STELLINGEN

behorende bij het proefschrift
"Transport Phenomena in Chemical Vapor Deposition Reactors"
doctor Chris Kleijn

1. Het optreden van recirculerende gasstromingen boven het begin van de
verhitte susceptor in horizontale CVD reactoren met gekoelde wanden
wordt voornamelijk bepaald door de waarde van het quotiënt van het
Grashofgetal en het Reynoldsgetal tot de macht $\kappa$, waarbij $\kappa$ gelijk is
aan 1 voor lage waarden van het Reynoldsgetal en gelijk aan 2 voor hoge
waarden van het Reynoldsgetal.
(dit proefschrift)

2. Transportverschijnselen, zoals stroming en diffusie van reactanten en
reactieproducten, zijn van grote invloed op de eigenschappen van de
gevormde films in CVD processen, ook wanneer de snelheid waarmee deze
films worden gevormd wordt gelimiteerd door de snelheid van de
heterogene depositiereacties.
(dit proefschrift)

3. De vaak gesuggereerde analogie tussen het Nusseltgetal voor de warmte-
overdracht en het Sherwoodgetal voor de transportgelimiteerde stof-
overdracht aan het oppervlak van de verhitte susceptor in CVD reactoren
is niet geldig wanneer de wanden van de reactor gekoeld zijn.
(dit proefschrift)

4. De interactie van gedwongen en vrije convectie in laminaire stromingen
can leiden tot stabiele asymmetrische stromingspatronen in symmetrische
configuraties.

5. Bij het mengen van mengbare vloeistoffen in turbulent geroerde vaten
dragen de dichtheidsverschillen tussen de vloeistoffen in hogere mate
bij tot lange mengtijden dan de viscositeitsverschillen.

6. De door van Doormaal en Raithby ter verbetering van het SIMPLE
algoritme voorgestelde behandeling van de drukcorrectievergelijking op
randen met een snelheidsrandvoorwaarde leidt bij gebruik van iteratieve
oplossmethoden tot divergentie van de oplossing.

7. Het belangrijkste nadeel van veel commercieel verkrijgbare computercodes
voor stroomssimulatie is dat het voor het gebruik van deze codes niet
noodzakelijk is om te beschikken over elementaire kennis op het gebied
van stromingsleer en numerieke wiskunde.
8. Het werken met gespecialiseerde redacteuren die verantwoordelijkheid dragen voor de publicaties op een bepaald deelgebied van het door een wetenschappelijk tijdschrift bestreken vakgebied is te verkiezen boven een systeem waarbij de individuele redacteuren ieder verantwoordelijk zijn voor de publicaties die afkomstig zijn uit een bepaalde regio van de wereld.

9. De spektakulaire ontwikkelingen in de mogelijkheden en beschikbaarheid van grafische plotters en de bijbehorende software zullen vooralsnog niet leiden tot een verbetering van de kwaliteit van de in wetenschappelijke tijdschriften gepubliceerde tekeningen en grafieken.

10. Het streven van onderwijsgevenden naar een betere aansluiting van de aangeboden leerstof op de "belevingswereld" van de leerlingen ontslaat hen niet van hun maatschappelijke en opvoedkundige plicht om de leerlingen interesse voor en nieuwsgierigheid naar nieuwe kennis omtrent de hen omringende wereld bij te brengen.

11. Judo is geen individuele sport.

12. Het gangbare gebruik om de bijbehorende stellingen als een losbladig addendum aan wetenschappelijke dissertaties toe te voegen vormt een goede garantie voor het feit, dat deze stellingen weer snel daar belanden, waar zij gezien hun wetenschappelijke kwaliteiten veelal thuishoren.
1. The occurrence of recirculating flows above the leading edge of the heated susceptor in horizontal CVD reactors with cooled walls is mainly determined by the ratio of the Grashof number and the Reynolds number to the power $\kappa$, with $\kappa$ equal to one for low Reynolds numbers and $\kappa$ equal to two for high Reynolds numbers.

(this dissertation)

2. Transport phenomena, such as flow and diffusion of reactants and reaction products, have a great influence on the properties of the films that are grown in CVD processes, even when the growth rate of these films is limited by the rate of the heterogeneous deposition reaction.

(this dissertation)

3. The commonly assumed analogy between the Nusselt number for heat transfer and the Sherwood number for transport limited mass transfer at the surface of the heated susceptor in CVD reactors is not valid when the walls of the reactor are cooled.

(this dissertation)

4. The interaction between forced and free convection in laminar flows may lead to stable asymmetric flows in symmetric configurations.

5. In the mixing of miscible liquids in turbulent stirred vessels, differences in density between the liquids are more likely to cause long mixing times than differences in viscosity.

6. The treatment of the pressure correction equation on boundaries with a prescribed velocity, proposed by van Doormaal and Raithby as an enhancement of the SIMPLE algorithm, leads to divergent solutions when used in combination with iterative solution procedures.

(J.P. van Doormaal en G.D. Raithby, Num. Heat Transfer, 7, 1984, 147)

7. The most important disadvantage of many commercially available computer codes for computational fluid dynamics is that they can be used without elementary knowledge of fluid dynamics and numerical techniques.
8. A system in which specialized editors are responsible for the publications in a particular sector of the total field of research covered by a scientific journal is to be preferred above a system in which individual editors bear responsibility for those publications originating from a particular region of the world.

9. The spectacular developments in the possibilities and availability of graphical plotters and software will not, as yet, lead to an improvement in the quality of the illustrations that are published in scientific journals.

10. Striving for a closer connection between the contents of their lessons and the daily experience of their pupils, does not discharge teachers from their educational and social duty to impart to the pupils an interest for and curiosity about new knowledge about the world surrounding them.

11. Judo is not an individual sport.

12. The common practice of printing the theses belonging to a scientific dissertation on a separate sheet guarantees that they will soon end up where they usually belong in view of their scientific qualities.
TRANSPORT PHENOMENA IN
CHEMICAL VAPOR DEPOSITION REACTORS

Chris Kleijn
TRANSPORT PHENOMENA IN CHEMICAL VAPOR DEPOSITION REACTORS

Proefschrift

ter verkrijging van de graad van doctor aan de Technische Universiteit Delft, op gezag van de Rector Magnificus, prof. drs. P.A. Schenck, in het openbaar te verdedigen ten overstaan van een commissie aangewezen door het College van Dekanen op maandag 16 december 1991 te 14.00 uur

door

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geboren te Voorburg

natuurkundig ingenieur
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aan mijn moeder

ter nagedachtenis aan mijn vader
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1 INTRODUCTION

1.1 THIN FILMS AND CHEMICAL VAPOR DEPOSITION

The use of thin solid films is widespread. Insulating, semiconducting or conducting layers are used in many technological areas, such as microelectronics (integrated circuits, transistors), optical devices (lasers, fibers, mirror or lens coatings), magnetic materials (recording tapes), solar energy conversion (photovoltaics, antireflection and spectral selective coatings) and as decorative or protective coatings in for instance the automobile and the ceramics industry.

These applications require deposition processes capable of producing solid films of a wide variety of materials with precisely defined and highly reproducible electrical, optical, chemical and mechanical properties. Furthermore, these deposition processes need to fulfill specific requirements with regard to throughput, safety, economics etc. The most widely used deposition techniques are evaporation, sputtering and Chemical Vapor Deposition (CVD). Compared to other deposition techniques, CVD is very versatile and offers good control of film structure and composition, excellent uniformity and sufficiently high growth rates. Perhaps the most important advantage of CVD over other (physical) deposition techniques is its capability of conformal deposition, i.e. depositing films of uniform thickness on highly irregularly shaped surfaces. Chemical Vapor Deposition and other thin film processes are reviewed in several books and survey papers [e.g. Bryant, 1977; Vossen and Kern, 1978; Bunshah, 1982; Hess et al., 1985; Jensen, 1987; Sherman, 1987].

Chemical Vapor Deposition processes use chemically reacting gases to deposit thin solid films. The chemical reactions involved distinguish it from physical deposition processes, such as sputtering and evaporation. Thus, a CVD system is a chemical reactor and the concept behind the CVD process is actually rather simple. Reactive molecules that contain the atoms of the material to be deposited are introduced as a gas (more or less diluted with an inert carrier gas) into the controlled environment of the process chamber in which the substrates on which deposition takes place are positioned. The energy required to drive the chemical reactions is usually thermal, although photons (Photo CVD - PCVD) or electric discharges (Plasma Enhanced CVD - PECVD) are also used. Surface reactions take place on the substrates as a result of which a thin film is deposited. Depending on
the process and the process conditions, homogeneous gas-phase reactions may also take place. Basically, the several steps that occur in every CVD reaction process are as follows:

(i) Convective and diffusive transport of reactants from the reactor inlet to the reaction zone within the reactor chamber.

(ii) Chemical reactions in the gas-phase, leading to a multitude of new reactive species and byproducts.

(iii) Convective and diffusive transport of the initial reactants and the reaction products from the homogeneous reactions to the susceptor surface.

(iv) Adsorption or chemisorption of these species on the susceptor surface.

(v) Surface diffusion of adsorbed species over the surface.

(vi) Heterogeneous surface reactions catalyzed by the surface, leading to the formation of a solid film.

(vii) Desorption of gaseous reaction products.

(viii) Diffusive transport of reaction products away from the surface.

(ix) Convective and/or diffusive transport of reaction products away from the reaction zone to the outlet of the reactor.

Since some CVD processes are considered to be fully heterogeneous, step (ii) in the above scheme does not take place for those cases. The above is illustrated in figure 1.1, taken from Jensen [1988].

figure 1.1: Schematic representation of basic steps in CVD [after Jensen, 1988].
The technological and scientific fields of the investigation, development and application of CVD processes are typically multidisciplinary and interdisciplinary. Engineers and scientists working in the fields of materials research, equipment manufacturing, chemistry, physics, fluid dynamics, electronics, process control etc. have contributed to the rapid and extensive growth of CVD applications. In this thesis, the main interest is in the fluid dynamics and transport phenomena in the gas mixture, in the chemical reactions in the gas-phase and at the surfaces, and in their influence on the film qualities in CVD processes for the microelectronics and optoelectronics industry. At the same time, this study leaves many important aspects of CVD processes undiscussed, such as the chemical, physical and mechanical properties of the deposited films, details of the physical and chemical processes taking place within the film during and after deposition, the applications of the deposited films in microelectronic and optoelectronic devices and the economic and environmental aspects of the processes. Nevertheless, this first chapter starts with a short introduction into some more general aspects of CVD techniques as applied in the microelectronics and optoelectronics industry.

1.2 CHEMICAL VAPOR DEPOSITION IN THE IC INDUSTRY

Since the announcement of the transistor in 1948 and the realization of the first silicon-based bipolar transistor in 1954, the microelectronics industry has made an impressive progress to the present state in which microelectronics form a crucial element of the industrialized society. It is possible to fabricate all kinds of microelectronic components, and, moreover, all these components can be integrated in one piece of silicon. The amount of integration in these so-called Integrated Circuits (IC's) has increased rapidly, from one component per chip (small scale integration, SSI) in 1960 to over 1 million components per chip (very large scale integration, VLSI), at present. Simultaneously, the typical feature lengths of IC's have decreased from 300 μm in SSI to 1 μm in VLSI. Present research and development efforts are aimed at the development of sub-micron devices in so-called ultra large scale integration (ULSI).

Thin film deposition techniques in the microelectronics and optoelectronics industry need to fulfill some general requirements, such as: (i) A sufficiently high growth rate; (ii) A uniform deposition (across the wafer, from wafer to wafer and from run to run); (iii) A good step coverage
(conformality); (iv) No (or limited, controlled) reaction with underlying layers; (v) Low stress in the film, or stress matched to the stresses in the adjoining layers; (vi) Minimal particulate generation; (vii) Minimal (unwanted) impurities; (viii) A good adhesion to underlying films, and (ix) An economic use of reactants.

Its capability of fulfilling the above requirements has made Chemical Vapor Deposition to be a very important technology for the fabrication of IC’s from the earliest days of microelectronics industry. Today, thin films of silicon dioxide, polysilicon, epitaxial silicon, silicon nitride, tungsten and tungsten silicide deposited by CVD play an important role in the manufacture of VLSI and ULSI circuits. Complex CMOS IC’s produced in the early 1980’s contained typically five to six thin films, most of which were formed by CVD techniques. In table 1.1 some common CVD processes in the silicon IC industry are summarized [Jensen, 1987; Sherman, 1987].

Although the semiconductor industry still considers silicon to be the major semiconductor material, III-V compounds, composed of group III and group V elements of the periodic table (such as GaAs, AlₙGa₁₋ₙAs and InₓGa₁₋ₓAs₁₋ₚₚᵧ) find increasing use in high speed electronic devices and optoelectronic components. These materials are most often deposited using so

<table>
<thead>
<tr>
<th>deposited film</th>
<th>reactants</th>
<th>pressure (Pa)</th>
<th>temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epitaxial silicon</td>
<td>SiHₓ₋ₓClₓ + H₂</td>
<td>10⁴-10⁵</td>
<td>1050-1450</td>
</tr>
<tr>
<td>(x = 0,2,3,4)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>poly silicon</td>
<td>SiH₄</td>
<td>~10²</td>
<td>850-950</td>
</tr>
<tr>
<td>doped poly silicon</td>
<td>SiH₄ + PH₃</td>
<td>~10²</td>
<td>850-950</td>
</tr>
<tr>
<td>SiO₂</td>
<td>SiH₂Cl₂ + N₂O</td>
<td>~10²</td>
<td>1100-1200</td>
</tr>
<tr>
<td></td>
<td>SiH₄ + O₂</td>
<td>~10²</td>
<td>650-700</td>
</tr>
<tr>
<td></td>
<td>SiH₄ + N₂O</td>
<td>~10²</td>
<td>900-1100</td>
</tr>
<tr>
<td></td>
<td>Si(O₆C₄H₅)₄</td>
<td>~10²</td>
<td>900-1000</td>
</tr>
<tr>
<td>Si₃N₄</td>
<td>SiH₂Cl₂ + NH₃</td>
<td>~10²</td>
<td>1000-1100</td>
</tr>
<tr>
<td>Tungsten</td>
<td>WF₆ + H₂</td>
<td>10²-10⁴</td>
<td>600-750</td>
</tr>
<tr>
<td></td>
<td>WF₆ + SiH₄</td>
<td>10²-10³</td>
<td>500-700</td>
</tr>
<tr>
<td></td>
<td>WF₆ + GeH₄</td>
<td>10¹-10²</td>
<td>600-800</td>
</tr>
<tr>
<td>WS₁₂</td>
<td>WF₆ + SiH₄</td>
<td>10²-10³</td>
<td>500-700</td>
</tr>
<tr>
<td>Aluminum</td>
<td>Al(C₄H₉)₃</td>
<td>~10²</td>
<td>500-600</td>
</tr>
</tbody>
</table>
table 1.2: Examples of MOCVD processes

<table>
<thead>
<tr>
<th>deposited film</th>
<th>reactants</th>
<th>pressure (Pa)</th>
<th>temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td>Ga(CH₃)₃ + AsH₃</td>
<td>10⁴-10⁵</td>
<td>900-1100</td>
</tr>
<tr>
<td>AlₓGa₁₋ₓAs</td>
<td>Ga(CH₃)₃ +</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Al₂(CH₃)₆ + AsH₃</td>
<td>10⁴-10⁵</td>
<td>900-1100</td>
</tr>
</tbody>
</table>

called MOCVD techniques, which use metal organic (MO) compounds as sources of the group III elements, whereas the group V elements are introduced in the form of hydrides. Some examples of such processes are shown in table 1.2.

Various types of CVD reactors are used in the microelectronics and optoelectronics industry. Here, we will limit ourselves to thermal CVD systems, not discussing photon or plasma enhanced CVD systems. Some examples of CVD reactor configurations with their most common names are illustrated in figure 1.2. The horizontal reactor (fig. 1.2a) is a classical configuration, which is now only used in research and in compound semiconductor epitaxial growth. Recently, single-wafer reactors have been developed which are based on the vertical impinging jet or stagnation flow reactor configuration (fig. 1.2b). This type of reactor is discussed in more detail below. Pancake reactors and barrel reactors (fig. 1.2c and 1.2d) are the most important tools for epitaxial silicon growth. The continuous belt reactor (fig. 1.2e) is mainly used to deposit silicon dioxide. The horizontal hotwall multiple-wafer-in-tube reactor (fig. 1.2f), operating at low pressures around 100 Pa, is most widely used in the silicon based IC industry and most low pressure processes from table 1.1 are run in this type of reactor. A multitude of other reactor configurations is in use as laboratory CVD systems in research and development environments.

Next to these large differences in reactor geometries, also a wide variety in operating conditions is found: Operating pressures in CVD reactors may vary from ~ 0.1 Torr (~ 10 Pa) to atmospheric pressure. Usually, processes operated at ~ 0.1-10 Torr (~ 10⁻¹⁰⁻⁻³ Pa) are referred to as low pressure CVD processes (LPCVD), whereas processes operated at 0.1-1 bar (10⁴⁻⁻⁻⁻⁵ Pa) are referred to as atmospheric pressure CVD processes (APCVD). The operating temperatures in thermal CVD processes may vary from
figure 1.2: Sketch of some commonly used CVD reactors.
500 K to 1500 K. In some cases, only the wafer surfaces are heated (coldwall CVD reactors), whereas in hotwall reactors the entire process chamber is heated. Heating may be done by means of radiant heaters, resistance heaters, RF coil or induction coil. The reactant gases may be used diluted in an inert carrier gas or undiluted (mol fractions $10^{-4}$-1). The total flow may vary from 100 standard cm$^3$ per minute (sccm) to 10 standard liters per minute (slm) (standard conditions are taken as $1.01325\cdot10^6$ Pa and 298.15 K, so 1 sccm of an ideal gas corresponds to $\approx 6.813\cdot10^{-7}$ mols per second).

Presently, most IC fabrication is done on wafers with 3 or 4 in. (1 in. = 0.0254 m) diameters. Some pilot lines processing 6 in. wafers have been taken into operation. For the near future the wafer diameter is believed to increase even further, up to 8-12 in. diameters. With this increase in wafer dimension the interest in single-wafer low pressure CVD reactors, processing one wafer at a time, has grown considerably. Some other trends in IC manufacturing have also led to the need for new types of CVD reactors such as the single-wafer reactor. The decrease in the typical dimensions of IC components (down to 0.25 $\mu$m within the next decade) puts high demands on the conformality of the deposition process and on the integrity of interfaces between subsequent layers. The increase in the number of components on one chip causes the need for the deposition of many layers of dielectrics and multi-level metallization, leading to an increase from 5-6 CVD films on a wafer at present to 15-20 films in the near future. Together, these demands necessitate the development of new, highly sophisticated CVD reactors and processes.

Although single-wafer reactors may have a lower throughput than batch type reactors which process many wafers at a time, several other factors make single-wafer reactors attractive. First, there are some economic and logistic arguments in favor of single-wafer reactors, such as the relatively low price, the small floor area occupied in the cleanroom and the easy automatic wafer handling. There are also more fundamental arguments for using single-wafer reactors. The most important are the excellent uniformity of the deposited films on large wafers at high growth rates and the effective removal of reaction byproducts from the wafer surface. The gasflow can be "tuned" precisely in such a way, that these demands are fulfilled. Moreover, the vertical "impinging jet" and "stagnation point flow" configurations (figure 1.3), on which most single-wafer reactors are based, offer excellent uniformity by themselves, because of the uniform boundary layers that are formed in these types of flow [Schlichting, 1965]. Compared
to conventional LPCVD in hotwall multiple-wafer-in-tube reactors the growth rate in single-wafer LPCVD reactors will have to be increased by a factor 10-100, in order to obtain acceptable throughput. Therefore, the pressure will be somewhat higher than in conventional LPCVD and possibly also the temperature will be increased. To prevent deposition on the walls of the reactor, these will be cooled.

At present, the situation seems to be that processes that cannot be operated successfully in hotwall multiple-wafer-in-tube reactors, e.g. because they can only be realized when the gas is refreshed at a high rate, are done in single-wafer reactors, whereas other processes are still carried out successfully in conventional LPCVD reactors. Also, single-wafer reactors are widely used for research and development purposes.

1.3 TRANSPORT PHENOMENA AND CHEMICAL REACTIONS IN CVD REACTORS

In all CVD processes, we are dealing with the change from one state, i.e. the initial reactant gases, to another, i.e. the final state with some solid deposits and some gaseous reaction products. In practice, this change must be completed within a reasonable time and so the rate of change from initial to final state is important. This rate is determined by the chemical
kinetics of the process and by the gas flow and transport phenomena (heat transfer, species diffusion) in the reactor. As a result, CVD process and film qualities are highly determined by transport phenomena in the gas mixture and by chemical reactions in the gas mixture and at the wafer surfaces. In particular, the growth rate and the growth uniformity strongly depend on these phenomena. The study of fundamental aspects of CVD will therefore involve both chemical kinetics and transport phenomena.

However, depending on the specific process characteristics, it is sometimes possible to make useful studies of CVD process aspects neglecting either the influence of chemical kinetics or the influence of transport phenomena. For this purpose, it is useful to distinguish between two extreme operating conditions: In the first extreme, the rate of incorporation of reactive species into the solid film is extremely slow compared to the maximum rate in which these species can be transported from the bulk gas flow to the wafer surface by convection and/or diffusion. In this case, the film growth rate will be determined by the chemical reaction rates at the wafer surface. This kind of CVD operation is often referred to as kinetically-limited CVD growth. Clearly, the gas flow and transport phenomena will have little influence on the film growth rate in this kind of CVD operation. In the other extreme, the rate of incorporation of reactive species into the solid film of the wafer surface is extremely fast compared to the maximum rate in which these species can be transported to the wafer surface. Now, any molecule of the reactive species that makes it to the surface will react instantaneously and the concentration of reactive species just above the wafer surface will be close to zero, i.e. the surface concentration will be much smaller than the concentration in the bulk. In this case, the growth rate is determined by the rate in which the reactive species can be transported to the wafer surface and fully depends on the gas flow and transport phenomena in the reactor, whereas the precise mechanisms and kinetics of the chemical reactions have less influence on the growth rate. This is often referred to as (mass-) transport-limited or diffusion-limited growth.

It is useful to have a more detailed look at the mechanisms that determine the growth rate in CVD. Consider the situation in figure 1.4. Here we have the bulk gas flow, in which the reactant concentration is equal to some bulk concentration. From the bulk flow, the reactant has to diffuse to the wafer surface through some kind of diffusion zone over a diffusion length $L$. In a first approximation, the maximum diffusion flux $J_{\text{max}}$ of the
reactant to the wafer may be approximated by $j^{\text{max}} = \frac{D \cdot c_{\text{bulk}}}{L}$, where $D$ is the effective diffusion coefficient of the reactant in the gas mixture and $c_{\text{bulk}}$ is the species bulk concentration. The surface reaction rate $\mathcal{R}$ for a $\beta$-th order surface reaction equals $\mathcal{R} = k \cdot c_{\text{surface}}^\beta$, where $k$ is the reaction rate constant and $c_{\text{surface}}$ is the reactant concentration at the wafer surface. When $j^{\text{max}} \gg \mathcal{R}$ (kinetically-limited growth), all reactive species molecules reacting at the wafer surface will be replaced instantaneously by fresh molecules from the bulk and the surface concentration $c_{\text{surface}}$ will be approximately equal to the bulk concentration $c_{\text{bulk}}$. This is the case when the surface Damköhler number (see section 4.3) $Da^S = \frac{\mathcal{R}}{j^{\text{max}}} = \frac{kL}{D \cdot c_{\text{bulk}}}^{1-\beta} \ll 1$. Similarly, when $Da^S \gg 1$ the process is transport-limited. For a first order reaction rate ($\beta = 1$) this leads to a criterion for the transition from kinetically to transport-limited growth which is often cited in CVD literature: $kL/D \ll 1$: kinetically-limited growth; $kL/D \gg 1$: transport-limited growth. In general, $k$ increases very rapidly with temperature according to an Arrhenius type of expression, whereas $D$ increases relatively slow with temperature. Thus, most CVD processes become transport-limited at high temperatures, leading to the well known transition in Arrhenius type plots of the logarithmic growth rate versus the reciprocal temperature (figure 1.5).

There are some rather fundamental differences between atmospheric pressure (AP) and low pressure (LP) CVD processes, both with respect to the transport phenomena and the chemistry in the reactor. The mean free path
length of the molecules is much larger in LPCVD processes, and for very small typical dimensions, such as the distance between wafers in hotwall multiple-wafer-in-tube reactors, the gas mixture shows a free molecular flow behavior, rather than a continuum flow behavior. The strongly reduced number of intermolecular collisions at low pressures also leads to reduced reaction rates for the gas-phase reactions. Furthermore, at fixed total mass flow rate, the average gas velocity is inversely proportional to the total pressure. As a result, the residence time of the gases in the reactor chamber will be much shorter in LPCVD than in APCVD reactors, leading to a further reduction of the importance of gas-phase chemistry. Therefore, and also due to the fact that APCVD processes usually operate at higher temperatures, the growth rates in APCVD are often much higher than in LPCVD. A third difference can be found in the mixed convection behavior of the gas flow in coldwall APCVD and LPCVD reactors. The dimensionless Rayleigh and Grashof numbers, which determine the occurrence of buoyancy driven mixed convection flows (see sections 2.2 and 4.3), are proportional to the square of the total pressure. Therefore, mixed convection flow phenomena are usually absent in LPCVD reactors, whereas they may be very important in coldwall APCVD reactors.
1.4 THE USE OF MATHEMATICAL MODELING IN CVD REACTOR DESIGN AND PROCESS OPTIMIZATION

The modern microelectronics and optoelectronics industry put severe demands on the qualities of CVD processes and films. As discussed, these qualities are highly determined by the interacting influences of hydrodynamics, transport phenomena and chemical reactions in the CVD reactor chamber. In turn, fluid flow, transport phenomena and chemical reactions strongly depend on the process conditions such as pressure, temperature, species concentrations, flowrate etc. and on the reactor geometry. As a result, the development and optimization of CVD processes and reactors, fulfilling the increasing demands in the electronics industry, is a difficult and time-consuming task, which until now is mainly done by methods of trial-and-error.

However, the need for mathematical CVD models, giving a detailed description of the relevant physical and chemical processes and relating process characteristics to process conditions and reactor geometry, has been recognized at an early stage. In the last two decades CVD models have evolved from simple analytical models to advanced numerical computer codes, describing the three dimensional hydrodynamics and the multi-step chemical reaction mechanisms involved [Jensen, 1987]. The ideal CVD model would consist of a set of mathematical equations, describing all the relevant macroscopic and microscopic physicochemical processes in the reactor and relating these phenomena to both microscopic and macroscopic qualities of the deposited films. Moreover, such a model should be generally applicable to various types of CVD processes and reactor configurations and should therefore be based on fundamental physical and chemical laws rather than process and reactor dependent correlations and fitting constants. Although considerable progress has been made in the development of CVD models, none of the models that have been developed until now incorporates all these properties. Nevertheless, by attacking the problem of CVD modeling from many different angles, CVD models have led to an enormous increase in the understanding of the important basic aspects of CVD processes and to valuable improvements in reactor designs and process characteristics.

Traditionally, CVD modeling has been aimed at atmospheric pressure CVD in conventional coldwall systems, such as the horizontal reactor, the barrel reactor and the pancake reactor, and at low pressure CVD in hotwall multiple-wafer-in-tube batch reactors. In the last five years it became clear that these conventional types of reactors are unsuitable for the
purpose of unraveling basic CVD mechanisms. Instead, reactor geometries with a simple and well-defined flow and temperature field, such as stagnation flow, impinging jet and rotating disk reactors, have been suggested for fundamental experimental and modeling studies [Hess et al., 1985; Jensen, 1987]. In the idealized case, the hydrodynamics in these configurations can be described by means of one-dimensional transport equations [Schlichting, 1968; Evans and Greif, 1988]. This simplification allows for the inclusion of complex chemical mechanisms in the CVD model. At the same time, as discussed above, the interest in coldwall single-wafer LPCVD reactors has grown considerably. As a basic concept for these reactors, the main interest is again in impinging jet, stagnation flow and rotating disk configurations. However, in actual single-wafer reactors the ideal hydrodynamic behavior is disturbed by buoyancy-driven mixed convection flows, edge effects, the influence of the reactor walls and symmetry breaking effects [Houtman et al., 1986; Evans and Greif, 1987ab; Fotiadis et al., 1990a; Weber et al., 1990], necessitating a two- or even three-dimensional approach. Despite of its theoretical and industrial relevance, the modeling of low pressure single-wafer reactors has not yet received as much attention as conventional low pressure and atmospheric pressure CVD reactors.

CVD models may be used for two main purposes: (i) In fundamental process research and development, the use of CVD models may be vital in the identification and correct interpretation of diagnostic experiments. These experiments are hampered by the fact that the process conditions at the wafer surface, where deposition takes place, are usually highly unknown, since they depend on the transport phenomena and chemical reactions in the reaction chamber and may differ significantly from the reactor inlet conditions. As a result, the validity of experimental data is often limited to a particular reactor configuration, making it hard to distinguish between fundamental process characteristics and reactor-dependent artifacts. Mathematical CVD models, relating the wafer conditions to the reactor inlet conditions, may resolve these problems. Usually, this involves some kind of iterative procedure, using the model to evaluate experiments, and experimental data to improve the model. (ii) Once a reliable model has been established, it may be used to optimize reactor design and process conditions with respect to all the relevant and often conflicting process demands. This may contribute to a reduction of the time involved in the development of new processes and reactors, to better process and equipment design, to reduced costs and improved IC manufacturing.
1.5 SCOPE AND AIMS OF THIS STUDY

In light of the previous discussions on the importance of a detailed knowledge of the transport phenomena and chemical reactions in CVD reactors, and of the availability of flexible and accurate CVD simulation models, the aims of the study described in this thesis are fourfold:

(i) The first aim is to develop a mathematical framework (a mathematical model), describing the hydrodynamics, transport phenomena and homogeneous and heterogeneous chemical reactions in thermal Chemical Vapor Deposition reactors, and their influence on the properties of the deposited layers, as well as numerical techniques for the solution of the equations appearing in this model. The model should be based on fundamental physical and chemical laws and theories, rather than empirical correlations, and should be generally applicable to a large variety of thermal CVD processes and reactors.

(ii) Secondly, it is the aim of this study to apply the model to a number of CVD techniques with highly dissimilar process characteristics, at widely varying process conditions and in different reactor geometries, and to compare the outcome of model simulations to experimental results. Thus, the validity of the model is tested and its general applicability to various processes is illustrated. Moreover, this approach underlines the fact that the basics of most CVD processes are very much the same and can be described by the same fundamental equations.

(iii) A third aim is to obtain more insight in the physical and chemical phenomena that play an important role in three particular CVD processes: (a) The deposition of polysilicon from silane in a coldwall single wafer reactor; (b) The deposition of tungsten from tungstenhexafluoride in this same reactor, and (c) The deposition of galliumarsenide from trimethylgallium and arsine in a horizontal atmospheric pressure reactor.

(iv) The final aim, which is in fact the final aim of all CVD modeling, is to use the model in order to optimize the process conditions and reactor geometry for the above CVD processes and reactors.

The mathematical model and the numerical techniques for its solution are described in chapters 2 and 3 of this thesis, which deal particularly with some uncommon and complicating aspects of CVD modeling and its numerics, such as multicomponent (thermal) diffusion phenomena, mixture composition dependent gas properties, and multiple homogeneous and heterogeneous reactions.
A second large part of this study, described in chapters 4, 5 and 6, deals with the transport phenomena and chemical reactions in a particular axisymmetric, coldwall single-wafer LPCVD reactor. In chapter 4 the gas flow and heat and mass transfer in this reactor are studied for a highly idealized and simplified LPCVD process. Thus, some general insights in the transport phenomena in this reactor are obtained. Also in this chapter, a comparison is made between model simulations and experimental measurements of the flow in an isothermal scale model of the single-wafer reactor. In chapter 5 a detailed study is made of the deposition of pure and in situ doped poly-silicon from silane as an example of a process in which the deposition is determined by multiple homogeneous and heterogeneous chemical reactions. In chapter 6 the deposition of tungsten from tungstenhexafluoride and hydrogen or silane is studied as an example of an LPCVD process in which the film qualities are mainly determined by transport phenomena and heterogeneous reactions.

In contrast to the two-dimensional, steady-state approach in chapters 4, 5 and 6, the third part of this thesis, described in chapter 7, deals with the three-dimensional and transient flow and transport phenomena in horizontal atmospheric pressure CVD reactors. In particular, the growth of gallium arsenide from trimethylgallium and arsine is studied as an example of a transport limited deposition process.

Finally, in chapter 8, the results from the previous chapters are reviewed and discussed and some general conclusions are formulated.
2 THE MATHEMATICAL MODEL

2.1 INTRODUCTION
A generally applicable CVD simulation model consists of a set of partial
differential equations with appropriate boundary conditions, describing the
gas flow, the transport of energy and species and the chemical reactions in
a CVD reactor. In these equations, several properties of gas species and
mixtures appear in relation to the temperature, pressure and composition of
the gas mixture. The chemical reactions in the gas-phase and at the wafer
surface can be described in a general way, suitable for many different
processes. However, for the actual modeling of a particular process
knowledge of the chemical mechanisms and kinetics is necessary. This
knowledge must be obtained from experiments and/or theoretical
considerations on the CVD chemistry for that particular process.

In section 2.2 some basic assumptions which are generally applicable to
CVD processes and which have been included in the model are explained. In
sections 2.3 and 2.4 the partial differential equations describing gas flow,
heat and gas species transport are presented. In sections 2.5 and 2.6 we
describe the boundary conditions for these equations and in section 2.7 it
is described how unknown properties of gas species can be predicted from
kinetical theory of gases.

2.2 BASIC ASSUMPTIONS
Some assumptions have been made which largely reduce the complexity of the
problem and the computational effort needed for the solution of the modeling
equations and which are so generally justified for CVD conditions that they
do not essentially limit the accuracy and the applicability of the model for
CVD applications.

(i) The gas mixture is assumed to behave as a continuum. This assumption is
valid when the mean free path length of the molecules is much smaller than
the characteristic dimensions in the reactor geometry, or

\[ \text{Kn} = \frac{\xi}{L} < 1 \]  \hspace{1cm} (2.1)

where Kn is the Knudsen number, \( \xi \) the mean free path length of the molecules
Table 2.1: Mean free path lengths in CVD

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Mean free path length</th>
<th>Nitrogen</th>
<th>Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 Torr (≈13.3 Pa)</td>
<td>1.2×10^{-3} m</td>
<td>1.9×10^{-3} m</td>
<td></td>
</tr>
<tr>
<td>1.0 Torr (≈133 Pa)</td>
<td>1.2×10^{-4} m</td>
<td>1.9×10^{-4} m</td>
<td></td>
</tr>
<tr>
<td>10 Torr (≈1330 Pa)</td>
<td>1.2×10^{-5} m</td>
<td>1.9×10^{-5} m</td>
<td></td>
</tr>
<tr>
<td>760 Torr (≈10^5 Pa)</td>
<td>1.6×10^{-7} m</td>
<td>2.6×10^{-7} m</td>
<td></td>
</tr>
</tbody>
</table>

and L a typical dimension for the regions in which the relevant physical phenomena take place, e.g. the thickness of boundary layers in which large gradients appear. In general, the continuum approach is valid for Kn < 0.01 [Kogan, 1969]. Approximate values for the mean free path lengths of the molecules in hydrogen and nitrogen gases at 700 K are shown in table 2.1. For pressures > 1 Torr and typical dimensions > 0.01 m we may safely use the continuum approach. For very low pressures and small typical dimensions however, we enter the so called slip flow or the transition regime, where the continuum assumption cannot be justified.

(ii) The gases are considered to be ideal gases, behaving in accordance with the ideal gas law and Newton's law of viscosity, which is a valid assumption for the gases, pressures and temperatures used in CVD.

(iii) The gas flow in the reactor is assumed to be laminar. In general, the gas flow will become turbulent when either the Reynolds number Re or the Rayleigh number Ra (both defined in section 4.3) becomes very large. For total gasflows of 0.1-10 slm and typical reactor dimensions of 0.01-0.10 m we find Re = 10^2-10^3 for hydrogen and Re = 10^1-10^2 for nitrogen, independent of the total pressure. So, in general, the Reynolds number in CVD reactors is below values at which the onset of turbulence might be expected (= 2.3×10^3 for pipe flow, ≈ 1.5×10^3 for a free jet flow [Tennekes and Lumley, 1983]). For the Rayleigh number in coldwall CVD reactors, heated from below, with typical vertical dimensions of 0.01-0.10 m and susceptor temperatures of 500-1500 K we find values as in table 2.2. Turbulent motion in a horizontal gas layer heated from below will develop at Rayleigh numbers > 10^5 [Krishnamurti, 1970, 1973, Hollands et al., 1975]. A superimposed forced convection flow as in CVD has a stabilizing effect, delaying the
### Table 2.2: The Rayleigh Number in CVD Reactors

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Rayleigh Number</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nitrogen</td>
</tr>
<tr>
<td>0.1 Torr (=13.3 Pa)</td>
<td>$10^{-4}$ - $10^{-1}$</td>
</tr>
<tr>
<td>1.0 Torr (=133 Pa)</td>
<td>$10^{-2}$ - $10^{1}$</td>
</tr>
<tr>
<td>10 Torr (=1330 Pa)</td>
<td>$10^{0}$ - $10^{3}$</td>
</tr>
<tr>
<td>760 Torr (=10$^{6}$ Pa)</td>
<td>$10^{4}$ - $10^{7}$</td>
</tr>
</tbody>
</table>

...transition to turbulent motion to even higher Rayleigh numbers [Chiu et al., 1987]. So, when using hydrogen as a carrier gas the flow will always be laminar. With nitrogen as a carrier gas, the flow in LPCVD ($10^{1}$–$10^{3}$ Pa) will be laminar also, but in APCVD ($10^{4}$–$10^{5}$ Pa) reactors with large vertical dimensions the flow may become turbulent due to heating from below. Note, that the above applies to coldwall systems with the heated susceptor facing upward only. In hot wall systems and in coldwall systems with the heated susceptor facing downward no instabilities in the flow will occur.

*(iv)* We assume that the gases are transparent for heat radiation from the heated walls and susceptor. Some reactant gases in CVD do absorb infrared heat radiation. However, these gases are present in low partial pressures, either because they are highly diluted (APCVD) or because the total pressure is very low (LPCVD). Thus, the absorption of heat radiation by these gases will be small.

*(v)* We neglect the heat that is consumed or released by the gas phase reactions. This is a valid assumption in APCVD, because the reactants are highly diluted, and in LPCVD where gas-phase reactions are highly suppressed.

*(vi)* We neglect viscous heating due to dissipation, which is allowed for gas flows in CVD reactors where no large velocity gradients appear and the Brinkman number, which is a measure of the extent to which viscous heating is important relative to the conductive heat flow [Bird et al., 1960, p. 278], is typically < 0.01.

*(vii)* We neglect the effects of pressure variations in the energy equation, which is also obviously correct for the low Mach number flows in CVD reactors.
2.3 FLUID FLOW AND HEAT TRANSFER

The gas flow in the reactor is described by (all principal symbols and their units are explained in the list of symbols):

1. the continuity equation:

\[
\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \mathbf{v})
\]  \hspace{1cm} (2.2)

where \( \rho \) is the density of the gas, \( t \) the time and \( \mathbf{v} \) the velocity vector, and

2. the Navier-Stokes or momentum balance equation:

\[
\frac{\partial (\rho \mathbf{v})}{\partial t} = -\nabla \cdot (\rho \mathbf{v} \mathbf{v}) + \nabla \cdot \mathbf{t} - \nabla P + \rho \mathbf{g}
\]  \hspace{1cm} (2.3)

where \( P \) is the pressure, \( \mathbf{g} \) the gravity vector and where the viscous stress tensor \( \mathbf{t} \) takes the form

\[
\mathbf{t} = \mu \left( \nabla \mathbf{v} + (\nabla \mathbf{v})^\dagger \right) + (\kappa - \frac{2}{3} \mu) (\nabla \cdot \mathbf{v}) \cdot \mathbf{1}
\]  \hspace{1cm} (2.4)

with \( \kappa \) the volume viscosity, \( \mu \) the dynamic viscosity, \( \mathbf{1} \) the unity tensor and \( \dagger \) denoting a transposed vector. Due to buoyancy effects, these equations are coupled to the energy equation, describing the temperature field and the heat transfer in the reactor, which may be written as:

\[
c_p \frac{\partial}{\partial t} (\rho T) = -c_p \nabla \cdot (\rho \mathbf{v} T) + \nabla \cdot (\lambda \nabla T) + \nabla \cdot \left( RT \sum_{i=1}^{N} \frac{\mathbf{D}_i^T}{m_i} \nabla (\ln f_i) \right)
\]  \hspace{1cm} (2.5)

where \( c_p \) represents the specific heat of the gas mixture, \( T \) its absolute temperature, \( \lambda \) its thermal conductivity, \( R \) the universal gas constant, \( m_i \) the mole mass of species \( i \) in the \( N \) species mixture, \( f_i \) its mole fraction and \( \mathbf{D}_i^T \) its multicomponent thermal diffusion coefficient. The last term in equation 2.5 represents the Dufour effect (or diffusion-thermo effect), which is the "reciprocal process" to the Soret effect (thermal diffusion). The Dufour effect causes an energy flux in a gas mixture as a result of concentration gradients, whereas the Soret effect causes species diffusion fluxes in a gas mixture as a result of temperature gradients. This is further discussed in sections 2.4.3 and 2.7.4.

The above equations 2.2, 2.3 + 2.4 and 2.5 are given in 3D cartesian \((x,y,z)\) and 2D cylindrical \((r,z)\) form in Appendix A. In the equations, the
fluid properties $\lambda$, $\mu$, $\rho$, $D_i^T$ and $c_p$ are not only functions of temperature and pressure, but also of the composition of the gas mixture. Thus, the energy and flow equations given above are coupled to the species concentration equations.

2.4 SPECIES TRANSPORT AND CHEMICAL REACTIONS IN THE GAS PHASE

Gas diffusion in a CVD reactor may result from concentration gradients (ordinary diffusion), but also from temperature gradients (thermal diffusion, Soret effect). There are many different ways of expressing species concentrations and diffusion velocities [Bird et al., 1960, pp. 495-502]. Here we will use mass fractions and diffusive mass fluxes relative to the mass averaged velocity of the gas mixture. The main advantage of this procedure is the fact that the mass averaged velocity is obtained from the Navier–Stokes equations and further also that the resulting convection-diffusion equation is very similar in form to the energy equation and to each of the components of the Navier-Stokes equations. This is favorable for the numerical solution of the equations (see chapter 3).

2.4.1 Species concentration equations

We define the mass averaged velocity $\bar{v}$ in an $N$ component gas mixture as

$$\bar{v} = \sum_{i=1}^{N} \omega_i \bar{v}_i$$

(2.6)

and the diffusive mass flux vector $\mathbf{j}_i$ of species $i$ as

$$\mathbf{j}_i = \rho \omega_i (\bar{v}_i - \bar{v})$$

(2.7)

where $\omega_i$ is the mass fraction of species $i$ and $\bar{v}_i$ the velocity vector of species $i$. We further assume that $K$ reversible chemical reactions take place in the gas-phase, with a forward reaction rate $R_k (k = 1,K)$ and a reverse reaction rate $R_k$. This is further described in section 2.4.4. Now, the balance equation for gas species $i$, in terms of mass fractions and diffusive mass fluxes, can be written as
\[ \frac{\partial (\rho \omega_i)}{\partial t} = -\nabla \cdot (\rho \nu \omega_i) - \nabla \cdot j_i + m_i \sum_{k=1}^{K} \nu_{ik} (R_k - R_{-k}) \]  

(2.8)

with \( m_i \) the mole mass of species \( i \) and \( \nu_{ik} \) stoichiometric coefficients for the gas-phase reactions.

The total diffusive mass flux \( j_i \) of species \( i \) is composed of diffusion fluxes due to concentration gradients \( j_i^c \) (see section 2.4.2) and diffusion fluxes due to thermal diffusion \( j_i^T \) (section 2.4.3).

\[ j_i = j_i^c + j_i^T \]  

(2.9)

In an \( N \) component gas mixture there are \( N-1 \) independent species concentration equations of the form of equation 2.8 since the mass fractions must sum up to 1.

\[ \sum_{i=1}^{N} \omega_i = 1 \]  

(2.10)

### 2.4.2 Ordinary diffusion

In a binary gas mixture (\( N = 2 \)) the ordinary diffusive mass flux of species \( i \) is given by Fick's Law:

\[ j_i^c = -\rho D_{12} \nabla \omega_i \]  

(2.11)

with \( D_{12} \) the binary diffusion coefficient for ordinary diffusion in the pair of gases 1 and 2, which is essentially independent of the mixture composition.

A general expression for the diffusion fluxes \( j_i^c \) due to concentration gradients in a multicomponent gas mixture is given by the Stefan-Maxwell equations. They form a set of equations relating the diffusive fluxes of all species in the mixture to all concentration gradients. Written in terms of mole fractions and -fluxes we have

\[ \nabla f_i = \frac{1}{c} \sum_{j=1}^{N} \frac{1}{D_{ij}} \left( f_i j_{ij}^c - f_j j_{ij}^c \right) \]  

(2.12)
with \( f_i \) the mole fraction of species \( i \), \( c \) the total mole concentration of the gas mixture (\( = P/RT \)), \( D_{ij} \) the binary diffusion coefficient for gas species \( i \) and \( j \) and \( j_i^c \) the diffusive mole flux of species \( i \). In terms of mass fractions and fluxes we obtain

\[
V \omega_i + \omega_i V(\ln m) = \frac{m}{\rho} \sum_{j=1}^{N} \frac{1}{m_j D_{ij}} \left( \omega_i j_j^c - \omega_j j_i^c \right) \tag{2.13}
\]

with \( m \) the average mole mass of the mixture

\[
m = \sum_{i=1}^{N} f_i m_i \tag{2.14}
\]

and \( m_i \) the mole mass of species \( i \). Again, in an \( N \) component gas mixture there are \( N-1 \) independent equations of the form of equation 2.13. Together with the additional equation

\[
\sum_{i=1}^{N} j_i^c = 0 \tag{2.15}
\]

they form a closed set of equations from which the \( N \) diffusive mass fluxes \( j_i^c \) can be solved directly. From equation 2.13 we can derive an explicit expression for \( j_i^c \), assuming that all the other fluxes \( j_j^c \) are known

\[
j_i^c = -\rho D_i V \omega_i - \rho \omega_i D_i V(\ln m) + m \omega_i \sum_{j=1}^{N} j_j^c \sum_{j=1}^{N} m_j D_{ij} \tag{2.16}
\]

with \( D_i \) an effective diffusion coefficient for species \( i \)

\[
D_i = \left( \sum_{j=1}^{N} \frac{f_j}{D_{ij}} \right)^{-1} \tag{2.17}
\]

The above expressions 2.16 and 2.17 can be used to solve the set of Stefan-Maxwell equations iteratively.

As an alternative to the Stefan-Maxwell equations an approximate expression for the diffusive fluxes in a multicomponent gas mixture has been derived by Wilke [Wilke, 1950]. Here the diffusion of species \( i \) in a multicomponent mixture is written in the form of Fick's law of diffusion
with an effective diffusion coefficient $D'_i$ instead of the binary diffusion coefficient:

$$j^C_i = -pD'_i \nu_i \omega_i$$  \hspace{1cm} (2.18)

with

$$D'_i = (1-f_i) \left( \sum_{j=1}^{N} \frac{f_j}{D_{ij}} \right)^{-1}$$  \hspace{1cm} (2.19)

In the case of a highly diluted species ($f_i \omega_i \ll 1$) the full Stefan-Maxwell equations and Wilke's approximation are identical. For binary mixtures ($N = 2$) both approaches lead to Fick's law of diffusion. When Wilke's approximation is used to calculate the diffusive fluxes in a multicomponent mixture, the $N$ species concentration equations of the form of equation 2.8 form an independent set, which is not consistent with equation 2.10, stating that the species concentrations must sum up to 1. Therefore, in order to be able to fulfill this constraint, one of the concentration equations must be dropped and be replaced by equation 2.10. Wilke's approximation to the full Stefan-Maxwell equations, as well as other approximations, have been discussed by Coffee and Heimerl [1981].

### 2.4.3 Thermal diffusion

Due to the effect of thermal diffusion (or Soret effect), the gas species in an initially homogeneous gas mixture will separate under the influence of a temperature gradient. This effect is usually small compared to ordinary diffusion, but in CVD in coldwall reactors thermal diffusion may be an important effect because of the large temperature gradients present. In general, thermal diffusion causes large, heavy gas molecules to concentrate in cold regions of the reactor, whereas small, light molecules concentrate in the hotter parts of the reactor.

The thermal diffusion coefficient was first calculated from the rigorous kinetic theory of gases by Chapman and Enskog and its value was later confirmed experimentally. The thermal diffusion effect cannot easily be explained from simple kinetical considerations based on the concept of mean free path. An elementary derivation, showing the existence and sign of
the effect for molecules repelling one another with a force \( F = -K/r^S \), with \( r \) the distance between the molecules, has been given by Frankel [Frankel, 1940]. General overviews on thermal diffusion theory are presented by Clark Jones and Furry [1946], Crew and Ibbs [1952] and Hirschfelder et al. [1963].

The diffusive mass fluxes due to thermal diffusion are given by

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

(2.20)

in which \( D_i^T \) is the multicomponent thermal diffusion coefficient for species \( i \). In general, \( D_i^T \) is a function of the temperature and the composition of the gas mixture, but is independent of the pressure, and \( D_i^T > 0 \) for large, heavy molecules and \( D_i^T < 0 \) for small, light molecules. Note that \( D_i^T \) is defined in such a way that its dimension equals the dimension of \( \rho D_{ij} \), the value of which is also independent of the pressure.

### 2.4.4 Gas phase reactions

The last term in the concentration equation 2.8 represents the creation and destruction of species \( i \) due to homogeneous gas-phase reactions. Assume that this is a result of \( K \) reversible chemical reactions. Since different species may act as products and reactants in each of the \( K \) reactions, we use the following general notation for these reactions:

\[
\sum_{i=1}^{N} \nu_{ik} \dot{A}_i \xrightleftharpoons[k_{-k}]{k_k} \sum_{i=1}^{N} \nu_{ik} \dot{A}_i \quad (k=1,K)
\]  

(2.21)

Here, the \( A_i \) (\( i = 1,N \)) represent the different gaseous species, \( k_k \) the forward reaction rate constant and \( k_{-k} \) the reverse reaction rate constant of gas-phase reaction \( k \) (\( k = 1,K \)) and \( \nu_{ik} \) the stoichiometric coefficients for species \( i \) in gas-phase reaction \( k \). Note that in the above notation for the reversible reactions, the summation is over the same \( N \) species on both sides of the reaction. Now, by taking

\( \nu_{ik} > 0 \) for the products of the forward reaction
\( \nu_{ik} < 0 \) for the reactants of the forward reaction

and by defining
\[ |\nu_{ik}| = \nu_{ik} \text{ and } |-\nu_{ik}| = 0 \text{ for } \nu_{ik} \geq 0 \]
\[ |\nu_{ik}| = 0 \text{ and } |-\nu_{ik}| = \nu_{ik} \text{ for } \nu_{ik} \leq 0 \]
equation 2.21 represents a general equilibrium reaction, with the reactants appearing on the left-hand side and the products appearing on the right-hand side.

When the forward reaction rate constant \( k_k \) and the reverse reaction rate constant \( k_{-k} \) are known, the reaction rates \( \mathcal{R}_k \) and \( \mathcal{R}_{-k} \) may be obtained from

\[ \mathcal{R}_k = k_k \cdot \prod_{i=1}^{N} \left( f_i P \frac{RT}{P} \right)^{\nu_{ik}} = k_k \cdot \prod_{i=1}^{N} c_i \nu_{ik} \]  
(2.22)

and

\[ \mathcal{R}_{-k} = k_{-k} \cdot \prod_{i=1}^{N} \left( f_i P \frac{RT}{P} \right)^{\nu_{ik}} = k_{-k} \cdot \prod_{i=1}^{N} c_i \nu_{ik} \]  
(2.23)

with \( c_i \) the mole concentration of species \( i \), \( f_i \) the mole fraction of species \( i \) and \( P \) the total pressure. Usually, the values of \( k_k \) and \( k_{-k} \) depend strongly on the temperature and are independent of the pressure for sufficiently high pressures. At low pressures however, \( k_k \) and \( k_{-k} \) may depend on the pressure ("pressure fall-off regime"). So, in general

\[ k_k = k_k(P,T) \]  
(2.24)

\[ k_{-k} = k_{-k}(P,T) \]  
(2.25)

When either \( k_k \) or \( k_{-k} \) is known the reaction speed in the opposite direction may be calculated from the reaction equilibrium thermochemistry. Using tabulated values for the standard heat of formation \( \mathcal{H}^0_{298,i} \) and standard entropy \( \mathcal{S}^0_{298,i} \) at \( P^0 = 1 \text{ atm} \) and \( T^0 = 298 \text{ K} \) and values for the specific heat \( c_p,i \) as a function of the temperature for species \( i \) [e.g. Wagman et al., 1982, Coltrin et al., 1986] the standard Gibbs energy change of formation \( \mathcal{G}^0_i(T) \) at temperature \( T \) for species \( i \) may be calculated from

\[ \mathcal{G}^0_i(T) = \mathcal{H}^0_{298,i} - T \mathcal{S}^0_{298,i} + \frac{1}{m_i} \int_{T^0}^{T} c_{p,i}(T) dT - \frac{T}{m_i} \int_{T^0}^{T} \frac{c_{p,i}(T)}{T} dT \]  
(2.26)
Values for the thermodynamic properties $H^{0}_{298}$, $S^{0}_{298}$ and $c_p$ for several gases relevant for the CVD processes discussed in this thesis are given in Appendix B.

