTIP + TTIP \rightarrow I + P$$

The rate of the bimolecular collision between TTIP and TTIP to form the intermediate species I in Reaction (4.1) is assumed to have the form:

$$r_1 = k_1[TTIP]^2$$

(4.2)

The rate constant $k_1$ is for second order kinetics. In contrast, the rate constant $k_r$ defined in chapter 3 is for pseudo first-order kinetics.

Based on previous results, we also assume an Arrhenius temperature dependence:

$$k_1 = k_1^0 \exp\left(\frac{-E_1}{RT}\right)$$

(4.3)

where $k_1^0$ is the pre-exponential factor in cm$^3$/mole/s.
The rest of the reaction mechanism is the same as section 3.1. The adsorption rate is expressed in Equation (3.7), and the surface reaction is expressed in Equation (3.9).

Another difference from the treatment in chapter 3 is the fact that the rate of reaction at the surface cannot be simplified as in Equation (3.11). Instead, the full Langmuir-Hinshelwood dependence must be retained:

\[ r_2 = \frac{k_2k_3[I]}{k_3 + k_2[I]} \]  \hspace{1cm} (4.4)

At low temperature and high TTIP inlet pressure, the surface decomposition reaction becomes rate limited and the overall rate saturates. For example, at 493 K and 2 Torr, the value of \( k_3 = 10^{-10} \) mole/cm\(^2\)/s is much smaller than the value of \( k_2[I] = 10^{-5} \) mole/cm\(^2\)/s.

### 4.2 Lumped Parameter Model

In this section I first derive the species balance equations for the pure TTIP experiments using the LP model. The reaction mechanism described in section 4.1 is incorporated into the species balance equations. The gas-phase rate constant in the proposed mechanism will be estimated by comparing with the growth rates measured by Siefering and Griffin (1990a). Then, I will present the concentration behavior for TTIP and intermediate. Finally, the sensitivity of the growth rate and kinetic parameter to the model assumptions will be discussed.
4.2.1 Governing Equations

The species balance equation for TTIP (species A) is:

\[ Q(C_A - C_{A0}) = -V k_1^{LP} C_A^2 \quad (4.5) \]

where \( k_1^{LP} \) will be defined below. The right side of the equation assumes a second-order dependence on TTIP concentration, in contrast to the first-order dependence assumed when analyzing the carrier gas experiments.

The species balance equation for the intermediate (species B) is:

\[ QC_B = V k_1^{LP} C_A^2 - A k_2^{LP} (C_B - C_B^s) \quad (4.6) \]

where \( k_2^{LP} \) is defined as in Equation (3.18). The last term in Equation (4.6) introduces a new variable, \( C_B^s \), which represents the intermediate concentration at the surface. Due to the saturation effects at the high TTIP pressure, we can no longer assume that this concentration is zero.

The addition of the new variable \( C_B^s \) in Equation (4.6) means that a third species balance equation must be added. The species balance equation for the intermediate (species B) at the surface is:

\[ k_2^{LP} (C_B - C_B^s) = \frac{k_2 k_3 C_B^s}{k_3 + k_2 C_B^s} \quad (4.7) \]

I will keep the Arrhenius dependence for \( k_3 \) (cf. Equation 3.10).
Finally, the TiO$_2$ film growth rate is given by:

\[ G = r_2 = \frac{k_2 k_3 C_B^s}{k_3 + k_2 C_B^s} \quad (4.8) \]

The new parameter $k_1^{LP}$ is defined identically to $k_1^{LP}$ in Equation (3.16):

\[ k_1^{LP} = \frac{1}{V} k_1^0 \int \exp \left( \frac{-E_1}{RT(V)} \right) dV \quad (4.9) \]

The value of $k_1^{LP}$ predicted by Equation (4.9) for the present cold-wall reactor geometry is different for different substrate temperatures. The ratio between the $k_1^{LP}$ and the value evaluated at the substrate temperature is defined to be $\gamma$. The value of $\gamma$ is listed in Table 4.1 for each substrate temperature.

### 4.2.2 Parameter Estimation

Siefering and Griffin (1990a) have determined values for the parameters $E_3$ and $k_3^o$. In this section we will determine a value for $E_3$ and $k_3^o$, using the more accurate LP model with the methods described below.

I proceed by solving Equations (4.5), (4.6), and (4.7) using the method of successive approximation. The parameters values are listed in Table 3.1. First we solve Equation (4.5) for the TTIP concentration ($C_A$). Using a trial value of $C_A$, we next solve Equation (4.7) for the intermediate concentration at the surface ($C_B^s$).
Table 4.1  Summary of $\gamma$ values for each Substrate Temperature using the 1-D SPFR Temperature Profile in Pure TTIP Experiments

<table>
<thead>
<tr>
<th>Substrate Temperature ($^\circ$C)</th>
<th>Substrate Temperature (K)</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>573</td>
<td>0.29</td>
</tr>
<tr>
<td>280</td>
<td>553</td>
<td>0.30</td>
</tr>
<tr>
<td>250</td>
<td>523</td>
<td>0.32</td>
</tr>
<tr>
<td>220</td>
<td>493</td>
<td>0.35</td>
</tr>
</tbody>
</table>
Finally, I solve Equation (4.6) for the new value of $C_B$ using the values of $C_A$ and $C_B^*$. I repeat the procedure until the value of $C_B$ has converged. The $\text{TiO}_2$ film growth rate is then determined by Equation (4.8).

The entire process is repeated using different values of $E_1$ and $k_{1o}$, and the optimum value is chosen to fit all the experimental data. This procedure yields optimized values of $E_1 = 45 \text{ kJ/mole}$ and $k_{1o} = 4.0 \times 10^{11} \text{ cm}^3/\text{mole/s}$. The coefficient of determination is about 0.8. The calculated growth rates are compared to the measured values in Figure 4.1.

### 4.2.3 Concentration Behavior

The calculated TTIP concentration as a function of inlet TTIP pressure is shown in Figure 4.2 for four different temperatures. The dimensionless TTIP concentration ($C_A/C_{A0}$) is close to unity at low TTIP inlet pressure for all four substrate temperatures. On the other hand, the value decreases to about 0.87 at the highest operating temperature (573 K) and pressure (2 Torr). This is the result of the second-order kinetics. In contrast, for the carrier gas experiments the calculated dimensionless TTIP concentration was independent of TTIP inlet pressure, because of the assumed first-order dependence.

Figure 4.3 shows the dimensionless concentration of the intermediate in the bulk ($C_b/C_{A0}$) and at the surface ($C_b^*/C_{A0}$) calculated for different inlet TTIP pressures. At low inlet TTIP pressure, both dimensionless concentrations increase linearly with increasing inlet TTIP pressure.
Figure 4.1  Order Plot for TiO₂ Films from Pure TTIP Experiments using LP Model
Figure 4.2 Dimensionless TTIP Concentration from Pure TTIP Experiments using LP Model
Figure 4.3  Dimensionless Intermediate Concentration from Pure TTIP Experiments using LP Model
However, the surface concentration is much lower because the Langmuir-Hinshelwood surface reaction is in the first-order regime \((k_1 > k_2 C_{\text{ns}}^+\)). As inlet TTIP pressure increases, the surface begins to saturate \((k_1 < k_2 C_{\text{ns}}^+)\). As the surface becomes blocked, this causes first \(C_{\text{ns}}^+\) and eventually \(C_{\text{ns}}\) to increase sharply. At the highest inlet TTIP pressures, \(C_{\text{ns}}^+\) approaches \(C_{\text{ns}}\).

### 4.2.4 Discussion

The uncertainty associated with the optimized value of \(k_1^n\) can be estimated in the same manner as in section 3.2.3 using the sensitivity information listed in Table 4.2. The second column is defined same as Equation (3.19). The third column, \(S_{k_1/x}\), shows the sensitivity of \(k_1^n\) to uncertainties in the parameters of interest, defined as follows:

\[
S_{k_1/x} = -\frac{S_{G/x}}{S_{G/k_1}}
\]

Four operating regimes are examined for the sensitivity effects. At high substrate temperature and low inlet TTIP pressure, I note that the sensitivity of the calculated rate with respect to the rate constant, \(S_{G/k_1}\), is equal to unity. This reflects the fact that the calculated fractional conversion of TTIP is 0.3 percent at these conditions. This means that the growth rate is not conversion limited, and is dependent on the rate constant associated with the intrinsic kinetics. This is also reflected by the weak sensitivity to the flow rate (cf., \(S_{G/q} = -0.19\)).
Table 4.2  Summary of Sensitivity Studies for LP Model in Pure TTIP Experiments

<table>
<thead>
<tr>
<th>Parameter (X)</th>
<th>Substrate Temperature, $T_s = 573$ K</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$P_{Ao} = 0.04$ Torr</td>
<td>$P_{Ao} = 2.0$ Torr</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$S_{G/X}$</td>
<td>$S_{k1/X}$</td>
<td>$S_{G/X}$</td>
<td>$S_{k1/X}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_1^e$</td>
<td>1.00</td>
<td>---</td>
<td>0.58</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>$k_{2\text{CSTR}}$</td>
<td>0.35</td>
<td>-0.35</td>
<td>0.19</td>
<td>-0.33</td>
<td></td>
</tr>
<tr>
<td>$Q$</td>
<td>-0.19</td>
<td>0.19</td>
<td>0.04</td>
<td>-0.06</td>
<td></td>
</tr>
<tr>
<td>$V$</td>
<td>1.00</td>
<td>-1.00</td>
<td>0.58</td>
<td>-1.00</td>
<td></td>
</tr>
<tr>
<td>$A$</td>
<td>-0.80</td>
<td>0.80</td>
<td>-0.59</td>
<td>1.03</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter (X)</th>
<th>Substrate Temperature, $T_s = 493$ K</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$P_{Ao} = 0.04$ Torr</td>
<td>$P_{Ao} = 2.0$ Torr</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$S_{G/X}$</td>
<td>$S_{k1/X}$</td>
<td>$S_{G/X}$</td>
<td>$S_{k1/X}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_1^e$</td>
<td>1.00</td>
<td>---</td>
<td>0.00</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>$k_{2\text{CSTR}}$</td>
<td>0.20</td>
<td>-0.20</td>
<td>0.00</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>$Q$</td>
<td>-0.19</td>
<td>0.19</td>
<td>0.00</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>$V$</td>
<td>1.00</td>
<td>-1.00</td>
<td>0.00</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>$A$</td>
<td>-0.80</td>
<td>0.80</td>
<td>0.00</td>
<td>---</td>
<td></td>
</tr>
</tbody>
</table>
Similarly, $S_{G,k_1}$ is equal to unity at the low substrate temperature and low inlet TTIP pressure. It is expected that there should be lower conversion at lower temperature. Thus, the growth rate is also dependent on the rate constant associated with the intrinsic kinetics. This is also reflected by the weak sensitivity to the flow rate (cf., $S_{G,q} = -0.19$).

However, I find that the sensitivity of the calculated rate with respect to the rate constant, $S_{G,k_1} = 0.58$, is not close to unity at high TTIP inlet pressure and high substrate temperature. This reflects the fact that the calculated fractional conversion of TTIP is 13 percent at these conditions. This means that the growth rate is starting to become conversion limited, and is only moderately dependent on the rate constant associated with the intrinsic kinetics. This is reflected by the moderate sensitivity to the flow rate (cf., $S_{G,q} = -0.04$).

Finally, the sensitivity factors are indeterminate at low substrate temperature and high TTIP pressure (cf., $T_s = 493$ K and $P_{A_o} = 2.0$ Torr). This is the saturation region, so that the parameters of the gas phase step do not affect the growth rate. Instead, the growth rate is determined entirely by $k_3$, the rate constant for the surface decomposition step.

4.3 1-D SPFR Model

In this section I apply the 1-D SPFR model to analyze the pure TTIP experimental results reported by Siefering and Griffin (1990a). I use the same momentum and energy equations from Section 3.3.2. I modify the species balance equations for the pure TTIP experiments using the reaction mechanism described in Section 4.1. Differences occur
in the reaction terms in the species balance equations and in the boundary conditions of
the intermediate balance equation. I will estimate the kinetic parameters $k_i^0$ and $E_i$ for
this model. The velocity, temperature, concentration profiles will be discussed. Finally,
I will present the sensitivity of $k_i^0$ to various model assumptions.

4.3.1 Transformation Equations

I reduce the 2-D partial differential equations into ordinary differential equations
in the same manner as Section 3.3.2. The reactor geometry of 1-D SPFR model can be
found in Figure 3.2. The transformed momentum and energy equations are the same as
Equations (3.30) and (3.31), respectively. The differences occur in the species equations
for TTIP (species A) and intermediate (species B).

The transformed balance equation for species A becomes:

$$\frac{d}{dz} \left( D \frac{dC_A}{dz} \right) + \frac{2f}{\rho} \frac{dC_A}{dz} - k_1 C_A^2 = 0 \quad (4.11)$$

The transformed species equation for species B becomes:

$$\frac{d}{dz} \left( D \frac{dC_B}{dz} \right) + \frac{2f}{\rho} \frac{dC_B}{dz} + k_1 C_A^2 = 0 \quad (4.12)$$
The TiO₂ film growth rate is the same as Equation (3.34):

\[ G = -D \frac{dC_B}{dz} \quad (4.13) \]

where \( G \) is in terms of flux units (1 mole/cm²/s = 6.75 x 10⁸ µm/h).

### 4.3.2 Boundary Conditions

The boundary conditions required to solve the above transformed balance equations are mostly the same as in Section 3.3.3. At the end of the inlet tube (\( z = 0 \)), the velocities, temperature, and concentration are governed by Equations from (3.35) to (3.39). At the face of the susceptor (\( z = L \)), the velocities, temperature, and concentration of TTIP are governed by Equations from (3.40) to (3.43).

However, the boundary condition for intermediate concentration (species B) at the face of the susceptor is different from Equation (3.44):

\[ -D \frac{dC_B}{dz} = \frac{k_2k_3C_B}{k_3 + k_2C_B} \quad (4.14) \]

The rate at which species B reacts on the susceptor is governed by the Langmuir-Hinshelwood rate equation.

### 4.3.3 Transport Properties

For pure TTIP precursor, the reactor pressure varies with the pressure of TTIP. Therefore, the transport properties are dependent on both the temperature and pressure.
First, the density is assumed to follow the ideal gas law:

\[ \rho = \frac{M P_o}{R T_o} \frac{P T_o}{P_o T} \Rightarrow \rho = 1.52 \times 10^{-5} \left( \frac{P}{P_o} \right) \left( \frac{T_o}{T} \right) \]  (4.15)

where \( M \) is molecular weight of TTIP (Table 4.3). \( P_o \) is the reference pressure of 1 Torr and \( T_o \) is the reference temperature of 300K.

Both absolute viscosity and thermal conductivity are independent of pressure. Then, the temperature dependence of the absolute viscosity, \( \mu \), and thermal conductivity, \( k \), are based on the Chapman-Enskog formula (Bird et al., 1960):

\[ \mu = \mu_o \left( \frac{T}{T_o} \right)^{0.5} \Rightarrow \mu = 9.04 \times 10^{-5} \left( \frac{T}{T_o} \right)^{0.5} \frac{g}{cm \ sec} \]  (4.16)

\[ k = k_o \left( \frac{T}{T_o} \right)^{0.5} \Rightarrow k = 3.32 \times 10^{-6} \left( \frac{T}{T_o} \right)^{0.5} \frac{cal}{cm \ sec \ K} \]  (4.17)

where both \( \mu_o \) and \( k_o \) are calculated from the Chapman-Enskog method at the reference temperature. The required parameters are listed in Table 4.3. The heat capacity of \( N_2 \), \( c_p \), varies only slightly between the inlet and substrate temperatures. Thus, an average value of \( c_p \) is estimated to be 0.0279 cal/g/K.

Finally, the diffusion coefficient for the gas mixture TTIP-TTIP is based on the method by Fuller, Schettler, and Giddings (Perry’s Handbook, Page 3-285). The required parameters are listed in Table 4.3.
Table 4.3  Physical Parameters of TTIP

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gas</strong></td>
<td><strong>TTIP</strong></td>
</tr>
<tr>
<td>Molecular Weight, M (g/gmole)</td>
<td>284.26</td>
</tr>
<tr>
<td>Boiling Point, T_b (°C)</td>
<td>170</td>
</tr>
<tr>
<td>Density at T_b, d (g/cm³)</td>
<td>1.033</td>
</tr>
<tr>
<td>Molar Volume, V (cm³/gmole)</td>
<td>275.2</td>
</tr>
<tr>
<td>ε/κ (K)</td>
<td>509.5</td>
</tr>
<tr>
<td>σ (Å)</td>
<td>7.584</td>
</tr>
<tr>
<td>Ω_p (600K)</td>
<td>1.5</td>
</tr>
<tr>
<td>Diffusion Volume, ΣV (Å³)</td>
<td>276</td>
</tr>
</tbody>
</table>
The temperature and pressure dependence is expressed as:

\[
D = D_0 \left( \frac{P_0}{P} \right) \left( \frac{T}{T_0} \right)^{1.75} \Rightarrow D = 8.13 \left( \frac{P_0}{P} \right) \left( \frac{T}{T_0} \right)^{1.75} \ \frac{cm^2}{sec}
\]  (4.18)

where \( D_0 \) is calculated at the reference temperature of 300K, and the reference pressure of 1 Torr.

