SIMULATION OF SILICON DIOXIDE
LPCVD FROM TEOS

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Master's thesis

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Acknowledgement

After ten months of work, my project comes to an end. The work done, however, would not have been realized without the help from my supervisor Dr. Kleijn, who gave good and solid guidance to a not sharply defined project and I would like to thank him for it. I am also grateful for the cooperation I received from ASM International, namely from Dr. Huussen, Dr. Ter Horst and Dr. Oosterlaken, who provided me with information where needed. I look back on these ten months with pleasure and I would like to thank Prof. Van den Akker for providing me with the opportunity to do my Masters project in the 'Kramers Laboratorium voor Fysische Technologie'.

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George Schoof
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Abstract

In this study, a model is constructed as a basis for an optimization tool for silicon dioxide low pressure chemical vapor deposition (LPCVD) from the precursor gas tetra-ethyl-ortho-silicate (TEOS) in ASM International's A412, hot wall, vertical 300 mm multi-wafer reactor. The model consists of a chemistry model based on elementary reactions and a transport model for multi-component gas flow, heat and mass transfer. Model simulation results have been validated against experimental data on growth rate and uniformities. The model semi-quantitatively predicts the dependence of growth rate and uniformity on pressure, TEOS flow rate and temperature. It also provides a basis for understanding experimental observations, such as the importance of the interwafer distance, the need for the use of multiple inlets and the need for a wafer rotation. The developed simulation tool can be used in further optimization studies with respect to reactor design and process operation.
Extended abstract

In this study, a basis is provided for an optimization tool for silicon dioxide low pressure chemical vapor deposition (LPCVD) from the precursor gas tetra-ethyl-ortho-silicate (TEOS) in a hot wall 300 mm multi-wafer reactor as produced by ASM International, based on computer simulations rather than expensive and time consuming experiments.

From an extensive literature review on models describing the chemical reaction mechanism by which silicon dioxide is deposited from TEOS, the chemical model as proposed by Coltrin and coworkers was selected as the best starting point for this study, because of its applicability to various circumstances. This reaction mechanism consists of a set of four gas phase and eight surface reactions. Deposition of silicon dioxide is assumed to take place through two parallel reaction routes: direct sticking and decomposition of TEOS on the surface and gas-phase decomposition of TEOS into the intermediate species TES, followed by sticking and decomposition of TES on the surface.

Together with a simplified representation of the industrially used 300 mm multi-wafer reactor, the chemistry model is fed to a commercially available CFD program called CFD-ACE+. In this program full scale 2-dimensional and 3-dimensional simulations are performed under varying circumstances. The N-component gas mixture is treated as a continuum, ideal gas and the flow is assumed to be laminar. The transport of mass, momentum, heat and chemical species are described by the continuity equation, the Navier-Stokes equations, the transport equation for thermal energy, and N-1 transport equations for the gas species, respectively. Multi-component diffusion is calculated by the Stefan-Maxwell equations.

The original Coltrin model was first investigated using the SPIN package (a 1-dimensional simulation package for a stagnation point/rotating disk reactor). It was concluded that the Coltrin model can be simplified through the omission of three out of four gas-phase reactions and modeling seven out of eight surface reactions irreversibly, without loss of accuracy or applicability.

Both the simplified and the full chemistry model were found to lead to growth rate predictions that are 50 % lower than experimental values. Therefore, the model was further modified by fitting one of the rate constants in the model in order to reproduce experimental growth rates at the most common operating conditions, i.e.
928 K, 200 sccm TEOS flow rate and 0.5 Torr. This was done, one-by-one, for the three most sensitive reactions in the model, leading to three different versions of the chemistry model.

These three models were used in running isothermal, 2-dimensional simulations in CFD-ACE+, for various pressures, TEOS flow rates and temperatures. For these circumstances, experimental results were provided by ASM International, so that a comparison could be made between simulation and experiment.

From simulations it became clear that the chemistry model in which the pre-exponential rate constant for sticking of TES has been fitted to experiments, predicts variations in growth rate with pressure, TEOS flow rate and temperature (other than those conditions to which the model had originally been fitted) most accurately. It further correctly predicts trends in intra-wafer non-uniformity. It is therefore concluded that this model should be used as a basis for further design optimization.

This model was also used in examining the effect of replacing the isothermal boundary conditions of the reactor by radiative heat transfer in a diffuse, gray manner in a 2-dimensional model, using the Discrete Ordinate Method. Simulations showed that the 2-dimensional model is unsuitable for investigating radiative heat transfer, since the gas heats up to reactor temperature before it reaches the wafer batch, and thus operation here is isothermal as well.

Finally, 3-dimensional simulations were performed to study the effect of non-symmetric features of the actual reactor. Although the model now takes these features into account, results are not very accurate, because the grid at some points (e.g. near the inlets) is not sufficiently fine to describe the behavior accurately. It does however provide a basis for further 3-dimensional investigations of the deposition behavior in the reactor.

In conclusion, a basis has been provided for an optimization tool, based on 2-dimensional modeling using the modified chemistry model in combination with a detailed transport model. The model predicts that average wafer growth rates increase with pressure, temperature and TEOS flow rate, as is confirmed by experiments. It further predicts absolute values of wafer averaged growth rate relatively accurately, especially for variations of growth rate with temperature. Furthermore, trends in uniformity correspond to those found in experiments, with the observation that uniformity deteriorates for increasing pressure and temperature and decreasing TEOS flow rate.

Subsequently, we have also gained insight in the reaction mechanism of silicon dioxide deposition from TEOS and have laid foundations to extend the model to 3-dimensional simulations and inclusion of radiative heat transfer.

This model can now be used to optimize reactor geometry and process conditions for silicon dioxide LPCVD from TEOS to obtain high efficiencies and high yields in the overall process, while simultaneously improving uniformity.
Uitgebreide samenvatting

In dit onderzoek is een basis gevormd om het proces van chemische vorming van silicium dioxide laagjes uit damp bij lage druk vanuit tetra-ethyl-ortho-silicaat te optimaliseren door middel van numerieke computer simulaties in plaats van dure en tijdrovende experimenten.

Na een uitgebreid literatuuronderzoek, werd het reactiemodel, zoals dat door Coltrin en collega’s is opgesteld, gekozen als de basis van het numerieke model vanwege het feit dat dit model toepasbaar is in een breed scala van condities. Het reactiemodel bestaat uit vier gas-fase en acht oppervlakte reacties. De vorming van de silicium dioxide film wordt verondersteld plaats te vinden rechtstreeks uit direcht aanhechten en uiteenvallen van TEOS en uit omzetting van TEOS in een intermediare stof TES, die vervolgens direct aanhecht en uiteenvalt.

Dit reactiemodel wordt gecombineerd met een model van de A412, de industrieel verkrijgbare warme wand, 300 mm multi wafer reactor, zoals die door ASM International geproduceerd wordt, en deze twee modellen worden ingevoerd in het CFD programma CFD-ACE+, dat samen met tranportvergelijkingen voor massa, impuls, warmte en de afzonderlijke componenten, simulaties uitvoert. Deze simulaties vinden plaats op volle reactor schaal in zowel twee als drie dimensies.

Nader onderzoek aan het reactiemodel met het programma SPIN (een 1-dimensionaal computer pakket voor roterende wafer reactoren) toonde aan dat het model verder vereenvoudigd kon worden. Hiertoe werden drie van de vier gas fase reacties weggelaten en werden zeven van de acht oppervlakte reacties irreversibel gemodelleerd, zonder dat de accuraatheid van het model geweld werd aangedaan.

Aangezien zowel het volledige model als de versimpelde versie hiervan nog steeds de voorspelde groeisnelheden met ongeveer 50 % onderschatte, werd het model verder veranderd door een reactiesnelheidsconstante te fitten aan experimenteel gevonden groeisnelheden bij de meest voorkomend procescondities (in dit geval 928 K, 0.5 Torr en 200 sccm TEOS debiet). Aangezien uit een gevoeligheids analyse bleek dat drie reactiestappen een grote invloed hebben op de groeisnelheid, werd van deze drie reacties de snelheidsconstante een voor een gefit, wat dus resulteerde in drie verschillende chemie modellen.
Deze modellen werden vervolgens gebruikt in 2-dimensionale simulaties in CFD-ACE+ onder procescondities, waarvoor experimentele gegevens beschikbaar waren, zodat een vergelijk getrokken kon worden. De experimenten zijn door ASM International verricht.

Uit simulaties blijkt dat het model, waarvoor de reactiesnelheidsconstante van het aanhechten van TES is gefit aan de groeisnelheden bij genoemde condities, de beste overeenstemming geeft met de experimenten, ook voor andere procescondities. Het model voorspelt trends in zowel variaties in groeisnelheden als wafer uniformiteiten met druk, TEOS debiet en temperatuur vrij nauwkeurig. Dit model zal dan ook gebruikt worden voor eventuele verdere optimalisatie studies.

Verder is dit model gebruikt om de invloed van warmtetransport door middel van straling te onderzoeken in een diffuus, grijze benadering, gebruikmakend van de Discrete Ordinaten Methode. Simulaties laten zien dat het 2-dimensionale model ongeschikt is om het niet-isotherme gedrag van de reactor te onderzoeken, omdat het koude gas al opgewarmd is naar reactortemperatuur tegen de tijd dat het de wafer rand bereikt. Er vind dus ook hier isotherme operatie plaats.

Ook zijn er 3-dimensionale simulaties uitgevoerd om de invloed van asymmetrische elementen in de reactor op de groeisnelheid te onderzoeken. Ondanks dat deze elementen in het 3-dimensionale model wel gemodelleerd konden worden, bleken de resultaten niet nauwkeurig genoeg te zijn. Dit werd veroorzaakt doordat het grid rond deze asymmetrische elementen niet fijn genoeg is om te effecten hiervan nauwkeurig te beschrijven. Met dit in gedachte, kan het 3-dimensionale model in de toekomst wel gebruikt worden als basis om nauwkeurige 3-dimensionale simulaties uit te voeren.

Samenvattend is er een fundament gelegd voor een numeriek model om optimalisaties te kunnen uitvoeren. Het model bestaat uit het aangepaste chemie model van Coltrin, de 2-dimensionale versimpeling van de werkelijke reactor geometrie en een stelsel van transportvergelijkingen. Het voorspelt niet alleen globale trends in groeisnelheden met druk, TEOS debiet en temperatuur, maar ook absolute waarden van die groeisnelheid, vooral tegen variaties in de temperatuur. Verder voorspelt het model correct dat de uniformiteit binnen een enkele wafer achteruit gaat met toenemende druk en temperatuur en afnemend TEOS debiet. Deze studie geeft een goed beeld van de mechanismen die een rol spelen in dit proces en legt een basis voor eventuele verdere 3-dimensionale simulaties.

Dit model kan nu verder gebruikt worden om reactor geometrie en procescondities te optimaliseren door bijvoorbeeld zowel de efficiency van het proces als de uniformiteit binnen wafers te verhogen.
List of symbols

\( A_i \) Pre-exponential rate constant
\( a_{ij} \) Thermal diffusion factor
\( c \) Molar concentration of mixture
\( c_i \) Concentration of species \( i \)
\( c_k \) Exponential pressure coefficient
\( c_p \) Specific heat
\( D \) Diffusion coefficient
\( D_{SM} \) Stefan - maxwell diffusion coefficient
\( D \) Characteristic diameter of reactor
\( D_{T} \) Thermal diffusion coefficient of species \( i \)
\( D_{ij} \) Binary diffusion coefficient
\( E_{a,k} \) Activation energy for reaction \( k \)
\( E_b \lambda \) Spectral distribution of emissive power of a black body
\( F_{ij} \) View factor
\( f_j \) Surface site density
\( g \) Gravitational constant
\( h \) Planck constant
\( H_i \) Specific enthalpy of species \( i \)
\( j_i \) Flux of species \( i \)
\( j_i^C \) Flux of species \( i \) due to concentration gradient
\( j_i^T \) Flux of species \( i \) due to temperature gradient
\( K_{k}^g \) Equilibrium constant for gas – phase reaction \( k \)
\( K_{l}^f \) Equilibrium constant for surface reaction \( l \)
\( k_b \) Boltzmann constant
\( k_{k,b}^g \) Reverse rate constant gas – phase reaction \( k \)
\( k_{k,f}^g \) Forward rate constant gas – phase reaction \( k \)
\( k_{l,b}^s \) Reverse rate constant surface reaction \( l \)
\( k_{l,f}^s \) Forward rate constant surface reaction \( l \)
\( k_s \) Surface reaction rate constant
\( L \) Characteristic length of reactor
\( m_i \) Molar mass of species \( i \)
\( p \) Pressure
\( q_b \) Blackbody radiative heat flux
\( q_{i,rad} \) Foreign radiative heat flux

consistent units

\(-\)

\( \text{mol/m}^3 \)

\( J/\text{mol} \cdot \text{K} \)

\( m^2/s \)

\( m \)

\( 	ext{kg/m}^2 \text{s} \)

\( m/s \)

\( J/\text{mol} \)

\( W/\text{m}^2 \cdot \mu \text{m} \)

\( \text{mol/m}^2 \)

\( 9.81 \text{ m/s}^2 \)

\( 6.626 \cdot 10^{-34} \text{ J/s} \)

\( \text{J/mol} \)

\( \text{mol/m}^2 \cdot \text{s} \)

\( \text{mol/m}^2 \cdot \text{s} \)

\( \text{mol/m}^2 \cdot \text{s} \)

consistent units

consistent units

consistent units

consistent units

consistent units

consistent units

\( 1.38 \cdot 10^{-23} \text{ J/K} \)

consistent units

consistent units

consistent units

consistent units

consistent units

\( \text{m} \)

\( \text{g/mol} \)

\( \text{Pa} \)

\( J/\text{m}^2 \cdot \text{s} \)

\( J/\text{m}^2 \cdot \text{s} \)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tr>
<td>$q_{n,\text{rad}}$</td>
<td>Net radiative heat flux</td>
</tr>
<tr>
<td>$q_{t,\text{rad}}$</td>
<td>Total radiative heat flux</td>
</tr>
<tr>
<td>$q_{s,\text{rad}}$</td>
<td>Own radiative heat flux</td>
</tr>
<tr>
<td>$R$</td>
<td>Universal gas constant</td>
</tr>
<tr>
<td>$R_{k,b}^0$</td>
<td>Backward rate of gas-phase reaction $k$</td>
</tr>
<tr>
<td>$R_{k,f}^0$</td>
<td>Forward rate of gas-phase reaction $k$</td>
</tr>
<tr>
<td>$R_{l,b}^0$</td>
<td>Backward rate of surface reaction $l$</td>
</tr>
<tr>
<td>$R_{l,f}^0$</td>
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</tr>
<tr>
<td>$S_i$</td>
<td>Specific entropy of species $i$</td>
</tr>
<tr>
<td>$\mathbf{s}$</td>
<td>Radiation beam directional vector</td>
</tr>
<tr>
<td>$T_{r,\text{ef}}$</td>
<td>Reference temperature</td>
</tr>
<tr>
<td>$v$</td>
<td>Gas velocity</td>
</tr>
<tr>
<td>$x_i$</td>
<td>Species molar fraction</td>
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**Greek symbols**

<table>
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<tr>
<td>$\alpha_{\text{rad}}$</td>
<td>Radiation absorption</td>
</tr>
<tr>
<td>$\beta_k$</td>
<td>Exponential temperature coefficient</td>
</tr>
<tr>
<td>$\Gamma_m^0$</td>
<td>Surface site density in bulk phase $m$</td>
</tr>
<tr>
<td>$\gamma_i$</td>
<td>Sticking coefficient for species $i$</td>
</tr>
<tr>
<td>$\Delta H_k^0$</td>
<td>Reaction enthalpy for gas-phase reaction $k$</td>
</tr>
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<td>$\Delta S_k^0$</td>
<td>Reaction entropy for gas-phase reaction $k$</td>
</tr>
<tr>
<td>$\Delta H_l^0$</td>
<td>Reaction enthalpy for surface reaction $l$</td>
</tr>
<tr>
<td>$\Delta S_l^0$</td>
<td>Reaction entropy for surface reaction $l$</td>
</tr>
<tr>
<td>$\Delta T$</td>
<td>Temperature difference</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>Lennard–Jones potential parameter</td>
</tr>
<tr>
<td>$\varepsilon_{\text{rad}}$</td>
<td>Radiation emissivity</td>
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<tr>
<td>$\theta_j$</td>
<td>Site occupancy of species $j$</td>
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<tr>
<td>$\kappa_{\text{rad}}$</td>
<td>Absorption coefficient</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Thermal conductivity</td>
</tr>
<tr>
<td>$\lambda_{\text{rad}}$</td>
<td>Wavelength of radiation</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Viscosity</td>
</tr>
<tr>
<td>$\nu_k$</td>
<td>Stoichiometric coefficient of species $i$ in reaction $k$</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density</td>
</tr>
<tr>
<td>$\rho_{\text{rad}}$</td>
<td>Radiation reflectivity</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Collision diameter</td>
</tr>
<tr>
<td>$\sigma_{\text{SB}}$</td>
<td>Stefan–Boltzmann's constant</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Stress tensor</td>
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<tr>
<td>$\tau_{\text{rad}}$</td>
<td>Radiation transmittivity</td>
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<tr>
<td>$\Phi(r, s', s)$</td>
<td>Phase function energy transfer</td>
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<tr>
<td>$\phi(r)$</td>
<td>Interaction potential function</td>
</tr>
<tr>
<td>$\xi$</td>
<td>Mean free path</td>
</tr>
<tr>
<td>$\Omega_i$</td>
<td>Potential function from kinetic gas theory</td>
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<tr>
<td>$\Omega_D$</td>
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<tr>
<td>$\omega_i$</td>
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### Dimensionless numbers

