Reactor Scale Simulation of Atomic Layer Deposition

Mohammad Reza Shaeri

University of Wisconsin-Milwaukee

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REACTOR SCALE SIMULATION OF ATOMIC LAYER DEPOSITION

by

Mohammad Reza Shaeri

A Dissertation Submitted in
Partial Fulfillment of the
Requirements for the Degree of

Doctor of Philosophy

in Engineering

at

The University of Wisconsin-Milwaukee

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ABSTRACT
REACTOR SCALE SIMULATION OF ATOMIC LAYER DEPOSITION

by

Mohammad Reza Shaeri

The University of Wisconsin-Milwaukee, 2014
Under the Supervision of Professor Tien-Chien Jen

In order to modify the characteristics of an atomic layer deposition (ALD) process, a numerical model to simulate a general ALD process in a reactor scale is presented. Simulations are described by deposition of Al₂O₃ from trimethylaluminum and ozone as the metal and oxygen sources, respectively, and inert argon as the purge gas, inside viscous flow reactors. The simulations are performed for a fixed operating pressure of 10 Torr (1330 Pa) and two substrate temperatures at 250 °C and 300 °C. The flow inside the reactor is a continuum; therefore, the Navier-Stokes, energy and species transport equations are discretized through the finite volume method to simulate transient, laminar and reacting flows. The chemistry mechanism used includes both gas-phase and surface reactions. The accuracy of the numerical model is validated with the benchmark solutions. By using the presented numerical model, the ALD characteristics of Al₂O₃ at different reactor design parameters are investigated.
Dedication

This thesis is dedicated to my beloved sister Katayoon for her endless love, support, encouragement and sacrifice.
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\(a_i-a_7\): coefficients of the polynomial functions for calculation of thermodynamics properties of gaseous species

\(A\): Pre-exponential factor in an Arrhenius expression (\(m^3/mol.s\))

\(b'\): reactant stoichiometric coefficient of a bulk species in a surface reaction

\(b''\): product stoichiometric coefficient of a bulk species in a surface reaction

\(B\): bulk species in a surface reaction

\(Br\): Brinkman number

\(C_p\): specific heat (\(J/Kg.K\))

\(D\): inlet, outlet, and substrate diameter (m)

\(D_T\): thermal diffusion coefficient (\(Kg/m.s\))

\(D_{ij}\): binary diffusion coefficient (\(m^2/s\))

\(E\): Activation energy in an Arrhenius expression (\(J/mol\))

\(f\): mole fraction

\(g'\): reactant stoichiometric coefficient of a gaseous species in a surface reaction

\(g''\): product stoichiometric coefficient of a gaseous species in a surface reaction

\(g\): gravitational acceleration vector (\(m/s^2\))

\(G\): gaseous species in a surface reaction

\(h\): mixture enthalpy (\(J/Kg\))

\(H\): enthalpy (\(J/mol\))

\(H^0\): standard state enthalpy (\(J/mol\))

\(I\): unity tensor
\( \hat{j} \): direction in \( Y \) coordinate

\( \bar{J} \): diffusive mass flux (Kg/m\(^2\).s)

\( J^n \): diffusive mass flux normal to the substrate (Kg/m\(^2\).s)

\( k_f \): forward reaction rate constant (consistent units)

\( k_b \): backward reaction rate constant (consistent units)

\( K \): mixture thermal conductivity (W/m.K)

\( \bar{K} \): species thermal conductivity (W/m.K)

\( K_B \): Boltzmann constant (J/K)

\( \dot{m} \): mass flow rate (Kg/s)

\( \dot{M}_{\text{dep}} \): mass deposition rate on the substrate (Kg/m\(^2\).s)

\( N \): total number of gaseous species inside the gaseous mixture

\( N_b \): total number of bulk species in a surface reaction

\( N_g \): total number of gaseous species in a surface reaction

\( N_R \): total number of gas-phase reactions

\( N_s \): total number of surface species in a surface reaction

\( N_{\text{surf}} \): total number of surface reactions

\( P \): pressure (Pa)

\( P_{\text{atm}} \): atmospheric pressure (Pa)

\( R \): gas constant (J/mol.K)

\( R^g \): molar reaction rate in a gas-phase reaction (mol/m\(^3\).s)

\( \mathcal{R} \): molar reaction rate in a surface reaction (mol/m\(^2\).s)

\( \text{Re} \): Reynolds number
\(s':\) reactant stoichiometric coefficient of a surface species in a surface reaction

\(s'':\) product stoichiometric coefficient of a surface species in a surface reaction

\(S:\) surface species in a surface reaction

\(S^0:\) standard state entropy (J/mol.K)

\(t:\) time (s)

\(T:\) temperature (K)

\(v':\) reactant stoichiometric coefficient in a gas-phase reaction

\(v'':\) product stoichiometric coefficient in a gas-phase reaction

\(\vec{V}:\) velocity vector (m/s)

\(W:\) molecular weight (Kg/mol)

\(X, Y, Z:\) Cartesian coordinates

\(y:\) mass fraction

\(z:\) site coverage

**Greek symbols**

\(\beta:\) temperature exponent in an Arrhenius expression

\(\gamma:\) sticking coefficient

\(\Gamma:\) total surface site concentration (Kgmol/m\(^2\))

\(\varepsilon:\) maximum energy of attraction (J)

\(\eta':\) rate exponent of a gaseous species in a surface reaction

\(\lambda:\) gas mean-free path (m)

\(\mu:\) mixture viscosity (Kg/m.s)

\(\bar{\mu}:\) species viscosity (Kg/m.s)

\(\rho:\) mixture density (Kg/m\(^3\))
\( \sigma \): Lennard-Jones collision diameter (m)

\( \Phi \): third bodies effects in a gas-phase reaction (mol/m\(^3\))

\( \psi' \): rate exponent of a surface species in a surface reaction

\( \Omega_D \): collision integral for diffusion (dimensionless)

\( \Omega_\mu \): collision integral for viscosity (dimensionless)

**Subscript**

Ar: respect to argon

in: respect to the inlet

i: respect to the \( i \)th species

j: respect to the \( j \)th species

O\(_3\): respect to ozone

r: respect to the \( r \)th reaction

s: respect to the substrate

TMA: respect to trimethylaluminum

**Superscript**

\( * \): respect to a surface species

B: respect to a bulk species
Chapter 1: Introduction

Deposition of thin films in a range of few nanometers to several tens of microns from gaseous precursors on different solid materials is a crucial requirement in industrial applications such as semiconductors, solar cells, photonics, microelectronics, MEMS, and nano-structures (Lin et al., 2009; Cho et al., 1999; Houtman et al., 1986; Luo et al., 2004; Kleijn et al., 2007; Jensen et al., 1991). Among different deposition techniques, atomic layer deposition (ALD) is widely recognized as a key enabling nanotechnology with capability to deposit ultrathin, conformal and pinhole-free nano-films on complex structures (Wind and George, 2010). ALD was developed with a name of atomic layer epitaxy (ALE) in the late 1970s by Suntola and co-workers in Finland (Ritala and Leskela, 2002; George, 2010). However, ALD has been known by different names as listed in Table 1.1.

Table 1.1: Different names of ALD, provided by Puurunen (2005).

<table>
<thead>
<tr>
<th>Name</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic layer deposition</td>
<td>ALD</td>
</tr>
<tr>
<td>Atomic layer epitaxy</td>
<td>ALE</td>
</tr>
<tr>
<td>Atomic layer evaporation</td>
<td>ALE</td>
</tr>
<tr>
<td>Atomic layer growth</td>
<td>ALG</td>
</tr>
<tr>
<td>Chemical assembly</td>
<td></td>
</tr>
<tr>
<td>Molecular deposition</td>
<td></td>
</tr>
<tr>
<td>Molecular lamination</td>
<td></td>
</tr>
<tr>
<td>Molecular layer epitaxy</td>
<td>MLE</td>
</tr>
<tr>
<td>Molecular layering</td>
<td>ML</td>
</tr>
<tr>
<td>Molecular stratification</td>
<td></td>
</tr>
</tbody>
</table>
In nature, ALD is a derivative of chemical vapor deposition (CVD) where in an ALD a binary reaction \( a + b \rightarrow c + d \) is split into self-limiting surface reactions between the gaseous precursors \( a \) and \( b \), and the absorbed species on a substrate in a cyclic manner (Kim et al., 2010). Therefore, in an ALD process, each precursor is pulsed to the reactor alternately, and the pulses are separated by inert gas purging periods (Rahtu and Ritala, 2002). Purging the reactor is an essential step in a cycle to prevent interactions and CVD between two precursors since a CVD adversely affects the uniformity of the deposited films. In a self-limiting condition, the same amount of film is deposited on all the surface of the substrate, if the dose of the precursor is high enough (Jones and Hitchman, 2009). Due to self-limiting characteristic of an ALD process, large areas of a complicated structure can be uniformly and conformally coated by ultrathin films, and the film thicknesses can be simply and accurately controlled in an atomic scale by the number of deposition cycle (Ritala et al., 1999). In addition, the low growth temperature is another big advantage of ALD compared with other deposition methods (Kim and Rossnagel, 2002). The ALD characteristics are listed in Table 1.2.

<table>
<thead>
<tr>
<th>ALD characteristics</th>
<th>Results on the film deposition</th>
<th>Practical advantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>1- Self-limiting</td>
<td>1-1- Film growth depends only on the number of deposition cycle.</td>
<td>1-1-1- Accurate and simple thickness control.</td>
</tr>
</tbody>
</table>
|                     | 1-2- There is no need for reactant flux homogeneity. | 1-2-1- Large area capability.  
|                     |                                                | 1-2-2- Large batch capability.  
|                     |                                                | 1-2-3- Excellent conformality.  |
| 1-3- Atomic level control of material composition. | 1-2-4- No problem with inconstant vaporization rates of solid precursors.  
1-2-5- Good reproducibility.  
Straightforward scale-up. |
|-------------------------------------------------|---------------------------------------------------------------------------------------------------------------|
| 1-3-1- Capability to produce sharp interfaces and superlattices.  
1-3-2- Possibility to interface modification. |

<table>
<thead>
<tr>
<th>2- Sequential precursor pulsing</th>
<th>2-1- No gas phase reactions</th>
<th>2-1-1- Favors precursors highly reactive towards each other, thus enabling effective material utilization.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-2- Sufficient time is provided to complete each reaction step.</td>
<td>2-2-1 High-quality materials are obtained at low processing temperatures.</td>
<td></td>
</tr>
</tbody>
</table>

| 3- Wide temperature operation | 3-1- Processing conditions of different materials are readily matched. | 3-1-1- Capability to prepare multilayer structures in a continuous process. |

In an ALD process, films are deposited on the substrate during four step as: (i) forming a new layer on the substrate due to the self-limiting surface reactions at the first precursor exposure, (ii) purging the reactor from the by-products and the unreacted precursors by using an inert gas, (iii) deposition of the desired film due to the self-limiting surface reactions between the second precursor and the adsorbed species on the
substrate, and (iv) purging the reactor form the by-products and the unreacted precursors by using an inert gas (Kim, 2003; Kim et al., 2009). These four steps form one ALD cycle and each cycle is characterized by a timing-sequence of \( t_1 \)-\( t_2 \)-\( t_3 \)-\( t_4 \) such that \( t_1 \) and \( t_3 \) correspond the exposures of the first and the second precursor, respectively, and \( t_2 \) and \( t_4 \) represent the first and the second purge times, respectively (Feng et al., 2011; Tamm et al., 2012).