4.3.4 Dimensionless Groups

The dimensionless momentum and energy equations are the same as Equations (3.60) and (3.61). I only need to rewrite the species equations using the dimensionless variables and groups defined in Section 3.3.5. However, I need to redefine the Damköhler number in Equation (3.59) for the gas phase reaction:

\[
Da_g^o = \frac{LC_{Ao} k_1^o}{u_o}
\]  (4.19)

At the same time, I will introduce a dimensionless activation energy and Damköhler number for the surface reaction:

\[
\Sigma_3 = \frac{E_3}{RT_o}
\]  (4.20)

\[
Da_s^o = \frac{Lk_2 k_3^o}{D \left[ k_3^o \exp \left( - \frac{\Sigma_3}{\theta_s} \right) + k_2 C_{Ao} \gamma_B \right]}
\]  (4.21)
The balance equation for species A becomes:

\[
\frac{1}{Pe_m} \frac{\partial}{\partial \zeta} \frac{\partial}{\partial \zeta} \gamma_A'' + \left[ \frac{7Pe_m}{4} \theta^4 \phi - \phi \right] \gamma_A' - Da^e \exp \left( - \frac{\Sigma_i}{\theta} \right) \gamma_A^2 = 0
\]  

(4.22)

The balance equation for species B becomes:

\[
\frac{1}{Pe_m} \frac{\partial}{\partial \zeta} \frac{\partial}{\partial \zeta} \gamma_B'' + \left[ \frac{7Pe_m}{4} \theta^4 \phi - \phi \right] \gamma_B' + Da^e \exp \left( - \frac{\Sigma_i}{\theta} \right) \gamma_A^2 = 0
\]  

(4.23)

At the end of the inlet tube (\(\zeta = 0\)), the velocities, temperature, and concentration are governed by Equation from (3.64) to (3.66). At the face of the susceptor (\(\zeta = 1\)), the velocities, temperature, and TTIP concentration are governed by Equation (3.67). However, the boundary condition for the intermediate concentration at the face of the susceptor becomes:

\[
\frac{d\gamma_B}{d\zeta} - Da^e \exp \left( \frac{\Sigma_3}{\theta_s} \right) \gamma_B = 0
\]  

(4.24)

4.3.5 Parameter Estimation

In this section I will determine the value for \(k_1^o\) and \(E_1\) using the 1-D SPFR model. I obtain the velocity, temperature, and concentration profiles by the methods described in Section 3.3.5. Using trial values of \(k_1^o\) and \(E_1\), I obtain the intermediate concentration profile (see next section). The TiO\(_2\) film growth rate is determined using
Equation (4.13). The process is repeated using different values of $k_1^o$ and $E_1$, and the optimum value is obtained using non-linear regression to fit all the experimental data.

This procedure yields an optimized value of $k_1^o = 5.5 \times 10^{11}$ cm$^3$/mole/s and $E_1 = 45$ kJ/mole. The coefficient of determination is 0.855. The calculated growth rates are compared to the measured values in Figure 4.4.

4.3.6 1-D Profiles

Calculated 1-D axial and radial velocity profiles are shown in Figure 4.5. Both axial and radial velocity profiles are very similar to the profiles for the carrier gas case. Four curves are shown to demonstrate the effect of substrate temperature (220 °C vs. 300 °C) and inlet TTIP pressure (0.04 Torr vs. 2.0 Torr). These correspond to the range of operating conditions studied by Siefering and Griffin (1990a).

The various operating conditions lead to small differences in the calculated velocity profiles. Both axial and radial velocity profiles shift slightly toward the substrate plane with decreasing temperature and increasing pressure. These differences appear to be due to the change in Reynolds number (Re). From Equation (3.55), Re is directly proportional to the reactor pressure and inversely proportional to the temperature. Thus, the Re increases in moving from the dashed line to the solid line shown in Figure 4.5. Larger Re will lead to larger convective force, so that the inlet momentum persists further toward the substrate.

Figure 4.6 shows the calculated 1-D temperature profiles for four substrate temperatures and two inlet TTIP pressures (0.04 Torr vs. 2.0 Torr) studied by Siefering
Figure 4.4 Order Plot for TiO₂ Films from Pure TTIP Experiments using 1-D SPFR Model
Figure 4.5  Axial and Radial Velocity Profiles for 1-D SPFR Model
Figure 4.6  Axial Temperature Profile for 1-D SPFR Model
and Griffin (1990a). The larger inlet TTIP pressure causes the calculated temperature profiles to shift towards the substrate plane for all four temperatures. These differences are due to the change in thermal Pelet number ($\text{Pe}_h$). From Equation (3.56), $\text{Pe}_h$ is directly proportional to the reactor pressure and inversely proportional to the temperature. Thus, the $\text{Pe}_h$ increases in moving from the solid line to the dotted line shown in Figure 4.6. Larger $\text{Pe}_h$ will lead to larger convection force, so that the inlet temperature persists further towards the substrate.

Figure 4.7 shows the calculated dimensionless TTIP concentration profiles ($C_A/C_{A_0}$). The concentration decreases from the inlet to susceptor, due to the gas phase reaction. The drop of concentration is larger at the higher substrate temperature, when the reaction rate is faster. Similar behavior appears here as in Figure 3.6.

Figure 4.8 shows the calculated dimensionless concentration of the intermediate ($C_B/C_{A_0}$) at low inlet TTIP pressure. The concentration is higher at the higher temperature because more intermediate molecules are generated. The concentration approaches zero near the susceptor because the surface reaction is fast enough to provide vacant sites for more intermediate to react. The intermediate concentrations remain high at the inlet because of the large diffusion at low operating pressure.

Figure 4.9 shows the behavior of $C_B/C_{A_0}$ at high inlet TTIP pressure. The values are dramatically different from Figure 4.8. The concentration is much higher for the high inlet TTIP pressure, compared with the low inlet TTIP pressure. This is because of the second-order kinetics. The temperature dependence of the concentration profile shows a maximum at 250 °C.
Figure 4.7 Axial TTIP Dimensionless Concentration Profiles for 1-D SPFR Model at inlet TTIP Pressure of 2.0 Torr
Figure 4.8 Axial Intermediate Dimensionless Concentration Profiles for 1-D SPFR Model at inlet TTIP Pressure of 0.04 Torr
Figure 4.9  Axial Intermediate Dimensionless Concentration Profiles for 1-D SPFR Model at inlet TTIP Pressure of 2.0 Torr
Between 220 and 250 °C, the concentration increases with temperature because of the increase in gas phase reaction rate. At the same time, the surface is saturated, causing the concentration gradient at the substrate to approach zero. Above 250 °C the concentration decreases with increasing temperature. This occurs in spite of the increase in gas phase activation rate, because the rate of surface reaction is increasing more rapidly with temperature. This also causes the surface to become unsaturated, so that the concentration of the intermediate approaches zero at the substrate.

4.3.7 Discussion

The uncertainty associated with the optimized value of $k_1^0$ can be estimated in the same manner as in Section 4.2.4 using the sensitivity information listed in Table 4.3. Two inlet TTIP pressures are examined at $T_s = 573$ K for sensitivity effects.

At the low inlet TTIP pressure, the sensitivity of the calculated rate with respect to the rate constant, $S_{G/k1}$ is equal to unity. This reflects the fact that the calculated fractional conversion of TTIP is 3% at these conditions. This means that the growth rate is not conversion limited, and is dependent on the rate constant associated with the intrinsic kinetics. This is also reflected by the weak sensitivity to the axial velocity (cf., $S_{G/uo} = 0.05$).

At the high TTIP inlet pressure, we find that the sensitivity of the calculated rate with respect to the rate constant is significantly less than unity ($S_{G/k1} = 0.60$). This partially reflects the fact that the calculated fractional conversion of TTIP is 13% at these conditions. This means that the growth rate is becoming conversion limited, and is only
Table 4.4  Summary of Sensitivity Studies for 1-D SPFR Model in Pure TTIP Experiments

<table>
<thead>
<tr>
<th>Parameter (X)</th>
<th>Substrate Temperature, ( T_s = 573 ) K</th>
<th>( P_{\Lambda_0} = 0.04 ) Torr</th>
<th>( P_{\Lambda_0} = 2.0 ) Torr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( S_{G/X} )</td>
<td>( S_{k1/X} )</td>
<td>( S_{G/X} )</td>
</tr>
<tr>
<td>( k_i^o )</td>
<td>1.0</td>
<td>---</td>
<td>0.60</td>
</tr>
<tr>
<td>Gas Phase Reaction</td>
<td></td>
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</tr>
<tr>
<td>( k_N^o )</td>
<td>0.0</td>
<td>0.0</td>
<td>0.25</td>
</tr>
<tr>
<td>Surface Reaction</td>
<td></td>
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</tr>
<tr>
<td>( u_0 )</td>
<td>0.05</td>
<td>-0.05</td>
<td>0.21</td>
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<tr>
<td>Inlet Axial Velocity</td>
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<tr>
<td>( D )</td>
<td>-0.07</td>
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<td>0.11</td>
</tr>
<tr>
<td>Diffusion Coefficient</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( L )</td>
<td>1.0</td>
<td>-1.0</td>
<td>0.51</td>
</tr>
<tr>
<td>Reactor Height</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
moderately dependent on the rate constant associated with the intrinsic kinetics. This is reflected by the moderate sensitivity to the axial velocity (cf., \( S_{G/\text{int}} = 0.21 \)). The loss of sensitivity to \( k_1^o \) is also due to the increasing sensitivity to the pre-exponential factor for surface reaction rate \( k_1 \) (cf., \( S_{G/k_1} = 0.25 \)).

Finally, there is very little uncertainty in the estimated rate constant associated with the diffusivity at either inlet TTIP pressure. For example, calculated concentration profiles indicate that an increase in the diffusivity would be accompanied by a compensating decrease in the concentration of the intermediate. As a result, the flux of intermediate to the surface remains relatively unchanged.

### 4.4 2-D SPFR Model

In this section I apply the 2-D SPFR model to analyze the pure TTIP experimental results reported by Siefering and Griffin (1990a). I use the same continuity, momentum and energy equations from Section 3.4.1. I modify the species balance equations for the pure TTIP experiments using the reaction mechanism described in Section 4.1. Differences occur in the reaction terms in the species equations and in the boundary conditions of the intermediate balance equation. I will estimate the kinetic parameters \( k_1^o \) and \( E_1 \) for this model. The velocity vectors, temperature and concentration contours will be discussed. Finally, I will present the sensitivity of \( k_1^o \) to various model assumptions.
4.4.1 Axisymmetric Balance Equations

The reactor geometry was shown in Figure 3.7. The continuity, momentum and energy equations are the same as Equations (3.68), (3.69), and (3.70) respectively. The differences occur in the species equations for TTIP (species A) and intermediate (species B).

The species equation for species A becomes:

\[
\frac{1}{r} \frac{\partial}{\partial r} (rv_r C_A) + \frac{\partial}{\partial z} (v_z C_A) = \frac{1}{r} \frac{\partial}{\partial r} \left( D \frac{\partial C_A}{\partial r} \right) + \frac{\partial}{\partial z} \left( D \frac{\partial C_A}{\partial z} \right) - k_1 C_A^2 \tag{4.25}
\]

The species balance equation for species B is:

\[
\frac{1}{r} \frac{\partial}{\partial r} (rv_r C_B) + \frac{\partial}{\partial z} (v_z C_B) = \frac{1}{r} \frac{\partial}{\partial r} \left( D \frac{\partial C_B}{\partial r} \right) + \frac{\partial}{\partial z} \left( D \frac{\partial C_B}{\partial z} \right) + k_1 C_A^2 \tag{4.26}
\]

The TiO\textsubscript{2} film growth rate is same as Equation (3.74):

\[
G = -D \frac{\partial C_B}{\partial n} \tag{4.27}
\]

where \( G \) is in terms of flux units (1 mole/cm\textsuperscript{2}/s = 6.75 x 10\textsuperscript{8} \mu m/h). Here \( n \) is the outward normal to the reactive or susceptor surfaces.
4.4.2 Boundary Conditions

The boundary conditions required to solve the above transformed balance equations are mostly the same as in Section 3.4.2. The velocities and temperature are governed by Equations (3.75) to (3.79). The species concentration for non-reactive surfaces are governed by Equation (3.80). For the inlet, they are governed by Equations (3.83) and (3.84). The boundary condition for the TTIP (species A) at the susceptor surface is governed by Equation (3.81).

However, the boundary condition for the intermediate (species B) at the susceptor is different from Equation (3.82):

$$-D \frac{dC_B}{dn} = \frac{k_1 k_2 C_B}{k_3 + k_2 C_B}$$

(4.28)

The rate at which species B reacts on the susceptor is governed by the Langmuir-Hinshelwood rate equation.

4.4.3 Parameter Estimation

In this section I will determine the values for $E_t$ and $k_i^n$ using the 2-D SPFR model. I obtain the velocity vectors and temperature and concentration contours by the methods described in Section 3.4.3. Using trial values of $E_t$ and $k_i^n$, I obtain the intermediate concentration contours (see next section). The average TiO$_2$ film growth rate is determined using Equation (4.27) at the centerline. The process is repeated using
different values of $E_q$ and $k_q''$, and the optimum value is obtained using non-linear regression to fit all the experimental data.

This procedure yields an optimized values of $E_q = 55$ kJ/mole, and $k_q'' = 4.8 \times 10^{12}$ cm$^3$/mole/s. The coefficient of determination is 0.927. The calculated average growth rates are compared to the measured values in Figure 4.10.

4.4.4 2-D Profiles

A calculated velocity vector plot for pure experiments is similar to the one shown in Figure 3.9 for the carrier gas experiments. This is because we have the same reactor geometry and boundary conditions.

Figures 4.11 and 4.12 compare the calculated 2-D temperature contours for two substrate temperatures ($T_s = 220$ °C and $T_s = 300$ °C) studied by Sielering and Griffin (1990a). The temperature of the walls is 100 °C. The temperature over most of the inlet region is below 120 °C for both substrate temperatures. The temperature of the end of the inlet tube is about 130 °C for $T_s = 220$ °C, but the temperature of the end of the inlet tube is about 150 °C for $T_s = 300$ °C.

Figures 4.13 and 4.14 show the calculated dimensionless 2-D TTIP concentration contours ($C_A/C_{A_0}$) for the two substrate temperatures ($T_s = 220$ °C and $T_s = 300$ °C). The concentration decreases from the inlet to susceptor, due to the gas phase reaction. The drop of concentration is larger at the higher substrate temperature, when the reaction rate is faster. Similar behavior appears here as in Figure 3.6. At the inlet, the $C_A/C_{A_0}$ is less
Figure 4.10  Order Plot for TiO$_2$ Films from Pure TTIP Experiments using 2-D SPFR Model
Figure 4.11  Temperature Contours for 2-D SPFR Model of Pure TTIP Experiments at Substrate Temperature of 220 °C
Figure 4.12  Temperature Contours for 2-D SPFR Model of Pure TTIP Experiments at Substrate Temperature of 300 °C
Figure 4.13  Dimensionless TTIP Concentration Contours \( \left( \frac{C_A}{C_{A_0}} \right) \) for 2-D SPFR Model of Pure TTIP experiments at Substrate Temperature of 220°C and Inlet TTIP Pressure of 2.0 Torr
Figure 4.14  Dimensionless TTIP Concentration Contours ($C_N/C_{No}$) for 2-D SPFR Model of Pure TTIP experiments at Substrate Temperature of 300°C and Inlet TTIP Pressure of 2.0 Torr
than unity due to the Danckwerts’ boundary condition. The contours remain quite uniform near the susceptor and the outlet regions. The $C_n/C_{A_0}$ near the susceptor for $T_s = 220 \, ^\circ C$ is 0.92, but the $C_n/C_{A_0}$ near the susceptor for $T_s = 300 \, ^\circ C$ is 0.78.

Figures 4.15 and 4.16 show the calculated dimensionless concentration of the intermediate ($C_n/C_{A_0}$) at low inlet TTIP pressure (0.04 Torr) for substrate temperatures of 220 and 300 \, ^\circ C, respectively. The concentration is higher at the higher temperature because more intermediate molecules are generated.

At the substrate temperature of 220 \, ^\circ C, the maximum value of $C_n/C_{A_0} \approx 1.2 \times 10^{-5}$ near 4.8 cm from the substrate. At a substrate temperature of 300 \, ^\circ C, the maximum value of $C_n/C_{A_0} \approx 2.6 \times 10^{-5}$ near 4.0 cm from the substrate.

The concentration approaches zero near the susceptor because the surface reaction is fast enough to provide vacant sites for more intermediate to react. The intermediate concentrations remain high at the inlet because of the large diffusion at low operating pressure. The concentration gradient towards the substrate is higher for $T_s = 300 \, ^\circ C$ than $T_s = 220 \, ^\circ C$, reflecting the higher growth rate.

Figures 4.17 and 4.18 show the behavior of $C_n/C_{A_0}$ at high inlet TTIP pressure for substrate temperature of 220 and 300\, ^\circ C. They are dramatically different from Figures 4.15 and 4.16. The intermediate concentration is much higher for the high inlet TTIP pressure, compared with the low inlet TTIP pressure. This is because of the assumed second-order dependence of the activation step on total pressures.
Figure 4.15  Dimensionless Concentration Contours of Intermediate ($C_i/C_{Ao}$) for 2-D SPFR Model of Pure TTIP Experiments at Substrate Temperature of $220^\circ$C and Inlet TTIP Pressure of 0.04 Torr
Figure 4.16  Dimensionless Concentration Contours of Intermediate ($C_p/C_{Ac}$) for 2-D SPFR Model of Pure TTIP Experiments at Substrate Temperature of 300°C and Inlet TTIP Pressure of 0.04 Torr
Figure 4.17  Dimensionless Concentration Contours of Intermediate ($C_{n}/C_{m}$) for 2-D SPFR Model of Pure TTIP Experiments at Substrate Temperature of 220°C and Inlet TTIP Pressure of 2.0 Torr.
Figure 4.18  Dimensionless Concentration Contours of Intermediate (C_w/C_a) for 2-D SPFR Model of Pure TTIP Experiments at Substrate Temperature of 300°C and Inlet TTIP Pressure of 2.0 Torr
At substrate temperature of 220 °C, the surface is saturated, causing the concentration gradient at the substrate to approach a constant value. On the other hand, the concentration contour of intermediate at substrate temperature of 300 °C is very different. The rate of surface reaction is increasing more rapidly with temperature. This causes the surface to become unsaturated, so that the concentration of the intermediate approaches zero at the substrate. A maximum value of $C_i/C_{Ai} = 0.02$ occurs near 0.8 cm from the substrate.