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<td>$Da_s$</td>
<td><em>Surface Damköhler number</em></td>
<td>–</td>
</tr>
<tr>
<td>$Gr$</td>
<td>Grashof number</td>
<td>–</td>
</tr>
<tr>
<td>$Kn$</td>
<td>Knudsen number</td>
<td>–</td>
</tr>
<tr>
<td>$Re$</td>
<td><em>Reynolds number</em></td>
<td>–</td>
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Chapter 1

Introduction

The invention of the microprocessor was the technological spark that led to the computer revolution. Since then, the complexity and performance of digital systems have been increasing at great speeds. It has become a basic stride for mankind to develop faster and better microprocessors. Integrated circuits (IC) play a key role in this development. IC’s are encountered in a wide variety of appliances, each with their own characteristics and specifications, but the use in microprocessors sets the highest standards when it comes to performance. In particular, the development of Very Large Scale Integration (VLSI) is a major boost for the realisation of high-performance IC’s. The variety of IC’s, together with more stringent demands on performance, have led to an increase in the number of steps it takes to complete an IC, varying between 30 and 300 [Badgwell et al., 1995]. Steps vary from simple procedures like (wet) chemical cleaning, (atmospheric) diffusion and oxidation, to more complex ones such as low-pressure chemical vapor deposition (LPCVD) or sputtering of films, patterning of these films and doping. The most common process steps are summarized in 1.1.

Figure 1.1: Overview of process steps in IC industry
1.1 Chemical Vapor Deposition

Deposition processes are used to apply solid layers with uniform thickness of a specific chemical composition onto surfaces. This deposition can be achieved either physically (by evaporation or sputtering) or chemically. Chemical vapor deposition (CVD) may be defined as the deposition of a solid on a surface from a chemical reaction in the vapor phase [Pierson, 1999]. The advantage of CVD over other techniques is that CVD can deposit conformal films (i.e. films of highly uniform thickness) on very irregularly shaped surfaces with deep recesses. Furthermore, the deposition rate is high (lower for low pressure processes than for atmospheric ones) and the process is flexible when it comes to conditions and materials that can be deposited.

Atmospheric deposition is mainly used for the deposition of epitaxial films. The deposition rate is high and is limited by the transport of reactants to the surface and products from the surface. Low pressure deposition is used for deposition of polycrystalline and amorphous films. The growth rates of the films are generally lower and deposition rate is limited by the kinetics of the heterogeneous reactions. These low pressure deposition processes are the focus of this study.

1.1.1 History

The first practical use of CVD was developed in the 1880s, in the production of incandescent lamps. Simultaneously, the carbonyl process, developed by Ludwig Mond, used CVD for the production of pure nickel. In the next fifty years this was the main purpose of CVD: extraction and pyrometallurgy for the production of high-refractory metals. The ease with which a film could be deposited on a substrate using CVD was not realized until the end of World War II. The early 60s saw the introduction of CVD in various fields, such as semiconductor fabrication and cutting-edge tools, of which the former nowadays comprises 75 % of all CVD production [Pierson, 1999]. Until 1976, the standard process for CVD was the cold wall reactor, operating under atmospheric pressure. The low temperature prevented deposition from taking place on the reactor walls. To stimulate the reaction, the wafers were heated through the wafer carrier. However, various studies of low pressure CVD led to a general switch to low pressure CVD (LPCVD) reactors in 1976 due to their extremely favourable economics. This was a result of the increased packing density of wafers, now that transport limitations were taken away by increased diffusion at this low pressure (<1 Torr). Conversely, the rate limiting deposition step led to an increased uniformity within and between wafers [Rosler, 1977]
1.1.2 Reactors

LPCVD reactors are mostly operated between 30-250 Pa, at temperatures of 500-1200 K. LPCVD processes are generally surface reaction-rate controlled. The two reactors mainly used for LPCVD are the hot wall multi-wafer reactor (see Fig. 1.2a) and the cold-wall single wafer reactor (see Fig. 1.2b). The advantage in a cold wall single wafer reactor is that the wafer can be heated up and cooled down quickly and no material is deposited on the wall. High deposition rates are needed to secure high throughput and efficiency. Because of steep thermal gradients (between wafer and wall) and the mass-transport limitation that often occurs, numerical modeling is quite important for these reactors.

The present study focusses on multi-wafer reactors. These reactors have hot walls, controlled by separate resistances to be able to apply gradients in temperature to compensate for downstream depletion, and a high throughput. The multi-wafer hot-wall reactors were initially placed horizontally, but are now placed vertically because of efficient clean room usage. For both the cold wall single wafer and hot wall multi-wafer reactor types the same requirements apply [Kuijlaars, 1996]:

- Thickness uniformity, within one wafer and, in the case of multi-wafer processing, between wafers. Non-uniformities of around 2% are acceptable.
- Conformal step coverage, i.e. the ability to fill trenches and holes with a uniform film. The step coverage is usually defined as the ratio of the thickness of the deposit on the sidewall of a trench over the thickness on the top surface.
- Absence of solid particulates which, when formed in the gas phase, may lead to defects in the film.
- Selectivity of the process with respect to susceptor material.

Figure 1.2: a) Multi-wafer hot wall reactor (left) and b) Single wafer cold wall reactor (right)

Until recently, 200 mm wafers were the cutting edge technology. However, as of 2000 larger 300 mm wafers are being processed. The larger diameter results in a
higher throughput (since the wafer area is increased). As the edge increases with diameter and the area increases with the diameter squared, the yield may be increased as well since most defects find themselves at the edge. The disadvantage is the decreased uniformity because of increased depletion, and higher concentrations of intermediates and by-products.

1.2 Fundamentals of CVD

As with all reactive processes, CVD is governed by thermodynamics (i.e. in which direction the reaction is going) and kinetics (i.e. how fast it is moving in that direction). The interaction between the chemistry and thermodynamics of the process on one hand, and the hydrodynamics on the other, form the framework in which the behavior of a CVD reactor can be modeled. Although well-established models and equations can describe the transport phenomena in LPCVD [C.R. Kleijn in M. Meyappan, 1995], the chemistry remains the bottleneck for accurate modeling and optimization.

![Diagram of CVD reactor](image)

**Figure 1.3: Main factors affecting CVD performance**

1.2.1 Thermodynamics

Although CVD processes are essentially non-equilibrium processes, thermodynamics tells us something about the feasibility of certain reactions and the state attainable. For simple reactions, where an a-priori knowledge of the system is available, a straightforward minimization of the Gibbs energy can provide enough information. When reactions become more complex (i.e. at high temperatures with many intermediate species), a minimization of the Gibbs energy can be accomplished by calculating the number densities at equilibrium for large number of species [Vossen
1.2. Fundamentals of CVD

and Kern, 1991; Sherman, 1987]. However, this still requires knowledge of thermochemical data.

1.2.2 Kinetics

Main reactions to be considered in CVD are gas-phase reactions (whose relative importance increases with higher pressures and temperatures), and surface reactions. Although these reactions can be represented straightforwardly by an Arrhenius or Langmuir-Hinshelwood expression, respectively, there are some complications that have to be taken into account.

1.2.2.1 Gas phase chemistry

Gas phase reactions mostly consist of decomposition due to collisions or thermal energy, leading to the precursors that actually adsorb on the surface and form the deposit. Whether this decomposition is a unimolecular (i.e. thermal) or bi-molecular (i.e. collisional) process, is determined by the pressure. At high pressures and temperatures the thermal energy present is enough for molecules to decompose, meaning a uni-molecular reaction. In the limit of low pressures the rate of energizing collisions becomes small relative to the rate of reaction of the energized molecule, and the decomposition becomes bi-molecular. The pressure, at which this change occurs, is referred to as the fall-off pressure. This crossover is usually calculated by RRKM (Rice-Ramsberger-Kassel and Marcus) theory [Holbrook et al, 1996]. For a molecule with many vibrational degrees of freedom, the internal energy efficiently thermalizes, leading to unimolecular decomposition which therefore remains of first order at low pressures. An accurate representation of the reaction schemes should take this behaviour into consideration, unless it is only valid for a specified pressure range.

1.2.2.2 Surface chemistry

Surface chemistry is a complex system of adsorption, surface diffusion, reaction and re-emission. This process can be described by a classical Langmuir-Hinshelwood expression (modified or not), but this expression only describes adsorption, thereby ignoring mechanisms that under certain circumstances can play a large role in deposition. Furthermore, although the L-H expression often provides the correct dependence of growth rate on partial pressure, the assumption of gas/surface equilibrium does not hold for a growth process.

Especially where irregular or patterned surfaces are involved, the L-H equations fall short. Usually the trenches in these surfaces are small compared to the mean free path of the molecules, and therefore the gas phase collisions are less likely than
molecule to wall collisions. To solve for the problems mentioned here a concept called the Reactive Sticking Coefficient (RSC) has been introduced. The RSC is the probability that a molecule, upon impinging on a surface, will 'stick' and react. For a film to be uniformly deposited, a combination of re-emission and surface diffusion needs to take place for the precursor to spread out over surfaces and deposit itself in trenches and recesses. Surface diffusion is negligible in LPCVD applications. Re-emission is a combination of physiosorption, chemisorption and desorption. Since even for the simplest processes information on these events is unavailable, they are modeled through the RSC.

1.2.3 Hydrodynamics

Although LPCVD processes are mostly kinetically controlled, hydrodynamics and transport phenomena, on both reactor scale and molecular level, play a significant role.

In theory the diffusion of species in and out of the intrawafer region should be much faster than any surface reaction, thereby assuring a uniform deposition profile. Uniformity is thus achieved by low surface reaction rates (obtained by decreasing the temperature) and high diffusion rates (obtained by decreasing pressure). However, decreasing temperature and pressure also leads to a strongly decreased deposition rate. The relative speed of surface reaction and diffusion is characterized by the (surface) Damköhler number, defined as reaction rate over diffusion rate:

$$D_{as} = \frac{k_s L}{D}$$

(1.1)

In this equation $k_s$ is the surface reaction rate constant, $L$ is a characteristic dimension for diffusion such as a boundary layer and $D$ a diffusion coefficient. The
closer $Da_s$ is to 0, the more uniform the deposition profile will be. In semiconductor manufacturing, where throughput (quantity) is as big an issue as uniformity (quality), reactors are operated on the edge, meaning highest possible reaction rates with minimal non-uniformity. It is this tolerated non-uniformity, or more properly, presence of gradients that makes hydrodynamics an important issue. One aspect of hydrodynamics is turbulence. Turbulence can arise due to either shear forces or buoyancy forces, characterized by the Reynolds and Grashof number respectively.

\[
Re = \frac{\rho v D}{\mu} \tag{1.2}
\]

\[
Gr = \frac{g \rho^2 H^3 \Delta T}{\mu^2 T_{ef}} \tag{1.3}
\]

In these equations $\rho$ stands for the density, $v$ for the gas velocity, $D$ is a characteristic dimension for convective transport such as a tube diameter, $\mu$ is the viscosity, $g$ is the gravity constant and $H$ is a characteristic dimension for heat transport such as the distance between a cold and hot wall. The low flow rates used in LPCVD make sure $Re$ is well below the transition to turbulent flows. Since the aim is to operate the reactor, employed in this study, isothermally, also the buoyancy forces play a minor role in causing turbulent flows.

Pressure and temperature relationships are accurately described by the ideal gas law, since the pressures in LPCVD are much lower than 10-100 bar, and temperatures are higher than the critical temperatures.

On a molecular level, hydrodynamic issues focus on the behavior of molecules. First of all, at low pressures it is essential to establish in which flow regime the molecules find themselves. One measure is the mean free path ($\xi$) of the molecules:

\[
\xi = \frac{1}{\pi \sqrt{2}} \frac{k_B T}{p \sigma^2} \tag{1.4}
\]

compared to a characteristic dimension of the reactor $L$. If the ratio $\xi$ over $L$ (i.e. the Knudsen number) approaches unity, we enter the regime of transitional flow or slip flow. In this regime, Monte Carlo simulations can be used to describe the interactions between gas molecules and the surface. If $Kn$ is sufficiently small ($< 0.01$), the flow can be described by conventional continuum mechanics. In most LPCVD reactors, and also in the reactor at hand, this is the case.
1.3 Project goal

In this work, from an extensive literature study, a reaction mechanism has been chosen for the deposition of SiO$_2$ by tetra-ethyl-ortho-silicate (TEOS). This mechanism will be used together with a two- and three-dimensional model of a hot wall, 300 mm, vertical multi-wafer LPCVD reactor. More specific, this reactor is the industrially used A412 vertical reactor, produced by ASM International. These two components will be fed into a commercially available computational fluid dynamics (CFD) modeling software package, CFD-ACE+. Together with the boundary conditions, the problem will be solved on an orthogonal grid (2D) and curvilinear non-orthogonal grid (3D), under steady-state conditions by a finite-volume method.

The simulation results will be validated against experimental results, provided by ASM International. Special attention will be given to the dependencies of growth rate and radial and axial deposition uniformity on process parameters such as temperature, pressure and flow rate, and the validity of the chemical reaction mechanism in explaining observed deposition and concentration profiles.

The aim of this project is to validate simulation results against experimental results, both for the A412 reactor, and thus provide a basis for an optimization tool, based on straightforward and cheap computer simulations rather than expensive and time-consuming real-life experiments.

Where discrepancies between the simulations and the experiments arise, these differences will be interpreted in terms of the model and, where possible, recommendations will be made to improve the model.
Chapter 2

Theory

Design and optimization of CVD equipment are traditionally based on empirical research. However, the awareness is rising that a fundamental understanding of transport phenomena and the chemistry taking place in the reactor should be the main focal point for the process of design and optimization. This is becoming possible through the availability of more computational power.

The first modelling studies of CVD processes consisted of analytical solutions for transport equations coupled with strongly simplified chemical reaction mechanisms. Later on, detailed \textit{ab initio} chemistry models with a large number of species and reactions in gas-phase and surface have been developed, which were coupled to simple one-dimensional models for the fluid flow. The models will be most accurate when the complex reaction mechanisms and transport phenomena can be combined into one single model. This makes the modelling of CVD reactors a time consuming process, but nevertheless very important. In this chapter the basis of design, that is, the equations and chemical reaction mechanisms that will eventually make up the model, will be treated. For an explanation of the symbols used, see the list of symbols in the beginning of this report.