To deposit metal oxide films by an ALD process, one precursor is used as the metal source and another is the oxidant (oxygen source) (Xu and Musgrave, 2004). Table 1.3 provides some metal oxides films with corresponding precursors.

<table>
<thead>
<tr>
<th>Film material</th>
<th>Metal source</th>
<th>Oxidant</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{B}_2\text{O}_3 )</td>
<td>( \text{BBr}_3 )</td>
<td>( \text{H}_2\text{O} )</td>
</tr>
<tr>
<td>( \text{MgO} )</td>
<td>( \text{MgCp}_2 )</td>
<td>( \text{H}_2\text{O} )</td>
</tr>
<tr>
<td>( \text{Al}_2\text{O}_3 )</td>
<td>( \text{AlCl}_3 )</td>
<td>( \text{H}_2\text{O} )</td>
</tr>
<tr>
<td>( \text{Al}_2\text{O}_3 )</td>
<td>( \text{AlCl}_3 )</td>
<td>( \text{O}_2 )</td>
</tr>
<tr>
<td>( \text{Al}_2\text{O}_3 )</td>
<td>( \text{AlBr}_3 )</td>
<td>( \text{H}_2\text{O} )</td>
</tr>
<tr>
<td>( \text{Al}_2\text{O}_3 )</td>
<td>( \text{Al(CH}_3\text{)}_3 )</td>
<td>( \text{H}_2\text{O} )</td>
</tr>
<tr>
<td>( \text{Al}_2\text{O}_3 )</td>
<td>( \text{Al(CH}_3\text{)}_3 )</td>
<td>( \text{H}_2\text{O}_2 )</td>
</tr>
<tr>
<td>( \text{Al}_2\text{O}_3 )</td>
<td>( \text{Al(CH}_3\text{)}_3 )</td>
<td>( \text{O}_3 )</td>
</tr>
<tr>
<td>( \text{Al}_2\text{O}_3 )</td>
<td>( \text{Al(CH}_3\text{)}_3 )</td>
<td>( \text{N}_2\text{O} )</td>
</tr>
<tr>
<td>( \text{Al}_2\text{O}_3 )</td>
<td>( \text{Al(CH}_3\text{)}_3 )</td>
<td>( \text{NO}_2 )</td>
</tr>
<tr>
<td>( \text{Al}_2\text{O}_3 )</td>
<td>( \text{Al(CH}_3\text{)}_3 )</td>
<td>( \text{N}_2\text{O}_4 )</td>
</tr>
<tr>
<td>( \text{SiO}_2 )</td>
<td>( \text{SiCl}_4 )</td>
<td>( \text{H}_2\text{O} )</td>
</tr>
<tr>
<td>( \text{SiO}_2 )</td>
<td>( \text{SiCl}_3\text{H} )</td>
<td>( \text{H}_2\text{O} )</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>SiCl$_2$H$_2$</td>
<td>O$_3$</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>TiCl$_4$</td>
<td>H$_2$O</td>
</tr>
<tr>
<td>ZnO</td>
<td>Zn</td>
<td>O$_2$</td>
</tr>
<tr>
<td>Y$_2$O$_3$</td>
<td>YCp$_3$</td>
<td>H$_2$O</td>
</tr>
<tr>
<td>HfO$_2$</td>
<td>HfCl$_4$</td>
<td>H$_2$O</td>
</tr>
<tr>
<td>HfO$_2$</td>
<td>HfCl$_4$</td>
<td>O$_2$</td>
</tr>
<tr>
<td>HfO$_2$</td>
<td>HfCl$_4$</td>
<td>O$_3$</td>
</tr>
</tbody>
</table>

ALD of Al$_2$O$_3$ from trimethylaluminum, Al(CH$_3$)$_3$ and water, H$_2$O, is one of the most studied ALD systems (Wilson et al., 2005). The surface chemistry mechanism during one cycle of this ALD is described as follows (George, 2010; Wilson et al., 2005; Groner et al., 2004):

(A) $\text{Al} - \text{OH}^* + \text{Al}(\text{CH}_3)_3 \rightarrow \text{Al} - \text{O} - \text{Al}(\text{CH}_3)^* + \text{CH}_4$

(B) $\text{Al} - \text{CH}_3^* + \text{H}_2\text{O} \rightarrow \text{Al} - \text{OH}^* + \text{CH}_4$

where the asterisks represent the surface species, and the remaining elements are the gaseous species. At the first precursor exposure, Al(CH$_3$)$_3$ is pulsed into the reactor and reacts with the adsorbed hydroxyl groups on the substrate. Then, an inert gas evacuates the reactor from the unreacted Al(CH$_3$)$_3$ and the by-product CH$_4$. At the second precursor exposure, H$_2$O is pulsed into the reactor and reacts with the methyl groups. Then, an inert gas evacuates the reactor from the unreacted H$_2$O and the by-product CH$_4$. The desired thickness of Al$_2$O$_3$ will be deposited by an ABAB… reaction sequence (Groner et al., 2004). Figure 1.1 describes the different steps of ALD of Al$_2$O$_3$ from Al(CH$_3$)$_3$ and H$_2$O.
Figure 1.1(a): Pulse of Al(CH$_3$)$_3$. Figure is provided from Savannah User Manual (2009).

Figure 1.1(b): The first purge. Figure is provided from Savannah User Manual (2009).
Figure 1.1(c): Pulse of H$_2$O. Figure is provided from Savannah User Manual (2009).

Figure 1.1(d): Monolayer formed after the second purge. Figure is provided from Savannah User Manual (2009).
Chapter 2: Motivation of This Study

2.1. Previous ALD Simulations

ALD reactors are divided into two groups as viscous flow reactors and molecular flow reactors (Ritala and Leskela, 2002). With much faster film depositions, viscous flow reactors are often used in ALD processes (Elam et al., 2002). Generally, the feature and reactor scales are two main length scales inside an ALD process. A feature scale corresponds to microscopic trenches and pores on the substrate surface, and a reactor scale represents macroscopic reactor geometrical dimensions such as a substrate/inlet/outlet diameter. Usually operating pressures of viscous flow reactors in ALD processes are in the range of 1-10 Torr (133-1330 Pa) (Schuisky et al., 2002; Jones and Hitchman, 2009). At these low pressures, it is possible that mean-free paths of gases are comparable with microscopic lengths in a feature scale while macroscopic lengths in a reactor scale are much larger than mean-free paths. Therefore, in an ALD process, both very large and very small Knudsen numbers coexist that result in simultaneous existences of molecular flows and continuum flows, respectively. Although employing the Navier-Stokes equations with no-slip boundary conditions is appropriate to simulate flows with very small Knudsen numbers (continuum flows), the validity of the continuum approach fails for large Knudsen numbers (molecular flows). Therefore, flow transports must be modeled through other methods such as Boltzmann equations (Misdanitis et al., 2012; Ganguly et al., 2012; Aristov et al., 2012).

Most ALD simulations were performed on large Knudsen numbers in feature scales. Gilmer et al. (2000) applied the Monte Carlo method to simulate film depositions
into small trenches. Mazaleyrat et al. (2005) presented a new kinetic Monte Carlo method to investigate the ALD of alumina onto silicon. Hu et al. (2009) investigated film density, composition, roughness, and growth rate in ALD of $\text{Al}_2\text{O}_3$ through molecular dynamics simulations. Gou et al. (2007) used the molecular dynamics simulation method to simulate $\text{SiF}_3$ continuously bombarding silicon surface. Adomaitis (2010) developed a multi-scale model by using the Monte Carlo method and the continuum approach to simulate film growths within a nanoporous material. Ahn et al. (2010) simulated the surface evolution by using the concepts of deposition probability and an imaginary substrate consisting. Rose and Bartha (2009) proposed a method to determine the sticking coefficient of precursor molecules used in ALD. In another study, Rose et al. (2010) investigated the temperature dependence of the sticking coefficient of precursor molecules in an ALD process. Nilsen et al. (2007) developed a tool for simulating the growth of amorphous thin films in an ALD process, based on purely geometrical considerations. Gobbert et al. (2002a, 2002b) simulated the interactions between gas-phase transports and surface reactions by using a Boltzmann equation based in a feature scale. Gordon et al. (2003) developed a simple theory in a feature scale to deposit a film with uniform thickness in narrow holes. Dendooven et al. (2009) extended the model proposed by Gordon et al. (2003) in order to predict a film thickness as a function of depth inside a hole. Makinen et al. (2011) simulated the ALD of $\text{Al}_2\text{O}_3$ on an OH-terminated $\text{TiO}_2(101)$ anatase surface by employing density functional theory. Heyman and Musgrave (2004) simulated the ALD of $\text{Al}_2\text{O}_3$ from $\text{AlCl}_3$ and $\text{H}_2\text{O}$ using density functional theory. Widjaja and Musgrave (2002) simulated the ALD of $\text{Al}_2\text{O}_3$ from trimethylaluminum and $\text{H}_2\text{O}$ by using the density functional theory. Kwon et al. (2008)
simulated the ALD of Al$_2$O$_3$ from trimethylaluminum and ozone by using the density functional theory. Elliott and Greer (2004) used the density functional theory to investigate atomic scale characteristics of surface reactions in an ALD process. Mastail et al. (2012) simulated the ALD of HfO$_2$ by using the density functional theory. Some research in atomic scale simulations of ALD processes is addressed in Table 2.1.

Table 2.1: Atomic scale simulations of ALD processes, provided by Elliott (2012).