Figure 4.19 shows the calculated growth rate profiles for two substrate temperatures (220 vs. 300 °C) and two inlet TTIP pressures (0.04 vs. 2.0 Torr) studied by Siefering and Griffin (1990a). The behavior described in Section 3.4.4 can be applied to the low inlet TTIP pressure (0.04 Torr) for both substrate temperatures. On the other hand, the growth rate profiles are very uniform for the high inlet TTIP pressure and low substrate temperature, due to the saturation effect.

4.4.5 Discussion

The uncertainty associated with the optimized value of $k_i$ can be estimated in the same manner as in Section 4.2.4 using the sensitivity information listed in Table 4.5. Two inlet TTIP pressures are examined at $T_s = 300°C$ for sensitivity effects.

At the low inlet TTIP pressure, the sensitivity of the calculated rate with respect to the rate constant, $S_{w/k}$, is unity. This reflects the fact that the calculated fractional conversion of TTIP is less than 1% at these conditions. This means that the growth rate
Figure 4.19 Thickness Profiles for TiO$_2$ Films from Pure TTIP Experiments using 2-D SPFR Model
Table 4.5 Summary of Sensitivity Studies for 2-D SPFR Model in Pure TTIP Experiments

<table>
<thead>
<tr>
<th>Parameter (X)</th>
<th>Substrate Temperature, $T_s = 300^\circ$C</th>
<th>$P_{Ao} = 0.04$ Torr</th>
<th>$P_{Ao} = 2.0$ Torr</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1^o$ Gas Phase Reaction</td>
<td>1.00</td>
<td>---</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>---</td>
</tr>
<tr>
<td>$k_1^o$ Surface Reaction</td>
<td>0.0</td>
<td>0.0</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-0.74</td>
</tr>
<tr>
<td>$u_e$ Inlet Axial Velocity</td>
<td>-0.01</td>
<td>0.01</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-0.53</td>
</tr>
<tr>
<td>$D$ Diffusion Coefficient</td>
<td>-0.03</td>
<td>0.03</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-0.07</td>
</tr>
<tr>
<td>$L_i$ Length of Inlet Tube</td>
<td>0.03</td>
<td>-0.03</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-0.05</td>
</tr>
<tr>
<td>$L_{is}$ Distance from Inlet Tube to Susceptor</td>
<td>0.23</td>
<td>-0.23</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-0.69</td>
</tr>
<tr>
<td>$R_{ws}$ Distance from Reactor Wall to Susceptor</td>
<td>0.16</td>
<td>-0.16</td>
<td>-0.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.17</td>
</tr>
<tr>
<td>$R_s$ Susceptor Radius</td>
<td>-0.03</td>
<td>0.03</td>
<td>-0.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.18</td>
</tr>
<tr>
<td>$L_s$ Susceptor Thickness</td>
<td>-0.08</td>
<td>0.08</td>
<td>-0.07</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.14</td>
</tr>
</tbody>
</table>
is not conversion limited, and is dependent on the rate constant associated with the intrinsic kinetics. This is also reflected by the weak sensitivity to the axial velocity (cf., $S_{g/k} = -0.01$).

At the high TTIP inlet pressure, I find that the sensitivity of the calculated rate with respect to the rate constant is significantly less than unity ($S_{g/k} = 0.51$). This partially reflects the fact that the calculated fractional conversion of TTIP is 24% at these conditions. This means that the growth rate is becoming conversion limited, and is only moderately dependent on the rate constant associated with the intrinsic kinetics. This is reflected by the moderate sensitivity to the axial velocity (cf., $S_{g/u} = 0.27$). The loss of sensitivity to $k_1^0$ is also due to the increasing sensitivity to the pre-exponential factor for surface reaction rate $k_3$ (cf., $S_{g/k_3} = 0.38$).

For low inlet TTIP pressure, it is not very sensitive to any parameter. This is due to differential conversion and is gas phase reaction limited. On the other hand, the pre-exponential factor, $k_1^0$ is very sensitive to $k_3$ at high TTIP inlet pressure. This is because the substrate surface reaches saturation at this regime. At the same time, $k_1^0$ is sensitive to the axial velocity and the distance between inlet plane and substrate. This is because both parameters are related to the residence time.

4.5 Comparison of Different Reactor Models

I have examined three reactor models in the last three sections (i.e., the LP, 1-D SPFR, and 2-D SPFR models). The assumptions involved for each model can be found in Sections 4.2, 4.3, and 4.4, respectively. The concentration profiles of TTIP and the
intermediate species are compared for all three models. Finally, I compare the optimized pre-exponential factor and activation energy obtained using each model.

### 4.5.1 Concentration Profiles of TTIP and Intermediate

The concentration profiles for all three models are obtained based on equal growth rates. This requires different optimized pre-exponential factor values of $k_i^o$ and $E_i$. The details of the parameter estimation can be found in Sections 4.2.2, 4.3.5, and 4.4.3 for the LP, 1-D and 2-D SPFR models, respectively.

**Concentration of TTIP.** The concentration profiles of TTIP (species A) for all three models are shown in Figures 4.20 and 4.21 at two different substrate temperatures. The concentration profiles obtained by 1-D and 2-D models are quite similar, and both are lower than the LP model. The average concentration profile obtained by the 2-D model is higher than the 1-D model.

Both 1-D and 2-D models predict a modest axial concentration gradient, with a maximum variation of 40%. For example, the TTIP varies from 0.97 to 0.92 between the inlet plane and the substrate for $T_s = 220 \, ^oC$. The TTIP varies from 0.93 to 0.77 between the inlet plane and the substrate for $T_s = 300 \, ^oC$. The modest gradients reflect a high value of diffusivity.

**Concentration of Intermediate.** Figures 4.22 and 4.23 show the concentration profiles of intermediate (species B) at two different substrate temperatures for all three models. At substrate temperature of 220 $^oC$, the concentration for all three models reaches a constant value at the substrate surface, due to the saturation effect. On the
Figure 4.20  TTIP Centerline Concentration Profiles at $T_s = 220 \, ^\circ C$ and $P_{\text{Ao}} = 2.0 \, \text{Torr}$ for Different Reactor Models in Pure TTIP Experiments
Figure 4.21  TTIP Centerline Concentration Profiles at $T_e = 300 \, ^\circ C$ and $P_{\lambda_0} = 2.0 \, \text{Torr}$ for Different Reactor Models in Pure TTIP Experiments
Figure 4.22 Centerline Concentration Profiles of the Intermediate at $T_s = 220 \, ^\circ\mathrm{C}$ and $P_{Ao} = 2.0 \, \text{Torr}$ for Different Reactor Models in Pure TTIP Experiments
Figure 4.23 Centerline Concentration Profiles of the Intermediate at $T_s = 300$ °C and $P_{\text{in}} = 2.0$ Torr for Different Reactor Models in Pure TTIP Experiments
other hand, the concentration for all three models reaches zero at the substrate surface at substrate temperature of 300 °C. This is because the intermediate reacts very fast at this temperature.

4.5.2 Kinetic Parameters

The comparison of pre-exponential factor and activation energy for the three reactor models is listed in Table 4.6. The first two columns list the optimized values of \( k^* \) and \( E \) for each model. As discussed above, I use the value of the activation energy determined in 1-D SPFR model (cf., Section 4.3) for the LP model.

The value of the activation energy for the 2-D SPFR model is determined in Section 4.4. This accounts for most of the difference in \( k^* \) value for the 1-D and 2-D models. In addition, the main difference among all three models is the activation energy, and the difference of the activation energy between 1-D and 2-D models is 10 kJ/mole.

The difference in the activation energy is caused by the temperature profiles from the different models. The value of \( \gamma \) depends on the substrate temperature (cf., Table 4.7). The temperature profile is different for 1-D and 2-D SPFR models. The difference of activation energy from the arrhenius plots for \( \gamma_{1D} \) and \( \gamma_{2D} \) is about 8 kJ/mole. Therefore, it is consistent with the activation energy for the rate constant.

Siefering and Griffin (1990a) reported the activation energy for the TTIP gas phase decomposition was 35.2 kJ/mole. This is smaller than the value obtained using our 2-D SPFR model. Those authors did not include the temperature efficiency factor for the lumped parameter reactor, \( \gamma \), when they analyzed their results. Because \( \gamma \) itself is
Table 4.6  Comparison of Pre-exponential Factor and Activation Energy for Different Reactor Models in Pure TTIP Experiments

<table>
<thead>
<tr>
<th>Reactor Model</th>
<th>Pre-exponential Factor, $k_0$ (cm^3/mole/s)</th>
<th>Activation Energy, $E_i$ (kJ/mole)</th>
<th>Rate Constant at 220°C, $k_1 (220°C)$ (cm^3/mole/s)</th>
<th>Rate Constant at 300°C, $k_1 (300°C)$ (cm^3/mole/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LP</td>
<td>4.0 x 10^{11}</td>
<td>45</td>
<td>6.82 x 10^6</td>
<td>3.16 x 10^7</td>
</tr>
<tr>
<td>1-D SPFR</td>
<td>5.5 x 10^{11}</td>
<td>45</td>
<td>9.38 x 10^6</td>
<td>4.35 x 10^7</td>
</tr>
<tr>
<td>2-D SPFR</td>
<td>4.8 x 10^{12}</td>
<td>55</td>
<td>7.14 x 10^6</td>
<td>4.65 x 10^7</td>
</tr>
</tbody>
</table>

Table 4.7  Summary of $\gamma$ Values for Different Substrate Temperatures and Reactor Models in the Pure TTIP Experiments

<table>
<thead>
<tr>
<th>Substrate Temperature (°C)</th>
<th>$\gamma_{1-D}$</th>
<th>$\gamma_{2-D}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>220</td>
<td>0.35</td>
<td>0.08</td>
</tr>
<tr>
<td>250</td>
<td>0.32</td>
<td>0.07</td>
</tr>
<tr>
<td>280</td>
<td>0.30</td>
<td>0.06</td>
</tr>
<tr>
<td>300</td>
<td>0.29</td>
<td>0.05</td>
</tr>
</tbody>
</table>
decreasing function of temperature (cf., Table 4.7), its neglect will lead to an erroneously smaller value of the activation energy.

The last two columns in Table 4.6 show the rate constant $k_1$ evaluated at 220 and 300 °C, based on the parameter values for each model. The rate constant obtained by the 2-D SPFR model should be the best estimate, because this model includes both axial and radial gradients, as well as the most accurate treatment of wall effects.

The values for each temperature are fairly consistent. The LP model differs from the 2-D model by 5 to 31% for 220 to 300 °C. On the other hand, the 1-D model differs from the 2-D model by 32 to 7% for 220 to 300 °C. These variations are well within the limits of uncertainty for each model.

4.6 Comparison of Different TiO$_2$ Thin Film Experiments

I have examined two reaction paths to produce TiO$_2$ thin films. In Chapter 3, I estimated the pre-exponential factor for the gas phase reaction in the carrier gas experiments. Siefering and Griffin (1990b) described the gas phase collision between TTIP and N$_2$, with a rate constant, $k_{TTIP-N_2}$. Due to limitations in their model, they were unable to report an absolute value for $k_{TTIP-N_2}$.

In my work, I defined a pseudo first-order rate constant, $k_1$, that incorporates the N$_2$ concentration. I now define $k^{n}_{TTIP-N_2}$ as the pre-exponential factor for the rate constant of TTIP and N$_2$. Therefore, I can relate $k^{n}_{TTIP-N_2}$ to $k_1^n$ using Equations (3.4), (3.5), and (3.6), based on N$_2$ pressure of 5 Torr and temperature of 300 °C. The values of $k^{n}_{TTIP-N_2}$ derived from the carrier gas experiments using three reactor models are listed in the middle column of Table 4.8.
Table 4.8 Comparison of Pre-exponential Factors for the Carrier Gas and Pure TTIP Experiments

<table>
<thead>
<tr>
<th>Reactor Model</th>
<th>Carrier Gas Experiments $k_{TTIPN_2}$ (cm$^3$/mole/s) (Chapter 3)</th>
<th>Pure TTIP Experiments $k_{TTIPTTIP}$ (cm$^3$/mole/s) (Chapter 4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LP</td>
<td>$4.2 \times 10^{11}$</td>
<td>$4.0 \times 10^{11}$</td>
</tr>
<tr>
<td>1-D SPFR</td>
<td>$6.1 \times 10^{11}$</td>
<td>$5.5 \times 10^{11}$</td>
</tr>
<tr>
<td>2-D SPFR</td>
<td>$5.7 \times 10^{12}$</td>
<td>$4.8 \times 10^{12}$</td>
</tr>
</tbody>
</table>
In the earlier sections of this chapter, I estimated the pre-exponential factor for the gas phase reaction in the pure TTIP experiments. In this case, Siefering and Griffin (1990a) proposed the limiting gas phase elementary step was a collision between TTIP and TTIP, with a second-order rate constant, $k_{TTIP/TTIP}$. I also define $k^{o}_{TTIP/TTIP}$ as the pre-exponential factor for the rate constant of TTIP-TTIP collisions. Therefore, $k^{o}_{TTIP/TTIP}$ is the same as $k_i^{o}$ listed in Table 4.6. These values are reproduced in the third column of Table 4.8 for the three reactor models.

The rate constants for the carrier gas experiments and the pure TTIP experiments agree to within 20 percent. This differs from the conclusion of Siefering and Griffin, who reported that $k_{TTIP/N2}$ was 2.5 times smaller than $k_{TTIP/TTIP}$. Part of this difference may be caused by the fact that the carrier gas experiments were performed at significant extents of conversion. Siefering and Griffin did not incorporate the TTIP conversion in their analysis (i.e., they implicitly assumed differential conversion).

The absolute collision efficiency can be discussed in terms of the steric factor, $p$ (Gardiner, 1972):

$$p = \frac{k^{o}_{TTIP/TTIP}}{Z_{TTIP/TTIP}} \quad (4.29)$$

Here $Z_{TTIP/TTIP}$ is hard-sphere collision frequency factor (molecular units):

$$Z_{TTIP/TTIP} = \left( \frac{8 \pi kT}{\mu_{TTIP/TTIP}} \right)^{1/2} \sigma_{TTIP/TTIP}^{2} \quad (4.30)$$
where $k$ is the Boltzmann's constant ($1.38 \times 10^{-16}$ g cm$^2$ s$^{-2}$ K$^{-1}$), $\mu_{ij}$ is the reduced mass of collision pair, and $\sigma_{ij}$ is related to the characteristic collision diameter. The latter two parameters are defined below:

$$
\mu_{ij} = \frac{M_i M_j}{M_i + M_j} \tag{4.31}
$$

$$
\sigma_{ij} = \frac{1}{2} (\sigma_i + \sigma_j) \tag{4.32}
$$

In this calculation, we have $M_{TTIP} = 284.25$ g/gmole and assume $\sigma_{TTIP} = 8.8$ Å, estimated from the density of liquid TTIP (0.995 g/cm$^3$). After converting to the molar units, this yields $Z_{TTIP/TTIP} = 4.36 \times 10^{-14}$ cm$^3$/mole/s. Using the pre-exponential factor from 2-D SPFR model, the absolute steric factor is about 0.01; i.e., the reactive cross section is 100X smaller than the kinetic theory cross section. A list of steric factors for the bimolecular gas reactions can be found in Table 4.1 of Gardiner (1972). The range of $\rho$ values lies between 1.0 and 0.00001, with the most common values around 0.01. In general, smaller values of $\rho$ are associated with more complex molecules.

The present results can also be expressed in terms of the relative collisional efficiency of TTIP and TTIP vs. TTIP and N$_2$. The relative efficiency, $\phi'_{N2/TTIP}$, is defined in Equation (5.35) of Weston and Schwarz (1972):

$$
\phi'_{N2/TTIP} = \left( \frac{k^0_{TTIP/N2}}{k^0_{TTIP/TTIP}} \right) \left( \frac{\mu_{TTIP/N2}}{\mu_{TTIP/TTIP}} \right)^{1/2} \left( \frac{\sigma_{TTIP/TTIP}}{\sigma_{TTIP/N2}} \right)^2 \tag{4.33}
$$
In this calculation, we obtain $\sigma_{N_2} = 3.6 \text{ Å}$ from Bird et al. (1960), and use the 2-D values for $k_{\text{TTIP}/N_2}^0$ and $k_{\text{TTIP}/\text{TTIP}}^0$. This yields $\phi_{\text{N}_2/\text{TTIP}} = 1.02$. This implies that a collision between TTIP and a $N_2$ molecule is just as efficient for activating TTIP as is a collision with a second TTIP molecule. This suggests that the TTIP molecule is large enough that the pattern of energy redistribution among its internal vibrational modes is independent of the size of the collision partner.
CHAPTER 5
LITERATURE REVIEW OF COPPER FILMS

5.1 Applications of Cu Films

Copper film is a potential material for high performance microelectronic devices due to its superior electrical and thermal properties. Metallization or metallic interconnects is the major application. Metal lines connect various transistors, resistor, capacitors, and diodes to each other inside computer chips. Multilevel metallization (MLM) schemes are proposed to optimize the usefulness of ULSI devices and circuits (Steigerwald et al., 1993; Eisenbraun et al., 1993).