2.1 Transport equations

The four main equations governing the behavior of CVD reactors are the transport equations for mass, momentum, heat and the concentrations of the various chemical components. These equations form a set of coupled partial differential equations. The gas flow in CVD reactors is given by the equation for the conservation of mass, or continuity equation:

\[
\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \vec{v}) \tag{2.1}
\]

and the equation for the conservation of momentum, or Navier-Stokes equation:

\[
\frac{\partial (\rho \vec{v})}{\partial t} = -\nabla \cdot (\rho \vec{v} \vec{v}) + \nabla \tau - \nabla p + \rho \vec{g} \tag{2.2}
\]
with \( \rho \) the gas density, \( t \) the time, \( \vec{v} \) the gas velocity vector, \( p \) the pressure and \( \vec{g} \) the gravity vector. The stress tensor \( \tau \), as used in CVD processes where we deal with Newtonian fluids, takes the form

\[
\tau = \mu (\nabla \vec{v} + (\nabla \vec{v})^T) - \frac{2}{3} \mu (\nabla \cdot \vec{v}) \cdot \mathbf{I}
\] (2.3)

where \( \mathbf{I} \) is the unity tensor and \( \mu \) the viscosity. For non-isothermal operation (as is quite common in CVD reactors) the temperature gradients can greatly affect the flow of gas. Therefore, the transport of thermal energy must be included in the model:

\[
\frac{\partial (\rho c_p T)}{\partial t} \quad \text{transient} \quad = \quad -\nabla (\rho c_p \vec{v} T) \quad + \quad \nabla (\lambda \nabla T) \quad + \quad \frac{D_p}{D_t} \quad + \quad \nabla \left( R T \sum_{i=1}^{N} \frac{D_T^T}{m_i} \nabla \ln(x_i) \right) \quad - \quad \sum_{i=1}^{N} j_i \cdot \nabla \frac{H_i}{m_i} \quad - \quad \sum_{i=1}^{N} \sum_{k=1}^{K} H_i \nu_{ik} (R_{k,f}^q - R_{k,b}^q) \quad - \quad \nabla \cdot q_{i,rad} \quad \text{Radiative heat flux}
\] (2.4)

The fourth equation is the transport equation for the \( i \)th species, defined by:

\[
\frac{\partial \rho \omega_i}{\partial t} \quad \text{transient} \quad = \quad -\nabla \cdot (\rho \vec{v} \omega_i) \quad - \quad \nabla \cdot \frac{z_i}{z_i} \quad + \quad m_i \sum_{k=1}^{K} \nu_{ik} (R_{k,f}^q - R_{k,b}^q) \quad \text{reaction}
\] (2.5)

Obviously, in an \( N \)-component gas mixture, there are \( N - 1 \) independent species equations like the one in Eq. 2.5. The equations 2.1 through 2.5 are the basis of any CFD reactor model. In the case of LPCVD, there are several assumptions possible which can simplify these equations and save computational effort.

### 2.2 Multi-component diffusion

Diffusion plays an important role in LPCVD processes and it is therefore essential to describe diffusion accurately into the model. There are a number of ways to do this:

- Stefan-Maxwell; fluxes based on multi-component diffusion coefficients and concentration gradients. This representation is most accurate but also time consuming.
- Fick; valid for dilute mixtures where a single component is in large excess.
- Wilke; valid for non-dilute mixtures in which one species diffuses through a stagnant medium
2.3. Transport and thermodynamic properties

Studies have shown that for most LPCVD studies the full Stefan-Maxwell equations are needed [Kuijlaars, 1996]. For an $N$-component gas mixture the following expression for the diffusive fluxes in terms of mole fractions can be written [Hirschfelder et al., 1967]:

\[
\sum_{j=1}^{N} \frac{x_i m_i j_j - x_j m_j j_i}{m_i m_j c D_{ij}} = \nabla x_i - \nabla (\ln T) \sum_{j=1}^{N} \frac{x_i m_i D_{ij}^T - x_j m_j D_{ij}^T}{m_i m_j c D_{ij}}
\] (2.6)

which can be rewritten into mass fractions using

\[
\omega_i = \frac{x_i m_i}{m}; \quad c = \frac{\rho}{m}; \quad m = \sum_{i=1}^{N} x_i m_i
\] (2.7)

This leads to the following Stefan-Maxwell relation on a mass fraction base:

\[
\frac{m}{\rho} \sum_{j=1,j\neq i}^{N} \omega_j \tilde{j}_j - \omega_i \tilde{j}_i = \nabla \omega_i + \omega_i \frac{\nabla m}{m} - \nabla (\ln T) \frac{m}{\rho} \sum_{j=1,j\neq i}^{N} \omega_j D_{ij}^T - \omega_i D_{ii}^T \frac{m_j D_{ij}}{m_{ij} D_{ij}}
\] (2.8)

In order to distinguish between diffusion due to concentration gradients and diffusion due to temperature gradients, diffusion fluxes can be split as:

\[
\tilde{j}_i = \tilde{j}_i^C + \tilde{j}_i^T
\] (2.9)

After rewriting Eq. 2.8 the components break down as:

\[
\tilde{j}_i^T = -D_i^T \nabla (\ln T)
\] (2.10)

\[
\tilde{j}_i^C = -\rho D_i^{SM} \nabla \omega_i - \rho \omega_i D_i^{SM} \frac{\nabla m}{m} - m \omega_i D_i^{SM} \sum_{j=1,j\neq i}^{N} \frac{j_j^C}{m_j D_{ij}}
\] (2.11)

where a diffusion coefficient $D_i^{SM}$ has been defined as:

\[
D_i^{SM} = \left( \sum_{j=1,j\neq i}^{N} \frac{x_i}{D_{ij}} \right)^{-1}
\] (2.12)

The expression for $\tilde{j}_i$ thus obtained, contains a Fick term (first term on right hand side) and two multi-component terms. The binary diffusion coefficient is discussed further below in 2.3. The main advantage is that this equation can be handled numerically in the same way as the transport equations, which is beneficial to the iteration process.

2.3 Transport and thermodynamic properties

Since transport coefficients greatly depend on temperature, pressure and composition of the mixture, models have to be constructed that relate these quantities to
each other. As stated before in 1.2.3, the gases obey the ideal gas law and the density can be calculated straightforward from:

$$\rho = \frac{\rho_m}{RT}$$  \hspace{1cm} (2.13)

For other transport properties the calculations are not as easy and the kinetic gas theory [Bird et al., 1960; Reid and Sherwood, 1966; Hirschfelder et al., 1967] provides good estimates for viscosity, thermal conductivity and binary and thermal diffusion coefficients. The basis of this theory is the interaction potential function $\phi(r)$ as given by the Lennard-Jones potential:

$$\phi(r) = 4\epsilon \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6}$$  \hspace{1cm} (2.14)

This potential function in itself forms the basis for the integral functions $\Omega_\mu$ and $\Omega_D$. The two main parameters in the potential function $\phi(r)$ are $\sigma_i$ and $\epsilon_i/k_B$ for every gas species $i$. Using this theory, commonly referred to as the Chapman-Enskog theory, we find for the viscosity and thermal conductivity of one species $^1$

$$\mu_i = 8.441 \times 10^{-25} \frac{\sqrt{m_i T_i}}{\sigma_i^2 \Omega_\mu (T_i^*)}$$  \hspace{1cm} (2.15)

$$\lambda_i = \left[ \frac{15}{4} + 1.32 \left( \frac{c_p m_i}{R} - \frac{5}{2} \right) \right] \frac{R}{m_i} \mu_i$$  \hspace{1cm} (2.16)

Extending this to the entire mixture we get

$$\mu = \sum_{i=1}^{N} \left( \frac{x_i \mu_i}{\sum_{j=1}^{N} x_j \Phi_{ij}} \right) \text{ with } \Phi_{ij} = \left[ 8 \left( 1 + \frac{m_i}{m_j} \right) \right]^{-\frac{1}{2}} \left[ 1 + \left( \frac{\mu_i}{\mu_j} \right) \frac{1}{2} \left( \frac{m_j}{m_i} \right) \right]^2$$  \hspace{1cm} (2.17)

$$\lambda = \sum_{i=1}^{N} \left( \frac{x_i \lambda_i}{\sum_{j=1}^{N} x_j \Phi_{ij}} \right) \text{ with } \Phi_{ij} = \left[ 8 \left( 1 + \frac{m_i}{m_j} \right) \right]^{-\frac{1}{2}} \left[ 1 + \left( \frac{\lambda_i}{\lambda_j} \right) \frac{1}{2} \left( \frac{m_j}{m_i} \right) \right]^2$$  \hspace{1cm} (2.18)

For the binary diffusion coefficient we have:

$$D_{ij} = 5.88 \times 10^{-24} \frac{T_i^{\frac{3}{2}}}{p_i^\frac{1}{4}(\sigma_i + \sigma_j)^2 \Omega_\rho (T_i^*)} \left( \frac{m_i + m_j}{m_i m_j} \right)^{\frac{1}{2}}$$  \hspace{1cm} (2.19)

Thermal diffusion coefficients can also be calculated from kinetic theory. This leads to elaborate equations, which can be found in literature [C.R. Kleijn in M. Meyappan, 1995].

$$D_{ij}^T = \sum_{j=1,j\neq i}^{N} \rho \omega_i \omega_j D_{ij} a_{ij}$$  \hspace{1cm} (2.20)

For the thermodynamic properties of a large number of gases sufficient data are available in the form of thermodynamic tables and databases, which are correlated

$^1 \text{T}_i = k_B T / \epsilon_i$
2.4. Radiation

through polynomial fits to temperature (as used in the CHEMKIN III package; see 3.1 on page 19):

$$
\frac{C_{p,i}(T)}{R} = a_{1,i} + a_{2,i}T + a_{3,i}T^2 + a_{4,i}T^3 + a_{5,i}T^4
$$

(2.21)

$$
\frac{H_i^0(T)}{RT} = a_{1,i} + \frac{a_{2,i}T}{2} + \frac{a_{3,i}T^2}{3} + \frac{a_{4,i}T^3}{4} + \frac{a_{5,i}T^4}{5} + \frac{a_{6,i}}{T}
$$

(2.22)

$$
\frac{S_i^0(T)}{R} = a_{1,i}\ln(T) + a_{2,i}T + \frac{a_{3,i}T^2}{2} + \frac{a_{4,i}T^3}{3} + \frac{a_{5,i}T^4}{4} + a_{7,i}
$$

(2.23)

These equations are based on the NASA chemical equilibrium code and CHEMKIN database and is more commonly referred to as the JANAF method, named after the rocket engineering department of the US military that developed the theory.

2.4 Radiation

Electromagnetic radiation is emitted by all substances due to the changes in the internal molecular and atomic energy states. One important difference between radiation and other modes of heat transport is that radiation does not use a medium as the carrier of energy. The theory of radiation starts with a blackbody: a perfect emitter and absorber of radiation. It is shown by Planck that the spectral distribution of the emissive power of a blackbody is

$$
E_{\lambda \text{rad}} = \frac{2\pi h c^2}{\lambda^5 \text{rad} \left( e^{(hc/\lambda \text{rad} T)} - 1 \right)}
$$

(2.24)

From this equation it is clear that the energy emitted at all wavelengths increases with temperature and the peak spectral emissive power shifts toward a smaller wavelength as the temperature increases. Integrating this equation over all the wavelengths results in the Stefan-Boltzmann equation:

$$
q_b = \sigma_{SB}T^4
$$

(2.25)

All real substances, however, do not behave as blackbodies, but have a certain emissivity ($\varepsilon_{\text{rad}}$) between 0 and 1. In general, this emissivity is a function of material, surface roughness, wavelength of the radiation and temperature of the surface. If emissivity is assumed the same for all circumstances, this assumption is called 'gray' body radiation.

When radiation is incident on a surface, three things happen: part of the energy is absorbed, part of it transmitted and part of it reflected, characterized by the fraction $\alpha_{\text{rad}}, \tau_{\text{rad}}$ and $\rho_{\text{rad}}$. Naturally:

$$
\alpha_{\text{rad}} + \tau_{\text{rad}} + \rho_{\text{rad}} = 1
$$

(2.26)

If we combine this with Kirchhoff’s law:

$$
total \ radiation = own \ emission + reflection \ foreign \ radiation
$$

(2.27)

$$
q_{t,\text{rad}} = \varepsilon_{\text{rad}} q_{s,\text{rad}} + (1 - \alpha_{\text{rad}}) q_{i,\text{rad}}
$$

(2.28)

$$
etal \ radiation = own \ emission - absorption \ foreign \ radiation
$$

(2.29)

$$
q_{n,\text{rad}} = \varepsilon_{\text{rad}} q_{s,\text{rad}} - \alpha_{\text{rad}} q_{i,\text{rad}}
$$

(2.30)
we find that the emissivity coefficient equals the absorption coefficient, i.e. \( \epsilon_{\text{rad}} = \alpha_{\text{rad}} \) [Beek and Mutzzall, 1972].

To extend these formulas to a set of different surfaces that exchange radiation with each other, view factors \( F_{ij} \) are introduced, which signify what part of the radiation emitted by surface \( i \) is felt by surface \( j \). The method is based on the area of the surfaces involved and the angle between them. This leads to a summation of products of radiation terms and view factors:

\[
\sum_{i=1}^{n} F_{ij} q_{i,\text{rad}} = q_{j,\text{rad}} - \epsilon_j \sigma_B T_j^4 A_j
\]

In more general terms, the heat transfer equation for an emitting-absorbing and scattering gray medium can be written as:

\[
\frac{dI}{ds} = \vec{s} \cdot \nabla I(r, \vec{s}) = -(\kappa_{\text{rad}}(r) + \sigma_{\text{rad}}(r)) I(r, \vec{s}) + \kappa_{\text{rad}}(r) I_b(r) + \frac{\sigma_{\text{rad}}(r)}{4\pi} \int_{\Omega = 4\pi} I(r, \vec{s}^\prime) \Phi(r, \vec{s}, \vec{s}^\prime) d\Omega^\prime
\]

In this equation \( \vec{s} \) is the direction of the propagation of a beam, \( r \) is its present position, \( I \) is the radiation intensity, \( I_b \) is the intensity of the blackbody radiation at the medium temperature, \( \Omega \) is the solid angle (i.e. the projection of one surface onto another) and \( \Phi \) is the phase function of the energy transfer from the incoming \( \vec{s}^\prime \) direction to the outgoing direction \( \vec{s} \) [Modest, 1993]. We see that the change in intensity of a beam, when crossing through a participating medium, is caused by the three terms on the right; absorption and outscattering (\( \kappa \) and \( \sigma \)), emission(\( \kappa I_b \)) and in-scattering(\( \Phi \)) respectively. Once the intensity \( I \) is determined, the total radiative heat flux can be calculated by integrating the intensity over all the solid angles:

\[
q_{t,\text{rad}} = \int_{4\pi} I \vec{n} \cdot \vec{s} \, d\Omega
\]

A number of techniques have been developed to solve this equation, each with its own assumptions:

- **Surface-to-surface method:** Assumes that the optical thickness of the participating medium is very thin and therefore equals the right-hand side of equation 2.32 to zero. This method does not account for semi-transparent solids.

- **Spherical Harmonics Method:** Converts Eq. 2.32 to relatively simple partial differential equations. However, the method is an improvement for optically thick media only. The thinner the medium, the higher the order of the equations becomes and with it the computational effort.

- **Discrete Ordinate Method:** Replaces Eq. 2.32 by a discrete set of equations for a finite number of ordinate directions. The integrals in the radiative heat transfer equation are replaced by a summation over the total number of ordinates. This method is not very accurate for optically thin media and encounters troubles when modeling specular (i.e. non-diffuse) radiation.
• **Monte Carlo method:** A statistically sampling method that treats radiation more in a continuous way (as opposed to the Discrete Ordinate method) by tracing a large number of rays through the discrete control volumes and accounting for the various events (absorption, emission and scattering) occurring in these volumes. Obviously, this method is the most accurate and the most computer-time-consuming.

## 2.5 Chemistry models

As seen earlier on in the thermal energy and species transport equation (2.4 and 2.5), the creation and destruction of species can have a considerable effect on these equations and will therefore be examined in further detail below. Detailed chemistry models have been developed for various CVD processes with varying success. The most accurate models are the ones that consist of a system of elementary reactions, since these are extendable to circumstances beyond the ones in which they are initially tested.