Now we define the standard Gibbs energy change of reaction $\Delta G^0_k$ for reaction $k$ as

$$\Delta G^0_k(T) = \sum_{i=1}^{N} \nu_{ik} C^0_{i}(T)$$  \hspace{1cm} (2.27)

The equilibrium constant $K_k$ for reaction $k$, defined as

$$K_k = \prod_{i=1}^{N} \left( \frac{f_{i, eq}}{P^{0}} \right) \nu_{ik}$$  \hspace{1cm} (2.28)

with $f_{i, eq}$ the mole fraction of species $i$ in equilibrium, may then be calculated from

$$K_k(T) = e^{-(\Delta G^0_k(T))/RT}$$  \hspace{1cm} (2.29)

From eqs. 2.22, 2.23 and 2.28 it may be deduced, that $k_k(P,T)$ and $k^{-k}(P,T)$ are related through

$$k^{-k}(P,T) = \frac{k_k(P,T)}{K_k(T)} \left( \frac{RT}{P^0} \right)^{\sum_{i=1}^{N} \nu_{ik}}$$  \hspace{1cm} (2.30)

### 2.4.5 Final equations for species concentrations

From the general equation for species transport and chemical reactions, the approximate and exact expressions for ordinary diffusion, the expressions for thermal diffusion and the expressions for the gas-phase reactions we can derive the following equations for calculating the species concentrations:
Approximate method (eqs. 2.8, 2.9, 2.18, 2.19 and 2.20):

\[
\frac{\partial (\rho \omega_i)}{\partial t} = -\nabla \cdot (\rho \omega_i) + \nabla \cdot (\rho D_i \nabla \omega_i) + \nabla \cdot (D_i \nabla (ln \; T))
\]
\[
+ \sum_{k=1}^{K} \nu_{ik} (R_k - R_{-k})
\]

(2.31)

Stefan–Maxwell equations (eqs. 2.8, 2.9, 2.16, 2.17 and 2.20):

\[
\frac{\partial (\rho \omega_i)}{\partial t} = -\nabla \cdot (\rho \omega_i) + \nabla \cdot (\rho D_i \nabla \omega_i)
\]
\[
+ \nabla \cdot (\rho \omega_i D_i \nabla (ln \; m)) - \nabla \cdot (m \omega_i D_i \sum_{j=1}^{N} \frac{\sum_{j=1}^{N} \frac{N_j}{m_j D_j}}{j \neq i})
\]
\[
+ \nabla \cdot (D_i \nabla (ln \; T)) + \sum_{k=1}^{K} \nu_{ik} (R_k - R_{-k})
\]

(2.32)

where \( R_k \) and \( R_{-k} \) are calculated from eqs. 2.21-2.30. The above equations are given in 3D cartesian \((x,y,z)\) and 2D cylindrical \((r,z)\) form in Appendix A.

2.5 SURFACE REACTIONS

At the wafer surface \( S \) surface reactions, transforming gaseous reactants into solid and gaseous reaction products, will take place of the form

\[
\sum_{i=1}^{N} \sigma_{is} A_i \rightarrow \sum_{i=1}^{N} \sigma_{is} A_i + \sum_{j=1}^{M} \chi_{js} B_j \quad (s=1,S)
\]

(2.33)

with \( A_i \) the gaseous reactants and reaction products \((i = 1,N)\) and \( B_j \) the solid reaction products \((j = 1,M)\). The \( \sigma_{is} \) and \( \chi_{js} \) represent the stoichiometric coefficients for the gaseous and solid species for surface reaction \( s \) \((s = 1,S)\). With respect to the sign of the stoichiometric coefficients and the definition of \( \sigma_{is} \), the same convention has been followed as in section 2.4.4. From 2.33 the growth rate \( \dot{g}_j \) \((\text{Ang} \cdot \text{min}^{-1})\) of solid species \( j \) may be deduced:

\[
\dot{g}_j = 60 \cdot 10^{10} \sum_{s=1}^{S} \frac{m_j}{\rho_j} \frac{S}{R_m} \chi_{js}
\]

(2.34)
with \( m_j \) the mole mass of species \( B_j \) and \( \rho_j \) its density in the solid phase.

Usually, heterogeneous surface reactions are characterized by complicated reaction mechanisms consisting of a number of different steps and the surface reaction speed \( \mathcal{R}_s \) of surface reaction number \( s \) will depend on the the partial pressures of the gaseous species, the rate constants of the individual reaction steps as a function of the temperature, and the surface properties. However, usually little or no information on the individual reaction steps and rate constants is available. Therefore, what is usually done is to propose a mechanism and to assume that one of the steps in this mechanism is rate limiting whereas all the other steps are in equilibrium. With these assumptions an expression for the reaction rate of the overall reaction in the form

\[
\mathcal{R}_s = \mathcal{R}_s(P_1, \cdots, P_N, T)
\]  

(2.35)

may be found, with \( P_i \) the partial pressure of species \( i \) and \( T \) the temperature. From a comparison of predictions from this expression with the experimentally observed growth rates one can now judge the validity of the assumptions made and make an estimate of the value of several unknown constants in the expression 2.35.

As an example, we look at the most simple surface reaction, the monomolecular surface dissociation of a gaseous species \( A \) into a solid species \( B \) and a gaseous species \( C \):

\[
A(\text{gas}) \xrightarrow{\mathcal{R}_s} B(\text{solid}) + C(\text{gas})
\]  

(2.36)

Now we assume that the mechanism for this reaction is described by the following chain of reaction steps

1. \textit{adsorption of } \( A \): \( A(\text{gas}) \leftrightarrow A(\text{ads}) \)  
2. \textit{surface reaction}: \( A(\text{ads}) \leftrightarrow B(\text{ads}) + C(\text{ads}) \)  
3. \textit{desorption of } \( C \): \( C(\text{ads}) \leftrightarrow C(\text{gas}) \)  

(2.37a, 2.37b, 2.37c)

When the surface reaction (2.37b) is rate limiting and irreversible, we find the following expression for the overall surface reaction rate \( \mathcal{R}_s \) of reaction 2.36:

\[
\mathcal{R}_s = \frac{c_1 P_A}{1 + c_2 P_A}
\]  

(2.38)
with \( c_1 \) and \( c_2 \) constants (which depend on the rate constants of the individual reaction steps and which generally have to be obtained from experimental growth rates) and \( P_A \) the partial pressure of species A. Relationship 2.38 for the deposition process is called Langmuir kinetics. It predicts a growth rate which is first order in \( P_A \) at low \( P_A \) and zero order in \( P_A \) at high \( P_A \). In a similar way, expressions for \( \mathcal{R}^S \) may be obtained in the case when the adsorption of species A (2.37a) or the desorption of species C (2.37c) is rate limiting.

A concept often used to give expressions for the surface reaction rate of a monomolecular surface dissociation reaction is the so called "sticking coefficient" [e.g. Coltrin et al., 1984, 1986, 1989, Sherman, 1988, Moffat and Jensen, 1988]. It is defined as the ratio of the number of collisions of molecules A with the wafer surface and the number of molecules B which are incorporated into the deposited film per unit time. From kinetic theory it can be derived that the mole flux \( \mathcal{F}_A \) of gaseous molecules A colliding with the surface equals

\[
\mathcal{F}_A = \frac{P_A}{(2\pi m_A RT)^{1/2}}
\]  

(2.39)

Defining a sticking coefficient \( \gamma_A \) for species A we now find

\[
\mathcal{R}^S = \gamma_A \frac{P_A}{(2\pi m_A RT)^{1/2}}
\]  

(2.40)

with \( \gamma_A \neq 1 \). From the above it may be clear, that \( \gamma_A \) is not a constant, but will in general depend on the temperature and the partial pressure of species A.

2.6 BOUNDARY CONDITIONS

For every transport equation described in sections 2.2-2.4 a set of boundary conditions must be prescribed. Thus, we need boundary conditions for the velocity, the temperature and the species concentrations on solid, nonreacting walls, on the reacting surfaces and in the inflow and outflow of the reactor. The pressure must be prescribed in one point. In the following we present these different boundary conditions.
Solid, nonreacting walls

On solid, nonreacting walls we apply the no slip and impermeability conditions for the velocity vector,

\[ \mathbf{v} = 0 \]  \hspace{1cm} (2.41)

prescribed temperatures or zero temperature gradients normal to the wall for isothermal or adiabatic walls

\[ T = T_{\text{wall}} \]  \hspace{1cm} (2.42)

or

\[ \mathbf{n} \cdot \nabla T = 0 \]  \hspace{1cm} (2.43)

and zero total mass flux vectors normal to the surface for each of the species:

\[ \mathbf{n} \cdot (\mathbf{j}_i^c + \mathbf{j}_i^T) = 0 \]  \hspace{1cm} (2.44)

with \( \mathbf{n} \) a unity vector normal to the surface of the wall and \( T_{\text{wall}} \) the local wall temperature.

Reacting surfaces

Due to the surface reactions (2.33) there will be a net mass production rate \( \mathcal{P}_i \) of gaseous species \( i \) at the wafer surface

\[ \mathcal{P}_i = m_i \sum_{s=1}^{S} \sigma_{is} \mathcal{R}_s^s \]  \hspace{1cm} (2.45)

Now, we find a velocity component normal to the wafer surface according to

\[ \mathbf{n} \cdot \mathbf{v} = \frac{1}{\rho} \sum_{i=1}^{N} \sum_{s=1}^{S} m_i \sigma_{is} \mathcal{R}_s^s \]  \hspace{1cm} (2.46)

with \( \mathbf{n} \) a unity vector normal to the wafer surface. Assuming the no-slip condition to hold, the tangential component is zero:

\[ \mathbf{n} \times \mathbf{v} = 0 \]  \hspace{1cm} (2.47)

For the temperature we have
\[ T = T_{\text{wafer}} \] (2.48)

The net total mass flux of species \( i \) normal to the wafer surface must be equal to \( P_i \), so

\[ \mathbf{n} \cdot (\rho \omega_i \mathbf{v} + j_i^c + j_i^T) = m_i \sum_{s=1}^{S} \sigma_{is} \mathbf{R}^s \] (2.49)

**Inflow**

In the inlet we prescribe the flow \( Q_i \) (in standard liters per minute, slm) of each of the species \( i \). Now we find for the inflow velocity

\[ \mathbf{v}_{\text{in}} = \frac{T_{\text{in}}}{T^0} \frac{P^0}{P_{\text{in}}} \cdot \frac{1}{60} \cdot \frac{1}{A_{\text{in}}} \sum_{i=1}^{N} Q_i = 5.66 \cdot 10^{-3} \frac{T_{\text{in}}}{P_{\text{in}}} \sum_{i=1}^{N} Q_i \] (2.50)

with \( \mathbf{v}_{\text{in}} \) the inflow velocity, \( A_{\text{in}} \) the surface area of the inflow opening, \( P_{\text{in}} \) the pressure at the inlet of the reactor and \( T_{\text{in}} \) the inflow temperature. Now we take as boundary conditions for the velocity vector in the inflow

\[ \mathbf{n} \cdot \mathbf{v} = v_{\text{in}} \] (2.51)
\[ \mathbf{n} \times \mathbf{v} = 0 \] (2.52)

with \( \mathbf{n} \) a unity vector normal to the inflow opening.

The temperature in the inflow is prescribed as

\[ T = T_{\text{in}} \] (2.53)

To prohibit a conductive heat flow through the inflow opening, we prescribe

\[ \mathbf{n} \cdot (\lambda \nabla T) = 0 \] (2.54)

The total mass flow of species \( i \) into the reactor must correspond to \( Q_i \), according to

\[ \mathbf{n} \cdot (\rho \omega_i \mathbf{v} + j_i^c + j_i^T) = 5.66 \cdot 10^{-3} \frac{Q_i m_i}{R A_{\text{in}}} \] (2.55)

with \( R \) the universal gas constant. This is most easily done by taking each
of the inlet concentrations $\omega_i$ fixed as

$$\omega_i = \frac{m_i Q_i}{\sum_{j=1}^{N} m_j Q_j}$$  \hspace{1cm} (2.56)$$

and by prohibiting species diffusion through the inflow

$$\mathbf{n} \cdot (\mathbf{j}_i + \mathbf{j}_i^T) = 0$$  \hspace{1cm} (2.57)$$

**Outflow**

In the outflow we assume zero gradients in the direction normal to the outflow opening for the total mass flux vector and zero heat and species diffusion fluxes. Furthermore, we assume that the direction of the velocity is normal to the outflow opening

$$\mathbf{n} \cdot (\nabla \rho \mathbf{v}) = 0, \ \mathbf{n} \times \mathbf{v} = 0$$  \hspace{1cm} (2.58)$$

$$\mathbf{n} \cdot (\lambda \nabla T) = 0$$  \hspace{1cm} (2.59)$$

$$\mathbf{n} \cdot (\mathbf{j}_i + \mathbf{j}_i^T) = 0$$  \hspace{1cm} (2.60)$$

with $\mathbf{n}$ a unity vector normal to the outflow opening. Finally, the pressure is prescribed in the outlet of the reactor.

**Modeling of wall temperatures**

It is not always possible to use simple boundary conditions such as the isothermal boundary condition (eq. 2.42) or the adiabatic boundary condition (eq. 2.43) for the temperatures of solid walls. In CVD reactors we often have to do with reactor walls which adopt a certain temperature profile as a result of the conjugate heat exchange with their surroundings through radiation and convection. In that case, side wall temperatures may be obtained from detailed thermal energy balance models, accounting for heat conduction in the wall material, and radiative and convective heat exchange fluxes between susceptor, reactor gases, reactor walls and surroundings. An example of such a side wall temperature model will be discussed in section 7.3.1.
2.7 PREDICTION OF TRANSPORT PROPERTIES

In the absence of experimental data, the transport properties of gas species and gas mixtures may be calculated from kinetic theory. This is discussed in the following sections.

2.7.1 Properties of gas species

The density $\rho_i$ of a gas species $i$ which is assumed to behave as an ideal gas may obviously be obtained from

$$\rho_i = \frac{P_i m_i}{RT} \quad (2.61)$$

The thermal conductivity and the dynamic viscosity of a gas species are functions of the temperature and, for the pressures common in CVD, independent of the pressure. For gases like H$_2$, He, N$_2$ and Ar experimental data are available [e.g. Maitland and Smith, 1972, l'Air Liquide, 1976 and Weast, 1979]. For less common gases, the thermal conductivity and dynamic viscosity may be predicted from kinetic theory [Svehla, 1962, Reid and Sherwood, 1966, Hirschfelder et al, 1967, Bretsznajder, 1971]. In doing so, we have to make some assumptions on the intermolecular potential energy function $\varphi(r)$. For non-polar molecules a commonly used and reasonably accurate intermolecular potential energy function is the Lennard-Jones (6-12) potential:

$$\varphi(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \quad (2.62)$$

where $r$ is the distance between the molecules, $\sigma$ the collision diameter of the molecules and $\varepsilon$ the maximum energy of attraction. Using the Lennard-Jones potential, a gas species $i$ is characterized by three parameters: the mole mass $m_i$, the collision diameter $\sigma_i$ (in Ång) and the maximum energy of attraction $\varepsilon_i$, usually given as $(\varepsilon/k)_i$ (in K), with $k$ Boltzmann's constant. These parameters may be estimated from experimental viscosity or thermal conductivity data or from critical properties of the species [Bird et al., 1960, p. 22]. Values for $m$, $\sigma$ and $\varepsilon/k$ for some gases that play a role in the CVD processes that will be discussed in this thesis are given in Appendix C. We define a reduced temperature $T^*$ as
\[ T_i^* = \frac{T}{(c/k)_i} \]  \hspace{1cm} (2.63)

and the integral function \( \Omega_i(T^*) \), which is a function of \( T^* \) only and which has been tabulated [Hirschfelder et al., 1967, pp. 1126-1127]. Polynomials for calculating \( \Omega_i \) are given in Appendix D. Now we have

\[
\mu_i = 2.6693 \cdot 10^{-6} \cdot \frac{(m_i T)^{1/2}}{\sigma_i^2 \Omega_i(T_i^*)} \hspace{1cm} (2.64)
\]

\[
\lambda_i = \frac{R}{m_i} \cdot \left[ \frac{15}{4} + 1.32 \left( \frac{c_p i m_i}{R} - \frac{5}{2} \right) \right] \cdot \mu_i \hspace{1cm} (2.65)
\]

with \( \mu_i \) the viscosity and \( \lambda_i \) the thermal conductivity of species \( i \).

The bulk viscosity \( \kappa \) is identically zero for low-density, mono-atomic gases and is probably not too important for poly-atomic and dense gases [Bird et al., 1960, p. 79]. Here, the bulk viscosity has been neglected.

The specific heat \( c_p i \) of a gas species \( i \) cannot be predicted from kinetic theory, but can be calculated from spectroscopic constants. Specific heats of gases are collected by Svehla [Svehla, 1962] and in the JANAF tables [JANAF, 1985].

### 2.7.2 Properties of gas mixtures

Using the values of the transport properties of the constituent species, the transport properties of a gas mixture may be calculated from (semi) empirical mixture rules. The density of a gas mixture may of course be calculated straightforward from

\[
\rho = \frac{\sum_{i=1}^{N} \rho_i}{\sum_{i=1}^{N} \frac{P_i m}{RT}} \hspace{1cm} (2.66)
\]

with \( m \) the average mole mass according to eq. 2.14.

Several methods for calculating the viscosity and thermal conductivity of a gas mixture have been evaluated by Bretsznajder [Bretsznajder, 1971]. Following his recommendations, the following relations were used:
\[ \mu = \sum_{i=1}^{N} \left( \frac{f_i \mu_i}{f_j \Phi_{ij}} \right) \]  \hspace{1cm} (2.67)

with

\[ \Phi_{ij} = \frac{1}{\sqrt{8}} \left( 1 + \frac{m_i}{m_j} \right)^{-\frac{1}{2}} \cdot \left( 1 + \frac{\mu_i}{\mu_j} \right)^{\frac{1}{4}} \]  \hspace{1cm} (2.68)

and

\[ \lambda = \zeta \sum_{i=1}^{N} \lambda_i f_i + (1-\zeta) \cdot \left( \frac{N \sum f_i}{\sum \lambda_i} \right)^{-1} \]  \hspace{1cm} (2.69)

in which \( \zeta \) is a fraction, the value of which depends on the mole fraction \( f_L \) of light gases (He, H\(_2\)) and may be approximated by [Bretschnajder, 1971, p. 283].

\[ \zeta = 0.312 + 0.325 f_L - 0.311 f_L^2 + 0.469 f_L^3 \]  \hspace{1cm} (2.70)

The specific heat of the gas mixture is simply the mass averaged specific heat

\[ c_p = \sum_{i=1}^{N} \omega_i c_{p,i} \]  \hspace{1cm} (2.71)

### 2.7.3 Ordinary diffusion coefficients

The binary diffusion coefficient \( D_{ij} \) for a gas pair \( i \) and \( j \) may also be calculated from kinetic theory. Its value depends on the temperature and the pressure, but is virtually independent of the mixture composition [Bird \textit{et al.}, 1960, p. 570]. We introduce the Lennard-Jones parameters \( \sigma_{ij} \) and \( (\epsilon/k)_{ij} \) and the reduced temperature \( T^*_ij \) for the gas pair \( i \) and \( j \)

\[ \sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \]  \hspace{1cm} (2.72)

\[ \left( \frac{\epsilon}{k} \right)_{ij} = \left[ \left( \frac{\epsilon_i}{k} \right) \left( \frac{\epsilon_j}{k} \right) \right]^{1/2} \]  \hspace{1cm} (2.73)
\[ T_{ij}^* = \frac{T}{(c/k)_{ij}} \]  \hspace{1cm} (2.74)

and the integral function \( \Omega_D(T_{ij}^*) \), which is a function of \( T_{ij}^* \) only and which has been tabulated [Hirschfelder et al., 1967, pp. 1126-1127]. Polynomials for calculating \( \Omega_D \) are given in Appendix D. Now we have [Bretschnajder, 1971, p. 339]:

\[ D_{ij} = \left( 0.0214-0.00492 \cdot \frac{m_i + m_j}{m_i m_j} \right)^{1/2} \cdot \frac{T^{3/2}}{p_{ij} \Omega_D(T_{ij}^*) \cdot \left( \frac{m_i + m_j}{m_i m_j} \right)^{1/2}} \]  \hspace{1cm} (2.75)

**2.7.4 Thermal diffusion coefficients**

In a binary gas mixture, the binary thermal diffusion coefficient for each of the species is given by:

\[ D^T_{1} = -D^T_{2} = \frac{P}{mRT} m_{12} \cdot D_{12} \cdot k_{12} \]  \hspace{1cm} (2.76)

where \( k_{12} \) is the thermal diffusion ratio, which may be obtained from kinetic theory [Hirschfelder et al., 1967, pp. 519 et seq.]. When species 1 moves to the cold region, \( k_{12} > 0 \) and when species 2 moves to the cold region \( k_{12} < 0 \). For a given gas pair, \( k_{12} \) is a function of the temperature and the mixture composition, and is independent of the pressure.

\[ k_{12} = -k_{21} = k_{12}(f_{1}, f_{2}, T) \]  \hspace{1cm} (2.77)

Unlike other transport properties, the thermal diffusion ratio is very sensitive to the assumed intermolecular potential energy function. When the Lennard-Jones (6-12) potential is assumed, \( k_{12} \) may be calculated from the set of equations given in Appendix E [Hirschfelder et al., 1967, pp. 534-541]. In figure 2.1a the calculated thermal diffusion ratio \( k_{12} \) for a \( H_2-N_2 \) gas mixture as a function of the temperature and the mixture composition is sketched. An often used quantity is the thermal diffusion factor \( a_{12} \):

\[ a_{12} = \frac{k_{12}}{f_{1} f_{2}} \]  \hspace{1cm} (2.78)
which is much less dependent on the mixture composition (figure 2.1b).

Using the binary thermal diffusion ratios, an approximate approach for calculating multi-component thermal diffusion coefficients, suggested by Clark Jones [Clark Jones, 1941], may be used. Thus we find

$$D_{i}^{T} = \sum_{j=1}^{N} \frac{P}{m_{j}^{i} m_{j}^{' i} j} D_{i}^{j} k_{i j} \quad (2.79)$$

which should be compared to eq. 2.76. The above approximation is exact for multicomponent mixtures of isotopes and for binary mixtures. Furthermore, this approach ensures that the sum of all thermal diffusion coefficients equals zero, as it should.

The exact equations for calculating multicomponent thermal diffusion coefficients are presented in Appendix F [Hirschfelder et al., 1967, pp. 538-543]. For an N component gas mixture, this calculation involves the computation of the value of one 2N×2N and N (2N+1)×(2N+1) determinants, the elements of which are complicated functions of the mole fractions and Lennard-Jones parameters of all species and of the temperature. Thus, this demands a great computational effort. Also, the values of thermal diffusion coefficients cannot practically be tabulated, due to their dependence on N
species mole fractions and the temperature, demanding a (N+1)-dimensional table.

2.7.5 Fitting relations for transport properties

The dependence of the dynamic viscosity $\mu_1$, thermal conductivity $\lambda_i$ and specific heat $c_{p,i}$ of the gas species $i$ on the temperature, the dependence of the binary diffusion coefficient for ordinary diffusion $D_{ij}$ for a gas pair $i$ and $j$ on the temperature and the pressure and the dependence of the binary thermal diffusion ratio $k_{ij}$ for a given gas pair $i$ and $j$ on the mole fractions and the temperature may be fitted fairly accurate by using relations of the following forms:

$$\lambda, \mu, c_p = c_0 + c_1 T + c_2 T^2$$  \hspace{1cm} (2.80)

$$D_{12} = D_{21} = (c_0 + c_1 T + c_2 T^2)/P$$  \hspace{1cm} (2.81)

$$k_{12} = -k_{21} = c_0 f_1 f_2 (1 + c_1 f_1 + c_2 f_1^2 + c_3 f_1^3)(1 + c_4 \exp(c_5 T))$$  \hspace{1cm} (2.82)
3 DISCRETIZATION AND NUMERICAL SOLUTION

3.1 INTRODUCTION

The mathematical model described in chapter 2 consists of a number of coupled non-linear partial differential equations with boundary conditions. This set of equations cannot be solved analytically in general. Nevertheless, for simple reactor geometries and by making many simplifying assumptions, useful analytical solutions may be obtained for particular CVD reactors and processes (e.g. Eversteijn et al. [1970], Kuiper et al. [1982], Van de Ven et al. [1986], van Sark et al. [1989, 1990abc]). In this study however, we wish to develop a general model, which can be applied to various reactor configurations and processes. Therefore, numerical methods have been used to find approximate solutions of the full set of equations.

For the type of computational fluid dynamics problems as appearing in CVD modeling, three classes of numerical methods can be used, each of which, in fact, has been used rather successfully in CVD modeling: (1) Finite element methods, which are especially useful for modeling complex geometries, have e.g. been used by Houtman et al. [1986], Lee et al. [1986], Moffat and Jensen [1986, 1988], Fotiadis et al. [1987, 1990abc] and Pons et al. [1990]. (2) Finite difference methods have mainly been used for the numerical solution of relatively simple models for the CVD hydrodynamics, e.g. by Pollard and Newman [1980], Júza and Cermák [1982], Michaelidis and Pollard [1984], Jenkinson and Pollard [1984], Coltrin et al. [1984, 1986, 1989], Chehouani et al. [1989] and Vinante et al. [1989]. (3) The finite volume method, which is a finite difference method in combination with a so-called control volume approach using a conservative formulation of the transport equations, has been used for modeling 2D and 3D hydrodynamics in CVD, e.g. by Wahl [1977], Evans and Greif [1987ab, 1989], Rhee et al. [1987], Ulacia et al. [1989], Gokoglu et al. [1989] and Ouazzani et al. [1988, 1990]. A comparison of the advantages and disadvantages of the three methods is made by e.g. Shih [1984] and in Minkowycz et al. [1988].

In general, the finite volume method, as introduced by Patankar and Spalding [1972], is the most widely used method for calculating heat and mass transfer in 2 and 3 dimensional variable property fluid flows with chemical reactions and has been used in this study also. The method has been described in detail by Patankar [1980] and in numerous other publications. Here we will give a brief description of the method only and we will
describe in detail how the method has to be adapted in order to include multicomponent diffusion phenomena, thermal diffusion and reacting walls in CVD modeling.

The implementation of the mathematical model described in chapter 2 by means of the numerical techniques described in this chapter has resulted in the development of a FORTRAN computer code "CVDMODEL", two versions of which are available: (i) a 2D version for 2D cartesian or axisymmetric calculations and (ii) a 3D cartesian version.

### 3.2 THE GENERAL TRANSPORT EQUATION

The equations in the mathematical model are of the convection-diffusion type and can be written in the general form:

\[
\frac{\partial}{\partial t} (\rho \phi) = -\nabla \cdot (\rho \mathbf{v} \phi) + \nabla \cdot (\Gamma \phi \nabla \phi) + S\phi
\]

\[\text{transient convection diffusion "source"}\] (3.1)

Here, \( \phi \) is the variable to be solved. The meaning of the factor \( \xi_\phi \), the diffusion coefficient \( \Gamma_\phi \) and the source term \( S_\phi \) for each of the equations is explained in table 3.1.

### Table 3.1: Terms in the General Transport Equation

<table>
<thead>
<tr>
<th>Equation</th>
<th>( \phi )</th>
<th>( \xi_\phi )</th>
<th>( \Gamma_\phi )</th>
<th>( S_\phi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Continuity (2.2)</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Navier-Stokes (2.3+2.4)</td>
<td>( \mathbf{v} )</td>
<td>1</td>
<td>( \mu ) ( \nabla \left( \mu (\nabla \mathbf{v})^T - \frac{2}{3} \mu (\nabla \cdot \mathbf{v}) I \right) )</td>
<td>( \nabla \cdot \mathbf{p} + \rho g )</td>
</tr>
<tr>
<td>Energy (2.5)</td>
<td>( T )</td>
<td>( c_p )</td>
<td>( \lambda ) ( \nabla \cdot \left( \frac{RT}{I} \sum_{i=1}^{N} D_{i} \nabla (ln f_i) \right) )</td>
<td></td>
</tr>
<tr>
<td>Species (appr., 2.31)</td>
<td>( \omega )</td>
<td>1</td>
<td>( \rho D_{i} ) ( \nabla \cdot (D_{i} \nabla (ln T)) ) + ( m_{i} \sum_{k=1}^{K} \nu_{i,k} (R_{k} - R_{-k}) )</td>
<td></td>
</tr>
<tr>
<td>Species (exact, 2.32)</td>
<td>( \omega )</td>
<td>1</td>
<td>( \rho D_{i} ) ( \nabla \cdot (D_{i} \nabla (ln T)) ) + ( m_{i} \sum_{k=1}^{K} \nu_{i,k} (R_{k} - R_{-k}) ) + ( \nabla \cdot (\rho \omega D_{i} \nabla (ln m)) ) - ( \nabla \cdot (m \omega D_{i} \sum_{j=1}^{N} D_{j} \nabla (ln D_{j})) )</td>
<td></td>
</tr>
</tbody>
</table>
In this study, eq. 3.1 has been solved in 2D (x, y) and 3D (x, y, z) cartesian and 2D axisymmetric (r, z) form. We then find for the general transport equation:

2D cartesian:
\[
\xi \phi \frac{\partial (\rho \phi)}{\partial t} = -\xi \phi \frac{\partial}{\partial x} (\rho v_x \phi) - \xi \phi \frac{\partial}{\partial y} (\rho v_y \phi) + \frac{\partial}{\partial x} (\Gamma \phi \frac{\partial \phi}{\partial x}) + \frac{\partial}{\partial y} (\Gamma \phi \frac{\partial \phi}{\partial y}) + S \phi
\]
\[ (3.2a) \]

3D cartesian:
\[
\xi \phi \frac{\partial (\rho \phi)}{\partial t} = -\xi \phi \frac{\partial}{\partial x} (\rho v_x \phi) - \xi \phi \frac{\partial}{\partial y} (\rho v_y \phi) - \xi \phi \frac{\partial}{\partial z} (\rho v_z \phi) + \frac{\partial}{\partial x} (\Gamma \phi \frac{\partial \phi}{\partial x}) + \frac{\partial}{\partial y} (\Gamma \phi \frac{\partial \phi}{\partial y}) + \frac{\partial}{\partial z} (\Gamma \phi \frac{\partial \phi}{\partial z}) + S \phi
\]
\[ (3.2b) \]

2D axisymmetric:
\[
\xi \phi \frac{\partial (r \rho \phi)}{\partial t} = -\xi \phi \frac{\partial}{\partial r} (r \rho v_r \phi) - \xi \phi \frac{\partial}{\partial z} (r \rho v_z \phi) + \frac{\partial}{\partial r} (r \Gamma \phi \frac{\partial \phi}{\partial r}) + \frac{\partial}{\partial z} (r \Gamma \phi \frac{\partial \phi}{\partial z}) + r S \phi
\]
\[ (3.2c) \]

Since all the transport equations can be written in the above general forms, we can use one numerical algorithm to solve all equations. In this chapter, the numerical method is explained for the 2D cartesian case. The extension to 2D axisymmetric and 3D cartesian situations is straightforward.

3.3 DISCRETIZATION OF THE GENERAL TRANSPORT EQUATION

The solution domain is divided into a number of adjoining rectangular control volumes, or grid cells, each of them surrounding one grid point in which all scalar variables (P, T, \( \omega_i \) (i = 1, N) and fluid properties) are calculated. The vector quantities (\( \mathbf{v}_x, \mathbf{v}_y, \mathbf{v}_z \) (i = 1, N)) are calculated in points located at the cell walls, halfway between the scalar grid points, using a so called staggered grid. This is illustrated in figure 3.1. (Note, that the grid point is not necessarily located in the center of the control volume). Consider the control volume surrounding the grid point P. In the 2D case, P has four neighboring grid points, indicated by N(orth), S(south), E(est) and W(est). The corresponding walls of the control volume are indicated by n, s, e and w. For the sake of clarity, we write \( v_x = u \) and \( v_y = v \) in the remainder of this chapter. Now, by integration of the equation
3.2a over the control volume $\Delta x\Delta y$ surrounding $P$ we find

\[
\iint_{\Delta x\Delta y} \left( \xi_\phi \frac{\partial}{\partial t}(\rho \phi) \right) \, dx \, dy = \\
\iint_{\Delta x\Delta y} \left( -\xi_\phi \frac{\partial}{\partial x}(\rho u \phi) - \xi_\phi \frac{\partial}{\partial y}(\rho v \phi) + \frac{\partial}{\partial x}(\Gamma_\phi \frac{\partial \phi}{\partial x}) + \frac{\partial}{\partial y}(\Gamma_\phi \frac{\partial \phi}{\partial y}) + S_\phi \right) \, dx \, dy
\]

(3.3)

By using the Gauss theorem, assuming that $\xi_\phi$ prevails over the control volume and by linearising the source term $S_\phi$ in $\phi$ according to

\[
S_\phi = S^C_\phi + S^P_\phi \cdot \phi
\]

(3.4)

we may write
\[ \xi_\phi \int_\Delta x \int_\Delta y \left( \frac{\partial}{\partial t} (\rho \phi) \right) \, dx \, dy = -\xi_\phi \left( \int_\Delta x \int_\Delta y \rho v \phi \, dx \, dy - \int_\Delta x \int_\Delta y \rho u \phi \, dy \, dx + \int_\Delta x \int_\Delta y \rho u \phi \, dx \, dy - \int_\Delta x \int_\Delta y \rho u \phi \, dy \, dx \right) \]

\[ + \int_\Delta x \int_\Delta y \left( \Gamma_\phi \frac{\partial \phi}{\partial y} \frac{\partial}{\partial y} \frac{\partial \phi}{\partial y} \right) \, dx \, dy - \int_\Delta x \int_\Delta y \left( \Gamma_\phi \frac{\partial \phi}{\partial x} \frac{\partial}{\partial x} \frac{\partial \phi}{\partial x} \right) \, dy \, dx + \int_\Delta x \int_\Delta y \left( S^C_{\phi} + S^P_{\phi \phi} \right) \, dx \, dy \]  

(3.5)

Now, the remaining integrals are approximated as

\[ \xi_\phi \frac{\rho_P \phi_P - \rho_P^0 \phi_P^0}{\Delta t} \Delta x \Delta y = \]

\[ -\xi_\phi \left( \rho_n v \phi_n \Delta x - \rho_s v \phi_s \Delta x - \rho_n u \phi_n \Delta y + \rho_s u \phi_s \Delta y \right) \]

\[ + \Gamma_\phi, n \frac{\partial \phi}{\partial y} \bigg|_n \Delta x - \Gamma_\phi, s \frac{\partial \phi}{\partial y} \bigg|_s \Delta x + \Gamma_\phi, e \frac{\partial \phi}{\partial y} \bigg|_e \Delta y - \Gamma_\phi, w \frac{\partial \phi}{\partial y} \bigg|_w \Delta y + \]

\[ (S^C_{\phi} + S^P_{\phi \phi}) \Delta x \Delta y \]  

(3.6)

where the superscript 0 indicates the value at the previous time step. Here, a first order backward time differencing has been used, which has first order accuracy in \( \Delta t \) and which is unconditionally stable for all \( \Delta t \). The densities and diffusion coefficients at the cell walls are approximated as

\[ \rho_n = \frac{1}{2} (\rho_p + \rho_N) \]  

(3.7)

\[ \Gamma_\phi, n = \frac{2 \Gamma_p \Gamma_N}{(\Gamma_p + \Gamma_N)} \]  

(3.8)

and similar for other walls. For the approximation of the value of the variable \( \phi \) and of its first derivative on the cell walls several methods have been proposed in literature, e.g.:

**central scheme:**

\[ \phi_n = \frac{1}{2} (\phi_p + \phi_N) \]  

(3.9a)

\[ \frac{\partial \phi}{\partial y} \bigg|_n = \frac{\phi_N - \phi_p}{\Delta y_n} \]  

(3.9b)

**1st order upwind scheme:**

\[ \phi_n = \begin{cases} 
\phi_p & \text{for } v_n \geq 0 \\
\phi_N & \text{for } v_n < 0 
\end{cases} \]  

(3.10a)

\[ \frac{\partial \phi}{\partial y} \bigg|_n = \frac{\phi_N - \phi_p}{\Delta y_n} \]  

(3.10b)
hybrid scheme:
\[
\phi_n = \begin{cases} 
\phi_N & \text{for } |Pe_{\Delta n}| < 2 \\
\frac{1}{2}(\phi_P^+ + \phi_N^-) & \text{for } |Pe_{\Delta n}| \leq 2 \\
\phi_P & \text{for } |Pe_{\Delta n}| > 2 
\end{cases} \quad (3.11a)
\]
\[
\frac{\partial \phi}{\partial y} \big|_{n} = \begin{cases} 
\frac{\phi_N - \phi_P}{\Delta y_n} & \text{for } |Pe_{\Delta n}| \leq 2 \\
0 & \text{for } |Pe_{\Delta n}| > 2 
\end{cases} \quad (3.11b)
\]

"Quick" (Quadratic Upstream Interpolation for Convection Kinematics)
\[
\phi_n = \begin{cases} 
\frac{1}{2}(\phi_P + \phi_N) - \frac{1}{8}(\phi_S - 2\phi_P + \phi_N) & \text{for } v \geq 0 \\
\frac{1}{2}(\phi_P + \phi_N) - \frac{1}{8}(\phi_P - 2\phi_N + \phi_{NN}) & \text{for } v < 0 
\end{cases} \quad (3.12a)
\]
\[
\frac{\partial \phi}{\partial y} \big|_{n} = \frac{\phi_N - \phi_P}{\Delta y_n} \quad (3.12b)
\]

where the cell Peclet number on the n-wall is defined as
\[
Pe_{\Delta n} = \frac{\rho_n v_n \Delta y_n}{\Gamma_n} \quad (3.13)
\]

and similar for other walls. The central scheme and the Quick scheme have second order accuracy in \(\Delta x\) and \(\Delta y\), but become unstable for large \(|Pe_{\Delta}|\), showing wiggles in the solution. The upwind scheme damps these wiggles, in turn for loss of accuracy: this scheme gives only first order accuracy and has a large numerical diffusion. The hybrid scheme is identical with the central scheme for \(|Pe_{\Delta}| \leq 2\). For \(|Pe_{\Delta}| > 2\), the hybrid scheme locally switches to the first order upwind scheme and sets the diffusion contribution to zero. Thus, the hybrid scheme combines some of the advantages of the first order upwind scheme (stability) and the central scheme (accuracy). In this study, the hybrid scheme has been used in all cases. Note however that, because of the low Reynolds numbers, and thus low cell-Peclet numbers, common in CVD, the hybrid scheme usually resulted in a central differencing scheme.

Now, using the hybrid differencing scheme and defining convection terms \(C_{nsew}\) and diffusion terms \(D_{nsew}\) according to
\[
C_n = \xi_{\phi_P} \rho_n v_n \Delta x \quad (3.14)
\]
\[
D_n = \frac{\Gamma_n \Delta x}{\Delta y_n} \quad (3.15)
\]
and similar for other walls, we can write eq. 3.6 as:

\[ a_P \phi_P = a_N \phi_N + a_S \phi_S + a_E \phi_E + a_W \phi_W + b \quad (3.16) \]

where

\[ a_N = 0 \quad \text{for } Pe_{\Delta n} > 2 \]
\[ a_N = D_n - \frac{1}{2} C_n \quad \text{for } |Pe_{\Delta n}| \leq 2 \]
\[ a_N = -C_n \quad \text{for } Pe_{\Delta n} < 2 \]
\[ a_S = C_n \quad \text{for } Pe_{\Delta s} > 2 \]
\[ a_S = D_n + \frac{1}{2} C_n \quad \text{for } |Pe_{\Delta s}| \leq 2 \]
\[ a_S = 0 \quad \text{for } Pe_{\Delta s} < 2 \quad (3.17) \]

and similar for the other walls, and

\[ a_P = a_N + a_S + a_E + a_W - S_P \Delta x \Delta y + \frac{\varepsilon_{\phi, P_P} \phi_P \Delta x \Delta y}{\Delta t} \quad (3.19) \]
\[ b = S_C \Delta x \Delta y + \frac{\varepsilon_{\phi, P_P} \phi_P \phi_P \Delta x \Delta y}{\Delta t} \quad (3.20) \]

### 3.4 THE HYDRODYNAMIC PROBLEM

The above discretization procedure was deduced for a scalar variable on a scalar grid point. A similar procedure can be followed for the discretization of each of the components of the Navier–Stokes equations for the different velocity components on the staggered grid points. The resulting discretized equation is identical to eq. 3.16. There is however one fundamental difficulty in the calculation of the velocity field, which can be found in the appearance of the (unknown) pressure gradient in the Navier–Stokes equation. There is no obvious equation for obtaining the pressure distribution. However, the pressure field is indirectly specified through the continuity equation: A correct pressure field will, when substituted in the Navier–Stokes equations, result in a velocity field which satisfies the continuity equation.

In this study, the coupling between the Navier–Stokes equations and the continuity equation through the pressure field has been accounted for using the SIMPLE (Semi Implicit Method for Pressure Linked Equations) algorithm by Patankar and Spalding [1972]. This algorithm has been described in numerous publications (e.g. Patankar [1980], Minkowycz et al. [1988]) and we will not discuss it in detail here. Basically, SIMPLE is an iterative procedure, in
which the Navier-Stokes equations are first solved for a guessed pressure distribution \( \hat{P} \). The resulting velocity field \( \hat{\mathbf{v}} \) will, in general, not satisfy continuity. The deviation from continuity is used to find a correction for the pressure field. For this purpose, a pressure correction equation is solved, which has the same basic form as the general convection-diffusion equation 3.1. From the pressure correction \( P' \) an approximate velocity correction \( \mathbf{v}' \) is obtained. Now, the corrected pressure field \( P = \hat{P} + P' \) and the corrected velocity field \( \mathbf{v} = \hat{\mathbf{v}} + \mathbf{v}' \) are used as an initial guess for the next iteration. If the procedure converges, \( \mathbf{v} \) and \( P \) will approach the correct velocity and pressure, satisfying both the momentum and the continuity equation, and \( P' \) and \( \mathbf{v}' \) will become zero.

In our computer code we have also implemented the optional use of the SIMPLEC procedure by van Doormaal and Raithby [1984], which is a modified version of SIMPLE. For our purpose however, SIMPLEC was found to give no significant improvement compared to SIMPLE.

3.5 SOLUTION OF THE DISCRETIZED EQUATIONS

The discretized transport equations 3.16 and pressure correction equation give rise to a matrix equation of the form

\[
A\phi = b, \tag{3.21}
\]

where \( \phi \) is a vector, representing all the unknown variables in all grid points and \( b \) is a vector representing the source terms \( b \) (eq. 3.20) in all grid points. The matrix \( A \) contains the coefficients "a", as defined in eqs. 3.17-3.19. Through the fluid properties and the velocities, both \( A \) and \( b \) are functions of \( \phi \). Therefore, eq. 3.21 is nonlinear and iterative solution procedures are necessary. Although a direct solution procedure could be used to solve eq. 3.21 after linearization, the size of the matrix \( A \) makes direct solution procedures prohibitive in computational effort. Also, direct solution procedures have a small range of convergence, necessitating an accurate initial guess. Therefore, in this study iterative procedures have been used, not only to deal with the nonlinearities, but also for the solution of the linearized matrix equation. The iterative nature of the solution procedure is introduced on three levels:

(1) First, the transport equations for the different variables (velocity components, temperature, pressure, species concentrations) represented
through eq. 3.21, are decoupled. Thus, a set of matrix equations

\[ A_n \phi_n = b_n \]  

(3.22)

is obtained, where \( \phi_n \) is a vector representing the values of the variable \( \phi_n \) in all grid points and \( A_n \) and \( b_n \) contain the coefficients and source terms for this variable. The coupling between the different \( \phi_n \) is now accounted for through the repeated, iterative solution of the equations 3.22 for all \( \phi_n \).

(iii) Equation 3.22 still contains non-linearities, which are linearized by evaluating the values of the coefficients in \( A_n \) and the source terms in \( b_n \) at the previous iteration level.

(iii) The resulting, linearized matrix equations are also solved iteratively.

Three different iterative matrix solution procedures have been implemented in the computer code and can optionally be used for the solution of eqs. 3.22 after linearization:

(a) A point-by-point Gauss-Seidel method. The discretized transport equation for a particular variable is solved in one grid point at a time, marching through the domain from point to point. After the variable has been solved in the whole domain, the same procedure is repeated for the next variable.

(b) A line-by-line Gauss-Seidel method, also known as the "method of lines". The discretized transport equation for one particular variable is solved for a series of grid points on a line parallel to one of the axes. The resulting tri-diagonal matrix is solved directly with an algorithm known as the Thomas algorithm or tri-diagonal matrix algorithm (TDMA) [Patankar, 1980]. This procedure is repeated on other lines, marching through the domain from line to line in alternating directions, using lines parallel to each of the axes. Again, one variable is solved in the whole domain before switching to the next variable.

(c) A plane-TDMA procedure, which is a two-dimensional extension of the line-TDMA procedure, and solves one variable in a plane parallel to one of the axes. After marching through the whole domain in this way, the next variable is solved.

All three methods have been described in detail by Post [1988].
3.6 BOUNDARY CONDITIONS

For every transport equation of the form of eq. 3.1 a set of discretized boundary conditions is needed. These boundary conditions may be imposed through the use of so called virtual points and by modification of coefficients and source terms. These methods have been described in numerous publications (e.g. Patankar [1980], Minkowycz et al. [1988], Post [1988]) and we will not go into details here. Instead, in the following, the methods are illustrated for two types of boundary conditions which are typical for CVD reactor modeling: the boundary conditions for the species concentrations in the inflow and the boundary conditions for the normal flow and the species concentrations on reacting walls.

inflow

In figure 3.2 an inflow opening normal to the y-direction has been illustrated. The computational domain is extended across the inflow boundary with one virtual point. For the species concentration equation we wish to impose the boundary conditions (2.56-2.57) on the n-wall of the control volume surrounding P, i.e. we want to set the diffusion fluxes (including thermal diffusion) through the inflow opening to zero and we want to give each of the species concentrations in the inflow opening a fixed value \( \omega_i = \omega_i, \text{in} \).

The first is simply done by setting the diffusion coefficients in the virtual \( N \)-point equal to zero, \( D_{i,N} = D_{i,N}^T = 0 \). Through eq. 3.8 we now find

![Figure 3.2: Inflow boundary condition](image)
zero diffusion coefficients on the $n$-wall of the cell, $D_{i,n} = D_{i,n}^T = 0$, and through eqs. 2.16 and 2.20 we then find $j_{i,y,n}^C = j_{i,y,n}^T = 0$. The second can be achieved by setting $\omega_{i,N} = \omega_{i,in}^i$. Since $D_{i,n} = 0$, the hybrid differencing scheme, through eqs. 3.13 and 3.11a, will then lead to $\omega_{i,n} = \omega_{i,N} = \omega_{i,in}^i$.

Note that the zero diffusion inflow boundary condition, which is not commonly used in the modeling of fluid flow with heat and mass transfer, is especially important in CVD modelling because of the low Reynolds (and thus low Peclet) numbers common in CVD, causing a diffusive species transport through the inflow opening which is significant relative to the convective transport.

**Reacting Wall**

In figure 3.3 we have illustrated a boundary formed by a reacting wall (e.g. a wafer surface). For the normal velocity on the $s$-wall of the control volume surrounding $P$ we want to impose the boundary condition 2.46, i.e.

$$ v_s = -\frac{1}{\rho_s} \sum_{i=1}^{S} m_i \sum_{s=1}^{S} \sigma_{is} R_s^S $$

(3.23)

This is simply done by setting $v_s$ to the desired value (no transport equation for $v_s$ is solved).

For the species concentration equations we want to impose eq. 2.49, i.e.

$$ \rho \omega_{i,s} v_s + j_{i,y,s}^C + j_{i,y,s}^T = -m_i \sum_{s=1}^{S} \sigma_{is} R_s^S $$

(3.24)

*figure 3.3: Reacting wall boundary condition*
The right-hand term in eq. 3.24 is found by evaluating the surface reaction rates \( R^S \) at the temperature, the pressure and the species concentrations in the grid point \( P \) from the previous iteration. For brevity, we write

\[
-S \sum_{s=1}^{m} \sigma_{is} R^S_{s}(T_P, P_P, \omega_{j,P}(j=1,N)) = \mathcal{F}_{\text{wall}} \tag{3.25}
\]

where \( \mathcal{F}_{\text{wall}} \) is the mass flux of species \( i \) deposited on the \( s \)-wall of the control volume. When we now equate the sum of the convective and diffusive fluxes through the \( s \)-wall to \( \mathcal{F}_{\text{wall}} \) and we write a balance equation over the control volume surrounding \( P \) similar to eq. 3.6, we get

\[
\frac{\rho_P \omega_P - \rho_P^0 \omega_P^0}{\Delta t} \Delta x \Delta y = \rho_n \omega_n \Delta x + \rho_u \omega_u \Delta y - \rho_w \omega_w \Delta y \\
+ \left[ \frac{\partial \omega}{\partial y} \right]_{n} \Delta x + \left[ \frac{\partial \omega}{\partial x} \right]_{e} \Delta y - \left[ \frac{\partial \omega}{\partial x} \right]_{w} \Delta y + \mathcal{F}_{\text{wall}} \Delta x + S \Delta x \Delta y \tag{3.26}
\]

We now find the following modifications in the source terms and coefficients of eq. 3.16:

1) Calculate \( a_N, a_S, a_E, a_W \), and \( b \) from eqs. 3.17-3.20.
2) Set \( a_S \) to zero
3) Calculate \( a_P \) from eq. 3.19
4) modify the source term \( b = b - \rho_S \omega_P^0 \Delta x + \mathcal{F}_{\text{wall}} \Delta x \)

In order to find the correct value for \( \rho^S \), we have to find appropriate values for the pressure \( P^S \) and the mass fractions \( \omega_{i,S} \) in the (virtual) South point. This is done by linear extrapolation as

\[
\phi_S = \phi_P + \frac{y_S - y_P}{y_N - y_P} (\phi_N - \phi_P) \tag{3.27}
\]
3.7 IMPLEMENTATION OF STEFAN-MAXWELL EQUATIONS AND THERMAL DIFFUSION

In the general convection-diffusion equation 3.1 it is assumed, that diffusive transport of the quantity $\phi$ is due to a gradient in $\phi$ only. For species diffusion in a multi-component gas mixture this is not true. From the Stefan-Maxwell equations 2.12-2.13 it is clear, that the diffusive flux of a species $i$ in an $N$ component mixture depends on the concentration gradients of all $N$ species. Furthermore, there is diffusion due to the Soret effect.

One strategy that could be followed for treating multicomponent ordinary diffusion is to set $\Gamma_\phi$ in eq. 3.1 equal to zero and to include the $\nabla \cdot j_i^c$ term in the "source" term $S_{\phi}$. The diffusive mass flux vectors $j_i^c$ ($i = 1,N$) may then be found through the solution of the matrix equation

$$
\frac{m \rho}{m_1} \begin{pmatrix}
\omega_j & \omega_1 & \cdots & \omega_1 \\
-\sum_{j \neq 1} \frac{m_j D_{1j}}{m_1 D_{11}} & & & \\
\frac{\omega_2}{m_2 D_{22}} & -\sum_{j \neq 2} \frac{m_j D_{2j}}{m_2 D_{22}} & & \\
\vdots & \vdots & \ddots & \\
\frac{\omega_N}{m_N D_{N1}} & \frac{\omega_N}{m_N D_{N2}} & \cdots & -\sum_{j \neq N} \frac{\omega_j}{m_j D_{Nj}}
\end{pmatrix}
\begin{pmatrix}
j_1^c \\
j_2^c \\
j_N^c
\end{pmatrix}
= \begin{pmatrix}
\nabla \omega_1 + \omega_1 \nabla (\ln m) \\
\nabla \omega_2 + \omega_2 \nabla (\ln m) \\
\vdots
\end{pmatrix}
$$

(3.28)

which is equivalent with eq. 2.13. This strategy, however, would dramatically change the character of the general convection-diffusion equation and of the numerical scheme, which has been based on this equation and which has been described above. This will probably deteriorate the rate of convergence of the iterative solution procedure. Moreover, the inversion of the $N \times N$ matrix equation 3.28 in each grid point demands a great computational effort.

Therefore, we have followed another strategy, in which the diffusive mass flux $j_i^c$ is written in a form which is as close to an ordinary gradient diffusion term as possible and which has led to eq. 2.16:

$$
j_i^c = -\rho D_i \nabla \omega_i - \rho \omega_i D_i \nabla (\ln m) + m \omega_i D_i \sum_{j=1}^{N} \frac{\omega_j}{m_j D_{ij}}
$$

(3.29)

(\therefore 2.16)
or, in the 2D case

\[ j_{i}^{C} = -\rho D_{i} \frac{\partial n_{i}}{\partial x} - \rho n_{i} D_{i} \frac{\partial \ln m}{\partial x} + m \omega_{i} \sum_{j=1}^{N} m_{j} D_{i j} \] (3.30a)

\[ j_{j}^{C} = -\rho D_{j} \frac{\partial n_{j}}{\partial y} - \rho n_{j} D_{j} \frac{\partial \ln m}{\partial y} + m \omega_{j} \sum_{j=1}^{N} m_{j} D_{j i j} \] (3.30b)

Here, the first terms on the right hand sides are of the gradient diffusion type and can be treated in the usual way as the diffusion term in the general convection-diffusion equation 3.1. The last two terms on the right hand sides, which were found to be generally much smaller than the first, are included in the "source" term \( S_{\phi} \). Their values are evaluated at the previous iteration level. For this purpose, the values of each of the components of the \( j_{i}^{C} \) vectors have to be stored. Therefore, after updating the species concentration values, we calculate and store the values of \( j_{i}^{C} \) and \( j_{j}^{C} \) (in the 2D case) from eqs. 3.30a–3.30b, making use of the latest updates of \( \omega_{i} \) and of the \( j_{i}^{C} \) and \( j_{j}^{C} \) from the previous iteration. As was done with the velocity components, the components of the \( j_{i}^{C} \) vectors are calculated on the walls of the scalar grid cells.

Summarizing, we have used a strategy for including the Stefan–Maxwell equations into an iterative solution procedure for species concentration convection-diffusion equations, which (i) maintains the basic character of a convection-diffusion equation with a gradient diffusion term, and (ii) solves the Stefan–Maxwell equations iteratively and can therefore easily be included in the overall iterative solution procedure. The main disadvantage of the method is the need to store \( 2N \) (in the 2D case) or \( 3N \) (in the 3D case) extra variables in each grid point.

The terms associated with the thermal diffusion fluxes in eqs. 2.31 and 2.32 have been included in the source term \( S_{\phi} \) of the general transport equation.

### 3.8 THE ITERATIVE SOLUTION PROCEDURE

In the previous sections we have described the discretization of the transport equations and the use of iterative solution procedures at various levels: (i) To decouple the coupled equations for the various variables,
(ii) To treat the non-linearities in the equations, (iii) To solve the linearized matrix equations, (iv) To couple the Navier-Stokes and continuity equations through the SIMPLE procedure and (v) To solve the Stefan-Maxwell equations. For clarity, we will now give an overview of the total procedure.

For stationary calculations, the iterative procedure is illustrated in figure 3.4. We start by making an initial guess for the values of all primary variables (velocity components, pressure, temperature and species concentrations) in all grid points. This initial guess may be extremely simple, e.g. by setting all velocities (except for the inflow) equal to zero and all temperatures and species concentrations (except at Dirichlet boundaries) and all pressures equal to their inlet value. All ordinary diffusion fluxes are set equal to zero. Because most fluid properties are related to molar concentrations of the species, we now calculate and store the species mole fractions from the species mass fractions. Consecutively, we calculate the fluid properties in all grid points. Then the iterative solution procedure is started. We first solve the u-velocity components in all grid points, through the solution of equations like eq. 3.16. This can e.g. be done by using a line TDMA method on North-South lines (sweeping through the domain from West to East and vice versa) and on East-West lines (sweeping to the domain from South to North and vice versa) or by using a plane TDMA method. The same procedure is repeated for the v-velocity component, the pressure correction $P'$ and the temperature. Finally, the species concentration equations are solved for all species except one, which is calculated from eq. 2.10. The numerical scheme was found to be most stable when this species was chosen to be the one present in the largest mass fraction. Note that each "solve" step in figure 3.4 may represent several consecutive solution steps for the variable in all grid points, using different solvers. We now update the fluid properties and ordinary diffusion fluxes. It was found, that this could be done only once in every 25-50 iterations, without seriously deteriorating the speed of convergence. Thus, a great saving in computational effort could be achieved. At the end of the iteration a number of convergence criteria are checked (see section 3.9). If these criteria are not fulfilled, the above procedure is repeated.