Copper film is of interest mainly because of its low resistivity, as well as its large electromigration resistance. Compared with the main interconnect material (aluminum), copper has close to 60% lower resistivity (1.7 μΩ-cm vs. 2.6 for Al). In integrated circuits (IC), the resistance-capacitance delays and current-resistance voltage drops are directly proportional to resistivities of metal lines (Jairath et al., 1993). For the next generation of ICs, faster operating frequencies and high speed performance will require the lowest resistivity metal lines.

High electromigration reliability also needs to be ensured for the higher device densities in next generation ICs. This is because miniaturization of transistors and interconnects increases current driving capabilities. Large currents must be conducted through thinner and longer metal lines (Chang et al., 1993; Nittaet al., 1993). Electromigration resistance translates into a large current carrying capability.
Jairath et al. (1993) reported that electromigration performance of copper is expected to be more than two orders of magnitude better than aluminum. Copper exhibited resistance to electromigration past $1 \times 10^4 \text{ A/cm}^2$, while Shacham-Diamand (1993) reported that the critical current density of aluminum is only $5 \times 10^5 \text{ A/cm}^2$.

In the design of the high performance ULSI chips, MLM schemes are suggested to maximize the use of available chip space and minimize interconnection length. These three dimensional structures create high aspect ratio vias and contacts, and the design rules or feature width will move below 0.5 μm. Therefore, highly pure materials like copper films by chemical vapor deposition (CVD) are needed for these complex architectures. At the same time, CVD can provide conformal layout for deposition of via and trench structures (Eisenbraun et al., 1993). Device speed can be increased to 1 GHz with six to seven levels of interconnects.

There have been several recent reports of copper used in industry. For example, most major Japanese chip makers plan to implement copper in 0.1 μm devices (Singer, 1993). IBM has fabricated 1K static RAM with single copper interconnect layer (Singer, 1993). Copper allows 1.5 times improvement in speed. This is because device frequency is an inverse function of the product of resistance of metal interconnect and the capacitance of the surrounding dielectric materials.

### 5.2 Precursors for Cu Films

High purity copper films with low resistivity can be deposited by thermal decomposition of metal-organic copper precursors. The copper precursors are grouped
into two classes based on the Cu oxidation state. The first class is Cu(I) compounds, which are reviewed by Kodas and Hampden-Smith (1994). The second class is Cu(II) compounds, which are reviewed by Griffin and Maverick (1994).

The Cu(I) compounds commonly contain one anionic ligand (X) and one two-electron donor or neutral ligand (L). Beach et al. (1990) reported the first Cu(I) compounds to deposit blanket copper films. Their Cu(I) complex is a metallocene, (triethylphosphine)cyclopentadienylcopper(I). Here cyclopentadienyl is the anionic ligand, and triethylphosphine is the neutral ligand. This complex is a solid at room temperature.

Since Beach et al. (1990) reported their Cu(I) complexes, most researchers have concentrated on the class of complexes with one hexafluoroacetylacetonate (hfac) as the anionic ligand. Four types of commonly used neutral ligand are alkyne (2-butyne), trialkylphosphine (PMe₃), 1,5-cyclooctadiene (COD), and vinyltrimethylsilane (VTMS).

Reynolds et al. (1991) reported CVD Cu film growth rates as high as 500 Å/min in a cold-wall reactor using (hfac)Cu(COD). Jain et al. (1991) reported growth rates as high as 9000 Å/min in a cold-wall reactor using (hfac)Cu(2-butyne). From the same group of researchers, Shin et al. (1991) reported growth rates as high as 1000 Å/min in a hot-wall reactor using (hfac)Cu(PMe₃).

From Schumacher, Norman et al. (1991) reported the copper film growth rates as high as 1000 Å/min in a cold-wall CVD reactor using (hfac)Cu(VTMS). This is reportedly the first liquid Cu(I) complex used for copper metalization. The substrate temperatures were between 120 and 420°C at reactor pressure between 0.1 and 40 Torr.
Argon carrier gas was bubbled at flow rates between 9.2 and 22.7 sccm through the liquid precursor. The vapor pressure of (hfac)Cu(VTMS) is about 1.0 Torr at the temperature of 40°C.

This type of Cu(I) precursor appears to disproportionate according to the stoichiometry (Doyle, 1985):

\[ 2Cu(hfac)L = Cu + Cu(hfac)_2 + 2L \]  (5.1)

According to Gladfelter (1993), the interest of most researchers working with Cu(I) compounds lies heavily on the side of precursor development. The CVD processing conditions for the Cu(I) precursors are not well-studied. Many questions about the relationship between the surface reaction and operating conditions need to be solved. On the other hand, Cu(II) compounds have been studied since 1965. Many efforts have been spent to understand the interaction between the film growth rate and processing parameters.

For the Cu(II) compounds, alkoxide, β-ketomine, and β-diketonate are common ligands. For the alkoxide ligand, Young (1993) recently used Cu(II) dimethylamino ethoxide to deposit copper onto strontium titanate substrates. For the β-ketomine ligand, Fine et al. (1990) reported that the copper growth rates as high as 700 Å/min in a cold-wall CVD reactor using Cu(nona-F)₂, which has nine fluorine atoms per ligand. Cu(acac)₂ and Cu(hfac)₂ are the common Cu(II) β-diketonate precursors.
The most studied β-diketonate compound for the CVD copper is Cu(hfac)$_2$. It was first used by Van Hemert et al. (1965) to deposit shiny copper films with reducing agent hydrogen:

$$\text{Cu(hfac)}_2 + \text{H}_2 \rightarrow \text{Cu} + 2\text{H(hfac)}$$

(5.2)

In the absence of H$_2$, Temple and Reisman (1989) reported copper films with relatively high resistivity of 3 to 7 $\mu\Omega$-cm. Kaloyeros et al. (1990) reported copper film growth rates as high as 1800 Å/min, and with lower resistivity (1.9 $\mu\Omega$-cm). Awaya (1991) reported that the copper film growth rate can be increased by the addition of water vapor.

One disadvantage of Cu(II) compounds is that they are all solid at room temperature. It is not easy to control the sublimation rate of a solid precursor. Zheng et al. (1992) reported a new liquid delivery approach using Cu(hfac)$_2$ dissolved in isopropanol or ethanol. They showed that reproducible and controllable flow rates of precursor-solvent mixtures can be delivered to reaction zone.

Lai et al. (1991) reported that the deposition rate of copper film reaches a saturation limit at high Cu(hfac)$_2$ concentration. They observed a first-order rate dependence on the hydrogen pressure, and a rate inhibition in the presence of excess H(hfac). Therefore, they derived a Langmuir-Hinselwood rate expression. Recently, Kim et al. (1993) also reported a similar rate expression for their low pressure results. Both kinetic expressions will be discussed and compared in next section.
5.3 Previous Mechanism Studies

Two type of mechanism studies have been reported for the reactions of Cu(hfac)$_2$. The first type consists of desorption studies under ultra high vacuum (UHV) conditions. Reactants do not always follow the same pathways as those occurring at "normal" CVD pressures. However, these studies are useful to identify the possible adsorbed species on the reactive surface. The second group is the kinetic studies under "normal" CVD conditions. Elementary steps are proposed to formulate the rate expression. The parameters from the rate expression are estimated from the experimental growth rate.

5.3.1 Adsorption Studies

Two groups of researchers have studied the adsorption of Cu(hfac)$_2$ on different substrate surfaces under UHV conditions. From IBM T.J. Watson Research Center, Cohen et al. (1992a; 1992b) studied the mechanism of Cu CVD on Ag and SiO$_2$ surfaces. From AT&T Bell Laboratories, Dubois et al. (1992) and Donnelly and Gross (1993) investigated thermal decomposition of Cu(hfac)$_2$ on Cu(100), Cu(111), and TiN surfaces.

Cohen et al. (1992a; 1992b) reported an absorption and decomposition mechanism for Cu(hfac)$_2$. They used x-ray photoelectron spectroscopy (XPS), high resolution electron energy loss spectroscopy (HREELS), and Auger electron spectroscopy (AES) to identify the surface adsorbed species. These authors proposed the mechanism as reduction of Cu(hfac)$_2$ to form adsorbed Cu(I)(hfac) and adsorbed (hfac) ligands on the Ag metal surface, and subsequent removal of (hfac) by reduction with H$_2$. Protonation of the excess (hfac) ligand was proposed as a rate limiting step. These authors also
studied the adsorption of Cu(hfac)$_2$ on both Ag and SiO$_2$ surfaces under the same conditions. They found that Cu(hfac)$_2$ is adsorbed intact on SiO$_2$ surface, in contrast to undergoing dissociative adsorption on Ag surface.

Dubois et al. (1992) observed the desorption and dissociation from the pyrolysis of Cu(hfac)$_2$ on both Cu(100) and Cu(111) surfaces between 77 and 327 C. They detected surface species by reflection-absorption infrared (RAIR) spectroscopy. They found the only species on the surface was the adsorbed (hfac) ligand. These authors did not observe any molecular Cu(hfac)$_2$ or H(hfac) on the Cu(100) and Cu(111) surfaces. Substantial carbon contamination was observed from the temperature programmed desorption (TPD) in the absence of H$_2$.

Donnelly and Gross (1993) studied the thermal decomposition of Cu(hfac)$_2$ by XPS, and TPD. They reported that the Cu was in the +1 oxidation state on the surface. Their explanation is that Cu(hfac)$_2$ is dissociatively chemisorbed at room temperature, with one of the hfac ligands still bound to Cu in a bidentate fashion, and the second hfac ligand involved in a surface mediated reduction of Cu(II) to Cu(I):

$$\text{Cu(II)(hfac)$_2$} \rightarrow \text{Cu(I)(hfac)}(\text{a}) + \text{(hfac)}(\text{a})$$  \hspace{1cm} (5.3)

5.3.2 Kinetic Studies

We first proposed a reaction mechanism for the growth of Cu films using Cu(hfac)$_2$ as a precursor (Lai et al., 1991 and Lai, 1991). The reactions were conducted under "normal" CVD conditions. We deposited Cu films on glass substrate under total
reactor pressure of 760 Torr in a hot wall horizontal flow reactor. A mixture of H₂ and He mixture was the carrier gas used to deliver the saturated vapor of the precursor from the evaporator to the reactor. The substrate temperature ranged from 200 to 275 °C. The precursor temperature ranged from 90 to 110 °C, and the corresponding precursor partial pressure was varied from 2 to 10 Torr. The H₂ partial pressure was varied approximately from 380 to 760 Torr. The flow rate of the carrier gas was varied from 16 to 41 sccm. The observed Cu growth rate ranged from 20 to 120 Å/min.

We determined the reaction kinetics by analyzing the axial thickness profiles of the Cu films under these operating conditions. We reported an activation energy of 80 kJ/mole for the ligand desorption step (see below). For substrate temperature between 200 and 250 °C, the growth rate exhibited saturation kinetics with respect to the precursor concentration, positive reaction order with respect to hydrogen pressure, and negative reaction order with respect to H(hfac) concentration.

Four elementary steps were proposed based on the experimental observations. The first step was irreversible, dissociative adsorption of the precursor at a vacant site to form Cu film and adsorbed (hfac) ligands (Reaction 5.4). The second step was reversible, dissociative adsorption of the H₂ (Reaction 5.5). The third step was the recombination of the volatile H(hfac) desorbed from the surface to generate vacant sites (Reaction 5.6). This step was reversible, so that readsorption of product could cause inhibition of the overall rate (Reaction 5.7). The third step was proposed to be the rate limiting step for the overall reaction.
This mechanism can be represented:

\[ \text{Cu(hfac)}_2(g) \rightarrow \text{Cu(s)} + 2\text{(hfac)}(a) \quad (5.4) \]
\[ H_2(g) \rightarrow 2H(a) \quad (5.5) \]
\[ \text{(hfac)}(a) + H(a) \rightarrow H\text{(hfac)}(g) \quad (5.6) \]
\[ H\text{(hfac)}(g) \rightarrow \text{(hfac)}(a) + H(a) \quad (5.7) \]

Under these specific operating conditions, the rate expression was expressed as:

\[ R = \frac{k_{a1}k_{d2}P_{H_2}C_{\text{Cu(hfac)}_2}}{k_{d2}P_{H_2} + [k_{a2}C_{H\text{(hfac)}} + 2k_{a1}C_{\text{Cu(hfac)}_2}]} \quad (5.8) \]

This rate expression was then combined with a simple reactor model to analyze the measured growth rates. By neglecting the gas-phase cross-sectional concentration gradients, the species balance equation for \( \text{Cu(hfac)}_2 \) assumes the form of the one dimensional plug flow reactor model with axial dispersion. The parameters estimated using this integral reactor model were:

\[ k_{a1} = k_{a2} = 0.1 \text{ \( \frac{cm}{s} \)} = 1.4 \times 10^{18} \text{ \( \frac{molecules}{cm^2 \ s \ atm} \)} \]
\[ k_{d2} = 2.2 \times 10^{23} \exp(-\frac{80kJ/mole}{RT}) \text{ \( \frac{molecules}{cm^2 \ s \ atm} \)} \]
From previous studies of Cu(I)(hfac) and (hfac) adsorbed species, Kim et al. (1993) recently proposed a new reaction mechanism for the growth of Cu films on TiSi$_2$-coated Si substrate. In their experiments, films were deposited on TiSi$_2$ surface under total reactor pressure of 10 Torr in a cold wall vertical flow reactor with H$_2$ and Ar mixture. The substrate temperature ranged from 300 to 400 °C. The precursor temperature ranged from 70 to 85 °C, and the corresponding precursor partial pressure ranged from 0.16 to 0.71 Torr. The H$_2$ partial pressure was varied from 2.5 to 9.5 Torr. The observed Cu growth rate ranged from 100 to 1000 Å/min.

They reported the overall activation energy is about 75 kJ/mole for substrate temperature between 300 and 350 °C. From 350 to 400 °C, the growth rate levels off and undergoes a transition from surface reaction to mass-transfer control. In the surface reaction controlled regime, they reported the film growth rate was 0.5 order in both precursor and hydrogen concentrations.

Five elementary steps were proposed in this regime. The first step was dissociative adsorption of the Cu(hfac)$_2$ to form Cu(I)(hfac) and (hfac) adsorbed species. In the second step, the surface reaction of Cu(I)(hfac) formed Cu film and (hfac) ligand. The third step was dissociative adsorption of the H$_2$. The fourth step was surface reaction to form H(hfac). Finally, volatile H(hfac) desorbed from the surface. Under their specific operating conditions, the rate expression was simplified to:

\[ R = 5.7 \times 10^8 \exp\left(-\frac{75 \text{ kJ/mole}}{RT}\right)P_{H_2}^{0.5}P_{\text{Cu(hfac)}_2}^{0.5} \]  

(5.9)
In this dissertation, I will re-examine the reaction mechanism proposed in Lai (1991), Lai et al. (1991), and Griffin et al. (1992), and also the rate expression proposed by Kim et al. (1993). I will then propose a revised mechanism, and test this new mechanism with the results obtained from our group (Little, 1992; Wang and Griffin, 1992). Little (1992) reported the growth of Cu films on both glass, Si, and TiN-coated substrates using Cu(hfac)$_2$ under total pressures ranging from 40 to 760 Torr in a warm wall horizontal flow reactor with pure H$_2$. The substrate temperature was varied from 250 to 350 °C. The precursor temperature was 80 °C, which corresponds to precursor partial pressure of about 0.66 Torr. The observed Cu growth rate ranged from 20 to 500 Å/min.

5.4 Reactor Modeling

The reactor configuration used to study the kinetics of CVD Cu films is a horizontal reactor in which gas flow is parallel to the substrate surface (Figure 5.1). The susceptor is made of copper, which provides uniform temperature. The top and side walls are warmed with warm heating oil to prevent condensation of Cu(hfac)$_2$ precursor. There have been various investigations to understand the complex transport processes in horizontal CVD reactors both experimentally and theoretically. The modeling of fluid flow, heat transfer, and mass transfer is complex because of the numerous physical phenomena occurring simultaneously.

For a complete three dimensional laminar flow model, Moffat and Jensen (1988) explored the effects of the side temperature boundary conditions and natural convection. They established where a full 2D model is not sufficient for Si film deposition from SiH$_4$
Figure 5.1  Horizontal Flow Over Substrate on Susceptor
diluted in H₂ carrier gas at atmospheric pressure. They reported that the slowing down of the axial velocity near sidewalls could lead to a greater reactant depletion near the walls. They showed that 3D transport effects may be important even in the absence of buoyancy effects. They reported that thermal diffusion could cause non-uniformity in the transverse direction.

Recently, Narusawa (1993) extended the above analysis and examined the effects of the (width/height) aspect ratio and the thermal boundary conditions on the distributions of the film growth rate. The inverse Graetz number may account for profile variations of the film growth rate due to changes in the inlet gas velocity and physical dimensions of the duct.

However, such complete 3D models are very complicated and do not provide rapid insight into the physical and chemical processes when interpreting experimental observations. With a proper design of the reactor, a simplified 2D model should be sufficient to describe the experiments. Therefore, several simpler 2D analytic and numerical models were proposed to take account for the actual growth rate distribution in horizontal CVD reactors.

Van de Ven et al. (1986) reported a 2D analytic studies on the gallium arsenide (GaAs) film growth rate as function of both axial and lateral position in laminar flow systems. They reported that Rayleigh number (Ra) was a good criterion for the characterization of the flow and growth rate under non-turbulent conditions with Reynolds number less than 2300. For Ra less than 700, they showed that the flow was dominantly forced laminar. They demonstrated very satisfactory agreement between experiments and
model even without parameter fitting. On the other hand, they showed that free convective effects were important and strong vortex motions were formed for Ra greater than 1700.