### 2.5.1 Gas-Phase Chemistry

Often, gas-phase chemistry plays a minor role in LPCVD processes and has more impact in APCVD. However, in the model used in this study (see 2.6) the gas-phase reactions produce a highly reactive intermediate which is responsible for most of the $\text{SiO}_2$ deposition and therefore deserves considerable attention. The reaction rates are defined through:

$$R_{k,f}^q = k_{k,f}^q \prod_{i=1}^{N} \sigma_i^{||\nu_{ik}||}, \quad R_{k,b}^q = k_{k,b}^q \prod_{i=1}^{N} \sigma_i^{||\nu_{ik}||}$$  \hspace{1cm} (2.34)

in which $\nu_{ik}$ is the stoichiometric coefficient of the $i^{th}$ species in the $k^{th}$ reaction. The way gas-phase reactions are given in CHEMKIN files (which is the standard way of representation), is that the forward reaction pre-exponential factor ($A_i$), activation energy ($E_a$) and $\beta_k$ are given according to:

$$k_{k,f}^q = A_i T^{\beta_k} \exp \left(-\frac{E_a}{RT}\right)$$  \hspace{1cm} (2.35)

There are modifications of these reactions possible to correct for fall-off behavior like the Lindemann or Tröe form, but since TEOS does not show fall-off behavior until 10 mTorr [Coltrin et al., 2000], these corrections are not relevant. The reverse rates for these reactions are calculated from the equilibrium constant, which in turn is obtained through a straightforward minimization of the Gibbs free energy $^2$:

$$K_k^q(T) = \exp \left(-\frac{\Delta H_k^0 - T \Delta S_k^0(T)}{RT}\right)$$  \hspace{1cm} (2.36)

$$k_{k,b}^q(p,T) = \frac{k_{k,f}^q(p,T)}{K_k^q(T)} \left(\frac{RT}{p^0}\right) \sum_{i=1}^{N} \nu_{ik}$$  \hspace{1cm} (2.37)

$^2$In these equations $\Delta H_k^0$ and $\Delta S_k^0$ are the net change in enthalpy and entropy over a reaction.
2.5.2 Surface Chemistry

Heterogeneous surface reactions are characterized by complex mechanisms consisting of several reaction steps. A detailed description includes adsorption of reactants and intermediates, their decomposition and desorption of reaction products. Thus, these processes must also be reflected in the rate equations by incorporating gas and surface species:

\[
R_{i,f}^t = k_{i,f}^s \prod_{i=1}^{N} p_i^{-\nu_i} \prod_{i=1}^{M} (f_{j}(\theta_j))^{-\mu_j} \quad R_{i,b}^t = k_{i,b}^s \prod_{i=1}^{N} p_i^{\nu_i} \prod_{j=1}^{M} (f_{j}(\theta_j))^{\mu_j} \tag{2.38}
\]

The rate constants in these equations are given in the same manner as gas phase reactions (see Eq. 2.35 on the preceding page). However, to calculate the backward reaction rate, again through the equilibrium, a slightly modified equation holds:

\[
K_f^s(T) = \left( \frac{P_{atm}}{RT} \right) \sum_{i=1}^{N} \nu_i \prod_{k=1}^{m} \left( \Gamma_{m}^0 \right)_{\nu_k} \prod_{j=1}^{M} e^{-\mu_j} \exp \left( -\frac{\Delta H_j^0 - T \Delta S_j^0(T)}{RT} \right) \tag{2.39}
\]

\[
k_{i,b}^s(p,T) = \frac{k_{i,f}^s(p,T)}{K_f^s(T)} \tag{2.40}
\]

in which the sum over the first exponent runs only over the gas-phase species and the sum in the second exponent runs only over surface species in surface phase \(m\) [Coltrin et al., 1996].

A different way of modelling the adsorption is by use of the RSC (see 1.2.2.2). This probability factor \(\gamma\) is usually defined in the same manner (thus by a \(A_i\), a \(\beta_k\) and a \(E_a\)), but they are applied differently:

\[
\gamma_i = \min \left[ 1, \frac{A_i T^{\beta_i} \exp \left( -\frac{E_{a,i}}{RT} \right) }{\Gamma_{tot}^{\gamma_i}} \right] \tag{2.41}
\]

\(^3\) To use these sticking coefficients as reaction rate we can convert these \(\gamma\)'s as:

\[
k_{i,f}^s = \frac{\gamma}{(\Gamma_{tot})^{\sum_{j=1}^{\nu_i} \nu_j}} \sqrt{\frac{RT}{2\pi m_a}} \tag{2.42}
\]

The assumption accompanying Eq. 2.42 is that the coefficient is much smaller than one. If not, the velocity distribution of these gas-phase species becomes skewed near the surface. This non-Maxwellian velocity distribution alters the net species flux near the surface. There are corrections dealing with this [Motz and Wise, 1960], but since this is not the case in the present problem, the equation will be omitted.

2.6 Deposition model for TEOS

TEOS or, more properly, tetra-ethyl-ortho-silicate, is part of the family of alkoxides whose use in deposition of oxides is becoming increasingly important for a number of reasons:

- Relatively low temperatures of deposition are needed to obtain high density films
- Kinetically controlled deposition enables good step coverage and conformality

\(^3\) Of course, the sticking coefficient can never exceed the value of '1', hence the minimum of two values
2.6. Deposition model for TEOS

- Single reactant system
- Safe and less explosive

The first reports of deposition through TEOS came in the early 80's. The deposition turned out to provide excellent step coverage and a good quality of film [Levin and Evans-Lutterodt, 1983; Kern and Rosler, 1977]. As this way of deposition became more important, the emphasis was increasingly put on finding a good understanding of the chemical reactions taking place in this deposition and a lot of studies have been published on this subject [Adams and Capio, 1979; Desu and Kalidindi, 1990; Schloëte et al., 1991; Raupp et al., 1992; McVittie et al., 1993]. The most recent one in this line, is a model developed by Coltrin [Coltrin et al., 2000]. The strength of this model is its applicability to a wide variety of circumstances (e.g. different temperatures and pressures) with fairly good correlation. Through an examination of all the possible reactions and a sensitivity analysis, Coltrin and co-workers came to a model consisting of four homogeneous reactions and eight heterogenous ones.

Gas-Phase reactions

\[
Si(OC_2H_5)_4 \leftrightarrow Si(OH)(OC_2H_5)_3 + C_2H_4
\]

\[
Si(OC_2H_5)_4 + H_2O \leftrightarrow Si(OH)(OC_2H_5)_3 + C_2H_5OH
\]

\[
Si(OH)(OC_2H_5)_3 + Si(OC_2H_5)_4 \leftrightarrow O(Si(OC_2H_5)_3) + C_2H_5OH
\]

\[
2Si(OH)(OC_2H_5)_3 \leftrightarrow O(Si(OC_2H_5)_3) + H_2O
\]

The most important step in this reaction is the thermal decomposition of TEOS: a \( \beta \)-hydride elimination of \( C_2H_4 \), resulting in tri-ethoxy-silanol (from now on referred to as TES). The reason for the relative importance of gas-phase reactions is that TES is the main precursor for deposition of \( SiO_2 \) in this model.

Surface reactions

\[
Si(OC_2H_5)_4 + SiG_3(OH) \leftrightarrow SiO_2(D) + SiGE_3 + C_2H_5OH
\]

\[
SiG_3E \leftrightarrow SiG_3(OH) + C_2H_4
\]

\[
SiG(OH)E_2 \leftrightarrow SiG(OH)_2E + C_2H_4
\]

\[
SiGE_3 \leftrightarrow SiG(OH)E_2 + C_2H_4
\]

\[
SiG(OH)_2E \leftrightarrow SiG_3(OH) + C_2H_5OH
\]

\[
SiG(OH)E_2 \leftrightarrow SiG_3E + C_2H_5OH
\]

\[
SiG(OH)_2E \leftrightarrow SiG_3E + H_2O
\]

\[
Si(OH)(OC_2H_5)_3 + SiG_3(OH) \leftrightarrow SiO_2(D) + SiGE_3 + H_2O
\]

The first and last surface reaction are the sticking reactions leading to deposition of \( SiO_2 \) from TEOS and TES, respectively. The rest of the reactions form a network of surface reactions which serve to replenish the \( SiG_3(OH) \) sites. This site is the site at which the TEOS and TES molecules adhere. A similarity with other models from literature [McVittie et al., 1993; Desu and Kalidindi, 1990] is the existence of a by-product formed from TEOS,

\(^4E\) stands for a surface ethoxy group \((OC_2H_5)_3\), 'G' indicates a glass bond, i.e. a surface silicon atom that is bonded to another silicon atom by an oxygen bond
which has a higher RSC than TEOS itself. In this model this species is thus identified as tri-ethoxysilanol \((Si(OH))(OC_2H_5)_3\). Schematically the surface reaction network can be represented as follows:

![Surface reaction network diagram]

*Figure 2.1: Surface reaction network*

Thanks to a number of reports on thermochemistry [Ho and Melius, 1995] and kinetical experiments [Chu et al., 1995; Herzler et al., 1997] on TEOS and TEOS-related products, combined with molecular beam experiments [Coltrin et al., 2000], some reliable reaction data have been obtained, which can be used to implement the model in the CFD simulations to be conducted.

### 2.7 Unit definition

In the CVD scientific community, it is common to speak about CVD processes in terms of Torr, sccm (or slm) and Å. This will also be the case in this thesis. To provide insight into these units the conversion factors are given below.

First of all, at the low pressures considered, Torr (from Torricelli’s tube) is a more common way of quantifying pressure. The conversion is as follows:

1 bar = 750.063755 Torr, or 1 Pa = 0.007501 Tcrr, or 1 Torr = 133.33 Pa

Conversion of sccm (standard cubic centimetres per minute) to the inlet velocity is a little bit more complex:

\[
\nu_{in} = \frac{10^{-6} \ T \ p^0 \ \phi_{in}}{60 \ T^0 \ p \ A_{in}} = 5.813 \cdot 10^{-4} \phi_{in} \frac{RT}{A_{in} p} \tag{2.43}
\]

in which equation \(\phi_{in}\) is given in sccm and the index '0' refers to standard temperature and pressure. Sccm can also be converted to mol/s using the ideal gas law:

\[
\phi_{in} = \frac{10^{-4} \ P}{60 \ RT} \tag{2.44}
\]

in which the term \(P/RT\) stands for the molar volume at chosen conditions. Finally, the Ångström (indicated as Å) is equal to \(1 \cdot 10^{-10}\) m or 0.1 nm.
Chapter 3

Numerical Tools

The following chapter contains a description of the tools used for modeling purposes, as well as a brief description of the attributes of the A412 multi-wafer LPCVD reactor, the basis of this modeling effort. Consequently, the different 2D and 3D models that are used in the simulations will be treated along with their simplifying assumptions.

3.1 Software

Most of the programs used in this project are to some extent well-known within the CVD modeling scientific community. This is especially true for the software developed by Sandia National Laboratories such as CHEMKIN III, SURFACE CHEMKIN III and SPIN. However, the main modeling task will be conducted in CFD-ACE+, a Computational Fluid Dynamics (CFD) program claimed to be specifically adapted for CVD purposes.

3.1.1 CHEMKIN III and SURFACE CHEMKIN III

The CHEMKIN package’s main purpose is to facilitate the formulation, solution and interpretation of problems involving elementary gas-phase chemical kinetics. It consists of an Interpreter (which reads the user-specified chemical reaction mechanism) and a Gas-Phase Subroutine Library (which is used to link thermodynamic properties, equations of state and chemical production rates). The thermodynamic properties and equations of state are calculated through Eq. 2.21 to 2.23, the production rates are calculated as stated in 2.5 on page 15 and simple files convey the relevant parameters. The SURFACE CHEMKIN package is built up roughly the same and its purpose lies in detailed surface chemistry.

3.1.2 SPIN

The SPIN package is used in combination with CHEMKIN and SURFACE CHEMKIN and TRANSPORT, a program used to evaluate gas-phase multi-component viscosities, thermal conductivities, diffusion coefficients, and thermal diffusion coefficients as described in 2.3 on page 11 [Miller et al., 1986]. SPIN provides species, temperature and velocity
profiles and deposition rates in a steady-state one-dimensional rotating disk or stagnation-point flow CVD reactor. The equations used are the one-dimensional, radially coordinated equivalents of Eq. 2.1 on page 9 to Eq. 2.5 on page 10, except for Eq. 2.4 in which the pressure, Dufour and radiative heat flux term have been grouped in a single source term. The program makes a straightforward and fast examination of the reaction mechanisms in interaction with flow and transport phenomena possible, in a geometry relevant for CVD. In this project it is used to examine the model developed by Coltrin more closely, and identify important and less important reaction paths.

3.1.3 CFD-ACE+

Like most CFD modeling software CFD-ACE+\(^1\) contains a number of sub-programs with their own specific function. In the case of CFD-ACE+ the program is roughly set up as follows: CFD-GEOM is an interactive CAD type geometry creation and fast grid generation

\(^1\)A product of CFD Research Corporation in Huntsville, Alabama, USA
3.2. Model setup

3.2.1 A412 multi-wafer reactor

The reactor under examination is the A412 hot wall multi-wafer LPCVD reactor. The reactor can process all conventional wafer sizes (100-200 mm diameter), but its main advantage is its ability to process 300 mm wafers.

![Figure 3.3: The A412, part of the Advance 400 series](image)

In a simplified manner, the reactor layout consists, from the outer shell moving inwardly, of the following components (see Fig. 3.4 on page 25):

- an outer shell of 5 separate circular heat resistances along the length of the reactor to be able to apply a temperature ramp
- an annulus filled with air to transfer the heat towards the inner reactor wall
- an inner reactorwall made of steel
- an outflow region for the processed gasses
- a steel wall, called the liner, separating the outflow region from the wafer batch
- the actual reaction section in which the wafer batch is located

The wafers are loaded into a boat cage, containing three support beams (see Fig. 3.5 on page 25. This cage is placed vertically on a pedestal, and both the pedestal and the cage are loaded into the reactor. Gases are transferred to the reactor through two perforated tubes, one for the bottom part and one for the top part of the reactor, which supply the
reactant(s) from the side at different heights in the wafer batch. The tubes are located in the dent of the liner (see Fig. 3.5 on page 25). The perforations in the tubes are gradually closer to each other, to compensate for pressure loss and thus decreased flow through these perforations.

The operation sequence follows a set cycle of the following operations:

- Boat insertion: 5 minutes
- Pumpdown: 30 minutes to operating pressure
- Stabilise: 45 minutes
- Actual deposition: around 10 minutes
- Purging: around 20 minutes
- Backfilling: around 20 minutes
- Boat unloading

The reactor is emptied, purged with \( N_2 \) and the sequence starts over again. Every now and then, the reactor walls are cleaned, because of the fact that deposition also takes place there and forms a heat resistance to the radiation.

### 3.2.2 2D Models

Although the hydrodynamics of the reactor influence the overall performance a great deal, some simplifying assumptions have to be made in translating the geometry from real life to the mathematical model, in order to increase speed of the convergence process, while trying to keep the solution as accurate as possible. First of all, for both the 2D and 3D model the front and end geometries have not been taken into account but instead the model boundaries are located at wafer \# 1 and at wafer \# 120. Consequently, the heating elements and outflow region have been omitted as well, meaning that the radial model boundary is located at the liner. In both models the boat tubes are also omitted. Further simplifications in the 2D model involve neglecting irregularities in the liner (i.e. the two 'dents').

Two 2D models are created. The first one has a single inlet in the annular flow region in the bottom of the wafer batch (see bottom of Fig. 3.6 on page 26, referred to from now on as 2DSI). The reason this geometry is used, is because simulations provide a more straightforward (and reactor-like) way of understanding the processes taking place (see section 4.2 on page 33). The second 2D model is one in which the side inlets are modeled as circular slits (inherent to the axisymmetrical nature of the model. This model is referred to as 2DMI (see top of Fig. 3.6 on page 26). Two remarks need to be made:

- In reality, the side inlets are small perforations in a tube, but are now modeled as circular slits. Since the surface area of this slit is much larger than that of a single inlet hole, inlet gas velocities in the 2D model are lower than in reality, and the local disturbance of the velocity and concentration fields may be smaller than in reality (see top 3.6 on page 26).

- In reality the pressure loss in a single inlet tube is compensated for by putting the inlet holes gradually closer to each other. In the model a velocity will be assigned to each inlet which is proportional to the distance to the previous inlet with the constraint that the overall velocity assigned equals the total flow rate.
3.2. Model setup

For modeling conveniences, the side inlets are modeled to be as thick as the wafer and are thus 'assigned' to a certain wafer. In this model inlet nozzles are located at wafer # 10, 21, 29, 36, 42, 47, 51, 55, 59, 62, 70, 80, 89, 96, 101, 106, 110, 114 and 118.

For both models, the liner is modeled as an isothermal boundary. Heat is supplied to the reactor through either specifying a set wafer and wall temperature (isothermal model), or only specifying a wall temperature and including heat transfer through radiation (radiation model). The model dimensions are summarized in table 3.1.