For transient calculations, the procedure is illustrated in figure 3.5. We now have to know the initial fields at $t = 0$. From here, $t$ is increased with a time step $\Delta t$ and the solution at the new time level is found iteratively. When the solution at a time level fulfills the convergence criteria, we move to the next time step.
Figure 3.4: Iterative solution procedure for stationary calculations
Initialization:
- Set initial solutions at $t=0$ for $u, v, (w), P, T, \omega_i (i=1,N)$
- Initiate the species mole fractions $f_i (i=1,N)$
- Initiate the fluid properties $\rho, \mu, \lambda, c_p, D_i, D_1 (i=1,N)$
- Initiate ordinary diffusion fluxes $j_{ix}^c, j_{iy}^c, (j_{iz}^c) (i=1,N)$

Next timestep:
- $t=t+\Delta t$

Next iteration:
- $k=k+1$

Solve:
- u-velocity components in all grid points
- v-velocity components in all grid points
- (w-velocity components in all grid points)

"SIMPLE" pressure correction method

Solve:
- the temperature $T$ in all grid points
- the species mass fractions $\omega_i (i=1,N-1)$
- Calculate $\omega_N$ from $\sum \omega_i = 1$

Update:
- species mole fractions $f_i (i=1,N)$
- fluid properties $\rho, \mu, \lambda, c_p, D_i, D_1 (i=1,N)$
- ordinary diffusion fluxes $j_{ix}^c, j_{iy}^c, (j_{iz}^c) (i=1,N)$

Convergence criterion

Calculate deposition rates etc.

Figure 3.5: Iterative solution procedure for transient calculations
3.9 CONVERGENCE AND RELAXATION

The iterative solution strategy described above will not automatically converge to the desired discrete solution. In order to prevent divergence and to speed up convergence relaxation of the iterative process is necessary. In this study two forms of relaxation were used:

(i) relaxation factors: The values $\phi^*_k$ obtained from applying the iterative solvers at a certain iteration level $k$ are only used partially to update the values $\phi_{k-1}$ from the previous iteration level:

$$\phi_k = \eta \phi^*_k + (1-\eta) \phi_{k-1}$$

(3.31)

Here, $\eta$ is the relaxation factor and $\eta < 1$ causes underrelaxation. In this study we used $\eta = 0.1-0.6$ for the velocity components, $\eta = 0.2-0.8$ for the temperature and $\eta = 0.2-0.8$ for the species concentrations. For the calculation of the ordinary diffusion fluxes from eqs. 3.30ab underrelaxation with $\eta = 0.5-0.8$ was used, whereas for the fluid properties relaxation factors of 0.5-0.8 were used. A similar underrelaxation technique was used for the pressure correction (see section 3.4):

$$P_k = P_{k-1} + \eta P'$$

(3.32)

with $\eta = 0.2-0.6$.

(ii) Limited maximum relative change: When gas-phase reactions play an important role in the species concentration equations (i.e., when the convection–diffusion equation 3.1 is largely determined by the source term $S_\phi$), the above relaxation method was not found to be satisfying. Better results were obtained when the maximum relative change in the concentration between one iteration and the next was limited to a small value:

$$\phi^{**}_k = \eta \phi^{**}_k + (1-\eta) \phi_{k-1}$$

(3.33)

$$\phi_k = \begin{cases} 
(1-\Delta) \phi_{k-1} & \text{if } \phi^{**}_k < (1-\Delta) \phi_{k-1} \\
\phi^{**}_k & \text{if } (1-\Delta) \phi_{k-1} \leq \phi^{**}_k \leq (1+\Delta) \phi_{k-1} \\
(1+\Delta) \phi_{k-1} & \text{if } \phi^{**}_k > (1+\Delta) \phi_{k-1}
\end{cases}$$

(3.34)

Here, $\eta$ is the relaxation factor as defined above and $\Delta$ is the maximum relative change in $\phi$ from one iteration to the next. This procedure can be
interpreted as an underrelaxation procedure with a variable relaxation factor \( \eta' \), where \( \eta' \to 0 \) for \( |(\phi_k^*-\phi_{k-1}^*)/\phi_{k-1}^*| > 1 \) and \( \eta' \to \eta \) for \( |(\phi_k^*-\phi_{k-1}^*)/\phi_{k-1}^*| < 1 \). In this study we have used \( \Delta = 0.01-0.05 \) for the species concentration equations in the presence of gas-phase reactions.

When the iterative solution procedure is converging to the desired solution, the iterations will be stopped when the difference between the iterated solution and the final solution is small enough. In this study we used several criteria for stopping the iterative procedure:

(i) From eq. 3.16 we can define an absolute, normalized residual \( R_P \) as

\[
R_P = \left| \frac{a_P \phi_P - a_N \phi_N - a_S \phi_S - a_E \phi_E - a_W \phi_W - b}{a_P \phi_{\text{ref}}} \right| \tag{3.35}
\]

where \( \phi_{\text{ref}} \) is a typical value for \( \phi \) in the computational domain. We now demand that the value of \( R_P \), averaged over all grid points, is below a certain small value for all \( \phi \).

(ii) For all variables in all grid points we demand that the relative change \( |(\phi_k^*-\phi_{k-1}^*)/\phi_{k-1}^*| \) from one iteration to another is below a certain small value.

(iii) Finally, we check that the error in the overall mass balance \( \Delta m \), with

\[
\Delta m = \left| \frac{\text{mass in} - \text{mass deposited} - \text{mass out}}{\text{mass in}} \right| \tag{3.36}
\]

is below a certain small value. In the absence of gas-phase reactions, this is also checked for the errors in the mass flows of each of the gas species.
4 FLOW, HEAT AND MASS TRANSFER IN A SINGLE-WAFER REACTOR

4.1 INTRODUCTION

As has been discussed in section 1.2, there is an increasing interest in the use of coldwall single-wafer LPCVD reactors in the IC industry. It has been stated that these reactors may in principle offer highly uniform growth rates on large wafers and that the gas flow may be "tuned" precisely in such a way that uniform deposition and efficient removal of reaction products are obtained. Therefore, a significant part of this thesis is devoted to the gas flow, transport phenomena and chemical reactions in cold-wall single-wafer LPCVD processes. In chapters 5 and 6 a detailed study of all relevant phenomena in single-wafer silicon and tungsten LPCVD will be made.

In this chapter however, a simplified study will be made of an idealized single-wafer LPCVD process. This will provide general information on the influence of the process conditions (pressure, temperature, type of gas, flowrate) and reactor geometry on the transport phenomena in the reactor. In sections 4.3 and 4.4 it will be shown, that such an analysis can be performed in terms of a small number of dimensionless numbers. The gas flow and heat transfer in the reactor are mainly determined by two dimensionless numbers only, the Reynolds and the Grashof number. Together with a third dimensionless number, the Schmidt number, these numbers also determine the reactant species concentration distribution and the mass transfer to the susceptor surface. Therefore, the gas flow and the heat and mass transfer in the reactor will be studied through model simulations as a function of the Grashof, Reynolds and Schmidt numbers, thus covering the whole range of common single-wafer LPCVD process conditions. In addition, experimental velocity measurements by means of Laser Doppler Anemometry in an isothermal scale-model of the studied single-wafer reactor will be compared to the flow simulations, in order to partially validate the mathematical model.

4.2 PROBLEM DESCRIPTION

In the simplified approach it is assumed that a single reactant, which is highly diluted \( f, \omega \ll 1 \) in a carrier gas, deposits at the susceptor surface with an infinite reaction rate and that homogeneous reactions are
negligible. Furthermore, the Dufour and Soret effects are neglected. Because of the low concentrations, the reactant species has no influence on the main gas flow and the heat transfer in the reactor. Thus, the species concentration equation is decoupled from the flow and energy equations. Due to the fast heterogeneous reaction and the absence of gasphase reactions, the deposition process is fully determined by the convective an diffusive transport of the reactant species to the susceptor surface and no chemical kinetics model is needed.

The studied single-wafer reactor, which has been developed by ASM International Inc. and has been designed for handling 0.20 m diameter wafers, is illustrated in figure 4.1. A small number of prototype reactors has been built and is being used as a research reactor for the development of Tungsten LPCVD processes. The experience that is gained with these prototype reactors may be used for the development of new single-wafer reactors, that can be used in commercial IC fabrication. The reactor is of the vertical impinging jet type and is cylinder symmetric. The walls of the stainless steel reactor chamber are water-cooled to room temperature. The wafer is placed on top of a 0.24 m diameter graphite susceptor on top of a quartz dome. The susceptor is heated indirectly by means of a resistance heating element, which is fixed against the inside of the upper wall of the quartz dome. The parts of the dome outside the susceptor are protected from

![Diagram of ASM coldwall single-wafer LPCVD reactor.](image)

*figure 4.1: The ASM coldwall single-wafer LPCVD reactor.*

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heating up by means of radiation shields. The gases are introduced radially into a 0.20 m diameter gas injection tube, which is positioned perpendicularly above the susceptor surface, and leave the reactor through the outflow. It is assumed, that deposition takes place exclusively on the wafer and susceptor surfaces. It is furthermore assumed, that the gas flow in the reactor is axisymmetric and steady-state. However, there is some indication, that asymmetric and unstable time-dependent flows may occur for certain process conditions. This is further discussed in section 4.10.

4.3 SOME REMARKS ON THE USE OF DIMENSIONLESS EQUATIONS AND DIMENSIONLESS NUMBERS IN CVD MODELING

The flow, heat and mass transfer in the reactor are described by the transport equations with boundary conditions and fluid property relations given in chapter 2. These equations have been presented in dimensional form. However, it is often useful to use dimensionless equations, in which the variables have been made dimensionless by scaling them with a reference value. As a result of this procedure certain dimensionless numbers, which may be interpreted as the ratio of the magnitude of two physical phenomena, appear in the equations and usually the number of problem defining parameters is reduced. In principle, the complete set of transport equations (2.2–2.5, 2.31/2.32), boundary conditions (2.41–2.60) and relations for the transport properties (2.61–2.79) could be written in dimensionless form. However, because of the complicated dependence of the transport properties on temperature, pressure and mixture composition in CVD reactors, a great number of dimensionless groups in addition to those that describe a constant property problem has to be introduced. Therefore, dimensional equations have been used throughout most of this study.

Nevertheless, dimensionless numbers may be very useful for the characterization of general features of CVD processes and as an easy way to check possible scale-up effects. Moreover, in the simplified case of a single highly diluted reactant in a carrier gas, as considered in this chapter, and when the Soret and Dufour effects are also neglected, the transport equations may relatively easy be written in dimensionless form. In doing so, several dimensionless groups appear, which, together with the geometric reactor configuration, give a complete definition of the fluid dynamics and chemical reactions in the reactor. In table 4.1 these dimensionless groups (as well as some other important dimensionless groups
### Table 4.1: Dimensionless groups in CVD

<table>
<thead>
<tr>
<th>Dimensionless group</th>
<th>Definition</th>
<th>Physical interpretation</th>
<th>Typical value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>APCVD</td>
</tr>
<tr>
<td>Reynolds (Re)</td>
<td>$\frac{\rho v L}{\mu_r}$</td>
<td>inertia forces viscosity forces</td>
<td>$10^{-2}$ - $10^5$</td>
</tr>
<tr>
<td>Grashof (Gr)</td>
<td>$\frac{g \rho_r \rho_v L^2 (T_h - T_c)}{\mu_r \rho_v}$</td>
<td>buoyancy forces viscosity forces</td>
<td>$10^5$ - $10^7$</td>
</tr>
<tr>
<td>Prandtl (Pr)</td>
<td>$\frac{\mu_r \rho_v}{\lambda_r}$</td>
<td>momentum diffusivity thermal diffusivity</td>
<td>$\approx 0.7$</td>
</tr>
<tr>
<td>Gay-Lussac (Ga)</td>
<td>$\frac{T_h - T_c}{T_r}$</td>
<td>temperature difference reference temp</td>
<td>$1$ - $1.3$</td>
</tr>
<tr>
<td>Schmidt (Sc)</td>
<td>$\frac{\mu_r}{\rho_r \rho_v}$</td>
<td>momentum diffusivity species diffusivity</td>
<td>$1$ - $10$</td>
</tr>
<tr>
<td>gas-phase Arrhenius</td>
<td>$\frac{E}{R T_r}$</td>
<td>activation energy potential energy</td>
<td>$0$ - $100$</td>
</tr>
<tr>
<td>surface Arrhenius</td>
<td>$\frac{E}{R T_r}$</td>
<td>activation energy potential energy</td>
<td>$0$ - $100$</td>
</tr>
<tr>
<td>gas-phase Damköhler</td>
<td>$\frac{L R_{ref}}{c_{in}^n}$</td>
<td>chemical reaction rate bulk rate</td>
<td>$10^{-3}$ - $10^3$</td>
</tr>
<tr>
<td>surface Damköhler</td>
<td>$\frac{L R_{ref}}{c_{in}^{n+1}}$</td>
<td>chemical reaction rate diffusion rate</td>
<td>$10^{-3}$ - $10^3$</td>
</tr>
<tr>
<td>Knudsen (Kn)</td>
<td>$\frac{E}{L}$</td>
<td>mean free path length characteristic dimension</td>
<td>$10^{-6}$ - $10^{-5}$</td>
</tr>
<tr>
<td>Rayleigh (Ra)</td>
<td>$Gr \cdot Pr$</td>
<td>buoyancy forces viscosity forces</td>
<td>$10^2$ - $10^7$</td>
</tr>
<tr>
<td>mass Peclet (Pe)</td>
<td>$Re \cdot Sc$</td>
<td>convective mass transfer diffusive mass transfer</td>
<td>$10^{-1}$ - $10^{-3}$</td>
</tr>
</tbody>
</table>

In CVD, these dimensionless groups are summarized, along with their physical interpretation and typical order of magnitude in APCVD (10^5 Pa) and LPCVD (10^2 Pa) reactors. In this table, L is a typical reactor dimension, V is a typical gas flow velocity, $c_{in}$ is the reactant inlet mole concentration (=$\phi$, P/RT), $T_h$ and $T_c$ are the hot susceptor temperature and the cold wall temperature respectively, $T_{ref}$ is the average gas temperature and $\phi_{ref}$ is the value of $\phi$ at the average gas temperature and pressure.

The Peclet, Grashof/Rayleigh, Reynolds, Damköhler and Knudsen numbers are particularly important for characterization of a CVD process. The relevance of the Knudsen number has been discussed in section 2.2. When the mass Peclet number is large, species transfer is mainly due to convection and downstream reaction products and impurities will not diffuse back into the reaction zone. When the mass Peclet number is small, the species transport is determined by diffusion mainly and the influence of the flow is
small. The Grashof and/or Rayleigh number are a measure for the occurrence of natural convection phenomena in the reactor. For large Rayleigh/Grashof numbers, natural and mixed convection phenomena are likely to disturb the flow field. When the surface Damköhler number is large, the surface reaction will be diffusion limited, whereas for small surface Damköhler numbers the deposition is kinetically limited. For large gas-phase Damköhler numbers, gas-phase chemistry will be important and the gases in the reactor will be close to thermodynamical equilibrium, whereas for small gas-phase Damköhler numbers the residence time in the reactor is too small for gas-phase reactions to proceed and the gas mixture will be in strong non-equilibrium. For the present simplified CVD process, the surface Damköhler number is infinite, whereas the gasphase Damköhler number is zero.

4.4 DIMENSIONAL ANALYSIS

In light of the above discussion on the advantages of using dimensionless equations, we will now make a dimensional analysis of the equations describing the simplified CVD process studied in this chapter. With the assumptions described in section 4.2, the continuity equation (eq. 2.2), the Navier–Stokes equation (eq. 2.3), the energy equation (eq. 2.5) and the species concentration equation (eq. 2.31) may be written as

\[
\nabla \cdot (\rho \mathbf{v}) = 0 \quad (4.1)
\]

\[
\nabla \cdot (\rho \mathbf{v} \mathbf{v}) = \nabla \cdot \left( \mu (\nabla \mathbf{v} + (\nabla \mathbf{v})^T) - \frac{2}{3} \mu (\nabla \cdot \mathbf{v}) \mathbf{I} \right) - \nabla P - \rho g e_z \quad (4.2)
\]

\[
\frac{c_p}{c} \nabla \cdot (\rho \mathbf{v} T) = \nabla \cdot (\mathbf{A} \nabla T) \quad (4.3)
\]

\[
\nabla \cdot (\rho \omega) = \nabla \cdot (\rho \mathbf{D} \mathbf{D} \mathbf{v}) \quad (4.4)
\]

with the following boundary conditions

\[
\text{reactor walls:} \quad \mathbf{v} = 0; \quad T = T_a \quad \frac{\partial \omega}{\partial n} = 0 \quad (4.5)
\]

\[
\text{susceptor surface:} \quad \mathbf{v} = 0; \quad T = T_{\text{susc}} \quad \omega = 0 \quad (4.6)
\]

\[
\text{Inflow:} \quad \mathbf{v}_n = \mathbf{v}_{in}; \quad T = T_a \quad \omega = \omega_{in}; \quad \mathbf{D} = 0 \quad (4.7)
\]

\[
\text{Outflow:} \quad \frac{\partial \rho \mathbf{v}}{\partial n} = 0; \quad \frac{\partial T}{\partial n} = 0; \quad \frac{\partial \omega}{\partial n} = 0 \quad (4.8)
\]

Here, \( n \) is the direction normal to the boundary. Because of the low reactant concentrations, the gas properties do not depend on the gas mixture composition, but on the temperature and pressure only. For most CVD carrier
gases and under common CVD conditions, these dependencies may be fitted through relations of the form

\[ \mu = c_1 T^{-0.7}; \quad \lambda = c_2 T^{-0.8}; \quad c_p = c_3 T^{-0.1}; \quad \rho = c_4 \rho_{\text{ref}}^{-1}; \quad D = c_5 T^{-1.7} P^{-1}_{\text{ref}} \] (4.9)

Here, \( c_1 - c_4 \) are constants, which depend on the type of carrier gas, and \( c_5 \) is a constant which depends on the combination of carrier gas and reactant. It is assumed, that the gas pressure is approximately equal to \( P_{\text{ref}} \) everywhere in the reactor chamber. From the above it is clear, that the gas flow and heat and species transfer are determined by the type of carrier gas and reactant, the pressure \( P_{\text{ref}} \), the susceptor and ambient temperatures \( T_{\text{susc}} \) and \( T_a \), the species inlet concentration \( \omega_{\text{in}} \) and the reactor dimensions.

The above equations are now made dimensionless by introducing the following dimensionless variables:

\[
\begin{align*}
\hat{v} &= \frac{v}{V} \\
\hat{T} &= \frac{(T - T_a)}{(T_{\text{ref}} - T_a)} \\
\hat{\omega} &= \frac{\omega}{\omega_{\text{in}}} \\
\hat{\rho} &= \frac{P}{\rho_{\text{ref}}} \\
\hat{\mu} &= \frac{\mu}{\mu_{\text{ref}}} \\
\hat{\lambda} &= \frac{\lambda}{\lambda_{\text{ref}}} \\
\hat{\phi} &= \frac{P - \rho_{\text{ref}} \gamma}{(\rho_{\text{ref}} V^2)} \\
\hat{\tau} &= \frac{L}{V} \\
\hat{c} &= \frac{c_p}{c_{p,\text{ref}}} \\
\hat{D} &= \frac{D}{D_{\text{ref}}} \\
\hat{c}_p &= \frac{c_p}{c_{p,\text{ref}}} \\
\hat{D} &= \frac{D}{D_{\text{ref}}} \\
\end{align*}
\] (4.10)

where \( \phi_{\text{ref}} \) is the value of the variable \( \phi \) at the average gas temperature \( T_{\text{ref}} = \frac{T_{\text{susc}} + T_a}{2} \), \( V \) is a characteristic velocity and \( L \) is a characteristic reactor dimension. This yields the following dimensionless transport equations:

\[
\begin{align*}
\text{continuity:} & \quad \hat{\nabla} \cdot (\hat{\rho} \hat{\nabla}) = 0 \\
\text{momentum:} & \quad \hat{\nabla} \cdot (\hat{\rho} \hat{\nabla} \hat{\nabla}) = \frac{1}{Re} \hat{\nabla} \cdot \left( \hat{\mu} \left( \hat{\nabla} \hat{\nabla} + (\hat{\nabla} \hat{\nabla})^T \right) - \frac{2}{3} \hat{\mu} (\hat{\nabla} \cdot \hat{\nabla}) \mathbb{I} \right) - \hat{\nabla} \hat{\rho} \\
& \quad \quad + \frac{Gr}{Re^2} \left( \frac{\hat{T} - \frac{1}{2}}{(\hat{T} - \frac{1}{2}) \text{Ga} + 1} \right) \hat{c}_p \\
\text{energy:} & \quad \hat{c}_p \hat{\nabla} \cdot (\hat{\rho} \hat{\nabla} \hat{T}) = \frac{1}{Re \cdot Pr} \hat{\nabla} \cdot (\hat{\lambda} \hat{\nabla} \hat{T}) \\
\text{species:} & \quad \hat{\nabla} \cdot (\hat{\rho} \hat{\nabla} \hat{\omega}) = \frac{1}{Re \cdot Sc} \hat{\nabla} \cdot (\hat{\rho} \hat{\nabla} \hat{\omega}) \\
\end{align*}
\] (4.11-4.14)

with the dimensionless boundary conditions:
reactor walls: \( \hat{y} = 0; \quad \hat{T} = 0; \quad \hat{\omega}/\hat{n} = 0 \) \hspace{1cm} (4.15)

susceptor surface: \( \hat{y} = 0; \quad \hat{T} = 0; \quad \hat{\omega} = 0 \) \hspace{1cm} (4.16)

Inflow: \( \hat{v}_n = v_{in}\sqrt{\nu}; \quad \hat{T} = 0; \quad \hat{\omega} = \omega_{in}; \quad \hat{\theta} = 0 \) \hspace{1cm} (4.17)

Outflow: \( \delta\rho\hat{u}/\delta n = 0; \quad \delta\hat{T}/\delta n = 0; \quad \delta\hat{\omega}/\delta n = 0 \) \hspace{1cm} (4.18)

and the dimensionless fluid properties

\[ \hat{\mu} = ((\hat{T} - \frac{1}{2}Ga + 1)^{0.7}; \quad \hat{\lambda} = ((\hat{T} - \frac{1}{2}Ga + 1)^{0.8}; \quad \hat{c}_p = ((\hat{T} - \frac{1}{2}Ga + 1)^{0.1} \]

\[ \hat{\rho} = ((\hat{T} - \frac{1}{2}Ga + 1)^{-1}; \quad \hat{\theta} = ((\hat{T} - \frac{1}{2}Ga + 1)^{1.7} \]

\hspace{1cm} (4.19)

Thus, the gas flow and heat transfer are determined by four dimensionless groups:

The Reynolds number \( Re = \frac{\rho_{ref} v L}{\mu_{ref}} \) \hspace{1cm} (4.20)

The Grashof number \( Gr = \frac{g\rho_{ref}^2 L^3 (T_{susc} - T_a)}{\mu_{ref}^2 T_{ref}} \) \hspace{1cm} (4.21)

The Prandtl number \( Pr = \frac{\mu_{ref} c_{p,ref}}{\lambda_{ref}} \) \hspace{1cm} (4.22)

The Gay-Lussac number \( Ga = \frac{T_{susc} - T_a}{T_{ref}} \) \hspace{1cm} (4.23)

In addition, the species transport is determined by

The Schmidt number \( Sc = \frac{\mu_{ref}}{\rho_{ref} D_{ref}} \) \hspace{1cm} (4.24)

For most CVD carrier gases under common CVD conditions, the Prandtl number is equal to \( \approx 0.7 \). Thus, the Prandtl number is not a parameter for the description of the process conditions. Also, there is only a small variation in the value of the Gay-Lussac number. For a wall temperature of 300 K and a susceptor temperature between 600 K and 900 K, \( Ga \) is between 0.67 and 1.0. In sections 4.9 and 7.6 it will be shown, that the influence of such variations in the Gay-Lussac number on the gas-flow in CVD reactors is relatively small. As a result, the gas flow and heat transfer depend mainly on the Reynolds and Grashof numbers only, whereas the reactant species transport depends on the Reynolds and Grashof numbers through the gas flow, and on the Schmidt number.
A further analysis of eq. 4.12 shows, that the gas flow is independent of the Grashof number for small values of the mixed convection parameter Gr/Re². In particular, an isothermal flow is determined by the value of Re only. For small values of Re, the inertial (i.e. the left hand side) term of the momentum equation is small compared to the viscous term (i.e. the first term on the right hand side) and may neglected. As a result, buoyancy induced mixed convection effects, which are counteracted by viscous effects, are mainly determined by the value of Gr/Re. Furthermore, from eqs. 4.13 and 4.14 it may be concluded, that the temperature and species concentration distributions are mainly determined by conduction/diffusion and virtually independent of the gas flow for small values of Re. So, in general, heat and mass transfer to the susceptor surface will be virtually independent of Re and Gr when Re is small, and virtually independent of Gr when Gr/Re² is small.

For the ASM single-wafer reactor configuration of figure 4.1, taking the 0.1 m radius Rp of the vertical inflow pipe as the characteristic dimension L and the average axial gas velocity in this pipe as the characteristic velocity V, we obtain the relations between the flowrate and reactor pressure and the Reynolds and Grashof numbers presented in table 4.2, for different susceptor temperatures and carrier gases. At a fixed reactor configuration and susceptor temperature, the Reynolds number depends on the type of gas and the flowrate only, whereas the Grashof number depends on the type of gas and the pressure only. In common single-wafer LPCVD operation, the flowrate is between 0.1 and 10 slm, whereas the pressure is between 10 and 1000 Pa, leading to $10^{-2} \leq Re \leq 10^1$ and $10^{-3} \leq Gr \leq 10^3$. For

<table>
<thead>
<tr>
<th>gas</th>
<th>Reynolds</th>
<th>Grashof</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{susc} =$</td>
<td>$T_{susc} =$</td>
</tr>
<tr>
<td></td>
<td>600 K</td>
<td>700 K</td>
</tr>
<tr>
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<td>0.24·Q</td>
<td>0.20·Q</td>
</tr>
<tr>
<td>H₂</td>
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<td>0.23·Q</td>
</tr>
<tr>
<td>N₂</td>
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</tr>
<tr>
<td>Ar</td>
<td>2.14·Q</td>
<td>1.79·Q</td>
</tr>
</tbody>
</table>

Table 4.2: Relations between the total flow Q (slm), the total pressure P (Pa) and the Reynolds and Grashof number in the ASM single-wafer reactor for different susceptor temperatures.

- 68 -
the Schmidt number of highly diluted reactants in different carrier gases, values between circa 0.8 and 3 are found, see table 4.3.

In this chapter, the gas flow and the heat and species mass transfer will be studied as a function of Re and Gr, at fixed Pr = 0.7, Ga = 0.8 and Sc = 1.0. In addition, the gas flow and heat and mass transfer will be studied as a function of Ga, at fixed Pr, Sc, Re and Gr, and as a function of Sc, at fixed Re, Gr, Pr and Ga.

<table>
<thead>
<tr>
<th>carrier gas</th>
<th>reactant</th>
<th>SiH₄</th>
<th>WF₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>helium</td>
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<td>2.8</td>
<td></td>
</tr>
<tr>
<td>hydrogen</td>
<td>1.8</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>nitrogen</td>
<td>0.9</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>argon</td>
<td>0.8</td>
<td>1.6</td>
<td></td>
</tr>
</tbody>
</table>

4.5 NUMERICAL SIMULATION

The steady-state transport equations with boundary conditions and relations for the gas properties eqs. 4.1-4.9 are solved in 2D axisymmetric form, using the control volume based finite difference method described in chapter 3. The equations are discretized on a non-uniform cylindrical grid, with 50 grid point in the radial and 70 grid points in the axial direction (figure 4.2). The grid is locally refined near the walls. Grid independence of the results has been checked by using a 75×100 grid for some representative situations. The local heat and mass transfer coefficients obtained on the finer grid differ less than 1% everywhere on the susceptor surface from those obtained on the standard grid.

The resulting equations were solved iteratively by using line-by-line TDMA and two-dimensional plane-TDMA methods (see chapter 3). For the momentum equations line TDMA methods on grid lines perpendicular to their coordinate direction were used: the axial momentum equation was solved on
horizontal grid lines, whereas the radial momentum equation was solved on vertical grid lines. The pressure correction and energy equations were solved by the line TDMA procedure on both horizontal and vertical grid lines. For the species concentration equation, both the line TDMA method on horizontal and vertical lines and the two-dimensional plane-TDMA method were used. For underrelaxation, standard relaxation techniques were used (eqs. 3.31-3.32), with $\eta = 0.4$ for the momentum equations $\eta = 0.8$ for the energy and species concentration equations and $\eta = 0.6$ for the pressure correction. Three convergence criteria were used: (i) the error in the global mass balance, $< 10^{-2}$ %; (ii) the residuals of the equations (eq. 3.35), averaged over all the grid points, and normalized with the maximum value for each variable, $< 10^{-5}$, and (iii) the relative changes from one iteration to the next in the heat and mass transfer coefficients at the center of the susceptor surface, $< 10^{-5}$. Negligible changes in the calculated heat and mass transfer coefficients occurred, when more severe convergence criteria were used. The calculations were carried out on a HP 9000-835 minicomputer. The number of iterations needed to satisfy the above convergence criteria
depends strongly on the value of the Reynolds number, varying from circa 400 iterations for $Re = 10$ to circa 1500 iterations for $Re = 0.01$, taking 3.5 seconds cpu time per iteration on the standard grid.

4.6 INFLUENCE OF THE REYNOLDS AND GRASHOF NUMBERS ON THE GAS FLOW

The gas flow has been simulated for fixed values of the Prandtl number ($Pr = 0.7$) and the Gay-Lussac number ($Ga = 0.8$), at varying Reynolds ($Re = 0.01$-10) and Grashof ($Gr = 10^{-3}$-$10^3$) numbers. The equations were solved in dimensional form and $Re$ and $Gr$ were varied by varying the carrier gas, flow rate and total pressure. It has been verified that the simulated flow and temperature fields, after being made dimensionless, were indeed identical for cases with different carrier gas, flow rate and pressure, but equal $Gr$ and $Re$ numbers.

Figures 4.3a-c illustrate the influence of the Grashof number on the flow in the reactor at fixed $Re = 1$. At $Gr = 30$, the flow is not disturbed by buoyancy effects and there are no flow recirculations. The normalized streamfunction values are between $\psi_{\min} = 0$ and $\psi_{\max} = 1$ everywhere in the reactor. At higher $Gr$ buoyancy induced recirculations are observed near the edge of the susceptor, rising up above the heated susceptor and coming down along the cold wall of the reactor. The amount of recirculation increases with increasing $Gr$. At $Gr = 100$, the maximum value of the streamfunction is $\psi_{\max} = 1.3$, whereas at $Gr = 300$ it has increased to $\psi_{\max} = 2.8$. The influence of these flow recirculations on the gas temperatures however is relatively small, as can be observed in figures 4.4a-c. At these conditions, the temperature distribution in the gas is mainly determined by heat conduction in the gas from the susceptor to the cold walls and the flow recirculations cause only a small uplifting of the hot gases. Figures 4.5a-c show the influence of the $Re$ number on the gas flow at a fixed value of $Gr = 300$. An increase in $Re$ from 1 to 3 strongly suppresses the buoyancy induced recirculating flows, reducing the maximum streamfunction value from $\psi_{\max} = 2.8$ to $\psi_{\max} = 1.2$. At even higher Reynolds numbers ($Re = 10$, figure 4.5c) another type of recirculating flow appears, which is induced by inertial effects. For this flow situation, the maximum streamfunction is $\psi_{\max} = 1.4$ and the minimum streamfunction is $\psi_{\min} = -0.2$. The influence of the Reynolds number on the temperature distribution is illustrated in figures 4.6a-c. At high $Re$, the thickness of the hot region above the
susceptor is strongly reduced and a relatively thin thermal boundary layer is formed.

To summarize the flow simulations, table 4.4 gives the minimum and maximum streamfunction values for all simulated combinations of Re and Gr. In general, buoyancy induced recirculations with $\Psi_{\text{max}} > 1$ are found for $\text{Re} \leq 3$ and $\text{Gr}/\text{Re} \geq 60$. For these flow parameters, the maximum streamfunction value is roughly equal to $\Psi_{\text{max}} = 1 + 0.007 \cdot (\text{Gr}/\text{Re} - 60)$. For $\text{Re} \geq 5$ two separate flow recirculations, caused by inertial effects, are found, leading to $\Psi_{\text{min}} < 0$ and $\Psi_{\text{max}} > 1$, respectively. These inertial rolls are absent for
Re ≤ 3. It should be stressed, that inertial rolls may be avoided by streamlining the reactor. To suppress the buoyancy induced rolls, the carrier gas, process conditions or reactor dimensions must be changed in order to reduce Gr or increase Re.
4.7 INFLUENCE OF THE REYNOLDS AND GRASHOF NUMBERS ON THE HEAT AND MASS TRANSFER TO THE SUSCEPTOR SURFACE

The influence of the Grashof and Reynolds number on the heat transfer and reactant species mass transfer is studied for different Gr and Re at fixed Ga = 0.8, Pr = 0.7 and Sc = 1.0. The heat flux from the susceptor to the reactor gas is made dimensionless with the thermal conductivity of the gas at the reference temperature \( \lambda_{\text{ref}} \), the vertical distance from the susceptor surface to the upper wall \( Z_{\text{tot}} \) and the temperature difference \( (T_{\text{susc}} - T_a) \) between the heated susceptor and the cooled reactor walls, leading to a Nusselt number \( Nu \) defined as

\[
Nu = \frac{Z_{\text{tot}}}{\lambda_{\text{ref}} (T_a - T_{\text{susc}})} \cdot \left( \frac{\partial T}{\partial z} \right)_{\text{susceptor}}
\]  \hspace{1cm} (4.25)

Thus, in case the heat transfer from the susceptor is purely caused by heat conduction to the cold upper reactor wall through a gas with \( \lambda = \lambda_{\text{ref}} \), we have \( Nu = 1 \). The reactant species mole flux from the gas to the susceptor is made dimensionless with the incoming mole flow of the species and with the reactive susceptor area, leading to a species transfer rate number \( M \), according to
where $A_{\text{susceptor}}$ is the susceptor area, $Q$ is the total gas supply in moles per second, $f_{\text{in}}$ is the inlet mole fraction of the reactant and $c$ (=P/RT) is the total mole concentration. In case all the incoming reactant would deposit on the susceptor surface, we would have $<\mathcal{M}> = 1$, with $<\mathcal{M}>$ the species transfer rate number $\mathcal{M}$ averaged over the susceptor surface. In general, we have $<\mathcal{M}> \leq 1$.

The calculated Nu numbers and species transfer rate numbers $\mathcal{M}$ for different Re and Gr are shown in figures 4.7a-d.

\begin{align*}
\mathcal{M} &= \frac{A_{\text{susceptor}}}{Q \cdot f_{\text{in}}} \cdot \left( cD \frac{\partial f}{\partial z} \right)_{\text{susceptor}} \\
\end{align*}

\text{(4.26)}

\text{figure 4.7: Nusselt (---) and } \mathcal{M} (----) \text{ numbers at the susceptor surface as a function of the normalized radius, for different Re and Gr (R = susceptor radius).}
Some conclusions can be drawn from these figures:

(i) A first important conclusion is, that the uniformity of $Nu$ and $M$, i.e. of the heat and species mass transfer to the susceptor surface, are quite dissimilar. Also, $Nu$ and $M$ show different dependencies on $Gr$ and $Re$. This is in clear contradiction with many CVD modeling studies, in which it is assumed that the Nusselt number for heat transfer is a measure for the transport limited species mass transfer (e.g. Houtman et al., [1986], Evans and Greif [1987ab]). This assumption is based on the mathematical equivalence of the energy equation (eq. 4.13) and the species concentration equation (eq. 4.14) and of their respective boundary conditions at the susceptor surface (eq. 4.16). However, in cold-wall reactors the boundary conditions at the reactor walls for the temperature and the species concentration are not equivalent: The temperature has a fixed wall temperature Dirichlet boundary condition, whereas the species concentration has a zero gradient Neumann boundary condition (eq. 4.15). Also, the inflow boundary conditions are different: For the temperature, there is a fixed inlet temperature Dirichlet boundary condition, whereas for the species concentration there is a fixed species concentration in combination with a zero diffusion flux inlet condition (eq. 4.17). As a result, the temperature and species concentration distribution may be quite dissimilar. As an example, figure 4.8 shows dimensionless temperature and species mole fraction distributions for $Re = 1$ and $Gr = 10$. Also when adiabatic thermal boundary conditions are assumed on the reactor walls, as was done by Evans and Greif [1987a], the Nusselt number is not a good measure for the species

![figure 4.8: Dimensionless temperatures and species mole fractions, for Re = 1 and Gr = 10.](image-url)
mass transfer. In this case the reactor walls will locally become hot, leading to reactant deposition, and the boundary conditions for the temperature and species concentration are again not equivalent. On the other hand, the inflow boundary conditions for the temperature and the species concentration do become equivalent for large Reynolds numbers. Also, for large \( Re \) the temperature and concentration boundary layers above the susceptor will be thin and not influenced by the reactor walls. Therefore, the heat and mass transfer uniformity become identical for large \( Re \), as can be observed from the \( Nu \) and \( M \) curves for \( Re = 10 \) in figures 4.7a-d. So, in general, the Nusselt number for heat transfer is not a good measure for the transport limited species mass transfer to the heated susceptor surface in cold-wall reactors, except when the Reynolds number of the flow is large.

(ii) Secondly, it is found that the calculated \( Nu \) and \( M \) as a function of radius are virtually independent of the Grashof number for \( Gr \leq 30 \) and for all \( Re \) numbers studied. This is due to two different effects, which have both been discussed in section 4.4: First, at low Reynolds numbers the heat and mass transfer are mainly determined by conduction and diffusion and are insensitive to the gas flow. Thus, although \( Gr \) has a large influence on the gas flow for these low \( Re \), its influence on \( Nu \) and \( M \) is small. At higher values of \( Re \) on the other hand, \( Gr \) has little influence on the gas flow since the mixed convection parameter \( Gr/Re^2 \) is small. As a result, \( Nu \) and \( M \) are again independent of \( Gr \).

(iii) Also in accordance with the theoretical analysis in section 4.4, the heat and mass transfer to the susceptor surface are virtually independent of the Reynolds number for small values of \( Re \). For the range of \( Gr \) studied, the calculated Nusselt and species transfer rate number distributions for \( Re = 0.01 \) are virtually identical to those for \( Re = 0.1 \), whereas a further increase to \( Re = 1 \) has only a small effect on \( Nu \) and \( M \).

(iv) Finally, it is clear that in general the heat transfer to the susceptor surface is much less uniform and much more sensitive to the flow conditions than the species mass transfer. For relatively small \( Re \) (\( Re \leq 3 \)) and \( Gr \) (\( Gr \leq 100 \)) a reasonably good mass transfer uniformity is found on a large part of the susceptor surface. Moreover, in this regime the uniformity is rather insensitive to the values of \( Gr \) and \( Re \). The heat transfer however is rather non-uniform and very sensitive to the process conditions for most combinations of \( Re \) and \( Gr \).

In general, it may be concluded, that the heat and mass transfer uniformity at the susceptor surface in the present reactor configuration are
not as good as might be expected. The ideal uniform temperature and concentration boundary layers for an impinging jet flow are highly disturbed by the influence of the reactor walls, side effects at the edge of the susceptor, and for large Grashof numbers also by buoyancy induced mixed convection flow phenomena. However, it should be stressed that the deposition rate in actual single-wafer LPCVD processes is usually determined by reaction kinetics, rather than species mass transfer, and may be more uniform than the transport limited mass transfer rates presented in this section. Nevertheless, the present heat and mass transfer rates are of relevance for finding the optimum process conditions and reactor geometry: A uniform species transfer rate number $\mathcal{N}$ for transport limited deposition processes corresponds to a uniform reactant concentration at the susceptor surface in deposition processes that are limited by heterogeneous kinetics. A uniform Nu number corresponds to a uniform thickness of the thermal boundary layer above the susceptor, which will lead to a uniform contribution of gasphase reactions in the hot gases and to a uniform influence of the Soret effect. Finally, a uniform heat flux from the susceptor to the reactor gases will make it more easy to obtain a uniform temperature in the resistance heated susceptor.

In section 4.11, attempts will be made to optimize the present reactor configuration in order to improve the uniformity of both Nu and $\mathcal{N}$.

4.8 INFLUENCE OF THE REACTOR ORIENTATION

It is often assumed, that an inversion of the reactor orientation (i.e. with a downward facing susceptor and an upward moving flow) may lead to a suppression of mixed convection phenomena in cold-wall reactors. Our simulations show, that this is not the case. Figure 4.9 shows the calculated streamlines for $Re = 1$ and $Gr = 300$, for the two reactor orientations.

Also in the case of an inverted reactor orientation there is a strong buoyancy induced flow recirculation. Although the location of the recirculation changes, the total amount of recirculation is similar for both orientations. Figure 4.10 shows Nu and $\mathcal{N}$ for the two reactor orientations. The inverted reactor has a somewhat better heat transfer uniformity, but a somewhat deteriorated mass transfer uniformity.
4.9 INFLUENCE OF THE SCHMIDT AND GAY-LUSSAC NUMBERS

In the previous sections, the gas flow and heat and mass transfer to the susceptor were studied as a function of Gr and Re, at fixed Pr, Sc and Ga. From eqs. 4.12, 4.14 and 4.19 it can be seen, that flow, heat and mass transfer also depend on the Gay-Lussac number, and that the species mass transfer also depends on the Schmidt number. Therefore, we have studied the influence of Sc on $\mathcal{M}$ at fixed Gr, Re, Pr and Ga, and the influence of Ga on
the gas flow and on $\mathcal{M}$ and Nu, at fixed Gr, Re, Pr and Sc.

Figure 4.11 shows the dependence of $\mathcal{M}$ on Sc for $0.5 \leq \text{Sc} \leq 4$, at fixed $\text{Ga} = 0.8$, $\text{Gr} = 10$, and $\text{Re} = 1$ and 10 respectively. It is clear, that the Schmidt number influences the absolute value of $\mathcal{M}$ and that this influence decreases with decreasing Re. However, the Schmidt number has no influence on the uniformity of the species transfer rate. Therefore, all conclusions on mass transfer uniformity in this chapter that are obtained for Sc = 1 are also valid for combinations of carrier gas and reactant with different values of Sc.

Similarly, by varying Ga from 0.67 to 1.0, at various combinations of Re and Gr, it was found that the Gay-Lussac number has a significant influence on the absolute value of Nu, but a very small influence on its uniformity. Furthermore, the value of Ga has a negligible influence on both the value and the uniformity of the species transfer rate number $\mathcal{M}$. Thus, the conclusions on heat and mass transfer uniformity in this chapter that are obtained for a susceptor temperature of 700 K (Ga = 0.8) are valid for all susceptor temperatures between 600 K and 900 K ($0.67 < \text{Ga} < 1.0$). The same conclusion holds for the gas flow: The minimum and maximum streamfunction $\Psi_{\text{min}}$ and $\Psi_{\text{max}}$ at given Gr and Re are virtually independent of Ga for $0.67 \leq \text{Ga} \leq 1.0$. Thus, table 4.4, which was obtained for a susceptor temperature of 700 K (Ga = 0.8) is also valid with good accuracy for other common susceptor temperatures.
4.10 MULTIPLE FLOW SOLUTIONS

In the previous sections, and in fact throughout the rest of this thesis, it has been assumed, that the gas flow in the single-wafer LPCVD reactor is axisymmetric and steady-state. Furthermore, it is assumed that for each set of process conditions there is one unique solution to the flow equations. However, recently indications have been found, that the strongly nonlinear coupling between the viscous, inertial and buoyant terms in the momentum equations for mixed convection flow may in some cases cause bifurcations to multiple, stable and unstable, symmetric and asymmetric solutions. The existence of multiple stable solutions in axisymmetric CVD reactors similar to the one studied here has been found in numerical studies by Kusumoto et al. [1985] and Fotiadis et al. [1990a]. Flow visualization experiments by de Keijser et al. [1988] showed the existence of non-axisymmetric mixed convection flows in a vertical axisymmetric CVD reactor. This result was supported by measurements of non-symmetric growth rate distributions in the same reactor by Roksnoer et al. [1989]. Asymmetric flows have also been found in numerical studies by Fotiadis et al. [1990a].

The axisymmetric approach used in the present study, in combination with the iterative, quasi time-dependent solution procedure described in chapter 3, allows for stable, steady-state, symmetric solutions only. Nevertheless, we have found indications for the existence of non-unique stable flow fields. For \( Re = 3 \) and \( Gr = 1000 \) two different flow solutions could be obtained. From all combinations of \( Re \) and \( Gr \) studied (see table 4.4), this was the only one leading to such multiple solutions. Figures

![Flow Diagrams](image)

*figure 4.12: Two different stable flow solutions.*
4.12ab show the two different flow fields that were obtained and figure 4.13 shows the corresponding highly differing Nu number and species transfer rate number $M$. The flow field in figure 4.12a was found when the calculated velocity and temperature fields obtained for Re = 1 and Gr = 1000 where used as an initial guess for the iterative solution procedure. Figure 4.12b was obtained when the solution for Re = 10 and Gr = 1000 was used as an initial guess. In both cases, the iterative solution procedure was found to converge readily to a stable solution, which was also found to be independent of the grid refinement. Thus, there is some indication that both solutions are physically realistic and stable, and that the actual steady-state gas flow is determined by the start-up procedure of the reactor. However, it seems also possible that the actual flow will oscillate between these two solutions, or that a non-symmetric 3D flow, combining the two possible 2D flows, will develop. Further research, including the numerical solution of the full 3D time-dependent flow equations and a formal numerical stability analysis of the obtained solutions, is needed in order to unravel the actual behavior of the gas flow.
4.11 OPTIMIZATION OF THE REACTOR CONFIGURATION

Although the uniformities of the Nusselt and species transfer rate numbers as presented in the previous sections do not represent the growth uniformity in actual single-wafer LPCVD processes, these numbers may be valuable in optimizing the reactor configuration and process conditions. A uniform species transfer rate number $M$ number is important for processes which are determined by heterogeneous kinetics, whereas a uniform Nu number is especially important for processes which are determined by homogeneous reactions in the thermal boundary layer.

A built-in option in the ASM single-wafer reactor for the optimization of the deposition uniformity is the variable length of the inflow pipe, allowing the distance $Z_t$ to be varied. Figure 4.14 shows the influence of $Z_t$ on Nu and $M$ for $Re = 1$ and $Gr = 10$.

For most process conditions, a large value of $Z_t$ has a favorable effect on the uniformity of $M$. At $Z_t = 0.125$ m, the mass transfer rate is uniform within 10% over more than 80% of the 0.24 m susceptor diameter, for $0.1 \leq Re \leq 3$ and $Gr \leq 30$. However, the heat transfer uniformity is still highly non-uniform for all cases studied. Also studied is the influence of the radius $R_p$ of the inflow pipe on Nu and $M$, at fixed $Z_t = 0.10$ m. The results are shown in figure 4.15 for 0.6 sليم nitrogen at 130 Pa total pressure. For $R_p = 0.125$ m the species transfer rate number $M$ is uniform.

![Figure 4.14: Influence of the length of the inflow pipe on Nu and $M$.](image1)

![Figure 4.15: Influence of the inflow pipe radius $R_p$ on Nu and $M$, for 0.62 sليم $N_2$ gas flow and 130 Pa total pressure.](image2)
within 10% over more than 80% of the susceptor diameter for a wide range of process conditions (0.4-10 slm hydrogen at pressures \( \leq 1000 \) Pa, 0.1-2 slm nitrogen at pressures \( \leq 300 \) Pa). The heat transfer, however, is again very non-uniform. A significant improvement in the uniformity of Nu could be obtained by a strong reduction of the height of the reactor at the use of a large inflow pipe radius. The configuration in figure 4.16 leads to a Nusselt number which is uniform within 25% over more than 80% of the susceptor radius, for a wide range of process conditions. However, the uniformity of the species transfer rate number \( \mathcal{M} \) is rather bad for this configuration.

Concluding, an optimization of the reactor geometry may lead to a highly improved uniformity in either the heat or the mass transfer. However, it is very difficult to optimize the uniformity of Nu and \( \mathcal{M} \) at the same time. For the optimization of actual processes, a compromise must be sought, depending on the specific process characteristics.

4.12 EXPERIMENTAL VALIDATION OF ISOThERMAl FLOW SIMULATIONS

In order to partially validate the flow simulations, velocity measurements using Laser Doppler Anemometry have been performed in an isothermal scale model of the ASM single-wafer reactor. Laser Doppler Anemometry (LDA) is an accurate, non-intrusive technique for measuring flow velocities in gases and liquids. Details of this technique can be found in textbooks (e.g. Durst et al. [1976], Watrasiewicz and Rudd [1976]). In section 4.12.2 the LDA set-up that has been used in this study will be described briefly, without
going into details of the technique itself.

It is very difficult to perform LDA measurements of the gas flow under actual LPCVD conditions. However, since the gas flow in isothermal reactors is determined by the Reynolds number only, it may be replaced by any fluid flow with equal Reynolds number. In this study we have measured a viscous oil flow in a perspex model of the ASM reactor, instead of the gas flow in the actual reactor. These measurements are compared to model simulations of the viscous oil flow and to model simulations of the actual gas flow at equal Reynolds numbers. The scale model is described in section 4.12.1.

4.12.1 The scale-model reactor

Velocity measurements have been carried out in an isothermal scale-model of the reactor, in which a viscous oil mixture was flowing at low Reynolds numbers similar to those found in the actual reactor. The scale-model was made of perspex at a scale of 1:2.5 of the actual reactor, except for the inflow configuration, see figure 4.17. Initially, an inflow configuration similar to that of the actual reactor was used, but this configuration led

*figure 4.17: The scale model single-wafer reactor.*
to asymmetric flows, the velocity distributions of which were very unstable and sensitive to small variations in the flow rate. Therefore, a differently shaped inflow configuration and a very long vertical inflow pipe were used in order to obtain axisymmetric flow conditions. It is not clear, if these symmetry problems occur in the actual reactor as well.

In order to avoid problems with the LDA laser beams refracting at the curved walls of the reactor model, the axisymmetric model was milled out of a rectangular piece of perspex, and a viscous oil mixture with a refractive index equal to that of the perspex was used as the flowing liquid. In that way, the only refraction of the laser beams was at the plane air-perspex transition. As a liquid a mixture of 68 volume percent of Shell Ondina 68 medicinal oil and 32 volume percent of Shellsol R solvent was used. It was checked, that the mixture behaves as a Newtonian fluid for all practical deformation rates. The mixture is clear and transparent, has a light yellow color and a refractive index identical to that of the perspex. The properties of the mixture and their temperature dependence are summarized in table 4.5. For the arising of Laser Doppler signals, the presence of scattering particles in the flow is essential. Therefore, the fluid has to be seeded with small particles, which follow the flow accurately and effectively reflect the laser light. For this purpose, small glass beads with a diameter of 1-3 μm from Particle Information Services Inc. (Oregon, USA) were used.

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<th>( \frac{8\phi}{\delta T} )</th>
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<td>specific heat</td>
<td>1700 J·kg⁻¹·K⁻¹</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>
4.12.2 The Laser Doppler Anemometer

The optical LDA set-up that has been used is of the differential mode backscatter type [Durst et al., 1976]. It is composed of standard optical components from Dantec Electronics (Denmark) and is especially suited for the accurate measurement of low velocity flows. Figure 4.18 shows the optical configuration. A 632.8 nm He-Ne laser beam passes two λ/4-plates, allowing the optical system to be rotated about the optical axis while maintaining the direction of polarization fixed inside the optics. Afterwards, the beam is split by a beam splitter into two parallel beams of equal intensity at 30 mm distance. One of the beams passes a Bragg cell, introducing a fixed frequency difference of ± 40 MHz between the two beams. This allows the determination of the direction of the measured flow. The shifted beam is then displaced over 30 mm, yielding a total beam separation of 60 mm. The unshifted beam passes a glass rod to ensure that the shifted and unshifted beams have an equal beam path length. The two beams are focused by a front lens of 160 mm focal length. Their intersection forms the so-called measuring volume. The same front lens focuses the light that is scattered back from particles moving through the measuring volume. The received light passes a pinhole section, consisting of two 48 mm focal length lenses and a 0.5 mm diameter pinhole, which serves as a spatial filter and prevents reflections from external surfaces from entering the receiving optics. The receiving optics consists of a 45° mirror, a receiving lens, a pinhole spatial filter and a photomultiplier. Through the electronic

![Diagram of the Laser Doppler Anemometer set-up](image)

*Figure 4.18: The optical set-up for the LDA experiments.*
downmixing of the signals from the photomultiplier, the ± 40 MHz optical frequency shift introduced by the Bragg cell can be brought down in steps to effective frequency shifts of ± 5-450 kHz.

The Doppler frequency of the light scattered back from the particles is equal to

$$\ell_d = \frac{2U \sin(\theta/2)}{\lambda_\ell}$$  \hspace{1cm} (4.27)

where $\theta$ is the angle between the two beams leaving the front lens, $U$ is the velocity component of the particle perpendicular to the optical axis in the plane of the two laser beams, and $\lambda_\ell$ is the wavelength of the laser light. Since the finally detected frequency $\ell$ is the sum of the effective preshift frequency $\ell_p$ and the Doppler frequency $\ell_d$, the velocity component equals

$$U = \frac{\lambda}{2 \sin(\theta/2)} \cdot (\ell - \ell_p) = C \cdot (\ell - \ell_p)$$  \hspace{1cm} (4.28)

For the present LDA configuration, $C = 1.69 \text{ mm} \cdot \text{s}^{-1} \cdot \text{kHz}^{-1}$. Effective preshift frequencies of 10 and 25 kHz have been used, allowing the measurement of velocities up to ± 16.9 mm/s and ± 42.3 mm/s respectively.

After downmixing, band-pass filtering and 40 dB amplification, the signal from the photomultiplier is analyzed by a TSI-1980A signal processing counter. In this counter the signal is again band-pass filtered to remove high- and low-frequency noise, and amplified. A threshold detector senses the presence or absence of a Doppler signal by the amplitude of the incoming signal. A Schmitt trigger converts the analog signal into a digital pulse train. A timing circuitry, activated by the threshold detector, measures the time needed for a fixed number of pulses to pass and thus determines the frequency of the Doppler signal, which is a measure for the velocity of the particle passing through the measuring volume through eq. 4.28.

The radial and axial velocity components were measured in a vertical plane of symmetry of the scale-model reactor. Since the flow is laminar and steady-state, the two velocity components may be measured separately. First, one of the velocity components was measured on different locations, by determining the average Doppler frequency of 100 individual particles per location. Then the optics were rotated over 90° along the optical axis, allowing the measurement of the other velocity component on different locations in the same plane of measurement.