<table>
<thead>
<tr>
<th>Product film</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$</td>
<td>Xu and Ye, 2010; Delabie et al., 2011; Ren et al., 2008b</td>
</tr>
<tr>
<td>BN</td>
<td>Arvidsson and Larsson, 2007</td>
</tr>
<tr>
<td>C</td>
<td>Hukka et al., 1996</td>
</tr>
<tr>
<td>CdS</td>
<td>Tanskanen et al., 2010</td>
</tr>
<tr>
<td>Co</td>
<td>Kwon et al., 2012</td>
</tr>
<tr>
<td>Cu</td>
<td>Pirolli and Teplyakov, 2006</td>
</tr>
<tr>
<td>Er$_2$O$_3$</td>
<td>Nolan and Elliott, 2010</td>
</tr>
<tr>
<td>GaAs</td>
<td>Mochizuki et al., 1994</td>
</tr>
<tr>
<td>HfO$_2$</td>
<td>Fenno et al., 2005</td>
</tr>
<tr>
<td>HfN</td>
<td>Xu and Musgrave, 2005</td>
</tr>
<tr>
<td>La$_2$O$_3$</td>
<td>Elliott, 2007</td>
</tr>
<tr>
<td>MgO</td>
<td>Lu et al., 2009</td>
</tr>
<tr>
<td>MoN</td>
<td>Miikkulainen et al., 2008</td>
</tr>
<tr>
<td>Nitrides</td>
<td>Widjaja et al., 2000</td>
</tr>
<tr>
<td>Ni</td>
<td>Li et al., 2009</td>
</tr>
<tr>
<td>PbS</td>
<td>Lee et al., 2010</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>Chen et al., 2011</td>
</tr>
<tr>
<td>Si$_3$N$_4$</td>
<td>(Mui et al., 2004)</td>
</tr>
<tr>
<td>HfSiO$_x$</td>
<td>(Ren et al., 2008a)</td>
</tr>
<tr>
<td>Material</td>
<td>Reference</td>
</tr>
<tr>
<td>---------------</td>
<td>------------------------------------</td>
</tr>
<tr>
<td>SnO₂</td>
<td>(Olivier et al., 2008)</td>
</tr>
<tr>
<td>SrO, SrTiO₃</td>
<td>(Holme and Prinz, 2007)</td>
</tr>
<tr>
<td>Ta₂O₅</td>
<td>(Siodmiak et al., 2000)</td>
</tr>
<tr>
<td>TaN, TaCN</td>
<td>(Xie et al., 2011; Rodriguez-Reyes and Teplyakov, 2008)</td>
</tr>
<tr>
<td>TiO₂</td>
<td>(Hu and Turner, 2007)</td>
</tr>
<tr>
<td>WN, WCN</td>
<td>(Rodriguez-Reyes and Teplyakov, 2008)</td>
</tr>
<tr>
<td>ZnO</td>
<td>(Ren, 2009)</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>(Ren et al., 2011)</td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>(Ren et al., 2009)</td>
</tr>
</tbody>
</table>

However, a feature scale simulation is extremely time-consuming and usually requires advanced computational techniques. For instance, Gobbert et al. (2007) applied a parallel computational technique with high performance computers on a distributed-memory cluster to simulate film depositions in a CVD process through transient Boltzmann equations. In another study, Cheimarios et al. (2013) modeled a CVD process through a multi-scale simulation by using a continuum approach and a ballistic model in a reactor scale and a feature scale, respectively. However, Cheimarios et al. (2013) applied multi processors as well as the Message Passing Interface (MPI) technique for their simulations. Therefore, it is advantageous to model an ALD process through a reactor scale simulation to overcome the expensive feature scale simulations. However, reactor scale simulations of ALD processes are rare. As one of the most successful studies, Ho et al. (2003) deposited Al₂O₃ from trimethylaluminum (TMA) and ozone for different substrate temperatures through both experiments and reactor scale simulations, and despite some deviations, obtained overall good agreements between experimental and numerical deposition rates. The major reason for deviations between numerical and
experimental results in (Ho et al., 2003) was the lack of an accurate chemistry mechanism. In fact, developing a precise chemistry mechanism to describe a surface reaction has remained a big challenge due to many unsolved and extremely complicated phenomena in a surface reaction.

2.2. Objective of This Study

This study is to present a numerical model to simulate a general ALD process in a reactor scale to improve ALD characteristics due to either reactor design parameters or operating conditions. In this study, the numerical approach is validated with the benchmark solutions. The simulation process is specified by deposition of Al₂O₃ from trimethylaluminum (TMA) and ozone as the precursors, and inert argon as the purge gas in an operating pressure of 10 Torr (1330 Pa) and two substrate temperatures of 250 °C and 300 °C inside viscous flow reactors.

A numerical procedure for a reactor scale simulation of a general ALD process is presented in chapter 3. Then, by using the proposed numerical model, the ALD characteristics of Al₂O₃ are investigated at different reactor design parameters and operating conditions in chapters 4, 5 and 6.
Chapter 3: Reactor Scale Simulation of a General ALD Process

3.1. Problem Description

At this chapter, the numerical procedure for the reactor scale simulation of a general ALD process is described by deposition of Al₂O₃ from TMA, Al(CH₃)₃, and ozone, O₃, as the metal and oxygen sources, respectively, based on the global reaction

$$2\text{Al(CH}_3)_3 + \text{O}_3 \rightarrow \text{Al}_2\text{O}_3 + 3\text{C}_2\text{H}_6$$  \hspace{1cm} (Kim et al., 2002; Shen et al., 2012)

Al₂O₃ films are deposited on the substrate inside the reactor illustrated in Figure 3.1. This reactor is prepared based on a lower size of the real reactor illustrated in Figure 3.2. An inert argon, Ar, is used as the purge gas to remove unreacted precursors and reaction products from the reactor. In an ALD process, an inert gas is also used as a carrier gas to transport the precursors into the reactor. In this study, a carrier gas is omitted to improve the computational times. However, a carrier gas can be simply considered by pulsing a mixture of a precursor and argon at each precursor exposure.

The reaction mechanism used is retrieved from the software package CHEMKIN-PRO (CHEMKIN-PRO, 2013). This mechanism includes three irreversible surface reactions and two reversible gas-phase reactions, as follows:

(S1) $$\text{Al(CH}_3)_3 + \text{O}^* \xrightarrow{k_f} \text{Al(CH}_3)_2^* + 0.5\text{C}_2\text{H}_6 \quad \gamma = 0.1$$

(G1) $$\text{O}_3 + \text{M} \xrightarrow{k_f} \text{O}_2 + \text{O} + \text{M} \quad A = 4.51 \times 10^9 \text{ m}^3/\text{mol.s}, \beta = 0, E = 100416 \text{ J/mol}$$
(G2) $O + O_3 \xrightarrow{k_f} 2O_2 \quad A = 2.96 \times 10^7 \: \text{m}^3/\text{mol.s}, \: \beta = 0, \: E = 25104 \: \text{J/mol}$

(S2) $2\text{Al}(\text{CH}_3)_2^* + \text{O} \xrightarrow{k_f} \text{Al}(\text{CH}_3)\text{OAl}(\text{CH}_3)^* + \text{C}_2\text{H}_6 \quad \gamma = 1.0$

(S3) $0.5\text{Al}(\text{CH}_3)\text{OAl}(\text{CH}_3)^* + \text{O} \xrightarrow{k_f} \text{O}^* + 0.5\text{C}_2\text{H}_6 + 0.5(\text{Al}_2\text{O}_3)^\text{B} \quad \gamma = 1.0$

where the asterisk and B superscripts represent surface and bulk species, respectively, and the remaining elements are gaseous species. The chemistry mechanism used in this study is simplified for illustration purposes only and should not be used as a source of kinetic data (CHEMKIN-PRO, 2013).

A timing-sequence of 1-2-72-5 is used for each ALD cycle that corresponds to (i) injection the pure TMA for 1 s, (ii) purging the reactor with pure argon for 2 s, (iii) injection the pure ozone for 72 s, and (iv) purging the reactor with pure argon for 5 s. Such a timing-sequence is established by several tests such that 1 s and 72 s are long enough to cover at least 99.90% of the substrates by $\text{Al}(\text{CH}_3)_2^*$ and $\text{O}^*$, respectively, during the TMA and ozone exposures. Also, 2 s and 5 s are sufficiently long to fill more than 99.0% of the reactor volumes by pure argon at the first and the second purges, respectively. The TMA exposure includes only the surface reaction S1 while other reactions all occur during the ozone exposure.

The inlet conditions are $T_{in} = 300 \: \text{K}, \: f_{\text{TMA}} = 1.0$ and $V_{in} = 0.6 \: \text{m/s}$ for the TMA exposure, $T_{in} = 300 \: \text{K}, \: f_{\text{O}_3} = 1.0$ and $V_{in} = 0.6 \: \text{m/s}$ for the ozone exposure, and $T_{in} = 300 \: \text{K}, \: f_{\text{Ar}} = 1.0$ and $V_{in} = 4.2 \: \text{m/s}$ for both purges. At the outlet, zero axial gradients for all the variables are set. The remaining faces are walls at a fixed temperature same to the substrate. Except for the substrate, no-slip boundary conditions and zero
diffusive mass fluxes normal to the faces are imposed for the other walls. At the substrate, \( \text{Al}_2\text{O}_3 \) films are deposited due to the surface reactions as described in the following section.

The simulations are performed for a fixed operating pressure of 10 Torr (1330 Pa) and two substrate temperatures of \( T_s = 250 \, ^\circ\text{C} \) and \( T_s = 300 \, ^\circ\text{C} \).

![Diagram of reactor](image1)

Figure 3.1: Reactor used in the simulation.

![Image of reactor](image2)

Figure 3.2: Real reactor chamber.
3.2. Numerical Model

3.2.1. Governing Equations

In this study, the maximum Knudsen number, \( \lambda / D = K_B T / \sqrt{2} \pi P \sigma^2 D \) (Yuan and Sunden, 2013; Woudberg and Du Plessis, 2008), is less than 0.01 by using

\[ K_B = 1.38 \times 10^{-23} \text{ J/K} \]

as the Boltzmann constant, \( \sigma = 2.75 \times 10^{-10} \text{ m} \) as the smallest collision diameter provided from (CHEMKIN-PRO, 2013), \( T = 573 \text{ K} \) as the maximum temperature, \( P = 1330 \text{ Pa} \) as the pressure, and \( D = 0.002 \text{ m} \) as the smallest physical length scale inside the reactor. Therefore, due to \( \lambda / D < 0.01 \), using the continuum flow assumption with no-slip boundary conditions is accurate to simulate flow fields inside the reactors (Avdiaj et al. 2013; Dreyer et al., 2014; Dienel et al., 2012; Hashemi et al., 2013; Gharamaleki and Shams, 2011). As a result, the governing equations are set as follows:

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{V}) = 0 \tag{3.1}
\]

\[
\frac{\partial (\rho \mathbf{V})}{\partial t} + \nabla \cdot (\rho \mathbf{V} \mathbf{V}) = -\nabla P + \nabla \left[ \mu \left( \nabla \mathbf{V} + (\nabla \mathbf{V})^T \right) - \frac{2}{3} \mu (\nabla \cdot \mathbf{V}) I \right] + \rho \mathbf{g} \tag{3.2}
\]

\[
\frac{\partial (\rho h)}{\partial t} + \nabla \cdot (\rho \mathbf{V} h) = \nabla \cdot (K \nabla T) - \sum_{i=1}^{N} \left( \mathbf{J}_i \cdot \mathbf{V} \frac{H_i}{W_i} \right) - \sum_{i=1}^{N} \sum_{r=1}^{N_{g}} \left[ H_i (v''_{i,r} - v'_{i,r}) R_{r}^{g} \right] \tag{3.3}
\]

\[
\frac{\partial (\rho y_i)}{\partial t} + \nabla \cdot (\rho \mathbf{V} y_i) = -\nabla \cdot \mathbf{J}_i + W_i \sum_{r=1}^{N_{g}} \left[ (v''_{i,r} - v'_{i,r}) R_{r}^{g} \right] \tag{3.4}
\]

\( h \) and \( H_i \) are the mixture enthalpy and enthalpy of the \( i \)th species that are described as follows:
\[ h = \sum_{i=1}^{N} y_i \frac{H_i}{W_i} \]  \hspace{1cm} (3.5)

\[ H_i = H_i^0 + W_i \left( T - 298.15 \right) \int C_{p,i} \,dT \]  \hspace{1cm} (3.6)

where \( H_i^0 \) is the standard state enthalpy of the \( i \)th gaseous species.