<table>
<thead>
<tr>
<th>Component</th>
<th>Dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wafer radius</td>
<td>0.15 m</td>
</tr>
<tr>
<td>Wafer thickness</td>
<td>0.775 mm</td>
</tr>
<tr>
<td>Interwafer distance</td>
<td>6.86024 mm</td>
</tr>
<tr>
<td>Liner radius</td>
<td>0.186 m</td>
</tr>
<tr>
<td>Reactor length</td>
<td>0.908 m</td>
</tr>
<tr>
<td>Number of wafers</td>
<td>120</td>
</tr>
</tbody>
</table>

Table 3.1: 2D Model dimensions

3.2.3 3D Model

The 3D model here is again a simplified version of the reactor discussed. Improvements over the 2D model are that the asymmetrical features in the liner are incorporated, and that the inlets are more like the ones used in the actual reactor (i.e. holes in stead of slits). Furthermore, the wall is subdivided into three heat resistance zones, to be able to apply a temperature ramp. Dimensions, obviously, remain the same, except for a few additional elements in the model:

<table>
<thead>
<tr>
<th>Component</th>
<th>Dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed tube dent outer radius</td>
<td>0.212 m</td>
</tr>
<tr>
<td>Feed tube dent angle</td>
<td>33 °</td>
</tr>
<tr>
<td>Heat resistance zone # 1</td>
<td>0-0.16 m</td>
</tr>
<tr>
<td>Heat resistance zone # 2</td>
<td>0.16-0.54 m</td>
</tr>
<tr>
<td>Heat resistance zone # 3</td>
<td>0.54-0.91 m</td>
</tr>
</tbody>
</table>

Table 3.2: Additional 3D Model dimensions

3.2.4 Model setting

The physical model settings in CFD-ACE+ are divided among several sections and all have their special attributes that need to be specified.

Problem Type  Specifies which modules need to be activated to obtain the appropriate solution. Main modules in this modeling effort are 'Flow', 'Heat', 'Chemistry' and (where applicable) 'Radiation'.
Table 3.3: Calculation of properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Model</th>
<th>Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density ($\rho$)</td>
<td>Ideal Gas Law</td>
<td>2.13 on page 12</td>
</tr>
<tr>
<td>Viscosity ($\eta$)</td>
<td>Mix Kinetic Theory</td>
<td>2.15 on page 12</td>
</tr>
<tr>
<td>Specific Heat ($c_p$)</td>
<td>Mix JANAF Method</td>
<td>2.21 to 2.23</td>
</tr>
<tr>
<td>Thermal conductivity ($k$)</td>
<td>Mix Kinetic Theory</td>
<td>2.16 on page 12</td>
</tr>
<tr>
<td>Mass Diffusion (D)</td>
<td>Multi-component Diffusion</td>
<td>–</td>
</tr>
<tr>
<td>Conservation of species</td>
<td>Stefan-Maxwell distribution</td>
<td>2.8 on page 11</td>
</tr>
</tbody>
</table>

Model options  Under this tab, the axi-symmetric nature of the 2D model and the steady-state are specified. Furthermore, the reference pressure and gas-phase reaction mechanism are entered here. Gravity forces are set to the appropriate values (zero for isothermal cases). For radiation, the Discrete Ordinates Method (see section 2.4 on page 13) is chosen, and different absorption and emissivity sets are defined. Radiation is set to be 'gray' (i.e. wavelength independent). Finally, the species mass fraction approach is chosen for its applicability to surface reactions, as opposed to a mixture mass fraction approach.

Volume conditions  Specifies ways of calculating properties for different volumes. Possible volume states are 'Fluid', 'Solid' (no flow) and 'Block' (no flow or heat transfer). Properties are calculated as stated in table 3.3. For radiation models, the predefined absorption and emissivity coefficients are assigned to the volumes.

Boundary Conditions  Specifies boundary states (e.g. 'Inlet', 'Outlet', 'Wall', 'Symmetry') along with its properties, such as gas velocity, pressure, temperature, gas composition and radiation parameters. Surface reactions are assigned to the wafer and wall boundaries. For isothermal cases, the wall and wafer temperatures are specified here as well.

Initial Conditions  Sets the starting values for the iterative process. Initial conditions are specified for the entire model and are usually all set to reasonable conditions (e.g. inlet conditions). Sometimes, however, solutions of previously run simulations are used as the starting point to obtain faster convergence.

Solver Control  Governs the different solvers and the parameters involved as well as the solution and solver output. Two important features are specified in this tab: spatial differencing and solver specification. For all simulations run, the 'First order Upwind' scheme is used [Patankar, 1980]. This is the most robust differencing scheme, although not the fastest. The solver used is a Conjugate Gradient Squared with preconditioning solver. Its main advantages over classical iterative methods are suitability for vectorization and lack of user-defined parameters [Saad, 1996].

Run  Runs and controls the simulation and produces information on the convergence process.
Figure 3.4: Horizontal and vertical cross-section of the A412

Figure 3.5: Loading sequence for LPCVD processing
Figure 3.6: 2D models used in simulations

Figure 3.7: 3D model used in simulations
Chapter 4

Results and discussion

In this chapter, the results from simulations are presented and compared with experimentally obtained results. First of all, in section 4.1, the reaction mechanism as proposed by Coltrin is examined in detail by taking a close look at thermodynamics and performing straightforward 1-D simulations using the SPIN package (see subsection 3.1.2 on page 19), to establish the relative importance of each reaction step in the mechanism.
Secondly, in section 4.2 the 2DSI model (see subsection 3.2.2 on page 22) is used to get acquainted with the main program CFD-ACE+, and to perform a first investigation of the reaction mechanism used.
Subsequently, in section 4.3, the reaction mechanism, and variations thereof, are used together with the 2DMI model (see subsection 3.2.2 on page 22) to examine variation in deposition behavior against variations in pressure, TEOS flow rate and temperature.
Finally, in sections 4.4 and 4.5, the study is extended to radiative heat transfer and 3D-simulations, for the reference conditions of 928 K, 0.5 Torr and 200 sccm TEOS flow rate only.

4.1 Preliminary examination of the chemical model

The chemical reaction mechanism for SiO$_2$ LPCVD from TEOS developed by Coltrin consists of four gas-phase reactions and eight surface reactions, all reversible. They are:

\[
\begin{align*}
\text{Si}(OC_2H_5)_4 & \leftrightarrow \text{Si}(OH)(OC_2H_5)_3 + C_2H_4 & G1 \\
\text{Si}(OC_2H_5)_4 + H_2O & \leftrightarrow \text{Si}(OH)(OC_2H_5)_3 + C_2H_5OH & G2 \\
\text{Si}(OH)(OC_2H_5)_3 + \text{Si}(OC_2H_5)_4 & \leftrightarrow O(\text{Si}(OC_2H_5)_3) + C_2H_5OH & G3 \\
2\text{Si}(OH)(OC_2H_5)_3 & \leftrightarrow O(\text{Si}(OC_2H_5)_3) + H_2O & G4
\end{align*}
\]
for the gas-phase reactions, and

\[
\begin{align*}
Si(OC_2H_5)_4 + SiG_3(OH) & \leftrightarrow SiO_2(D) + SiGE_3 + C_2H_5OH & S1 \\
SiG_3E & \leftrightarrow SiG_3(OH) + C_2H_4 & S2 \\
SiG(OH)E_2 & \leftrightarrow SiG(OH)_2E + C_2H_4 & S3 \\
SiGE_3 & \leftrightarrow SiG(OH)E_2 + C_2H_4 & S4 \\
SiG(OH)_3E & \leftrightarrow SiG_3(OH) + C_2H_5OH & S5 \\
SiG(OH)_2E & \leftrightarrow SiG_3E + C_2H_5OH & S6 \\
SiG(OH)_3E & \leftrightarrow SiG_3E + H_2O & S7 \\
Si(OH)(OC_2H_5)_3 + SIG_3(OH) & \leftrightarrow SiO_2(D) + SiGE_3 + H_2O & S8
\end{align*}
\]

for the surface reactions. An examination of this model and its performance is in place to interpret results obtained and trends observed.

### 4.1.1 Thermodynamics

The kinetic parameters of these reactions have been investigated in numerous studies [Chu et al., 1995; Herzler et al., 1997] and the parameters used in the present study, are those stated by Coltrin et al. [Coltrin et al., 2000]. The reaction enthalpy and entropy at the most common process temperature of 928 K were calculated as discussed in Section 2.3 on page 11, with thermodynamical parameters obtained in earlier studies [Ho and Melius, 1995]. The general form of the rate equations is given by Eq. 2.35 on page 15, except for S1 and S8, which are determined by the sticking coefficient and Eq. 2.41 on page 16, based on data obtained through molecular beam experiments [Coltrin et al., 2000].

**Table 4.1: Kinetic and thermodynamical data for Coltrin model**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( A_i )</th>
<th>( \beta )</th>
<th>( E_A ) (kJ/mol)</th>
<th>( \Delta H_r ) (kJ/mol)</th>
<th>( \Delta S_r ) (kJ/mol·K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>( 4.9 \cdot 10^{13} )</td>
<td>0</td>
<td>255</td>
<td>58.1</td>
<td>0.212</td>
</tr>
<tr>
<td>G2</td>
<td>( 1.0 \cdot 10^{11} )</td>
<td>0</td>
<td>100</td>
<td>35.6</td>
<td>0.165</td>
</tr>
<tr>
<td>G3</td>
<td>( 1.0 \cdot 10^{11} )</td>
<td>0</td>
<td>120</td>
<td>200</td>
<td>0.005</td>
</tr>
<tr>
<td>G4</td>
<td>( 1.0 \cdot 10^{11} )</td>
<td>0</td>
<td>120</td>
<td>193</td>
<td>-0.078</td>
</tr>
<tr>
<td>S1*</td>
<td>( 8.75 \cdot 10^{2} )</td>
<td>0</td>
<td>175</td>
<td>-3.45</td>
<td>0.01</td>
</tr>
<tr>
<td>S2</td>
<td>( 1.7 \cdot 10^{12} )</td>
<td>0</td>
<td>195</td>
<td>60</td>
<td>0.147</td>
</tr>
<tr>
<td>S3</td>
<td>( 3.4 \cdot 10^{12} )</td>
<td>0</td>
<td>195</td>
<td>60</td>
<td>0.144</td>
</tr>
<tr>
<td>S4</td>
<td>( 5.1 \cdot 10^{12} )</td>
<td>0</td>
<td>195</td>
<td>60</td>
<td>0.127</td>
</tr>
<tr>
<td>S5</td>
<td>( 2.0 \cdot 10^{12} )</td>
<td>0</td>
<td>183</td>
<td>-27.8</td>
<td>0.146</td>
</tr>
<tr>
<td>S6</td>
<td>( 2.0 \cdot 10^{12} )</td>
<td>0</td>
<td>183</td>
<td>-27.8</td>
<td>0.142</td>
</tr>
<tr>
<td>S7</td>
<td>( 2.0 \cdot 10^{12} )</td>
<td>0</td>
<td>183</td>
<td>-36.0</td>
<td>0.127</td>
</tr>
<tr>
<td>S8*</td>
<td>20</td>
<td>0</td>
<td>50</td>
<td>-9.9</td>
<td>-0.073</td>
</tr>
</tbody>
</table>

* Sticking reaction

From the numbers in Table 4.1 and Fig. 4.1 on page 31, it is clear that a complete cycle of deposition of SiO \(_2\) and replenishment of the SiG \(_3\)OH sites is endothermic. The deposition process has a larger overall heat effect than the gas-phase reactions. Simulations confirmed
4.1. Preliminary examination of the chemical model

this. However, because of the low concentration of the reactants, the overall effect of heats of reaction on temperature will be quite small. This observation is often found in literature, where temperature profiles in reactors are calculated from models based on thermal radiation and solid conduction only, independently of gas composition and flow, since convection, conduction and reactions have a small overall heat effect [Houf et al., 1993; Badgwell et al., 1994].

It is also interesting to notice that the sticking reaction of TES (S8) proceeds in the direction of positive Gibbs free energy (i.e. the equilibrium of S8 lies on the reactant side). H2O will push the reaction in the opposite direction, making H2O a deposition inhibiting by-product. The sticking coefficient of S8 is several orders of magnitude larger than that of S1.

4.1.2 1D simulations

To gain more insight into the deposition behavior of the mechanism proposed by Coltrin, the SPIN package is used to examine the sensitivity of deposition rate to the various reaction steps in a one-dimensional stagnation flow/rotating disk reactor. The reason this program is used, is that, although the SPIN geometry is incomparable to the reactor under examination (compare Fig. 3.1 on page 20 with Fig. 3.6 on page 26), it provides a straightforward tool for determining the relative impact of the separate reaction steps on the overall deposition rate. Simulations are all performed at the reference conditions of 928 K, 0.5 Torr and 200 sccm TEOS flow rate. The rotational speed of the disk is set at 10 revolutions per minute (an arbitrary choice) and the distance between gas entrance and deposition surface is 5 cm. Assuming that no significant reaction takes place under 800 K, we identify a region from the wafer surface upward of 1 cm, in which the temperature is above 800 K and in which it is safe to say that most of the reaction takes place. In this geometry, the sensitivity of the deposition rate to various simplifications of the chemistry model is studied.

First of all, in Table 4.2 the different steps in the gas-phase reaction mechanism are removed one-by-one separately, and the influence is measured on key criteria like deposition rate, surface fraction of the main sticking site (SiG3OH), and TEOS and TES flux to the surface. The same procedure is repeated in Table 4.3 for the surface reactions, but here complete reaction loops are removed. Subsequently, in Table 4.4, the importance of reversibility of surface reactions is investigated.

From Table 4.2 we see that in the gas-phase, the most important step is G1, the decomposition of TEOS into TES and C2H4. In fact, reactions G2-G4 apparently play a minor role, since deposition is not affected by it. The surface reaction loops in Table 4.3 have an influence on deposition rate varying between -20 % to +7 % when compared to the full reaction mechanism and should therefore all be included in the simulation. However, reversibility of surface reactions is only an issue for S8, the sticking reaction of TES (see Table 4.4).

From these one-dimensional simulations, the following conclusions can be drawn:

- G2-G4 can be omitted, when using the reaction mechanism as proposed by Coltrin.
- Only the TES sticking reaction (S8) has to be modeled reversibly, all other surface reactions (S2-S7) can be modeled irreversibly.
- The surface reaction network (see Fig. 4.1 on page 31) can be used to tune the simulated deposition rate to the experimentally established deposition rate by changing the rate parameters of these reactions.
Table 4.2: Spin results for gas-phase reactions

<table>
<thead>
<tr>
<th>Case</th>
<th>Deposition Rate (Å/min)</th>
<th>Surface fraction SiG₃(OH) (-)</th>
<th>TEOS flux (g/cm²s)</th>
<th>TES flux (g/cm²s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Full model</td>
<td>10.32</td>
<td>0.9103</td>
<td>-2.759 · 10⁻⁹</td>
<td>-1.106 · 10⁻⁷</td>
</tr>
<tr>
<td>G1 Removed</td>
<td>2.412</td>
<td>0.998</td>
<td>-3.073 · 10⁻⁹</td>
<td>1.971 · 10⁻⁴</td>
</tr>
<tr>
<td>G2 Removed</td>
<td>10.32</td>
<td>0.9103</td>
<td>-2.759 · 10⁻⁹</td>
<td>-1.106 · 10⁻⁷</td>
</tr>
<tr>
<td>G3 Removed</td>
<td>10.32</td>
<td>0.9103</td>
<td>-2.759 · 10⁻⁹</td>
<td>-1.106 · 10⁻⁷</td>
</tr>
<tr>
<td>G4 Removed</td>
<td>10.32</td>
<td>0.9103</td>
<td>-2.759 · 10⁻⁹</td>
<td>-1.106 · 10⁻⁷</td>
</tr>
<tr>
<td>G2, G3, G4 Removed</td>
<td>10.32</td>
<td>0.9103</td>
<td>-2.759 · 10⁻⁹</td>
<td>-1.106 · 10⁻⁷</td>
</tr>
</tbody>
</table>

Table 4.3: Spin results for surface reactions

<table>
<thead>
<tr>
<th>Case</th>
<th>Deposition Rate (Å/min)</th>
<th>Surface fraction SiG₃(OH) (-)</th>
<th>TEOS flux (g/cm²s)</th>
<th>TES flux (g/cm²s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Full model</td>
<td>10.32</td>
<td>0.9103</td>
<td>-2.759 · 10⁻⁹</td>
<td>-1.106 · 10⁻⁷</td>
</tr>
<tr>
<td>S5, S6 Removed</td>
<td>7.928</td>
<td>0.8982</td>
<td>-2.722 · 10⁻⁹</td>
<td>-8.449 · 10⁻⁸</td>
</tr>
<tr>
<td>S6 Removed</td>
<td>9.121</td>
<td>0.9171</td>
<td>-2.779 · 10⁻⁹</td>
<td>-9.748 · 10⁻⁸</td>
</tr>
<tr>
<td>S5 Removed</td>
<td>9.829</td>
<td>0.9054</td>
<td>-2.743 · 10⁻⁹</td>
<td>-1.058 · 10⁻⁷</td>
</tr>
<tr>
<td>S3, S5, S7 Removed</td>
<td>10.78</td>
<td>0.8962</td>
<td>-2.722 · 10⁻⁹</td>
<td>-1.161 · 10⁻⁷</td>
</tr>
<tr>
<td>S7 Removed</td>
<td>10.91</td>
<td>0.9127</td>
<td>-2.769 · 10⁻⁹</td>
<td>-1.167 · 10⁻⁷</td>
</tr>
<tr>
<td>S2, S6, S7 Removed</td>
<td>11.02</td>
<td>0.9296</td>
<td>-2.824 · 10⁻⁹</td>
<td>-1.182 · 10⁻⁷</td>
</tr>
</tbody>
</table>