Van de Ven et al. (1986) also reported that the ratio of Grashof (Gr) and Reynolds (Re) numbers was not a reliable measure to characterize the effect of natural convection. They showed that the aspect ratios larger than four would provide good lateral growth rate homogeneity for over 70% of the susceptor width.

For the 2D numerical model, Ouazzani et al. (1988) examined the limitations on their assumptions. They performed a systemetric numerical study and compared with experimental data for the CVD GaAs by Van de Ven et al. (1986). They showed that 2D models can produce realistic predictions only for reactors with large aspect ratios, that are operated at subcritical Ra. They claimed that the thermal (Soret) diffusion must be included in the model. Furthermore, they insisted that velocity corrections for finite aspect ratios must be made. They suggested that the buoyancy effects can be significant in the entrance region, and 2D modeling could not correctly predict the growth rate.

Holstein et al. (1989) studied the effects of thermal diffusion using 2D numerical model. Their model represented conditions occurring in reactors with large aspect ratios in the absence of longitudinal roll waves, conductive to the best growth uniformity. Thermal diffusion was found to be a significant term in the mass transfer equation, decreasing growth rate by about 30% near the front of the susceptor and by lesser amounts further downstream.
Holstein and Fitzjohn (1989) showed that fluid flow in the thermal transition regions is influenced by the ratio of buoyancy and inertial forces, represented by $Gr/Re^2$. They reported that gas recirculation in the form of transverse roll waves occurs over both the leading and trailing edges of the susceptor at high $Gr/Re^2$. They showed that longitudinal roll waves can arise from the side wall effects and an instability characterized by $Ra$. They suggested that buoyancy effects could be reduced at low pressure.

Fotiadis et al. (1990) and Chinoy et al. (1991) included the thermal radiation analysis in their studies. Both studies showed that the simulated temperature fields were closely match with experimental results. They showed that wall heating had a substantial effect on the velocity and temperature fields. They compared the temperature distribution along the wall for the radiation case with the isothermal case.

In this work, I will apply a simplified 2D model which does not include thermal diffusion and buoyancy effects. I should obtain a reasonable prediction of the film growth rate in axial direction, due to the low Re and Ra in our reactor conditions. This simplified model will be adequate to describe the observed growth rate profiles, which are relatively smooth and well-behaved. I will assume a rectangular cross-section, to model the semi-circular cross-section used in our horizontal CVD reactor. Therefore, the partial differential balance equations in rectangular coordinates will be used. The SIMPLE finite volume method, developed by Patankar (1980) is used for the 2-D reactor analysis. Patankar’s SIMPLE numerical scheme has been used by some authors mentioned above (Ouazzani et al., 1988; Chinoy et al., 1991; and Narusawa, 1993).
CHAPTER 6
EXPERIMENTAL

In this chapter, I will describe the apparatus and procedure used to prepare copper thin films by chemical vapor deposition (CVD) for kinetic studies. The CVD apparatus consists of three main parts. The first part is the copper precursor delivery system, described in Section 6.1 and 6.2. These sections describe the handling of the carrier gas (both H\textsubscript{2} and He), the precursor evaporator, and the FTIR spectrometer for monitoring the precursor concentration. The calibration of the precursor delivery rate at different points of the delivery system is discussed in Section 6.3.

The second part of the apparatus is the horizontal warm-wall CVD reactor itself, described in Section 6.4. The next sections are Section 6.5 and 6.6, where I report the preparation of the substrates used for Cu film deposition and the thickness measurements of the deposited Cu film. Finally, the experimental results in Section 6.7 provide the basis for the subsequent kinetic analysis (Chapter 7).

6.1 Precursor Source

For all our CVD Cu films, copper(II) hexafluoroacetylacetonate hydrate [Cu(hfac)\textsubscript{2}\cdot xH\textsubscript{2}O] is used as a copper precursor. A 25g bottle of solid Cu(hfac)\textsubscript{2}\cdot xH\textsubscript{2}O with molecular weight of 495.66 g/gmole is obtained from Aldrich Chemical Company, Inc. Its melting point is between 130-134 °C. This hydrate form of Cu(hfac)\textsubscript{2} is a green crystalline power. On the other hand, the anhydrous form of Cu(hfac)\textsubscript{2} with molecular
weight of 477.64 g/gmole can be obtained from Strem Chemicals, Inc. It is a dark green power with a melting point of 91-93 °C.

The precursor evaporator is shown in Figure 6.1. As the Cu(hfac)$_2$·xH$_2$O is solid at room temperature, a packed bed evaporator configuration is employed to create the vapor phase of precursor. The solid precursor is held by a metal screen inside a half-inch stainless steel tube. The vapor pressure of Cu(hfac)$_2$ was reported by Wolf et al. (1972), and ranges from 0.9 Torr at 76 °C to 2.9 Torr at 90 °C. The standard enthalpy of vaporization is approximately 87 kJ/mole. However, the mass transport rate of the precursor can be varied with different operating conditions.

The typical initial weight and height of the solid bed are 2.0 gram and 3.0 cm, respectively. A one-eighth-inch tubing is inserted through the metal screen, and the opening is below the solid bed. This allows the carrier gas to pass through the heated solid precursor from the bottom of the screen. Then, the precursor vapor and the carrier gas leave the evaporator through a quarter-inch tubing. The temperature of the evaporator is kept constant with a constant temperature oil bath by Fisher Scientific (Isotemp Model 8000). The tubing around the oil bath is wrapped with heating tapes to keep the temperature 10 °C above the oil bath temperature.

Both hydrogen and helium cylinders from Liquid Air Corp. supply the carrier gas for the CVD experiments. The flow rate is controlled by mass flow controllers (MFC) (MKS Instruments Model 1159B), which are calibrated with a burette soap-film flowmeter placed at the reactor outlet. By closing valve 3, I allow both MFCs to reach steady state for the flow of carrier gas before entering either the evaporator or the reactor.
Figure 6.1  From Carrier Gas Handling System to Precursor Evaporator, and then the Precursor is Monitored with IR Cell before Entering the CVD Reactor
By closing valves 1 and 6, I allow the carrier gas to pass through the evaporator to start the mass transport rate or film growth experiments. I stop the experiments by closing both valves 4 and 5, and opening valve 6 (by-pass). This by-pass also allows only the carrier gas to pass through the reactor region at the end of the experiments.

6.2 Fourier Transform Infrared (FTIR) Spectroscopy

Before the mixture of precursor vapor and the carrier gas enters the reactor, the concentration of the precursor is examined using a FTIR spectrometer (Nicolet 60SX). The principle of IR spectroscopy is based on the vibrational motion of bonds between two atoms; i.e., the oscillation of atoms around their fixed equilibrium positions (Conley, 1966). The gas phase of precursor can be characterized from a range of IR frequencies. The absorbance at each frequency is deconvoluted from the interferometer signal detected by mercury-cadmium-telluride detector with resolution of 5 cm\(^{-1}\).

The IR cell shown in Figure 6.1 was designed by Mr. Qingming Zhang of our group. It is made of an aluminum tube, and it has two NaCl windows tightened with o-ring seals at both ends. The inside volume of the IR cell is about 30 cm\(^3\). The NaCl windows transmit frequencies from 625 to 4000 cm\(^{-1}\) to characterize the vapor phase of the copper precursor. The IR cell is wrapped with heating tape and aluminum foil to keep the cell temperature at 150 °C. The quarter-inch tubing along the evaporator, in and out of the IR cell, and the inlet of the horizontal CVD reactor are also wrapped with heating tape to avoid condensation.
A wavenumber of 1117 cm$^{-1}$ is chosen to monitor the precursor concentration before entering the CVD reactor (Lai, 1991). From Beer’s law, the concentration of the precursor is approximately proportional to the absorbance signal. The calibration curve is obtained from the evaporation experiments using a cylindrical glass tube similar to the CVD reactor and which is cooled to act as a trap. The glass tube is connected to the outlet of the IR cell. Therefore, the amount of the solid precursor collected and the absorbance signal are recorded at the same time. The concentration of the precursor ($C_A$) in µmole/cm$^3$ can be expressed in terms of absorbance ($A$):

$$C_A = \frac{A}{6.02 - 1.58A}$$  \hspace{1cm} (6.1)

### 6.3 Evaporation Rate

For the high substrate temperature experiments, the precursor temperature of 76°C is used, and the absorbance of 0.18 is recorded at 1117 cm$^{-1}$. Thus, the precursor concentration is estimated to be $3.0 \times 10^8$ mole/cm$^2$ or 0.66 Torr. For the low substrate temperature experiments, the precursor temperature of 90°C is used, and the absorbance of 0.4 is recorded at 1117 cm$^{-1}$. The precursor concentration is estimated to be $1.0 \times 10^7$ mole/cm$^2$ or 2.3 Torr. In both cases, the precursor pressure is lower than the vapor pressure values reported by Wolf et al. (1972). We suspect that the differences are due to the partial condensation inside the IR cell.

This is confirmed by measurements by Mr. Reginald Little, another member of our group. He connected a U-shaped glass tube condenser directly at the outlet of the
evaporator. At atmospheric pressure, the U-tube collected 2.4 mg/min at a precursor temperature of 90 °C and H₂ flow rate of 30 sccm. The precursor partial pressure is estimated to be 2.9 Torr. This is much closer to the saturation vapor pressure, based on the results of Wolf et al. (1972).

6.4 Horizontal Warm-Wall CVD Reactor

The Cu film growth rate experiments are performed inside a cold-wall type, horizontal flow reactor system shown in Figure 6.2. The reactor wall is heated above the evaporator temperature to avoid condensation of the precursor. The main reactor wall is made of pyrex glass tube with 2.5 cm inside diameter and 0.1 cm wall thickness. The inlet of the reactor is reduced to 0.7 cm outside diameter in order to connect to the quarter-inch tubing from the IR cell. An ULTRA-TORR union by Cajon Company is used to connect the metal and glass tubing with quick and finger-tight assembly.

The main reactor wall is surrounded by a heating jacket made of another concentric pyrex glass tube with outside diameter of 5 cm. Heated bath oil at about 80°C from a constant temperature oil bath flows between the two glass tubes from the outlet to the inlet of the reactor. This prevents the precursor from condensing or reacting on the warm reactor wall. The bath oil is obtained from Fisher Scientific (White Mineral Oil), and has a flash point of 180 °C. The recirculator is also from Fisher Scientific (Isotemp Model 8000).

The glass reactor is 25 cm in length. A 4 cm long copper susceptor is used to heat the substrate to deposition temperature. The susceptor is a 2.5 cm diameter hemi-
Figure 6.2  Warm-Wall Horizontal CVD Reactor with the Vacuum System
cylindrical block. The substrate is placed horizontally on the flat surface of this block. A 15 cm long aluminum block is placed between the inlet and the copper susceptor to help to create a uniform flow field. The susceptor is heated by two 200 Watt cartridge heaters (Watlow FIREOD). Two chromel-alumel thermocouples placed in the susceptor are used to measure the substrate temperature. The temperature can be controlled within 1°C by adjusting a variable autotransformer and an digital temperature controller (Omega).

A vacuum system designed by Dr. Jue Wang of our group allows the reactor to be operated at pressures from 760 Torr down to 40 Torr. The reaction product and the carrier gas from the pump are exhausted to the laboratory hood. A throughput of 38 sccm (standard cubic centimeter per minute) is held constant at all pressures by using the MFC (MKS Instruments Model 1159B). The throughput is calibrated by measuring the vacuum pump exhaust rate with a burette soap-film flowmeter placed inside the hood. At this throughput and for a substrate temperature of 350 °C, the average axial velocity increases from 0.53 to 10 cm/s as the reactor pressure is decreased from 760 to 40 Torr.

6.5 Substrate Preparation

Chemical vapor deposition (CVD) may involve both gas phase and surface reactions. In the case of surface reaction, controlled surface conditions are important for the film growth. Therefore, the source of the substrate and the cleaning procedure must be specified.
Two types of substrate surfaces are used for deposition of Cu Films. The first type of substrate surface is uncoated (i.e., only with native oxide) silicon wafers for the deposition temperature of 350°C. The second type of substrate surface is coated with 450Å thick titanium nitride (TiN) silicon wafers. According to Little (1992), a more reactive material like TiN is required for deposition at the lower temperature (250°C). All the six inch Si wafers were obtained from Silica-Source Technology Corp.

The substrates used in the CVD experiments are 2.5 cm wide and 4.0 cm long in order to fit the size of the susceptor. The Si wafers are broken along the principal crystal axis directions to form these rectangular pieces.

The substrate is boiled in trichloroethylene for 10 minutes, then washed with deionized water. It is then boiled in acetone for 10 minutes and rinsed with deionized water. Before the substrate is placed inside the CVD reactor, it is dried by flowing He over the surface. After the substrate has reached the desired deposition temperature from the susceptor, the copper precursor is passed over the surface of the substrate for the film growth experiments.

6.6 Thickness Measurement

In general, two methods are commonly used to measure the thin film thickness: optical interferometry and stylus profilometry. The stylus technique is chosen here because it is simple and rapid. The measurement is performed using a surface profiler by Tencor Instruments (Model Alpha-Step 200) in Professor Pratul Ajmera’s Solid State Laboratory in the Electrical Engineering Department at L.S.U.
To make a measurement, a baseline on the substrate is required. Therefore, the deposited copper film is cut using a scalpel knife to locate the baseline. Because both Si and TiN surfaces are harder than the scalpel knife, no damage should be caused on the substrate. Seven thickness measurements are made at the centerline in the axial direction with an equal interval of 0.5 cm. For each axial direction, six additional thickness measurements are performed in the radial direction for averaging.

After locating the measurement position on the X-Y stage, a diamond stylus is placed on the Cu thin film side by the baseline. The stylus is moved across the Cu film surface and the baseline, and the vertical movement of the stylus is detected by a transducer. A image of the thickness profile across the measurement position is displayed on the video screen. The value of the thickness of each position is also displayed on the screen. The minimum thickness measured by the surface profiler is about 1000Å.

6.7 Experimental Results

Dr. Jue Wang and Mr. Reginald Little in our group performed a series of CVD experiments at pressures between 760 and 40 Torr and substrate temperatures of 350 and 250 °C. From the pressure variation experiments at 350°C, they found that there are two regimes. The first regime shown in Figure 6.3 is considered to be atmospheric pressure, i.e., from 760 to 300 Torr. The other regime, which we label as low pressure, is shown in Figure 6.4. The results obtained at 250 °C are shown in Figure 6.5. These latter films were deposited at 380 and 120 Torr on a TiN coated substrate.
Figure 6.3  Cu Film Growth Rate Profiles on Uncoated Si substrate with Only Native Oxide at Substrate Temperature of 350°C
Figure 6.4 Cu Film Growth Rate Profile on Uncoated Si substrate with Only Native Oxide at Substrate Temperature of 350°C and Low H₂ Pressure (40 Torr)
Figure 6.5 Cu Film Growth Rate Profiles on TiN coated Si Substrate at Substrate Temperature of 250 °C
In the atmospheric pressure regime, the growth rate is highest at the leading edge of the substrate. The rate decays to nearly zero at the end of the substrate. The film growth rate profile increases with decreasing H\textsubscript{2} pressure. This is because the molar flow rate of the precursor is increased at low pressure (i.e., due to the higher velocity through the reactor). Growth rates as high as 600 Å/min can be reached at H\textsubscript{2} pressure of 300 Torr.

In the low pressure regime, the Cu film growth rate profile is relatively uniform. It only changes from 125 to 175 Å/min over the 3 cm length of the substrate. On the other hand, the growth rate is four times smaller than the rate at H\textsubscript{2} pressure of 300 Torr. Therefore, there must be a maximum in the growth rate between 40 and 300 Torr of H\textsubscript{2} pressure.

At the lower substrate temperature of 250°C, the Cu film growth rate profiles are quite uniform. They only vary within 10 Å/min over the 3 cm length of the substrate. However, the growth rate is ten times smaller than the rate at substrate temperature of 350°C.

Dr. Jue Wang in our group performed a preliminary kinetic analysis of the atmospheric regime results. However, he did not include the effect of ligand inhibition proposed by Lai et al. (1991). Our goal in this study is to propose a better reaction mechanism for the experimental results. We will support our findings with the 2-D temperature and concentration profiles.
CHAPTER 7

Cu FILMS FROM WARM-WALL EXPERIMENTS

In Chapter 6, I reviewed the copper thin film growth rates obtained by Dr. Jue Wang and Mr. Reginald Little in our group, using H₂ reduction of copper(II) hexa-fluoroacetylacetonate hydrate [Cu(hfac)_2]. In those experiments, the Cu(hfac)_2 vapor was transferred from the constant temperature evaporator to the chemical vapor deposition (CVD) reactor using H₂ as the carrier gas. Changing the H₂ pressures gave different molar flow rates of Cu(hfac)_2, and different thicknesses of Cu films were deposited on a heated substrate inside the CVD reactor. The results were reported in the form of a growth rate profile along the axial direction of the reactor.

In this chapter, I first introduce a simple two-dimensional (2-D) reactor model for our horizontal flow warm-wall CVD reactor to estimate the kinetic parameters for the proposed mechanism. This 2-D reactor model should provide the necessary information about the flow, temperature, and concentration fields. Initially, I use a power law rate expression to incorporate the surface reaction kinetics into the boundary conditions. Using the control volume finite difference method, I obtain the surface concentration profiles for both Cu(hfac)_2 and H(hfac) by matching the measured growth rate profiles.