Although the flow is laminar, a spreading in the Doppler frequencies
of the individual particles measured at one location was observed. The standard deviation in the measured Doppler frequency of 100 particles was typically 100-300 Hz, corresponding to a velocity of ~ 0.2-0.5 mm/s, independent of the average value of the Doppler frequency. This must be ascribed to signal noise, instabilities in the frequency shift and the downmixing, and counter inaccuracies. However, when several series of 100 measurements were performed on one location, the standard deviation in the average Doppler frequency was typically less than 50 Hz, corresponding to a velocity of ~ 0.1 mm/s.

4.12.3 Flow velocity measurements in the scale-model reactor and comparison to model simulations

To test the accuracy of the LDA set-up, test measurements of the laminar Poiseuille flow in a horizontal circular tube have been performed. The tube was made of perspex and its inner radius was \( R = 0.015 \) m. As fluid the oil/solvent mixture described in section 4.12.1 was used, with identical seeding. The axial velocity profile was measured at a downstream distance \( x = 15 \cdot R \), at flow rates of \( 2.5 \cdot 10^{-6} \) and \( 12 \cdot 10^{-6} \) m\(^3\)/s, corresponding to average flow velocities of 3.6 and 17 mm/s and to Reynolds numbers \( \rho \langle v \rangle R / \mu \) of 2.2 and 10 respectively. The results of the LDA velocity measurements,

![Figure 4.19: Comparison between LDA velocity measurements and theoretical velocity profiles in a horizontal cylindrical tube.](image)

- 89 -
compared to the theoretical velocity profile, are shown in figure 4.19. It may be concluded, that the LDA set-up is capable of measuring velocities < 35 mm/s in the present liquid mixture with an accuracy better than ± 1 mm/s.

After the above test of the LDA set-up, the axial and radial velocities in the scale-model reactor have been measured for oil flows of 0.036 and 0.059 liters per second, corresponding to Re numbers of 13 and 22 respectively, according to the definition of eq. 4.20. This corresponds to the upper limit of Re numbers found in the actual reactor. At lower flow rates it was not possible to obtain flow patterns which were both stable and symmetric. The results of the LDA flow measurements are shown in figure 4.20, together with the model simulations for this oil flow. There is a good correspondence between experimental and simulation results. Furthermore, it has been checked, that the simulated dimensionless flow velocities for the oil-flow were identical to the simulated dimensionless flow velocities for

\[ \phi_v = 0.036 \text{ l/s} \quad \text{Re} = 13 \]

\[ \phi_v = 0.059 \text{ l/s} \quad \text{Re} = 22 \]

(a) axial velocities

(b) radial velocities

*figure 4.20: Comparison between LDA velocity measurements in the scale model reactor and flow simulations.*
Isothermal gas flows, at equal Re number. Thus, it may be concluded that the simulation model accurately predicts laminar flow velocities in low Reynolds number isothermal flows in the present single-wafer reactor configuration.
5.1 INTRODUCTION

Of all CVD processes that are used to deposit thin films in the IC industry, the deposition of silicon from silane ($\text{SiH}_4$) is perhaps the most widely applied and studied. Depending on the process conditions, the silicon growth can be either epitaxial, polycrystalline or amorphous [Hitchman and Ahmed, 1984; Cullen and Corboy, 1984]. In the IC industry, epitaxial silicon is mostly grown at (near) atmospheric pressures ($10^4$-$10^5$ Pa) and high temperatures (1100-1500 K). For this purpose several reactor types, such as the barrel reactor and the pancake reactor (see section 1.2), are being used [Bloem and Giling, 1985; Sherman, 1987], whereas most explorative research and process development has been carried out in horizontal reactors [Eversteijn et al., 1970; Eversteijn, 1971; Claassen and Bloem, 1981]. Polycrystalline silicon is deposited at low pressures (LPCVD, 10-100 Pa) and low temperatures (850-950 K), mostly in batch type horizontal tube reactors with hot walls, containing a large number of closely packed wafers [Rosler, 1977; Brown and Kamins, 1977; van den Brekel and Bollen, 1981; Kuiper et al., 1982; Claassen et al., 1982; Sherman, 1987].

In spite of the increasing interest in coldwall, low pressure, single-wafer reactors in IC manufacturing (see section 1.2), the use of single-wafer reactors for silicon LPCVD has not yet evolved. An important drawback seems to be the low growth rate obtained in silicon LPCVD, leading to an unacceptably low throughput in single-wafer reactors. In order to obtain higher rates, the process conditions will have to be modified compared to those in conventional batch type reactors. Especially, the temperature and the pressure must be increased. This will probably increase the contribution of gas-phase reactions to the deposition process, which may in turn affect the film properties. It is generally assumed, that gas-phase reactions are negligible in poly-silicon LPCVD from silane under conventional LPCVD conditions. On the other hand, homogeneous reactions play an important role in atmospheric pressure silicon CVD from silane. Complex, multiple step reactions in the gas-phase lead to the formation of a large number of reactive intermediates, which highly contribute to the growth of silicon. Therefore it may be expected that a change of the process conditions in silicon LPCVD towards higher pressures and temperatures will also lead to an increase in the importance of gas-phase chemistry.
Several models for silicon CVD under atmospheric pressure conditions have been published. These models have either been aimed at a detailed description of the chemistry in simplified hydrodynamic situations [e.g. Coltrin and coworkers, 1984, 1986, 1989] or at the detailed description of the hydrodynamics, using relatively simple models for the chemistry [e.g. Lord, 1987; Rhee et al., 1987; Moffat and Jensen, 1988; Gokoglu et al., 1989]. Besides, models have been published for silicon LPCVD in batch type hotwall reactors [e.g. Charlier, 1981; Jensen and Graves, 1983; Roenigk and Jensen, 1985; Middleman and Yeckel, 1986]. In these LPCVD models, gas–phase reactions have been neglected and the hydrodynamical problem is highly simplified, since homogeneous reactions and gas flow are relatively unimportant in these types of reactors.

In this chapter, we describe a mathematical model for the hydrodynamics and the heterogeneous and homogeneous chemical reactions in silicon LPCVD in a single-wafer reactor of the vertical impinging jet type. In these reactors, the qualities of the film layers are highly determined by the complex interaction of hydrodynamics and chemical reactions. Therefore, the model combines a full description of the hydrodynamics with a rather detailed model of the heterogeneous and homogeneous chemical reactions. The model is used to study the applicability of a low pressure, coldwall, single-wafer reactor for silicon growth on large (0.20–0.25 m diameter) wafers. Starting from process conditions that are common in conventional silicon LPCVD, several options for increasing the growth rate are explored, such as an increase of the temperature, an increase of the total pressure and an increase of the silane inlet mole fraction. Special attention is paid to the influence of gas–phase reactions under these varying process conditions. We also study the possibility of growing in situ doped polysilicon films in a single-wafer reactor and we try to optimize the reactor geometry in order to obtain uniform deposition.

5.2 PROBLEM DESCRIPTION

We study silicon LPCVD from silane in the ASM coldwall single-wafer reactor that has been described in section 4.2 (figure 4.1). The silane gas is more or less diluted with a carrier gas (N₂, H₂, He). After introduction of the gas mixture into the reactor, homogeneous chemical reactions lead to the formation of silicon containing reactive intermediate species. Both silane and the reactive intermediates react at the wafer surface to form solid
silicon and gaseous hydrogen. In this chapter we assume, that deposition takes place on the 0.24 m diameter susceptor surface exclusively. The remaining silane and reactive intermediates, the formed hydrogen and the carrier gas leave the reaction chamber through the reactor outflow.

To study all the above phenomena, we use a combination of a hydrodynamical model for the gas flow and transport phenomena in the reactor and a chemical model for the homogeneous and heterogeneous reactions. The hydrodynamical model is generally applicable to different CVD processes and has been described in chapter 2. Here, we consider the hydrodynamics to be stationary and fully axisymmetric. Therefore, the transport equations are solved in stationary, 2D axisymmetric form. In doing so, we neglect the fact that the gas flow may become asymmetric and time dependent for certain process conditions, even when the configuration is symmetric and the process conditions are stationary (see section 4.10). The chemistry model is specific for the considered CVD process and consists of reaction mechanisms and reaction rate constants which can be substituted in the general model described chapter 2. The chemistry model is described in the next section.

5.3 CHEMISTRY MODEL

5.3.1 Homogeneous reaction model

It is generally assumed, that gas-phase reactions are negligible in poly-silicon LPCVD from silane under conventional LPCVD conditions and that silicon growth is almost completely due to the heterogeneous decomposition of silane into silicon and hydrogen on the wafer surface. Experimental evidence for this assumption can be found in the fact that the deposition rate decreases dramatically (i.e. with about a factor 25) when small amounts of phosphine, blocking the free surface sites for silane adsorption, are added to the gas mixture [Meyerson and Olbricht, 1984]. On the other hand, gas-phase reactions seem to play a dominating role in atmospheric pressure epitaxial silicon CVD from silane. Modeling work by Coltrin and coworkers [1984, 1986, 1989] in combination with experimental research by Breiland, Ho and coworkers [Breiland and Hushner, 1983; Ho and Breiland, 1984; Breiland, Ho and Coltrin, 1986; and Breiland, Coltrin and Ho, 1986] demonstrated, that under these conditions silicon growth may be almost completely due to reactive intermediates formed in the gasphase and that a full treatment of the gas-phase kinetics can involve as much as 20 different reactive
intermediates and homogeneous chemical reactions.

In this study, we want to develop a model for the gasphase chemistry in single-wafer silicon LPCVD at temperatures and pressures intermediate between conventional LPCVD and atmospheric pressure epitaxial CVD conditions. In view of the above, such a model should involve a rather detailed multi-step chemical mechanism. However, since we want to couple our chemistry model to a complete hydrodynamic model for the gas flow and transport phenomena, the chemistry model cannot be too detailed, due to computational constraints. Moreover, under LPCVD conditions most of the homogeneous decomposition reactions are in their pressure falloff regime and little is known about the kinetics of the reactions. Therefore, too much detail in a chemistry model does not seem justified. Because of this, we use a relatively closed subsystem of the full kinetic model that was used by Coltrin and coworkers, including five reversible gas-phase reactions, leading to the formation of four reactive intermediates: The initial homogeneous decomposition of silane, which is the key reaction in the kinetic mechanism, leads to the formation of silylene (SiH₂) and hydrogen [Purnell and Walsh, 1966; Newman et al., 1979]. Silylene is easily inserted into silane to form disilane (Si₂H₆), and into disilane to form trisilane (Si₃H₈) [John and Purnell, 1973]. The main decomposition path for disilane is to silane plus silylene, with a decomposition to silylsylene (Si₂H₄) plus hydrogen competing at higher temperatures [Dzarnoski et al., 1982; Beccera and Walsh, 1987]. Finally, we have included the insertion of silylene into itself to form silylsylene. Thus, we used the following reaction mechanism:

\[
\begin{align*}
\text{G1:} & \quad \text{SiH}_4 \quad \xrightleftharpoons[k_{-1}]{k_1} \quad \text{SiH}_2 + \text{H}_2 \\
\text{G2:} & \quad \text{Si}_2\text{H}_6 \quad \xrightleftharpoons[k_{-2}]{k_2} \quad \text{SiH}_4 + \text{SiH}_2 \\
\text{G3:} & \quad \text{Si}_3\text{H}_8 \quad \xrightleftharpoons[k_{-3}]{k_3} \quad \text{Si}_2\text{H}_6 + \text{SiH}_2 \\
\text{G4:} & \quad \text{Si}_2\text{H}_4 \quad \xrightleftharpoons[k_{-4}]{k_4} \quad \text{SiH}_2 + \text{SiH}_2 \\
\text{G5:} & \quad \text{Si}_2\text{H}_6 \quad \xrightleftharpoons[k_{-5}]{k_5} \quad \text{Si}_2\text{H}_4 + \text{H}_2
\end{align*}
\] (5.1) (5.2) (5.3) (5.4) (5.5)

Although the above system will probably not reflect all the details of the homogeneous thermal decomposition of silane and the subsequent reactions of...
intermediate species, it is believed that it is adequate for the prediction of silicon growth rates under single-wafer LPCVD conditions. Coltrin and coworkers [1984, 1986, 1989] found that silicon deposition under atmospheric pressure CVD conditions at moderate temperatures (< 1100 K) is mainly due to SiH₄, SiH₂ and Si₂H₄. The formation of these species is essentially reflected in the above reaction mechanism. Furthermore, we will show that the predicted growth rates are relatively insensitive to the precise details of the reaction mechanism.

The low pressure reaction rate constants \( k_1 \) and \( k_2 \) as a function of total pressure and temperature were taken from a Rice-Ramsperger-Kassel-Marcus analysis by Roenigk and coworkers [1987]. The values for \( k_1 \) are in good agreement to those reported by Meyerson and Jasinski [1987]. The reverse reaction rate \( k_{-3} \) was taken from experimental data by Jasinski and Chu [1988] at 300 K and 133-1330 Pa pressures. A zero activation energy \( E_{-3} \) was assumed, as was done for the high pressure reaction rate by Coltrin and coworkers [1989]. For G4 and G5 no pressure falloff kinetic data have been published. As a rough estimate of their low pressure kinetics, we have assumed that \( k_4 \) and \( k_5 \) show the same pressure falloff behavior as \( k_2 \), according to

\[
k_4(P,T) = k_4(P_{\infty},T) \frac{k_2(P_{\infty},T)}{k_2(P,T)} \tag{5.6}
\]
\[
k_5(P,T) = k_5(P_{\infty},T) \frac{k_2(P_{\infty},T)}{k_2(P,T)} \tag{5.7}
\]

where the high pressure reaction rate constants \( k_4(P_{\infty},T) \) and \( k_5(P_{\infty},T) \) have been taken from Coltrin et al. [1986] and the pressure falloff correction \( k_2(P,T)/k_2(P_{\infty},T) \) has been taken from Roenigk et al. [1987]. The reaction rates in the opposite directions (\( k_{1'}, k_{-2'}, k_3, k_4 \) and \( k_{-5} \)) were calculated from the chemical reaction equilibria (eq. 2.30). The thermodynamic properties for silane, disilane, trisilane, silylsylene and hydrogen were taken from Coltrin et al. [1986]. For silylene the recently revised value for the standard heat of formation from Coltrin et al. [1989] was taken, which is in good agreement with the findings of Roenigk et al. [1987]. The thermodynamic properties of the different species are listed in Appendix B. The reaction rate constants for both the forward and the reverse reactions were fitted as \( k = A \cdot P^k \cdot \exp(-E/RT) \) for temperatures from 300 K to 1100 K and pressures from 133 Pa to 1330 Pa. The resulting fits are presented in table
5.1. Note, that the negative activation energies for some of the reverse reactions are a result of the pressure falloff behavior of the forward reactions.

5.3.2 Heterogeneous reaction model

For the silicon growth at the wafer surface from silane and the reactive intermediates we use the following set of surface reactions:

\[
\begin{align*}
\text{S1:} \quad & \text{SiH}_4(g) \overset{\mathcal{R}_1}{\longrightarrow} \text{Si(s)} + 2 \text{H}_2(g) \\
\text{S2:} \quad & \text{SiH}_2(g) \overset{\mathcal{R}_2}{\longrightarrow} \text{Si(s)} + \text{H}_2(g) \\
\text{S3:} \quad & \text{Si}_2\text{H}_6(g) \overset{\mathcal{R}_3}{\longrightarrow} 2 \text{Si(s)} + 3 \text{H}_2(g) \\
\text{S4:} \quad & \text{Si}_3\text{H}_8(g) \overset{\mathcal{R}_4}{\longrightarrow} 3 \text{Si(s)} + 4 \text{H}_2(g) \\
\text{S5:} \quad & \text{Si}_2\text{H}_4(g) \overset{\mathcal{R}_5}{\longrightarrow} 2 \text{Si(s)} + 2 \text{H}_2(g)
\end{align*}
\]

The surface reaction rates $\mathcal{R}^S$ were calculated using the concept of reactive
sticking coefficients (see chapter 2.5, eq. 2.40). The reactive sticking coefficients (RSC) \( \gamma_1 \) and \( \gamma_3 \) of silane and disilane on polycrystalline silicon surfaces have been studied by Buss and coworkers [1988] for a wide range of temperature and pressure conditions. The sticking coefficients were found to have a non-Arrhenius temperature dependence and to be dependent on the flux of molecules colliding with the surface. Rather complex models for the chemical mechanisms involved in the heterogeneous thermal decomposition of silane and disilane on silicon surfaces were proposed to fit the data. However, these models do not seem to reflect the fact that the growth rate in silicon LPCVD is first order in silane for low silane pressures and zero order in silane for high silane pressures [Claassen et al., 1982], i.e. that the silane RSC is independent of the silane flux for low fluxes and inversely proportional to the silane flux for high fluxes. Therefore, we propose a different model, which reflects the desired flux dependence and accurately fits experimental data over a wide range of temperatures and silane pressures.

In our model, we assume that the heterogeneous thermal decomposition of silane takes place according to a simple two-step adsorption/desorption + heterogeneous reaction mechanism:

\[
\begin{align*}
\text{SiH}_4(g) + \ast & \xrightarrow{k_1^S} \text{SiH}_4^* \\
\text{SiH}_4^* & \xrightarrow{k_2^S} \text{Si(s)} + 2 \text{H}_2(g)
\end{align*}
\]  

(5.13)  

(5.14)

where \( \ast \) indicates a free surface site and \( \text{SiH}_4^* \) is adsorbed silane. Since there is some experimental evidence that hydrogen inhibits silane adsorption [Holleman and Aarnink, 1981; Claassen et al., 1982], we also include the dissociative adsorption of \( \text{H}_2 \) on free surface sites:

\[
\begin{align*}
\text{H}_2 + 2\ast & \xleftrightarrow{k_{3}^S} 2 \ast \text{H}^* \\
\end{align*}
\]  

(5.15)

Applying steady-state conditions to \( \text{SiH}_4^* \) and \( \ast \text{H}^* \) we find
\[ k_{S_{C=1}}^{S_{SiH_4}} ([S]-[SiH_4^*]-[H^*]) = (k_{-1}^S + k_2^S)[SiH_4^*] \]  
\[ k_{S_{H_2}}^{S_{C=3}} ([S]-[SiH_4^*]-[H^*])^2 = k_{-3}^S [H^*] \]

(5.16)

(5.17)

where \( C_i \) is the species \( i \) mole concentration and \([S]\) the surface site density. Now, with \( \phi = [SiH_4^*/[S]], \phi = [H^*/[S]], c_1 = 4k_1^S[S]/\gamma_{SiH_4}, c_{-1} = k_{-1}^S[S], c_2 = k_2^S[S], c_3 = 4k_3^S[S]/\gamma_{H_2} \) and \( c_{-3} = k_{-3}^S[S] \) and \( \gamma_1 = \frac{1}{4} \frac{c_1 \gamma_{SiH_4}}{c} \) we find

\[ c_{1} \frac{\gamma_{SiH_4}}{c_{S_{H}}} (1-\phi - \phi) = (c_{-1} + c_2) \phi \]

(5.18)

\[ c_{3} \frac{\gamma_{H_2}}{c_{S_{H}}} (1-\phi - \phi)^2 = c_{-3} \phi \]

(5.19)

From these equations, \( \phi_s \) and \( \phi_h \) can be solved. For \( \phi_s \) we get

\[ \phi_s = \frac{c_1 \gamma_{SiH_4}}{(c_{-1} + c_2)(1 + c_3^{1/2} \gamma_{H_2}^{1/2}) + c_1 \gamma_{SiH_4}} \]

(5.20)

where \( C_3 = c_3/c_{-3} \). Now, with with the molar deposition rate \( D \) equal to \( D = k_2^S[SiH_4^*] = c_2 \phi_s \) and the sticking coefficient \( \gamma_1 \) equal to \( \gamma_1 = D/\gamma_{SiH_4} \), we obtain the following equation for the RSC of silane:

\[ \gamma_1 = \frac{c_1 c_2}{(c_{-1} + c_2)(1 + c_3^{1/2} \gamma_{H_2}^{1/2}) + c_1 \gamma_{SiH_4}} \]

(5.21)

The constants \( c_1, c_{-1}, c_2, c_{-3}, C_3 \) in our model equation 5.21 have been fitted to a large set of experimental data, obtained in coldwall very low pressure (VLPCVD) reactors and molecular beam configurations [Donahue and Reif, 1986; Buss et al., 1988; Comfort and Reif, 1989], and in conventional hotwall LPCVD reactors [van den Brekel and Bollen, 1981; Holleman and Aarnink, 1981; Kuiper et al., 1982; Claassen et al., 1982; Meyerson et al., 1986; Foster and Learn, 1986]. There seems to be a systematic difference between the RSC obtained in these two types of reactors. Therefore, Buss and coworkers [1988] suggested, that the adsorption rate constant (i.e. \( c_1 \) in our present model) may be a function of the temperature (energy) of the impinging gas molecules rather than the surface temperature. Indeed, we found that data from both types of reactor could be fitted by taking \( c_1 \) a function of the gas temperature. Thus, we obtain the following values for the model constants:

- 100 -
\[ c_1 = 8.0 \cdot 10^{-2} \cdot \exp(-7500/RT_{gas}) \]
\[ c_{-1} = 1.2 \cdot 10^{-6} \cdot \exp(49000/RT_{wafer}) \text{ mole} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \]
\[ c_2 = 1.7 \cdot 10^4 \cdot \exp(-153800/RT_{wafer}) \text{ mole} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \]
\[ C_3 = 0.61 \text{ mole}^{-1} \cdot \text{m}^2 \cdot \text{s} \]

Note that, due to insufficient experimental data, no temperature dependence could be determined for \( C_3 \).

A similar model for the heterogeneous thermal decomposition of disilane, not taking into account adsorption of hydrogen on free surface sites since there is no experimental indication that \( H_2 \) inhibits disilane adsorption, leads to the following expression for the disilane RSC:

\[ \gamma_3 = \frac{c_4 c_5}{c_{-4} + c_5 + c_4 \frac{g}{\text{Si}_2\text{H}_6}} \quad (5.22) \]

For the determination of the constants in this expression we only used the data from the very low pressure experiments by Buss et al. [1988]. Experimental silicon growth rate data from disilane in conventional LPCVD reactors have been published [Meyerson et al., 1986; Nakayama et al., 1984, 1986], but the RSC calculated from these data are much lower (i.e. a factor 5-10) than those obtained by Buss and coworkers. This is most likely due to the gas-phase reactions and depletion effects influencing the growth rate in conventional LPCVD reactors. Thus, we obtained

\[ c_4 = 4.5 \cdot 10^{-2} \]
\[ c_{-4} = 4.3 \cdot 10^{-4} \text{ mole} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \]
\[ c_5 = 1.7 \cdot 10^4 \cdot \exp(-153800/RT_{wafer}) \text{ mole} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \]

Due to insufficient experimental data, no temperature dependence could be determined for \( c_4 \) and \( c_{-4} \).

Figure 5.1 shows a comparison between experimental data and our model predictions for the temperature dependence of the silane and disilane RSC (\( \gamma_1 \) and \( \gamma_3 \)) at low molecular fluxes (i.e. in the flux independent region). Figures 5.2 and 5.3 show the flux dependence of the silane RSC (\( \gamma_1 \)) for different temperatures in hotwall LPCVD and coldwall VLPCVD reactors respectively. Figure 5.4 shows the flux dependence of the disilane RSC (\( \gamma_3 \)) in a coldwall VLPCVD reactor. From these comparisons it can be concluded,
**figure 5.1:**
Comparison between model predictions and experimental data for the silane and disilane RSC as a function of the wafer temperature in cold wall VLP CVD reactors at low molecular fluxes.

**figure 5.2:**
Comparison between model predictions and experimental data for the silane RSC as a function of the silane molecular flux at different temperatures in hot wall LPCVD reactors.

**figure 5.3:**
Comparison between model predictions and experimental data for the silane RSC as a function of the different wafer temperatures in coldwall VLP CVD reactors.

**figure 5.4:**
Comparison between model predictions and experimental data for the disilane RSC as a function of the disilane molecular flux in a cold wall VLP CVD reactor.
that our present models accurately predict the reactive sticking coefficients of silane and disilane on silicon for a wide range of operating conditions.

No experimental data are available for the reactive sticking coefficients of silylene, trisilane and silylsilene. However, experiments on the chemisorption of silane, disilane and trisilane on silicon surfaces [Gates et al., 1987] indicate, that trisilane is much more reactive than disilane. It is also very likely, that the unstable species silylene and silylsilene will be highly reactive on a heated silicon surface. Therefore, we assume that silylene, trisilane and silylsilene react at the surface with unit probability, i.e. \( \gamma_2 = \gamma_4 = \gamma_5 = 1 \), as was done by Coltrin et al. [1984, 1986, 1989]. We will show, that the model predictions are rather insensitive to the assumed values for \( \gamma_2, \gamma_4 \) and \( \gamma_5 \).

### 5.4 NUMERICAL SIMULATION

The discretized 2D axisymmetric transport equations (see chapters 2 and 3 and appendix A) were solved on a non-uniform grid with 55 grid points in the axial direction and 35 grid points in the radial direction. Near the susceptor surface, the grid was locally very refined in order to accurately capture the concentration boundary layers of the reactive intermediates formed by the gas-phase reactions. In all cases, there were at least 10 grid points within the thinnest of these boundary layers. The grid is illustrated in figure 5.5. Grid independence of the results was checked by using a 95 × 60 grid for some representative situations. The calculated deposition rates due to each of the individual surface reactions obtained on this refined grid differed less than 4% from those obtained on the standard grid in each location on the susceptor surface. The total deposition rate (due to the combined effect of all surface reactions) in each location of the susceptor surface, as well as the growth uniformity, differed less than 1%.

The resulting matrix equations were solved iteratively by using line-by-line TDMA and two-dimensional plane-TDMA methods (see chapter 3). For the momentum equations line TDMA methods on grid lines perpendicular to their coordinate direction were used. The pressure correction and energy equation were solved on both horizontal and vertical grid lines, traversing against the main flow direction. Both the line TDMA method on horizontal and vertical lines and the two-dimensional plane-TDMA method were used to solve the species concentration equations. The fluid properties and the species
diffusive mass fluxes were calculated only once in every 50 iterations. For the momentum and energy equation and for the pressure correction, standard relaxation techniques were used (see section 3.9), with the underrelaxation factor $\eta = 0.4$ for the momentum equations, $\eta = 0.8$ for the energy equation and $\eta = 0.6$ for the pressure correction. As described in section 3.9, standard underrelaxation techniques do not lead to convergence when the species concentration equations are strongly determined by gas-phase reactions (i.e. strongly source term dominated). This is due to the fact, that the relative change in the species concentrations from one iteration to the next may be extremely large ($> 10^5$), especially in the beginning of the iterative solution procedure. Therefore, we limited the maximum relative change of the species concentrations from one iteration to the next to a maximum value $\Delta$, according to eqs. 3.33-3.34. For all cases discussed in this chapter, convergence could be obtained by using a combination of $\Delta = 0.01-0.05$ and $\eta = 0.2-0.8$.

Four convergence criteria were used: (i) the error in the global mass balance, $< 10^{-2}$ %, (ii) the residuals of the equations (eq. 3.32), averaged
over all the grid points, $< 10^{-5}$ for each variable, (iii) the relative changes of the variables from one iteration to the next in a representative monitor point, $< 10^{-5}$ for each variable and (iv) the relative changes from one iteration to the next in the deposition rates in the center of the wafer, $< 10^{-5}$ for each of the deposition reactions. The monitor point was located on the axis of the reactor, at 0.01 m above the susceptor surface.

In this region the maximum concentrations of the reactive intermediates occurred. Negligible changes in the calculated deposition rates occurred, when more severe convergence criteria were used. The calculations were carried out on a HP 9000-835 minicomputer. Using the standard grid, the computer code needs 2.8 Mbyte of working memory. To reach a converged solution, circa 5000 iterations, taking 18 seconds cpu time per iteration, were needed when starting from a guessed initial solution.

5.5 RESULTS FOR THE BASE CASE

As a base case, we have chosen process conditions similar to those common in silicon LPCVD in conventional batch type hotwall horizontal tube reactors, i.e. a total pressure of 133 Pa, a wafer temperature of 900 K, a total flowrate of 1000 sccm, and a silane inlet mole fraction of 0.1 in nitrogen carrier gas. The inlet gas temperature was 293 K. Expressed in the dimensionless numbers introduced in chapter 4, we have $Re = 1.2$, $Gr = 8$, $Pr = 0.7$, $Ga = 1$ and $Sc = 0.9$. The resulting flow, temperature and

![Diagram](image)

*figure 5.6 + 5.7: Calculated streamlines (left) and isotherms (right) for the base case. Normalized streamfunction values are 0.1, 0.2, ..., 0.9.*
*figure 5.8 - 5.13: Calculated species mole fractions for the base case.*

concentration fields are shown in figures 5.6-5.13. Due to gasphase reactions, reactive intermediates are formed in the heated zone above the susceptor, which diffuse either away from the heated zone or to the susceptor surface, where deposition takes place. Silylene is found in a very
figure 5.14: Total growth rate and growth rates due to gas-phase intermediates for the base case.

thin layer above the susceptor only, whereas the other reactive intermediates are distributed more gradually over the reactor volume. For all reactive intermediates, the maximum concentration is found at a distance of 5-15 mm above the center of the susceptor surface. The calculated growth rates as a function of radial position due to each of the silicon-containing species are shown in figure 5.14. The reactive intermediates lead to strongly nonuniform growth (note the logarithmic scale), which is higher in the center than at the edge of the susceptor. Because of the relatively low sticking coefficient, the growth rate due to disilane is more uniform than due to the other intermediate species. It is clear, that SiH₂ and Si₂H₆ are the most important intermediates under the considered process conditions. In contrast to the reactive intermediates, silane leads to a very uniform growth. Since the growth rate as a result of the direct heterogeneous decomposition of silane is much larger than the growth due to the intermediate species, the total growth rate is very uniform also. So, in general, it may be concluded that excellent uniformity on large deposition areas may be obtained in a coldwall single-wafer reactor operated at conventional LPCVD process conditions and that the contribution of gas-phase reactions to the total growth is negligible under these conditions.
5.6 INFLUENCE OF PROCESS PARAMETER VARIATIONS

Although the above process conditions lead to excellent uniformity on large wafers, the growth rate is far too low for successful economic application of single-wafer reactors for silicon CVD in the IC industry. For this purpose, the growth rate has to be increased by about a factor 10. Apart from turning to other chemistries, there seem to be three options for increasing the growth rate: (i) increasing the total pressure in the reactor, (ii) increasing the silane concentration in the gas mixture and (iii) increasing the susceptor temperature. In this section, we will systematically study the influence of each of these parameter variations on the growth rate, the uniformity and the relative importance of gas-phase reactions.

First, we increase the wafer temperature from 900 K to 1100 K, keeping the other parameters fixed as in the base case. The resulting growth rates in the center of the susceptor surface (i.e. at r = 0) are shown in figure 5.15. Due to the temperature increase, both the rate for the direct heterogeneous decomposition reaction of silane and the rates for the gas-phase reactions increase dramatically. As a result, the total growth rate is increased by a factor 8 compared to the base case, when the

![figure 5.15: Total growth rate and growth rates due to gas-phase intermediates at r=0 as a function of temperature for 133 Pa total pressure, 13.3 Pa silane partial pressure and nitrogen carrier gas.](image)

- 108 -
temperature is increased to 1000 K, and by more than a factor 30 when the temperature is further increased to 1100 K. We also see a small increase in the relative contribution of the gas-phase reactions to the total growth, from 0.5 % at 900 K to 1.9 % at 1100 K, and a shift in the relative importance of the intermediate species from Si$_2$H$_6$ to Si$_2$H$_4$. However, even at the highest temperature the contribution of the gas-phase reactions to the silicon growth is small. Also, the growth uniformity is still very good: The model predicts a uniformity > 98 %, i.e. the minimum growth rate on the 0.24 m diameter deposition area is more than 98 % of the maximum growth rate. Thus, an increase in the operating temperature compared to conventional silicon LPCVD seems to be an attractive option for increasing the throughput in single-wafer reactors. Of course, such a temperature increase will have an influence on film qualities such as morphology and stress, which cannot be predicted by the present model. In conventional silicon LPCVD in batch type hotwall reactors, the temperature seems to be limited to about 900 K by uniformity demands mainly. However, silicon LPCVD at higher temperatures has been reported [Holleman and Aarnink, 1981; Claassen et al., 1982] and a temperature of 1000 K, leading to a growth rate of more than 1000 Ång/min, seems to be acceptable from a film quality point of view.

A second option for increasing the growth rate could be an increase of the total pressure in the reactor. We have simulated processes at total pressures from 133 to 1330 Pa, at wafer temperatures of 900 K and 1000 K. The resulting growth rates at $r = 0$ are shown in figure 5.16. It is clear, that an increase in the total pressure leads to a spectacular increase in the contribution of gas-phase reactions from circa 1 % at 133 Pa to more than 50 % at 1330 Pa total pressure. The growth rate due to direct heterogeneous silane decomposition is almost independent of the total pressure. This is due to the fact, that the heterogeneous reaction rate is zero order in silane for these high silane pressures. As a result, the total growth rate increases by only a factor 2-3, when the pressure is increased from 133 to 1330 Pa. The growth uniformity however is seriously deteriorated due to the increased importance of gas-phase reactions. At 1330 Pa total pressure the uniformity is less than 60 %, which is of course unacceptable for commercial applications. Thus, an increase in the total pressure leads to a relatively small increase in the growth rate and a severe loss of uniformity due to gas-phase reactions, and therefore is not a suitable option for increasing the throughput in silicon CVD in the present.
**Figure 5.16:**
Total growth rate and growth rate due to gas-phase intermediates at \( r = 0 \) as a function of total pressure for 900 K and 1000 K wafer temperatures and 10% silane in nitrogen carrier gas.

**Figure 5.17:**
Idem, as a function of the inlet silane mole fraction, at 133 Pa total pressure and with nitrogen carrier gas.

Finally, we have studied the influence of the silane partial pressure at a fixed total pressure of 133 Pa, by increasing the inlet silane mole fraction, keeping the other process conditions fixed as in the base case. The resulting growth rates at \( r = 0 \) are shown in figure 5.17. Due to the increased silane partial pressure the gas-phase reactions are enhanced and their contribution to the deposition is increased. At 900 K susceptor temperature, the silicon growth due to gas-phase reactions increases from 0.5% to 4% of the total growth when the silane mole fraction is increased from 0.1 to 1. For a susceptor temperature of 1000 K we see an increase from 1.4% to 15%. The total growth however, which is again mostly due to direct heterogeneous silane decomposition, is almost independent of the silane partial pressure. Just as before, this is due to the fact that at these silane pressures the silane RSC is inversely proportional to the silane pressure. So, as was the case when the total pressure was increased, the effect of an increase in the silane partial pressure at fixed total pressure on the total growth rate is small, whereas uniformity is deteriorated.
Concluding, we find that an increase in the susceptor temperature will lead to a highly increased growth rate, while the contribution of gas-phase reactions remains relatively small and uniformity is still very good. An increase in the total pressure or the silane partial pressure however, leads to a relatively small increase in the growth rate, a large increase in the contribution of gas-phase reactions and a highly deteriorated uniformity. In general, the contribution of gas-phase reactions to the silicon growth was roughly found to be small (i.e. \( \leq 10\% \)) for \( P_{\text{total}} \cdot P_{\text{SiH}_4} < \phi \), with \( \phi \approx 3 \cdot 10^4 \text{ Pa}^2 \) for \( T_{\text{wafer}} = 900 \text{ K} \) and \( \phi \approx 1 \cdot 10^4 \text{ Pa}^2 \) for \( T_{\text{wafer}} = 1000 \text{ K} \) in the present reactor configuration.

5.7 INFLUENCE OF THE CARRIER GAS

It seems likely, that the use of hydrogen as a carrier gas will suppress the gas-phase chemistry, since the initial homogeneous decomposition of silane (reaction G1) is suppressed in a hydrogen ambient. Besides, the type of carrier gas will also have an effect on the transport phenomena (gas flow, diffusion, thermal diffusion etc.) in the reactor. We have studied the influence of the carrier gas under those process conditions which, of all cases studied, led to the most significant contribution of gas-phase chemistry. Thus, we have simulated a process at 1330 Pa total pressure, 1000 K wafer temperature and a silane inlet mole fraction of 0.1, using nitrogen, hydrogen and helium as carrier gases. The resulting growth rates due to gas-phase reactions and the total growth rates as a function of radius are shown in figure 5.18. In contrast to what might be expected from a chemistry point of view, there is a large difference between the growth rates obtained with the two inert carrier gases helium and nitrogen, whereas on the other hand the results obtained with hydrogen and helium are very similar. This indicates, that the observed differences are due to transport phenomena rather than chemical effects. There are two important effects of the carrier gas on the transport phenomena: First, due to the increased buoyancy effects, nitrogen as a carrier gas causes strong recirculations in the gas flow (see chapter 4), thus increasing the thickness of the thermal boundary layer and the importance of gas-phase reactions. Secondly, thermal diffusion effects, causing silane and the reactive intermediates to diffuse away from the heated susceptor, are much weaker in nitrogen than in helium or hydrogen. Both effects cause a larger growth rate in nitrogen than in helium or hydrogen. On the other hand, the very small difference between
hydrogen and helium carrier gases indicates, that the suppression of reaction G1 in hydrogen carrier gas is small. This may be understood from the fact that hydrogen will have a suppressing effect on reaction G1 only, if this reaction is close to local equilibrium. In this case, the local formation of silylene by the forward reaction G1 and its destruction by the reverse reaction will be of equal importance and the addition of hydrogen will cause a shift in the local equilibrium towards less silylene. In figure 5.19 the local equilibrium ratios $\Psi_g$, defined as

$$\Psi_g = \frac{\Pi_{products} (f_i P_i P_0^i)^1}{\Pi_{reactants} (f_i P_i P_0^i) K_g}$$  \hspace{1cm} (5.23)$$

as a function of the height above the susceptor (at $r = 0$) are shown for the different gas-phase reactions in the case of helium carrier gas. Local equilibrium is reached for $\Psi_g = 1$. When $\Psi_g \ll 1$ (or $\Psi_g \gg 1$) the reaction is far from equilibrium and the amount of formed species is determined by the kinetics of the forward (backward) reaction, rather than the reaction thermochemistry. It is clear, that reaction G1 is far from equilibrium and that the amount of formed silylene is determined by the forward reaction.
Figure 5.19: Local equilibrium ratios $\Psi_e$ at r=0 as a function of the height above the susceptor for 1000 K wafer temperature, 1330 Pa total pressure and 10% silane in helium carrier gas.

only. Therefore, addition of hydrogen will have little influence on the formation of silylene. Reactions G4 and G5 are also far from local equilibrium, whereas G2 and G3 are very close to equilibrium. The above illustrates that gas-phase reactions in CVD may be far from equilibrium and that one should be careful in using equilibrium arguments when predicting the influence of parameter variations on process performance. It also shows the importance of transport phenomena and chemical kinetics in CVD processes.

Concluding we find, that the carrier gas does have an influence on the silicon growth rate. This influence, however, is a result of the differences in the transport phenomena in different carrier gases, rather than chemical effects. The strong thermal diffusion effects in hydrogen and helium carrier gases cause the reactive intermediates to diffuse away from the susceptor, resulting in a decreased growth rate. In nitrogen carrier gas, thermal diffusion is less important and the silicon growth due to reactive intermediates is larger, resulting in a less uniform deposition.
5.8 OPTIMIZATION OF IN SITU DOPED POLYSILICON DEPOSITION

In the previous sections it was shown, that gas-phase reactions have a deteriorating effect on the deposition uniformity. However, it may not always be desirable to suppress these gas-phase reactions in order to obtain uniform growth. A significant contribution of gas-phase reactions may e.g. be desired when growing in situ Phosphorus doped poly-silicon through the addition of phosphine to the gas-mixture. This will prevent silicon growth from direct heterogeneous silane adsorption (see section 5.3.1). Therefore, to grow uniform films of in situ P doped polysilicon films, we have to optimize the reactor geometry and the process conditions in order to obtain a uniform deposition of reactive intermediates formed in the gas-phase. For this purpose, both the silane concentration boundary layer and the temperature boundary layer above the susceptor surface must be uniform, as has been discussed in chapter 4.

In this section we will use the model for such an optimization. We set the silane sticking coefficient $\gamma_1$ to zero and assume that the sticking coefficients of the intermediates are not influenced by the phosphine addition. We now try to obtain a high and uniform deposition rate on a 0.20 m diameter wafer. From the process conditions studied in the previous sections, we take those that lead to a large deposition rate of gas-phase intermediates, i.e. a total pressure of 1330 Pa, a wafer temperature of 1000 K and a silane inlet mole fraction of 0.1. We use helium as a carrier gas in order to suppress buoyancy driven mixed convection flows. Expressed in the dimensionless numbers introduced in chapter 4, these process conditions lead to $Re = 0.26$, $Gr = 36$, $Pr = 0.24$, $Ga = 1.1$ and $Sc = 1.9$. Note that the Prandtl number of the silane-helium mixture highly deviates from the usual $Pr = 0.7$ for pure gases. Figure 5.20 shows the highly non-uniform growth rate due to reactive intermediates for these process conditions. We will now vary the flowrate and the reactor geometry in order to try to improve this uniformity.

5.8.1 Influence of the flowrate

A first option to improve the growth uniformity seems to be a variation of the total flowrate. There are two effects primarily influencing the growth uniformity: (i) The uniformity of the thermal boundary layer above the susceptor surface and (ii) The uniformity of the silane transport to the
susceptor. An increased flow will lead to less silane depletion and possibly a more uniform silane concentration at the susceptor surface. Also, the flowrate may influence the thickness of the thermal boundary layer. Finally, an increased flowrate leads to a reduced residence time of the gases in the reactor, and thus influences the gas phase reactions.

In figure 5.20 the growth rate distributions for total flows of 0.25, 1 and 4 slm (Re = 0.06, 0.26 and 1.0 respectively) are compared. In all three cases, the growth rate is maximum in the center of the wafer. This is due to the fact that the thermal boundary layer thickness is maximum at r = 0 (correspondingly, the Nusselt has a minimum at r = 0). In contrast to what might be expected, an increase of the total flow leads to a decreased uniformity. This can be explained from two effects of an increased flowrate: First, it has been shown in section 4.7, that the thickness of the thermal boundary layer is almost unaffected by the flowrate at low Re and Gr numbers (figure 4.7a). The same is found for the present situation. In figure 5.20 the three curves for Nu as a function of radius for 0.25, 1 and 4 slm total flow practically coincide (within 5 %), and for clarity only the curve for 1 slm has been shown. Thus, the thickness uniformity of the thermal boundary
layer is hardly influenced by an increased flow rate. On the other hand, the total flow does have an effect on the silane concentration at the wafer surface. At low flowrates, the silane surface concentration is low due to strong depletion effects and has a minimum at \( r = 0 \). For high flowrates the silane surface concentration increases due to less depletion, and has a maximum at \( r = 0 \). These effects are superimposed on the aforementioned temperature effect, causing the growth rate to be higher and less uniform for higher flowrates.

5.8.2 Optimization of the reactor geometry

Secondly, we try to optimize the reactor geometry in order to obtain uniform deposition.

As discussed in section 4.11, a built-in feature of the ASM single-wafer reactor is the variable length of the inflow tube which is positioned perpendicularly above the susceptor surface. By varying the length of this tube, the distance \( Z_t \) (figure 4.1) from the susceptor surface to the end of the inflow tube can be varied. This is expected to influence the deposition uniformity. In figure 5.21 we compare the calculated growth rates for \( Z_t = 0.025 \text{ m}, 0.050 \text{ m} \) and \( 0.100 \text{ m} \). The length of the inflow tube does have some influence on the growth rate uniformity, due to its influence

\[ \text{figure 5.21: Deposition rate as a function of radius for different } Z_t. \]
on the thermal and concentration boundary layers. However, uniform deposition cannot be obtained by varying $Z_t$ in the present reactor configuration.

Thus, a more rigorous modification of the reactor geometry seems necessary in order to improve the deposition uniformity. In chapter 4 it was found, that a decrease of the reactor height and the use of a large inflow pipe radius lead to an improvement of the thermal boundary layer uniformity. Based on these findings, a reactor configuration optimization study was made, using the simulation model to study the effect of various geometrical variations on the growth uniformity. This study has led to the reactor configuration in figure 5.22. The resulting distribution of the silane surface concentration, the Nusselt number and the growth rate are shown in figure 5.23. The growth uniformity is better than 96% over a 0.20 m diameter wafer surface. This good uniformity is not limited to the process conditions chosen for our optimization study. We varied the total pressure from 1330 Pa to 400 Pa, the susceptor temperature from 1000 K to 900 K and the total flow from 1 slm to 3 slm and we have switched from He to $N_2$ carrier gas. In all cases, the growth uniformity was better than 90% over a 0.20 m diameter wafer. Thus we have obtained a reactor geometry allowing the deposition of uniform layers of in situ Phosphorus doped poly-silicon layers on large wafers at reasonably high deposition rates. Moreover, the process conditions used in this reactor are not critical to the obtained uniformity. However, it should be noted, that the 0.36 m diameter deposition area in the optimized reactor configuration is much larger than the 0.20 m wafer diameter, leading to a relatively large amount of silicon deposition outside the wafer surface. This may be unwanted.
The above may serve as an illustration of the use of advanced computer simulation models as an aid in the optimization of CVD processes and reactors. Of course, experimental validation of the predicted results and further refinement of the design will still be necessary. Nevertheless, an optimization study as the above may largely reduce the time and costs involved in the trial-and-error optimization procedures common in CVD reactor and process development up to now.

5.9 CHEMICAL MODEL SENSITIVITY ANALYSIS

The used model for the heterogeneous and homogeneous chemical reactions contains a number of uncertainties. First, as stated before, the homogeneous reaction model will most probably not reflect all the details of the gas-phase chemistry. Secondly, there are rather large uncertainties in the rate constants for the homogeneous reactions. Finally, there may be errors in the values for the sticking coefficients. Therefore, we have studied the sensitivity of our model to variations in the homogeneous reaction rate constants, the reactive sticking coefficients and the homogeneous reaction model.

To study the influence of the reaction rates, we have systematically varied the homogeneous rate constants and the sticking coefficients for a case with 1330 Pa total pressure, 1000 K wafer temperature and 0.1 inlet
### Table 5.2: Sensitivity of the chemistry model

<table>
<thead>
<tr>
<th>parameter variation:</th>
<th>percentage influence on:</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>growth due to gas phase reactions</td>
<td>r=0</td>
<td>r=0.10 m</td>
<td>r=0</td>
<td>r=0.10 m</td>
</tr>
<tr>
<td>$A_1, A_1 \times 10$</td>
<td>+138 % +273 %</td>
<td></td>
<td></td>
<td>+85 % +122 %</td>
<td></td>
</tr>
<tr>
<td>$A_2, A_2 \times 10$</td>
<td>+ 0 % - 2 %</td>
<td></td>
<td></td>
<td>+ 0 % - 1 %</td>
<td></td>
</tr>
<tr>
<td>$A_3, A_3 \times 10$</td>
<td>+ 0 % + 0 %</td>
<td></td>
<td></td>
<td>+ 0 % + 0 %</td>
<td></td>
</tr>
<tr>
<td>$A_4, A_4 \times 10$</td>
<td>- 6 % - 7 %</td>
<td></td>
<td></td>
<td>- 4 % - 3 %</td>
<td></td>
</tr>
<tr>
<td>$A_5, A_5 \times 10$</td>
<td>+ 32 % + 13 %</td>
<td></td>
<td></td>
<td>+20 % + 6 %</td>
<td></td>
</tr>
<tr>
<td>$E_1$ - 10 kJ/mole</td>
<td>+ 91 % +125 %</td>
<td></td>
<td></td>
<td>+57 % +56 %</td>
<td></td>
</tr>
<tr>
<td>$E_2$ - 10 kJ/mole</td>
<td>- 14 % - 11 %</td>
<td></td>
<td></td>
<td>- 9 % - 5 %</td>
<td></td>
</tr>
<tr>
<td>$E_3$ - 10 kJ/mole</td>
<td>+ 0 % + 0 %</td>
<td></td>
<td></td>
<td>+ 0 % + 0 %</td>
<td></td>
</tr>
<tr>
<td>$E_4$ - 10 kJ/mole</td>
<td>+ 6 % + 3 %</td>
<td></td>
<td></td>
<td>+ 4 % + 1 %</td>
<td></td>
</tr>
<tr>
<td>$E_5$ - 10 kJ/mole</td>
<td>+ 16 % + 6 %</td>
<td></td>
<td></td>
<td>+10 % + 3 %</td>
<td></td>
</tr>
<tr>
<td>$r_1 \times 0.1$</td>
<td>+ 20 % + 14 %</td>
<td></td>
<td></td>
<td>-20 % - 43 %</td>
<td></td>
</tr>
<tr>
<td>$r_2 \times 0.1$</td>
<td>+ 2 % + 2 %</td>
<td></td>
<td></td>
<td>+ 1 % + 1 %</td>
<td></td>
</tr>
<tr>
<td>$r_3 \times 0.1$</td>
<td>- 7 % - 16 %</td>
<td></td>
<td></td>
<td>- 5 % - 7 %</td>
<td></td>
</tr>
<tr>
<td>$r_4 \times 0.1$</td>
<td>+ 0 % + 0 %</td>
<td></td>
<td></td>
<td>+ 0 % + 0 %</td>
<td></td>
</tr>
<tr>
<td>$r_5 \times 0.1$</td>
<td>+ 0 % + 0 %</td>
<td></td>
<td></td>
<td>+ 0 % + 0 %</td>
<td></td>
</tr>
</tbody>
</table>

mole fraction silane in nitrogen carrier gas. At these conditions, 37 % of the total growth (at r = 0) is due to direct heterogeneous decomposition of silane and 63 % is due to reactive intermediates formed in the gas-phase. First, we have one by one increased the homogeneous reaction rate constants for both the forward and the reverse reactions by a factor 10 (thus keeping the equilibrium constants fixed). Next, we have one by one decreased the activation energies of the forward reactions by 10 kJ/mole at fixed reaction rates for the reverse reactions (thus shifting the equilibrium of the reactions). Finally, we have one by one decreased the RSC of the silicon containing species by a factor 10. Table 5.2 shows the influence of these variations on the predicted growth rates at r = 0. The deposition results are very sensitive to the kinetics of reaction G1, which however is rather well known. On the other hand, the predicted growth rates are relatively insensitive to variations in the rates for reactions G2-G5, which mostly result in a shuffle of the contributions of the different reactive
Table 5.3: Representative situations used for studying
the influence of the homogeneous reaction
model the predicted growth rates.

<table>
<thead>
<tr>
<th>Wafer temperature</th>
<th>Total pressure</th>
<th>SiH₄ inlet fraction</th>
<th>Carrier gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>I 900 K</td>
<td>1330 Pa</td>
<td>0.1</td>
<td>N₂</td>
</tr>
<tr>
<td>II 1000 K</td>
<td>133 Pa</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>III 1000 K</td>
<td>1330 Pa</td>
<td>0.1</td>
<td>N₂</td>
</tr>
<tr>
<td>IV 1000 K</td>
<td>1330 Pa</td>
<td>0.1</td>
<td>H₂</td>
</tr>
<tr>
<td>V 1100 K</td>
<td>133 Pa</td>
<td>0.1</td>
<td>N₂</td>
</tr>
</tbody>
</table>

intermediates, but have little influence on the total growth rate. The model
is of course very sensitive to the silane RSC, but appears to be relatively
insensitive to the values assumed for the other sticking coefficients.
Concluding we may say, that the used model is very sensitive to the kinetics
of the initial homogeneous decomposition reaction of silane and to the value
of the silane sticking coefficient, which however are both known rather
accurately, whereas it is rather insensitive to the other homogeneous and
heterogeneous rate constants.

To get an impression of the sensitivity of the predicted growth rates
to the amount of detail in the homogeneous reaction model, we have repeated
our simulations for some representative situations, summarized in table 5.3,
using a highly reduced reaction mechanism, containing reactions G1 and G2
and Si-S3 only. Thus, the simplified model includes the formation of SiH₂
and Si₂H₆ in the gas-phase, but neglects the formation of Si₃H₈ and Si₂H₄. A
comparison of the calculated total growth rates and the growth rates due to
reactive intermediates only, using both the full chemical model (G1-G5,
Si-S5) and the simplified chemical model (G1-G2, Si-S3) is presented in
table 5.4. It can be seen that the predicted growth rates are relatively
insensitive to the amount of details in the homogeneous reaction model for
the process conditions studied in this chapter. Even in case III, where the
full model predicts a significant (35%) contribution of Si₃H₈ and Si₂H₄ to
the total growth, the simplified model leads to a small (4%) error in the
total growth. Thus we conclude, that the model used in this study, although
probably not reflecting all the detailed features of the reaction mechanism,
Table 5.4: Influence of the homogeneous reaction model on the predicted growth rates.

<table>
<thead>
<tr>
<th></th>
<th>growth rate due to intermediates at ( r=0 )</th>
<th>total growth rate at ( r=0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>full</td>
<td>simplified</td>
</tr>
<tr>
<td>I</td>
<td>173</td>
<td>148 (-14 %)</td>
</tr>
<tr>
<td>II</td>
<td>210</td>
<td>206 (-2 %)</td>
</tr>
<tr>
<td>III</td>
<td>1950</td>
<td>1822 (-7 %)</td>
</tr>
<tr>
<td>IV</td>
<td>823</td>
<td>726 (-12 %)</td>
</tr>
<tr>
<td>V</td>
<td>88</td>
<td>88 (-0 %)</td>
</tr>
</tbody>
</table>

will predict the silicon growth rate in single-wafer LPCVD reactors with reasonable accuracy.