A Brinkman number, \( Br = \frac{\mu |\vec{V}|^2}{K (T_s - T_i)} \), is an indicator of viscous dissipations strength. To measure the effects of viscous dissipations, \( Br_{in} \) is used instead of local Brinkman numbers in this study. At the present operating conditions, the inlet mixture viscosity, and thermal conductivity range from 1.03×10^{-5} Kg/m.s to 2.44×10^{-5} Kg/m.s, and 0.013 W/m.K to 0.024 W/m.K, respectively. Therefore, in this study 5.6×10^{-7} < Br_{in} < 1.5×10^{-4}. Due to such small values of Brinkman numbers, viscous dissipations are neglected in the energy equation.

The diffusive mass flux as a concentration and temperature-dependent variable is calculated as follows for a non-dilute multi-component mixture:

\[ J_i = -\rho \frac{1}{\sum_{j,j \neq i} D_{ij}} \nabla y_i - D_i^p \nabla \frac{T}{T} \]  \hspace{1cm} (3.7)

The density field of the gaseous mixture is obtained from the ideal gas law for a multi-component mixture, as shown below:
The molar reaction rate for the \( r \)th reversible gas-phase reaction is described as follows (CHEMKIN-CFD, 2011):

\[
R^r_{i} = \Phi_r \left[ k_{f,r} \prod_{\text{reactants}} \left( \frac{P_f}{RT} \right)^{v_i^r} - k_{b,r} \prod_{\text{products}} \left( \frac{P_f}{RT} \right)^{v_i^r} \right]
\]  

(3.9)

where \( \Phi_r \) represents the effect of third bodies in the \( r \)th reaction. The forward and the backward reaction rate constants for the \( r \)th gas-phase reaction are calculated from an Arrhenius expression and the reaction equilibrium constant, respectively, as follows (Kleijn, 2000):

\[
k_{f,r} = A_r T^{\beta_r} \exp\left( -\frac{E_r}{RT} \right)
\]  

(3.10)

\[
k_{b,r} = \frac{k_{f,r}}{\exp\left( \frac{\Delta S_r^0(T)}{R} - \frac{\Delta H_r^0(T)}{RT} \right) \sum_{i=1}^{N} (v_i^r - v_i^r)} \left( \frac{RT}{P_{\text{atm}}} \right)^{\sum_{i=1}^{N} v_i^r}
\]  

(3.11)

with

\[
\Delta H_r^0(T) = \sum_{i=1}^{N} \left[ (v_i^r - v_i^r) H_i^0(T) \right]
\]  

(3.12)
\[
\Delta S_i^0 (T) = \sum_{i=1}^{N} \left[ (v''_{i,r} - v'_{i,r}) S_i^0 (T) \right]
\]

where \( H_i^0 (T) \) and \( S_i^0 (T) \) are the enthalpy and entropy of the \( i \)th gaseous species at the temperature \( T \) and the atmospheric pressure.

The general form for the \( r \)th irreversible surface reaction is as follows (ANSYS FLUENT Theory Guide, 2011):

\[
\sum_{i=1}^{N_g} g'_{i,r} G_i + \sum_{i=1}^{N_b} b'_{i,r} B_i + \sum_{i=1}^{N_s} s'_{i,r} S_i \rightarrow \sum_{i=1}^{N_g} g''_{i,r} G_i + \sum_{i=1}^{N_b} b''_{i,r} B_i + \sum_{i=1}^{N_s} s''_{i,r} S_i
\]

where \( G, B, \) and \( S \) correspond the gas-phase species, the bulk species, and the surface species, respectively, with the total numbers of \( N_g, N_b, \) and \( N_s \), respectively, inside the \( r \)th reaction. \( g', b', \) and \( s' \) are the stoichiometric coefficients of the reactants, and \( g'', b'' \) and \( s'' \) are the stoichiometric coefficients of the products. The surface reaction rate constant is specified in terms of a sticking coefficient as follows (CHEMKIN-CFD, 2011):

\[
k_f = \frac{\gamma}{\Gamma^m} \sqrt{\frac{RT}{2\pi W}}
\]

where \( T \) is the substrate temperature, \( W \) is the molecular weight of gaseous reactant, \( \Gamma \) is the total surface site concentration, and \( m \) is the summation of stoichiometric coefficients.
of surface species reactants. In this study, $\Gamma = 2.72 \times 10^{-8}$ Kgmol/m$^2$ for all the surface reactions (CHEMKIN-PRO, 2013).

The molar reaction rate for the $r$th irreversible surface reaction is calculated as follows (ANSYS FLUENT Theory Guide, 2011):

$$\mathcal{R}_r = k_{f,r} \left( \prod_{i=1}^{N_g} [G_i]_{s}^{\eta_{i,r}} \right) \left( \prod_{j=1}^{N_s} [S_j]_{s}^{\psi_{j,r}} \right)$$

(3.16)

with

$$[G_i]_s = \frac{(\rho y_i)_s}{W_i}$$

(3.17)

$$[S_i]_s = \Gamma z_i$$

(3.18)

where $[ \ ]_s$ corresponds the concentration of a species (only gaseous and surface species) at the substrate, and $\eta_{i,r}$ and $\psi_{j,r}$ are the rate exponents for the $i$th gaseous species and the $j$th surface species, respectively, in the $r$th surface reaction. Also, $z_i$ is the site coverage of the surface species $i$ and $\sum_{i=1}^{N_s} z_i = 1$ where the summation is over all the surface species, including O*, Al(CH$_3$)$_2^*$, and Al(CH$_3$)OAl(CH$_3$)*.
3.2.2. Boundary Conditions at the Substrate

In the simulations, the substrate temperatures are set at 250 °C and 300 °C.

Due to the surface reactions, the net vertical mass flux of the \(i\)th gaseous species into the substrate balances with its net consumption/production rate on the substrate, as follows (ANSYS FLUENT Theory Guide, 2011; Kleijn, 2000):

\[
\left( J_i^n - \dot{M}_{dep,y_i} \right)_s = W_i \sum_{r=1}^{N_{surf}} \left[ (g_{i,r}'' - g_{i,r}')R_r \right] \tag{3.19}
\]

where the mass deposition rate on the substrate is calculated as shown below:

\[
\dot{M}_{dep} = \sum_{i=1}^{N_b} W_i \sum_{r=1}^{N_{surf}} \left[ (b_{i,r}'' - b_{i,r}')R_r \right] \tag{3.20}
\]

3.2.3. Species Transport and Thermal Properties

In the ALD reactor, transport coefficients and thermal properties of species are described as temperature-dependent variables due to large variations in the temperature.

3.2.3.1. Thermodynamics Properties of Species

Specific heat, heat of formation, and entropy of the \(i\)th gaseous species are obtained based on the temperature-dependent polynomial functions available in (CHEMKIN-PRO, 2013) as the following forms:

\[
C_{p,i} = a_{1,i} + a_{2,i}T + a_{3,i}T^2 + a_{4,i}T^3 + a_{5,i}T^4 \tag{3.21}
\]
The thermal diffusion coefficient of the $i$th species is calculated from the empirically-based composition-dependent expression provided in (ANSYS FLUENT User’s Guide, 2011; Jin and Shaw, 2010) as follows:

\[
H_i^0 = a_{i,1}T + \frac{a_{i,2}}{2}T^2 + \frac{a_{i,3}}{3}T^3 + \frac{a_{i,4}}{4}T^4 + \frac{a_{i,5}}{5}T^5 + a_{i,6}
\]  \hfill (3.22)

\[
S_i^0 = a_{i,1}\ln T + a_{i,2}T + \frac{a_{i,3}}{2}T^2 + \frac{a_{i,4}}{3}T^3 + \frac{a_{i,5}}{4}T^4 + a_{i,7}
\]  \hfill (3.23)

### 3.2.3.2. Transport Properties of Species

The binary diffusivity, viscosity and thermal conductivity of each species are obtained through the correlations in the kinetic theory of gases as follows (McGee, 1991; Bird et al., 2002):

\[
D_{ij}^T = -2.59 \times 10^{-7}T^{0.659} \left[ \sum_{j=1}^{N} \left( \frac{W_{ij}^{0.511} f_i}{W_{ij}^{0.511} f_j} \right) \right] - y_i \left[ \sum_{j=1}^{N} \left( \frac{W_{ij}^{0.511} f_i}{W_{ij}^{0.511} f_j} \right) \right]
\]  \hfill (3.24)

**Binary diffusivity:**

\[
\mathcal{D}_{ij} = 1.8583 \times 10^{-3} \sqrt{T^3 \left( \frac{1}{W_i} + \frac{1}{W_j} \right) \frac{1}{P \sigma_{ij}^2 \Omega_p}}
\]  \hfill (3.25)

with
\[
\sigma_{ij} = \frac{1}{2} \left( \sigma_i + \sigma_j \right) 
\] (3.26)

where the units of the binary diffusivity is in cm\(^2/s\) if the units of \(P\), \(T\), and \(\sigma_{ij}\) are in atm, K, and angstrom, respectively. Also, \(\Omega_D\) as the collision integral for diffusion is a function of dimensionless temperature \(K_BT/\epsilon_{ij}\) with:

\[
\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j} 
\] (3.27)

*Viscosity of the \(i\)th species:*

\[
\bar{\mu}_i = 2.6693 \times 10^{-5} \sqrt{\frac{W_i T}{\sigma_i^2 \Omega_{\mu}}} 
\] (3.28)

where \(\bar{\mu}_i\) is in g/cm.s, \(W_i\) is in Kg/mol, \(T\) is in K, and \(\sigma_i\) is in angstrom. In addition, \(\Omega_{\mu}\) as the collision integral for viscosity is a function of the dimensionless temperature \(K_BT/\epsilon_i\).

*Thermal conductivity of the \(i\)th species:*

\[
\bar{K}_i = \bar{\mu}_i \left[ C_{p,i} + \frac{5}{4} \frac{R}{W_i} \right] 
\] (3.29)
To use the kinetic theory correlations, the Lennard-Jones parameters as required for each species are obtained from the transport data in (CHEMKIN-PRO, 2013) and listed in Table 3.1.

Table 3.1: Molecular weights and Lennard-Jones parameters for the gaseous species provided from (CHEMKIN-PRO, 2013).

<table>
<thead>
<tr>
<th>Species</th>
<th>( W_i ) (Kg/Kmol)</th>
<th>( \sigma_i ) (Angstrom)</th>
<th>( \varepsilon_i / K_B ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMA</td>
<td>72.086</td>
<td>5.3</td>
<td>471</td>
</tr>
<tr>
<td>Ar</td>
<td>39.948</td>
<td>3.33</td>
<td>136.5</td>
</tr>
<tr>
<td>O</td>
<td>15.999</td>
<td>2.75</td>
<td>80</td>
</tr>
<tr>
<td>( O_2 )</td>
<td>31.999</td>
<td>3.458</td>
<td>107.4</td>
</tr>
<tr>
<td>( O_3 )</td>
<td>47.998</td>
<td>4.1</td>
<td>180</td>
</tr>
<tr>
<td>( C_2H_6 )</td>
<td>30.070</td>
<td>4.302</td>
<td>252.3</td>
</tr>
</tbody>
</table>

3.2.3.3. Mixture Properties

The viscosity and thermal conductivity of the mixture are calculated as follows (Hsueh et al., 2010; Zarvandi et al., 2012):

\[
\mu = \sum_{i=1}^{N} \frac{f_i \bar{\mu}_i}{\sum_{j=1, j \neq i}^{N} f_j \phi_{ij}}
\]

(3.30)

\[
K = \sum_{i=1}^{N} \frac{f_i \bar{K}_i}{\sum_{j=1, j \neq i}^{N} f_j \phi_{ij}}
\]

(3.31)

with
\[
\phi_{ij} = \frac{1 + \left( \frac{\bar{\mu}_i}{\mu_j} \right)^{0.5} \left( \frac{W_j}{W_i} \right)^{0.25}}{8 \left( 1 + \frac{W_i}{W_j} \right)^{0.5}} \]

(3.32)

3.3. Numerical Procedure

3.3.1. Grid and Time-Step Size Independence Tests

The grid independence tests are performed through steady state CVD of Al₂O₃ at \(P=10\) Torr (1330 Pa), \(T_{in}=300\) K, \(T_s=573\) K, \(V_{in}=1\) m/s \(\hat{j}\), \(f_{TMA}=0.1\), \(f_{O_3}=0.3\) and \(f_{Ar}=0.6\) for different grid structures with 13456, 22020, 31965, 48288, 83940, 102630, 140010, 177390, 225240 and 259284 computational cells. A grid with 31965 cells is appropriate for the simulations since by further increases in the numbers of cells from 31965, the changes in the magnitudes of deposition rates, heat transfer coefficients, and skin friction coefficients on the substrate remain below 4%.

To obtain an independency between the deposition rates and the time-step sizes, a very small time-step size is required that leads to extremely time-consuming computations. Therefore, to save the computational time, an independency between deposition rates and time-step sizes is ignored and a time-step independency is obtained by using a transient and multi-component non-reactive flow with the same characteristics for the previous CVD process. The tests are performed for 20 s by using the grid with 31965 cells and time-step sizes of 0.1 s, 0.05 s, 0.01 s, 0.005 s, 0.001 s, 0.0005s, and 0.0001 s. The time-step size of 0.005 s is accurate enough for the simulations since by
using smaller time-step sizes, the magnitudes of time-averaged heat transfer coefficients and skin friction coefficients on the substrate remain below 4% and 0.03%, respectively.

A time-averaged property of $\xi$ is calculated as $\langle \xi \rangle = \frac{1}{t} \int_{t_0}^{t} \xi \, dt$ (Xu et al., 2012).

### 3.3.2. Solution Method

The momentum, energy and species transport equations are discretized spatially and temporally by using the second-order upwind and the first order implicit methods, respectively, through the finite volume approach. Also, source terms in the transport equations are linearized. The pressure and velocity components are coupled by the PISO algorithm. The PISO algorithm is a robust and recommended procedure for transient flow calculations especially with large time-step sizes (Luo et al., 2013). The solutions are considered to be converged when the residual values are less than $1 \times 10^{-5}$ for the continuity, velocity components, and temperature, and less than $1 \times 10^{-4}$ for the gaseous species at each time-step.

The transport equations are solved by using ANSYS FLUENT 14.0. The chemistry is simulated through an advanced chemistry solver CHEMKIN-CFD provided by Reaction Design. The software CHEMKIN-CFD is linked to FLUENT to enhance the accuracy and stability of chemistry simulations. Also, a user-defined function (UDF) is developed and loaded in FLUENT to change the inlet boundary conditions at each ALD cycle.
3.4. Accuracy Validation of the Numerical Model

The CVD benchmark results provided by Kleijn (2000) are used to validate the accuracy of the present numerical procedure. CVDs of silicon from a mixture of silane and helium in a two-dimensional axi-symmetric reactor illustrated in Figure 3.3(a) were simulated in (Kleijn, 2000) through a full multi-component transport model, multi-species and multi-reaction chemistry. In this study, the same boundary conditions and chemistry mechanisms in (Kleijn, 2000) are used and the comparisons of selected results in two studies are shown in Figure 3.3. The excellent agreements between the results prove the good accuracy of the numerical process in this study. Therefore, the ALD characteristics are illustrated in the following section by using the validated numerical model.

Figure 3.3(a): Comparisons of total deposition rates in our study and (Kleijn, 2000).

Figure 3.3(b): Comparisons of axial velocity and temperature profile in our study and (Kleijn, 2000).
Chapter 4: ALD Characteristics of Al₂O₃ at Different Substrate Temperatures

4.1. Problem Description

Al₂O₃ films are deposited in the reactor illustrated in Figure 4.1. The chemistry mechanism, the boundary conditions, the timing-sequence, and the operating conditions are the same as those mentioned in section 3.1.

![Figure 4.1: Reactor.](image)

4.2. Results

The mass flow rates during one cycle are illustrated in Figure 4.2. Based on the inlet mixture viscosities \( 1.03 \times 10^{-5} \text{ Kg/m.s} < \mu_{in} < 2.44 \times 10^{-5} \text{ Kg/m.s} \), a Reynolds number, \( \text{Re} = 4\dot{m}_{in} / \pi D \mu_{in} \), changes between 1 and 18 at the present operating conditions. Therefore, the flow inside the reactor is perfectly laminar.
In an ALD process, a substrate is saturated with a surface species at the end of each precursor exposure. Based on Figure 4.3(a), both substrates are quickly saturated with $\text{Al(CH}_3\text{)}_2^*$ in almost 0.3 s from the TMA injection. Since a TMA exposure includes only one surface reaction, and the reactant is injected directly into the reactors, the substrate is saturated with $\text{Al(CH}_3\text{)}_2^*$ quickly.

However, an ozone exposure includes four reactions with two dependent surface reactions and the most important, oxygen atoms as the reactant for both surface reactions must be generated from ozone decompositions. Therefore, based on Figure 4.3(b), a substrate oxidation takes much longer than a substrate saturation at the TMA exposure. The bulk temperature inside the reactor including the hotter substrate is larger than that of the reactor at $T_s = 250 \, ^\circ\text{C}$. Therefore, gas-phase reactions take place faster inside the reactor with $T_s = 300 \, ^\circ\text{C}$ that result in more ozone decompositions, and more $\text{O}_2$ and
oxygen atoms productions as illustrated in Figure 4.4. More oxygen atoms over the hotter substrate lead to a faster substrate oxidation such that less than 15 s from the ozone exposure, more than 90% of the hotter substrate is oxidized compared with only 50% for the colder substrate at the same time. At the end of the ozone exposure more than 99.910% and 99.983% of the substrates with $T_s = 250 \, ^\circ\text{C}$ and $T_s = 300 \, ^\circ\text{C}$, respectively, are oxidized.

![Figure 4.3(a): Substrate coverage during the TMA exposure in one cycle.](image1)

![Figure 4.3(b): Substrate coverage during the ozone exposure in one cycle.](image2)

![Figure 4.4: Mass fractions of gaseous species inside the reactors during the ozone exposure for one cycle.](image3)
Figure 4.5 illustrates the deposition rate distributions for five ALD cycles. At each substrate temperature, the deposition distributions are the same among all cycles. Steeper slopes of the deposition curves for the hotter substrate indicate earlier film depositions in the result of a faster substrate oxidation. A higher substrate temperature, and more oxygen atoms over a substrate result in a larger surface reaction rate constant, and greater gaseous concentrations at the substrate, respectively. Therefore, surface reaction rates and consequent mass deposition rates are larger for the hotter substrate. For this reason, based on Figure 4.4, more C$_2$H$_6$ as the gaseous product of the surface reactions is generated inside the reactor with the hotter substrate.

![Figure 4.5: Deposition rate distributions for 5 cycles.](image)

Contours of substrate coverage with $\text{Al(CH}_3)_2^*$ at different times are shown in Figure 4.6. Also, Figure 4.7 shows the contours of deposition rates at different times for $T_s = 300 \, ^\circ\text{C}$. 
In an ALD process, depositions start from the area covered by Al(CH\textsubscript{3})\textsuperscript{3} in the vicinity of oxygen atoms. At the beginning of the ozone exposure, films are deposited at the leading edge of a substrate that is the closest area to the reactor inlet; therefore, deposition rates are the highest at the leading edge. When some parts of the leading edge are oxidized, the maximum deposition rates are shifted to the next area with the highest density of Al(CH\textsubscript{3})\textsuperscript{3}. The shifting of the maximum deposition rates continues until all
Al(CH$_3$)$_2^*$ on the substrate are consumed or, in other words, the whole substrate is oxidized.

Figure 4.7: Contours of deposition rates at $T_s = 300 \, ^\circ$C. (i): 1 s after ozone injection, (ii): 10 s after ozone injection, (iii): 70 s after ozone injection.