To improve the power law rate expression, I review the mechanisms for Cu(hfac)_2 reduction proposed by Lai et al. (1991) and Kim et al. (1993). However, both of the previous mechanisms are not able to describe our recent experiments results. Therefore, a non-competitive adsorption model is proposed for the results. The kinetic parameters
will be estimated based on the results at $H_2$ pressures between 760 and 40 Torr for two substrate temperatures (350 and 250°C). I will compare the measured and calculated growth rates for different pressures at both high and low substrate temperatures. Finally, I discuss the optimized parameters by comparing with the available literature values for the adsorption behavior of the reactants and products.

7.1 Reactor Model

Most of the Cu films growth rates measured by Dr. Jue Wang and Mr. Reginald Little were obtained at high reactant conversions (cf., Figure 7.5). Therefore there are significant concentration gradients present within the reactor. In order to extract kinetic parameters from measured growth rates, it is necessary to develop a transport model for the reactor. This model will relate the concentrations of reactants and products at the substrate surface to the inlet conditions for the reactor, based on the growth rate at the surface.

First, I formulate the balance equations by expressing the general balance equations described in Section 3.3.1 in rectangular coordinates. Then, I will specify the boundary conditions for the flow, temperature, and concentration fields. The reaction rates are defined in the boundary conditions for the reactive surfaces. The transport properties of the $H_2$ carrier gas are determined from the existing literature. In this section, where I only seek to identify the transport effects and concentration gradients within the reactor, it is sufficient to use a simple power law rate expression to approximate the observed growth rate. (More realistic rate expressions will be considered in later sections.)
The balance equations are solved using the control volume finite difference method developed by Patankar (1980). I will present the concentration profiles obtained using the power law rate expression with optimized coefficients. The results are shown for the experiments performed at 350°C, where a first-order $H_2$ pressure dependence is observed, and at 250°C, where I find an one-half order $H_2$ pressure dependence. In the later sections, these calculated gas phase concentrations will be used to evaluate different rate expressions based on more realistic mechanism proposals.

### 7.1.1 Balance Equations

The reactor geometry is modeled as two parallel plates (i.e., side wall effects are neglected). Therefore, I am able to apply the balance equations in rectangular coordinates to describe the behavior of the reactor vertically above the substrate (x-component) and axially along the reactor length (z-component). The active geometry of the 2-D HFR model is chosen to be the region between the channel above the aluminum block and the end of the copper susceptor (cf. Figure 7.1). Both the inlet and outlet of the reactor have a width of 2.5 cm. The length between the inlet and outlet is assumed to be 10 cm. The height of the reactor is 1.0 cm. The distance from the inlet to the leading edge of susceptor is 4.0 cm.

The momentum, energy, and species balance equations in rectangular coordinates are developed in the same manner described by Patankar (1980).

The continuity equation is:

$$\frac{\partial}{\partial x} (\rho v_x) + \frac{\partial}{\partial z} (\rho v_z) = 0$$  \hspace{1cm} (7.1)
Figure 7.1 Reactor Geometry for 2-D HFR Model
The x-momentum balance equation is:

\[
\frac{\partial}{\partial x}(\rho v_x v_x) + \frac{\partial}{\partial z}(\rho v_x v_z) = \frac{\partial}{\partial x}(\mu \frac{\partial v_x}{\partial x}) + \frac{\partial}{\partial z}(\mu \frac{\partial v_x}{\partial z}) - \frac{\partial p}{\partial x}
\]  \hspace{1cm} (7.2)

The z-momentum balance equation is:

\[
\frac{\partial}{\partial x}(\rho v_x v_x) + \frac{\partial}{\partial z}(\rho v_x v_z) = \frac{\partial}{\partial x}(\mu \frac{\partial v_z}{\partial x}) + \frac{\partial}{\partial z}(\mu \frac{\partial v_z}{\partial z}) - \frac{\partial p}{\partial z}
\]  \hspace{1cm} (7.3)

The energy balance equation is:

\[
\frac{\partial}{\partial x}(\rho c_p v_x T) + \frac{\partial}{\partial z}(\rho c_p v_z T) = \frac{\partial}{\partial x}\left(k \frac{\partial T}{\partial x}\right) + \frac{\partial}{\partial z}\left(k \frac{\partial T}{\partial z}\right)
\]  \hspace{1cm} (7.4)

The species balance equation for Cu(hfac)_2 (species A) is:

\[
\frac{\partial}{\partial x}(v_x C_A) + \frac{\partial}{\partial z}(v_z C_A) = \frac{\partial}{\partial x}\left(D_{AH} \frac{\partial C_A}{\partial x}\right) + \frac{\partial}{\partial z}\left(D_{AH} \frac{\partial C_A}{\partial z}\right)
\]  \hspace{1cm} (7.5)

The species balance equation for H(hfac) (species B) is:

\[
\frac{\partial}{\partial x}(v_x C_B) + \frac{\partial}{\partial z}(v_z C_B) = \frac{\partial}{\partial x}\left(D_{BH} \frac{\partial C_B}{\partial x}\right) + \frac{\partial}{\partial z}\left(D_{BH} \frac{\partial C_B}{\partial z}\right)
\]  \hspace{1cm} (7.6)
The Cu film growth rate is determined from:

$$ G = -D_{AH} \frac{\partial C_A}{\partial x} \quad (7.7) $$

where $G$ is in terms of flux units (1 mole/cm²/s = 4.27 x 10¹⁰ Å/min). Here $x$ is the outward normal to the reactive or susceptor surfaces.

### 7.1.2 Boundary Conditions

Boundary conditions are required to solve the above balance equations. The velocity boundary conditions are: no tangential velocity at the walls, block and susceptor; no normal velocity at the walls, block and susceptor; uniaxial flow at the inlet; and no axial gradient at the outlet. For the temperature boundary conditions, we have fixed temperature at the walls and the susceptor. A short temperature profile is assumed along the block in front of the susceptor. There is no axial gradient at the outlet. The above conditions can be expressed as:

At the inlet,

$$ V_x = 0 \ ; \ V_z = u_o \ ; \ T = T_o \quad (7.8) $$

At the outlet,

$$ V_x = 0 \ ; \ \frac{\partial V_z}{\partial z} = 0 \ ; \ \frac{\partial T}{\partial z} = 0 \quad (7.9) $$
At the walls,

\[ V_x = 0 ; \quad V_z = 0 ; \quad T = T_w \quad (7.10) \]

At the susceptor,

\[ V_x = 0 ; \quad V_z = 0 ; \quad T = T_s \quad (7.11) \]

At the block,

\[ V_x = 0 ; \quad V_z = 0 ; \quad T = T_o + (T_s - T_o)\exp[-m(L_o - z)] \quad (7.12) \]

where \( m \) is a decay constant based on the properties of the Al block.

The concentration boundary conditions are based on the rate expression described in Section 7.1. The assumption of no net normal flux is used on all non-reactive boundaries (i.e., walls and outlet). At the reactive surface, Cu(hfac)\(_2\) (= species A) reacts, to form H(hfac) (= species B). The concentrations across the inlet are assumed to follow Danckwerts' boundary conditions. The above conditions can be expressed as:

At non-reactive surfaces,

\[ \frac{\partial C_A}{\partial x} = \frac{\partial C_B}{\partial x} = 0 \quad (7.13) \]
At the reactive surfaces,

\[- D_{AH} \frac{\partial C_A}{\partial x} = G \]  \hspace{1cm} (7.14)

\[- D_{AH} \frac{\partial C_B}{\partial x} = -2G \]  \hspace{1cm} (7.15)

At the inlet,

\[ u_o (C_{Ao} - C_A) = -D_{AH} \frac{dC_A}{dz} \]  \hspace{1cm} (7.16)

\[-u_o C_B = -D_{BH} \frac{dC_B}{dz} \]  \hspace{1cm} (7.17)

### 7.1.3 Transport Properties

Since the concentration of the H\(_2\) carrier gas is much larger than the precursor, the physical properties of the gas mixture are based on the H\(_2\) carrier gas. First, the temperature dependence of density is assumed to follow the ideal gas law:

\[ \rho = \frac{PM}{RT} \frac{g}{cm^3} \]  \hspace{1cm} (7.18)

where M is molecular weight of H\(_2\) and R is universal gas constant. The temperature dependence of the absolute viscosity, \( \mu \), and thermal conductivity, \( k \), are based on the
experimental data from Kreith and Bohn (1986). The viscosity and thermal conductivity are fitted with experimental values by a power law:

\[ \mu = 8.96 \times 10^{-5} \left( \frac{T}{T_o} \right)^{0.67} \frac{g}{cm \ sec} \]  (7.19)

\[ k = 4.35 \times 10^{-4} \left( \frac{T}{T_o} \right)^{0.78} \frac{cal}{cm \ sec \ K} \]  (7.20)

where \( T_o \) is the reference temperature of 300K. The heat capacity of \( H_2 \), \( c_p \), varies only slightly between the inlet and substrate temperatures. Thus, an average value of \( c_p \) is 3.46 cal/g/K. Finally, the diffusion coefficients for the gas mixture \( \text{Cu(hfac)}_2\text{H}_2 \) (\( D_{\text{AH}} \)) and \( \text{H(hfac)}\text{H}_2 \) (\( D_{\text{BH}} \)) are based on the Chapman-Enskog method (Bird et al., 1960). The required parameters for the Chapman-Enskog method are listed in Table 7.1 and 7.2. The temperature and pressure dependence are expressed by fitting to a power law:

\[ D_{\text{AH}} = 0.182 \left( \frac{T}{T_o} \right)^{1.77} \left( \frac{P_o}{P} \right) \frac{cm^2}{sec} \]  (7.21)

\[ D_{\text{BH}} = 0.338 \left( \frac{T}{T_o} \right)^{1.73} \left( \frac{P_o}{P} \right) \frac{cm^2}{sec} \]  (7.22)

where \( T_o \) is the reference temperature of 300K, and \( P_o \) is the reference pressure of 760 Torr.
Table 7.1  Physical Properties of Cu(hfac)$_2$, H(hfac) and H$_2$

<table>
<thead>
<tr>
<th>Gas</th>
<th>Cu(hfac)$_2$</th>
<th>H(hfac)</th>
<th>H$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M (g/gmole)</td>
<td>495.66</td>
<td>208.06</td>
<td>2.016</td>
</tr>
<tr>
<td>Melting/Boiling</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Point (°C)</td>
<td>134</td>
<td>71</td>
<td>---</td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>1.349</td>
<td>1.470</td>
<td>---</td>
</tr>
<tr>
<td>$\nu_m/\nu_b$</td>
<td>367.4</td>
<td>141.5</td>
<td>---</td>
</tr>
<tr>
<td>$\sigma$ (Å)</td>
<td>8.752</td>
<td>6.077</td>
<td>2.915</td>
</tr>
<tr>
<td>$\varepsilon/\kappa$ (K)</td>
<td>781.4</td>
<td>396</td>
<td>38</td>
</tr>
</tbody>
</table>

Table 7.2  Physical Properties of Gas Mixtures Cu(hfac)$_2$-H$_2$ and H(hfac)-H$_2$

<table>
<thead>
<tr>
<th>Gas Mixture</th>
<th>Cu(hfac)$_2$-H$_2$</th>
<th>H(hfac)-H$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1/M_i + 1/M_H2)</td>
<td>0.498</td>
<td>0.5008</td>
</tr>
<tr>
<td>$\sigma_H$ (Å)</td>
<td>5.834</td>
<td>4.496</td>
</tr>
<tr>
<td>$\varepsilon_{hi}/\kappa$ (K)</td>
<td>172.3</td>
<td>122.7</td>
</tr>
<tr>
<td>$\Omega_D$ (300-700K)</td>
<td>1.1-0.88</td>
<td>1.0-0.82</td>
</tr>
</tbody>
</table>
7.1.4 Method of Solution

The assumed parameters for the 2-D HFR model are listed in Table 7.3. I use a control volume-based finite volume method (Pantankar 1980) to solve the partial differential balance equations for the velocity vectors, and the temperature and concentration contours. Based on this method, the partial differential balance equations are solved by program SOUR2 described in Chapter 3. The equations are discretized into a uniform, rectangular grid with grid spacing of 0.1 cm. The grid consists of 100 cells in the axial direction and 10 cells in the radial direction. To reach a fully converged solution takes about 3 minutes of CPU time and 2000 iterations.

7.2 Transport Effects

From the growth rate results at the substrate temperature of 350°C, the reactant is almost completely consumed. Therefore, a large concentration gradient across is expected. To perform a kinetic studies on CVD copper film, it is necessary to consider the transport effects such as velocity, temperature, and concentration.

7.2.1 Velocity Profile

The velocity vectors for the horizontal flow over a heated substrate are shown in Figure 7.2. The velocity at the inlet is assumed to be uniform. There is an entrance effect near the inlet. The parabolic velocity is observed a few centimeters from the inlet. The velocity is zero at the wall and susceptor surfaces. The velocity vectors move a little upward when they approach the heated substrate.
**Table 7.3 Parameters for 2-D HFR Model**

<table>
<thead>
<tr>
<th>Type</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor Geometry</td>
<td>Inlet and Outlet Width</td>
<td>$W = 2.5$ cm</td>
</tr>
<tr>
<td></td>
<td>Inlet and Outlet height</td>
<td>$H = 1.0$ cm</td>
</tr>
<tr>
<td></td>
<td>Inlet to the Leading Edge of the Susceptor</td>
<td>$L_o = 4.0$ cm</td>
</tr>
<tr>
<td></td>
<td>Susceptor length</td>
<td>$L_s = 4.0$ cm</td>
</tr>
<tr>
<td></td>
<td>Inlet to Outlet</td>
<td>$L = 10$ cm</td>
</tr>
<tr>
<td>Operating Conditions</td>
<td>Inlet Throughput Controlled by MFC</td>
<td>$Q = 38$ sccm</td>
</tr>
<tr>
<td></td>
<td>Inlet Temperature</td>
<td>$T_o = 80$ °C</td>
</tr>
<tr>
<td></td>
<td>Wall Temperature</td>
<td>$T_w = 80$ °C</td>
</tr>
<tr>
<td></td>
<td>Substrate Temperature</td>
<td>$T_s = 350$ and 250°C</td>
</tr>
<tr>
<td></td>
<td>Al Block Thermal Decay Constant</td>
<td>$m = 1.17$ cm$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>Inlet Cu(hfac)$_2$ Pressure</td>
<td>$P_{Cu} = 0.66$ Torr</td>
</tr>
<tr>
<td></td>
<td>Reactor or H$_2$ Pressure</td>
<td>$P = 760 - 40$ Torr</td>
</tr>
</tbody>
</table>
Figure 7.2  Velocity Vector of Horizontal Flow Over a Heated Substrate for 2-D HFR Model
7.2.2 Temperature Contours

The temperature contours within the reactor for a substrate temperature of 350°C are shown in Figure 7.3. The temperature at the inlet is 80 °C, and the substrate temperature is 350°C. The surface temperature along the Al block reflects the balance between heat conduction from the susceptor and heat loss to the reactor walls. Based on visual observation, the Al block becomes hot enough to support measurable Cu deposition at a distance of about 1 cm from the leading edge of the susceptor.

7.2.3 Concentration Profiles

Because the measured growth rates are available for each set of reactor conditions that has been studied, it is possible to calculate the concentration profiles for Cu(hfac)$_2$ and H(hfac) without explicit knowledge of the reaction mechanism and rate expression. As expressed in the boundary conditions at the substrate surface (cf. Equations 7.14 and 7.15), it is possible to solve the reactor transport model by setting the diffusive fluxes (i.e., which are proportional to the concentration gradients) equal to the observed rate, multiplied by the stoichiometric coefficient for the reactant or product, respectively. In this section, I use a simple power law expression with a single adjustable parameter to represent the empirical growth rate. The present goal is simply to calculate the concentration profile, in order to show the magnitude of mass transport effects in the reactor. In Section 7.3, I will consider more physically realistic rate expressions.
Figure 7.3   Temperature Profile for 2-D HFR Model
High Substrate Temperature. For the experiments performed at a substrate temperature of 350°C, I am able to reproduce the observed growth rate using the expression:

\[
G = r_1 = k_{350} P_{\text{Cu(hfac)}_2} P_{H_2}
\]  

(7.23)

A single parameter search provided the optimum value of the coefficient:

\[
k_{350} = 1.96 \times 10^6 \text{ Å} \frac{1}{\text{min atm}^2}
\]  

(7.24)

High Pressure. At the substrate temperature of 350°C, I observe two pressure regimes. The first regime is near atmospheric pressure from 760 to 300 Torr. The results obtained at this regime exhibit clear evidence of transport limited effects. In Figure 7.4, the measured growth rates are compared with calculated growth rates. I observe that as the H\textsubscript{2} pressure is decreased, the growth rate of Cu films increases from 300 to 600 Å/min near the leading edge of the susceptor. The increase is mainly due to the increase of the molar flow rate of the Cu(hfac)\textsubscript{2} with decreasing H\textsubscript{2} pressure; i.e., since the throughput is held constant, the velocity increases as the pressure is decreased. At the same time, the decreasing pressure also causes an increase in the reactant diffusivity.

In Figure 7.5, I show the dimensionless concentration of reactant, Cu(hfac)\textsubscript{2}, above the substrate surface starting from 4 cm in front of the substrate to 2 cm beyond the substrate. The largest concentration gradient appears near the leading edge of the
Figure 7.4 Effect of H₂ Pressures on Cu Film Growth Rate Profiles at High Substrate Temperature
Figure 7.5  Dimensionless Cu(hfac)$_2$ Concentration Contours ($C_n/C_{Ao}$) for 2-D HFR Model at Substrate Temperature of 350°C and H$_2$ Pressure of 760 Torr
substrate. High conversion of reactant is calculated at the end of the reactor. Due to the high conversion, the Cu film growth rate is not strongly sensitive to changes in growth rate constant. Therefore, this regime is considered to be near the transport (diffusion) limited regime.