Table 4.4: Influence of reversibility of surface reactions

<table>
<thead>
<tr>
<th>Case</th>
<th>Deposition Rate (Å/min)</th>
<th>Surface fraction SiG₃(OH) (-)</th>
<th>TEOS flux (g/cm²s)</th>
<th>TES flux (g/cm²s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Full model</td>
<td>10.32</td>
<td>0.9103</td>
<td>-2.759 · 10⁻⁹</td>
<td>-1.106 · 10⁻⁷</td>
</tr>
<tr>
<td>S1 irreversible</td>
<td>10.32</td>
<td>0.9103</td>
<td>-2.759 · 10⁻⁹</td>
<td>-1.106 · 10⁻⁷</td>
</tr>
<tr>
<td>S2-S7 irreversible</td>
<td>10.32</td>
<td>0.9103</td>
<td>-2.759 · 10⁻⁹</td>
<td>-1.106 · 10⁻⁷</td>
</tr>
<tr>
<td>S8 irreversible</td>
<td>40.23</td>
<td>0.6504</td>
<td>-1.968 · 10⁻⁹</td>
<td>-4.392 · 10⁻⁷</td>
</tr>
</tbody>
</table>

To verify these observations, two simulations were run using the 2DMI model (see subsection 3.2.2 on page 22), one with the full chemistry model, and one with the modifications concerning omission of reaction G2-G4 and irreversibility of reaction S1-S7, as discussed above. The most important variable to look at in comparing these simulations, is the concentration of TES throughout the reactor, since this precursor is mainly responsible for SiO₂ deposition. This is shown in Fig. 4.2 on the facing page. The simulations in Fig. 4.2 suggest that the modifications made to the Coltrin model are valid for this set of circumstances. Based on these observations, reactions G2 to G4 will be omitted and only S8 will be modeled reversibly.¹

To circumvent one shortcoming of CFD-ACE+ (its inability to calculate backward surface reaction rates through minimization of Gibbs energy), the backward reaction rates are calculated by modifying the sticking parameter γ into a conventional reaction rate (using Eq. 2.42), and calculating the backward rate by hand through minimization of Gibbs energy. Doing this at various temperatures, yields a curve from which the pre-exponential rate constant and activation energy for the backward reaction can be calculated (see Fig. 4.3 on page 32.). For the backward sticking reaction of TES (S8s) these values are:

¹Not only TES concentration profiles but all other profiles were identical for the two simulations
4.1. Preliminary examination of the chemical model

Figure 4.1: Surface reaction network.

Figure 4.2: Simulated TES concentration profiles (mol/m$^3$) with full Coltrin model (left) and modified model (right). Simulations run at 200 sccm, 928 K and 0.5 Torr.
$A_{S8} = 1.9 \cdot 10^{20} \text{ m/s}$
$E_A = 127.84 \text{ kJ/mol}$

![Graph showing rates and model parameters for reverse TES sticking reaction.]

*Figure 4.3: Model parameters for reverse TES sticking reaction.*

### 4.1.3 Sensitivity analysis

As stated earlier, removing one reaction or a loop of reactions pushes deposition through the remaining reaction pathways. In order to be able to tune the surface reactions to the experimentally determined deposition rate, the influence of every reaction step on the deposition was investigated by changing the pre-exponential rate constant of each reaction step in the surface reaction mechanism separately and measuring its effect on the deposition rate. From Table 4.5, it is clear that the reaction through which all loops proceed, S4, and the TES sticking reaction, S8, have the biggest influence on deposition, but also TEOS sticking reaction S1 plays a role.

*Table 4.5: Sensitivity analysis of pathways*

<table>
<thead>
<tr>
<th>Reaction</th>
<th>% Response in deposition rate to a 10 % increase in rate constant</th>
<th>% Response in deposition rate to a 10 % decrease in rate constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>1.02</td>
<td>-1.03</td>
</tr>
<tr>
<td>S2</td>
<td>-0.53</td>
<td>0.41</td>
</tr>
<tr>
<td>S3</td>
<td>0.28</td>
<td>-0.32</td>
</tr>
<tr>
<td>S4</td>
<td>4.62</td>
<td>-4.30</td>
</tr>
<tr>
<td>S5</td>
<td>-0.32</td>
<td>0.24</td>
</tr>
<tr>
<td>S6</td>
<td>-0.45</td>
<td>0.32</td>
</tr>
<tr>
<td>S7</td>
<td>0.28</td>
<td>-0.28</td>
</tr>
<tr>
<td>S8</td>
<td>3.17</td>
<td>-3.43</td>
</tr>
</tbody>
</table>
4.2 2D Simulations of the Single Inlet configuration

To test CFD-ACE+ and its various features, the 2DSI model (as discussed in subsection 3.2.2 on page 22) is used together with the modified Coltrin model (as discussed in the previous subsection), but for the gas-phase reactions only (subsection 4.2.1). In subsection 4.2.2, the surface reactions are included in the same model and a first examination of the deposition behavior of this reaction mechanism is made.

4.2.1 Simulations with only gas-phase chemistry

When using gas-phase reaction G1 only, the decrease in TEOS concentrations should be equal to the rise in TES concentration, which in turn should be equal to the rise in $C_2H_4$ concentration. However, it is shown here that certain outlet geometries can produce results in which TES and $C_2H_4$ concentrations deviate from each other and from the converted amount of TEOS significantly.

In Fig. 4.5, the various concentrations profiles are shown for four different combinations of inlet and outlet geometry. Inlet and outlet are either made equal to the annular flow radius (Large Inlet/Outlet; LI/LO) or equal to a small slit in this annular radius (Small Inlet/Outlet; SI/SO), as depicted in Fig. 4.4. This leads to four different possible combinations of inlet and outlet geometry.

![Figure 4.4: Large Inlet-Large Outlet geometry (left) and Small Inlet - Small Outlet geometry (right). Two other possibilities are Large Inlet-Small Outlet (LISO) and Small Inlet-Large Outlet (SILO). Back diffusion and outflow are the important transport phenomena in the outlets.](image)

From Fig. 4.5 on the next page, we see that for the cases with large outlets (SILO and LISO), large discrepancies exist between TES and $C_2H_4$ concentration. Only for the cases with small outlets, the consumption of TEOS is equal to the production of $C_2H_4$ and TES. Part of this can be explained by back diffusion in the reactor (see Fig. 4.4) in combination with the fact that TES and $C_2H_4$ have different diffusion coefficients. A small outlet creates a convective barrier through which no backward diffusion can take place and hence this difference is not observed for small outlet cases (SISO and LISO). Furthermore, we can see that the Small Inlet, Small Outlet case has a much lower conversion than all other cases. Apparently, diffusion through the inlet also plays a role when the inlet is large. Further reduction of the size of the inlet and outlet openings did not lead to any further changes in the concentration profiles.
Chapter 4. Results and discussion

Figure 4.5: Concentration profiles for different I/O geometries. Gas-phase reactions only.

4.2.2 Simulations with gas-phase and surface reactions

To understand the reaction mechanism and its deposition behavior in a, for this study, relevant geometry, simulations are conducted using the 2DSI model, as discussed in section 3.2.2 on page 22. The conditions under which these simulations are performed, are the reference conditions of 928 K, 0.5 Torr and 200 sccm TEOS flow rate. The difference with the simulations ran in subsection 4.2.1, is that surface reactions are now included. In Fig. 4.6 and Fig. 4.7 the concentration profiles are shown for the annular and interwafer region, respectively. Main observations from these figures are:

- In axial direction we see that within the first 50 to 60 wafers TEOS concentration drops and TES concentration rises to a steady concentration (see Fig. 4.6 on the next page).

- In radial direction, for the first 20 wafers the TES concentration increases towards the center and after wafer # 20, the TES concentration decreases towards the wafer center (see Fig. 4.7 on the facing page).

These observations are indicative of the intermediate nature of TES; for low TES concentrations (i.e. in the beginning of the reactor), production in the gas phase exceeds consumption at the surface and the concentration increases. After the concentration reaches a certain level, consumption and production should balance each other out. The reason that the TES concentration decreases slightly in the interwafer region, is because the high surface-to-volume (A/V) ratio is in favor of surface reactions. Concentrations of species created at the surface, such as $C_2H_4$, $C_2H_5OH$ and $H_2O$, rise steadily in concentration moving towards the wafer center.

Looking at the deposition profiles in Fig. 4.8 on page 36, we see that deposition rate decreases moving downstream, whereas radial non-uniformity (indicated by the difference in
4.2. 2D Simulations of the Single Inlet configuration

Figure 4.6: Axial profiles of concentration at wafer edge.

Figure 4.7: Radial profiles of concentration of key components, at wafer # 8, 20 and 60.
deposition rate between center and edge) increases. The decreasing deposition rate is due
to decreasing TEOS concentration, which apparently is not fully compensated for by the
increase of deposition from TES. This means that, although TES is responsible for a large
part of the deposition, TEOS, because of its high concentration, does play an important role
too.
The increase in radial non-uniformity is caused by the radial TES concentration profile. The
concave profile of TES (i.e. high concentration at the center, low concentration at the edge)
in the first wafers, flattens out the strongly convex TEOS profile, leading to a more uniform
deposition profile. However, moving down the wafer batch, the TES profile becomes less
concave and turns to convex after wafer # 23, thereby enhancing the convex deposition
profile and increasing the non-uniformity.

In Table 4.2.2, from the fractional surface coverage shown in the middle column (under
'single spacing'), we see that the surface site to which TEOS and TES adhere, is by far the
most abundant one. Variation across the wafer in SiG3OH coverage is +/- 0.9 %.

<table>
<thead>
<tr>
<th>Species</th>
<th>Single Spacing</th>
<th>Double Spacing</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiG3(OH)</td>
<td>0.959</td>
<td>0.914</td>
</tr>
<tr>
<td>SiG3E</td>
<td>0.025</td>
<td>0.055</td>
</tr>
<tr>
<td>SiGE3</td>
<td>0.010</td>
<td>0.021</td>
</tr>
<tr>
<td>SiG(OH)E2</td>
<td>0.05</td>
<td>0.08</td>
</tr>
<tr>
<td>SiG(OH)2E</td>
<td>0.01</td>
<td>0.02</td>
</tr>
</tbody>
</table>

For reaction mechanisms, in which an intermediate leading to deposition is formed in the
gas-phase and consumed at the surface, the surface-to-volume-ratio (A/V) in the reactor is
an important variable. In regions where A/V is low (e.g. near edges), the deposition rate
will be high, and vice versa. Therefore, it is interesting to see how the deposition process
discussed above, changes when the interwafer distance is doubled and the number of wafers thus decreased to 60. Again, axial and radial profiles of concentration are shown in Fig. 4.9 and 4.10, respectively, which should be compared to Fig. 4.6 on page 35 and 4.7 on page 35 for single-spaced wafers. The main differences are:

- Concentrations change continuously in the double spaced system to much higher (or lower, for TEOS; see Fig. 4.9) levels, whereas concentrations of gas-phase species rise more rapidly in the closer spaced system, but level off after a certain wafer number (see subsection 4.2.3 on page 39 for a detailed discussion).
- The only gas species that has not risen in concentration is \( \text{C}_2\text{H}_5\text{OH} \), the main by-product of TEOS sticking, suggesting that the increased TEOS conversion is mainly taking place in the gas-phase (as expected).
- The TES concentration profile never becomes convex in the entire reactor (see Fig. 4.10 on the next page.)

![Figure 4.9: Axial profiles of concentration at wafer edge for system with double wafer spacing.](image)

The deposition profiles in Fig. 4.11 on the following page show that there is a changeover from concave to convex around wafer # 18. This deposition behavior is, again, the net result of TES and TEOS sticking, and can be explained as follows: at the low concentrations of TES within the first 20 wafers, the concentration of TES increases much faster towards the wafer center than in the closer spaced system, because of the decreased A/V. TEOS concentration on the other hand, decreases slower, because of less sticking. The net result is a much stronger concave TES profile and a less convex TEOS profile, leading to a concave deposition profile. After wafer # 20, the concentration of TES has risen and production of TES in the interwafer region is less strong than in the first wafers. On the other hand, the increased TES concentration leads to increased deposition. Overall, the radial profiles of TES concentration flatten out, leading to an increasingly convex deposition profile.

This deposition behavior is not unknown. Studies have shown that concave deposition profiles are possible for some circumstances [Yeckel and Middleman, 1990] and that the A/V ratio can be used to influence the radial non-uniformity [Hitchman and Kane, 1981], but also for this particular reactor the same trend has been observed experimentally [Ter Horst and Oosterlaken, 2001].
Figure 4.10: Radial profiles of concentration of key components at wafer # 2, 9, 18 and 50 for system with double wafer spacing.

Figure 4.11: Deposition profile along the wafer batch for selected wafers in the system with double wafer spacing.
It is interesting to see that an increased deposition rate, as found for the system with double wafer spacing, is accompanied by a lower fractional surface coverage of the main adsorption site, $SiG_3(OH)$, as shown in the last column of Table 4.2.2.

### 4.2.3 Convective and diffusive transport

Looking at Fig. 4.6 on page 35, it seems strange that concentration profiles for TEOS and TES become flat; this would mean that no deposition would take place. If we calculate how much Si is needed to reach a deposition rate of 10 Å/minute on a single wafer, we find that this is already reached by $9.14 \cdot 10^{-5}$ mmol per wafer per second, or 0.011 mmol per batch per second. If this is compared to the 200 sccm TEOS that is fed to the reactor, which is equal to 0.14 mmol/s, we see that deposition consumes around 8% of the total amount of silicon fed to the reactor. Although the axial profiles of concentration become flat, deposition can very well still take place. Consequently, the large drop in TEOS concentration in the beginning of the reactor must thus be attributed to gas-phase decomposition of TEOS (reaction G1).

![Figure 4.12: Axial concentration profiles for silicon and oxygen, calculated from Fig. 4.6 on page 35.](image)

Now, if we convert the axial concentration profiles shown in Fig. 4.6 on page 35 to concentration profiles for elemental silicon (the sum of TEOS and TES concentration) and oxygen as is done in Fig. 4.12, we find that concentration of silicon drops from 8.6 mmol/m$^3$ to 5.4 mmol/m$^3$, much more than what is needed for deposition for the entire batch (0.011 mmol per batch per second). However, the concentration needs to be corrected for the different velocities in inlet and outlet, caused by acceleration through net gas production. We find for the inlet and outlet gas velocities 12.09 m/s and 18.12 m/s respectively, and these figures should comply to the overall mass balance for Si over the reactor:

$$v_{in}C_{in} = v_{out}C_{out} + \text{total deposition} \quad (4.1)$$

From the equation above we find a total deposition of 0.0129 mmol per batch per second, as opposed to the calculated deposited amount of 0.011 mmol. The discrepancy can be because deposition on the walls (1.06 m$^2$) was not considered in the calculation.

When we compare the axial concentration profiles in the systems for single and double wafer spacing (see Fig. 4.6 on page 35 and Fig. 4.9 on page 37 respectively), we already
made the observation that for the single spaced system the intermediate concentrations rise more rapidly but level off after a certain wafer number, whereas the concentrations in the double spaced system change slower, but continuously to higher (or lower for TEOS) levels. Although the A/V ratio is lower in the system with double wafer spacing and might thus favor gas-phase decomposition of TEOS more than in the system with single wafer spacing, it is strange that the profiles do not become constant.

An explanation can be, that instead of the concentrations, the concentration gradients tell us more about the deposition process in the reactor. Strong concentration gradients, as found in the case of double wafer spacing, could be an indication of high deposition rates. If we zoom in on an interwafer/annular region in the reactor (see Fig. 4.13) and neglect convective transport because of the low Péclet number in the annular zone, at first instance, we see that the difference between fluxes $J_{x,i}$ and $J_{x,i+1}$ must be equal to the total deposition in that particular interwafer region. Since the system with double wafer spacing has higher deposition rates (nearly twice as high), the difference between the fluxes in the annular region must be larger than in the system with single wafer spacing. In other words, because of the higher deposition rate the concentration gradient in the case of double wafer spacing must be larger than for single wafer spacing. This, together with an increased gas-phase decomposition, can explain the larger overall increase (or drop for TEOS) in concentration. The assumption of absence of convective transport is not entirely valid, since Péclet numbers are around unity, meaning that convection and diffusion contribute equally. The convection increases the concentration gradient for TEOS and decreases it for other species because of its set direction.