5.10 APPROXIMATE APPROACHES FOR MULTICOMPONENT DIFFUSION

In all modeling studies described in this chapter we have used the rigorous treatment of multicomponent ordinary diffusion described in section 2.4.2 (Stefan-Maxwell equations, eqs. 2.12-2.17) and the exact formulation for multicomponent thermal diffusion described in sections 2.4.3 (eq. 2.20) and appendix F (eqs. F.1-F.8). In section 2.4.2 (eqs. 2.18-2.19) we have described an approximate approach for modeling multicomponent ordinary diffusion which (i) requires less computational effort and (ii) leads to expressions which are very similar to Fick's law for ordinary diffusion and therefore can be implemented easily as a standard gradient diffusion term in the general transport equation 3.1. In section 2.7.4 (eq. 2.79) we have described an approximate method for calculating multicomponent thermal diffusion coefficients, which requires much less computational effort than the exact formulation. In this section we will study the accuracy of both approximate approaches for the processes considered in this chapter. We compare the six approaches in table 5.5. It can be seen that, for the present model implementations, the approximate approach for thermal diffusion leads to a 34% reduction of the required cpu time per iteration compared to the exact formulation, whereas the approximate approach for
table 5.5: Approximate approaches for multi-component (thermal) diffusion

<table>
<thead>
<tr>
<th></th>
<th>ordinary diffusion</th>
<th>thermal diffusion</th>
<th>Dufour effect</th>
<th>normalized CPU time per iteration</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>exact</td>
<td>exact</td>
<td>included</td>
<td>1.00</td>
</tr>
<tr>
<td>II</td>
<td>exact</td>
<td>exact</td>
<td>not</td>
<td>0.97</td>
</tr>
<tr>
<td>III</td>
<td>exact</td>
<td>appr.</td>
<td>included</td>
<td>0.66</td>
</tr>
<tr>
<td>IV</td>
<td>exact</td>
<td>not</td>
<td>not</td>
<td>0.61</td>
</tr>
<tr>
<td>V</td>
<td>appr.</td>
<td>exact</td>
<td>included</td>
<td>0.80</td>
</tr>
<tr>
<td>VI</td>
<td>appr.</td>
<td>appr.</td>
<td>not</td>
<td>0.46</td>
</tr>
</tbody>
</table>

ordinary diffusion leads to another 20% reduction. The inclusion of the Dufour effect requires relatively little additional cpu time. The total number of iterations required to obtain a converged solution is approximately the same for all the different approaches. We compare these 6 approaches for a process with 1330 Pa total pressure, 1000 K wafer temperature, 1 slm total flow and an inlet mole fraction silane of 0.1 in a carrier gas of nitrogen, helium or an equimolal mixture of nitrogen and hydrogen.

The resulting growth rates at \( r = 0 \) are compared in table 5.6. From this comparison we may conclude that (i) the influence of the Dufour effect on the predicted growth rate is negligible (compare I vs II); (ii) The influence of thermal diffusion can be very important when there is a large difference in molecular mass of the constituent species (compare I vs IV); (iii) The approximate approach for multicomponent thermal diffusion gives rather accurate results (compare I vs III) and (iv) The approximate approach for multicomponent ordinary diffusion leads to negligibly small errors (compare I vs V). Thus, by using the approximate approaches for ordinary and thermal multicomponent diffusion and by neglecting the Dufour effect we obtain a less complex computer code and we reduce the overall cpu time by more than 50%, while obtaining accurate growth rate predictions for the type of processes considered in this chapter (compare I vs VI).
Table 5.6: Influence of approximate approaches for multi-component (thermal) diffusion

<table>
<thead>
<tr>
<th>Growth Rate at r=0 (Å/min)</th>
<th>$N_2$ Carrier</th>
<th>He Carrier</th>
<th>$N_2$/$N_2$ Carrier</th>
</tr>
</thead>
<tbody>
<tr>
<td>I  3015</td>
<td>1845</td>
<td></td>
<td>2445</td>
</tr>
<tr>
<td>II 3018 (+0.1%)</td>
<td>1846 (+0.1%)</td>
<td>2444 (+0.0%)</td>
<td></td>
</tr>
<tr>
<td>III 3019 (+0.1%)</td>
<td>1915 (+3.8%)</td>
<td>2453 (+0.3%)</td>
<td></td>
</tr>
<tr>
<td>IV 3142 (+4.2%)</td>
<td>2840 (+54%)</td>
<td>2830 (+16%)</td>
<td></td>
</tr>
<tr>
<td>V  3018 (+0.1%)</td>
<td>1849 (+0.2%)</td>
<td>2435 (-0.4%)</td>
<td></td>
</tr>
<tr>
<td>VI 3018 (+0.1%)</td>
<td>1931 (+4.7%)</td>
<td>2448 (+0.1%)</td>
<td></td>
</tr>
</tbody>
</table>
6 TUNGSTEN LPCVD IN A SINGLE-WAFER REACTOR

6.1 INTRODUCTION

In the last few years, the interest in the use of tungsten in multilevel metallization submicron IC technology has grown considerably [e.g. Blewer, 1986a; Broadbent, 1987; Wells, 1988; Blewer and Mc Conica, 1989; Wong and Furukawa, 1990]. Tungsten can be used (a) as a diffusion barrier between silicon and aluminum, (b) as a shunting material on gate structures and (c) for the filling of vias and contact holes, see figure 6.1 [Miller and Beinglas, 1982; Broadbent and Stacy, 1985; Blewer, 1986b]. Tungsten is a suitable candidate for metallization purposes because it (i) has a low bulk resistivity, (ii) has a low contact resistance to TiSi2, (iii) is chemically stable, (iv) has a high resistance to electromigration and (v) has a coefficient of thermal expansion similar to that of silicon. Because of the poor conformality (step coverage) sputtering techniques are not suited for application in submicron devices and CVD techniques are required.

Tungsten CVD can be applied in either a selective or a blanket mode. Whether the process is selective or not is e.g. determined by the chemistry

![Diagram](image)

*figure 6.1: The use of tungsten as (a) diffusion barrier, (b) shunt material and (c) contact fill in multilevel metallization IC's. (after Granneman [1988])*
of the process, the reactor configuration, the process conditions and the pre-treatment of the wafer surface. In a selective mode, deposition takes place on metallic and silicon surfaces, but not on most oxides, such as SiO₂. This offers the possibility of filling contact holes without the need for subsequent backetching and has the advantage of an economic use of reactant gases (figure 6.2b). However, selective deposition for this purpose is only possible when all contact holes are equal in depth, which is not always the case. Moreover, until now efforts to develop commercially applicable selective tungsten LPCVD processes have not fully succeeded.

Blanket tungsten deposition processes with subsequent backetching (figure 6.2a) have been more successful. The filling of contact holes in a blanket mode requires deposition techniques capable of filling submicron, high aspect ratio holes with excellent conformality (high step coverage). Blanket tungsten LPCVD from tungstenhexafluoride (WF₆), using hydrogen as a reducing agent, according to the overall reaction:

$$WF₆ + 3 H₂ \rightarrow W + 6 HF$$  \hspace{1cm} (6.1)

is now widely used for this purpose [Schmitz et al., 1987, 1988, 1989a; Joshi et al., 1990] and has been included in (pilot) production lines of most major IC manufacturers. Like many other LPCVD processes, tungsten LPCVD from H₂-WF₆ was originally developed in hotwall multiple-wafer-in-tube LPCVD reactors [Miller and Beinglas, 1980; Broadbent and Ramiller, 1984; Pauleau and Lami, 1985; Lami and Pauleau, 1988; Kwakman et al., 1988], but the use
of coldwall single-wafer reactors is more common nowadays [McConica and Krishnamani, 1986; McConica et al., 1988a; Blumenthal and Smith, 1988; Kuiper et al., 1989, Cale et al., 1990]. Coldwall single-wafer reactors offer several advantages over conventional hotwall systems, such as low particle contamination, low WF₆ consumption, suppression of gas-phase reactions, efficient removal of reaction by-products, excellent uniformity on large wafers and easy automatic wafer handling. Moreover, selective deposition does not seem to be realizable in hotwall reactors.

Several important qualities of tungsten films deposited through LPCVD from hydrogen and tungstenhexafluoride seem to depend highly on the species concentrations, pressure and temperature distributions in the reactor and at the wafer surface. The growth rate appears to depend on the hydrogen pressure and the temperature only, at sufficiently high WF₆ pressures [Broadbent and Ramiller, 1984; McConica and Krishnamani, 1986]. At low tungstenhexafluoride pressures however, the growth rate has been found to depend on the WF₆ pressure also [van der Putte, 1987; Blumenthal and Smith, 1988]. Low temperatures, low WF₆ concentrations and low concentrations of reaction-products have been mentioned by several authors as factors favoring selective deposition [Carlsson and Boman, 1985; Pauleau and Lami, 1985; McConica, 1987; Kwakman et al., 1988; McConica et al, 1988a; Kato and Itsumi, 1988]. The step coverage appears to be improved by high tungstenhexafluoride partial pressures, low temperatures and low hydrogen partial pressures [McConica and Churchill, 1988b; Chatterjee and McConica, 1990; Schmitz et al., 1990; Hasper et al., 1990, 1991]. Encroachment (undesired W growth in contact windows just underneath SiO₂) has been found to decrease with decreasing temperature and tungstenhexafluoride pressure [Moriya et al., 1983].

From the above it is clear, that it is important to have precise knowledge of the concentration and temperature distributions in tungsten LPCVD reactors. These distributions are mainly determined by hydrodynamics and transport phenomena in the gas mixture in the reactor. Especially in single-wafer reactors with high deposition rates and cooled reactor walls, leading to a high rate of reactant consumption and reaction-product formation and to strong thermal diffusion effects, significant concentration and temperature gradients will be present. Detailed hydrodynamic models can be used to determine the species concentrations and temperature distributions in the gas mixture and at the wafer surface. Recently, some models for the hydrodynamics and chemical reactions in tungsten LPCVD in
coldwall single-wafer reactors have been published [Ulacia et al., 1989; Jasinski and Harshbarger, 1989; McInerney et al., 1990, Jasinski and Kang, 1991]. These models have been based on commercially available fluid dynamics computer codes and do not incorporate several aspects which are relevant for accurate coldwall single-wafer LPCVD modeling, such as multicomponent (thermal) diffusion and the influence of the gas mixture composition on the fluid properties. In this chapter the mathematical CVD model as described in chapter 2, which includes all these phenomena, is used to model blanket tungsten LPCVD from H₂-WF₆ in a single-wafer reactor and model predictions are compared to experimental results. The model is then used to optimize the process with respect to a high growth rate, a high step coverage in large aspect ratio contact holes and a high uniformity on large wafers in combination with a low WF₆ consumption. These results have been verified experimentally.

Recently, alternative processes using silane (SiH₄) or germane (GeH₄) instead of hydrogen as a reducing agent for tungstenhexafluoride have been discovered as attractive alternatives for tungsten LPCVD [Schmitz et al., 1987; Kusumoto et al., 1988; Ohba et al., 1989; van der Jeugd et al., 1990, 1991b]. Little is yet known on the reaction mechanisms and kinetics of these processes. Suggested overall mechanisms are

\[2 \text{WF}_6 + 3 \text{SiH}_4 \rightarrow 2 \text{W} + 3 \text{SiF}_4 + 6 \text{H}_2 \quad (6.2a)\]

\[\text{WF}_6 + 2 \text{SiH}_4 \rightarrow \text{W} + 2 \text{SiHF}_3 + 3 \text{H}_2 \quad (6.2b)\]

\[4 \text{WF}_6 + 3 \text{SiH}_4 \rightarrow 4 \text{W} + 3 \text{SiF}_4 + 12 \text{HF} \quad (6.2c)\]

\[\text{WF}_6 + 3 \text{GeH}_4 \rightarrow \text{W} + 3 \text{GeF}_2 + 6 \text{H}_2 \quad (6.3)\]

[Ohba et al., 1989, Park et al., 1989; Yu et al., 1990; Kobayashi et al., 1990; van der Jeugd et al., 1991b]. Although these processes offer many advantages over the hydrogen reduction process, such as a higher growth rate, smaller grain size and less interaction with silicon [Schmitz et al., 1987, 1989b; Rosler et al., 1988; Gorczyza et al., 1989; Park et al., 1989; Ohba et al., 1989, 1990; van der Jeugd et al., 1990, 1991b], the poor step coverage seems to make them unsuitable for contact hole filling in a blanket mode [Schmitz et al., 1990; Hasper et al., 1990, 1991]. In this chapter some preliminary simulation results for tungsten LPCVD by means of the silane reduction process will be presented. The simulations will illustrate the
need for an accurate account of transport phenomena in the interpretation of kinetic experiments.

6.2 PROBLEM DESCRIPTION

We study tungsten LPCVD from tungstenhexafluoride, using hydrogen or silane as a reducing agent, in the ASM coldwall single-wafer reactor configuration which has been described in detail in section 4.2 (figure 4.1). Our main interests are in (i) the growth rate and growth uniformity as a function of process conditions, (ii) the transition from kinetically-limited to transport-limited growth and its influence on growth rate and growth uniformity, (iii) the species concentration distributions at the wafer surface as a function of the inlet conditions and their influence on step coverage.

As was done in chapter 5, it is assumed that the hydrodynamics are stationary and axisymmetric and the transport equations are solved in stationary, 2D axisymmetric form. The deposition area is either a 3 in. (0.076 m diameter) wafer in the center of the susceptor, or the entire susceptor surface. In the chemistry models, homogeneous reactions are neglected and it is assumed that deposition is due to heterogeneous processes only. This is further discussed in section 6.3, in which the chemistry models are described.

6.3 CHEMISTRY MODELS

6.3.1 The hydrogen reduction process

The deposition rate of tungsten from hydrogen and tungstenhexafluoride in LPCVD appears to be fully determined by surface chemistry for the common process conditions (600–750 K, 10^2–10^3 Pa). These low pressures and temperatures suggest that gas-phase reactions are of limited importance. Indeed, a recent theoretical study of reaction kinetics in tungsten LPCVD from H_2-WF_6 by Arora and Pollard [1991] shows, that gas-phase reactions are unimportant for common process conditions. The fact that the process can be run in a selective mode is another indication for the fact that the deposition is determined by heterogeneous reactions mainly. The overall reaction rate is given by eq. 6.1. For sufficiently high tungsten-
hexafluoride concentrations, the deposition rate has been found to depend on the hydrogen partial pressure and the temperature, being independent of the WF$_6$ partial pressure, according to

$$R_{kin}^S = c_h [P_{WF_6}]^0 [P_{H_2}]^{1/2} \exp(-E/RT)$$  \hspace{1cm} (6.4)

where $R_{kin}^S$ is the reaction rate determined by the surface kinetics and $E \approx 67-73$ kJ/mole [Bryant, 1978; Broadbent and Ramiller, 1984; Broadbent and Stacy, 1985; Pauleau and Lami, 1985; McConica and Krishnamani, 1986]. At very low tungstenhexafluoride concentrations however, the overall growth rate cannot remain independent of the WF$_6$ pressure, because of supply and mass transfer limitations. It is also possible, that the heterogeneous reaction rate changes from zero order to nonzero order in tungstenhexafluoride at low concentrations. Indeed, at very low WF$_6$ partial pressures the growth rate has been found to decrease with decreasing WF$_6$ concentration [van der Putte, 1987; Blumenthal and Smith, 1988]. Blumenthal and Smith ascribed this to mass transfer limitations, whereas van der Putte assumed the reaction rate to change from zero order to $1/6$ order in tungstenhexafluoride at low WF$_6$ concentrations. In this chapter, it will be shown that the rate of the heterogeneous reaction probably remains zero order in WF$_6$ down to very low pressures.

We now assume, that the actual growth rate is described by a mechanism that considers the sequential processes of gas-phase diffusion of reactants to the wafer surface and a heterogeneous reaction, as was done by Ulacia et al. [1989]:

$$\frac{1}{R_{eff}^S} = \frac{1}{R_{kin}^S} + \frac{1}{j_{WF_6}^{max}} + \frac{3}{j_{H_2}^{max}}$$  \hspace{1cm} (6.5)

Here, $R_{eff}^S$ is the actual deposition rate, $R_{kin}^S$ is the reaction rate determined by the heterogeneous reaction kinetics and $j_i^{max}$ is the maximum diffusion flux of species $i$ to the wafer surface. Through eq. 6.5, the slowest of the three mechanisms: (i) heterogeneous reaction at the wafer surface, (ii) diffusion of tungstenhexafluoride to the wafer surface and (iii) diffusion of hydrogen to the wafer surface determines the deposition rate. Usually, a large excess of H$_2$ is used. Also, the diffusion coefficient of hydrogen in the gas mixture is much larger than the diffusion coefficient of tungstenhexafluoride. Therefore, $j_{H_2}^{max}$ is usually much larger than $j_{WF_6}^{max}$.
and the deposition rate is determined either by the heterogeneous reaction kinetics, or by the supply of tungstenhexafluoride to the wafer surface, or both.

Based on the extensive set of experimental growth rates obtained in a hotwall reactor published by Broadbent and Ramiller [1984], $R_k^S$ was calculated from eq. 6.4, using

$$c_H = 1.7 \text{ mole} \cdot \text{Pa}^{-1/2} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$$

$$E = 69 \text{ kJ} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$$

with a statistical error of $\pm 0.5 \text{ mole} \cdot \text{Pa}^{-1/2} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ (95%) in the value of $c_H$ at fixed $E$. The maximum mole flux $j_i^{\text{max}}$ of species $i$ to the wafer surface was taken as the maximum diffusive flux from the first discretization grid point to the wafer surface. The actual diffusive mole flux of species $i$ from the first grid point to the wafer surface in the direction normal to this surface is given by

$$j_i^{1{\rightarrow}0} = \frac{1}{m_i} \left( \rho \frac{\omega_i^1 - \omega_i^0}{\Delta} + D_i^T \ln \frac{T^1 - \ln T^0}{\Delta} \right)$$

(6.7)

where the superscript $^1$ denotes the value in the first grid point next to the wafer surface, the superscript $^0$ denotes the value at the wafer surface, and $\Delta$ denotes the distance from the wafer surface to the first grid point. Now, the maximum diffusive mass flux to the wafer surface may be calculated from eq. 6.7, assuming that the wafer concentration $\omega_i^0$ equals zero. As a result $D_i^T$ will also be zero, since $D_i^T \rightarrow 0$ for $\omega_i \rightarrow 0$. We now find for the maximum diffusive mole flux of species $i$ from the first discretization point to the wafer surface

$$j_i^{\text{max}} = \frac{\rho D_i \omega_i^1}{m_i \Delta}$$

(6.8)

The effective ordinary diffusion coefficient $D_i$ for species $i$ in the gas mixture may be calculated from

$$D_i = \frac{1}{\rho} \frac{n \cdot j_i^c}{n \cdot \nabla \omega_i}$$

(6.9)
with \( \mathbf{n} \) a unity vector normal to the wafer surface and \( \mathbf{j}^C_1 \) the ordinary diffusion mass flux vector of species 1.

6.3.2 The silane reduction process

There is little consensus in literature on the reaction mechanisms and kinetics of tungsten LPCVD from tungstenhexafluoride and silane. Even the overall reaction mechanism has not yet been clearly established. This seems mainly due to the complexity of the process. Depending on the process conditions (temperature, total pressure, SiH\(_4\):WF\(_6\) ratio) the deposited film consists of stable \( \alpha\)-W, metastable \( \beta\)-W or tungsten silicides (WSi\(_2\), W\(_5\)Si\(_3\)) [Park et al., 1989; Ohba et al., 1989; Schmitz et al., 1989]. The deposition kinetics and reaction mechanisms probably vary with the composition of the deposited film. Also, the role of gas-phase reactions has not yet been clearly established. However, Kobayashi et al. [1990] have found some indication for the fact that tungsten growth in the silane reduction process is also mainly due to heterogeneous processes under the common process conditions.

For SiH\(_4\):WF\(_6\) mole ratios less than 1.3 and deposition temperatures from about 475 K to 625 K stable \( \alpha\)-W is formed. Even within this small process window, there is a great deal of contradiction in the overall deposition rate expressions proposed in literature. Apparent activation energies of 7-28 kJ/mole [Gocke et al., 1990], 16-28 kJ/mole [Park et al., 1989] and 25-50 kJ/mole [Rosler et al., 1988] have been reported. Other authors find nearly temperature independent growth rates [Schmitz et al., 1987; Ohba et al., 1988, Kusumoto et al., 1988; Hasper et al., 1990] which may possibly be ascribed to mass-transfer-limited growth. The overall deposition rate order in tungstenhexafluoride has been reported as -0.6 by Ohba et al. [1988], as -0.2 - 0 by Rosler et al. [1988] and as 0 by Schmitz et al. [1987], Park et al. [1989] and Hasper et al. [1990]. For the overall deposition rate order in SiH\(_4\) most authors find a value of 1 [Schmitz et al., 1987; Rosler et al., 1988; Park et al., 1989; Hasper et al., 1990], but a value of 1.3 has been reported by Ohba et al. [1988]. Overall reaction mechanisms according to eqs. 6.2a, 6.2b and 6.2c have been reported. The reaction mechanism 6.2a seems to be the most generally accepted. However, by means of in situ infrared spectroscopy of reaction products, Kobayashi et al. [1990] have recently found indications for the fact that tungsten deposition from tungstenhexafluoride and silane is due to a combination of
reaction mechanism 6.2a and reaction mechanism 6.2b. Both mechanisms are concluded to be heterogeneous and no indication is found for the occurrence of homogeneous reactions. The first reaction (eq. 6.2a) is found to proceed preferably on metallic (tungsten) surfaces, whereas the second reaction mechanism (eq. 6.2b) proceeds on both tungsten and silicon dioxide substrate materials.

In this chapter, as a preliminary study, it will be assumed that deposition takes place due to a heterogeneous process, with the overall reaction eq. 6.2a, and an overall rate equation

$$\mathcal{R}_{kin}^S = c_s [P_{WF_6}]^0 [P_{SiH_4}]^1 \exp(-E/RT)$$  \hspace{1cm} (6.10)

where

$$c_s = 1.25 \cdot 10^{-2} \text{ mole} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$$  \hspace{1cm} (6.11)$$

$$E = 25 \text{ kJ/mole}$$

This expression reflects the first order rate dependence in silane and the zero order rate dependence in tungstenhexafluoride, reported by most authors. The activation energy has roughly been taken as the average of the values reported by those authors who do find an activation energy. The value of $c_s$ has been chosen in order to obtain a semi-quantitative agreement with growth rates observed by Schmitz et al. [1987] and Hasper et al. [1991]. However, a large number of published experimental data are not in agreement with this expression.

6.4 NUMERICAL SIMULATION

The discretized 2D axisymmetric transport equations were solved on a non-uniform grid with 35 grid points in the axial direction and 35 grid points in the radial direction. The grid is illustrated in figure 6.3. Grid independence of the results was checked on 50 $\times$ 50 and 70 $\times$ 70 grids for some representative situations. The calculated deposition rates and species concentrations at the wafer surface obtained on these fine grids differed less than 3% from those obtained on the standard grid on each point of the wafer surface.

To check the convergence of the iterative solution procedure, four criteria were used: (i) the error in the global mass balance for the total
flow, \( < 10^{-2} \% \); (ii) the error in the global mass balance for each of the gas species, \( < 1 \% \); (iii) the residuals of the equations (absolute values, summed over the grid, normalized by a characteristic value for the variable and normalized by the number of grid points), \( < 10^{-5} \) and (iv) the relative changes of the variables from one iteration to the next in a representative monitor point, \( < 10^{-5} \) for each variable. Changes of less than \( 1 \% \) in the calculated deposition rates and wafer surface concentrations occurred, when these criteria were reduced to \( 10^{-3} \%, 10^{-1} \%, \) and \( 10^{-6} \). The monitor point was taken on the axis of the reactor, in the first grid point next to the susceptor surface.

The calculations were carried out on a HP 9000-835 minicomputer. When using the standard \( 35 \times 35 \) grid and solving for 6 species concentrations, the computer code needs 1.8 Mbyte of working memory. Circa 2000-5000 iterations (depending on the process conditions) are needed to reach a converged solution when starting from a guessed initial solution, taking 6.2 seconds cpu time per iteration.
6.5 EXPERIMENTAL VALIDATION

Several diagnostic tools may be used for the validation of CVD reactor simulation models. The most straightforward way is to compare predicted growth rates and growth uniformities with experimental observations. In tungsten LPCVD from H\textsubscript{2}-WF\textsubscript{6} this method has limited value, because of the insensitivity of the growth rate to the WF\textsubscript{6} concentration (eq. 6.4) and the excess hydrogen which is commonly applied. However, the observed dependence of the growth rate on the WF\textsubscript{6} concentration at very low WF\textsubscript{6} concentrations [van der Putte, 1987; Blumenthal and Smith, 1988] may be used to test a simulation model. A second possibility is the combination of a reactor simulation model with models for the prediction of microscopic (feature scale) film qualities and to compare predictions of these combined models with experimental results. Step coverage models e.g. predict a strong dependence of the step coverage on the WF\textsubscript{6} concentration at the pore mouth [Mc Conica and Churchill, 1987; Schmitz et al., 1990; Chatterjee and McConica, 1990; Hasper et al., 1990, 1991]. Now, by using the WF\textsubscript{6} concentration at the wafer surface as calculated from the reactor model as a boundary condition at the pore mouth for the step coverage model and comparing predicted step coverages with experimental observations, the combination of reactor model and step coverage model may be tested [Hasper et al., 1990, 1991, McInerney et al., 1990]. A third possibility for the validation of a CVD reactor simulation model is the use of in situ laser diagnostic techniques for measuring temperatures and species concentrations in the gas mixture and to compare these values with model predictions [Breiland et al., 1986].

In this chapter, predicted growth rates and uniformities for the WF\textsubscript{6}-H\textsubscript{2} process at high and low WF\textsubscript{6} concentrations are compared to experimental results. Thus, it is possible to test the simulation model. At the same time more insight is gained in the processes influencing the growth rate at low WF\textsubscript{6} concentrations. This knowledge is important, because (i) for economic reasons it is interesting to use as little WF\textsubscript{6} as possible and (ii) for the accurate prediction of step coverage, precise knowledge of the mechanisms determining the growth rates at low WF\textsubscript{6} concentrations is essential, since the WF\textsubscript{6} concentration inside contact holes may be very low. Furthermore, the reactor scale transport phenomena model is coupled to a feature scale step coverage model, which uses the surface species concentrations from the reactor model as input to predict the step coverage in trenches and contact holes. The step coverage predicted by these combined models has been
compared to experimental values.

The experimental determination of tungsten growth rates and step coverages in the loadlocked, coldwall, single-wafer ASM reactor described in section 4.2 has been carried out in close collaboration at the Faculty of Electrical Engineering of Twente University by Hasper and Holleman. In the experiments, 3 in. (0.076 m diameter) p type 10 Ω·cm (100) wafers were used, which were placed in the center of an 8 in. silicon dioxide coated carrier wafer. Immediately before loading the wafer into the reactor a HF (1:100) dip of 30 seconds was applied. The purity of the gas sources (WF₆, Ar, H₂) employed was 99.999 %, according to manufacturer’s specifications. Very low WF₆ flows could be realized by putting a needle valve in series with the WF₆ massflow controller. Thus it was possible to adjust the WF₆ flow down to 0.4 sccm with an accuracy of ± 0.05 sccm. The silicon wafer temperature was measured by means of a dual wavelength pyrometer through a quartz window in the upper wall of the reactor. In this way, the wafer temperature (which may deviate substantially from the susceptor temperature in coldwall LPCVD reactors) was known with an accuracy of ± 5 K at the beginning of the deposition process. During the deposition process, the susceptor temperature as measured by a series of thermocouples was kept constant.

In the growth rate experiments, deposition took place selectively on the 3 in. wafer surface only and was stopped immediately at the moment selectivity was lost and deposition at the carrier wafer and susceptor was initiated. Layer thicknesses were determined by measuring the weight increase of the wafer and by using a profilometer. The measured layer thickness was corrected for the thickness of the initial, silicon reduced tungsten layer. By determining the weight increase, the wafer averaged growth rate could be determined with an accuracy of ± 20 Ång/min. The profilometer measures the local thickness, thus allowing the determination of growth rate uniformities. Profilometer measurements however suffer from inaccuracies due to surface roughnesses, which may be 10 % of the total layer thickness for hydrogen reduced tungsten films. For the step coverage experiments, rectangular trenches with a depth of 5-10 μm and widths ranging from 1 to 5 μm were etched into the silicon wafer surface. In these experiments, deposition took place on the 3 in. silicon wafer as well as on the 8 in. carrier wafer and the heated susceptor. The step coverage was determined by Scanning Electron Microscope observations with an accuracy of ± 5 %. More details about the experimental methods used can be found in the publications by Hasper, Kleijn and coworkers [Hasper et al. 1990, 1991;
6.6 RESULTS FOR THE HYDROGEN REDUCTION PROCESS

6.6.1 Examples of modeling results

In figure 6.4 some examples of modeling results for the hydrogen reduction process are shown. Figures 6.4a and 6.4b show calculated streamlines and isotherms for a total pressure of 133 Pa, a wafer temperature of 673 K and an inlet flow of 1000 sccm hydrogen, 100 sccm tungstenhexafluoride and 100 sccm argon. Expressed in the dimensionless numbers as discussed in chapter 4, these process conditions correspond to $Re = 1.9$, $Gr = 10$, $Ga = 0.8$ and $Pr = 0.21$. The growth rate is fully determined by surface reaction kinetics and is highly uniform, as is shown in figure 6.5. Due to the 460 Ång/min deposition on the 0.20 m diameter wafer, 3.6 sccm $WF_6$ and 10.8 sccm $H_2$ are consumed and 21.6 sccm HF is produced. In figures 6.4c and 6.4d the resulting hydrogenfluoride and tungstenhexafluoride mole fractions

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**figure 6.4:** Model predictions for 133 Pa total pressure, 673 K wafer temperature, 1000 sccm $H_2$ and 200 sccm $Ar + WF_6$.
(a–d = 100 sccm $WF_6$; e = 10 sccm $WF_6$, f = 1 sccm $WF_6$)
Figure 6.5: Predicted growth rates for 133 Pa total pressure, 673 K wafer temperature, 1000 sccm $H_2$, and 200 sccm $Ar + WF_6$.

in the reactor are shown. Although only 3.6% of the incoming $WF_6$ is consumed, the $WF_6$ concentration at the wafer surface is less than 50% of the inlet concentration. This is mainly due to the strong thermal diffusion effects, causing the heavy $WF_6$ molecules to move away from the hot susceptor. Furthermore, a concentration gradient between inlet and wafer surface is required in order to have diffusive transport of $WF_6$ to the wafer surface. In figure 6.4e the incoming $WF_6$ flow is reduced to 10 sccm, whereas the Ar flow is increased to 190 sccm, keeping all other parameters fixed as in figure 6.4a-d. In this case the growth rate is just beginning to be limited by $WF_6$ transport and has slightly decreased to 420 Ång/min (figure 6.5). Although the $WF_6$ consumption is only 33%, the $WF_6$ concentration at the wafer surface is less than 10% of the inlet concentration. In figure 6.4f the $WF_6$ inlet flow is further reduced to 1 sccm. Now, the growth rate is strongly limited by $WF_6$ transport and highly non-uniform (figure 6.5). The $WF_6$ concentration at the wafer surface is zero and the $WF_6$ consumption is 45%.

Figure 6.6 shows simulation results for (i) the deposition rate at $r = 0$, (ii) the ratio of the tungstenhexafluoride pressure at the wafer surface at $r = 0$ and the tungstenhexafluoride inlet pressure, and (iii) the amount of consumed (=deposited) tungstenhexafluoride as a fraction of the tungstenhexafluoride inflow, each as a function of the $WF_6$ inlet pressure,
Figure 6.6: Predicted growth rate and WF$_6$ surface partial pressure at r=0 and WF$_6$ consumption as a function of the WF$_6$ inlet pressure, for 133 Pa total pressure, 111 Pa hydrogen pressure, 673 K wafer temperature and 1.2 slm total flow.

For the above process conditions. For tungstenhexafluoride inlet pressures above a certain value $P_{\text{crit}}$, the growth rate is kinetically limited and independent of $P_{\text{in}}(\text{WF}_6)$, whereas for lower WF$_6$ inlet pressures the growth rate becomes transport limited and decreases linearly with decreasing $P_{\text{in}}(\text{WF}_6)$. The WF$_6$ consumption as a fraction of the WF$_6$ inlet flow is inversely proportional to $P_{\text{in}}(\text{WF}_6)$ for $P_{\text{in}}(\text{WF}_6) > P_{\text{crit}}$, whereas for lower $P_{\text{in}}(\text{WF}_6)$ the consumption reaches a maximum, which, for the present conditions, is 45% of the WF$_6$ inflow. The tungstenhexafluoride pressure at the wafer surface is substantially lower than the tungstenhexafluoride inlet pressure for all process condition studied, due to thermal diffusion effects and the ordinary diffusion concentration gradient. Note however that the WF$_6$ wafer pressure is of the same order of magnitude as the WF$_6$ inlet pressure for $P_{\text{in}}(\text{WF}_6) > P_{\text{crit}}$, whereas for $P_{\text{in}}(\text{WF}_6) < P_{\text{crit}}$ the WF$_6$ wafer concentration quickly drops to zero.

The above illustrates the influence of the WF$_6$ inlet pressure on the transition from kinetically limited to transport-limited growth, on the WF$_6$ consumption and on the growth rate and growth uniformity.
6.6.2 Comparison with experimental results

In this section the simulation results for the tungsten growth rate will be compared with experimental results obtained at Twente University by Hasper and Holleman. In figure 6.7 experimental results for the growth rate (averaged over the 3 in. wafer surface) as a function of the WF$_6$ inlet pressure are shown. In this series of experiments the wafer temperature was 673 K, the total pressure was 133 Pa, and the H$_2$ flow was 1000 sccm. The WF$_6$ flow was varied from 0.4 to 200 sccm, thus varying the WF$_6$ inlet pressure by almost three orders of magnitude from 0.044 to 22 Pa. Argon was used to keep the total flow fixed at 1200 sccm. Tungsten growth took place on the 0.076 m diameter wafer surface only. Also shown in figure 6.7 are results of model simulations for the same process parameters. The model fairly accurately predicts the WF$_6$ independent growth rate for large WF$_6$ inlet pressures, the linear dependence of the growth rate on the WF$_6$ inlet pressure for low inlet pressures and the transition point $P_{crit}$ between these two regions. It should be noted, that the model predictions in figure 6.7 were obtained without the introduction of any fitting parameter. It should also be noted, that the model assumes a heterogeneous reaction rate which is zero order in WF$_6$ for all WF$_6$ concentrations and that the decreasing growth rates for low

\[ \text{growth rate (Ång/min)} \]
\[ \begin{array}{c}
10^3 \\
10^2 \\
10^1 \\
10^{-2} \\
10^{-1} \\
10^0 \\
10^1 \\
10^2 \\
\end{array} \]
\[ \begin{array}{c}
\triangle \\
\triangle \\
\triangle \\
\triangle \\
\triangle \\
\triangle \\
\triangle \\
\end{array} \]

**Figure 6.7:** Model predictions and experimental data for the 3 in. wafer averaged growth rate wafer as a function of the WF$_6$ inlet pressure (133 Pa total pressure, 111 Pa Hydrogen inlet pressure, 673 K wafer temperature, 1200 sccm total flow)
WF₆ concentrations predicted by the model are caused by mass transfer limitations only. Because of the good agreement between model predictions and experimental observations, it is concluded that decreasing growth rates at low WF₆ inlet concentrations are caused by mass transfer limitations rather than a change in the reaction kinetics. More arguments supporting this conclusion will be discussed below.

When comparing model predictions and experimental results in detail, it can be seen that the model systematically overpredicts the growth rate in the region of low WF₆ concentrations. This may possibly be explained by relatively small errors in the transport properties, especially in the (thermal) diffusion coefficients, that were used in the model and that were obtained from theoretical predictions based on Chapman-Enskog kinetic theory and Lennard-Jones interaction potentials. When e.g. the binary ordinary diffusion coefficient for H₂ and WF₆ was reduced by 40% compared to the theoretical value, keeping all other parameters fixed, a very good match between model predictions and experimental results could be obtained for all process conditions studied. An error of 40% in the predicted diffusion coefficients for a gaspair like H₂ and WF₆ at high temperatures is not very unlikely, especially since the Lennard-Jones force parameters for WF₆ had to be estimated from critical parameters (Appendix C). Therefore, a corrected binary ordinary diffusion coefficient for hydrogen and tungstenhexafluoride of 0.6 times the theoretical value has been used in all further model simulations. Experimental determination of the binary diffusion coefficient for H₂-WF₆ is needed to further elucidate the above.

In figure 6.8, the experimental results from figure 6.7 are shown again, together with simulation results, using the corrected H₂-WF₆ diffusion coefficient. Also shown are comparisons between experimental and simulated growth rates for series of experiments at different wafer temperature and total pressure. With the corrected diffusion coefficient, the model accurately predicts the growth rate as a function of the tungstenhexafluoride inlet pressure for all cases considered. Both the experiments and the model simulations show, that the growth rate at low WF₆ concentrations is linearly proportional to the WF₆ inlet pressure, inversely proportional to the total pressure and independent of the wafer temperature (at fixed total flow and reactor geometry). This again is an indication for the fact, that decreasing growth rates at low WF₆ inlet concentrations are caused by mass transfer limitations rather than kinetical effects. Diffusion coefficients vary relatively little with temperature, causing the mass-
transfer-limited growth rate to be almost independent of temperature. On the other hand, diffusion coefficients are inversely proportional to the total pressure, causing the mentioned effect of total pressure on the transfer-limited growth rate at fixed WF₆ pressure.

When (at fixed wafer temperature, total pressure and inlet species partial pressures) the total flow is increased, the convective transport of WF₆ to the wafer surface is increased, so WF₆ will be less depleted and its concentration at the wafer surface will increase. Thus it is expected that the mass-transfer-limited growth rate increases with increasing total flow. This was confirmed by two experiments at an equal total pressure of 133 Pa, equal WF₆ and H₂ inlet partial pressures of 0.11 Pa and 111 Pa, and an equal wafer temperature of 673 K, but differing total flows of 1200 and 4800 sccm respectively. For these process conditions, eqs. 6.4 and 6.6 predict a surface kinetics determined growth rate of 460 Ång/min. The observed transport limited wafer averaged growth rates for these two experiments were 101 and 163 Ång/min respectively. In figure 6.9 these results are shown, together with model simulations for total flows between 300 and 9600 sccm. As expected, an increased total flow leads to an increased mass-transfer-limited growth rate. However, the effect of a large increase in total flow
Figure 6.9: Model predictions and experimental data for the 3 in. wafer averaged growth rate as a function of the total flow. The dashed curve shows the calculated WF$_6$ conversion. (0.11 Pa WF$_6$ and 111 Pa H$_2$ inlet pressure, 133 Pa total pressure, 673 K wafer temperature).

is relatively small, indicating that transport of WF$_6$ from reactor inlet to wafer surface is mainly due to diffusion rather than convection. Also note, that a low WF$_6$ consumption does not guarantee the exclusion of mass transfer limitations. Even at a total flow of 10 slm and a WF$_6$ conversion of only 3 % the growth rate is highly reduced by mass transfer limitations.

In figure 6.10 experimental and modeling results for the growth rate as a function of radius on a 3 in. wafer are shown for a total pressure of 133 Pa, a wafer temperature of 673 K, a hydrogen flow of 1000 sccm, a WF$_6$ flow of 1.3 sccm and an Ar flow of 198.7 sccm. The kinetically determined growth rate according to eqs. 6.4 + 6.6 is again 460 Ång/min. Both model predictions and experiments show a highly reduced, strongly non-uniform, mass-transfer-limited deposition. Large variations in experimental growth rates obtained at different locations at fixed radii were found, especially at the edge of the wafer, where the model predicts a strong variation of the growth rate with radius. These variations may possibly be ascribed to small asymmetries in the reactor configuration or the gas flow. Within this experimental error there is again a good agreement between model predictions and experimental results.

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6.6.3 A criterion for "gradientless" reactor operation

In the above it has been shown, that mass transfer and depletion phenomena may lead to strong concentration gradients in single-wafer LPCVD reactors, causing a large difference between the species inlet concentrations and the concentrations at the wafer surface. For fundamental CVD studies it is often desired to have precise knowledge of the species concentrations at the wafer surface. For this purpose, the concept of the "gradientless" CVD reactor, which is almost completely free of gradients in species concentrations, has been introduced [e.g. Raupp, 1988]. A gradientless CVD reactor is believed to be approximated under so called "differential" operating conditions, i.e. at a low (<10 %) reactant conversion. As was shown in this chapter, this is not a sufficient criterion: Even at very low reactant conversions, i.e. in the absence of supply limitations, concentration gradients may be significant due to transport limitations. In this section a criterion for the absence of transport limitations will be deduced.

In the previous sections it was shown that, for otherwise fixed process parameters, the growth rate is independent of the WF$_6$ inlet partial pressure above a certain value $P_{\text{crit}}$ and decreases linearly with decreasing WF$_6$ inlet pressure below $P_{\text{crit}}$. For WF$_6$ inlet pressures $\gg P_{\text{crit}}$ the WF$_6$ concentration
at the wafer surface is close to the WF$_6$ inlet concentration, as can be seen in figure 6.6, and we can speak of a "gradientless" reactor. However, even under these conditions, the WF$_6$ concentration at the wafer surface can be 25-60 % lower than the inlet concentration in coldwall reactors, due to thermal diffusion phenomena.

Now, for the determination of "gradientless" operation conditions, we have to determine $P_{\text{crit}}$. Of course, $P_{\text{crit}}$ can be determined accurately from detailed model simulations, as presented in this chapter, or from series of growth experiments as described in section 6.6.2. However, a first estimate of $P_{\text{crit}}$ may readily be obtained from global criteria for the absence of (i) transport limitations and (ii) supply limitations:

ad (i): Mass transport limitations are negligible when the surface reaction Damköhler number $Da^S$, which is the ratio of the chemical reaction rate at the surface and the diffusive species transport, is small ($Da^S \ll 1$) [Carberry, 1976]. Transition to mass transfer limited growth takes place for

$$Da^S = \frac{R_{k in}^S \mathcal{L}}{D_{WF_6} c_{WF_6, in}} \approx 1 \quad (6.12)$$

with $R_{k in}^S$ the kinetically determined deposition rate, $\mathcal{L}$ a characteristic length for diffusion, $D$ the effective diffusion coefficient and $c_{WF_6, in}$ the molar concentration of WF$_6$ in the reactor inlet. We thus find for the critical WF$_6$ inlet pressure $P_{\text{crit,transp}}$ at which the transition from kinetically to transport limited growth takes place

$$P_{\text{crit,transp}} = \frac{R_{k in}^S \mathcal{L}}{RT_{\text{ref}} D_{WF_6}} \quad (6.13)$$

or for the critical mole fraction $f_{\text{crit,transp}}$ of WF$_6$ in the reactor inlet

$$f_{\text{crit,transp}} = \frac{R_{k in}^S \mathcal{L} RT_{\text{ref}}}{D_{WF_6} P_{\text{tot}}} \quad (6.14)$$

with $T_{\text{ref}}$ the average gas temperature and $P_{\text{tot}}$ the total operating pressure.

In order to determine $P_{\text{crit,transp}}$ from eq. 6.13, an expression must be found for the diffusion length $\mathcal{L}$. For this purpose it should be realized, that diffusion of WF$_6$ to the wafer can occur in two directions: (a) In radial direction from the region above the non-reacting susceptor surface to
the region above the reacting wafer surface. A characteristic diffusion length in this direction is the wafer radius $R_W$. (b) In a direction perpendicular to the wafer surface, through a concentration boundary layer with thickness $L_B$. The concentration boundary layer thickness is a function of the total flowrate, or, when expressed in dimensionless form, $L_B/Z_{tot}$ is a function of the Peclet number $Pe = V \cdot Z_{tot} / D_{WF_6}$, where $V$ is the average gas velocity in the inflow pipe of the reactor and $Z_{tot}$ is the vertical distance from the susceptor surface to the upper reactor wall (figure 4.1). For high $Pe$, species transport is dominated by convection and there is a thin concentration boundary layer above the wafer, whereas for low $Pe$ species transport is dominated by diffusion and $L_B$ is approximately equal to $Z_{tot}$.

Figure 6.11 shows $WF_6$ concentration profiles as a function of height above the wafer surface on the axis of the reactor, for different total flowrates (Peclet numbers). The concentration boundary layer thickness may be defined as the thickness of the layer, where the $WF_6$ concentration is less than 95% of the maximum $WF_6$ concentration. It can be seen, that $L_B$ decreases with increasing $Pe$. From extensive series of simulations, the following approximate expression for $L_B$ in the present reactor configuration was obtained:
\[
\mathcal{L}_B/Z_{\text{tot}} = 1/(1 + 0.23 \cdot \text{Pe})
\]  \hspace{1cm} (6.15)

which was found to be accurate within 20% for \(1 \leq \text{Pe} \leq 60\). Now, the diffusion length \(\mathcal{L}\) in eqs. 6.13-6.14 may be estimated from \(\mathcal{L}_B\) and \(R_W\) as

\[
\mathcal{L} = \frac{1}{1/\mathcal{L}_B + 1/R_W}
\]  \hspace{1cm} (6.16)

and the critical WF₆ inlet concentration for the transition from kinetically limited to transport limited growth may be estimated from eqs. 6.4, 6.6, 6.13-6.16.

ad (ii): Supply limitations are negligible when the rate of supply of WF₆ gas is much larger than its rate of consumption. Transition from kinetically limited to supply limited growth occurs when these two are equal. We now find for the critical WF₆ inlet mole fraction

\[
f_{\text{crit, supply}} = \frac{A \cdot \mathcal{R}^S_{\text{kin}}}{Q_{\text{tot}}}
\]  \hspace{1cm} (6.17)

where \(Q_{\text{tot}}\) is the total gas supply (in mole·sec⁻¹) and \(A\) the deposition area.

Now, since the transport limitations and the supply limitations may be considered as resistances in series, we may combine eqs. 6.14 and 6.17 from (i) and (ii) to find the minimum WF₆ inlet mole fraction needed to exclude both transport limitations and supply limitations:

\[
f_{\text{crit}} = \frac{Q_{\text{crit,WF₆}}}{Q_{\text{tot}}} \approx \left(\frac{\mathcal{L}}{D_{\text{WF₆}}} \frac{RT_{\text{ref}}}{P_{\text{tot}}} + \frac{A}{Q_{\text{tot}}}\right) \mathcal{R}^S_{\text{kin}}
\]  \hspace{1cm} (6.18)

or

\[
P_{\text{crit}} = \left(\frac{\mathcal{L}}{D_{\text{WF₆}}} \frac{RT_{\text{ref}}}{P_{\text{tot}}} + \frac{A}{Q_{\text{tot}}}\right) \mathcal{R}^S_{\text{kin}}
\]  \hspace{1cm} (6.19)

A large number of model simulations, varying the flowrate \(Q\) (0.1-20 slm), the total pressure (13.3-1330 Pa), the deposition area (0.01-0.12 m diameter wafers), the wafer temperature (523-798 K), and the carrier gas (\(\text{H}_2, \text{N}_2\) and \(\text{Ar}\)), were performed to evaluate the accuracy the above equations. It was found, that \(P_{\text{crit}}\) was predicted within 30% for all simulated situations.

We have now found a general expression for the estimation of \(P_{\text{crit}}\) in
the present reactor configuration. As stated before, "gradientless" operation occurs for \( P_{\text{in}} (WF_6) > P_{\text{crit}} \). Note that, for most common single wafer LPCVD conditions, the first term in brackets in eqs. 6.18 and 6.19 is large compared to the second term. Also, for common flowrates, the dependence of \( \mathcal{L} \) on the flowrate (eq. 6.15, 6.16) is small. Therefore, an increase in the total flow at fixed WF\(_6\) inlet partial pressure is usually an ineffective way to obtain "gradientless" process conditions.

The above discussion, which was held for tungsten LPCVD from hydrogen and tungstenhexafluoride, can more generally be applied to heterogeneous CVD processes which are zero order in the reactant concentration.

6.6.4 Prediction of step coverage

When filling high aspect ratio contact holes using blanket tungsten deposition it is important that the step coverage is high and uniform over the entire wafer surface. In figure 6.12 a pore with initial diameter \( W_0 \) and depth \( L_0 \) is illustrated. The step coverage is defined as the ratio \( d_{1/2}/(1/2 W_0) \) in percent of the layer thickness \( d_{1/2} \) halfway the pore depth at the moment of pore closure, and the (initial) pore radius \( 1/2 W_0 \). A low step coverage will lead to undesirable void formation when filling contact holes. In this section the use of a reactor scale model as an aid in the prediction of step coverages will be discussed.

Since the dimensions of vias and contact holes in IC's are small compared to the mean free path length of the molecules at typical LPCVD conditions, transport of reactants in the pore is due to Knudsen diffusion.

![Figure 6.12: A high aspect ratio pore with deposited tungsten.](image-url)
The Knudsen diffusion coefficient for a species \( i \) in a high (depth-to-width) aspect ratio cylindrical pore or rectangular trench is given by

\[
D_i^K(W) = \frac{2W}{3} \left( \frac{8RT}{\pi \eta \mu_i} \right)^{1/2}
\]  

(6.20)

where \( W \) is the radius \( \frac{1}{2}w \) of the pore or the width \( w \) of the trench. We can now find an expression for the step coverage as a function of the pore or trench dimensions, the deposition rate, the \( \text{WF}_6 \) concentration at the pore mouth and its Knudsen diffusion coefficient. Such an analysis was first presented by McConica and Churchill [1988]. Consider a high (depth-to-width) aspect ratio pore (trench) as in figure 6.12. From an overall mass balance, equating the diffusive transport of \( \text{WF}_6 \) through the pore (trench) mouth to the amount of \( \text{WF}_6 \) deposited on its walls, we find that tungsten growth at a certain depth \( z = z_c \) will stop when the pore radius (trench width) \( W \) has diminished to a certain value \( W_{c'} \) with

\[
\frac{\pi W^2 \cdot D_i^K(W) \cdot c^0_{\text{WF}_6}}{z_c} = 2\pi W \cdot z_c \cdot \frac{R_S}{k_{\text{in}}}
\]

(6.21a)

for a pore, and

\[
\frac{W \cdot D_i^K(W) \cdot c^0_{\text{WF}_6}}{z_c} = 2z \cdot \frac{R_S}{k_{\text{in}}}
\]

(6.21b)

for a trench, with \( W_c \) the critical pore radius (trench width) and \( c^0_{\text{WF}_6} \) the \( \text{WF}_6 \) concentration at the pore mouth. So, for trenches and pores, we have

\[
W_c = \frac{2z \cdot \frac{R_S}{k_{\text{in}}}}{D_i^K(W) \cdot c^0_{\text{WF}_6}}
\]

(6.22)

Since \( D_i^K(W) = (W/W_0) \cdot D_i^K(W_0) \), we find that tungsten growth at \( z_c = \frac{1}{2}L_0 \) will stop when

\[
W_c^2 = \frac{L_0^2 \cdot \frac{R_S}{k_{\text{in}}}}{2 \cdot D_i^K(W_0) \cdot c^0_{\text{WF}_6}}
\]

(6.23)

We now introduce the dimensionless number \( \Phi \), which is often referred to as
the step coverage modulus,

$$\phi = \frac{L_0^2 R^S_{kin}}{W_0 \cdot D^K_{WF} (W_0) \cdot c^0_{WF}}$$  \hspace{1cm} (6.24)

which is closely related to the Thiele modulus $h_T$ for a zero order reaction [Hill, 1977], according to $\phi = \frac{1}{2} (h_T)^2$. This leads to the following expression for the step coverage in a cylindrical hole or rectangular trench

$$\text{step coverage} = \left(1 - \frac{W}{W_0}\right) \cdot 100\% = \left(1 - \sqrt[2]{\phi}\right) \cdot 100\%$$  \hspace{1cm} (6.25)

From eqs. 6.20, 6.24 and 6.25 it can be seen, that the step coverage modulus $\phi$ and the step coverage do not depend on the pore or trench dimensions, but on the (initial) aspect ratio $L_0/W_0$ only. For a trench, $\phi$ is four times smaller as for a cylindrical pore of equal initial depth and width. Figure 6.13 shows the step coverage in trenches and contact holes as a function of the step coverage modulus $\phi$ according to eq. 6.25. A high step coverage is obtained when $\phi$ is low. A 100% step coverage can never be obtained.

It is now clear that the step coverage in the kinetically limited growth regime is a function of the WF$_6$ concentration at the wafer surface. At fixed aspect ratio, wafer temperature and deposition rate, $\phi$ is inversely

![Figure 6.13: Theoretical and experimental step coverage as a function of the step coverage modulus.](image-url)

- 150 -
proportional to the WF$_6$ concentration at the pore mouth and a high step coverage is obtained for high WF$_6$ concentrations. Thus, in order to predict the step coverage, the WF$_6$ surface concentration must be known. The combination of macroscopic (reactor scale) hydrodynamic models, predicting the species concentration distributions in the reactor, and microscopic (feature scale) step coverage models has been found very useful in predicting step coverages (McInerney [1990], Hasper, Kleijn et al. [1990, 1991]). Conversely, the step coverage may also be used as a measure for the WF$_6$ surface concentration, thus offering an indirect way for the validation of the hydrodynamic reactor model.

We have used the present reactor model to calculate the WF$_6$ surface concentration for a series of experiments at varying process conditions (133-1064 Pa total pressure, 0.24-180 Pa tungstenhexafluoride inlet pressure, 648-713 K wafer temperature, 0.3-5 slm total flowrate), performed at the Faculty of Electrical Engineering of the University of Twente by Hasper and Holleman. The calculated WF$_6$ surface concentrations were used to calculate the step coverage modulus from eq. 6.24 and the theoretical step coverage from eq. 6.25 for trenches of varying dimensions (5-10 μm depth, 1-5 μm width, aspect-ratio 2-7), located on different locations of the wafer surface. For this range of process conditions and trench dimensions, $\Phi$ varied from 0.008 to 0.14 and the experimental step coverage varied from 95 % to 70 %. A good agreement was found between theoretical step coverages predicted from eqs. 6.24-6.25 and experimental values obtained from SEM cross sections, see figure 6.13. This may serve as a confirmation of the accuracy of the WF$_6$ surface concentrations predicted by our hydrodynamic LPCVD reactor model.

The above discussion neglects tungsten growth on the bottom of the pore, the influence of the finite pore length on the Knudsen diffusion coefficient and the fact that width of the pore will become a function of depth during deposition. Also note that the above discussion is not valid in the transport limited growth regime, where the deposition rate is no longer zero order in WF$_6$. These effects can be included in numerical step coverage models [Hasper et al., 1990, 1991; Schmitz et al., 1990]. For large aspect ratio pores and kinetically limited growth the results of such numerical models are very similar to those obtained with the above simplified analysis. A detailed discussion of the combined use of a numerical reactor model and a numerical step coverage model in the prediction of tungsten LPCVD step coverages may be found in the publications by Hasper, Kleijn and
coworkers [1990, 1991].

6.6.5 Process and reactor optimization for blanket contact fill

We may now use the LPCVD reactor model to optimize a blanket contact fill tungsten LPCVD process from $\text{H}_2-\text{WF}_6$. Such a process should have (i) a high and uniform growth rate, (ii) a high and uniform step coverage, and (iii) a low use of (expensive) $\text{WF}_6$ gas.

ad (i): The growth rate may be increased by increasing the hydrogen pressure or the temperature. With regard to multilevel metallization the maximum process temperature is limited to circa 700 K. In the present reactor, the maximum total pressure is limited to 1330 Pa. Within these constraints, the wafer temperature was set to 693 K, and the total pressure to 1064 Pa, leading to a growth rate of circa 1500 Ång/min. At this growth rate it will take $3^{2\over 3}$ min to fill a 1 μm diameter contact hole, allowing a throughput of circa 10 wafers/hour. This seems to be acceptable from an economic point of view.

ad (ii): With respect to the step coverage we demand that a 5:1 aspect ratio trench is filled with $\geq 95\%$ step coverage, requiring a step coverage modulus $\Phi \leq 0.005$. At the above process conditions, $\Phi = 0.005$ corresponds to a $\text{WF}_6$ partial pressure at the wafer surface of approximately 50 Pa.

ad (iii): In order to obtain a high tungstenhexafluoride partial pressure at low $\text{WF}_6$ flow and fixed total pressure, the total flow should be low. As a practical minimum we chose a total flowrate of 300 sccm, consisting of 200 sccm hydrogen, 0-100 sccm tungstenhexafluoride and 100-0 sccm argon.