In Figure 7.6, I show the calculated dimensionless Cu(hfac)$_2$ concentration profiles ($C_A/C_{Ao}$) at the reactive surface, where $x = 0.0$ cm in Figure 7.5. The Cu(hfac)$_2$ concentration decreases from the inlet to the susceptor due to the surface reaction. At the inlet, the $C_A/C_{Ao}$ is less than unity due to the Danckwerts' boundary condition. At the substrate temperature of 350°C, the $C_A/C_{Ao}$ approaches zero at the end of the reactor.

Figure 7.7 shows the dimensionless concentration of product, H(hfac), above the substrate surface starting from 4 cm in front of the substrate to 2 cm beyond the substrate. The largest concentration gradient also appears near the leading edge of the substrate. High conversion of product is calculated at the end of the reactor. This is consistent with the high conversion of reactant.

In Figures 7.8, I show the calculated dimensionless H(hfac) concentration contours ($C_p/C_{Ao}$) at the reactive surface, where $x = 0.0$ cm in Figure 7.7. The $C_p/C_{Ao}$ at the inlet is greater than zero, again due to Danckwerts' boundary condition. The H(hfac) concentration increases from the inlet towards the substrate due to generation by surface reaction, and it reaches its maximum value at the outlet of the reactor.

**Low Pressure.** Figure 7.9 shows the low pressure regime at 40 Torr. At this pressure the Cu film growth rate profile is quite uniform, and varies only from 150 to 200 Å/min. There is a modest increase in thickness along the length of the sample.
Figure 7.6  Dimensionless Cu(hfac)$_2$ Concentration Profiles at the Substrate Surface ($C_A/C_{A_o}$) for 2-D HFR Model at Substrate Temperature of 350$^\circ$C
Figure 7.7  Dimensionless H(hfac) Concentration Contours ($C_H/C_{Ao}$) for 2-D HFR Model at Substrate Temperature of 350°C and H$_2$ Pressure of 760 Torr
Figure 7.8  Dimensionless H(hfac) Concentration Profiles ($C_B/C_{Ao}$) at the Substrate Surface for 2-D HFR Model at Substrate Temperature of 350°C
Figure 7.9  Cu Film Growth Rate Profile at Low H₂ Pressure Regime
which is attributed most likely to a non-uniform temperature profile within the susceptor block.

In Figure 7.10, I show the dimensionless concentration profiles of $\text{Cu(hfac)}_2$ (= species A) and $\text{H(hfac)}$ (= species B) for the 40 Torr experiments. The $\text{Cu(hfac)}_2$ exit concentration remains quite high, and the fractional conversion is about 10%. Thus, the reaction is now kinetically limited, and the Cu film growth rate is sensitive to changes in the assumed rate constant. The $\text{H(hfac)}$ concentration along the reactor corresponds to the stoichiometry described in Reaction (7.23).

**Low Substrate Temperature.** For the experiments performed at a substrate temperature of 250°C, I am able to reproduce the observed growth rate using the expression:

$$ G = r_1 = k_{250} P_{\text{Cu(hfac)}_2} P_{\text{H}_2}^{0.5} $$

(7.25)

A single parameter search provided the optimum value of the coefficient:

$$ k_{250} = 6.41 \times 10^4 \text{ Å min atm}^{-1.5} $$

(7.26)

At the substrate temperature of 250°C, Mr. Reginald Little in our group deposited Cu films at two H$_2$ pressures (380 and 120 Torr). Figure 7.11 shows the comparison between the calculated and measured growth rate. The difference in the measured growth rate between two pressures is only about 20 Å/min near the leading edge (i.e., about 40% of the growth rate at 380 Torr). The measured growth rate for two pressures at the last 3 cm from the leading edge is quite uniform, their difference are only about 5 Å/min.
Figure 7.10  Dimensionless Concentration Profiles for Low H₂ Pressure using 2-D HFR Model
Figure 7.11  Cu Film Growth Rate Profiles at Low Substrate Temperature
In Figure 7.12, I show the dimensionless concentration profiles for both \( \text{Cu(hfac)}_2 \) (species A) and \( \text{H(hfac)} \) (species B). The \( \text{Cu(hfac)}_2 \) exit concentration is higher for the lower substrate temperature. The fractional conversions of \( \text{Cu(hfac)}_2 \) are about 5% and 30% for 120 and 380 Torr, respectively. At the same time, the fractional conversions of \( \text{H(hfac)} \) are two times higher than the ones of \( \text{Cu(hfac)}_2 \). This is consistent with the stoichiometry of the reaction.

### 7.3 Reaction Mechanism

The majority of previous studies on chemical vapor deposited Cu films have concentrated on identifying suitable reaction conditions, and on the characterization of the deposited films. Two groups of researchers have proposed reaction mechanisms to explain their experimental kinetic observations. Both groups used the \( \text{Cu(hfac)}_2 \) precursor with \( \text{H}_2 \) carrier gas.

Lai et al. (1991) was the first group to propose a Langmuir-Hinshelwood rate expression. They deposited Cu films at \( \text{H}_2 \) pressure of 760 Torr in a horizontal hot-wall reactor. Their conclusion was based on observed saturation effects in the growth kinetics at high reactant concentration. Recently, Kim et al. (1993) deposited Cu films at much lower \( \text{H}_2 \) pressure (10 Torr) in a vertical cold-wall reactor. They proposed a power law rate expression, which they justified as the lower coverage limit of a Langmuir-Hinshelwood mechanism. They also proposed that separate, non-competitive adsorption sites existed for \( \text{Cu(hfac)}_2 \) and \( \text{H}_2 \).
Figure 7.12  Dimensionless Concentration Profiles at the Substrate Surface for 2-D HFR Model at Substrate Temperature of 250°C
In this section, I will attempt to apply both of these previously proposed mechanisms to the present results. After showing the shortcomings of both previous mechanisms, I will propose a possible reaction mechanism that is able to describe our results.

### 7.3.1 Previous Rate Expressions

I first examined the rate expression proposed by Lai et al. (1991), which was reviewed in Chapter 3. Under their specific operating conditions, the rate expression was expressed as:

$$R = \frac{k_{a1}k_{d2}P_{H_2}C_{Cu(\text{fac})_2}}{k_{d2}P_{H_2} + [k_{a2}C_{H(\text{fac})} + 2k_{a1}C_{Cu(\text{fac})_2}]}$$  \hspace{1cm} (7.27)

In Chapter 3, the estimated parameters were:

$$k_{a1} = k_{a2} = 0.1 \frac{cm}{s}\hspace{1cm} (7.28)$$

$$k_{d2} = 2.2 \times 10^{23} \exp\left(-\frac{80kJ/mole}{RT}\right) \frac{molecules}{cm^2 s atm}\hspace{1cm} (7.29)$$

The comparison of the calculated and measured results are shown in Table 7.4. However, I am unable to obtain agreement with our present observed results. The calculated growth rates are much less than the measured growth rates for H\textsubscript{2} pressures from 760 to 300 Torr at substrate temperature of 350°C. On the other hand, the calculated growth rates are
Table 7.4  Comparison of Measured Growth Rates and Calculated Growth Rates from the Rate Expression Proposed in Lai et al. (1991)

<table>
<thead>
<tr>
<th>Substrate Temperature (°C)</th>
<th>H₂ Pressure (Torr)</th>
<th>Growth Rate at 2 cm from the Leading Edge (Å/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Measured</td>
<td>Original Parameters</td>
</tr>
<tr>
<td>350</td>
<td>760</td>
<td>45.0</td>
</tr>
<tr>
<td></td>
<td>540</td>
<td>109.6</td>
</tr>
<tr>
<td></td>
<td>380</td>
<td>192.8</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>285.3</td>
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<td></td>
<td>40</td>
<td>145.7</td>
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<tr>
<td>250</td>
<td>380</td>
<td>38.0</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>33.0</td>
</tr>
</tbody>
</table>
larger than the measured values for a H₂ pressure of 40 Torr. In addition, the calculated growth rates are higher than the measured rates at substrate temperature of 250°C for all H₂ pressures.

I next attempt to improve the fit by keeping the same form of the rate expression, but optimizing the parameters. First, I assume the adsorption rate is calculated from the gas kinetic theory with sticking coefficient of unity. The adsorption rate of H(hfac), $k_{a2}$ is higher than the adsorption rate of Cu(hfac)$_2$, $k_{a1}$. This is because the molecular weight of H(hfac) is smaller than the molecular weight of Cu(hfac)$_2$. The activation energy for the desorption rate of H(hfac), $k_{d2}$ is kept the same. However, I decrease the pre-exponential factor to best fit the measured rates. The optimized parameters are:

$$k_{a1} = 4.1 \times 10^3 \frac{cm}{s} ; \quad k_{a2} = 6.4 \times 10^3 \frac{cm}{s}$$

(7.30)

$$k_{d2} = 8.8 \times 10^{16} \exp\left(-\frac{80 \text{kJ/mole}}{RT}\right) \frac{\text{molecules}}{cm^2 \text{ s atm}}$$

(7.31)

However, the calculated growth rates for substrate temperatures of 350°C are still under-predicted when compared with the measured rates at H₂ pressures below 760 Torr (Table 7.4). Therefore, the reaction mechanism proposed by Lai et al. (1991) does not satisfy our latest measured growth rates.

I then examined the rate expression proposed by Kim et al. (1993), which was also reviewed in Chapter 5. Their rate expression was simplified to:

$$R = 5.7 \times 10^8 \exp\left(-\frac{75 \text{kJ/mole}}{RT}\right) P_{H_2}^{0.5} P_{Cu(hfac)_2}^{0.5}$$

(7.32)
Using their parameters, the calculated growth rates are higher than the measured growth rates for at substrate temperature of 350 and 250°C. The comparison of the calculated and measured results are shown in Table 7.5.

To improve the agreement between the calculated and measured growth rate, I need to decrease the pre-exponential factor and the activation energy. The optimized parameters and the rate expression are:

$$R = 1.3 \times 10^6 \exp\left(\frac{-57 \text{kJ/mole}}{RT}\right)P_{H_2}^{0.5}P_{Cu(hfac)_2}^{0.5} \quad (7.33)$$

In addition, half-order kinetics for $Cu(hfac)_2$ are unable to provide a consistent relationship between the observed growth rates and the observed fractional conversion for several of our 350°C results. Therefore, the reaction mechanism proposed by Kim et al. (1993) cannot satisfy our observed growth rates.

### 7.3.2 New Mechanism

To develop an accurate kinetic model for the CVD process, it is necessary to propose a reaction mechanism in terms of elementary steps. The six proposed elementary steps for the reaction taking place in the presence of $H_2$ carrier gas are:

$$Cu(hfac)_2_{(g)} + 2\theta_{V,1} \rightarrow Cu_{(s)} + 2\theta_{(hfac)} \quad (7.34)$$

$$Cu(hfac)_2_{(g)} + 2\theta_{V,1} \rightarrow Cu_{(s)} + 2\theta_{(hfac)} \quad (7.35)$$
Table 7.5  Comparison of Measured Growth Rates and Calculated Growth Rates from the Rate Expression Proposed in Kim et al. (1993)

<table>
<thead>
<tr>
<th>Substrate Temperature (°C)</th>
<th>H₂ Pressure (Torr)</th>
<th>Growth Rate at 2 cm from the Leading Edge (Å/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Measured</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>760</td>
</tr>
<tr>
<td></td>
<td>540</td>
<td>109.6</td>
</tr>
<tr>
<td></td>
<td>380</td>
<td>192.8</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>285.3</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>145.7</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>380</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>33.0</td>
</tr>
</tbody>
</table>
The coverage variables, \( \theta_{v,j} \), have been subdivided into two groups, reflecting the competitive adsorption behavior described below. The surface (hfac) species produced by the adsorption of Cu(hfac)_2 or H(hfac) is much more strongly bound than absorbed H atoms. Under all of the conditions examined below, absorbed (hfac) will almost completely displace adsorbed H atoms. Thus, H\(_2\) adsorption will have little competitive effect on those sites were (hfac) adsorption can occur.

However, adsorbed (hfac) groups are likely to require several adjacent Cu atoms as their adsorption sites. The lattice statistics of multi-site adsorbates imply that perfect coverage is not likely to be obtained: i.e., small regions of vacant Cu atoms are likely to be exposed at "gaps" between neighboring (hfac) groups that are not perfectly aligned. Since (hfac) groups are sterically inhibited from entering these gap sites, H\(_2\) adsorption can occur non-competitively at these sites.
The result of these assumptions is that the surface behaves as if it is comprised of two types of sites which adsorb each reactant non-competitively (i.e., as originally suggested by Kim et al. (1993)). The type I sites represent the maximum packing efficiency of (hfac) groups, while the type II sites represent the remaining surface sites that are accessible to H₂.

The adsorption rate of the Cu(hfac)₂ (A) to form the adsorbed (hfac) in Reaction (7.34) is assumed to have the form:

\[ r_{1a} = k_{1a} P_A \theta_{hfac}^2 \]  \hspace{1cm} (7.40)

Reaction (7.35) represents the desorption of the adsorbed (hfac) from the substrate as Cu(hfac)₂. Its rate can be expressed as:

\[ r_{1d} = k_{1d} \theta_{hfac}^2 \]  \hspace{1cm} (7.41)

The adsorption rate of the H₂ to form the adsorbed II in Reaction (7.36) is assumed to have the form:

\[ r_{2a} = k_{2a} P_{H₂} \theta_{II}^2 \]  \hspace{1cm} (7.42)

Reaction (7.37) represents the desorption of the adsorbed II from the substrate. Its rate can be expressed as:

\[ r_{2d} = k_{2d} \theta_{II}^2 \]  \hspace{1cm} (7.43)
The adsorption rate of the H(hfac) (B) to form the adsorbed (hfac) and H in Reaction (7.38) is assumed to have the form:

\[ r_{3a} = k_{3a} P_B \theta_{V,I} \theta_{V,II} \]  \hspace{1cm} (7.44)

Reaction (7.39) represents the desorption of the adsorbed (hfac) and H from the substrate. Its rate can be expressed as:

\[ r_{3d} = k_{3d} \theta_{(hfac)} \theta_H \]  \hspace{1cm} (7.45)

In the above equations, \( P_A \), \( P_{H_2} \) and \( P_B \) are the pressures of Cu(hfac), \( H_2 \) and H(hfac) in atm, respectively.

The balance equation for coverage of hfac ligand, \( \theta_{(hfac)} \), on type I sites is:

\[ 2r_{1a} - 2r_{1d} + r_{3a} - r_{3d} = 0 \]  \hspace{1cm} (7.46)

\[ 2k_{1a} P_A \theta_{V,I}^2 - 2r_{1d} \theta_{(hfac)}^2 + k_{3a} P_B \theta_{V,I} \theta_{V,II} - k_{3d} \theta_{(hfac)} \theta_H = 0 \]  \hspace{1cm} (7.47)

The balance equation for coverage of H atoms, \( \theta_H \), on type II sites is:

\[ 2r_{2a} - 2r_{2d} + r_{3a} - r_{3d} = 0 \]  \hspace{1cm} (7.48)

\[ 2k_{2a} P_{H_2} \theta_{V,II}^2 - 2r_{2d} \theta_H^2 + k_{3a} P_B \theta_{V,I} \theta_{V,II} - k_{3d} \theta_{(hfac)} \theta_H = 0 \]  \hspace{1cm} (7.49)
For non-competitive adsorption, I assume $\theta_{\text{A,I}} + \theta_{\text{hfac,I}} = 0.5$ for type I sites, and $\theta_{\text{A,II}} + \theta_{\text{hfac,II}} = 0.5$ for type II sites. Therefore, I have four unknown coverage variables and four balance equations.

### 7.3.3 Kinetic Parameters

The mechanism described above contains six kinetic parameters (rate constants). In order to reduce the difficulty of the optimization search, assumed values are used for several of these parameters. The adsorptions of Cu(hfac), and H(hfac) are assumed to have unit sticking coefficient (i.e., $S = 1$). The adsorption rate constant can be calculated based on gas kinetic theory:

$$
k_{i\alpha} = \frac{1}{4} \langle V \rangle = \frac{1}{4} \left( \frac{8RT}{\pi M_i} \right)^{0.5} \frac{cm}{s}
$$

Thus, the adsorption rate constant for Cu(hfac), becomes:

$$
k_{1\alpha} = 4.80 \times 10^{22} \quad cm^2 \quad s^{-1} \quad atm^{-1}
$$

and the adsorption rate constant for H(hfac) becomes:

$$
k_{3\alpha} = 7.42 \times 10^{22} \quad cm^2 \quad s^{-1} \quad atm^{-1}
$$

The adsorption and desorption rate constant and the equilibrium adsorption constant for $H_2$ on clean Cu(111) surfaces have been reported by Ovesen et al. (1992).
They can be expressed in term of an Arrhenius temperature dependence:

\[ k_{2a} = 5.78 \times 10^{23} \exp\left(\frac{-58 \text{ kJ/mole}}{RT}\right) \text{ cm}^{-2} \text{s}^{-1} \text{ atm}^{-1} \quad (7.53) \]

\[ k_{2d} = 1.38 \times 10^{28} \exp\left(\frac{-102 \text{ kJ/mole}}{RT}\right) \text{ cm}^{-2} \text{s}^{-1} \quad (7.54) \]

\[ K_2 = 4.17 \times 10^{5} \exp\left(\frac{44 \text{ kJ/mole}}{RT}\right) \text{ atm}^{-1} \quad (7.55) \]

Since I may not have the same surface conditions as reported by Ovesen et al. (1992), the adsorption and desorption rate constants may be different from the above values. I use these values as initial guesses, and then vary \( k_{2a} \) and \( k_{2d} \) in parallel by keeping \( K_2 \) constant.