Similar deposition rate distributions among all cycles at a fixed substrate temperature result in an identical film thickness at each cycle. Therefore, the desired film thickness can be controlled only by the numbers of ALD cycles. Based on Figure 4.8, Al$_2$O$_3$ growth rates of 3.78 angstrom/cycle and 4.52 angstrom/cycle are obtained for $T_s = 250 \, ^\circ$C and $T_s = 300 \, ^\circ$C, respectively. Films grow sharply from the beginning of an ozone exposure and reach a plateau until the end of a cycle that corresponds to the consumption of almost all Al(CH$_3$)$_2^*$ on the substrate. Therefore, the assigned length for the ozone exposure in this study is long enough to deliver a sufficiently oxidized substrate.
However, since the substrates are not fully oxidized at the end of the ozone exposures, still Al$_2$O$_3$ films are deposited at the beginnings of the second purges (shown as the small bumps in Figure 4.5) due to the oxygen atoms remaining inside the reactors. Based on Figure 4.9(a), due to the low amounts of the remaining oxygen atoms after an ozone exposure inside the reactor with $T_s = 250$ °C, Al$_2$O$_3$ films are not deposited on the substrate during the second purges.

Nevertheless, according to Figure 4.9(b), not only enough oxygen atoms are available over the substrate with $T_s = 300$ °C, but also both ozone and O$_2$ are removed from the reactor earlier than the oxygen atoms. Therefore, the oxygen atoms participate mostly in the surface reactions rather than in the gas-phase reactions; so, Al$_2$O$_3$ films are deposited on the substrate at the second purges. There are two sharp rises in the deposition rates shown in Figure 4.9(b). The first sharp rise corresponds to the start of the increase in the gap between the remaining oxygen atoms and other species (O$_3$ and O$_2$).
that results in more surface reactions compared with the gas-phase reactions. The second and biggest jump represents when the major $\text{O}_2$ and almost all the ozone are removed from the reactor, so the remaining oxygen atoms participate mainly in the surface reactions to deposit $\text{Al}_2\text{O}_3$. By the reduction in the oxygen atoms inside the reactor due to the purge, the deposition rates continuously decrease until they stop.

However, based on Figure 4.10, $\text{Al}_2\text{O}_3$ growth rates at the second purges are less than $2.3 \times 10^{-4}$ angstrom/cycle and $2.8 \times 10^{-2}$ angstrom/cycle for $T_s = 250 \, ^\circ \text{C}$ and $T_s = 300 \, ^\circ \text{C}$, respectively. Therefore, the deposition rates at the second purges for both substrate temperatures are negligible.

![Figure 4.9(a): Deposition rates and species mass fractions during the second purge in one cycle for $T_s = 250 \, ^\circ \text{C}$.](image1)

![Figure 4.9(b): Deposition rates and species mass fractions during the second purge in one cycle for $T_s = 300 \, ^\circ \text{C}$.](image2)
In order to compare the purge times between two different reactors, the argon mass fractions inside the reactor volumes are measured and shown in Figure 4.11. At the beginning of the TMA injection, a reactor is full with argon from the previous purge and since the length of the TMA exposure is short (1 s), the major part of a reactor will remain filled with argon after the TMA exposure. For this reason, the argon mass fractions are almost 0.6 at the beginning of the first purge, so a relatively short purge time is enough to evacuate the reactors from the remaining TMA and C$_2$H$_6$. As shown in Figure 4.11(a), the differences between the first purge times for the two reactors are negligible and both of them are evacuated at almost the same time.

However, the argon is removed completely from the reactors during an ozone exposure due to a long exposure time (72 s). Therefore, based on Figure 4.11(b), the second purge takes longer than the first purge since the argon mass fraction must increase from zero inside the reactors at the second purges. Although the differences in the second purge times for the reactors with different substrate temperatures are not significant, the reactor with a colder substrate is purged in a slightly shorter time. Generations of C$_2$H$_6$
due to Al$_2$O$_3$ depositions at the second purges inside the reactor with the hotter substrate could be the reason for a slightly longer purge time for the reactor with $T_s = 300\,^\circ$C.

Figure 4.11(a): Argon mass fractions inside the reactors at the first purge for one cycle.  
Figure 4.11(b): Argon mass fractions inside the reactors at the second purge for one cycle.
Chapter 5: ALD Characteristics of Al₂O₃ in Multi-Outlet

Viscous Flow Reactors

5.1. Problem Description

Al₂O₃ films are deposited inside the viscous flow reactors illustrated in Figure 5.1. The chemistry mechanism, the boundary conditions, the timing-sequence, and the operating conditions are the same as those mentioned in section 3.1.

Figure 5.1(a): Top view of a reactor with 1 outlet.  Figure 5.1(b): Top view of a reactor with 2 outlets.

Figure 5.1(c): Top view of a reactor with 3 outlets.  Figure 5.1(d): Side view of reactors.
5.2. Results

Figure 5.2 illustrates the mass flow rates, \( \dot{m} \), inside a cycle. At the present operating conditions, the inlet mixture viscosity ranges as

\[ 1.03 \times 10^{-5} - 2.44 \times 10^{-5} \text{ Kg/m.s} \]; therefore, the Reynolds number, \( \text{Re} = \frac{4\dot{m}_{in}}{\pi D \mu_{in}} \), changes between 1 and 18 that indicates perfectly laminar flows inside the reactors.

Surface coverages during TMA and ozone exposures are illustrated in Figures 5.3(a) and 5.3(b), respectively. Since during the TMA exposure only one surface reaction occurs, and TMA as the reactant is directly injected into the reactors, all the substrates are quickly and fully saturated with \( \text{Al(C}_3\text{H}_3)_{2}^* \) almost within 0.3 s after TMA injection.

However, due to existence of four reactions at the ozone exposure on one hand and production of oxygen atoms from ozone decomposition on the other hand, the substrate oxidation takes for a longer time. For a specific reactor type, the hotter substrate
is oxidized faster due to a larger amount of oxygen atoms over the substrate, in the result of a higher bulk temperature inside the reactor. A higher bulk temperature leads to faster ozone decompositions and more oxygen atoms generations. The comparisons of oxygen atoms inside the reactors are illustrated in Figure 5.4. Insignificant differences in oxidation times among the different reactors at a fixed substrate temperature in Figure 5.3(b) are due to almost the same amount of oxygen atoms over the substrates based on Figure 5.4.

![Figure 5.3(a): Substrate coverage during the TMA exposure for one cycle.](image1)

![Figure 5.3(b): Substrate oxidation during the ozone exposure for one cycle.](image2)

![Figure 5.4: Mass fractions of oxygen atoms inside the reactors during the ozone exposure for one cycle.](image3)
Figure 5.5 illustrates the deposition rate distributions for five ALD cycles. The same deposition rate distributions among all cycles for each ALD process indicate the equal film growth rate at each cycle and the dependency of the desired film thickness only on the number of cycles.

For a reactor with a fixed number of outlets, films are deposited earlier on the hotter substrate due to a faster substrate oxidation. In addition, mass deposition rates are larger for the hotter substrate due to (i) a larger surface reaction rate constant, and (ii) larger concentrations of oxygen atoms at the substrate.

![Deposition rate distributions for 5 cycles.](image)

However, the surface reaction rate constants are equal for the substrates with the same temperature. Therefore, concentrations of oxygen atoms at the substrates are the major parameters to compare the deposition rates among fixed-temperature substrates in different reactors. Although in Figure 5.5 the peaks of deposition rates are slightly higher
for a reactor with fewer outlets, no considerable differences are observed in film growth rates among multi-outlet reactors due to almost the same amount of oxygen atoms inside the reactors. Therefore, the deposited thickness is almost independent of the numbers of outlets. Based on Figure 5.6, Al₂O₃ growth rates for \( T_s = 250 \, ^\circ C \) and \( T_s = 300 \, ^\circ C \) are 3.78 angstrom/cycle and 4.52 angstrom/cycle, respectively. A growth plateau at each cycle in Figure 5.6 indicates that most parts of the substrate surfaces are oxidized and so, there is not enough \( \text{Al}(\text{CH}_3)_2^* \) left to deposit more Al₂O₃. Accordingly, the assigned length for the ozone exposure is sufficiently long in order to investigate ALD performances.

![Al₂O₃ film thickness plots](image)

Figure 5.6(a): Al₂O₃ film thickness at \( T_s = 250 \, ^\circ C \) for 5 cycles.

Figure 5.6(b): Al₂O₃ film thickness at \( T_s = 300 \, ^\circ C \) for 5 cycles.

Figure 5.7 compares the deposition rates for two substrate temperatures inside the reactor with two outlets. The higher deposition rates for the hotter substrate are observed at all times. According to surface reaction S2, more \( \text{Al}(\text{CH}_3)_2^* \) produces more \( \text{Al}(\text{CH}_3)\text{OAl}(\text{CH}_3)^* \). Since \( \text{Al}(\text{CH}_3)\text{OAl}(\text{CH}_3)^* \) as a product of surface reaction S2 is required as a reactant in surface reaction S3 to deposit Al₂O₃, the deposition rates are the
highest in those parts of a substrate where the density of $\text{Al(C}_2\text{H}_3)_2^*$ is the maximum. At the beginning of the ozone exposure, depositions start at the leading edge of the substrate that is the closest part to the reactor inlet with the maximum density of $\text{Al(C}_2\text{H}_3)_2^*$ . When a fraction of $\text{Al(C}_2\text{H}_3)_2^*$ in an area is consumed, the maximum deposition rates are shifted to the next part towards the outlet with a higher $\text{Al(C}_2\text{H}_3)_2^*$ density. This process continues until the whole $\text{Al(C}_2\text{H}_3)_2^*$ on the substrate is consumed (substrate is oxidized) and then the depositions stop.

Based on Figure 5.8, deposition patterns are almost the same for the different reactors at the same substrate temperature. Since a film uniformity is affected strongly by a deposition pattern, it can be concluded that a film uniformity is almost independent of the numbers of outlets.

Figure 5.7(a): Contours of deposition rates at 1 s after the ozone exposure for the reactor with two outlets. (i): $T_s = 250 \degree \text{C}$, (ii): $T_s = 300 \degree \text{C}$. 
Figure 5.7(b): Contours of deposition rates at 10 s after the ozone exposure for the reactor with two outlets. 
(i): $T_s = 250 \, ^\circ C$, (ii): $T_s = 300 \, ^\circ C$.

Figure 5.7(c): Contours of deposition rates at 70 s after the ozone exposure for the reactor with two outlets. 
(i): $T_s = 250 \, ^\circ C$, (ii): $T_s = 300 \, ^\circ C$.

Figure 5.8(a): Contours of deposition rates at 10 s after the ozone exposure for $T_s = 300 \, ^\circ C$. (i): one outlet, 
(ii): two outlets, (iii): three outlets.
Since at the end of ozone exposures the substrates are not fully oxidized, Al$_2$O$_3$ films are still deposited at the beginnings of the second purges due to the existence of oxygen atoms inside the reactors. These depositions are observed in Figure 5.5 as the small bumps. Figure 5.9 illustrates the deposition rates and gaseous species inside the reactors at the second purge. Based on Figure 5.9(a), due to the low remaining amounts of oxygen atoms inside the reactors with $T_s = 250 \degree$C, no more Al$_2$O$_3$ films are deposited at the early times of the second purge.