The reactor simulation model may now be used in order to find the minimum $\text{WF}_6$ flowrate leading to a tungstenhexafluoride surface pressure $\approx 50$ Pa. Figure 6.14 shows the calculated $\text{WF}_6$ surface pressure at $r = 0$ as a function of the $\text{WF}_6$ flow, for two different length of the inflow pipe, corresponding to $Z_1 = 0.025$ and 0.100 m. For the standard configuration, with $Z_1 = 0.100$ m, a flow of 50 sccm (i.e. a $\text{WF}_6$ inlet pressure of 177 Pa) leads to the required $\text{WF}_6$ surface pressure of circa 50 Pa..

The optimized process conditions deduced above (i.e. 1064 Pa total pressure, 693 K wafer temperature, 200 sccm hydrogen, 50 sccm tungstenhexafluoride and 50 sccm argon) were evaluated experimentally at the University of Twente by Hasper and Holleman [Hasper et al., 1991]. In the experiments, a 6 in. (0.15 m diameter) wafer was placed on a 8 in. (0.20 m
Figure 6.14: \( WF_6 \) surface partial pressure at \( r=0 \) as a function of the \( WF_6 \) flow (1064 Pa total pressure, 693 K wafer temperature, 200 sccm \( H_2 \), 100 sccm \( WF_6 + Ar \))

diameter) carrier wafer. Deposition took place on the entire (0.24 m diameter) susceptor surface. Trenches of 10×2 μm were used to evaluate the step coverage. Since the step coverage is a function of the feature aspect ratio only, the observed step coverage is expected to be obtained in submicron trenches with a 5:1 aspect ratio (and in submicron holes with a 2.5:1 aspect ratio) also. In Table 6.1 the predicted and experimentally observed process characteristics have been compared.

<table>
<thead>
<tr>
<th>predicted</th>
<th>experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>growth rate: 1450 Ång/min (±12 Ång/min over 8 in. wafer)</td>
<td>1430 Ång/min (uniform within exp. error over 6 in. wafer)</td>
</tr>
<tr>
<td>step coverage in 5:1 trench: 95.6% (±0.3% over 8 in. wafer)</td>
<td>&gt;93 % (uniform within exp. error over 6 in. wafer)</td>
</tr>
</tbody>
</table>
It can be seen that our optimization study by means of a reactor scale hydrodynamic model and a feature scale step coverage model has led to the desired process characteristics, i.e. a high and uniform growth rate and step coverage on a large wafer at a low use of tungstenhexafluoride. Figure 6.15 shows a SEM cross section of a $10 \times 2$ $\mu$m trench, filled with tungsten by means of the above process, again indicating the extraordinary good step coverage obtained with this process.

As shown in figure 6.14, the WF$_6$ wafer surface pressure increases when the length of the reactor inflow pipe is increased and the distance $Z_t$ from the wafer surface to the end of this pipe is decreased. This offers a possibility for a further optimization of the process. Figure 6.16 shows the predicted step coverage as a function of radius for a WF$_6$ flow of 25 sccm at different values of $Z_t$. For $Z_t = 0.025$ m a step coverage of circa 92 %, uniform over the entire 0.24 m diameter deposition area, is obtained. For $Z_t = 0.100$ m the same process conditions lead to a highly non-uniform step coverage, varying from 82 % in the middle to 92 % at the edge of the wafer. So, besides from optimization of the process conditions, small modifications in the reactor geometry may also highly improve the blanket tungsten contact fill process characteristics.
Figure 6.16: Step coverage as a function of radius for three different inflow tube lengths (1064 Pa total pressure, 693 K wafer temperature, 200 sccm H₂, 75 sccm Ar, 25 sccm WF₆).

6.7 PRELIMINARY RESULTS FOR THE SILANE REDUCTION PROCESS

As has been discussed in section 6.3.2, there is little consensus on the tungsten deposition kinetics, using the silane reduction process. In this section we will illustrate, that at least part of the confusion in literature may be due to the neglect of the influence of transport phenomena in the kinetic experiments that have been performed by various authors.

In figure 6.17 the calculated WF₆, SiH₄ and SiF₄ mole fractions are shown for a process with the following process conditions: 133 Pa total pressure, 623 K wafer temperature, 1250 sccm total flow (150 sccm WF₆, 100 sccm SiH₄ and 1000 sccm Ar) and a 0.20 m diameter deposition surface, assuming the overall reaction eq. 6.2a and the rate expressions eqs. 6.10 and 6.11. The growth rate is circa 2500 Ång/min. As a result, 13% of the incoming tungstenhexafluoride and 30% of the incoming silane are consumed. The silane and tungstenhexafluoride concentrations at the wafer surface are only 40% and 50% of their inflow values, respectively. Also, at the wafer surface the SiH₄ : WF₆ ratio differs significantly from the inlet value (1 : 2 at the wafer vs 1 : 1.5 in the inlet). Thus, when determining the growth rate as a function of the (ratio of the) species partial pressures, a large error can be made when species inlet pressures are used instead of their actual values at the wafer surface. This may lead to errors in the
observed rate order for the different reactants and in the observed activation energy. This is further illustrated in three series of simulations:

(i) First, the tungsten growth rate as a function of the wafer temperature is calculated for 133 Pa total pressure, and 100 sccm SiH₄, 150 sccm WF₆ and 1000 sccm Ar flows. To assure a low conversion of reactants, we let deposition take place selectively on a 0.076 m diameter wafer surface only. Thus, the silane conversion is less than 8% and the WF₆ conversion is less than 4% for all temperatures considered. The wafer averaged growth rate as a
function of temperature is shown in figure 6.18. Due to transport phenomena effects, the silane wafer concentration is less than its inlet concentration, and this effect becomes more pronounced at increased wafer temperatures. This causes a deviation in the observed activation energy from its actual value. Thus, an apparent activation energy of 18 kJ/mole (continuous line) is found instead of the actual value of 25 kJ/mole (dashed line).

(ii) Secondly, the growth rate on a 0.076 m diameter wafer has been simulated as a function of the silane inlet pressure, at 623 K wafer temperature. For all cases, the silane and tungstenhexafluoride consumption are less than 11% and 5%. In a first series, the total pressure is fixed at 133 Pa and the silane partial pressure is varied from 3.2 to 32 Pa, at a fixed SiH₄ : WF₆ = 1.5 : 1 inlet ratio and a fixed total flow of 1250 sccm. The simulated growth rate as a function of the silane inlet pressure is shown in figure 6.19 (circles). A first order rate dependence in silane is observed, in accordance with the rate equation 6.10, but the apparent value of cₛ is 40% lower than the actual value. In a second series, the total pressure is varied from 40 Pa to 400 Pa, at fixed 1250 sccm total flow, 100 sccm silane flow, and 150 sccm WF₆ flow, thus again varying the silane inlet pressure from 3.2 to 32 Pa. The resulting growth rates as a function
of the silane inlet pressure are shown in figure 6.19 (triangles). In this case, the apparent rate order in silane is 0.65, instead of the actual value of 1.

(iii) Finally, the influence of the deposition area on the simulated growth rate has been studied. At 623 K wafer temperature, 133 Pa total pressure, 100 sccm SiH₄, 150 sccm WF₆ and 1000 sccm Ar we have simulated tungsten growth on (a) a 0.20 m diameter wafer, (b) a 0.076 m diameter wafer, and (c) a (microscopically) patterned 0.076 m diameter, with 90% of the surface covered by silicon-oxide, were no deposition takes place, and 10% of the surface covered by silicon, were deposition takes place. The silane consumption rates are 30%, 6% and 1% respectively. The resulting growth rates as a function of radius are shown in figure 6.20. Also shown is the theoretical maximum growth rate, based on the rate expression 6.10 and the silane inlet pressure. Depending on the surface area on which deposition takes place, the observed growth rate may vary by as much as a factor 3, at fixed process conditions. It is also interesting to see, that in the case of a 0.076 m diameter wafer the uniformity is worse than in the case of a 0.20 m diameter wafer. In the case of a patterned wafer, the difference between the observed growth rate and the theoretical maximum value is very small.
Figure 6.20: Dependence of the growth rate on the deposition area. The dashed line shows the growth rate based on inlet concentrations. (623 K wafer temperature, 133 Pa total pressure, 1000 sccm Ar, 150 sccm WF₆, 100 sccm SiH₄).

These simulations, using an assumed but not unrealistic reaction mechanism and rate expression, illustrate that the apparent deposition kinetics observed in experiments may be seriously biased by transport phenomena in various ways. This may lead to large errors in the observed activation energy, reaction rate orders and proportionality constants. Therefore, it is very likely that the neglect of the influence of transport phenomena may be the cause of at least part of the apparent contradictions in the reported deposition kinetics for this process. This strongly suggests that kinetic experiments for the silane reduction process should always take into account the difference due to transport phenomena between species inlet concentrations and wafer concentrations. The most accurate way to perform these experiments is clearly to deposit tungsten selectively on a very small deposition area. The use of argon as a carrier gas will reduce concentration gradients due to thermal diffusion. The use of mathematical models for the transport phenomena in the reactor may contribute to more an accurate determination of the deposition kinetics.
6.8 APPROXIMATE APPROACHES FOR MULTICOMPONENT DIFFUSION

In the previous sections, the rigorous treatment of multicomponent ordinary diffusion (eqs. 2.12-2.17) and the exact formulation for multicomponent thermal diffusion (eqs. 2.20 and F.1-F.8) have been used. In section 5.10 the accuracy of approximate approaches for modeling multicomponent (thermal) diffusion in silicon LPCVD from silane has been evaluated. It was concluded, that these approaches may lead to very accurate results at highly reduced computational effort. Here the accuracy of these approximate methods in the modeling of tungsten LPCVD from hydrogen and tungstenhexafluoride will be studied. The gas mixture in the reactor consists of WF₆, H₂, Ar and HF. We use the six modeling approaches listed in table 5.5. The savings in cpu time per iteration are similar to those found in section 5.10, and the total number of iterations needed to reach a converged solution is again very similar for all six approaches. We now compare the accuracy of these six approaches for two different process conditions: (i) A process in the kinetically-limited growth regime, with 133 Pa total pressure, 673 K wafer temperature, 1000 sccm hydrogen, 100 sccm argon and 100 sccm tungstenhexafluoride and deposition on an 0.20 m diameter wafer. In this case, the growth rate is almost unaffected by transport phenomena in the gas mixture, but the species concentrations at the wafer surface are determined by convection and (thermal) diffusion phenomena. (ii) A process in the diffusion-limited growth regime, with 133 Pa total pressure, 673 K wafer temperature, 1000 sccm hydrogen, 199 sccm argon and 1 sccm tungstenhexafluoride and deposition on a 0.20 m diameter wafer. In this case, the growth rate is determined by the transport phenomena in the reactor. The accuracy of the approximate approaches is evaluated through their influence on the predicted WF₆ partial pressure at the wafer surface and on the growth rate at r = 0, for process (i) and (ii) respectively.

The results of these comparisons are presented in table 6.2. As was concluded for silicon deposition from silane in section 5.10, the influence of the Dufour effect is again negligible (compare I vs II) and the effect of thermal diffusion is very important (compare I vs IV). However, in contrast to what was found in section 5.10, the approximate approach to multicomponent thermal diffusion is not very accurate (compare I vs III). Also, the use of the approximate approach to multicomponent ordinary diffusion instead of the full Stefan-Maxwell equations leads to rather large errors (compare I vs V). Thus, for the accurate modeling of tungsten LPCVD from WF₆ and H₂, the exact formulations for multicomponent ordinary and thermal
### Table 6.2: Influence of approximate approaches for multi-component (thermal) diffusion

<table>
<thead>
<tr>
<th></th>
<th>(i) kinetically limited</th>
<th>(ii) transport limited</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>WF$_6$ partial pressure at wafer surface at r=0 (Pa)</td>
<td>Growth rate at r=0 (Ång/min)</td>
</tr>
<tr>
<td>I exact</td>
<td>5.26</td>
<td>47.8</td>
</tr>
<tr>
<td>II no Dufour effect</td>
<td>5.27 (+0%)</td>
<td>47.8 (+0%)</td>
</tr>
<tr>
<td>III approximate thermal diffusion</td>
<td>6.81 (+29%)</td>
<td>49.7 (+4%)</td>
</tr>
<tr>
<td>IV no thermal diffusion</td>
<td>10.11 (+92%)</td>
<td>60.9 (+27%)</td>
</tr>
<tr>
<td>V approximate ordinary diffusion</td>
<td>6.69 (+27%)</td>
<td>52.6 (+10%)</td>
</tr>
<tr>
<td>VI approximate thermal + ordinary diffusion</td>
<td>7.95 (+51%)</td>
<td>54.3 (+14%)</td>
</tr>
</tbody>
</table>

diffusion, which increase the total cpu time needed, should be used.

### 6.9 Influence of the Modeled Reactor Inlet

In chapters 4, 5 and 6 a simplified representation of the reactor inlet configuration has been used in the model simulations. In the actual reactor, the gases are led into a ring, which is put around the cylindrical inflow tube. In this way, the gases are distributed equally around the reactor. The inside of the ring consists of a fine-meshed wire gauze, allowing the gases to flow symmetrically from the ring into the large inflow tube (see upper part of figure 6.21). In the simulation model this inflow configuration was simplified to the geometry illustrated in the lower part of figure 6.21, where the gases flow radially inward between to circular plates at a distance $\Delta_P = 0.0025$ m. The plates have an outer radius $r_p = 0.20$ m and an inner radius $r_i = 0.10$ m, which is equal to the radius of the inflow tube. The boundary conditions (eqs. 2.50-2.57) are imposed at $r = r_p$.

To study the sensitivity of the model predictions to the precise form of the reactor inlet, various tungsten deposition processes from WF$_6$-H$_2$ in the transport limited and kinetically limited regime have been simulated for different inlet configurations, varying $\Delta_P$ from 0.0025 to 0.01 m and ($r_p$-$r_i$) from 0.025 to 0.10 m. The WF$_6$ surface pressure in the kinetically limited
regime and the growth rate in the transport limited regime were found to be virtually independent (within 2%) of the geometry of the inflow configuration, for all studied combinations of $\Delta p$ and $(r_p - r_t)$, both for very low and very high total flowrates. Thus it may be concluded, that the model predictions are insensitive to the way in which the reactor inlet is modeled and that the simplifications made in modeling the reactor inlet do not influence the accuracy of the model predictions significantly.
7.1. INTRODUCTION

In the study of the basic fundamentals of Chemical Vapor Deposition techniques, horizontal cold wall CVD reactors operating at (near) atmospheric pressures have always been in the center of interest. Although a classical configuration which is now only used in research and in compound semiconductor epitaxial growth, this type of reactor still provides a fruitful basis for the study of the underlying physicochemical processes in CVD. The appearance of multiple reaction gas phase and surface chemistry and the large influence of transport phenomena on the deposition process, in combination with a relatively simple reactor geometry, seem to make this type of CVD reactor very suitable for fundamental CVD studies. However, in view of the need for further process analysis it is crucial that one should be able to distinguish between chemical kinetics and transport phenomena effects.

Besides from experimental studies on gas flow patterns, temperature distributions, reactant diffusion and growth rates in horizontal CVD reactors [e.g. Eversteijn et al., 1970; Takahashi et al., 1972; Ban, 1978; Gilling, 1982ab; Van de Ven et al., 1986; Stock and Richter, 1986; Sato and Suzuki, 1987a, Fotiadis et al., 1990b, Fotiadis and Jensen, 1990c] there have been great efforts in the development of mathematical models, giving a more or less complete description of the relevant processes [e.g. Eversteijn et al., 1970; Takahashi et al., 1972; Coltrin et al., 1984, 1986; Van de Ven et al., 1986; Moffat and Jensen, 1986, 1988; Rhee et al., 1987; Sato and Suzuki, 1987b; Ouazzani et al., 1988; Field, 1989; Evans and Greif, 1989, 1991; Ouazzani and Rosenberger, 1990; van Sark et al., 1990abc; Chinoy et al., 1991]. Both from experimental and modeling studies it has been found, that fluid flow and transport phenomena strongly influence the performance of epitaxial processes in horizontal CVD reactors. In fact it has been found that, although complex multiple reaction chemistry plays an important role in epitaxial CVD, growth rates and uniformities can be predicted accurately by models based on the transport of the main reactive species only [Coltrin et al., 1984; Van de Ven et al., 1986; Moffat and Jensen, 1986; Ouazzani et al., 1988; Ouazzani and Rosenberger, 1990; van Sark et al., 1990c]. Thus, parallel to the important work done on unraveling the chemical reaction mechanisms and kinetics in CVD processes, considerable progress has been
made in the development of mathematical models of increasing complexity, describing the fluid flow and transport phenomena in epitaxial CVD.

Based on flow visualization experiments revealing the existence of longitudinal rolls and an apparent stagnant layer above the susceptor, Eversteijn et al. [1970] developed the so called stagnant layer model, which represents one of the very first attempts to describe the growth process in epitaxial CVD through an analytical mathematical model. However, this model was found to give some incorrect predictions and, moreover, it was found that the stagnant layer concept was physically unrealistic [Giling, 1982ab]. Van de Ven et al. [1986] developed an analytical similarity solution model for epitaxial growth in horizontal CVD reactors, based on boundary layer theory. This model, which is essentially 2-D and neglects the effects of thermal diffusion, axial diffusion and varying fluid properties on the transport of growth species, was found to give reasonable predictions of experimentally observed growth rates under low Rayleigh number conditions. By solving the 2-D transport equations numerically, Ouazzani et al. [1988] were able to include thermal diffusion, axial diffusion and variable fluid property effects into a mathematical model. It was concluded, that 2-D models can produce realistic predictions of growth rates in horizontal reactors with large width-to-height aspect ratios, operated under subcritical Rayleigh number conditions (Ra < 2·10³).

In small aspect ratio reactors and under supercritical Rayleigh number conditions however, three-dimensional flow effects become dominant. Therefore, Moffat and Jensen [1986, 1988] and Ouazzani and Rosenberger [1990] developed 3-D numerical models for CVD in horizontal epitaxial reactors. It was found that spiral rolls may develop with axes in the main flow direction, as was also observed in flow visualization experiments. These rolls have a large influence on both the axial and lateral growth rate distributions. The onset, magnitude and rotational direction of these rolls were found to be very sensitive to the inlet flow structure and to the thermal boundary conditions on the side walls. Therefore, a quantitative agreement between predicted and measured growth rates could not be obtained for supercritical Rayleigh number conditions. However, a good qualitative agreement was found. The 3-D models developed by Moffat and Jensen were based on the parabolised approximation of the transport equations, which is valid for high Reynolds (Peclet) number conditions (Re, Pe > 10) only and is unable to deal with reverse flows, caused by flow obstructions or thermal expansion effects at the leading edge of the heated susceptor or with large
slope tapered reactors. Ouazzani and Rosenberger used a fully elliptic
description of the problem.

In this chapter, we will use two and three-dimensional elliptic
numerical models to study the steady-state and transient transport phenomena
in horizontal epitaxial CVD reactors. Special attention will be given to the
accurate modeling of the side wall temperatures and to occurrence of
buoyancy driven mixed convection flow phenomena and their influence on
memory effects and growth uniformity. The simulations will be compared to
results from well-characterized Metal Organic CVD (MOCVD) growth experiments
by Van de Ven et al. [1986] and to results from flow visualization
experiments by Visser et al. [1989], performed parallel to the research
described in this chapter at the Catholic University of Nijmegen.

7.2 PROBLEM DESCRIPTION

The reactor geometry studied in this chapter is illustrated in figure 7.1.
It consists of a horizontal silica reactor tube with rectangular cross
section. The width of the reactor is 0.05 m, the length is 0.40 m, the
height varies from 0.008 to 0.05 m. The gas mixture flows in on one side of
the reactor tube, into a 0.15 m long isothermal entrance region. Usually,
the reactants are highly diluted (mole fractions < 10^{-3}) in a carrier gas
(e.g. hydrogen or nitrogen). In the deposition zone the reactor is heated
from below and water cooled on top across its full width. The reactants

![Figure 7.1: Schematic representation of the reactor configuration.](image)
deposit on the heated susceptor at the bottom of the reactor. The side walls of the reactor, as well as the upper and lower wall in the isothermal entrance region, are in free contact with the surrounding air.

The gas flow, heat transfer and chemical species transport in this reactor configuration are studied through the numerical solution of the transport equations described in chapter 2. The Navier-Stokes, continuity, species concentration and energy equations are solved in steady-state and transient, 2-D and 3-D cartesian form, for widely varying process conditions. In the 2-D formulation only the reactor mid plane is modeled.

The model simulations will focus on two aspects of the transport phenomena in horizontal CVD reactors:

(i) In sections 7.3–7.5 axial and lateral steady-state growth rate distributions in horizontal CVD reactors are studied by solving the 2-D and 3-D stationary transport equations. In the 3-D simulations a detailed model for the calculation of side wall temperature distributions is used. Model simulations for gallium arsenide growth rates from trimethylgallium and arsine are compared to experimental data by van de Ven et al. [1986].

(ii) In sections 7.6 and 7.7 recirculating flows due to the sudden heating of the gases at the leading edge of the susceptor, and their influence on memory effects are studied by solving the 2-D stationary flow and energy equations and the 2-D transient reactant species concentration equation. The flow simulations are compared to data from experimental flow visualizations by Visser et al. [1989].

7.3 SIMULATION OF STEADY-STATE GROWTH RATE DISTRIBUTIONS

The aim of the work presented in sections 7.3–7.5 is to develop a mathematical model predicting the steady-state axial and lateral distributions of the transport limited epitaxial growth rates in horizontal CVD reactors under widely varying conditions. To test its validity, the model predictions are compared to a series of well characterized growth experiments by Van de Ven et al. [1986]. In these experiments, epitaxial gallium arsenide (GaAs) is grown by Metal Organic (MO) CVD from trimethylgallium (Ga(CH₃)₃, TMGa) and arsine (AsH₃), according to the overall reaction

$$\text{Ga(CH}_3\text{)}_3 (g) + \text{AsH}_3 (g) \rightarrow \text{GaAs (s)} + 3 \text{ CH}_4 (g)$$  \hspace{1cm} (7.1)
table 7.1: Main parameters for the calculated situations

<table>
<thead>
<tr>
<th>Case</th>
<th>$H$ (m)</th>
<th>$u_{in}$ (m/s)</th>
<th>$f_{in, TMGa}$</th>
<th>$f_{in, AsH_3}$</th>
<th>Carrier gas</th>
<th>$Re_{gas}$</th>
<th>$Gr$</th>
<th>$W/H$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.008</td>
<td>0.069</td>
<td>0.0006</td>
<td>0.012</td>
<td>$H_2$</td>
<td>1.9</td>
<td>43</td>
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</tr>
<tr>
<td>2</td>
<td>0.018</td>
<td>0.020</td>
<td>0.0005</td>
<td>0.010</td>
<td>$H_2$</td>
<td>1.2</td>
<td>460</td>
<td>2.8</td>
</tr>
<tr>
<td>3</td>
<td>0.018</td>
<td>0.061</td>
<td>0.0005</td>
<td>0.010</td>
<td>$H_2$</td>
<td>3.6</td>
<td>460</td>
<td>2.8</td>
</tr>
<tr>
<td>4</td>
<td>0.018</td>
<td>0.092</td>
<td>0.0005</td>
<td>0.010</td>
<td>$H_2$</td>
<td>5.5</td>
<td>460</td>
<td>2.8</td>
</tr>
<tr>
<td>5</td>
<td>0.039</td>
<td>0.029</td>
<td>0.0005</td>
<td>0.010</td>
<td>$H_2$</td>
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<td>4700</td>
<td>1.3</td>
</tr>
<tr>
<td>6</td>
<td>0.039</td>
<td>0.058</td>
<td>0.0005</td>
<td>0.010</td>
<td>$H_2$</td>
<td>7.5</td>
<td>4700</td>
<td>1.3</td>
</tr>
<tr>
<td>7</td>
<td>0.039</td>
<td>0.087</td>
<td>0.0005</td>
<td>0.010</td>
<td>$H_2$</td>
<td>11</td>
<td>4700</td>
<td>1.3</td>
</tr>
<tr>
<td>8†</td>
<td>0.021-0.006</td>
<td>0.157</td>
<td>0.0005</td>
<td>0.010</td>
<td>$H_2$</td>
<td>6.7</td>
<td>170</td>
<td>3.8</td>
</tr>
<tr>
<td>9</td>
<td>0.018</td>
<td>0.061</td>
<td>0.0004</td>
<td>0.008</td>
<td>$N_2$</td>
<td>20</td>
<td>12000</td>
<td>2.8</td>
</tr>
</tbody>
</table>

† tapered reactor: tapering angle = 3.5°. $H = 0.021$ m for $x < 0$. $H = 0.006$ m for $x = 0.25$ m. $Re$, $Gr$ and $W/H$ are defined for $H = 0.013$ m.

The reactor geometry is sketched in figure 7.1. The total pressure in the reactor is $10^5$ Pa, the inflow temperature is 293 K, and the susceptor temperature is 973 K. Using these fixed parameters, the reactor height $H$, the carrier gas and the inflow velocity $u_{in}$ are varied, thus covering a wide range of aspect ratios, Grashof numbers and Reynolds numbers. All simulated situations are summarized in table 7.1.

The boundary conditions for the flow equations include a uniform horizontal velocity profile in the inflow, zero normal and tangential velocities on solid walls and zero velocity gradients in the outflow. On the susceptor surface there is a small normal velocity component, determined by the total mass deposition rate, and a zero tangential velocity (see section 2.6). For the energy equation a uniform inflow temperature of 293 K and a zero axial temperature gradient in the outflow are prescribed. In the entrance region all walls are assumed to be at the inflow temperature. The top wall temperature in the susceptor region is assumed to be 400 K, as was found experimentally by Gilling [1982a] and Van de Ven et al. [1986]. The susceptor temperature is set at 973 K. For the side walls in the susceptor region both adiabatic boundary conditions, fixed temperature profiles and a detailed energy balance model were used as a boundary condition. The latter is described in section 7.3.1. For the species balance equations, fixed
values for the mole fractions in the inflow, a constant gradient in the outflow and zero normal total mass fluxes on the nonreacting solid walls are used as boundary condition. At the susceptor surface a very high chemical reaction rate is assumed, leading to transport limited growth.

In the species concentration equations, the approximate methods for describing multi-component (thermal) diffusion (eqs. 2.18, 2.19, 2.20 and 2.79) have been used, which were found to be very accurate for the highly diluted gas mixtures studied in this chapter. The transport properties of the gas mixture were calculated from kinetic theory, as described in section 2.7. However, for the binary ordinary diffusion coefficient of TMG and H₂ experimental values have been reported by Suzuki and Sato [1985], which are almost 70 % higher than those obtained from kinetic theory. In the present study, the experimental values for the diffusion coefficient have been used, since these were found to give better results than the theoretical values from kinetic theory.

7.3.1 Calculation of side wall temperatures

The flow in horizontal CVD reactors is very sensitive to the temperature distribution in the side walls of the reactor [Moffat and Jensen, 1986, Ouazzani and Rosenberger, 1990]. This temperature distribution may be obtained from a detailed energy balance model, including heat conduction in the silica walls and radiative and convective heat transfer at the inside

\[ \text{figure 7.2: Calculation of side wall temperatures in horizontal CVD reactors.} \]
and outside surfaces of the walls.

Consider the configuration in figure 7.2. The upper wall is cooled to a fixed temperature $T_{\text{cold}}$ and the lower wall is heated to a fixed temperature $T_{\text{hot}}$. On the outside, the side walls are in free contact with the surrounding air. On the inside the reactor gases are flowing. Now consider the shaded wall element $j$. When a uniform temperature profile across the wall thickness is assumed (which is usually allowed since the walls are relatively thin and well conducting) the temperature distribution in the side walls is two dimensional and the energy balance for the wall element may be written as

$$
d \left( \lambda_w \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left( \lambda_w \frac{\partial T}{\partial y} \right) + q''_{\text{conv, inw}} + q''_{\text{conv, outw}} - q''_{\text{rad, inw}} - q''_{\text{rad, outw}} = 0 \tag{7.2}$$

with $d$ the thickness of the wall, $\lambda_w$ the thermal conductivity of the wall, $T_w$ the local wall temperature, $q''_{\text{conv, inw}}$ and $q''_{\text{conv, outw}}$ the convective heat fluxes from the reactor gases to the wall element and from the wall element to the surrounding air respectively and $q''_{\text{rad, inw}}$ and $q''_{\text{rad, outw}}$ the radiative heat fluxes from the reactor walls to the wall element and from the wall element to the surroundings respectively. Now we may find expressions for each of these four heat fluxes. For the convective heat flux from the inner wall we have

$$q''_{\text{conv, inw}} = -\lambda_g \left. \frac{\partial T}{\partial z} \right|_{\text{inner wall}} \tag{7.3}$$

with $\lambda_g$ the thermal conductivity of the reactor gases and $T_g$ the temperature of the reactor gases. For the convective heat flux from the outer wall, we have

$$q''_{\text{conv, outw}} = \alpha_{\text{conv}}(y) \cdot (T_w - T_a) \tag{7.4}$$

with $\alpha_{\text{conv}}(y)$ a convective heat transfer coefficient as a function of height and $T_a$ the ambient temperature. Based on the well-known relation

$$Nu_y = \frac{\alpha_{\text{conv}}(y) \cdot y}{\lambda} = \frac{0.508 \Pr^{1/2}}{(0.952 + \Pr^{1/4})^{1/4}} \text{Gr}^{1/4} \tag{7.5}$$
for the natural convection heat transfer from an isothermally heated vertical plate, we roughly estimated $\alpha_{\text{conv}} = 5.0 \cdot y^{-1/4}$ W/m$^2$K. The radiative heat flux from the outer wall to the surroundings is given by

$$q_{\text{rad, outw}} = \varepsilon_j \sigma_B (T_w^4 - T_a^4)$$  \hspace{1cm} (7.6)

with $\varepsilon_j$ the emissivity of the wall element $j$ and $\sigma_B$ the Stefan-Boltzmann constant. The net radiative heat flux $q_{\text{rad, inw}}$ to the inside surface of the wall element $j$, resulting from the radiative heat exchange between the wall element and all other walls, may be calculated using the Gebhart absorption factor method [Gebhart, 1958; Linthorst, 1985]. We divide the reactor walls into a number of surface elements $i$ ($i = 1, N$) with surface areas $A_i$ which are small enough to assume uniform temperature and optical properties across each surface element. Now, the net radiative heat flow to surface element $j$ is equal to

$$q_{\text{rad, inw, j}} = \frac{1}{A_j} \sum_{i=1}^{N} G_{ij} \varepsilon_i \sigma_B T_i^4 A_i - \varepsilon_j \sigma_B T_j^4$$  \hspace{1cm} (7.7)

where the $G_{ij}$ are the Gebhart absorption factors, which may be found through the inversion of the matrix equation

$$\begin{pmatrix}
F_{11}^{-1} & F_{12} \rho_2 & \cdots & F_{1N} \rho_N \\
F_{21} \rho_1 & F_{22}^{-1} \rho_2 & \cdots & F_{2N} \rho_N \\
\vdots & \vdots & \ddots & \vdots \\
F_{N1} \rho_1 & F_{N2} \rho_2 & \cdots & F_{NN}^{-1} \rho_N \\
\end{pmatrix} \times \begin{pmatrix}
G_{11} & G_{12} & \cdots & G_{1N} \\
G_{21} & G_{22} & \cdots & G_{2N} \\
\vdots & \vdots & \ddots & \vdots \\
G_{N1} & G_{N2} & \cdots & G_{NN} \\
\end{pmatrix} =$$  \hspace{1cm} (7.8)

$$\begin{pmatrix}
-F_{11} \alpha_1 & -F_{12} \alpha_2 & \cdots & -F_{1N} \alpha_N \\
-F_{21} \alpha_1 & -F_{22} \alpha_2 & \cdots & -F_{2N} \alpha_N \\
\vdots & \vdots & \ddots & \vdots \\
-F_{N1} \alpha_1 & -F_{N2} \alpha_2 & \cdots & -F_{NN} \alpha_N \\
\end{pmatrix}$$

Here, the $F_{ij}$ are the view factors, which are determined by the geometry of the configuration only, $\rho_i$ is the reflection coefficient of the wall element $i$ and $\alpha_i$ its absorption coefficient. Now, eqs. 7.2-7.7 determine the temperature of wall element $j$, which is a boundary condition for the
Table 7.2: Optical properties of reactor walls

<table>
<thead>
<tr>
<th></th>
<th>α</th>
<th>ρ</th>
<th>τ</th>
<th>ε</th>
</tr>
</thead>
<tbody>
<tr>
<td>Susceptor</td>
<td>0.7</td>
<td>0.3</td>
<td>0.0</td>
<td>0.7</td>
</tr>
<tr>
<td>Side walls</td>
<td>0.4</td>
<td>0.1</td>
<td>0.5</td>
<td>0.94 - 0.00051 \cdot T_w</td>
</tr>
<tr>
<td>Top wall</td>
<td>0.5</td>
<td>0.5</td>
<td>0.0</td>
<td>0.8</td>
</tr>
</tbody>
</table>

The temperature of the gases in the reactor. Note, that this boundary condition in turn depends on the gas flow in the reactor through eq. 7.3.

In the present study, because of the small height and width of the reactor compared to its length, the radiation was considered to be two-dimensional in the y-z plane and the wall conduction was considered to be one dimensional in the y direction. This simplification is justified in the downstream region of the heated zone, where axial temperature gradients in the side walls are small compared to the vertical temperature gradients. However, near the leading edge of the heated susceptor there may also be substantial temperature gradients in axial direction, making the above assumptions less accurate.

The 2-D view factors were calculated using Hottel’s crossed string method [Hottel, 1954]. The wavelength dependence of the radiative properties of the walls was accounted for approximately by evaluating the absorption and reflection coefficients of the side wall material at the susceptor temperature, whereas the emissivities were evaluated at the actual surface temperature. The reactor tube was assumed to consist of 2.5 mm thick silica glass, with a 2 mm thick silica susceptor on the bottom and a silver mirror on top of the upper wall. With data from Driscoll [1978] and Sala [1986] this led to the estimated optical properties in table 7.2. The temperature dependent thermal conductivity of silica \( \lambda_w \) was taken from Parnott and Stuckes [1975].

7.3.2 Chemistry model

To complete the description of the CVD process, the mathematical model for the transport phenomena should be extended with a chemical model, giving reaction mechanisms and rate expressions for heterogeneous and homogeneous reactions. However, for the MOCVD of GaAs from TMGa and AsH₃, which is the
topic of this chapter, the elementary kinetics are still largely unknown, despite a great amount of valuable experimental and theoretical research [e.g. Treep, 1982; Suzuki and Sato, 1985; Yoshida et al., 1985; Lee et al., 1987; Omstead et al., 1988; Tirtowidjojo and Pollard, 1988, 1989; Jensen et al., 1989].

Yet, it is widely believed that growth rates in MOCVD at the pressures and temperatures considered in this chapter and in excess AsH₃ are controlled by the mass transfer of the Ga containing species, which is slow compared to the heterogeneous reaction rate. Moreover, it has been found that growth rates may be predicted accurately by assuming that TMGa is the only Ga containing species, neglecting the gas phase reactions that will actually lead to the formation of cracking products such as Ga(CH₃)₂ and GaCH₃. Therefore, one effective overall surface reaction according to eq. 7.1 is assumed.

By setting the reactive sticking coefficient of TMGa equal to one, the deposition rate is determined by the transport of TMGa to the susceptor surface. The resulting surface reaction rate leads to a boundary condition for the normal total mass flux of AsH₃. Because of the low concentrations the formation of CH₄ is neglected.

7.3.3 Numerical solution

The transport equations with boundary conditions resulting from the above model were solved numerically in 2-D and 3-D cartesian form, using the control volume based finite difference method described in chapter 3. For the 2-D calculations, a non-uniform 30 × 15 (x × y) grid was used, which was locally refined near the reactor top and bottom wall and near the leading edge of the susceptor. Although rather coarse, this grid was found to give accurate predictions of the deposition rates, differing less than 4% from results obtained with 60 × 30 and 100 × 50 grids. For the 3-D calculations in small (= 1.3) and medium (= 2.8) width-to-height aspect ratio reactors a 30 × 15 × 15 (x × y × z) grid was used, which in the x-y plane was identical to the 2-D grid (figure 7.3). Deposition results obtained with this grid were found to differ less than 3% from those obtained with a 30 × 15 × 30 grid. For large (=6.3) aspect ratio reactors a 30 × 10 × 25 grid was used. No use was made of the fact that the configuration is symmetric in the z = ½W plane, which would allow a restriction of the computational domain to half the reactor width. However, it was found that this approach highly
reduced the rate of convergence of the iterative solution procedure.

Included in the iterative solution procedure was the iterative coupling of the flow equations to the side wall energy balance model (eq. 7.3). In the 2-D calculations, line TDMA solvers were used on vertical and horizontal grid lines. The relaxation factors used were \( \eta = 0.4 \) for the velocity components and \( \eta = 0.6 \) for the pressure, species concentration and energy equations. In the 3-D calculations, plane TDMA solvers were used. Within each iteration, the equations were solved on vertical (\( x = \text{constant} \)) planes, sweeping through the domain from inflow to outflow, on horizontal (\( y = \text{constant} \)) planes, sweeping through the domain from bottom to top and on vertical (\( z = \text{constant} \)) planes, sweeping alternately from the left to the right, and from the right to the left side wall. Relaxation factors were \( \eta = 0.1 \) for the velocity components and the temperature, \( \eta = 0.2 \) for the pressure, and \( \eta = 0.3 \) for the species concentrations.

As convergence criteria the error in the global mass balance for the total flow (\(< 10^{-3} \% \)) and each of the species flows (\(< 10^{-1} \% \)) were used, as well as the residuals of the equations (absolute values, summed over the grid, normalized by a characteristic value for the variable and normalized by the number of grid points, \(< 10^{-5} \)). No significant change in calculated growth rates occurred, when more severe criteria were used. After fulfilling
these criteria, the relative change from one iteration to the next at each grid point and for each dependent variable was typically less than $10^{-5}$. To reach a converged solution on the standard grids, circa 500 iterations were needed for the 2-D calculations, taking approximately 1.2 s CPU time per iteration on a HP 9000-835 mini computer, whereas for the 3-D calculations circa 2000 iterations were needed, taking approximately 18 s of CPU time per iteration. When using the standard $30 \times 15 \times 15$ grid and solving for three chemical species concentrations, the 3D code needs 5 Mbyte of core memory for execution.

7.4 RESULTS OF 2-D STEADY-STATE GROWTH RATE SIMULATIONS

The horizontal CVD reactor can be treated as a 2-D configuration for large width to height aspect ratios and in the absence of mixed convection flow effects, i.e. for subcritical Gr number conditions ($Gr = Ra/Pr \lesssim 2 \cdot 10^3$) [Gilden, 1982ab; Moffat and Jensen, 1986, 1988]. The average velocity in the vertical mid plane of a reactor of finite aspect ratio is somewhat higher than the overall average velocity, averaged over the rectangular cross section of the reactor. Therefore, when comparing 2-D model simulations to experimental results for the vertical mid plane of a 3-D reactor configuration, the inflow velocity used in the computations has to be corrected. Thus, the experimental mean inflow velocities were multiplied with the correction factors given in table 7.3 [Han, 1960], as was done by Ouazzani et al. [1988].

**Table 7.3**: Inflow velocity correction factors for 2-D simulation of finite aspect ratio reactors.

<table>
<thead>
<tr>
<th>Aspect ratio W/H</th>
<th>correction factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>1.40</td>
</tr>
<tr>
<td>1.50</td>
<td>1.37</td>
</tr>
<tr>
<td>2.00</td>
<td>1.33</td>
</tr>
<tr>
<td>3.00</td>
<td>1.24</td>
</tr>
<tr>
<td>4.00</td>
<td>1.18</td>
</tr>
<tr>
<td>6.00</td>
<td>1.13</td>
</tr>
<tr>
<td>8.00</td>
<td>1.09</td>
</tr>
<tr>
<td>$\infty$</td>
<td>1.00</td>
</tr>
</tbody>
</table>
Figure 7.4: Simulated TMGa mole fractions ($\times 10^4$) for case 3 without (a) and with (b) thermal diffusion. (For clarity, the figure has been expanded by a factor 3 in vertical direction).

Figure 7.4 shows TMGa mole fractions ($\times 10^4$) for case 3 of table 7.1, calculated without and with the inclusion of thermal diffusion effects. Figure 7.5 shows the corresponding growth rate distributions. Due to thermal diffusion, TMGa is driven away from the susceptor to the cold upper wall, causing a decreased growth rate in the upstream region of the susceptor. As a result, TMGa is conserved for downstream deposition, causing an increased growth rate further downstream. Thus it is clear, that thermal diffusion plays an important role and cannot be neglected in model simulations. Figure

Figure 7.5: Deposition rates for case 3, with and without thermal diffusion.
Figure 7.6: Relative magnitude of the mechanisms for TMGa transport for case 2. Within each cross section all fluxes are scaled in the same way, but a different scalings have been used on different cross sections.

7.6 shows the relative importance of the three transport mechanisms responsible for TMGa species transport (convection, ordinary diffusion and thermal diffusion), for case 2 of table 7.1. From all cases studied, this was the case with the lowest Re (and Pe) number. Even for this low Re number situation (Re = 1.2), species transport in the axial direction is almost completely due to convection, and axial diffusion may well be neglected. This may explain the success of analytical and numerical models such as those developed by Van de Ven et al. [1986] and Moffat and Jensen [1986] in predicting growth rates in horizontal epitaxial CVD reactors while neglecting axial diffusion. It also shows, that discrepancies between analytical models and experiments cannot be ascribed to the neglect of axial diffusion, as was done by Van de Ven et al. [1986]. Except at the beginning of the susceptor, vertical species transport is almost completely caused by the counteracting effects of ordinary and thermal diffusion. It should be noted, that the directions of ordinary and thermal diffusion fluxes are not exactly opposite and that the ratio of their magnitudes varies largely. Thus, thermal diffusion cannot be accounted for accurately by reducing the
Figure 7.7: Comparison between 2-D model predictions for the growth rates at $z = W/2$, and experimental results by Van de Ven et al. [1986].
ordinary diffusion coefficient, as was e.g. suggested by Everstieijn et al. [1970] and Van de Ven et al. [1986].

In figures 7.7(a-e) a series of comparisons is made between 2-D model predictions and experimental growth rates by Van de Ven et al. [1986] at the $z = \frac{1}{2}W$ reactor mid plane, under widely varying conditions. Figure 7.7a shows results for a large aspect ratio reactor operated under low Gr number conditions. The 2-D model accurately predicts experimental growth rates for this situation, especially when considering the experimental error, which, although not explicitly stated by Van de Ven, is probably 100-300 Ång/min. Also for the low Gr number situations in a medium aspect ratio reactor shown in figure 7.7b, the model predictions are quite accurate. However, at supercritical Gr number conditions (Gr $\geq 2 \cdot 10^3$) as shown in figures 7.7c and 7.7d, the 2-D model predictions are in large deviation from experimental growth rates. Finally, in figure 7.7e it can be seen that the model also accurately predicts growth rates in tapered cells operated at subcritical Gr numbers. The irregular shape of the calculated curve is caused by the fact that the tapered cell configuration was approximated on a rectangular grid, causing the reactor height to decrease in discrete steps. Using a finer grid this effect is strongly reduced (solid curve: $30 \times 15$ grid, dashed curve: $60 \times 30$ grid).

From the above it may be concluded that the 2-D model simulations accurately predict the growth rates in the mid plane of medium and large width-to-height aspect ratio horizontal CVD reactors, tapered or non tapered, when operated under subcritical Gr number conditions. Under high Gr number conditions however, the 2-D model can no longer be used successfully and 3-D calculations are necessary. Moreover, 3-D calculations are needed to predict lateral growth rate distributions, even at low Gr numbers.

### 7.5 RESULTS OF 3-D STEADY-STATE GROWTH RATE SIMULATIONS

Under supercritical Gr number conditions, 3-D mixed convection flow effects have a large influence on both the axial and lateral growth rate distributions. The precise nature of these effects has been found to depend strongly on the side wall temperatures [Moffat and Jensen, 1986, 1988]. However, in contrast to the upper and lower walls, which have well defined temperatures, it is not clear which boundary conditions should be used for the side wall temperatures. Moffat and Jensen have used both adiabatic and perfectly cooled side wall conditions. Of these two, the perfectly cooled
side wall assumption led to growth rate predictions which were in qualitative agreement with experimental observations. However, good quantitative agreement was not obtained and this was ascribed to the inaccurate side wall temperature modeling. Ouazzani and Rosenberger [1990] have used adiabatic, perfectly cooled and isothermal conditions at the average reactor temperature as thermal boundary condition on the side walls and found large differences in the lateral growth rate distributions for subcritical Gr number conditions. Supercritical Gr number conditions were not studied.

In reality, the side wall temperatures will be close to the susceptor temperature $T_s$ at $y = 0$, and close to the upper wall temperature $T_{up}$ at $y = H$, the precise $T_w(x,y)$ profile being determined by conductive, radiative and convective heat exchange between the side wall and its surroundings. In this section, the influence of the side wall temperatures on 3-D flow effects and lateral and axial growth rate distributions is studied in detail, using various thermal boundary conditions for the reactor side walls, as well as the detailed energy balance model described in section 7.3.1. A second important 3-D effect is the deposition of reactants on the reactor side walls. As has been observed experimentally by Van de Ven and coworkers [1986], deposition does not only take place on the susceptor surface, but also on hot parts of the side walls. The influence of this side wall deposition is also studied in this section.

### 7.5.1 Influence of side wall temperatures

Three-dimensional modeling calculations were made for the high Gr number situation of case 6 (table 7.1), using the prescribed $T_w(y)$ profiles illustrated in figure 7.8 (dashed curves a-e) for all $x \approx 0$. The temperature profile (a) approximates the "perfectly cooled" idealization, curve (c) represents a linear temperature profile and curve (e) approximates the "perfectly heated" idealization. The profiles (b) and (d) are intermediate to the others. Besides these five prescribed side wall temperature situations, calculations were also made using adiabatic side wall boundary conditions (the resulting side wall temperature profiles are not included in figure 7.8).

The axial growth rate distributions $G(x)$ at $z = \frac{1}{2}W$ predicted by the 3-D model for these six cases are shown in figure 7.9 (dashed curves). It can be seen, that the model predictions change drastically when the thermal
boundary conditions for the side walls are altered. The "heated side wall" cases (d) and (e) both predict growth rates which are far too high compared to experimental observations. With adiabatic side walls, predicted growth rates differ slightly from those obtained with heated side walls for small

**Figure 7.9:** Predicted deposition rates for different prescribed side wall temperature profiles (--- a-e), adiabatic side walls (...) and calculated side wall temperatures (--). The latter without (1) and with (2) side wall deposition.
x, whereas for large x almost identical growth rates are found. With the linear temperature profile (c) the predicted growth rates, although lower than in the previous cases, are still in large error with experiments. When assuming "cooled side walls" (curves a and b) the predicted growth rates are in good agreement with experiments for large x in both cases. For small x however, side wall temperature profile (a) leads to growth rates which are far too low, whereas the profile (b) leads to reasonably accurate growth rates predictions.

In figures 7.10(a-c-e) the flow mechanism behind the observed differences is illustrated. This figure shows transversal velocity vectors resulting from the $v_y$ and $v_z$ velocity components in four different y-z cross sections of the reactor, for the "perfectly cooled" side wall assumption (a), the linear temperature profile assumption (c) and the "perfectly heated" side wall assumption (e). Since the gas inflow temperature is 293 K and the side wall temperatures vary from 400 K to 973 K, the side wall temperatures are higher than the gas temperature for small x in all three cases. Therefore, buoyancy effects cause an upward movement along the side walls in the beginning of the susceptor region, resulting in negative vortex motion ($v_y < 0$ at $z = \frac{1}{2}W$, $v_y > 0$ near $z = 0$ and $z = W$) and increased growth rates in the $z = \frac{1}{2}W$ plane. Of course, because of the relatively hotter side walls, the rotation velocity of the negative vortex movement increases from case (a) to case (c) and (e). After entering the susceptor region, the gases

![Figure 7.10: Transverse velocities for case 6.](image)

(a) cooled side walls; (c) linear side wall temperature profile; (e) heated side walls.
are gradually heated up. In the case of cooled side walls this leads to a situation where the gas temperatures are higher than the side wall temperatures downstream from a certain x position. Here, the negative vortex motion changes into a positive vortex motion, moving downward along the side walls and upward in the reactor mid plane and causing a decrease in the growth rates in the $z = \frac{1}{2}W$ plane. After some distance a fully developed situation is reached and no further change in vortex motion is observed. In the case of a linear side wall temperature profile (c), it takes a longer distance for the gases to be heated up far enough to cause an inversion in the vortex direction. In figure 7.10c it can be seen that this inversion point is not yet reached at $x = 0.20 \text{ m}$. However, since for a linear side wall temperature profile the fully developed gas temperatures will be higher than those of the side walls, it is expected that for larger x a positive vortex motion will appear. Finally, when using the "heated side wall" assumption (e), the side wall temperatures are always higher than the gas temperatures, causing the vortex movement to be negative for all x. Due to the heating up of the gases the initial rotation velocity is slowed down, and finally a fully developed situation is reached.

The above may serve as an illustration of the large influence that side wall temperature boundary conditions may have on the predicted mixed convection flows and on the growth rate distributions in horizontal CVD reactors. It also shows, that simple assumptions such as perfectly cooled side walls or adiabatic side walls may lead to inaccurate modeling results. Although the effects were illustrated here for a supercritical Gr number situation, it must be stressed, that even under subcritical Gr number conditions in small and medium aspect ratio reactors, simple boundary conditions, such as the perfectly cooled side walls assumption, were found to lead to growth rate predictions which are largely in error. Thus, the need for a more detailed modeling of the side wall temperatures is clearly shown.

Using the detailed energy balance model described in section 7.3.1, the side wall temperature profiles $T_w(x, y)$ for $x \geq 0$ can be calculated. In figure 7.8 the calculated side wall temperatures for not too small x ($x \geq H$) are shown, for 0.008, 0.018 and 0.039 m high reactors. The shaded areas indicate variations of $T_w(y)$ with x ($x \geq H$), for the different carrier gases and inflow velocities studied. These variations are due to the convective heat losses to the reactor gases. It can be seen, that for small reactor heights the temperature profiles in the side walls are nearly linear,
whereas for larger \( H \) the side walls are relatively colder. Figure 7.11 shows the calculated side wall temperatures \( T_w(x,y) \) for case 5 (table 7.1). There is a rapid increase in the side wall temperature at the leading edge of the susceptor, which may in part be caused by the neglect of axial heat conduction in the side walls in the heat transfer model. The fully developed side wall temperature distribution is strongly non-linear in the \( y \) coordinate.

Using the calculated side wall temperatures, the growth rate distribution for case 6 (table 7.1) was calculated again and the result is shown in figure 7.9 (solid curve 1). When using the detailed energy balance model for calculating the side wall temperatures, the model predictions for the axial growth rate distribution at \( z = \frac{1}{2} w \) are in close agreement with experimental observations. Figure 7.12, showing the calculated distribution of growth rates over the susceptor surface from the 2-D model and from the 3-D model using different thermal boundary conditions for the side walls, gives another illustration of the importance of correct 3-D modeling for high Gr number situations.

7.5.2 Influence of deposition on the side walls

In all the 3-D calculations described above it was assumed that deposition takes place on the susceptor surface only. In reality there will also be deposition on the hot parts of the side walls. This causes an additional depletion of the reactor gases and increased concentration gradients in lateral direction. Therefore, the influence of deposition on the side walls on the predicted growth rates was investigated. For a detailed modeling of side wall deposition more insight in the TMGa decomposition mechanism, including the low temperature deposition range, would be needed. However, a first approximation of its influence on gas phase depletion can
Figure 7.12: Growth rate distributions in Ång/min, for case 6.
(a): 2-D calculations. (b): 3-D calculations, cooled side walls. (c): 3-D, adiabatic side walls 
(d): 3-D, calculated side wall temperatures 
(e): idem, with side wall deposition.

be made. Van de Ven et al. [1986] concluded, that TMGa decomposition is not complete in the gas phase and that at least the removal of the last methyl group must occur at a hot surface $\geq 700$ K. Therefore, we assumed that transport limited deposition takes place on those parts of the side walls with temperatures $\geq 700$ K and that zero deposition takes place on those parts of the side walls with temperatures $< 700$ K. In doing so, the total deposition surface is increased by circa 15 %, 30% and 40 % for 0.008, 0.018 and 0.039 m high reactors respectively.

In figure 7.9 it can be seen, that the difference in the axial growth rate distribution in the $z = \frac{1}{2} W$ plane, calculated with (solid curve 2) and without (solid curve 1) side wall deposition, is rather small. However, a
very significant effect is found when considering the lateral growth rate distributions (fig 7.12). Thus, the modeling of side wall deposition may be of great importance in the accurate prediction of lateral growth rate distributions. In all following cases, the above model for side wall deposition was included.

7.5.3 Comparison with experimental results

Now, with the above model for calculating side wall temperatures and deposition on the side walls, full 3-D simulations of the MOCVD process can be performed. As an example of the model predictions, figures 7.13(a-c) show the calculated transverse velocities, the temperatures and the TMGa mole fractions \((x \times 10^4)\) at four different vertical cross sections in the reactor, for case 6 of table 7.1. The inversion of the transverse vortex movement can be clearly observed, as well as its influence on the transverse temperature and TMGa concentration distributions.

In figures 7.14(a-e) the solid curves show 3-D modeling results for the axial growth rate distributions in the 9 cases of table 7.1, compared with the 2-D modeling results (dashed curves) described before. As was to be expected, 3-D and 2-D results are almost identical for the large aspect-ratio, low Gr number situation in figure 7.14a. In the medium aspect ratio, low Gr number situations shown in figure 7.14b, lower growth rates are found in the downstream region, when using the 3-D model. This is not caused by 3-D flow effects, which are rather unimportant in these low Gr

![Figure 7.13: 3-D model simulations for case 6. (a) Transversal velocities; (b) Isotherms; (c) TMGa mole fractions \((x10^4)\)](image-url)
Figure 7.14: Comparison between 2-D (---) and 3-D (-----) model predictions for the growth rates at $z = W/2$, and experimental results by Van de Ven et al. [1986].
number situations, but by diffusion effects in the z direction: First, near
the side walls the gas phase depletion is stronger than in the reactor mid
plane, due to the lower flow velocities. Therefore, TMGa concentrations are
lower near the side walls, causing lateral diffusion from the mid plane to
the side walls. Secondly, the side walls are somewhat colder than the gas
mixture in the developed gas temperature region. Therefore, thermal
diffusion will cause TMGa to move from the mid plane to the side walls.
Thirdly, the assumed deposition on the side walls causes an additional
depletion. The increased depletion in the 3-D calculations compared to the
2-D calculations seems to lead to a somewhat improved correspondence between
modeling results and experiments for larger x. In case 2 however, 2-D
results are somewhat better, which must probably be considered fortuitous.
On the whole, differences between 2-D and 3-D modeling are rather small for
low Gr number situations in large and medium aspect ratio reactors. For high
Gr number situations (figure 7.14c) on the other hand, 3-D modeling gives
rather accurate predictions of experimentally observed axial growth rate
distributions, whereas 2-D results are in large error. Here we can see the
large influence of 3-D mixed convection flow effects, as described above. In
figure 7.14e it can be seen that 3-D modeling results for a tapered reactor
cell under low Gr number conditions differ only slightly from 2-D results.
The irregular shape of the curve is again caused by the approximation of the
tapered geometry on a rectangular grid, as was explained in section 7.4.