The remaining unknown kinetic parameters are the desorption rate constants for Cu(hfac), and H(hfac): \( k_{1d} \) and \( k_{3d} \). These are related through the overall equilibrium constant, \( K_{eq} \). For an assumed value of \( K_{eq} \), I only need to identify one of the remaining rate constants.

The relationship between \( K_{eq} \) and the other rate constants is:

\[ K_{eq} = \frac{K_1 K_2}{K_3^2} = \frac{P_B^2}{P_A P_{H2}} \quad (7.56) \]

\[ K_{eq} = \left( \frac{k_{1a}}{k_{1d}} \right)^2 \left( \frac{k_{2a}}{k_{2d}} \right) \left( \frac{k_{3a}}{k_{3d}} \right)^2 \quad (7.57) \]
7.4 Results

In this section, I determine the optimized values of \( k_{1d} \) and \( k_{2d} \) to use with our new proposed mechanism. The parameters are first determined using the calculated surface concentrations and observed reaction rates, as discussed in Section 7.1. I then present the growth rate profiles calculated by inserting the optimized rate expression into the full reactor model (cf. Section 7.1).

7.4.1 Parameter Estimates

The kinetic parameter optimization can be performed without solving the full reactor transport model for each iteration. Instead, a separate optimization program was developed that uses the calculated surface concentrations of \( \text{Cu(hfac)}_2 \) and \( \text{H(hfac)} \) along with the measured growth rate at each axial position as the starting data. For each set of conditions, the steady-state coverage equations, Equations (7.47) and (7.49) are solved using the assumed rate constants.

The calculated coverages are then used to compute the deposition rate of Cu film:

\[
G = 2r_{1a} - 2r_{1d} \tag{7.58}
\]

\[
G = 2k_{1a}P_A \theta_{r,l}^2 - 2k_{1d} \theta_{(hfac)}^2 \tag{7.59}
\]

The process is repeated using different trial values of \( k_{1d} \) and \( k_{2d} \), until the best values are obtained.
This procedure yields optimum values of $k_{1d}$ and $k_{2a}$:

$$k_{1d} = 2.03 \times 10^{34} \exp\left(-\frac{244 \text{ kJ/mole}}{RT}\right) \text{ cm}^{-2} \text{ sec}^{-1}$$  \hspace{1cm} (7.60)

$$k_{2a} = 1.29 \times 10^{22} \exp\left(-\frac{62 \text{ kJ/mole}}{RT}\right) \text{ cm}^{-2} \text{ sec}^{-1} \text{ atm}^{-1}$$  \hspace{1cm} (7.61)

These results are then used to derive values for $k_{3d}$ and $k_{2d}$:

$$k_{3d} = 6.48 \times 10^{27} \exp\left(-\frac{101.5 \text{ kJ/mole}}{RT}\right) \text{ cm}^{-2} \text{ sec}^{-1}$$  \hspace{1cm} (7.62)

$$k_{2d} = 3.09 \times 10^{26} \exp\left(-\frac{106 \text{ kJ/mole}}{RT}\right) \text{ cm}^{-2} \text{ sec}^{-1}$$  \hspace{1cm} (7.63)

### 7.4.2 Growth Rate Profiles

The optimized parameters are then checked by incorporating them into the full reactor transport modeling program. The comparison of calculated and measured results are shown in Table 7.6. In addition, the calculated growth rate profiles are compared with the measured results in Figures 7.13, 7.14, and 7.15. Figures 7.13 and 7.14 show the results for the 350°C growth experiments for both the high and low pressure regimes. In particular, the proposed mechanism is able to account for the strong $H_2$ dependence much better than the half-order rate expression proposed by Kim et al. (1993).

At the same time, our mechanism is also able to reproduce the weaker $H_2$-order dependence observed at 250°C (cf. Figure 7.15). Our mechanism is also able to
Table 7.6 Comparison of Measured Growth Rates and Calculated Growth Rates from the New Proposed Rate Expression

<table>
<thead>
<tr>
<th>Substrate Temperature (°C)</th>
<th>H\textsubscript{2} Pressure (Torr)</th>
<th>Growth Rate at 2 cm from the Leading Edge (Å/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Measured</td>
</tr>
<tr>
<td>350</td>
<td>760</td>
<td>45.0</td>
</tr>
<tr>
<td></td>
<td>540</td>
<td>109.6</td>
</tr>
<tr>
<td></td>
<td>380</td>
<td>192.8</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>285.3</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>145.7</td>
</tr>
<tr>
<td>250</td>
<td>380</td>
<td>38.0</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>33.0</td>
</tr>
</tbody>
</table>
Figure 7.13 Effect of H$_2$ Pressures on Cu Film Growth Rate Profiles at High Substrate Temperature from the New Proposed Rate Expression
Non-competitive Adsorption Model

$T_s = 350 \, ^\circ C$

Figure 7.14  Cu Film Growth Rate Profiles in Low $H_2$ Pressure Regime from the New Proposed Rate Expression
Non-competitive Adsorption Model

$T_s = 250 \, ^\circ C$

Figure 7.15  Cu Film Growth Rate Profiles for Low Substrate Temperature from the New Proposed Rate Expression
qualitative difference between the slopes observed in the two growth rate profiles. There is a residual quantitative difference between the slopes of the calculated vs. measured profiles. We suspect this may be caused by a small temperature gradient along the sample. This would also account for the slight increase in thickness with axial distance that appears to be present in the growth rate profile measured at 120 Torr.

7.5 Discussion

The values for the adsorption and desorption rate constants for H\(_2\) determined in our analysis are similar to those reported by Ovesen et al. (1992) for adsorption on a clean Cu(111) surface (cf., Table 7.7). In our model, I am able to retain the same value for the equilibrium heat of adsorption (44 kJ/mole). It is necessary to increase the individual activation energies by 4 kJ/mole, and to decrease the pre-exponential factors by about a factor of 50. At least two physical factors might cause a difference of this magnitude. The growing Cu surface is likely to contain crystal planes other than the (111) surface. In addition, the presence of co-adsorbed (hfac) species may perturb the chemisorption behavior of H\(_2\) relative to adsorption on a clean surface.

The kinetic parameters for the H(hfac) desorption step (cf. Equation (7.62)) have not been previously determined. The pre-exponential factor is quite reasonable for a second-order bimolecular surface reaction, assuming a saturation coverage of order 10\(^{14}\) molecule/cm\(^2\). The activation energy for desorption (cf. 101.5 kJ/mole) is comparable to the sum of the desorption energies for adsorbed CH\(_2\)=O and CH\(_3\)O + H species on a copper surface (67 + 42 = 109 kJ/mole) (Shustorovich et al., 1991). The latter might be
Table 7.7  Comparison of Rate Constants for H₂ Adsorption

<table>
<thead>
<tr>
<th></th>
<th>Ovesen et al., 1992</th>
<th>Our Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_{2a} ) (cm² s⁻¹ atm⁻¹)</td>
<td>( 5.78 \times 10^{21} )</td>
<td>( 1.29 \times 10^{22} )</td>
</tr>
<tr>
<td>( E_{2a} ) (kJ/mole)</td>
<td>58</td>
<td>62</td>
</tr>
<tr>
<td>( k_{2d} ) (cm² s⁻¹ atm⁻¹)</td>
<td>( 1.38 \times 10^{28} )</td>
<td>( 3.09 \times 10^{26} )</td>
</tr>
<tr>
<td>( E_{2d} ) (kJ/mole)</td>
<td>102</td>
<td>106</td>
</tr>
</tbody>
</table>
taken as a reasonable approximation for the bonding energetics of a bi-dentate (hfac) group absorbed on the Cu surface.

The kinetic parameters for the Cu(hfac)$_2$ desorption step (cf. Equation (7.60)) are also previously undetermined. The values reported here are based in part on the assumed value of the equilibrium constant for the overall reaction. The latter has not been reported experimentally, although one group has reported a value for the enthalpy of reaction based on calorimetric measurements ($\Delta H_{rxn} = -85$ kJ/mole).

Our reported activation energy for desorption (244 kJ/mole) may be compared with the heat of sublimation for Cu atoms (339 kJ/mole). Using a bond-order conservation argument, I expect that it will be easier for a surface Cu atom to break its neighboring Cu-Cu bonds when there are absorbed (hfac) groups available to accommodate part of its bond order capacity.
CHAPTER 8
CONCLUSIONS AND RECOMMENDATIONS

8.1 Summary

Recent microelectronic applications of TiO₂ films were reviewed. TiO₂ film provides a high dielectric constant for use in memory chip technology. Kinetic studies performed by Siefering and Griffin (1990a; 1990b) were described. The TiO₂ films were deposited in a vertical cold wall low pressure chemical vapor deposition (LPCVD) reactor using two different precursor delivery methods (i.e., both with and without carrier gas).

Carrier gas experiments were performed at substrate temperature of 300°C and TTIP inlet pressures from 0.006 to 0.8 Torr under N₂ pressure of 5 Torr. Under these operating conditions, the reactor order plot showed that the growth rate of TiO₂ is first order dependent on the TTIP concentration. The surface reaction is very fast, so that no saturation effect is observed.

Pure TTIP experiments were performed using substrate temperatures from 220 to 300 °C and TTIP inlet pressures from 0.04 to 2 Torr. Low conversion of TTIP was observed under these operating conditions. The reactor order plot showed that the growth rate of TiO₂ is second order dependent on the TTIP concentration at low TTIP inlet pressures. The saturation effect is observed at high TTIP inlet pressures.
Conclusions of this work. Using a series of reactor models with different levels of approximation, I have estimated the kinetic parameters for both carrier gas and pure TTIP experiments. The simplest approximation was based on a lumped parameter model. The second approximation was based on a 1-D stagnation point flow reactor (SPFR) model using a similarity transformation. The most detailed approximation was based on a full 2-D SPFR model with a axisymmetric geometry.

The 2-D SPFR model gave the most accurate temperature field, including wall and susceptor effects. The 2-D SPFR model gave an improved value of 55 kJ/mole for the activation energy for the gas phase reaction. On the other hand, the 1-D SPFR model estimated the activation energy to be 45 kJ/mole. The magnitude of the pre-exponential factor is consistent with predictions by collision theory.

Cu CVD. In the second part of this dissertation, I reviewed recent applications of Cu films. Copper is considered to be the most promising advanced conducting material for multilevel interconnection application. The kinetic studies based on Lai et al. (1991) and Kim et al. (1993) were examined. Experimental techniques have been developed to study the growth kinetics in a horizontal warm wall reactor. Low resistivity Cu films (2.0 μΩ-cm, vs. 1.7 μΩ-cm for bulk) can be obtained.

The steady state inlet concentration of Cu(hfac), in the reactant stream was monitored by FTIR spectroscopy. The reactor wall was kept warm up to the evaporator temperature to avoid precursor condensation. The reactor pressures varied from 760 to 40 Torr. The substrate temperatures were 350 and 250°C. The thickness of the deposited Cu film was measured using a stylus profilometer.
Conclusions of this work. A two-dimensional horizontal flow reactor (HFR) model has developed to describe the transport effects. The velocity and temperature profiles were calculated for the warm wall reactor. The concentration profiles were first obtained using a simple power rate expression to fit the measured growth rates. The calculated surface concentrations of Cu(hfac), and H(hfac) were then used to evaluate more physically realistic rate rate expressions.

At the high substrate temperature (350°C), the growth rate exhibited first order dependence on H2 pressure. A transport limited regime was observed above 300 Torr of H2 pressure. At low H2 pressure (40 Torr), I noticed that the growth behavior became reaction limited. At the low substrate temperature (250°C), the growth rate was no longer first order dependent on H2 pressure. The reaction order must be reduced to an half to match the measured growth rates.

For a more physically realistic rate expression, a non-competitive adsorption model was proposed to describe the measured growth rate. All the species can adsorb and desorb from the surface. Two types of adsorption site are assumed. Type I sites are designated for hfac ligands, and type II sites are designated for H atoms. The estimated kinetic parameters are reported in Section 7.2.3.

8.2 Recommendations for Future Work

TiO x CVD. The gas phase reaction of TTIP above a heated substrate has been inferred from the carrier gas and pure TTIP experiments. We used the reactor transport model to get kinetic parameters. The next step is to gain more understanding of the gas
phase reaction. In order to study the interaction between TTIP and N₂, we need to change the N₂ pressure in the carrier gas experiments. In addition, we can identify the proposed gas phase intermediate and other products using mass spectrometer sampling.

According to the other researchers, water vapor and oxygen have significant effects on the growth rate. Therefore, added small amount of these species to the existing system can provide some insights of their interaction with TTIP.

Cu CVD. Dr. Wang and Mr. Little did a set of experiments using a horizontal warm wall reactor under different substrate temperatures and H₂ pressures. I proposed a reaction mechanism to describe their results, and obtained the kinetic parameters using a two-dimensional horizontal flow model. Lowering the operating pressure can allow us to study the reaction controlled regime. Therefore, we can perform more accurate reaction order studies on the reactants, Cu(hfac), and H₂, and on the product inhibition by H(hfac) for testing of the proposed rate expression.

Several groups have recently suggested dissolving Cu(hfac), in an alcohol solvent to improve delivery of the reactant. It would be useful to study the influence of alcohol vapors on the reaction kinetics. Other groups have reported that faster deposition rates can be obtained using various Cu(I) precursors. Because these compounds also contain (hfac) ligands, a comparison between the Cu(II) and Cu(I) complexes under the same operating conditions can give us a better understanding of the reaction mechanism.

In addition to obtaining more information about the chemistry of the reaction, it would be worthwhile to improve the reactor transport model. For integral conversions, the Stefan-Maxwell equations are more appropriate to describe the multicomponent gas
mixture than the binary diffusion flux. For both integral and differential conversions, thermal diffusion may be important when the temperature gradient is large. It may also be useful to examine buoyancy effects for high pressure.

Finally, we also suggest to examine issues relevant to the applications in multilevel metallization schemes. These include the selectivity, conformality, step coverage, and trench filling of surface microstructures. It would also be useful to extend our kinetic and reactor modeling studies to a commercial single wafer CVD reactor.
REFERENCES


Gordon, R. "Recent Advances in the MOCVD of Metal Nitrides and Oxides." Paper Y1.6, presented at the MRS Fall 1993 Meeting.


APPENDIX A
THE SIMPLE ALGORITHM

The two-dimensional model equations in this work were solved by the control volume based finite difference method introduced by Patankar (1980). The procedure that Patankar (1980) developed for the calculation of the flow field has been given the name SIMPLE, which stands for Semi-Implicit Method for Pressure-Linked Equations. The sequence of this algorithm is given in Chapter 6 of Patankar (1980):

1. Guess the pressure field $p^*$. 

2. Solve the $u$ and $v$ momentum equations, to obtain $u^*$ and $v^*$.

   Discretized $u$-momentum equation:
   \[
   a_e u_e^* = \Sigma a_{eb} u_{eb}^* + b + (p_p^* - p_E^*)A_e
   \]  
   (A.1)

   Discretized $v$-momentum equation:
   \[
   a_n v_n^* = \Sigma a_{nb} v_{nb}^* + b + (p_p^* - p_N^*)A_n
   \]  
   (A.2)

3. Solve the $p'$ equation.

   Discretized $p'$ equation:
   \[
   a_p p'_p = a_E p'_E + a_W p'_W + a_N p'_N + a_S p'_S + b
   \]  
   (A.3)

where $p'$ is called the pressure correction.
4. Calculate $p$ by adding $p^*$ to $p'$.

5. Calculate $u$ and $v$ from their starred values using the velocity-correction formulas:

\[ u_e = u_e^* + d_e(p_p' - p_e') \]  \hspace{1cm} (A.4)

\[ v_n = v_n^* + d_n(p_p' - p_n') \]  \hspace{1cm} (A.5)

6. Solve the discretization equation for other $\phi$'s, such as temperature and concentration.

7. Treat the corrected pressure $p$ as a new guessed pressure $p^*$, return to step 2, and repeat the whole procedure until a converged solution is obtained.
VITA

The author, Wing-Cheong Gilbert Lai, the son of Bob Shing and Kim Oi, was born on August 3, 1964, in Kowloon, Hong Kong. He has three brothers and one sister. He attended Tak Sun Primary School and Tang King Po Secondary School.

In August 1982, the author left Hong Kong to continue his education in Canada. He went to St. Joseph High School at Renfrew, Ontario, from which he graduated the top of the class in 1983. During the time in Canada, he heard a lot about the advanced technologies in the United State from his cousin, Wing Tak Lai, a Ph.D. Candidate at the University of Minnesota (U of M) in Minneapolis.

In August 1983, the author came to the United State from Canada. He pursued and obtained a Bachelor of Chemical Engineering from the U of M in June 1988. During his undergraduate studies, he completed a independent study on "Photoelectrochemical Studies of Zinc Oxide Films on Polycrystalline Zinc Surfaces" with Dr. William H. Smyrl from Corrosion Research Center at U of M. Because of the excellent materials program at the U of M, he developed a strong interests in advanced materials processing.

In August 1988, the author decided to start his graduate work with Dr. Gregory L. Griffin at the Louisiana State University (LSU) in Baton Rouge. He concentrated his research at the Advanced Materials Processing Laboratory. He obtained his Master of Science in Chemical Engineering from LSU in August 1991. To understanding more about chemical vapor deposition processes in semiconductor industry, he decided to continue his Ph.D. work with Dr. Griffin.
DOCTORAL EXAMINATION AND DISSERTATION REPORT

Candidate: Wing-Cheong Gilbert Lai

Major Field: Chemical Engineering

Title of Dissertation: Reactor Analysis of Chemical Vapor Deposition of TiO$_2$ and Cu Thin Films

Approved:

[Signatures]

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Date of Examination: May 3, 1994