![Figure 4.13: Schematic representation of a wafer/annulus region](image-url)
4.3 Model validation

The ultimate goal in this project is to first reach compliance between simulations and experimental results, and second, to use the validated model to predict ideal deposition circumstances and investigate in detail the deposition mechanism. The first part, the validation, will be conducted using experimental results provided by ASM International. The experimental results were taken from their own A412 reactor under varying circumstances. The cases tested are listed in Table 4.7. For the Reynolds and Péclet number the velocity in the annular region and the distance between annulus and wafer edge are taken. For the Damköhler number the sticking coefficients of TEOS and TES (reactions S1 and S8) are calculated into a conventional rate constant (using Eq. 2.42 on page 16) and the characteristic dimension is the wafer spacing distance. For the listed cases, detailed deposition data

<table>
<thead>
<tr>
<th>Case</th>
<th>P (mTorr)</th>
<th>$\Phi_{TEOS}^2$ (sccm)</th>
<th>T (K)</th>
<th>Kn (-)</th>
<th>Re (-)</th>
<th>Pe (-)</th>
<th>$Da_{S1}$ (-)</th>
<th>$Da_{S8}$ (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>500</td>
<td>200</td>
<td>928</td>
<td>1.30 $\cdot$ 10^{-2}</td>
<td>4.6</td>
<td>2.0</td>
<td>1.0 $\cdot$ 10^{-2}</td>
<td>2.8 $\cdot$ 10^2</td>
</tr>
<tr>
<td>$\Phi$</td>
<td>500</td>
<td>50</td>
<td>928</td>
<td>1.30 $\cdot$ 10^{-2}</td>
<td>1.9</td>
<td>0.8</td>
<td>1.0 $\cdot$ 10^{-2}</td>
<td>2.8 $\cdot$ 10^2</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>100</td>
<td>928</td>
<td>1.30 $\cdot$ 10^{-2}</td>
<td>3.4</td>
<td>1.5</td>
<td>1.0 $\cdot$ 10^{-2}</td>
<td>2.8 $\cdot$ 10^2</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>300</td>
<td>928</td>
<td>1.30 $\cdot$ 10^{-2}</td>
<td>6.2</td>
<td>2.7</td>
<td>1.0 $\cdot$ 10^{-2}</td>
<td>2.8 $\cdot$ 10^2</td>
</tr>
<tr>
<td>P</td>
<td>250</td>
<td>200</td>
<td>928</td>
<td>2.60 $\cdot$ 10^{-2}</td>
<td>4.6</td>
<td>2.0</td>
<td>5.2 $\cdot$ 10^{-3}</td>
<td>1.4 $\cdot$ 10^2</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>200</td>
<td>928</td>
<td>8.66 $\cdot$ 10^{-3}</td>
<td>4.6</td>
<td>2.0</td>
<td>1.6 $\cdot$ 10^{-2}</td>
<td>4.2 $\cdot$ 10^2</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>200</td>
<td>928</td>
<td>6.45 $\cdot$ 10^{-3}</td>
<td>4.6</td>
<td>2.0</td>
<td>2.1 $\cdot$ 10^{-2}</td>
<td>5.6 $\cdot$ 10^2</td>
</tr>
<tr>
<td></td>
<td>1500</td>
<td>200</td>
<td>928</td>
<td>4.31 $\cdot$ 10^{-3}</td>
<td>4.6</td>
<td>2.0</td>
<td>3.1 $\cdot$ 10^{-2}</td>
<td>8.4 $\cdot$ 10^2</td>
</tr>
<tr>
<td>T</td>
<td>500</td>
<td>200</td>
<td>903</td>
<td>1.26 $\cdot$ 10^{-3}</td>
<td>4.6</td>
<td>2.0</td>
<td>5.5 $\cdot$ 10^{-3}</td>
<td>2.3 $\cdot$ 10^2</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>200</td>
<td>953</td>
<td>1.33 $\cdot$ 10^{-2}</td>
<td>4.6</td>
<td>2.0</td>
<td>1.9 $\cdot$ 10^{-2}</td>
<td>3.3 $\cdot$ 10^2</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>200</td>
<td>978</td>
<td>1.37 $\cdot$ 10^{-2}</td>
<td>4.6</td>
<td>2.0</td>
<td>3.4 $\cdot$ 10^{-2}</td>
<td>4.0 $\cdot$ 10^2</td>
</tr>
</tbody>
</table>

is available for wafer numbers 16, 41, 66, 91 and 116 out of a batch of 120 wafers. Two remarks must be made about comparing simulation results and experimental data:

- Experimental results available are film thicknesses obtained after 10 minutes of deposition, which will have to be calculated back on a rate per minute. Any transients in these results will not be present in simulations.
- The simulations are all performed at a set temperature, whereas the experiments are conducted in a reactor with temperature gradients of around 5 to 10 K. The set temperature in the simulation is the average of the experimental reactor temperatures.

4.3.1 Model parameter fitting

When running the model at the reference conditions of 928 K, 500 mTorr, 200 sccm TEOS flow rate and 20 sccm $N_2$ flow rate, it is observed from Fig. 4.14 on the following page that the simulated results lead to structurally lower deposition rates (in the order of 10 Å/min) as compared to experimental data (which is around 20 Å/min), a deviation of almost 50 %. In Coltrin’s own work it is also shown that discrepancies exist in the reaction mechanism used when comparing simulations to experimental results, as can be seen in the same picture. Here, results are presented for a LPCVD reactor operating at approximately 0.2 Torr, but
at a much higher temperature. Although the relative difference here is much smaller ($\approx 12\%-15\%$), simulations also predict lower deposition rates than experimental results. This example, but also other studies [Labun et al., 2000; Cale et al., 2000], show that the reaction mechanism as proposed provides good correlation, but still needs further refinement. For the present study, the refinement will be sought in changing the pre-exponential rate constants of the surface reactions.

As stated in the sensitivity analysis (see Section 4.1.2 on page 29), three reaction steps are very distinct in their influence on the overall deposition rate, and these will be fitted one-by-one separately to the reference conditions through trial-and-error. Doing so, we now have five different reaction mechanisms and it is in place to define these mechanisms, as is shown in Table 4.3.1. A detailed description of the fitted models follows below:

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Modifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coltrin</td>
<td>Mechanism as found in literature [Coltrin et al., 2000]</td>
</tr>
<tr>
<td>Modified Coltrin</td>
<td>Reactions G2-G4 omitted and reactions S1-S7 modeled irreversibly</td>
</tr>
<tr>
<td>Modified S1</td>
<td>Same as 'Modified Coltrin' but with pre-exponential constant S1 fitted to experimental deposition rates</td>
</tr>
<tr>
<td>Modified S4</td>
<td>Same as 'Modified Coltrin' but with pre-exponential constant S4 fitted to experimental deposition rates</td>
</tr>
<tr>
<td>Modified S8</td>
<td>Same as 'Modified Coltrin' but with pre-exponential constant of the backward reaction of reaction S8 fitted to experimental deposition rates</td>
</tr>
</tbody>
</table>

**Table 4.8: Overview of reaction mechanism and modifications thereof**

S8 For reaction S8 (the sticking of TES), the reverse reaction rate constant is changed. This pre-exponential constant is chosen because it is not experimentally obtained, but calculated from other parameters. The value thus obtained is $5.1 \cdot 10^{19} \text{ m/s}$, rather than the calculated value of $1.9 \cdot 10^{20} \text{ m/s}$ stated in subsection 4.1.2.

It is possible to calculate this change back to a difference in the exponential term of Eq. 2.39 on page 16, i.e. the change in Gibbs free energy over reaction S8. A decrease in pre-exponential rate constant to roughly 25\% of its value, means a 10.7 kJ increase in the term.
4.3. Model validation

\[ (\Delta H - T\Delta S) \]. Since five species are involved in this reaction, an error in enthalpy of 2 kJ is not only plausible, but also beyond the accuracy of current measuring devices and theoretical prediction methods. Furthermore, since TES is a reactive intermediate, produced by TEOS, Coltrin had difficulty performing molecular beam experiments with pure TES. He finally tackled the problem by fitting hot and cold molecular beam data and assuming the difference between the two experiments is due to TES. Although this is the only way to do it, it is obviously not the most accurate way, and deviations are found in his own work as well [Coltrin et al., 2000].

\[ S1 \] Alternatively, to reach a fit through modification of the TEOS sticking coefficient, the pre-exponential constant was increased from $8.8 \cdot 10^8 \text{ [-]}$ to $7.9 \cdot 10^4 \text{ [-]}$.

\[ S4 \] As can be expected, the reaction step, through which all cycles leading to deposition and replenishment proceed, can have a considerable influence on the overall deposition rate. In this case, the pre-exponential constant of S4 has been increased from $5.1 \cdot 10^{12} \text{ m/s}$ to $2.04 \cdot 10^{13} \text{ m/s}$ to match the experimental results at reference conditions.

In the remaining section, the three models discussed above (i.e. 'Modified S8' or 'Modified S1' or 'Modified S4') will all be used in simulations under the circumstances listed in Table 4.7 on page 41. In other words, for each set of pressures, flow rates and temperatures, three simulations will be performed and each of these simulations will be compared to the experimentally obtained results.

4.3.2 Simulations with modified TES sticking

Below are presented the results for the various cases described in Table 4.7 on page 41 using the 'Modified S8' model.

4.3.2.1 Deposition rate as a function of total pressure

Performing the simulations for the various pressure data, we can see in Fig. 4.16 on page 45 a clear rise in deposition rate with pressure. Not surprising, higher pressures lead to higher concentrations of TEOS and TES, and thus to higher deposition, a trend also found in experimental data. For high pressures, the simulations show lower deposition rates than experiments. Higher pressures lead to higher concentrations, and thus higher deposition rates, but high pressures could also lead to surface site saturation, which could explain the non-linear behavior found in simulations and experiments.

Looking at the deposition profiles across a single batch in Fig. 4.15 on the next page we see that deposition rate first decreases and then increases moving down the wafer batch. This trend is also observed in experiments, and might suggest that the nozzle spacing has not been optimally designed. A second indication is the concentration profile (see appendix I), which shows an uneven concentration throughout the reactor. Subsequently, the concentration profiles explain why radial non-uniformity and deposition rate increase with pressure.

An important criterion for LPCVD processes is the radial non-uniformity, which can be expressed through the intrawafer standard deviation of the wafer thickness. Radial non-uniformity can be attributed to a variety of factors [Hitchman and Kane, 1981]:
Figure 4.15: Radial deposition profiles for a single batch at 928 K, 0.5 Torr and 200 sccm TEOS flow rate, for selected wafers.

- Low diffusivity and/or high surface reaction rates, leading to interwafer reactant depletion.
- Radial temperature variations.
- Wall effects (common in cases with reactive intermediates) through the A/V ratio, since the intermediate production is linear with V and its consumption linear with A. This effect can manifest itself through the boat tubes, that support the wafers, and which can decrease deposition on the edge of the wafer making deposition profiles more uniform.
- Growth inhibition due to by-products building up between wafers.

The high Damköhler numbers for TES sticking, suggest that the radial transport limitations for TES diffusion are the main factors affecting uniformity. TEOS sticking on the other hand seems to be kinetically limited. Furthermore, also by-product inhibition by H₂O may play a role. Radial temperature differences do not seem to be a plausible cause for radial variations in experimental growth rates, and are of course absent in the simulations.

The trends in standard deviation seen in Fig. 4.16 on the facing page can be interpreted in terms of the Damköhler number. The decreased diffusion increases the transport limitation and thus leads to an increased radial non-uniformity (larger Damköhler number).
Figure 4.16: Variation of growth rate and standard deviation of film thickness with pressure, for modified S8.
4.3.2.2 Deposition rate as a function of TEOS flow rate

In Fig. 4.17 on the next page it is shown that growth rate increases with flow rate. When TEOS flow rate is increased (and \( N_2 \) flow rate is kept constant), the dilution of TEOS is reduced. In contrast, an increase in flow rate leads to a decrease in residence time, and thus lower conversion of TEOS to TES, and lower deposition. Since both experiment and simulation show a positive trend, the reduced dilution is more predominant than the lowered residence time. Simulations give higher deposition rates than experiments for low and high flow rates.

The concentration profiles (see appendix) confirm the observation that radial non-uniformity decreases with increasing flow rate, meaning that the concentration becomes more even throughout an interwafer region.

In theory, the non-uniformity should remain unchanged, since the Damköhler number remains unaffected. From Fig. 4.17 on the facing page we see this is clearly not the case. One explanation can be that decreasing the flow rate leads to an increased residence time in the annular region and thus a higher TES concentration. The higher TES concentration in the annulus, and thus at the edge of the wafer, leads to more deposition from TES, which is transport limited according to the high Damköhler numbers, and less from TEOS, which is kinetically limited. Both effects lead to a less uniform deposition profile for lower flow rates.

4.3.2.3 Deposition rate as a function of temperature

The temperature results show a very good resemblance between simulation and experiment, meaning that the temperature dependency of deposition is adequately described by the model. The largest effect of increasing the temperature is that the rate constants are increased (especially for the surface sticking reactions), leading to a strongly increased non-uniformity and deposition rate.

The high deposition rates (\( \Delta 50 \, \text{Å} \)) are not caused by high TEOS and TES concentrations\(^3\), but because the sticking coefficient of reactions S1 and S8 (i.e. TEOS and TES sticking respectively) is strongly increased. This means that the process is still very much kinetically limited and that increasing concentration of reactants in the reactor by increasing pressure or flow rate has a small effect on deposition rate.

4.3.3 Simulations with modified TEOS sticking

Below are presented the results for the various cases described in Table 4.7 on page 41, using the 'Modified S1' model.

4.3.3.1 Deposition rate as a function of total pressure

Comparing Fig. 4.19 on page 49 to Fig. 4.16 on the page before, it is clear that the 'Modified S1' model exhibits a much larger pressure dependence than the 'Modified S8' model. While

\(^3\)Compare in Appendix 1 the concentration profiles for the pressure cases and the temperature cases
Figure 4.17: Variation of growth rate and standard deviation of film thickness with flow, for modified S8
Figure 4.18: Variation of growth rate and standard deviation of film thickness with temperature for modified S8
results for reference conditions are close to experimental results, results at lower and higher pressure are off. However, the linear trend is more like the experimentally found trend, as opposed to the case for modifying TES sticking (see Fig. 4.16 on page 45, where the curve levels off for high pressure).

The results for standard deviation are comparable to the results shown in Fig. 4.16 on page 45, which can suggest that deviations from experimental results is caused by other effects than TEOS and TES sticking. Also the high standard deviation for wafer # 16 and 166 is likely to be caused from difference in top and bottom zones between the model and the actual reactor.

![Graphs showing deposition rate and standard deviation vs. pressure](image)

*Figure 4.19: Variation of growth rate and standard deviation of film thickness with pressure, for modified S1.*

### 4.3.3.2 Deposition rate as a function of TEOS flow rate

The average growth rate results in Fig. 4.20 on the following page for variation of flow rate, show that the results are close to the experimental results for low flow rates, but not much
closer than for the 'Modified S8' model in Fig. 4.17 on page 47. However, results deviate significantly for higher flow rates. Obviously, the decreased residence time, a direct result of increasing the flow rate, results in a high concentration of TEOS which results in higher predicted deposition, now that the sticking coefficient for TEOS has been increased when compared to Fig. 4.17 on page 47.

The high TEOS concentration for high flow rates leads to an increase in standard deviation, as can be seen in Fig. 4.20 which is in better agreement with the experimental results than for the 'Modified S1 model' (see 4.17 on page 47).

![Graphs showing deposition rate and standard deviation](image)

*Figure 4.20: Variation of growth rate and standard deviation of film thickness with flow for modified S1.*

### 4.3.3.3 Deposition rate as a function of temperature

The same observations made for the variation of growth rate with flow rate can be made when looking at Fig. 4.21 on the next page. Growth rates are not as accurately predicted as by the 'Modified S8' model in Fig. 4.18 on page 48, but trends in standard deviation are...
in better agreement with the experimental results.