When using nitrogen as a carrier gas (fig. 7.14d), the predicted growth
rates for large x obtained from the 3-D model are in much better agreement
with experimental results than the 2-D model predictions. For small x
however, the 3-D model predictions do not agree with experimental results.
Two main causes for this discrepancy between model simulations and
experimental results may be identified: (i) First, the model assumes a
discrete temperature step at x = 0 at the reactor bottom, whereas in reality
a more gradual rise of the bottom temperature will be present. In nitrogen
carrier gas, the calculated growth rates in the first few centimeters were
found to be very sensitive to the way in which the temperature rise at x = 0
was modeled. For larger x however, the sensitivity was small. (ii) Secondly,
as stated in section 7.3.1, the neglect of axial temperature gradients in
the side wall energy balance model is not justified near the leading edge of
the heated susceptor. Again, when using nitrogen carrier gas, the growth
rates in the first few centimeters were found to be very sensitive to small
changes in the side wall temperatures near x = 0. When using hydrogen as a
carrier gas, the calculated growth rates were much less sensitive to the thermal boundary conditions at the bottom and side walls near \( x = 0 \), probably due to the fact that thermal entry lengths are much smaller in hydrogen [Giling, 1982ab].

Figure 7.15 shows the axial growth rate distributions at three different lateral positions for case 5 of table 7.1, calculated with different types of boundary conditions at the side walls, and compared to experimental results by Van de Ven et al. [1986]. The growth rate distributions near the side walls are even more sensitive to the side wall...
boundary conditions than the growth rate distribution in the reactor midplane. The use of perfectly cooled or adiabatic side wall conditions leads to highly erroneous results. With the use of the energy balance model for calculating the side wall temperatures a somewhat better agreement with experimental results is found. However, even when this detailed side wall boundary condition is used, there is no good quantitative agreement between model simulations and experiments. Moreover, the results are extremely sensitive to the way in which deposition on the side walls is modeled.

Thus, even more advanced energy balance models for the side wall thermal boundary conditions than the one used in this study, including three-dimensional radiative heat exchanges between the reactor walls and two-dimensional heat conduction within the reactor side walls, a detailed description of the bottom temperature rise near x = 0, as well as detailed models for the low temperature deposition on the reactor side walls, seem to be necessary in order to accurately predict the lateral growth rate distributions in low aspect ratio horizontal CVD reactors operated at high Gr number conditions. The weakest point in the present model seems to be the inaccurate treatment of the temperature rise in the bottom and side walls near x = 0.

The sensitivity of 3-D transport models to the highly unknown boundary conditions on the side walls, and the effort needed to accurately predict the side wall temperatures and deposition, gives rise to the question whether horizontal reactors as studied in this chapter are well suited for diagnostic experiments, aimed at unraveling the transport phenomena, chemical mechanisms and kinetics in epitaxial CVD. An important improvement would be the application of water-cooling not only to the upper wall but also to the side walls of the reactor. A better defined flow field can be obtained in vertical stagnation flow reactors with cooled walls.

### 7.6 Buoyancy Driven Recirculating Flows

In horizontal CVD reactors recirculating flows at the leading edge of the heated susceptor may occur due to the sudden gas expansion (figure 7.16a). These recirculating flows are considered to be highly unwanted, because of their possible action as a memory cell, when switching from one reactant gas source to another. Especially in compound semiconductor fabrication it is important to be able to switch gas sources abruptly in order to obtain thin layers, sharp interfaces and precise control over composition and dopant
levels. Special designs for rapid gas switching systems have been developed [Norris et al., 1984] and many efforts have been put in the design of streamlined reactor configurations in order to avoid dead volumes [Gilling, 1985]. In a systematic study of the factors impairing the abruptness of junctions, Opdorp and Leys [1987] have pointed out the importance of recirculating flows with respect to memory effects.

Recirculating flows at the leading edge of the heated susceptor are caused by the interaction of the main gas flow and buoyancy-induced secondary flows. Mixed convection phenomena in horizontal rectangular channels heated from below have been the subject of many studies, both theoretical [e.g. Hwang and Cheng, 1973; Incropera and Schutt, 1985; Mahanay et al., 1987; Chou and Hwang, 1987] and experimental [e.g. Ostrach and Kamotani, 1975; Hwang and Liu, 1976; Osborne and Incropera, 1985; Maughan and Incropera, 1987; Incropera et al., 1987]. However, these studies were primarily aimed at the heat transfer increase caused by longitudinal rolls, i.e. buoyancy-induced spiral rolls with axes in the main flow direction (figure 7.16b). These rolls occur when the Rayleigh number based on the height of the reactor exceeds a critical value \( Ra_{cr,\text{long}} \approx 2 \times 10^3 \), independent of the imposed main flow. Longitudinal rolls have a large influence on axial and lateral growth rate uniformities in horizontal CVD reactors, as has been discussed in section 7.5, but do not cause memory effects. Memory effects are caused by transversal rolls with axes in the cross stream direction (figure 7.16a). Little is known about the occurrence
of these rolls.

Here the occurrence of recirculating flows at the leading edge of the heated susceptor in horizontal CVD reactors will be studied as a function of the dimensionless parameters which describe the flow conditions. For this purpose, a theoretical analysis of the flow equations is described in the next section. Since we are interested in recirculating flows with axes in the cross stream direction, caused by vertical temperature gradients aligned with the gravitation field, we consider the hydrodynamics to be two-dimensional. Thus, the stationary flow and energy equations are solved in 2-D cartesian form. However, there is some indication that the flow becomes unsteady for certain flow conditions. This will be discussed in the next sections.

The simulation results are compared to results from flow-visualization experiments by means of TiO\textsubscript{2} particle injections into the gas flow, performed by Visser and coworkers at the Catholic University of Nijmegen. More details on these experiments can be found in Visser et al. [1989].

### 7.6.1 Theoretical analysis

We consider the 2-D flow configuration depicted in figure 7.17. The steady-state flow and temperature distribution are described by the Navier-Stokes, continuity and energy equations (eq. 2.2-2.5) in 2-D cartesian, stationary form, with the following boundary conditions:

- **inflow** \( x = -\infty \): \( u = u_{\text{in}} \), \( v = 0 \), \( T = T_c \)
- **outflow** \( x = \infty \): \( \delta(pu)/\delta x = 0 \), \( \delta T/\delta x = 0 \)
- **upper wall** \( y = H \): \( u = 0 \), \( v = 0 \), \( T = T_c \)
- **lower wall** \( y = 0, x \leq 0 \): \( u = 0 \), \( v = 0 \), \( T = T_c \)
- **susceptor** \( y = 0, x > 0 \): \( u = 0 \), \( v = 0 \), \( T = T_h \)  \( (7.9) \)

where \( u \) is the horizontal and \( v \) is the vertical velocity component.

As described in section 4.4, the fluid properties of the gas can be approximated accurately by relations of the form:

\[
\rho = c_1 P_{\text{ref}} T^{-1}, \quad \mu = c_2 T^{0.7}, \quad \lambda = c_3 T^{0.8}, \quad c_p = c_4 T^{0.1}
\]  \( (7.10) \)

where \( c_1...c_4 \) are constants, depending on the type of carrier gas, and where it has been assumed that the pressure is approximately equal to \( P_{\text{ref}} \).
Figure 7.17: 2-D reactor configuration for the numerical study of recirculating flows.

everywhere in the reactor. Thus, the hydrodynamics are described by six parameters: $u_{in}$, $T_h$, $T_c$, $P_{ref}$, $H$ and the type of gas (it is assumed that the length of the entrance and exit regions are long enough not to play a role in the problem description).

Now, to reduce the number of problem describing parameters, the equations are put in a dimensionless form. The analysis is very similar to the one in section 4.4. When we introduce dimensionless parameters, according to

$$
\begin{align*}
\hat{u} &= u/u_{in} \\
\hat{v} &= v/u_{in} \\
\hat{\lambda} &= (T-T_c)/(T_h-T_c) \\
\hat{x} &= x/H \\
\hat{y} &= y/H \\
\hat{P} &= (P - P_{ref}g)/(\rho_{ref}u_{in}^2) \\
\hat{\rho} &= \rho/\rho_{ref} \\
\hat{\gamma} &= \mu/\mu_{ref} \\
\hat{\lambda} &= \lambda/\lambda_{ref} \\
\hat{c}_p &= c_p/c_{p,ref}
\end{align*}
\tag{7.11}
$$

where $\phi_{ref}$ is the value of the fluid property $\phi$ at the reference temperature $T_{ref} = (T_h + T_c)/2$, we obtain the following dimensionless equations with boundary conditions:

**continuity:**

$$
\frac{\partial (\hat{\rho} \hat{u})}{\partial \hat{x}} + \frac{\partial (\hat{\rho} \hat{v})}{\partial \hat{y}} = 0 \tag{7.12}
$$

**momentum:**

$$
\frac{\partial (\hat{\rho} \hat{u}^2)}{\partial \hat{x}} + \frac{\partial (\hat{\rho} \hat{u} \hat{v})}{\partial \hat{y}} = \frac{1}{Re} \left[ \frac{\partial}{\partial \hat{x}} \left( \frac{4}{3} \mu \hat{u} \hat{v} - \frac{2}{3} \mu \hat{v} \right) - \frac{\partial}{\partial \hat{y}} \left( \frac{\mu}{\hat{v}} \hat{u} \hat{v} + \frac{\mu}{\hat{v}} \right) \right] - \frac{\partial \hat{P}}{\partial \hat{x}} \tag{7.13}
$$
\[
\frac{\partial (\rho \hat{v})}{\partial \hat{x}} + \frac{\partial (\rho \hat{v}^2)}{\partial \hat{y}} = \frac{1}{Re} \left[ \frac{\partial}{\partial \hat{y}} \left( \frac{4}{3} \frac{\partial \hat{v}}{\partial \hat{x}} - \frac{2}{3} \frac{\partial \hat{u}}{\partial \hat{y}} \right) + \frac{\partial}{\partial \hat{x}} \left( \frac{\partial \hat{u}}{\partial \hat{y}} + \frac{\partial \hat{v}}{\partial \hat{x}} \right) \right] - \frac{\partial \hat{T}}{\partial \hat{y}} + \frac{Gr}{Re^2} \left[ \frac{(\hat{T}-\frac{1}{2})}{(\frac{1}{2}Ga+1)} \right]
\]  
(7.14)

energy:
\[
\hat{c}_p \frac{\partial (\rho \hat{u} \hat{T})}{\partial \hat{x}} + \hat{c}_p \frac{\partial (\rho \hat{v} \hat{T})}{\partial \hat{y}} = \frac{1}{Re \cdot Pr} \left[ \frac{\partial}{\partial \hat{x}} \left( \lambda \frac{\partial \hat{T}}{\partial \hat{x}} \right) + \frac{\partial}{\partial \hat{y}} \left( \lambda \frac{\partial \hat{T}}{\partial \hat{y}} \right) \right]
\]  
(7.15)

boundary conditions:
- inflow \( \hat{x} = -\infty \): \( \hat{u} = 1 \) \( \hat{v} = 0 \) \( \hat{T} = 0 \)
- outflow \( \hat{x} = \infty \): \( \partial (\rho \hat{u})/\partial \hat{x} = 0 \) \( \hat{v} = 0 \) \( \hat{T}/\partial \hat{x} = 0 \)
- upper wall \( \hat{y} = 1 \): \( \hat{u} = 0 \) \( \hat{v} = 0 \) \( \hat{T} = 0 \)
- lower wall \( \hat{y} = 0 \), \( \hat{x} \leq 0 \): \( \hat{u} = 0 \) \( \hat{v} = 0 \) \( \hat{T} = 0 \)
- susceptor \( \hat{y} = 0 \), \( \hat{x} > 0 \): \( \hat{u} = 0 \) \( \hat{v} = 0 \) \( \hat{T} = 1 \)

fluid properties:
\[
\hat{\rho} = \left( (\frac{1}{2}Ga+1) \right)^{-1}; \quad \hat{\mu} = \left( (\frac{1}{2}Ga+1) \right)^{0.7}
\]  
\[
\hat{\lambda} = \left( (\frac{1}{2}Ga+1) \right)^{0.8}; \quad \hat{c}_p = \left( (\frac{1}{2}Ga+1) \right)^{0.1}
\]  
(7.17)

We can now see, that the hydrodynamics are determined by four dimensionless groups:

The Reynolds number \( Re = \frac{\rho \text{ref} u_{in} H}{\mu \text{ref}} \)  
(7.18)

The Grashof number \( Gr = \frac{g \rho \text{ref} H^3 (T_{\text{h}} - T_{\text{c}})}{\mu \text{ref}^2 T \text{ref}} \)  
(7.19)

The Prandtl number \( Pr = \frac{\mu \text{ref} c_p \text{ref}}{\lambda \text{ref}} \)  
(7.20)

The Gay-Lussac number \( Ga = \frac{(T_{\text{h}} - T_{\text{c}})}{T \text{ref}} \)  
(7.21)

As in chapter 4, the Prandtl number can be dropped as a problem determining
parameter, since Pr ≈ 0.7 for all common CVD gases at common CVD temperatures and pressures. Moreover, for Ga ≪ 1, the dimensionless temperature difference also vanishes from the equations. In that case, mixed convection flow phenomena are determined by the Grashof and Reynolds numbers only.

The buoyancy term (last term on the r.h.s. of eq. 7.14) depends on the mixed convection parameter Gr/Re^2. The buoyancy forces are counteracted by viscous and inertial forces. For very low Re, inertial forces are negligible and the inertial terms can be omitted in the vertical momentum equation, which then becomes:

\[
(Ga \ll 1, \; Re \ll 1) \quad 0 = \left[ \frac{\partial}{\partial \hat{y}} \left( 4 \frac{\partial \hat{u}}{\partial \hat{y}} - 2 \frac{\partial \hat{u}}{\partial \hat{x}} \right) + \frac{\partial}{\partial \hat{x}} \left( \mu \frac{\partial \hat{u}}{\partial \hat{y}} + \mu \frac{\partial \hat{v}}{\partial \hat{x}} \right) \right] - Re \frac{\partial \hat{\rho}}{\partial \hat{y}} + \frac{Gr}{Re} \left( \hat{T} - \frac{1}{2} \right) \quad (7.22)
\]

In this case, the occurrence of buoyancy induced transversal rolls is expected to be determined by Gr/Re.

For very large Re, the viscous terms can be neglected and we obtain for the vertical momentum equation

\[
(Ga \ll 1, \; Re \gg 1) \quad \frac{\partial (\hat{\rho} \hat{u})}{\partial \hat{x}} + \frac{\partial (\hat{\rho} \hat{v})}{\partial \hat{y}} = - \frac{\partial \hat{\rho}}{\partial \hat{y}} + \frac{Gr}{Re^2} \left( \hat{T} - \frac{1}{2} \right) \quad (7.23)
\]

In that case, the occurrence of buoyancy induced transversal rolls is expected to be determined by Gr/Re^2.

Neglecting the small differences in Pr for different gases we will study the occurrence of recirculating flows as a function of Gr, Re and Ga.

In accordance with the values in realistic CVD operation, Re will be varied from 0.1 to 20 and Gr from 10^0 to 10^4, for Ga = 1.0 (T_h = 900 K, T_c = 300 K) and Ga = 1.2 (T_h = 1200 K, T_c = 300 K). For a further evaluation of the influence of Ga, we will also study the Boussinesq limit Ga = 0.01 (T_h = 303 K, T_c = 300 K).

7.6.2 Numerical solution

The stationary, 2-D cartesian Navier-Stokes, continuity and energy equation with the above boundary conditions and fluid property relations were solved
in dimensional form. In the axial direction, the computation domain extended from \( x = -5 \) H to \( x = 10 \) H. The hydrodynamic and thermal entrance lengths in laminar gas flow in channels are \( L_T = 0.04 \text{ Re} \cdot \text{H} \) and \( L_H = 0.28 \text{ Re} \cdot \text{H} \) respectively (Giling, 1982a). Thus, for \( \text{Re} \leq 20 \) as in the present study, the hydrodynamic entrance length \( L_H \leq 0.8 \) H and the thermal entrance length \( L_T \leq 5.6 \) H.

A uniform grid with 90 grid points in axial and 30 grid points in vertical direction was used for most calculations. Grid independence of the results was checked on 180 \( \times \) 30, 90 \( \times \) 60 and 135 \( \times \) 45 grids for some representative situations with strong flow recirculations. The minimum and maximum value of the stream function and the value of the largest negative horizontal velocity obtained on these grids, differed less than 1% from those obtained on the standard grid.

The equations were solved iteratively, using the TDMA line procedure on vertical lines, sweeping through the solution domain from the inflow to the outflow of the reactor. Underrelaxation was done through the use of standard relaxation factors \( \eta = 0.4 \) for the momentum equations, \( \eta = 0.6 \) for the pressure correction, \( \eta = 0.8 \) for the energy equation). Three convergence criteria were used:

1. Error in the overall mass balance, \( < 10^{-2} \% \),
2. Residuals of the discretized equations (absolute values, summed over the grid, normalized by the maximum value for the variable and by the number of grid points) \( < 10^{-5} \) and
3. Relative changes from one iteration to the next in the values of the variables in a representative monitor point, \( < 10^{-5} \).

On the standard grid 250-750 iterations (taking 2.3 CPU s. per iteration on a HP 9000-835 minicomputer) were needed to fulfill these convergence criteria. No significant changes in the solution were observed when more severe convergence criteria were used. For certain process conditions, convergence according to the above criteria could not be reached, as will be discussed later. In those cases, the iteration process was stopped after 2500 iterations.

### 7.6.3 Results

The flow and temperature distribution in the reactor were simulated for a wide range of process conditions. By varying the type of gas (hydrogen and nitrogen), the reactor height (0.01-0.05 m), the gas flowrate (1-100 slm per meter reactor width), the pressure (\( 10^3 - 10^5 \) Pa) and the susceptor temperature (303 K, 900 K and 1200 K) the Reynolds number was varied from
Figure 7.18: Normalized streamlines for the four different types of flow. In all cases, Re = 1.0 and rt = 1.0.
(For clarity, the figure has been expanded with a factor 2 in the vertical direction)
(a) Gr = 10^1: no recirculating flow;
(b) Gr = 10^2: transitional flow;
(c) Gr = 10^3: recirculating flow;
(d) Gr = 10^4: wavy flow.

0.1 to 20 and the Grashof number from 10^0 to 10^4 at values of the
dimensionless temperature difference Ga = 0.01, 1.0 and 1.2.

Figures 7.18(a-d) show four typical solutions for the streamlines of
the flow at fixed values of Re = 1 and Ga = 1.0 and increasing Gr (10^1-10^4):
(i) At low Gr, as in figure 7.18a, the flow is almost undisturbed by the
sudden heating at the leading edge of the susceptor, except for the fact
that the flow adapts to a new, asymmetric velocity profile due to the
temperature dependence of the viscosity. For the minimum and maximum values
of the streamfunction, normalized at the incoming mass flow, we have
Ψ_{min} = 0 and Ψ_{max} = 1.
(ii) At larger Gr, as in figure 7.18b, the streamlines are clearly disturbed near
the leading edge of the heated susceptor, but there is no significant
flow recirculation. The maximum streamline value Ψ_{max} is slightly larger
than one.
(iii) A further increase in Gr, as in figure 7.18c, leads to a strong flow
recirculation above the leading edge of the heated susceptor (Ψ_{max} > 1);
(iv) Finally, in figure 7.18d, an even further increase of Gr leads to a wavy flow, with a large recirculation above the leading edge of the heated susceptor \( \Psi_{\text{max}} > 1 \) and many smaller recirculating flows in opposite direction in the heated susceptor region \( \Psi_{\text{min}} < 0 \). For this latter type of solution it was found that the iterative solution procedure of the steady-state flow equations did not lead to convergence. Oscillating solutions were found, even when very small values of the relaxation factors were used. This is further discussed below.

According to the four flow types illustrated above, we have divided our simulation results into four groups:

(i) No recirculating flow: \( \Psi_{\text{min}} = 0; \ \Psi_{\text{max}} = 1 \)
(ii) Transitional flow: \( \Psi_{\text{min}} = 0; \ 1.0 < \Psi_{\text{max}} \leq 1.1 \)
(iii) Recirculating flow: \( \Psi_{\text{min}} = 0; \ \Psi_{\text{max}} > 1.1 \)
(iv) Wavy flow: \( \Psi_{\text{min}} < 0; \ \Psi_{\text{max}} > 1.1; \) no convergence

Figure 7.19a shows results, presented according to the above classification, for a large series of simulations at strongly varying process conditions, thus varying Gr from \( 10^0 \) to \( 10^4 \) and Re from 0.1 to 20 at fixed Ga = 1.2. In accordance with the previous theoretical analysis, the occurrence of recirculating flows depends on the values of the Gr and Re numbers only (at fixed Ga). Moreover, again in agreement with the theoretical analysis, it is found that recirculating flows are present for \( \text{Gr/Re} > \alpha_{\text{crit}} \) at low values of Re (Re < \( \text{Re}_1 \)), whereas for larger Re (Re \( \approx \text{Re}_1 \)), recirculating flows

### Table 7.4: Critical parameters for the occurrence of recirculating flows

<table>
<thead>
<tr>
<th>Ga</th>
<th>( \text{Re}_1 )</th>
<th>( \alpha_{\text{crit}} )</th>
<th>( \alpha^*_{\text{crit}} )</th>
<th>( \text{Re}_1 )</th>
<th>( \alpha_{\text{crit}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>7 ± 3</td>
<td>360 ± 100</td>
<td>460</td>
<td>≈ 8</td>
<td>190 ± 60</td>
</tr>
<tr>
<td>1.0</td>
<td>4 ± 2</td>
<td>170 ± 50</td>
<td>220</td>
<td>6 ± 2</td>
<td>80 ± 20</td>
</tr>
<tr>
<td>1.1</td>
<td>3 ± 1</td>
<td>130 ± 40</td>
<td>170</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( \alpha_{\text{crit}} \) deduced from figure 7.19
\( \alpha^*_{\text{crit}} \) deduced from figure 7.20
occur for $\text{Gr}/\text{Re}^K > \beta_{\text{crit}}$, with $\kappa > 1$. Although there are insufficient data to determine the value of $\kappa$ accurately, it seems plausible that $\kappa = 2$, in accordance with the theoretical analysis. Similar results, with different values for $\alpha_{\text{crit}}$ and $\text{Re}_1$, are found for $\text{Ga} = 1.0$ (figure 7.19b) and $\text{Ga} = 0.01$ (figure 7.19c). We thus find the following criterion for absence of recirculating flows:
\begin{align*}
\text{Gr}/\text{Re} &< \alpha_{\text{crit}}(\text{Ga}) \quad \text{for} \quad \text{Re} < \text{Re}_1(\text{Ga}) \\
\text{Gr}/\text{Re}^2 &< \alpha_{\text{crit}}(\text{Ga})/\text{Re}_1(\text{Ga}) \quad \text{for} \quad \text{Re} \geq \text{Re}_1(\text{Ga})
\end{align*}

(7.24a)  \quad (7.24b)

The values of $\alpha_{\text{crit}}$ and $\text{Re}_1$ at different $\text{Ga}$, deduced from figures 7.19(a-c) are presented in table 7.4. It is clear, that both $\alpha_{\text{crit}}$ and $\text{Re}_1$ decrease with increasing $\text{Ga}$. However, the influence of $\text{Ga}$ on the occurrence of recirculating flows is relatively small.

A second possibility for the determination of $\alpha_{\text{crit}}$ is illustrated in figure 7.20. Here, the maximum value $\Psi_{\text{max}}$ of the streamfunction in the reactor (normalized at the incoming mass flow) is presented as a function of $\text{Gr}/\text{Re}$, for $\text{Re} = 0.1$ and $\text{Ga} = 0.01, 1.0$ and 1.2. A linear least squares fit through all points with $\Psi_{\text{max}} \geq 1.5$ gives the following results:

\begin{align*}
\text{Ga} = 0.01: & \quad \Psi_{\text{max}} - 1 = 0.0011 \cdot (\text{Gr}/\text{Re} - 460) \\
\text{Ga} = 1.0: & \quad \Psi_{\text{max}} - 1 = 0.0021 \cdot (\text{Gr}/\text{Re} - 220) \\
\text{Ga} = 1.2: & \quad \Psi_{\text{max}} - 1 = 0.0028 \cdot (\text{Gr}/\text{Re} - 170)
\end{align*}

(7.25a)  \quad (7.25b)  \quad (7.25c)

The resulting values for $\alpha_{\text{crit}}$ which are very similar to those obtained from figures 7.19(a-c), are presented as $\alpha^*$ in table 7.4. Again, $\alpha_{\text{crit}}$ is found to decrease with increasing $\text{Ga}$.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure7.20.png}
\caption{Maximum normalized streamfunction as a function of $\text{Gr}/\text{Re}$ for different values of $\text{Ga}$.}
\end{figure}
7.6.4 Comparison with experimental results

Parallel to the theoretical and numerical study described in the previous sections, flow visualization experiments on recirculating flows in horizontal CVD reactors were performed by Visser and coworkers at the Catholic University of Nijmegen [Visser et al., 1989]. Smoke particles of TiO₂ were added to the hydrogen gas flowing through a horizontal quartz reactor with rectangular cross section (height: 40 mm, width: 50 mm). In the deposition zone, the reactor was water cooled on top and resistance heated from below across its full width. The smoke particles were illuminated from above by a sheet of laser light. Recirculating flows caused a locally high concentration of smoke particles, which could easily be observed visually. It was indicated, that fall-out and thermophoresis effects are relatively small in the region of interest where recirculating flows may occur and that the smoke particles follow the motion of the gas quite accurately.

At an inflow temperature $T_c = 293$ K and susceptor temperatures $T_h = 870$ K (Ga = 1.0) and $T_h = 1020$ K (Ga = 1.1), the flowrate was varied from 0.2 to 12 slm and the pressure was varied from $0.15 \times 10^5$ to $1.0 \times 10^5$ Pa, thus varying Re from 0.2 to 12 and Gr from $10^2$ to $5 \times 10^3$. The results of these experiments, again presented as a function of Re and Gr at fixed Ga and divided into undisturbed, transitional and recirculating flows, are shown in figure 7.2.1. As was predicted by the theoretical analysis.

![Figure 7.2.1: The occurrence of recirculating flows as a function of Gr and Re, for different values of Ga, according to flow visualization experiments by Visser et al. [1989].](image)
and the numerical simulations, the occurrence of recirculating flows is
determined by the value of $Gr/Re$ at low $Re$. The resulting values for $\alpha_{crit}$
are presented in table 7.4 and are in rather good agreement with those
predicted numerically. Also in agreement with the numerical simulations,
$\alpha_{crit}$ decreases when $Ga$ increases. However, the dependence of $\alpha_{crit}$ on $Ga$
seems to be more pronounced in the experiments than in the simulations. For
$Ga = 1.1$ there is some indication that the critical parameter changes from
$Gr/Re$ at low $Re$ to $Gr/Re^2$ at high $Re \cong Re_l$, but the value of $Re_l$ is somewhat
higher than predicted numerically. For $Ga = 1.0$ such a transition could not
be discerned for the range of $Re$ values studied.

From the results of the numerical flow simulations and the flow
visualization experiments the following engineering criterion, valid for the
full range of hydrodynamic conditions commonly used in horizontal epitaxial
CVD reactors, may be deduced: To make sure, that no buoyancy induced
recirculating flows will occur at the leading edge of the heated susceptor,
the mixed convection parameter $Gr/Re = (\rho_{ref} g H^2 \Delta T)/(\mu_{ref} T_{ref} u_{in})$
should be $\ll 100$.

### 7.6.5 Flow instabilities

As stated in sections 7.6.2 and 7.6.3, stable solutions of the steady-state
flow equations could not always be obtained. At very high values of $Gr$ the
iterative solution procedure was found to lead to oscillating solutions,
even at very low values of the relaxation factors. Figure 7.22 shows the
calculated temperature in a monitor point at half the reactor height and
halfway down the heated susceptor as a function of the iteration number, for
$Re = 1$, $Gr = 10^4$ and $Ga = 1.0$. The calculated temperature oscillates with a
fixed amplitude and "frequency". Figure 7.23 shows the calculated
temperature fields at the different stages of the iteration procedure
indicated in figure 7.22. Traveling waves are found, which lead to a
periodic solution as a function of the iteration number. It seems reasonable
to assume, that this behavior of the pseudo time-dependent iterative
solution procedure that was used to solve the steady-state flow equations
(see chapter 3), reflects the fact that the actual flow is unsteady. This
may be associated with the unsteady flow behavior for large Grashof numbers,
that was observed experimentally by Chiu and Rosenberger [1987a] and with
the traveling wave instabilities in horizontal channels heated from below
that were predicted theoretically by Gage and Reid [1968] and from transient
Figure 7.22: Calculated temperature at $x = 5H$, $y = H/2$, as a function of the iteration number ($Re = 1$, $Gr = 10^4$ and $Ga = 1.0$).

numerical simulations by Evans and Greif [1989, 1991] and observed experimentally by Luijkx et al. [1981].

As in the above studies, flow instabilities in the present simulations were observed for $Gr > Gr_{cr,trans}(Re)$, with $Gr_{cr,trans}$ increasing with $Re$ and $Gr_{cr,trans}(Re) > Gr_{cr,long}$. Figure 7.24 shows that the values of $Gr_{cr,trans}(Re)$ are considerably larger in the present study than the values predicted by Gage and Reid [1968]. However, their criterion applies to a horizontal channel of infinite length. As was found by Evans and Greif [1989, 1991], wavelike flow instabilities may start to develop at large downstream positions for large Re. For $Re = 40$ and $Gr = 10^4$ for instance, flow instabilities were found for $x > 20H$ only. Since the length of the susceptor zone was only $10H$ in the present study, stable solutions may have been found for cases which, further downstream, might have become unstable. In addition, the pseudo time-dependent solution procedure may have a stabilizing effect, postponing the occurrence of flow instabilities to higher $Gr$ numbers.
Figure 7.23: Calculated temperatures at different stages of the iteration process ($Re = 1$, $Gr = 10^4$ and $Ga = 1.0$, see also fig. 7.22)
Figure 7.24: Unstabilities in the present flow simulations
for \( r_T = 0.01 \), \( \times = \text{unstable}, - = \text{stable} \),
compared to the stability criterion from Gage
and Reid (—).

7.7 INFLUENCE OF RECIRCULATING FLOWS ON MEMORY EFFECTS

The interest in return flows, as studied in the previous sections, is
motivated by their possible influence on memory effects, when switching from
one gas source to another. In this section the influence of return flows on
memory effects is studied through the time dependent solution of the
transient reactant species concentration equation. As an example the
deposition of GaAs from TMGa and arsine will be taken.

For \( t < 0 \), the process is running in steady-state. At \( t = 0 \) the TMGa
supply is switched off. Due to memory effects, the TMGa concentration in the
reactor will not be zero instantaneously and a finite amount of GaAs will be
deposited after the TMGa supply has been switched off. Starting from the
steady-state solution for the flow, temperature and species concentration
equations, the time-dependent TMGa concentration equation is solved for
\( t \geq 0 \). Since TMGa is highly diluted in the carrier gas and arsine is present
in large excess, it is assumed that the flow, the temperature and the arsine
concentration distribution in the reactor remain unchanged for \( t \geq 0 \). By
comparing the time dependent growth rate and the total deposition between
\( t = 0 \) and \( t \to \infty \) for different process conditions the influence of return
flows on the memory effects in the reactor is studied.
7.7.1 Numerical solution

The transient species concentration equation (eqs. 2.8, 2.18, 2.20 and 2.85) in 2-D cartesian form is discretized using the control volume method described in chapter 3. The time is discretized fully implicitly with a time step of $10^{-3}$ s. For the spatial discretization, a uniform $90 \times 30$ ($x \times y$) grid has been used. At an average gas velocity of 0.1 m/s and a reactor length of 0.4 m, the above combination of grid size and time step corresponds to a residence time of the gases in each grid cell of approximately 40 time steps. Within each time step, the concentration equation was solved iteratively using the line TDMA algorithm on vertical and horizontal grid lines, sweeping through the domain from inflow to outflow and from bottom to top wall respectively. For underrelaxation, a relaxation factor $\eta = 0.4$ was used. As convergence criteria the relative change from one iteration to the next in the calculated deposition rates ($< 10^{-5}$) and the residuals of the equation (absolute values, summed over the grid, normalized by the number of grid points and by the maximum concentration, $< 10^{-5}$) were used. Depending on the process conditions, 4-10 iterations per time-step were needed to fulfill these convergence criteria, taking 1.4 s CPU time per iteration on a HP 9000-835 minicomputer.

The accuracy of the spatial and temporal discretization used has been studied by comparing the results from the numerical model to the exact solution for a simplified situation for which an analytical solution can be found. For a plug flow with velocity $v_0$ in the x-direction and an initially zero species concentration, the time dependent species concentration $C(x,t)$ after a species inlet concentration $c_0$ at $x = 0$ has been switched on at $t = 0$, is described by the following differential equation with initial and boundary conditions in dimensionless form

$$\frac{\partial C(\xi, \tau)}{\partial \tau} = -Pe \frac{\partial C(\xi, \tau)}{\partial \xi} + \frac{\partial^2 C(\xi, \tau)}{\partial \xi^2}$$  \hspace{1cm} (7.26a)

$$\begin{align*}
\tau = 0: & \quad C(\xi, 0) = 0 \quad \forall \ \xi \\
\tau > 0: & \quad C(0, \tau) = 1 \quad \forall \ \tau > 0 \\
C(\infty, \tau) = 0 \quad \forall \ \tau > 0
\end{align*}$$  \hspace{1cm} (7.26b)

where $C = c/c_0$, $\xi = x/L$, $\tau =Dt/L^2$ and $Pe = v_0 L/\text{D}$, $\text{D}$ is the diffusion coefficient of the species in the carrier gas and $L$ is a characteristic length. The solution for $C(\xi, \tau)$ may be obtained by means of Laplace transformation [Breedveld, 1990], and is given by

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\[ C(\xi, \tau) = e^{\frac{\xi}{2Pe}} \left[ e^{-\frac{1}{4}Pe^2\tau} \text{erfc} \left( \frac{\xi}{2\sqrt{\tau}} \right) + \frac{1}{4}Pe^2 \int_0^{\tau} e^{-\frac{1}{4}Pe^2\tau'} \text{erfc} \left( \frac{\xi}{2\sqrt{\tau'}} \right) d\tau' \right] \] (7.27)

which can be evaluated numerically with great accuracy. Thus, the exact solution of the problem depends on the Pe number \( v_0L/D \) only. For common MOCVD processes, with \( D \approx 2 \times 10^{-4} \text{ m}^2/\text{s} \) and \( v_0 \approx 0.1 \text{ m/s} \) and taking \( L = 1 \text{ m} \), Pe is typically 500. We have compared the numerical solution of \( C(\xi, \tau) \) with the exact solution from eq. 7.27 for grid sizes \( 0.002 \text{ m} \leq \Delta x \leq 0.020 \text{ m} \), time steps \( 0.001 \text{ s} \leq \Delta t \leq 1 \text{ s} \) and \( 100 \leq \text{Pe} \leq 2000 \). The average error in the numerical solution, defined as the sum over all grid points of the absolute difference between the numerical and the exact solution at \( \tau = 0.2/\text{Pe} \), normalized by the number of grid points and by \( c_0 \), was found to decrease with decreasing grid size, decreasing time step and decreasing Pe number. For \( \Delta x = 0.0044 \text{ m} \) and \( \Delta t = 0.001 \text{ s} \) (as was used in the full 2-D simulations of the actual problems) the average error was found to be 0.2 \% for Pe = 100 and 1 \% for Pe = 2000.

The accuracy of the numerical solutions was further studied by evaluating the influence of grid size, time step and convergence criteria on the numerical solution for a representative realistic problem. A reduction by a factor 2 of the time step and of the grid size in both directions and

\[ -0.07 \text{ m/s} \]

\[ x=2.5 \text{ H} \quad x=0 \quad x=2.5 \text{ H} \]

**Figure 7.25:** Calculated steady-state flow velocities for different total pressures. (a) 35 kPa total pressure; (b) idem, \( g=0 \); (c) 10 kPa total pressure.
Figure 7.26(a): Calculated TMGa mole fractions ($\times 10^4$) at different times at 35 kPa total pressure

the use of more severe convergence criteria led to very small changes (< 1 %) in the calculated deposition rates.

7.7.2 Results

Figure 7.25a shows the calculated velocities in a 0.04 m high reactor at 35 kPa total pressure, 20 slm total flow per meter width (average inflow velocity 0.024 m/s), 973 K wafer temperature, and hydrogen carrier gas. When expressed in the dimensionless groups introduced in section 7.6.1, we have $Re = 1.5$, $Gr = 1650$ and $Ga = 1.1$. A strong flow recirculation is observed. In steady-state operation at $t < 0$, the inlet mole fractions of TMGa and
arsine are $5 \cdot 10^{-4}$ and $1 \cdot 10^{-2}$ respectively. At $t = 0$ the TMGa supply is switched off. Figure 7.26a shows the calculated TMGa concentrations as a function of time for $t \geq 0$. The memory effect caused by the recirculating flow can clearly be observed. It takes 10 s to reduce the TMGa concentration to $5 \cdot 10^{-5}$ everywhere in the reactor. Figure 7.27a shows the axial growth rate distributions for different $t \geq 0$. It takes roughly 10 s for the growth rate to decrease to one tenth of its steady-state value. The total thickness of the GaAs film that is grown after TMGa has been switched off is shown in figure 7.28 and corresponds to many atomic layers.

To evaluate the contribution of the recirculating flow to the memory effects, we have repeated the above simulations for identical process
Figure 7.26(c): Calculated TMGa mole fractions ($\times 10^4$) at different times at 10 kPa total pressure

conditions, artificially setting the gravity constant $g$ to zero. Thus, the recirculating flow vanishes completely (figure 7.25b). The time dependent TMGa concentrations and the growth rate distributions for different $t \geq 0$ are shown in figure 7.26b and 7.27b respectively. The absence of a recirculating flow has only a small effect on the rinsing time of the reactor and it still takes roughly 10 s to reduce the growth rate to one tenth of its steady-state value. Also, the influence of the recirculating flow on the total amount of GaAs deposited for $t \geq 0$ is relatively small, as can be seen in fig. 7.28. In fact, the presence of a recirculating flow causes a somewhat larger film thickness at small axial distances and a somewhat smaller film thickness at larger axial distances.

An effective way of reducing the memory effects in horizontal CVD
Figure 7.27: Axial growth rate distributions at different t ≥ 0. 
(a) 35 kPa total pressure; (b) idem, zero gravity; 
(c) 10 kPa total pressure.

Reactors is the reduction of the total pressure at fixed total flowrate and 
species flow rates. Thus, the Gr number is reduced, leading to a 
disappearance of recirculating flows, and more importantly, the average gas 
velocity is increased and the rinsing time is decreased, at virtually 
identical steady-state growth rates. Figure 7.25c shows the calculated 
velocities for the above process conditions, when the total pressure is 
reduced to 10 kPa. Figures 7.26c and 7.27c show the time dependent TMGa 
concentrations and the axial growth rate distributions for these conditions.
Figure 7.28: Total film growth for $t \geq 0$, for the three cases from figures 7.25-7.27.

It now only takes approximately 3 s to reduce the TMGa to below $5 \times 10^{-5}$ everywhere in the reactor and to reduce the growth rate to one tenth of its steady-state value. The total film thickness grown after $t = 0$ is shown in figure 7.28 and is significantly smaller than for the two cases at 35 kPa.

From the above examples and other transient simulations that are not discussed here, it may be concluded that memory effects in horizontal CVD reactors are mainly caused by the finite rinsing time of the reactor and that the contribution of recirculating flows to the total memory effect is relatively small for all common process conditions. A reduction of the total pressure at fixed reactant and carrier gas flow rates leads to reduced memory effects at similar steady-state growth rates.
Having arrived at the end of this thesis, we now look back at the primary aims of this study, as formulated in section 1.5, and we review and discuss the main conclusions.

8.1 Development of a CVD simulation model

It has been shown, that a mathematical simulation model for the detailed prediction of the gas flow, transport phenomena and chemical reactions in thermal CVD reactors can be formulated on basis of fundamental equations from fluid dynamics, physics and chemistry. In order to be generally applicable to different CVD processes, such a model should incorporate specific aspects which are not commonly encountered in chemical reactor models: The laminar flows of the multicomponent gas mixtures in CVD reactors necessitate the accurate evaluation of molecular transport properties, which depend on the temperature, pressure and composition of the gas mixture. In absence of experimental data, these properties may be calculated from the kinetic theory of gases. However, indications have been found for the fact that there may be relatively large errors in the predicted diffusion coefficients, leading to inaccuracies in the model predictions. Multicomponent ordinary diffusion can be modeled with the use of the Stefan-Maxwell equations, which can be written in a form consisting of a dominant gradient diffusion term and additional terms for non gradient multicomponent effects. This form allows for the incorporation of the Stefan-Maxwell equations in a standard numerical scheme for the solution of convection-diffusion transport equations. Thermal diffusion phenomena are very important in cold wall reactors. The calculation of multicomponent thermal diffusion coefficients from kinetic theory is extremely time consuming. The approximate methods which have been formulated for modeling multicomponent ordinary and thermal diffusion reduce the amount of computation needed and may lead to accurate results for certain processes. However, especially in the case of undiluted multicomponent mixtures of gases with very dissimilar molecular masses, the exact formulations are needed in order to obtain accurate predictions. The Dufour effect was found to be negligible for all processes studied. Special care must be taken of the treatment of the boundary conditions in the inflow of the reactor, in
order to prohibit species diffusion through the inflow opening, and at the reacting walls. The temperatures of the reactor walls can be calculated with the use of energy balance models, including wall conduction and convective and radiative heat exchange with the environment.

The general expressions for homogeneous and heterogeneous chemical reactions as formulated in this study allow for the flexible definition of reaction mechanisms and kinetics. However, the reaction pathways, reactive intermediates and rate constants cannot be obtained self-consistently from the present model and must be supplied separately.

The finite volume discretization method was found to be very well suited for the incorporation of all the above phenomena into a numerical simulation model. Special care had to be taken of the underrelaxation procedure in the iterative solution of species concentration equations which are dominated by gasphase reactions. The finite volume method in combination with the use of iterative solvers allows for the modeling of relatively complex two and three-dimensional systems on relatively small computers. Using the techniques developed in this study, the three dimensional simulation on $n \times 10^4$ grid points of complex CVD processes with $\sim 10$ gaseous species seems to be feasible on the present generation workstations.

8.2 Application and validation of the model

The developed CVD simulation model has successfully been applied to different CVD processes at largely varying process conditions in different reactor geometries. From the experimental validation of many model predictions it may be concluded that the present model accurately describes a wide range of thermal CVD processes. Laser Doppler velocity measurements indicated, that the model correctly predicts the isothermal laminar flow in the studied single-wafer reactor. Furthermore, the model correctly predicted the kinetically limited and the transport limited growth rates in tungsten LPCVD from tungstenhexafluoride and hydrogen in this reactor. Also, the use of the calculated tungstenhexafluoride surface concentrations as input for a feature scale model led to accurate step coverage predictions. The model predictions of the occurrence of return flows in the horizontal epitaxial reactor were in accordance with flow visualization experiments. The axial growth rate distributions for MOCVD of galliumarsenide were also predicted with good accuracy, whereas the discrepancies in the side wall temperature model, causing the incorrect prediction of lateral growth rate
distributions, have clearly been indicated. No experimental data are available for the evaluation of the simulation results for polysilicon deposition. However, it was shown that the model predictions are relatively insensitive to the assumed mechanisms and kinetics.

The broad applicability of a fundamental simulation model, as illustrated in this study, underlines the fact that the fundamental phenomena in all thermal CVD processes are basically the same and can be described very similarly.

8.3 Transport phenomena and chemical reactions in the studied CVD processes

The detailed simulation of the chemical reactions and transport phenomena in the studied CVD processes has led to a number of insights, which will briefly be reviewed here.

In polysilicon LPCVD from silane in a coldwall single-wafer reactor at conventional LPCVD conditions the growth rate is almost completely due to heterogeneous decomposition of silane. The reaction rate is relatively low and almost independent of the silane partial pressure. As a result, uniform growth rates can be obtained on large (0.20 m diameter) wafers. An increase of the wafer temperature appears to be the most suitable way for increasing the growth rate. An increase in the total pressure or the silane partial pressure leads to increased gasphase chemistry and decreased uniformity. However, the increased gasphase reactions may be used for the deposition of in situ phosphorus doped polysilicon, where phosphorus blocks the direct heterogeneous reaction pathways. The carrier gas influences the process qualities through its influence on gas flow and transport phenomena. The influence of the carrier gas on the chemistry is small.

In single-wafer tungsten LPCVD through the hydrogen reduction of tungstenhexafluoride the growth rate is normally determined by the heterogeneous reaction rate, which is independent of the tungstenhexafluoride partial pressure and very uniform. However, when the tungstenhexafluoride infow partial pressure is low, the deposition becomes transport limited and highly non-uniform. The critical tungstenhexafluoride inflow partial pressure for this transition depends on various process parameters and an approximate relation for its determination has been deduced. When the tungstenhexafluoride inflow pressure is below the critical value for transport limited growth, the concentration gradients in the
reactor are large, even though the total reactant conversion may be small. Even in the absence of transport limitations, ordinary and thermal diffusion effects may lead to relatively large concentration gradients. As a result, the tungstenhexafluoride concentration at the wafer surface, which influences the step coverage of the process, may deviate significantly from the inlet concentration. Preliminary simulations of the silane reduction of tungstenhexafluoride show, that the species concentrations at the wafer surface are also very different from the inlet concentrations under common process conditions. This obscures the results from kinetic experiments in which growth rates are related to inflow conditions, and may (partially) account for the conflicting kinetic results in literature.

The growth rates in the MOCVD of galliumarsenide from trimethylgallium and arsine in an atmospheric pressure horizontal reactor are highly determined by three dimensional mixed convection flows, especially for low width-to-height aspect ratio reactors and under high \( (> 2 \cdot 10^3) \) Grashof number flow conditions. The longitudinal flow rolls are very sensitive to the thermal conditions at the reactor side walls. In these walls a non linear temperature profile is adopted which is determined by conjugate heat transfer to the inside and outside of the reactor. For low aspect ratio, high Grashof number conditions, the longitudinal rolls are moving upward near the reactor sidewalls and downward in the reactor midplane at small axial distances. Further downstream, an inversion in the rotational direction of the rolls occurs. Both the axial and the lateral growth rate distributions are very sensitive to the behavior of the longitudinal rolls. Besides, the lateral growth rate distributions are strongly influenced by deposition on the side walls. At the leading edge of the susceptor recirculating flows occur with axes in the cross stream direction, when the mixed convection parameter Grashof/Reynolds\(^K\) exceeds a certain critical value. It was found that \( \kappa = 1 \) for small \((< 5)\), and \( \kappa = 2 \) for large Reynolds numbers. For very large Grashof numbers the flow becomes unstable, leading to time dependent, periodic, wavelike flow patterns. In contrast to what is often assumed, the influence of recirculating flows on memory effects in horizontal MOCVD reactors is small.

8.4 Reactor design and process optimization

Throughout this thesis, the simulation model has been used to evaluate various possibilities for the improvement of reactor geometries and for the
optimization of process conditions, with respect to different process demands.

For most common process conditions the thermal boundary layer above the susceptor in the studied single-wafer reactor is strongly non-uniform, as is the concentration boundary layer for transport limited deposition processes. The ideal uniform boundary layers are disturbed by edge effects, by the influence of the reactor walls and for certain process conditions by mixed convection flows. The shapes of the thermal and concentration boundary layers are very dissimilar, due to the different effects of the reactor walls. As a result, it is difficult to optimize the uniformity of both layers simultaneously. Nevertheless, uniform growth rates can be obtained on large wafers for the both the studied LPCVD processes.

Due to the relatively low heterogeneous reaction rate and its small dependence on the silane partial pressure, the growth rate in the polysilicon process is very uniform, as long as deposition is mainly determined by heterogeneous kinetics. For the studied process conditions (i.e. silane partial pressures between 10 and 100 Pa and total pressures between 100 and 1000 Pa), this is the case when the product of the total pressure and the silane partial pressure is much smaller than $10^4 \text{ Pa}^2$. Uniform polysilicon growth rates of $\sim 1000 \text{ Ång/min}$ are obtained at $\sim 100 \text{ Pa}$ total pressure, $\sim 10 \text{ Pa}$ silane partial pressure and $\sim 1000 \text{ K}$ wafer temperature. When gas phase reactions become important, i.e. at increased total pressure and silane partial pressure, the non uniformity of the thermal boundary layer causes non uniform deposition. This may be improved by a reduction of the height of the reactor and an increase of the susceptor diameter. When thus modified, 500 Ång/min in situ phosphorus doped polysilicon may be grown uniformly on 0.20 m diameter wafers at 1000 K wafer temperature, $\sim 1000 \text{ Pa}$ total pressure and $\sim 100 \text{ Pa}$ silane partial pressure.

Due to the zero order rate dependence in tungstenhexafluoride, very uniform tungsten growth rates are obtained in LPCVD from tungstenhexafluoride and hydrogen in the kinetically limited regime. In the transport limited regime, the growth becomes non uniform. A relation has been given for the critical tungstenhexafluoride inlet pressure for the transition from kinetically limited to transport limited growth. In order to eliminate transport limitations, an increase of the tungstenhexafluoride inlet mole fraction at fixed total flow is more effective than an increase of the total flow at fixed tungstenhexafluoride inlet concentration. In contrast to the growth rate, the step coverage of the kinetically limited
deposition process strongly depends on the tungstenhexafluoride partial pressure. With the use of the simulation model, optimized process conditions, combining a high and uniform growth rate and step coverage with a low use of tungstenhexafluoride, have been found. At \( \sim 1000 \) Pa total pressure, \( \sim 700 \) K wafer temperature, 50 sccm tungstenhexafluoride flow and 300 sccm total flow, a uniform growth rate of \( \sim 1500 \) Ång/min is obtained on 0.20 m diameter wafers, with a \( > 95 \% \) step coverage in 5:1 aspect ratio trenches. These process characteristics have been verified experimentally. An increase of the length of the inflow pipe further improves the step coverage of the process.

Our model simulations confirm earlier results from literature, that uniform axial growth rate distributions can be obtained in tapered horizontal MOCVD reactors. In order to reduce the sensitivity of the lateral growth rate distributions on the side wall temperatures and the side wall deposition, these walls should be cooled. For common MOCVD conditions recirculating flows at the leading edge of the susceptor are absent for Grashof/Reynolds \( < 100 \). The most effective way to reduce memory effects, which are mostly caused by the finite rinsing time of the reactor and only very little by flow recirculations, is a reduction of the pressure, at fixed flowrate, leading to increased gas velocities and decreased residence times at similar steady-state growth rates.

8.5 Final remarks

Due to the worldwide efforts by many researchers, there has been an impressive evolution in the development of numerical simulation models for CVD chemistry and hydrodynamics in the last ten years. At present, major progress is made in the integration of detailed chemistry models and multidimensional hydrodynamic models and in the application of these models for the study and optimization of realistic reactors and processes. In this thesis some contributions have been made to the latter development. The model that has been developed and tested in this study combines a full two or three dimensional hydrodynamics model with detailed models for multicomponent transport phenomena and multiple homogeneous and heterogeneous chemical reactions. Such models have now come to a point were they can be used successfully in reactor design and process optimization, as has been illustrated in this thesis.