However, the remaining amounts of oxygen atoms inside the reactors with $T_s = 300 \degree$C are large enough to deposit Al$_2$O$_3$ at the second purge. Based on Figure 5.9(b), not only ozone and O$_2$ are removed from the reactors earlier than oxygen atoms, but also oxygen atoms leave the reactors slowly until the reactors are completely purged of ozone and O$_2$. Therefore, oxygen atoms have more chance to participate in the surface reactions rather than in the gas-phase reactions. The first peak in deposition rates in Figure 5.9(b) occurs at the start of the increase in the gap between the mass fractions of oxygen atoms and other species (O$_3$ and O$_2$). The second and biggest jump corresponds to when almost all the ozone and most of the O$_2$ are removed from the reactors and

Figure 5.8(b): Contours of deposition rates at 15 s after the ozone exposure for $T_s = 300 \degree$C. (i): one outlet, (ii): two outlets, (iii): three outlets.
therefore, the remaining oxygen atoms participate mainly in the surface reactions. Then, the depositions stop when the reactors are emptied of the oxygen atoms.

However, based on Figure 5.10, Al₂O₃ growth rates at the second purge are less than $2.7 \times 10^{-4}$ angstrom/cycle and $3 \times 10^{-2}$ angstrom/cycle at $T_s = 250 \degree C$ and $T_s = 300 \degree C$, respectively. Therefore, the deposited thicknesses at the second purges are negligible, especially for the substrates at lower temperatures.

Figure 5.9(a): Deposition rates and species mass fractions during the second purge in one cycle for $T_s = 250 \degree C$.

Figure 5.9(b): Deposition rates and species mass fractions during the second purge in one cycle for $T_s = 300 \degree C$.

Figure 5.10(a): Al₂O₃ film thickness at the second purges for $T_s = 250 \degree C$.

Figure 5.10(b): Al₂O₃ film thickness at the second purges for $T_s = 300 \degree C$. 
In order to investigate the purge times, argon mass fractions inside the reactors are measured at the purges. At the beginning of TMA exposure, the reactor is full with argon from the previous purge and since the TMA exposure takes a short time (1 s), much of the reactor is still filled with argon at the end of the TMA exposure. Therefore, the first purge takes a short time, as illustrated in Figure 5.11(a). Also, the first purge times are almost the same for all the reactors with different substrate temperatures.

However, since the ozone exposure takes for a much longer time, the remaining argon inside a reactor from the first purge is completely removed during the ozone exposure. Therefore, based on Figure 5.11(b), the second purge takes longer than the first purge. In addition, for a reactor with a specific number of outlets, the second purge takes a slightly longer at \( T_s = 300 \, ^\circ\text{C} \) due to generations of \( \text{C}_2\text{H}_6 \) in the results of \( \text{Al}_2\text{O}_3 \) depositions at the early times of the second purge. Moreover, at a specific substrate temperature, the second purge times are slightly shorter for a reactor with fewer numbers of outlets.

![Figure 5.11(a): Argon mass fractions inside the reactors at the first purge in one cycle.](image1)

![Figure 5.11(b): Argon mass fractions inside the reactors at the second purge in one cycle.](image2)
Chapter 6: Effects of Reactor Inlet Locations on ALD

Characteristics of Al₂O₃

6.1. Problem Description

Al₂O₃ films are deposited inside the viscous flow reactors illustrated in Figure 6.1. In the top-inlet reactor (TIR), the gases are injected directly into the substrate from the top surface of the reactor while in the bottom-inlet reactor (BIR) gases are injected into the reactor from the bottom of the reactor and close to the substrate. The chemistry mechanism, the boundary conditions, the timing-sequence, and the operating conditions are the same as those mentioned in section 3.1. $\hat{V}_{in} = -\hat{V}_{in} \hat{j}$ and $\hat{V}_{in} = \hat{V}_{in} \hat{j}$ for the TIR and the BIR, respectively.

Figure 6.1(a): Top-inlet reactor (TIR).
Figure 6.1(b): Bottom-inlet reactor (BIR).
6.2. Results

Inlet mass flow rates are illustrated in Figure 6.2. According to the ranges for the inlet mixture viscosities, \( 1.03 \times 10^{-5} \text{ Kg/m.s} < \mu_{in} < 2.44 \times 10^{-5} \text{ Kg/m.s} \), the Reynolds number, \( \text{Re} = \frac{4\dot{m}_{in}}{\pi D \mu_{in}} \), changes between 1 and 18 at the present operating conditions. Therefore, flows are perfectly laminar inside the reactors.

Figure 6.3 illustrates the argon mass fractions during one cycle. At the beginning of TMA exposure, the reactor is filled with argon. Moreover, since the TMA exposure takes for a short time (1 s), still argon remains inside the reactor at the end of TMA exposure. Therefore, a short time for the first purge is enough to remove unreacted TMA and by-product \( \text{C}_2\text{H}_6 \) from the reactor. However, due to a long ozone exposure (72 s), remaining argon inside the reactor from the first purge is completely removed during the ozone exposure. As a result, a relatively longer time for the second purge is required to evacuate the reactor from \( \text{O}_3, \text{O}_2, \text{O}, \) and \( \text{C}_2\text{H}_6 \).

![Figure 6.2: Mass flow rates during one cycle.](image)
In an ALD process, a substrate is saturated with a surface species at the end of each precursor. Based on Figure 6.4(a), the substrates are quickly saturated with $\text{Al} (\text{CH}_3)_2^*$ after TMA injection because the TMA exposure includes only one reaction, and the gaseous reactant is directly injected into the reactor. The coverage times are almost the same for the different substrate temperatures at a specific reactor type. However, at a fixed substrate temperature, a substrate in the TIR is saturated faster because TMA covers a wider area of the substrate in the TIR compared with the BIR due to almost axi-symmetric TMA injections in the TIR.
Nevertheless, the substrate oxidation takes much longer since (i) the ozone exposure includes four reactions, (ii) surface reaction S3 depends on the surface reaction S2, and the most important, (iii) the oxygen atoms as the gaseous reactants for the surface reactions must be produced from the gas-phase reactions. As shown in Figure 6.4(b), for a specific reactor type, the hotter substrate is oxidized faster due to (i) a larger surface reaction rate constant, and (ii) greater concentrations of oxygen atoms at the substrate. The produced amount of oxygen atoms in a reactor is proportional to the bulk temperature inside a reactor. Since a bulk temperature is higher inside a reactor with a hotter substrate, gas-phase reactions take place faster inside the reactor with $T_s = 300$ °C. As a result, more ozone is consumed and more O$_2$ and oxygen atoms are generated inside the reactor including the hotter substrate. Figure 6.5 illustrates the gaseous species inside the reactor volumes during the ozone exposure.

However, at a fixed substrate temperature, surface reaction rate constants are equal. Therefore, the concentrations of reactants at the substrates are the only major parameters to compare the speed of surface coverages.
Due to almost axi-symmetric ozone injections inside the TIR, oxygen atoms are distributed more uniformly over the whole substrate surface in the TIR compared with the BIR. Therefore, if there are sufficiently large amounts of oxygen atoms inside the reactors, oxidation occurs faster for the substrate in the TIR due to a higher $[O]_s$ otherwise, a substrate in the BIR is oxidized faster. Based on Figure 6.5(c), there are significantly less amounts of oxygen atoms inside the reactors with $T_s = 250 \, ^\circ\text{C}$ compared with the reactors at $T_s = 300 \, ^\circ\text{C}$. On the other hand, among all the oxygen atoms inside a reactor volume, only those atoms that are over the substrate participate in the surface reactions. As a result, there are not sufficient oxygen atoms over the colder substrates. So, at $T_s = 250 \, ^\circ\text{C}$, $[O]_s$ is lower in the TIR that results in a faster substrate oxidation for the BIR. The same justifications are true at the beginnings of the ozone exposure inside the reactors with $T_s = 300 \, ^\circ\text{C}$. Therefore, the hotter substrate is oxidized faster in the BIR until the amounts of oxygen atoms reach to the highest value inside the reactors after almost 8 s from the ozone exposure, as shown in Figure 6.5(c). Of this time, the oxidation trends are changed as shown in Figure 6.4(b) due to a higher $[O]_s$ at the substrate in the TIR.

However, since a sufficiently long time is assigned for the ozone exposure in this study, the final fractions of the substrates that are oxidized are independent of the reactor type such that at the end of the ozone exposure, almost 99.910% of both substrates at $T_s = 250 \, ^\circ\text{C}$ and 99.983% of both substrates at $T_s = 300 \, ^\circ\text{C}$ are oxidized. A long enough time for an ozone exposure is a crucial parameter to analyze deposition rates.
Figure 6.5(a): Mass fractions of ozone inside the reactors during the ozone exposure in one cycle.

Figure 6.5(b): Mass fractions of O₂ inside the reactors during the ozone exposure in one cycle.

Figure 6.5(c): Mass fractions of oxygen atoms inside the reactors during the ozone exposure in one cycle.

Figure 6.5(d): Mass fractions of C₂H₆ inside the reactors during the ozone exposure in one cycle.

Figure 6.6 illustrates the deposition rate distributions for five ALD cycles. For a specific reactor type, the mass deposition rates are higher on the hotter substrate due to both larger surface reaction rate constant and more oxygen atoms over the substrate. However, surface reactions rate constants are equal for the substrates at the same temperature. Therefore, [O]ₜ is the major parameter to compare the mass deposition rates.
on the fixed-temperature substrates in different reactor types. Figure 6.7 illustrates the deposition rate distributions at $T_s = 250$ °C for one ALD cycle. Since the substrate at $T_s = 250$ °C is oxidized faster in the BIR, $[O]_s$ is larger in the BIR at specific times during the deposition process. A faster substrate oxidation inside the BIR can be found by steeper slopes of deposition curves for the BIR in Figure 6.7. However, since the peaks of deposition rates are almost the same for two substrates in Figure 6.7, the maximum values of $[O]_s$ should be almost equal for both the BIR and the TIR. In fact, when depositions are stopped on the substrate in the BIR due to a faster oxidation, films are still being deposited on the substrate in the TIR due to a long ozone exposure. As shown in Figure 6.7, at the end of the ozone exposure, the area under the deposition curve in the TIR is larger than that of the deposition curve in the BIR. As a result, at $T_s = 250$ °C, a thicker Al$_2$O$_3$ film is deposited on the substrate inside the TIR, although the substrate in the BIR is oxidized faster.

However, at $T_s = 300$ °C, the peaks of deposition rates are much higher inside the TIR as shown in Figure 6.6; therefore, $[O]_s$ is larger at the TIR due to sufficiently high amounts of oxygen atoms inside the reactors. Figure 6.8 compares the distributions of oxygen atoms right above the substrates at $T_s = 300$ °C at a specific time. Although $[O]_s$ is higher in some areas of the substrate in the BIR, the area-averaged of $[O]_s$ is much larger in the TIR. As a result, at $T_s = 300$ °C, the deposition rates are larger on the substrate in the TIR.
Figure 6.6: Deposition rate distributions for 5 ALD cycles.

Figure 6.7: Deposition rate distributions for one ALD cycle at $T_s = 250$ °C.
Figure 6.8: Mass fractions of oxygen atoms on the substrates at $T_s = 300 \degree C$ after 12 s from the ozone exposure. (i): BIR, (ii): TIR.

As mentioned earlier, among entire oxygen atoms inside a reactor volume, only those parts that are right above the substrate participate in the surface reactions. For this reason, based on Figure 6.8, $[O]_s$ is larger for the TIR despite almost equal amounts of oxygen atoms inside the volumes of both the BIR and the TIR in Figure 6.5(c). In addition, at a specific substrate temperature, more produced $C_2H_6$ shown in Figure 6.5(d) inside the TIR indicates the larger deposition rates on the substrate in the TIR.

Figure 6.9 shows the contours of deposition rates on the substrates at $300 \degree C$ at three different times. Depositions start from the area that is covered with $Al(CH_3)_2^*$ in the vicinity of oxygen atoms. In the BIR, deposition starts at the leading edge of the substrate that is the closest area to the reactor inlet; therefore, deposition rates are the highest at the leading edge. When some parts of $Al(CH_3)_2^*$ at the leading edge is consumed, the maximum deposition rates shift to the next area that is mostly covered with $Al(CH_3)_2^*$. The shifting of the maximum deposition rates continues until all
$\text{Al(CH}_3\text{)}_2^*$ on the substrate is consumed or, in other words, the whole substrate is oxidized. However in the TIR, depositions are more uniform compared with the BIR because whole the substrate surface in the TIR is covered by the oxygen atoms at each time. Based on Figure 6.9, depositions are almost axi-symmetric in the TIR. In addition, Figure 6.9(c) indicates a sufficiently long ozone exposure in this study since while depositions are nearly stopped on the substrate that has been almost oxidized, still films are being deposited on another substrate that has not been oxidized yet.

Figure 6.9(a): Contours of deposition rates at $T_s = 300 \, ^\circ\text{C}$ after 1 s from the ozone exposure. (i): BIR, (ii): TIR.

Figure 6.9(b): Contours of deposition rates at $T_s = 300 \, ^\circ\text{C}$ after 12 s from the ozone exposure. (i): BIR, (ii): TIR.
The same deposition distributions among all the cycles in Figure 6.6 for each ALD process result in a constant film growth rate at each cycle. As a result, the desired film thickness can be controlled only by the numbers of ALD cycles. Based on Figure 6.10, the film growth rates at $T_s = 250$ °C are equal to 3.78 and 4.43 angstrom/cycle in the BIR and the TIR, respectively, and the film growth rates at $T_s = 300$ °C are equal to 4.52 and 6.49 angstrom/cycle in the BIR and the TIR, respectively. Also, the plateaus in film growths at each cycle in Figure 6.10 indicate both the terminations of $\text{Al}_2\text{O}_3$ depositions and a sufficiently long ozone exposure.

However, due to non-fully oxidized substrates at the end of an ozone exposure, $\text{Al}_2\text{O}_3$ films are deposited at the early times of the second purge in the results of available oxygen atoms inside the reactors. These depositions are observed as the very small bumps in Figure 6.6. Although depositions at the second purges can be avoided by assigning a longer ozone exposure, the computational times increase significantly. But, based on Figure 6.11, the film growth rates at the second purges are less than $3.3 \times 10^{-4}$ angstrom/cycle and $2.8 \times 10^{-2}$ angstrom/cycle for $T_s = 250$ °C and $T_s = 300$ °C.
respectively. Therefore, the deposited thicknesses at the second purges can be neglected without any penalty in the accuracy of the deposited film thicknesses.

Figure 6.10: Deposited Al₂O₃ film thicknesses during 5 ALD cycles.

Figure 6.11(a): Deposited Al₂O₃ film thicknesses at the second purges for \( T_s = 250 \, ^\circ\text{C} \).

Figure 6.11(b): Deposited Al₂O₃ film thicknesses at the second purges for \( T_s = 300 \, ^\circ\text{C} \).
Chapter 7: Conclusions and Future Works

7.1. Conclusions

A validated numerical model to simulate a general ALD process in a reactor scale is presented. The simulation process is specified by depositions of Al₂O₃ for five ALD cycles by using TMA and ozone as the metal source and the oxidant, respectively. An inert argon is used as the purge gas, and simulations are performed for an operating pressure of 10 Torr (1330 Pa) and two substrate temperatures of 250 °C and 300 °C, respectively. By using the proposed numerical model, ALD characteristics of Al₂O₃ are investigated at different reactor design parameters.

7.1.1. ALD Characteristics of Al₂O₃ at Different Substrate Temperatures

Substrates with different temperatures are saturated quickly and almost at the same time with Al(CH₃)₂⁺ at the TMA exposure while substrate oxidations take much longer due to existence of four reactions, dependent surface reactions, and generations of oxygen atoms from ozone decompositions at the ozone exposure.

A higher bulk temperature inside the reactor with \( T_s = 300 \, ^\circ\text{C} \) results in faster ozone decompositions and more oxygen atoms productions. Therefore, oxidations and film depositions take place more quickly on the hotter substrate. Moreover, deposition rates are higher for the hotter substrate due to both the larger surface reaction rate constant and the greater concentrations of oxygen atoms at the substrate.
At a fixed substrate temperature, deposition rate distributions are the same among all cycles; therefore, the desired film thickness can be controlled only by the number of deposition cycles. Al₂O₃ growth rates of 3.78 ångstrom/cycle and 4.52 ångstrom/cycle are obtained for the substrate temperatures of 250 °C and 300 °C, respectively. Also, plateaus in film growths indicate a long enough time for the ozone injection in this study to deliver a sufficiently oxidized substrate.

Film depositions at the second purges are negligible since the growth rates are less than 2.3×10⁻⁴ ångstrom/cycle and 2.8×10⁻² ångstrom/cycle for \( T_s = 250 \) °C and \( T_s = 300 \) °C, respectively, during the second purges.

### 7.1.2. ALD Characteristics of Al₂O₃ in Multi-Outlet Viscous Flow Reactors

For a reactor with a fixed number of outlets, the hotter substrate is oxidized earlier due to more oxygen atoms over the substrate. Also, deposition rates are higher on the hotter substrate due to a larger surface reaction rate constant, and larger concentrations of oxygen atoms at the substrate. However, the deposition rates are almost the same on the substrates at a fixed temperature in different reactors, due to equal surface reaction rate constants and almost the same amount of oxygen atoms over the substrates.

For each ALD process, deposition rate distributions are the same among all the cycles that indicate a constant deposited thickness at each cycle; as a result, film growth rates of 3.78 ångstrom/cycle and 4.52 ångstrom/cycle are obtained for the substrate temperatures of 250 °C and 300 °C, respectively. Therefore, deposition film thicknesses are independent of the number of reactor outlets. The film growth plateaus correspond to a long enough time for the ozone exposure to deliver a sufficiently oxidized substrate.
Although the substrates are not fully oxidized at the end of the ozone exposure, film growths at the beginning of the second purges are negligible.

### 7.1.3. Effects of Reactor Inlet Locations on ALD Characteristics of Al₂O₃

The substrates are saturated quickly at the TMA exposure. The coverage times are almost independent of the substrate temperatures for a specific reactor type. However, the substrates in the TIR are saturated faster than those inside the BIR due to distributions of TMA on wider areas of the substrates in the TIR.

Assigning a long enough time for an ozone exposure is a crucial parameter to investigate oxidation times and film deposition rates. Inside a specific reactor type, the hotter substrate is oxidized faster while depending on the substrate temperature, the oxidation trends are different in the TIR and the BIR. However, due to a long assigned time for the ozone exposure in this study, the same amounts of substrates at a fixed temperature are oxidized at the end of the ozone exposure.

Inside a specific reactor type, the mass deposition rates are higher on the hotter substrate due to both the larger surface reaction rate constant and the greater concentrations of oxygen atoms on the substrate. At a fixed substrate temperature, higher deposition rates are obtained by using the TIR.

The deposition rate distributions are the same among all the cycles for each ALD process that indicate a constant growth rate at each cycle. The Al₂O₃ growth rates at $T_s = 250 \degree C$ are equal to 3.78 and 4.43 angstrom/cycle in the BIR and the TIR, respectively, and the films growth rates at $T_s = 300 \degree C$ are equal to 4.52 and 6.49 angstrom/cycle in the BIR and the TIR, respectively.
Due to non-fully oxidized substrates at the end of the ozone exposure, Al₂O₃ films are deposited at the beginning of the second purge. However, the growth rates at the second purges are less than $3.3 \times 10^{-4}$ angstrom/cycle and $2.8 \times 10^{-2}$ angstrom/cycle for $T_s = 250 \, ^\circ\mathrm{C}$ and $T_s = 300 \, ^\circ\mathrm{C}$, respectively. Therefore, depositions at the second purge can be neglected without any penalty in the thicknesses of the final films.

7.2. Future Works

Since the present research is among the first studies in a reactor scale simulation of an ALD process, more investigations are suggested to improve the present numerical model, as follows:

1- More accurate chemistry mechanisms should be used with the present numerical model.

2- Simulations should be extended for a wider range of substrate temperatures, and operating pressures.

3- The effects of precursor flow rates on ALD characteristics should be investigated.

4- Full oxidation of a substrate should be obtained through different numerical techniques without any penalty in computational times.

5- The ALD characteristics should be investigated by using a viscous flow reactor with adiabatic walls. At this study, all the reactor walls are at the same temperature of the substrate.
References


CHEMKIN-CFD for FLUENT Module 20112, Reaction Design: San Diego, 2011.


Pirolli, L., Teplyakov, A.V., 2006. Molecular view of copper deposition chemistry: (Hexafluoroacetylacetonate)Cu(vinyltrimethylsilane) on a Si(100)-2x1 surface. Surface Science 600, 3313-3320.


Wind, R.A., George, S.M., 2010. Quartz crystal microbalance studies of Al\textsubscript{2}O\textsubscript{3} atomic layer deposition using trimethylaluminum and water at 125 °C. The Journal of Physical Chemistry A 114, 1281-1289.


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