Figure 4.21: Variation of growth rate and standard deviation of film thickness with temperature for modified S1.

4.3.4 Simulations with modified S4

Below are presented the results for the various cases described in Table 4.7 on page 41 using the 'Modified S4' model.

4.3.4.1 Deposition rate as a function of total pressure

The results stated in Fig. 4.22 on the following page shows fairly good correlation between experiments and simulation, comparable to the agreement obtained in Fig. 4.16 on page 45. The same can be said when looking at the results about standard deviation.
Figure 4.22: Variation of growth rate and standard deviation of film thickness with pressure, for modified S4.
4.3.4.2 Deposition rate as a function of TEOS flow rate

The results in Fig. 4.23 show that deposition rate, when using the 'Modified S4' model, is more or less invariant to variations in flow rate. In other words, although the ratio of TEOS to TES concentration might change due to a change in annular residence time, each ratio results in more or less the same deposition rate. Results for variation in standard deviation are comparable to 4.17 on page 47.

![Deposition rate graphs](image)

*Figure 4.23: Variation of growth rate and standard deviation of film thickness with flow, for modified S4.*

4.3.4.3 Deposition rate as a function of temperature

As is the case when using the 'Modified S8' mode, the correlation between simulations and experiments shown in Fig. ?? on page ?? is very good and even slightly better. The standard deviation indicates the same trends as experiments.
Figure 4.24: Variation of growth rate and standard deviation of film thickness with temperature, for modified S4.
4.3.5 Modified models compared

The simulations above were conducted using different chemical models, each differing one rate parameter from the 'Modified Coltrin' model, to establish which model predicts experimental behavior most accurately. It is fair to say that the 'Modified S8' model is the most accurate one. For the 'Modified S1' model we find strong deviations from experimental results in the growth rate against pressure (see Fig. 4.19 on page 49, and moderate deviations against flow rate and temperature (see Fig. 4.20 on page 50 and Fig. 4.21 on page 51 respectively). Strong similarities exist between the 'Modified S8' model and the 'Modified S4' model, but the flow invariance exhibited in Fig. 4.23 on page 53 and accompanying deviations from experimental results, indicate that the 'Modified S8' model is the one model out of the three possible modified models, on which future simulations should be based.

4.4 Radiation

Until now, simulations have been run using isothermal boundary conditions for the reactor. In reality the temperature is not even throughout the reactor, but gradients exist, which are determined by radiative heat transfer and solid conduction in reactor wall and wafers. To gain some more insight in this process, a first investigation is conducted here using radiation and conduction to determine temperature profiles, instead of isothermal conditions. When running simulations with radiative heat transfer, a few choices have to be made about the radiative properties.

First of all a choice had to be made about whether or not radiation is specular or diffuse. Although studies have been performed in which the difference in performance between a diffuse and a specular approach is minimal [Coronel and Jensen, 1994], the full-scale reactor model is most accurately when specular reflection is included, at the cost of more computational effort. For an examination of radiative heat transfer however, the less time-consuming diffuse approach is used.

Furthermore, the radiative properties can be wavelength dependent (i.e. non-gray) or not. This, in turn, is of course dependent on the properties of the materials used. For the silicon wafer, the emissivity becomes constant with a value of 0.68 for the wavelengths involved in radiation from liner to wafer (i.e. 1.2 to 10 μm) [Badgwell et al., 1994] above a temperature of 600 °C.

The liner is a quartz tube with an emissivity of 0.95, which remains nearly constant over the wavelength range used. Gases can absorb radiation and use the energy to change vibrational or rotational energy. The attenuation (κ) thus achieved in a gas is proportional to the collision between molecules and photons, which in its turn is proportional to the density of gases (ρ ∝ p/T) and their average molecular speed (v ∝ √T). Absorption is related to the attenuation factor through:

\[ \alpha_{rad} = 1 - e^{-\kappa s} \]  

(4.2)

in which s is the distance traveled through the medium. A molecule like TEOS has many degrees of rotational and vibrational freedom (also manifest in its low fall-off pressure), and therefore might be quite susceptible to radiation. Since no data is available for TEOS, data will be used taken from similar molecules like ethene, ethanol and silicon dioxide. Average absorption factors for these species at 300 K and 1 bar are around 0.05 to 0.3 m⁻¹, resulting in attenuation factors of 0.03 to 0.35 using Eq. 4.2, for the characteristic distance from reactor wall to wafer edge of 3.6 cm. Correcting this to 928 K and 0.5 Torr (0.0004
bar), through collision proportionalities stated above, the attenuation factor at these new conditions becomes 0.0002 m$^{-1}$, meaning that absorption at these conditions is next to non-existent. It is therefore safe to say that the fluid can be treated as a transparent, and thus wavelength independent, medium.

From these considerations it is clear that for our case the radiative heat transfer process can be treated as wavelength independent (i.e. gray).

For the diffuse, gray approximation (solved by the Discrete Ordinates Method) we find that operation is almost completely isothermal and therefore not much different to the situations discussed in the previous section. A probable cause is the way the inlets are defined; by modeling the inlets all around, the velocity through each nozzle is lowered, leading to smaller heat-up lengths. If it is initially assumed that the inlet velocity does not decrease and penetration theory is used to calculate the heat up length using the term $\sqrt{\pi \nu t}$, it is found that over 15 mm the temperature difference between the gas inlet and its surroundings drops to 20% of its original value. Furthermore, penetration theory for momentum (using $\sqrt{\pi \nu t}$) the velocity of the jet drops to 20% of its value over a distance of 12 cm. Since the distance from inlet to wafer edge is 3.6 cm, it is plausible that the temperature difference between gas and surroundings are long gone before the gas reaches the wafer (an observation made in other studies as well [Roenigk and Jensen, 1987]). This effect is visualised in simulations in Fig. 4.25. From this simulation and the consideration

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure4.25.png}
\caption{Temperature profile for 2D model with radiative heat transfer. Temperature of feed set at 300 K}
\end{figure}

stated above, it is clear that this particular 2-dimensional geometry is unsuitable to examine the effect of temperature radiations on radial non-uniformities. Non-uniformity can thus be attributed to gas flow only, which is, as stated in subsection 4.1.1., negligible.
4.5 3D simulation

In this section 3-dimensional simulations are performed to investigate the effect of the inlet jets on the overall performance of the reactor. The three dimensional model as described in section 3.2.3 on page 23 is used to reproduce results at the reference case of 928 K, 0.5 Torr and 200 sccm TEOS flow rate and 20 sccm N₂. In this simulation the 'Modified S8' model is used. Any difference between the 2- and 3-dimensional case should be interpreted in terms of the irregularities in the liner and, more importantly, the jet effects, both in velocity and concentration, of the inlet nozzles (see subsection 3.2.2 on page 22).

In Figs 4.26 to 4.28, the concentration profiles show strong radial variation and, hence, the deposition profiles have also strong radial variations. Concentrations and deposition rate are very similar to those found using the 2D model (see Appendix 1 and Fig. 4.16 on page 45).

The large, almost linearly varying, concentration differences over the wafer surfaces ob-

![Figure 4.26: Concentration profiles for TES and TEOS.](image)

viously caused by the asymmetrical inlet geometry, are counteracted by rotating the wafer batch, and thus radially averaging the concentration and deposition profiles over the wafer. To take this rotation into account in the simulations, radial averaging over the wafer can be performed numerically. The results are shown in Fig. 4.29 on page 59, where also a comparison is made with experimental results. The main observation is that the averaged deposition profiles are much flatter (and thus much more uniform) than the experimentally obtained profiles. This could be an indication that the rotational speed of the wafer batch in the actual reactor is not large enough. This can be established by looking at the scatter of measured points at a certain radius for experimental results. A large scatter would thus indicate that the wafer boat is not rotated fast enough. In Fig. 4.31 on page 60 the scatter of experimentally determined points (closed squares) is compared to the scatter of
Figure 4.27: Concentration profiles for $C_2H_4$ and $C_2H_5OH$.

Figure 4.28: Concentration profile for $H_2O$ and deposition rate.
the simulated, non-rotating, 3-dimensional simulations (open circles), where it is clear that the experimentally obtained points exhibit considerably less scattering and also indicating a clear trend in deposition profile. The large scattering of point obtained from simulation confirm that no, or not fast enough, rotation leads to large scattering.

If we compare deposition profiles, obtained from 2-dimensional and 3-dimensional simulations, in Fig. 4.30 on the next page we see that the 3-dimensional deposition profiles are not only much flatter but also concave. Apparently, the profiles are caused by a too low deposition rate on the wafer edge near the inlets (see ?? on page ??, which results in a low deposition rate average at the wafer edge. The low deposition rate near the inlets is most likely to be caused by a too low TES concentration as compared to the 2-dimensional results. This low TES concentration (or low TEOS conversion) must be a result of the jet effect of the inlet nozzles and the discrepancy with experimental results might be explained by a too rough grid used for the inlet holes.

Although the 3-dimensional model works well and shows some interesting results, to accurately predict deposition behavior the grid density is not high enough near the inlets to describe the jet effect and should be increased.

![Figure 4.29: Radial deposition profiles, radially averaged from simulations, compared with experimental results for wafer #16 and wafer #66.](image-url)
Figure 4.30: Radial deposition profiles for wafer # 16 and # 66, obtained from 2D (dotted) and 3D (straight) simulations using the 'Modified S8' model at 928 K, 0.5 Torr and 200 sccm TEOS flow rate.

Figure 4.31: Separate points for simulations and experiment for wafer # 66
Chapter 5

Conclusions and recommendations

5.1 Conclusions

In this report, a comprehensive model was presented for the gas flow, transport phenomena and chemical reactions in low pressure chemical vapor deposition of silicon dioxide from TEOS in the ASM A412 vertical reactor for 300 mm wafers. The model was constructed by combination of a model for elementary gas phase and surface reactions, as proposed by Coltrin and coworkers, and the computational fluid dynamics code CFD-ACE+.

The main goals of the study were twofold:

1. To gain insight in the underlying physical and chemical phenomena of the process, in order to better understand experimentally observed process characteristics.

2. To develop a reliable simulation code, preferably based on fundamental chemistry and physics rather than empirical fits, that can be used in process and equipment optimization. However, it was necessary to include some fitting to experimental data into the modelling: The chemistry model as proposed by Coltrin was found to underpredict experimentally observed growth rates by some 50%.

It is shown in this study that the resulting model provides a good basis for an optimization tool for silicon dioxide LPCVD from TEOS. The modified chemistry model, together with the 2-dimensional simplified representation of the reactor, provides useful information about the trends and characteristics of the process, when used in combination with equations describing the transport of mass, momentum, heat and chemical species. This is done in many commercially available CFD programs, but the program used here is CFD-ACE+.

The modifications made to the chemistry model by changing the pre-exponential rate constant of the backward reaction of TES sticking, predict experimental growth values accurately for a wide variety of circumstances (0.25-1.5 Torr, 50-300 sccm TEOS flow rate and 903 - 978 K), others than those to which the model was fitted (viz. 0.5 Torr, 200 sccm
TEOS flow rate and 928 K). Two other possibilities to fit the chemistry model to experimental growth rate data, by modifying the rate constants of two other elementary reaction steps, were also studied. However, these models were much less successful in reproducing experimental data over the entire range of studied process conditions, and were therefore discarded.

From the simulations, we clearly see that increases in pressure, temperature and TEOS flow rate, lead to an increase in the deposition rate. The increase in deposition rate with temperature is the strongest, suggesting that the process is still very strongly kinetically limited.

From the results for pressure variations, we see that growth rates obtained from simulations and, to a lesser extent, from experiments, sublinearly increase with pressure, indicating that maybe surface site saturation occurs.

Trends in standard deviation of film thickness over a wafer surface suggest that intra-wafer uniformity deteriorates with an increase in temperature or pressure or a decrease in TEOS flow rate. The deteriorating uniformity can be qualitatively explained from increasing Damköhler numbers. For the TEOS flow rate, this is explained by the changing ratio of the precursor TEOS to the gas-phase intermediate TES at the edge of a wafer. This is furthermore indicative of another characteristic of this process: both TEOS and TES play an important role in predicting not only the absolute value of growth rate, but also the uniformity with a wafer and the form of the deposition profile. In general, it can be said that the more silicon dioxide is deposited by TES, the more the radial uniformity deteriorates, which explains why uniformity increases with decreasing temperature or pressure and increasing flow rate; the extent to which TEOS is converted to TES is reduced in the same direction.

The model simulations have clarified the phenomena leading to some experimental observations, some of which were only partly understood until now:

- Comparing 2-D simulations with a single inlet and multiple inlets confirms the experimental observation that the application of multiple inlets along the height of the reactor is crucial for obtaining good wafer-to-wafer uniformity. The simulations also showed that optimal distribution of the gas inlets along the height is needed to obtain a good wafer-to-wafer uniformity. Continued simulation studies can assist in finding this optimum. Furthermore, 3-D simulations showed that non-symmetric gas injection through multiple inlets from the side of the reactor causes large growth rate differences over the wafers. Continued simulation studies, more accurately accounting for the 3-D effects near the inlets, could show to what extent this non-uniformity can be evened out by slowly rotating the wafers.

- The surface to volume ratio A/V, which can be varied by changing the interwafer distance, was found to have a large impact on the intra-wafer uniformity. In fact, the experimentally observed transition from concave deposition profiles for the first wafers to convex profiles for the wafers further downstream was qualitatively reproduced by the simulations, and could be explained from variations in the relative contributions of TEOS and TES to the deposition.

- The cold gas jets entering the reactor through multiple inlet holes from the side, were found to heat up to the reactor temperature very rapidly. In fact, these jets completely disappear before the gas enters the interwafer region.
5.2 Recommendations

Future work should focus on two fields; consolidation of the work done and extension to practical implementations.

- First of all, there still are some discrepancies present in our current model. It has to be established whether or not this is due to assumed simplifications in the bottom and top of the reactor geometry, since these deviations are most markedly present for wafers in the beginning and end of the batch. However, it could also be that the chemistry model needs to be expanded with species or reaction steps that start playing an important role for high pressure and short residence times.

- Secondly, the model should be studied in more detail in 3-dimensional simulations with a much finer grid near asymmetries in the reactor. In this 3-dimensional model the radiative heat transfer might also result in non-isothermal simulation, especially when bottom and top geometries have been taken into account, and can thus provide more understanding of axial or radial non-uniformities.

- Finally, the present 2-dimensional model can be used to optimize process conditions and reactor geometries. The inlet geometry can be optimized further to provide a more even concentration profiles throughout the reactor and thus a more even deposition profile. Also wafer spacings can be varied, since it is shown that the A/V ratio in the reactor can have a large impact on the deposition rates and uniformities.
Appendix A

TEOS and TES concentration profiles for 'Modified S8'
Appendix B

Radial deposition profiles for 'Modified S8'
base case, \# 16, r = 0: 58 - P \rightarrow 22
58 - q \rightarrow 19
50 - T \rightarrow 19
51 - P \rightarrow 20
51 - Q \rightarrow 19
51 - T \rightarrow 19

\# 116, r = 0: 58 - P \rightarrow 22
58 - q \rightarrow 19
58 - T \rightarrow 20

\# 91, r = 21

\# 116, P = 22
Q = 19
T = 20

\text{Deposition rate (A/min)}

\text{Radial position (m)}

\text{Wafer #91}

\text{Wafer #116}
Appendix B. Radial deposition profiles for 'Modified S8'

![Graphs showing deposition rate vs radial position for different wafers (16, 41, 66). Each graph uses symbols for different gas flow rates (50, 100, 200, 300) and show trends in deposition rate with radial position.](image-url)

- **Wafer #16**
  - Deposition rate vs radial position graph
  - Symbols for gas flow rates: 50, 100, 200, 300

- **Wafer #41**
  - Deposition rate vs radial position graph
  - Symbols for gas flow rates: 50, 100, 200, 300

- **Wafer #66**
  - Deposition rate vs radial position graph
  - Symbols for gas flow rates: 50, 100, 200, 300
Appendix B. Radial deposition profiles for 'Modified S3'
Appendix C

TEOS and TES concentration profiles for 'Modified S1'
Appendix C. TEOS and TES concentration profiles for 'Modified S1'
Appendix D

Radial deposition profiles for 'Modified S1'
Appendix D. Radial deposition profiles for 'Modified S1'
Appendix D. Radial deposition profiles for 'Modified S1'
Appendix E

TEOS and TES concentration profiles for 'Modified S4'
Appendix E. TEOS and TES concentration profiles for 'Modified S4'
Appendix F

Radial deposition profiles for 'Modified S4'