Nevertheless, many important challenges remain for the near future. In
particular, the insufficient knowledge of the reaction pathways and kinetics in CVD processes is an important bottle-neck for the further evolution and application of CVD simulation models. As indicated in this thesis, diagnostic kinetic experiments should be performed together with numerical simulations of the transport phenomena, in order to accurately unravel the chemistry of the relevant CVD processes. The tendency to operate CVD processes at very low pressures necessitates the development of non-continuum models for the transport phenomena in CVD reactors. Finally, in order to actually contribute to the development of better processes and reactors, and to reduced costs for research and development, numerical CVD simulation models should become more easy accessible for non-expert engineers, working on the design and development of new reactors and processes. For this purpose, flexible and user friendly computer codes have to be further developed. This study has explored many of the aspects that should be included in such codes.
**PRINCIPAL SYMBOLS**

- \(A\) Pre-exponential factor in rate expressions for homogeneous chemical reactions (for units see table 5.1)
- \(c\) mole concentration (=P/RT for ideal gas), mole\cdot m^{-3}
- \(c_p\) specific heat of the gas mixture, J\cdot kg^{-1}\cdot K^{-1}
- \(D\) binary ordinary diffusion coefficient, m^2\cdot s^{-1}
- \(D'\) effective multicomponent diffusion coefficient, m^2\cdot s^{-1}
- \(D^{T}\) approximate multicomponent diffusion coefficient, m^2\cdot s^{-1}
- \(D^{K}\) multicomponent thermal diffusion coefficient, kg\cdot m^{-1}\cdot s^{-1}
- \(D^{k}\) Knudsen diffusion coefficient, m^2\cdot s^{-1}
- \(E\) activation energy for homogeneous reaction, kJ\cdot mole^{-1}
- \(E^{S}\) activation energy for surface reaction, kJ\cdot mole^{-1}
- \(f\) species mole fraction
- \(\mathcal{F}\) flux of molecules colliding with a surface, mole\cdot m^{-2}\cdot s^{-1}
- \(g\) gravity vector (\(g_z = -9.81\ m\cdot s^{-2}\))
- \(G^0\) standard Gibbs energy change of formation, kJ\cdot mole^{-1}
- \(\Delta G^0\) standard Gibbs energy change of reaction, kJ\cdot mole^{-1}
- \(H^0\) standard heat of formation, kJ\cdot mole^{-1}
- \(I\) unity tensor
- \(j\) diffusive mass flux vector, kg\cdot m^{-2}\cdot s^{-1}
- \(J\) diffusive mole flux vector, mole\cdot m^{-2}\cdot s^{-1}
- \(k^k\) forward reaction rate constant for the \(k^{th}\) homogeneous reaction, in m^3, mole and s, depending on the reaction order
- \(k^{-k}\) reverse reaction rate constant for the \(k^{th}\) homogeneous reaction, in m^3, mole and s, depending on the reaction order
- \(k^r\) reaction rate constant for heterogeneous reaction, in mole, m and s, depending on the order of the reaction
- \(K\) number of gas phase reactions
- \(K^k\) equilibrium constant for gasphase reaction number \(k\)
- \(L\) characteristic reactor dimension, m
- \(L_0\) initial depth of trench or contact hole, m
- \(L\) characteristic diffusion length, m
- \(m\) mole mass, kg\cdot mole^{-1}
- \(M\) number of different solid deposits
- \(M\) dimensionless mass transfer rate
- \(n\) unity vector normal to the inflow/outflow opening or wall
- \(N\) number of gaseous species in the mixture
P  pressure, Pa
\( P^0 \)  standard pressure = 1.013 \cdot 10^5 Pa
Q  volume flow rate at standard conditions, slm = standard liters per minute (1 slm = 6.813 \cdot 10^{-4} \text{mole} \cdot \text{s}^{-1} \) for an ideal gas
Q'  molar flowrate, mole \cdot \text{s}^{-1}
q'  heat flux, W \cdot m^{-2}
\( r, z \)  axisymmetric coordinates, m
R  universal gas constant = 8.314 J \cdot \text{mole}^{-1} \cdot \text{K}^{-1}
R_k  forward reaction rate of the \( k^{th} \) gasphase reaction, mole \cdot m^{-3} \cdot \text{s}^{-1}
R_{-k}  reverse reaction rate of the \( k^{th} \) gasphase reaction, mole \cdot m^{-3} \cdot \text{s}^{-1}
R_S  surface reaction rate, mole \cdot m^{-2} \cdot \text{s}^{-1}
S^0  standard entropy, J \cdot \text{mole}^{-1} \cdot \text{K}^{-1}
S  number of surface reactions
S_\phi  source term in general transport equation
[S]  density of free surface sites, m^{-2}
t  time, s
T  temperature, K
T^0  standard temperature = 298.15 K
T^*  reduced temperature = kT/\epsilon
\( \nabla \)  velocity vector, m \cdot \text{s}^{-1}
\langle \nabla \rangle  average molecular velocity = (8RT/\pi\epsilon)^{1/2}, m \cdot \text{s}^{-1}
V  reference gas velocity
W  trench width or contact hole radius, m
\( x, y, z \)  cartesian coordinates, m
\( \| x \| \)  = x for x \geq 0; = 0 for x < 0

**greek symbols**

\( \alpha_{\text{conv}} \)  convective heat transfer coefficient, W \cdot m^{-2} \cdot \text{K}^{-1}
\( \gamma \)  reactive sticking coefficient (RSC)
\( \Gamma_\phi \)  diffusion coefficient in general transport equation for \( \phi \)
\( \Delta x, \Delta y \)  grid size in x and y direction, m
\( \epsilon \)  radiative emissivity
\( \epsilon/k \)  ratio of maximum energy of attraction in Lennard-Jones interaction potential and the Boltzmann constant, K
\( \eta \)  relaxation factor
\( \phi \)  fraction of covered surface sites
\( \kappa \)  volume viscosity, kg \cdot m^{-1} \cdot \text{s}^{-1}
\( \kappa \) pressure coefficient in rate expressions for homogeneous chemical reactions (see table 5.1)

\( \lambda \) thermal conductivity of the gas mixture, \( W \cdot m^{-1} \cdot K^{-1} \)

\( \mu \) dynamic viscosity of the gas mixture, \( kg \cdot m^{-1} \cdot s^{-1} \)

\( \nu \) stoichiometric coefficient for gas phase reaction

\( \xi \) mean free path length, m

\( \xi_\phi \) factor in general transport equation for variable \( \phi \)

\( \rho \) density, \( kg \cdot m^{-3} \)

\( \sigma_B \) Stefan-Boltzman constant = \( 5.6703 \cdot 10^{-8} \) \( W \cdot m^{-2} \cdot K^{-4} \)

\( \sigma \) collision diameter in Lennard-Jones interaction potential, Ång

\( \sigma_i \) stoichiometric coefficient for surface reaction

\( \tau \) viscous stress tensor, \( N \cdot m^{-2} \)

\( \phi \) general variable

\( \chi \) stoichiometric coefficient for surface reaction

\( \omega \) species mass fraction

\( \psi \) streamfunction

\( \psi_g \) local equilibrium ratio for \( g \)th gas phase reaction

\( \Omega_\mu \) tabulated function of \( \tau^* \) for calculating \( \mu \) (see Appendix D)

\( \Omega_D \) tabulated function of \( \tau^* \) for calculating \( D \) (see Appendix D)

**subscripts**

\( a \) ambient

\( \text{bulk} \) in the bulk of the gas flow

\( i,j \) with respect to the \( i^{th}/j^{th} \) gas species

\( ij \) with respect to gas pair \( i-j \)

\( k \) with respect to the \( k^{th} \) gas phase reaction

\( \text{in} \) in the inflow of the reactor

\( n,s,e,w \) at the north, south, east or west wall of a grid cell

\( N,S,E,W \) in the North, South, East or West neighbour grid point

\( P \) in the grid point \( P \)

\( r,z \) in the \( r, z \) direction

\( \text{ref} \) at the reference temperature

\( s \) with respect to the \( s^{th} \) surface reaction

\( \text{wafer} \) at the wafer surface

\( \text{wall} \) at the wall of the reactor

\( x,y,z \) in the \( x, y, z \) direction
superscripts
0  at standard temperature and pressure
C  due to ordinary diffusion
(o  at the previous time step
T  due to thermal diffusion
†  transposed vector

dimensionless groups (see also table 4.1)
Arrh^G  gas-phase Arrhenius  Nu  Nusselt
Arrh^S  surface Arrhenius  Pr  Prandtl
Da^G    gas-phase Damköhler  Pe  Peclet
Da^S    surface Damköhler  Ra  Rayleigh
Ga      Gay-Lussac  Re  Reynolds
Gr      Grashof  Sc  Schmidt
Kn      Knudsen
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APPENDIX A

Transport equations in 3D cartesian \((x,y,z)\) and 2D cylindrical \((r,z)\) form

3D cartesian:

Continuity equation (eq. 2.2):

\[
\frac{\partial \rho}{\partial t} = - \left( \frac{\partial (\rho v_x)}{\partial x} + \frac{\partial (\rho v_y)}{\partial y} + \frac{\partial (\rho v_z)}{\partial z} \right) \tag{A.1}
\]

Navier-Stokes equations (eqs. 2.3 + 2.4):

\[
\frac{\partial}{\partial t}(\rho v_x) = - \frac{\partial}{\partial x}(\rho v_x v_x) - \frac{\partial}{\partial y}(\rho v_y v_x) - \frac{\partial}{\partial z}(\rho v_z v_x) \\
+ \frac{\partial}{\partial x}(\mu \frac{\partial v_x}{\partial x}) + \frac{\partial}{\partial y}(\mu \frac{\partial v_x}{\partial y}) + \frac{\partial}{\partial z}(\mu \frac{\partial v_x}{\partial z}) \\
+ \frac{\partial}{\partial x}(\mu \frac{\partial v_x}{\partial x}) + \frac{\partial}{\partial y}(\mu \frac{\partial v_x}{\partial y}) + \frac{\partial}{\partial z}(\mu \frac{\partial v_x}{\partial z}) \\
+ \frac{\partial}{\partial x}\left( \kappa - \frac{2}{3}\mu \right) \frac{\partial v_x}{\partial x} + \frac{\partial v_x}{\partial y} + \frac{\partial v_x}{\partial z} \right) - \frac{\partial P}{\partial x} + \rho g_x \tag{A.2a}
\]

\[
\frac{\partial}{\partial t}(\rho v_y) = - \frac{\partial}{\partial x}(\rho v_x v_y) - \frac{\partial}{\partial y}(\rho v_y v_y) - \frac{\partial}{\partial z}(\rho v_z v_y) \\
+ \frac{\partial}{\partial x}(\mu \frac{\partial v_y}{\partial x}) + \frac{\partial}{\partial y}(\mu \frac{\partial v_y}{\partial y}) + \frac{\partial}{\partial z}(\mu \frac{\partial v_y}{\partial z}) \\
+ \frac{\partial}{\partial x}(\mu \frac{\partial v_y}{\partial x}) + \frac{\partial}{\partial y}(\mu \frac{\partial v_y}{\partial y}) + \frac{\partial}{\partial z}(\mu \frac{\partial v_y}{\partial z}) \\
+ \frac{\partial}{\partial y}\left( \kappa - \frac{2}{3}\mu \right) \frac{\partial v_y}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_y}{\partial z} \right) - \frac{\partial P}{\partial y} + \rho g_y \tag{A.2b}
\]

\[
\frac{\partial}{\partial t}(\rho v_z) = - \frac{\partial}{\partial x}(\rho v_x v_z) - \frac{\partial}{\partial y}(\rho v_y v_z) - \frac{\partial}{\partial z}(\rho v_z v_z) \\
+ \frac{\partial}{\partial x}(\mu \frac{\partial v_z}{\partial x}) + \frac{\partial}{\partial y}(\mu \frac{\partial v_z}{\partial y}) + \frac{\partial}{\partial z}(\mu \frac{\partial v_z}{\partial z}) \\
+ \frac{\partial}{\partial x}(\mu \frac{\partial v_z}{\partial x}) + \frac{\partial}{\partial y}(\mu \frac{\partial v_z}{\partial y}) + \frac{\partial}{\partial z}(\mu \frac{\partial v_z}{\partial z}) \\
+ \frac{\partial}{\partial z}\left( \kappa - \frac{2}{3}\mu \right) \frac{\partial v_z}{\partial x} + \frac{\partial v_z}{\partial y} + \frac{\partial v_z}{\partial z} \right) - \frac{\partial P}{\partial z} + \rho g_z \tag{A.2c}
\]
Energy equation (eq. 2.5):

\[
c_p \frac{\partial}{\partial t}(\rho T) = -c_p \left( \frac{\partial}{\partial x}(\rho v_x T) + \frac{\partial}{\partial y}(\rho v_y T) + \frac{\partial}{\partial z}(\rho v_z T) \right)
+ \frac{\partial}{\partial x} \left( \lambda \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left( \lambda \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z} \left( \lambda \frac{\partial T}{\partial z} \right)
+ \frac{\partial}{\partial x} \left( RT \sum_{i=1}^{N} \frac{D_i^T}{m_i f_i} \frac{\partial f_i}{\partial x} \right) + \frac{\partial}{\partial y} \left( RT \sum_{i=1}^{N} \frac{D_i^T}{m_i f_i} \frac{\partial f_i}{\partial y} \right) + \frac{\partial}{\partial z} \left( RT \sum_{i=1}^{N} \frac{D_i^T}{m_i f_i} \frac{\partial f_i}{\partial z} \right) \tag{A.3}
\]

Species concentration equation:

Approximate method (eq. 2.31):

\[
\frac{\partial(\rho \omega_i)}{\partial t} = -\frac{\partial}{\partial x}(\rho v_x \omega_i) - \frac{\partial}{\partial y}(\rho v_y \omega_i) - \frac{\partial}{\partial z}(\rho v_z \omega_i)
+ \frac{\partial}{\partial x}(\rho D_i \frac{\partial \omega_i}{\partial x}) + \frac{\partial}{\partial y}(\rho D_i \frac{\partial \omega_i}{\partial y}) + \frac{\partial}{\partial z}(\rho D_i \frac{\partial \omega_i}{\partial z})
+ \frac{\partial}{\partial x} \left( \frac{D_i^T}{T} \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left( \frac{D_i^T}{T} \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z} \left( \frac{D_i^T}{T} \frac{\partial T}{\partial z} \right)
+ m_k \sum_{k=1}^{K} v_{ik} (R_k - R_{-k}) \tag{A.4}
\]

Stefan-Maxwell equations (eq. 2.32):

\[
\frac{\partial(\rho \omega_i)}{\partial t} = -\frac{\partial}{\partial x}(\rho v_x \omega_i) - \frac{\partial}{\partial y}(\rho v_y \omega_i) - \frac{\partial}{\partial z}(\rho v_z \omega_i)
+ \frac{\partial}{\partial x}(\rho D_i \frac{\partial \omega_i}{\partial x}) + \frac{\partial}{\partial y}(\rho D_i \frac{\partial \omega_i}{\partial y}) + \frac{\partial}{\partial z}(\rho D_i \frac{\partial \omega_i}{\partial z})
+ \frac{\partial}{\partial x} \left( \rho \frac{\omega_i D_i}{m} \frac{\partial m}{\partial x} \right) + \frac{\partial}{\partial y} \left( \rho \frac{\omega_i D_i}{m} \frac{\partial m}{\partial y} \right) + \frac{\partial}{\partial z} \left( \rho \frac{\omega_i D_i}{m} \frac{\partial m}{\partial z} \right)
- \frac{\partial}{\partial x} \left( m \omega_i D_i \sum_{j=1}^{N} \frac{j \omega_j D_j}{m_j D_j} \right) - \frac{\partial}{\partial y} \left( m \omega_i D_i \sum_{j=1}^{N} \frac{j \omega_j D_j}{m_j D_j} \right) - \frac{\partial}{\partial z} \left( m \omega_i D_i \sum_{j=1}^{N} \frac{j \omega_j D_j}{m_j D_j} \right)
+ m_k \sum_{k=1}^{K} v_{ik} (R_k - R_{-k}) \tag{A.5}
\]
2D cylindrical:

Continuity equation (eq. 2.2):

\[
\frac{\partial (\rho p)}{\partial t} = - \left( \frac{\partial (\rho p v_r)}{\partial r} + \frac{\partial (\rho p v_z)}{\partial z} \right) \tag{A.6}
\]

Navier–Stokes equations (eqs. 2.3+2.4):

\[
\frac{\partial (\rho p v_r)}{\partial t} = - \frac{\partial}{\partial r}(\rho p v_r v_r) - \frac{\partial}{\partial z}(\rho p v_r v_z) \\
+ \frac{\partial}{\partial r}(\rho \mu \frac{\partial v_r}{\partial r}) + \frac{\partial}{\partial z}(\rho \mu \frac{\partial v_r}{\partial z}) + \frac{\partial}{\partial r}(\rho \mu \frac{\partial v_z}{\partial r}) + \frac{\partial}{\partial z}(\rho \mu \frac{\partial v_z}{\partial z}) \\
+ \frac{\partial}{\partial r}(k - \frac{2}{3} \mu) \left( \frac{1}{r} \frac{\partial}{\partial r}(r v_r) + \frac{\partial v_z}{\partial z} \right) - \frac{2 \mu v_r}{r} - r \frac{\partial P}{\partial r} + r p g_r \tag{A.7a}
\]

\[
\frac{\partial (\rho p v_z)}{\partial t} = - \frac{\partial}{\partial r}(\rho p v_r v_z) - \frac{\partial}{\partial z}(\rho p v_z v_z) \\
+ \frac{\partial}{\partial r}(\rho \mu \frac{\partial v_z}{\partial r}) + \frac{\partial}{\partial z}(\rho \mu \frac{\partial v_z}{\partial z}) + \frac{\partial}{\partial r}(\rho \mu \frac{\partial v_z}{\partial r}) + \frac{\partial}{\partial z}(\rho \mu \frac{\partial v_z}{\partial z}) \\
+ \frac{\partial}{\partial z}(k - \frac{2}{3} \mu) \left( \frac{1}{r} \frac{\partial}{\partial r}(r v_r) + \frac{\partial v_z}{\partial z} \right) - r \frac{\partial P}{\partial z} + r p g_z \tag{A.7b}
\]

Energy equation (eq. 2.5):

\[
c p \frac{\partial}{\partial t}(\rho T) = -c_p \left( \frac{\partial}{\partial r}(\rho p v_r T) + \frac{\partial}{\partial z}(\rho p v_z T) \right) + \frac{\partial}{\partial r}(\lambda \rho \frac{\partial T}{\partial r}) + \frac{\partial}{\partial z}(\lambda \rho \frac{\partial T}{\partial z}) \\
+ \frac{\partial}{\partial r} \left( R T r \sum_{i=1}^{N} \sum_{k=1}^{m_i} \frac{D_i^T}{m_i} \frac{\partial f_i}{\partial r} \right) + \frac{\partial}{\partial z} \left( R T r \sum_{i=1}^{N} \sum_{k=1}^{m_i} \frac{D_i^T}{m_i} \frac{\partial f_i}{\partial z} \right) \tag{A.8}
\]

Species concentration equation:

Approximate method (eq. 2.31):

\[
\frac{\partial (\rho p \omega_i)}{\partial t} = - \frac{\partial}{\partial r}(\rho p v_r \omega_i) - \frac{\partial}{\partial z}(\rho p v_z \omega_i) \\
+ \frac{\partial}{\partial r}(\rho p D_i^T \frac{\partial \omega_i}{\partial r}) + \frac{\partial}{\partial z}(\rho p D_i^T \frac{\partial \omega_i}{\partial z}) \\
+ \frac{\partial}{\partial r} \left( \frac{D_i^T}{T} \frac{\partial T}{\partial r} \right) + \frac{\partial}{\partial z} \left( \frac{D_i^T}{T} \frac{\partial T}{\partial z} \right) \\
+ \kappa \sum_{k=1}^{K} \nu_{ik} (R_{ik} - R_{ik}) \tag{A.9}
\]

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Stefan–Maxwell equations (eq. 2.32):

\[
\frac{\partial (r \rho \omega_1)}{\partial t} = - \frac{\partial}{\partial r} (r \rho \nu_r \omega_1) - \frac{\partial}{\partial z} (r \rho \nu_z \omega_1)
\]

\[
+ \frac{\partial}{\partial r} (r \rho \Omega_1 \frac{\partial \omega_1}{\partial r}) + \frac{\partial}{\partial z} (r \rho \Omega_1 \frac{\partial \omega_1}{\partial z})
\]

\[
+ \frac{\partial}{\partial r} \left( \frac{r \rho \omega_1 \Omega_1 m_1}{m} \frac{\partial m_1}{\partial r} \right) + \frac{\partial}{\partial z} \left( \frac{r \rho \omega_1 \Omega_1 m_1}{m} \frac{\partial m_1}{\partial z} \right)
\]

\[
- \frac{\partial}{\partial r} \left( r m \omega_1 \sum_{j=1}^{N} j \frac{C_{j1}}{m_j D_{1j}} \right) - \frac{\partial}{\partial z} \left( r m \omega_1 \sum_{j=1}^{N} j \frac{C_{j1}}{m_j D_{1j}} \right)
\]

\[
+ \frac{\partial}{\partial r} \left( \frac{D_{1T}}{T} \frac{\partial T}{\partial r} \right) + \frac{\partial}{\partial z} \left( \frac{D_{1T}}{T} \frac{\partial T}{\partial z} \right)
\]

\[
K
\]

\[
+ r m_1 \sum_{k=1}^{K} \nu_{1k} (R_k - R_{-k})
\]

(A.10)
**APPENDIX B**

Thermodynamic properties of some CVD gases

- standard heat of formation $H_{298}^0$ [kJ.mole$^{-1}$] and
- standard entropy $S_{298}^0$ [J.mole$^{-1}$.K$^{-1}$]

<table>
<thead>
<tr>
<th>gas</th>
<th>$H_{298}^0$</th>
<th>$S_{298}^0$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>0</td>
<td>154.8</td>
<td>[Weast, 1984]</td>
</tr>
<tr>
<td>AsH$_3$</td>
<td>66.44</td>
<td>222.8</td>
<td>[Weast, 1984]</td>
</tr>
<tr>
<td>Ga(CH$_3$)$_3$</td>
<td>-45.5</td>
<td>368.0</td>
<td>[Kee et al., 1990]</td>
</tr>
<tr>
<td>H$_2$</td>
<td>0</td>
<td>130.7</td>
<td>[Coltrin et al., 1986]</td>
</tr>
<tr>
<td>HF</td>
<td>-271.1</td>
<td>173.8</td>
<td>[JANAF, 1985]</td>
</tr>
<tr>
<td>N$_2$</td>
<td>0</td>
<td>191.6</td>
<td>[Weast, 1984]</td>
</tr>
<tr>
<td>SiF$_4$</td>
<td>-1615</td>
<td>282.5</td>
<td>[Weast, 1984]</td>
</tr>
<tr>
<td>SiH$_2$</td>
<td>268.8</td>
<td>206.5</td>
<td>[Coltrin et al., 1989]</td>
</tr>
<tr>
<td>SiH$_4$</td>
<td>34.3</td>
<td>204.0</td>
<td>[Coltrin et al., 1986]</td>
</tr>
<tr>
<td>Si$_2$H$_4$</td>
<td>239.9</td>
<td>273.0</td>
<td>[Coltrin et al., 1986]</td>
</tr>
<tr>
<td>Si$_2$H$_6$</td>
<td>79.8</td>
<td>273.4</td>
<td>[Coltrin et al., 1986]</td>
</tr>
<tr>
<td>Si$_3$H$_8$</td>
<td>120.8</td>
<td>347.8</td>
<td>[Coltrin et al., 1986]</td>
</tr>
<tr>
<td>WF$_6$</td>
<td>-1722</td>
<td>341.1</td>
<td>[JANAF, 1985]</td>
</tr>
</tbody>
</table>

**c$_p$** [J.kg$^{-1}$.K$^{-1}$] = $a_0 + a_1 T + a_2 T^2$

<table>
<thead>
<tr>
<th>gas</th>
<th>$a_0$</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>5.20·10$^2$</td>
<td>0.00·10$^0$</td>
<td>0.00·10$^0$</td>
<td>[Svehla, 1962]</td>
</tr>
<tr>
<td>AsH$_3$</td>
<td>2.45·10$^2$</td>
<td>1.08·10$^0$</td>
<td>4.24·10$^{-4}$</td>
<td>[Svehla, 1962]</td>
</tr>
<tr>
<td>Ga(CH$_3$)$_3$</td>
<td>3.36·10$^2$</td>
<td>2.54·10$^0$</td>
<td>-9.27·10$^{-4}$</td>
<td>[Kee et al., 1990]</td>
</tr>
<tr>
<td>H$_2$</td>
<td>1.44·10$^4$</td>
<td>-2.61·10$^{-1}$</td>
<td>8.67·10$^{-4}$</td>
<td>[Svehla, 1962]</td>
</tr>
<tr>
<td>HF</td>
<td>1.48·10$^3$</td>
<td>-1.20·10$^{-1}$</td>
<td>1.47·10$^{-4}$</td>
<td>[Svehla, 1962]</td>
</tr>
<tr>
<td>N$_2$</td>
<td>1.03·10$^3$</td>
<td>4.58·10$^{-3}$</td>
<td>1.34·10$^{-4}$</td>
<td>[Svehla, 1962]</td>
</tr>
<tr>
<td>SiF$_4$</td>
<td>4.73·10$^2$</td>
<td>9.73·10$^{-1}$</td>
<td>-4.55·10$^{-4}$</td>
<td>[Svehla, 1962]</td>
</tr>
<tr>
<td>SiH$_2$</td>
<td>9.02·10$^2$</td>
<td>9.32·10$^{-1}$</td>
<td>-2.07·10$^{-4}$</td>
<td>[Coltrin et al., 1986]</td>
</tr>
<tr>
<td>SiH$_4$</td>
<td>4.74·10$^2$</td>
<td>3.26·10$^0$</td>
<td>-1.08·10$^{-3}$</td>
<td>[Coltrin et al., 1986]</td>
</tr>
<tr>
<td>Si$_2$H$_4$</td>
<td>5.83·10$^2$</td>
<td>2.24·10$^0$</td>
<td>-9.97·10$^{-4}$</td>
<td>[Coltrin et al., 1986]</td>
</tr>
<tr>
<td>Si$_2$H$_6$</td>
<td>3.44·10$^2$</td>
<td>3.57·10$^0$</td>
<td>-1.55·10$^{-3}$</td>
<td>[Coltrin et al., 1986]</td>
</tr>
<tr>
<td>Si$_3$H$_8$</td>
<td>3.71·10$^2$</td>
<td>3.44·10$^0$</td>
<td>-1.55·10$^{-3}$</td>
<td>[Coltrin et al., 1986]</td>
</tr>
<tr>
<td>WF$_6$</td>
<td>3.25·10$^2$</td>
<td>4.69·10$^{-1}$</td>
<td>-2.94·10$^{-4}$</td>
<td>[JANAF, 1985]</td>
</tr>
</tbody>
</table>
# Appendix C

Lennard-Jones parameters for some CVD gases

<table>
<thead>
<tr>
<th>gas</th>
<th>m (kg/mole)</th>
<th>σ (Å)</th>
<th>ε/k (K)</th>
<th>Reference for σ and ε/k</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>39.944</td>
<td>3.542</td>
<td>93.3</td>
<td>[Svehla, 1962]</td>
</tr>
<tr>
<td>AsH₃</td>
<td>77.95</td>
<td>4.145</td>
<td>259.8</td>
<td>[Holstein, 1988]</td>
</tr>
<tr>
<td>Ga(CH₃)₃</td>
<td>114.83</td>
<td>5.68</td>
<td>398</td>
<td>[Holstein, 1988]</td>
</tr>
<tr>
<td>H₂</td>
<td>2.016</td>
<td>2.827</td>
<td>59.7</td>
<td>[Svehla, 1962]</td>
</tr>
<tr>
<td>HF</td>
<td>20.01</td>
<td>3.138</td>
<td>330</td>
<td>[Svehla, 1962]</td>
</tr>
<tr>
<td>N₂</td>
<td>28.02</td>
<td>3.798</td>
<td>71.4</td>
<td>[Svehla, 1962]</td>
</tr>
<tr>
<td>SiF₄</td>
<td>104.09</td>
<td>4.880</td>
<td>171.9</td>
<td>[Svehla, 1962]</td>
</tr>
<tr>
<td>SiH₂</td>
<td>30.10</td>
<td>3.803</td>
<td>133.1</td>
<td>[Coltrin et al., 1986]</td>
</tr>
<tr>
<td>SiH₄</td>
<td>32.12</td>
<td>4.084</td>
<td>207.6</td>
<td>[Svehla, 1962]</td>
</tr>
<tr>
<td>Si₂H₄</td>
<td>60.21</td>
<td>4.601</td>
<td>312.6</td>
<td>[Coltrin et al., 1986]</td>
</tr>
<tr>
<td>Si₂H₆</td>
<td>62.23</td>
<td>4.828</td>
<td>301.3</td>
<td>[Coltrin et al., 1986]</td>
</tr>
<tr>
<td>Si₃H₈</td>
<td>92.33</td>
<td>5.562</td>
<td>331.2</td>
<td>[Coltrin et al., 1986]</td>
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<tr>
<td>WF₆</td>
<td>297.84</td>
<td>5.21</td>
<td>338</td>
<td>Estimated¹</td>
</tr>
</tbody>
</table>

¹ estimated from critical parameters [Bird et al., 1960, p. 22], using T_c = 443 K, T_b = 290.2 K, V_c = 227.9 cm³/mole, V_b = 86.83 cm³/mole, P_c = 42.7 bar [l’Air Liquide, 1976]
APPENDIX D
Polynomials for approximation of $\Omega_\mu(T^*)$, $\Omega_\nu(T^*)$, $A^*(T^*)$, $B^*(T^*)$ and $C^*(T^*)$ for calculating transport properties for the Lennard-Jones (6-12) potential.

All functions are approximated with third order polynomials

$$\phi = a_0 + a_1 T^* + a_2 (T^*)^2 + a_3 (T^*)^3$$

in the interval $0.3 \leq T^* \leq 30$.

<table>
<thead>
<tr>
<th>$\phi$</th>
<th>T* interval</th>
<th>a_0</th>
<th>a_1</th>
<th>a_2</th>
<th>a_3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Omega_\mu$</td>
<td>$0.3 \leq T^* &lt; 1$</td>
<td>$4.0384 \times 10^0$</td>
<td>$-5.2953 \times 10^0$</td>
<td>$4.0846 \times 10^0$</td>
<td>$-1.2414 \times 10^0$</td>
</tr>
<tr>
<td></td>
<td>$1 \leq T^* &lt; 3$</td>
<td>$2.7015 \times 10^0$</td>
<td>$-1.6152 \times 10^0$</td>
<td>$5.6831 \times 10^{-1}$</td>
<td>$-7.1633 \times 10^{-2}$</td>
</tr>
<tr>
<td></td>
<td>$3 \leq T^* &lt; 10$</td>
<td>$1.3824 \times 10^0$</td>
<td>$-1.6174 \times 10^{-1}$</td>
<td>$1.7603 \times 10^{-2}$</td>
<td>$-7.1058 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>$10 \leq T^* \leq 30$</td>
<td>$9.8307 \times 10^{-1}$</td>
<td>$-1.9520 \times 10^{-2}$</td>
<td>$4.4911 \times 10^{-4}$</td>
<td>$-3.8432 \times 10^{-6}$</td>
</tr>
<tr>
<td>$\Omega_\nu$</td>
<td>$0.3 \leq T^* &lt; 1$</td>
<td>$4.2639 \times 10^0$</td>
<td>$-7.1400 \times 10^0$</td>
<td>$6.6722 \times 10^0$</td>
<td>$-2.3599 \times 10^0$</td>
</tr>
<tr>
<td></td>
<td>$1 \leq T^* &lt; 3$</td>
<td>$2.4130 \times 10^0$</td>
<td>$-1.4086 \times 10^0$</td>
<td>$4.9307 \times 10^{-1}$</td>
<td>$-6.2149 \times 10^{-2}$</td>
</tr>
<tr>
<td></td>
<td>$3 \leq T^* &lt; 10$</td>
<td>$1.2729 \times 10^0$</td>
<td>$-1.5195 \times 10^{-1}$</td>
<td>$1.6376 \times 10^{-2}$</td>
<td>$-6.4903 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>$10 \leq T^* \leq 30$</td>
<td>$8.9722 \times 10^{-1}$</td>
<td>$-1.9064 \times 10^{-2}$</td>
<td>$4.4207 \times 10^{-4}$</td>
<td>$-3.7962 \times 10^{-6}$</td>
</tr>
<tr>
<td>$A^*$</td>
<td>$0.3 \leq T^* &lt; 1$</td>
<td>$8.7140 \times 10^{-1}$</td>
<td>$8.5547 \times 10^{-1}$</td>
<td>$1.0310 \times 10^0$</td>
<td>$4.0751 \times 10^{-1}$</td>
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<td>$-3.1927 \times 10^{-2}$</td>
<td>$9.6617 \times 10^{-3}$</td>
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<td>$-1.2018 \times 10^{-2}$</td>
<td>$1.2583 \times 10^{-3}$</td>
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<td>$1.0950 \times 10^0$</td>
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<td>$0.0000 \times 10^0$</td>
<td>$0.0000 \times 10^0$</td>
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<td>$0.3 \leq T^* &lt; 1$</td>
<td>$9.4008 \times 10^{-1}$</td>
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<td>$5.5896 \times 10^{-1}$</td>
<td>$-2.0409 \times 10^{-1}$</td>
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<td>$7.6201 \times 10^{-1}$</td>
<td>$9.0169 \times 10^{-2}$</td>
<td>$-1.6830 \times 10^{-2}$</td>
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APPENDIX E

Equations for calculating the binary thermal diffusion ratio $\kappa_{12}$ for the Lennard-Jones (6-12) potential function.
(see Hirschfelder et al., 1967, pp. 534-541)

\[ \kappa_{12} = \frac{f_1 f_2}{6 \lambda_{12}} \frac{S^{(1)} f_1 - S^{(2)} f_2}{X_\lambda^* + Y_\lambda^*} \left( 6C^* - 5 \right) \]  \hspace{1cm} (E.1)

with $\kappa_{12}$ the binary thermal diffusion ratio, $f_1$ and $f_2$ the mole fractions of species 1 and 2 and

\[ S^{(1)} = \frac{m_1 + m_2}{2 m_2} \frac{\lambda_{12}}{\lambda_1} - \frac{15}{4 A_{12}^*} \left( \frac{m_2 - m_1}{2 m_1} \right) - 1 \]  \hspace{1cm} (E.2)

\[ S^{(2)} = \frac{m_1 + m_2}{2 m_1} \frac{\lambda_{12}}{\lambda_2} - \frac{15}{4 A_{12}^*} \left( \frac{m_1 - m_2}{2 m_2} \right) - 1 \]  \hspace{1cm} (E.3)

\[ \lambda_{12} = 0.0831 \left( \frac{T/m_1}{\mu_1} \right)^{1/2} \frac{\sigma^2 \Omega}{A_{12}} \Omega \left( T^* \right) \]  \hspace{1cm} (E.4)

\[ \lambda_1 = 0.0831 \frac{(T/m_1)^{1/2}}{\sigma^2 \Omega \left( T^* \right)} \]  \hspace{1cm} (E.5)

and similar for $\lambda_2$

\[ X_\lambda = \frac{f_1^2}{\lambda_1^*} + \frac{2 f_1 f_2}{\lambda_{12}^*} + \frac{f_2^2}{\lambda_2^*} \]  \hspace{1cm} (E.6)

\[ Y_\lambda = \frac{f_1^2}{\lambda_1^*} U^{(1)} + \frac{2 f_1 f_2}{\lambda_{12}^*} U^{(Y)} + \frac{f_2^2}{\lambda_2^*} U^{(2)} \]  \hspace{1cm} (E.7)

\[ U^{(1)} = \frac{4}{15 A_{12}^*} \frac{1}{12} \left( \frac{12 B_{12}^*}{5} - 1 \right) m_1 \frac{m_1 - m_2}{m_2} - \frac{1}{2} \frac{(m_1 - m_2)^2}{m_1 m_2} \]  \hspace{1cm} (E.8)

\[ U^{(2)} = \frac{4}{15 A_{12}^*} \frac{1}{12} \left( \frac{12 B_{12}^*}{5} - 1 \right) m_2 \frac{m_2 - m_1}{m_1} + \frac{1}{2} \frac{(m_2 - m_1)^2}{m_1 m_2} \]  \hspace{1cm} (E.9)

\[ U^{(Y)} = \frac{4}{15 A_{12}^*} \frac{(m_1 + m_2)^2}{4 m_1 m_2} \frac{\lambda_{12}^2}{\lambda_1 \lambda_2} - \frac{1}{12} \left( \frac{12 B_{12}^*}{5} - 1 \right) \frac{5}{32 A_{12}^*} \frac{12 B_{12}^*}{5} - 5 \]  \hspace{1cm} (m_2 - m_1)^2 \]  \hspace{1cm} (E.10)

A_{12}^*, B_{12}^* and C_{12}^* are tabulated functions of T_{12}^* [Hirschfelder et al., 1967, pp. 1128-1129]. Polynomials for approximating these functions can be found in Appendix D.

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APPENDIX F

Equations for calculating the multicomponent thermal diffusion coefficient $D_k^T$ for species $k$ in an $N$ component gas mixture for the Lennard-Jones (6-12) potential function.
(see Hirschfelder et al, 1967, pp.538-543)

\[
D_k^T = -\frac{8m_k}{5R} f_1 \delta_{ik} \cdots f_N \delta_{nk} 0 \cdots 0 0
\]

with $D_k^T$ the multicomponent thermal diffusion coefficient of species $k$ in an $N$ component gas mixture, $m_k$ the mole mass of species $k$, $R$ the universal gas constant, $f_i$ the mole fraction of species $i$, $\delta_{ij}$ the Kronecker delta function and
\[ L_{11}^{oo} = 0 \] (F.2)

\[ L_{ij}^{oo} = \frac{2 f_i f_j}{A_{1j} \lambda_{1j}} + \sum_{n=1}^{\infty} \frac{2 f_i f_n m_j}{m_1 A_{1n} \lambda_{1n}} \] (1\#j) (F.3)

\[ L_{11}^{01} = 5 \sum_{n=1}^{\infty} \frac{f_i f_n m_n (\delta_{C_{1n}} - 1)}{(m_1 + m_n) A_{1n} \lambda_{1n}} \] (F.4)

\[ L_{ij}^{01} = -5 \frac{f_i f_j m_j (\delta_{C_{1j}} - 1)}{(m_1 + m_j) A_{1j} \lambda_{1j}} \] (1\#j) (F.5)

\[ L_{1i}^{10} = \frac{m_j}{m_1} L_{1j}^{01} \] (F.6)

\[ L_{11}^{11} = -\frac{4 f_1^2}{\lambda_1} - \sum_{n=1}^{\infty} \frac{2 f_1 f_1 \left( \frac{15}{2} m_1^2 + \frac{25}{4} m_2^2 - 3 m_1 m_2 + 4 m_1 m_n A_{1n}^* \right)}{(m_1 + m_n)^2 A_{1n} \lambda_{1n}} \] (F.7)

\[ L_{1j}^{11} = \frac{2 f_1 f_j m_j}{(m_1 + m_j)^2 A_{1j} \lambda_{1j}} \left( \frac{55}{4} - 3 B_{1j}^* - 4 A_{1j}^* \right) \] (1\#j) (F.8)

\[ A_{1j}^*, B_{1j}^*, C_{1j}^* \text{ and } A_{1n}^*, B_{1n}^*, C_{1n}^* \text{ are tabulated functions of } T_{1j}^* \text{ and } T_{1n}^* \text{ [Hirschfelder et al., 1967, pp. 1128-1129]. Polynomials for approximating these functions can be found in Appendix D. Expressions for } \lambda_1, \lambda_j \text{ and } \lambda_{ij} \text{ can be found in Appendix E.} \]
SUMMARY

A mathematical model has been developed for the prediction of the laminar gas flow, transport phenomena and chemical reactions in Chemical Vapor Deposition (CVD) reactors for the growth of thin solid films. The model is based on the fundamental transport equations for mass, momentum, heat and chemical species. The transport properties of the gas mixture as a function of temperature, pressure and mixture composition are evaluated from the kinetic theory of gases. Multi-component ordinary diffusion phenomena are described by means of the Stefan-Maxwell equations. The model includes thermal diffusion (Soret) and diffusion-thermo (Dufour) effects. As an alternative to the exact formulations, approximate methods for multi-component (thermal) diffusion have also been included. The model accounts for the formation and destruction of gaseous species due to multiple surface and gasphase reactions. Submodels have been added for the calculation of reactor wall temperatures.

Numerical techniques, based on the finite volume discretization method, have been adapted and computer codes have been developed for the numerical solution of the model equations in 2D axisymmetric or 3D cartesian form. The numerical solution procedure includes the iterative inversion of the Stefan-Maxwell equations, special treatments of reacting boundaries and of the inflow boundaries in low Reynolds number flows, and relaxation techniques for solving source-term dominated transport equations. The chemical reaction pathways and rate constants may be specified separately. The number of reactive species and homogeneous and heterogeneous reactions is unlimited, although in practice limitations may occur due to computer limitations.

The influence of the Soret and Dufour effects and the accuracy of the approximate approaches for multicomponent diffusion have been evaluated for different processes. The neglect of thermal diffusion in coldwall reactors generally leads to large errors, whereas the influence of the Dufour effect is negligible. The approximate methods for describing multicomponent diffusion reduce the computational effort and may lead to accurate results for particular process conditions. However, in general the full treatment is needed in order to obtain accurate predictions.

The model is used to study several aspects of different processes in two reactor configurations. The axisymmetric hydrodynamics and chemical reactions in a coldwall single-wafer reactor of the vertical impinging jet type have been studied for three different low pressure CVD processes:

First, general insights in the transport phenomena in this reactor have been obtained from the study of a hypothetical process with a single, highly diluted reactant, negligible gasphase reactions and fast heterogeneous deposition kinetics. The gas flow is determined by its Grashof and Reynolds number. Buoyancy induced recirculating flows occur for Reynolds < 3 and Grashof/Reynolds > 30. The inversion of the reactor orientation does not lead to a suppression of buoyancy effects. For Re > 5 recirculating flows appear which are caused by inertial effects. For particular combinations of Reynolds and Grashof multiple stable flow solutions were obtained. Laser Doppler flow velocity measurements in an isothermal scale model of the reactor were in good agreement with results from the simulation model. The uniformities of the heat and mass transfer to the susceptor surface are also determined by the Reynolds and Grashof numbers and are virtually independent of the process conditions for low Reynolds (< 1) and Grashof (< 30) numbers. The uniformity of the heat and mass transfer are very dissimilar and cannot easily be optimized simultaneously.

Secondly, a comprehensive simulation study has been made of the single-wafer low pressure deposition of polysilicon from silane. In this process, the deposition is determined by multiple homogeneous and heterogeneous
reactions. The used chemistry model included five gaseous and five surface reactions. Expressions for the pressure fall-off behavior of the homogeneous rate constants and for the heterogeneous sticking coefficients of silane and disilane have been formulated. Starting from conventional polysilicon LPCVD conditions the deposition rate and uniformity have been studied for varying susceptor temperatures, silane partial pressures, total pressures, and carrier gases. For standard process conditions, gaseous reaction rates were found to be negligible and an excellent uniformity was obtained on a 0.24 m diameter deposition area. An increased temperature led to increased growth rates and still relatively unimportant gaseous chemistry. An increased total pressure or silane partial pressure caused an increase of the gaseous chemistry and a reduced uniformity. The carrier gas was found to influence the growth rates through its influence on the transport phenomena, but the effect of using hydrogen instead of inert helium was found to be small. Suggestions for reactor and process optimization have been made in order to obtain high and uniform growth rates of in situ phosphorus doped poly-

silicon on large wafers. The model predictions were relatively insensitive to the assumed reaction mechanisms and rate constants.

Thirdly, a study has been made of the deposition of tungsten from tungstenhexafluoride and hydrogen or silane. In these processes, the film properties are mainly determined by heterogeneous reactions and transport phenomena in the gaseous phase. It is shown, that transport phenomena cause large concentration gradients in the gas mixture, even at low reactant conversions, and that the process conditions at the wafer surface may be very dissimilar from the inflow conditions. A criterion is deduced for "gradientless" reactor operation. The predicted growth rate in the hydrogen reduction process becomes transport limited at low tungstenhexafluoride inflow concentrations, leading to a growth rate which is linearly proportional to the tungstenhexafluoride inflow pressure and inversely proportional to the total pressure. These model predictions were confirmed by experimental results obtained at the University of Twente. The predicted tungstenhexafluoride surface concentrations were used as input for a step coverage model and the combined models were used to optimize a blanket tungsten feature filling process. The predicted step coverages were in good agreement with experimental results and the properties of the optimized process, combining a high and uniform deposition rate and step coverage with a low use of tungstenhexafluoride, have been verified experimentally. It is shown, that the neglect of the influence of transport phenomena may be a cause for the apparent contradictions in literature on the kinetics of the tungstenhexafluoride/silane process.

Besides from these low pressure processes in a vertical single-wafer reactor, the transport phenomena in a horizontal atmospheric pressure reactor have been studied. Two and three-dimensional simulations were performed for a wide range of process conditions. The deposition was assumed to be due to a single, fast heterogeneous reaction. The three-dimensional model included a detailed model for the calculation of the reactor side wall temperatures. The predicted growth rates for Metal Organic CVD of gallium arsenide from trimethylgallium and arsine were compared to experimental data from literature. The two-dimensional model accurately predicted axial growth rate distributions in large and medium width-to-height aspect ratio reactors at low Grashof number conditions. In small aspect ratio reactors and at high Grashof number conditions, the growth was found to be influenced by three-
dimensional flows, which were very sensitive to the side wall thermal boundary conditions. Using the side wall temperature model, an accurate prediction of axial growth rate distributions was obtained, but the lateral growth rate distributions could not be predicted accurately. The occurrence of buoyancy induced flow recirculations at the leading edge of the heated
susceptor was studied through two-dimensional flow simulations. Recirculating flows were found to occur when the mixed convection parameter $\text{Gr}/\text{Re}^\kappa$ exceeded a certain critical value, with $\kappa = 1$ for small Re and $\kappa = 2$ for large Re. The flow behavior depended only slightly on the susceptor temperature, at fixed Re and Gr. These results were confirmed by flow visualization experiments, performed at the Catholic University of Nijmegen.

From the solution of the transient species concentration equation it was concluded, that memory effects are mainly caused by the finite rinsing time of the reactor and that the influence of return flows on memory effects is small. The best way to suppress memory effects is to reduce the total pressure at fixed total flowrate.

From these studies of the transport phenomena and chemical reactions in a number of highly dissimilar thermal CVD processes in different reactors by means of basically the same simulation model, and from the experimental validation of many model predictions, it is concluded that the fundamentals of a wide range of processes can be described by the same basic equations. The use of simulation models in the interpretation of experimental data and in the optimization of process conditions and reactor geometry has been illustrated in various ways. It is concluded, that the most important bottle-neck in CVD modeling at present is the insufficient knowledge of the chemical reaction mechanisms and rate constants, and that diagnostic experiments in well defined reactor configurations in combination with model simulation studies may provide this knowledge.
SAMENVATTING

In deze studie werd een mathematisch model ontwikkeld voor de beschrijving van de laminair gasstroom, de transportverschijnselen en de chemische reacties in Chemical Vapor Deposition (CVD) reactoren voor de groei van dunne vaste films. Het model is gebaseerd op de fundamentele transportvergelijkingen voor massa, impuls, warmte en chemische stof. De transportcoëfficiënten van het gasmengsel als functie van druk, temperatuur en samenstelling, worden berekend met behulp van de kinetische gastheorie. Voor de beschrijving van de concentratie diffusie wordt gebruik gemaakt van de Stefan-Maxwell vergelijkingen. Ook thermodiffusie (Soret effect) en diffusie-thermo (Dufour effect) verschijnselen zijn in het model opgenomen. Naast de exacte beschrijving voor meer-componenten (thermo) diffusie zijn vereenvoudigde benaderende methoden gemodelléerd. De modelvergelijkingen bevatten tevens de vorming en destructie van gasvormige componenten ten gevolge van heterogene en homogene chemische reacties. Tenslotte zijn submodellen ontwikkeld voor de berekening van reactorwandtemperaturen.

Voor het oplossen van de modelvergelijkingen in 2D axisymmetrische en 3D cartesische vorm zijn numerieke technieken en computer codes ontwikkeld, gebaseerd op de eindige volume discretisatie methode. De numerieke oplosmethode omvat de iteratieve inversie van de Stefan-Maxwell vergelijkingen, een speciale behandeling de randvoorwaarden op reagerende wanden en van de randvoorwaarden in de instroom voor stromingen met lage Reynolds getallen. De onderrelaxatie van de iteratieve oplosmethode werd geschikt gemaakt voor het oplossen van transportvergelijkingen welke sterk worden bepaald door brontermen. Het aantal reactanten en chemische reacties is in principe onbeperkt, doch wordt in de praktijk gelimiteerd door de beschikbare computerfaciliteiten.

De invloed van het Soret en Dufour effect zijn bestudeerd voor verschillende CVD processen. Het Dufour effect kan in de regel worden verwaarloosd, maar het Soret effect heeft een grote invloed op de transportverschijnselen in koude wand reactoren. De benaderende beschrijvingen voor meer componenten (thermo) diffusie leiden tot een aanzienlijke vermindering van de benodigde hoeveelheid rekenwerk en leiden voor een aantal processen tot nauwkeurige resultaten. In het algemeen is echter de exacte beschrijving noodzakelijk om te komen tot nauwkeurige voorspellingen.

Het model is gebruikt in de bestudering van uiteenlopende CVD processen in verschillende reactoren. De transportverschijnselen en chemische reacties in een vertikale, axisymmetrische koude wand enkelspits lage druk reactor zijn bestudeerd voor drie verschillende processen:

Ten eerste is, ter verkrijging van algemene inzichten in de transportverschijnselen in deze reactor, een studie gemaakt van een hypothetisch proces waarbij één enkele, sterk verdunde reactant wordt gedeponeerd ten gevolge van een snelle oppervlakte reactie, terwijl gasfase reacties verwaarloosbaar zijn. De gasstroom in de reactor bleek volledig te worden bepaald door de dimensieloze Grashof en Reynolds getallen. Door dichtheidsverschillen veroorzaakte recirculerende stromingen traden op voor Reynolds < 3 en Grashof/Reynolds > 30. Het omkeren van de reactor leidde niet tot onderdrukking van deze verschijnselen. Voor Reynolds > 5 traden stromingsrecirculaties op welke worden veroorzaakt door traagheids effecten. Bepaalde combinaties van Reynolds en Grashof leidden tot meervoudige stabiele oplossingen van de stromingsvergelijkingen. Laser Doppler snelheidsmetingen in een isotherm schaalmodel van de reactor waren in goede overeenstemming met de modellsimulaties. De uniformiteit van de warmte en stofoverdracht naar de verhitte susceptor wordt eveneens volledig bepaald door de Reynolds en Grashof getallen. Voor lage Reynolds (< 1) and Grashof (< 30) bleek deze uniformiteit vrijwel onafhankelijk van de stromings-
condities. De thermische en concentratie grenslagen zijn zeer verschillend van vormen het bleek zeer gecompliceerd om de uniformiteit van beide gelijktijdig te optimaliseren.

Vervolgens is een volledige simulatiestudie verricht van de depositie van polysilicium uit silaan in een enkelplaks lage druk reactor. De depositie wordt bepaald door meervoudige oppervlakte en gasfase reacties. In de modelstudie werden vijf homogene en vijf heterogene reacties meegenomen. Er werden modellen geformuleerd voor de lage druk gasfase reactiesnelheidsconstanten en voor de reactieve plakkans van silaan en disilaan op silicium. Uitgaande van standaard polysilicium LPCVD procescondities werden de depositiesnelheid en -uniformiteit bestudeerd voor variërende susceptor-temperaturen, totale drukken, silaan partieeldrukken en draaggassen. Onder standaard procescondities bleken de gasfase reacties verwaarloosbaar en de depositie op de 0.24 m diameter susceptor zeer uniform. Een verhoging van susceoptortemperatuur leidde tot een sterke toename van de groeisnelheid, terwijl de relatieve invloed van gasfase reacties gering bleef en de uniformiteit hoog. Een verhoging van de silaan partieeldruk of de totaaldruk leidde tot een toename van de gasfase reacties en een verminderde uniformiteit. Het gebruikte draaggas bleek een grote invloed op de depositie te hebben vanwege de invloed op de transportverschijnselen. Het gebruik van waterstof in plaats van inert helium had echter een geringe invloed. Met behulp van het simulatiemodel zijn mogelijkheden onderzocht voor de optimalisatie van de procescondities en de reactorgeometrie, teneinde uniforme in situ fosfor gedoteerde polysilicium lagen met een hoge groeisnelheid te kunnen deponeren op grote wafers. De modelvoorspellingen waren relatief ongevoelig zijn voor variaties in de reactiesnelheidsconstanten en -mechanismen.


Naast deze lage druk processen in een axisymmetrische enkelplaksreactor is ook een studie verricht naar de transportverschijnselen in een horizontale atmosferische drum reactor. Twee- en driedimensionale simulaties zijn uitgevoer voor uiteenlopende procescondities, waarbij werd aangenomen
dat de depositie wordt bepaald door een enkelvoudige snelle oppervlakte-reactie. Bij de driedimensionale simulaties werd gebruik gemaakt van een gedetailleerd model voor de berekening van de temperaturen van de reactor zijwanden. De voorspelde groeisnelheden voor de depositie van gallium-arsenide uit trimethylgallium en arsine zijn vergeleken met experimentele resultaten uit de literatuur. Voor stromingscondities bij lage Grashof getallen in reactoren met een grote of middelgrote breedte-hoogte verhouding levert het twee-dimensionale model nauwkeurige voorspellingen op van de axiale groeisnelheidsverdeling. Bij kleine breedte-hoogte verhoudingen of grote Grashof getallen hebben driedimensionale gemengd convectieve stromingen een grote invloed op de groeisnelheid. Deze stromingen zijn zeer gevoelig voor de thermische condities op de reactor zijwanden. Met behulp van het zijwand temperatuurmodel konden deze redelijk nauwkeurig worden berekend, hetgeen leidde tot een accurate voorspelling van de axiale groei-

snelheidsverdelingen. De laterale groeisnelheidsverdelingen konden niet nauwkeurig worden voorspeld. Het optreden van recirculerende stromingen aan het begin van de verhitte susceptor is bestudeerd met behulp van twee-
dimensionale stromingssimulaties. Recirculaties bleken op te treden wanneer de gemengde convectie parameter $\text{Gr}/\text{Re}^k$ groter werd dan een bepaalde criticale waarde. Hierbij is $k = 1$ voor lage Reynolds en $k = 2$ voor hoge Reynoldsgetallen. Het stromingsgedrag hangt in geringe mate af van de susceptortemperatuur, bij gegeven Re en Gr. Deze resultaten zijn bevestigd door stromingsvisualisaties experimenten verricht aan de Katholieke Universiteit Nijmegen. De invloed van stromingsrecirculaties op geheugeneffecten in horizontale CVD reactoren is onderzocht door het oplossen van de transiente concentratievergelijking. Deze invloed bleek slechts gering. Daarentegen worden de geheugeneffecten voornamelijk beïnvloed door de eindige spoeltijd van de reactorgassen. De aangewezen manier om geheugeneffecten te verminderen bleek een verlaging van de druk te zijn, bij gelijk-

blijvend gasdebit.

Uit deze studies naar de transportverschijnselen en chemische reacties in uiteenlopende thermische CVD processen in verschillende reactoren, met behulp van in essentie één en hetzelfde simuliemodel, en uit de experimentele bevestiging van vele modelvoorspellingen, kan worden geconcludeerd dat de fundamentele verschijnselen in deze CVD processen kunnen worden beschreven met behulp van dezelfde basisvergelijkingen. Het gebruik van simuliemodellen bij de interpretatie van experimentele data en in de optimalisatie van procescondities en reactor-ontwerpen is op diverse manieren geïlustreerd. Geconcludeerd wordt, dat de onvoldoende kennis van de reactiemechanismen in CVD processen momenteel de belangrijkste belemmering vormt voor de volledige simulatie van CVD processen. Zorgvuldige diagnostische experimenten in goed gedefinieerde reactoren, in combinatie met modelsimulaties, kunnen bijdragen tot een vermeerdering van deze kennis.
EPILOGUE

In the sometimes lonely task of preparing this thesis, it was good to experience the help and support of many people. Here, I want express my deep gratitude to all those people who contributed to the final result.

At first, I owe many thanks to Professor C.J. Hoogendoorn for his guidance and support during the past five years of research, and for his useful criticism on the draft versions of this thesis. It is good to learn the art of scientific research from a true artist.

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CURRICULUM VITAE

Christiaan Rudolf Kleijn was born on 18 November 1960 in Voorburg, The Netherlands. In 1979 he got his Gymnasium B diploma at the "St. Maartenscollege" in Voorburg. From 1979 to 1986 he studied Applied Physics at the Delft University of Technology in the Netherlands. The final phase of the study took place in the Heat Transfer Section of Transport Phenomena Group of the Department of Applied Physics. Under the supervision of Professor C.J. Hoogendoorn he performed studies on the suppression of natural convection in solar collectors, and on the numerical simulation of stratified turbulent air flows. The degree of "ingenieur" was received in June 1986. From 1982 to 1983 he was a teacher of Physics at the "St. Petrus Scholengemeenschap" in Zoetermeer, The Netherlands. From 1986 to 1991 he performed a Ph.D. research project on transport phenomena in Chemical Vapor Deposition reactors, again in the Heat Transfer group and under the supervision of Professor C.J. Hoogendoorn. The results of this study have been described in this thesis. Since June 1991 he is a member of the scientific staff of the "Kramers Laboratorium voor Fysische Technologie" of the Department of Applied Physics of the Delft University of Technology.
RELATED PUBLICATIONS

Parts of this thesis have been based on the following publications:


