Improving atomic layer deposition process through reactor scale simulation

Mohammad Reza Shaeri \(^a\), Tien-Chien Jen \(^{a,b,*}\), Chris Yingchun Yuan \(^a\)

\(^a\) Department of Mechanical Engineering, University of Wisconsin-Milwaukee, Milwaukee, WI 53211, USA

\(^b\) School of Engineering, University of Alaska Anchorage, Anchorage, AK 99508, USA

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**A B S T R A C T**

In order to modify atomic layer deposition (ALD) characteristics of Al₂O₃, three-dimensional gas transports and film depositions are investigated through reactor scale simulations inside two different viscous flow reactors. In the top-inlet reactor (TIR), the gaseous species are directly injected into the substrates from the upper surface of the reactor while in the bottom-inlet reactor (BIR), the inlet is at the bottom of the reactor and next to the substrate. The numerical procedure to simulate the ALD process is thoroughly explained by using the multi-species and multi-reaction chemistry phenomena. The reactants are trimethylaluminum (TMA) and ozone, and the simulations are performed in an operating pressure of 10 Torr (1330 Pa) and two substrate temperatures of 250 °C and 300 °C. Due to the chemistry mechanism used in this study, a long ozone exposure is a crucial parameter to deliver a sufficiently oxidized substrate. For a specific reactor type, deposition rates are higher on the hotter substrate due to both a larger surface reaction rate constant and greater concentrations of the oxygen atoms on the substrate. At a fixed substrate temperature, higher deposition rates are obtained by using the TIR. The same deposition rate distributions are obtained among all cycles for each ALD process that result in the dependency of the film thickness only on the numbers of ALD cycles. For the substrate at 250 °C, the growth rates are equal to 3.78 Å/cycle and 4.43 Å/cycle in the BIR and the TIR, respectively, and for the substrate at 300 °C, the growth rates are equal to 4.52 Å/cycle and 6.49 Å/cycle in the BIR and the TIR, respectively.

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1. Introduction

Atomic layer deposition (ALD) is a key enabling nanotechnology derived from a chemical vapor deposition (CVD), but in an ALD process a substrate is sequentially exposed to gaseous reactants (precursors) to grow ultrathin and monolayer-by-monolayer films \([1]\). In an ALD process, films are deposited on the substrate in a cyclic manner in four steps, as follows: (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 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 from the by-products and the unreacted precursors by an inert gas \([2,3]\). 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 \(t_2\) correspond to the exposures of the first and the second precursors, respectively, and \(t_3\) and \(t_4\) represent the first and the second purge times, respectively \([4]\). Purging the reactor is an essential step in a cycle to prevent interactions and CVD between two precursors inside the reactor, as a CVD adversely affects the uniformity of the deposited films. The self-limiting characteristic of a surface reaction results in excellent advantages such as high conformal thin films over complex structures, good reproducibility, precise thickness control in an atomic scale, and growth rates dependent only on the number of ALD cycles \([5,6]\).

Generally, 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 geometrical dimensions inside the reactor such as a substrate/inlet/outlet diameter. Since the operating pressures inside viscous flow reactors in ALD processes are ranged 1–10 Torr (133–1330 Pa) \([7]\), it is possible that mean-free paths of gases are comparable with microscopic lengths while macroscopic lengths are much larger than mean-free paths. Therefore, coexistences of both very large and very small Knudsen numbers as indicators of molecular flows and continuum flows, respectively, result in challenging and complicated simulation processes.
Although a comprehensive numerical study of an ALD process is obtained through a multi-scale simulation, either computational times increase significantly or advanced numerical techniques are required. For instance, Cheimarios et al. [8] used multi processors as well as the Message Passing Interface (MPI) technique for multi-scale simulations of CVD processes. However, depending on a research goal, using either a feature scale simulation or a reactor scale simulation can lead to satisfactory results. For example, a feature scale simulation is appropriate for an investigation of ALD characteristics on a porous substrate, although large length scales render it unusable when it comes to studying reactor performance. Using a reactor scale simulation, however, is a reasonable approach for the latter purpose. Our literature reviews show that most ALD simulations were performed in feature scales/multi-scales [9-12] while reactor scale simulations were rarely performed. Ho et al. [13] deposited Al₂O₃ from trimethylaluminum (TMA) and ozone for different substrate temperatures through both experiments and reactor scale simulations. In their study, numerical and experimental deposition rates were not in good agreement, due to a weak temperature-dependent chemistry mechanism – such that the deposition rates remain almost unchanged for the substrate temperatures from 300 °C to 450 °C. In fact, the lack of a precise chemistry mechanism in a surface reaction has remained as an inevitable limitation due to extremely complicated processes and many unsolved phenomena inside the reaction.

**Nomenclature**

\[ a_1-a_7 \] coefficients of the polynomial functions for calculation of thermodynamics properties of gaseous species

\( A \) pre-exponential factor in an Arrhenius expression \((\text{m}^3/\text{mol} \cdot \text{s})\)

\( b^r \) reactant stoichiometric coefficient of a bulk species in a surface reaction

\( b^s \) 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 \((\text{J/kg} \cdot \text{K})\)

\( D \) inlet, outlet, and substrate diameter \((\text{m})\)

\( D_f \) bulk diffusion coefficient \((\text{kg/m}^2 \cdot \text{s})\)

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

\( E \) activation energy in an Arrhenius expression \((\text{J/mol})\)

\( f \) mole fraction

\( g^r \) reactant stoichiometric coefficient of a gaseous species in a surface reaction

\( g^s \) product stoichiometric coefficient of a gaseous species in a surface reaction

\( g \) gravitational acceleration vector \((\text{m/s}^2)\)

\( G \) gaseous species in a surface reaction

\( h \) mixture enthalpy \((\text{J/kg})\)

\( H \) enthalpy \((\text{J/mol})\)

\( h^0 \) standard state enthalpy \((\text{J/mol})\)

\( i \) unity tensor

\( J \) direction in \( Y \) coordinate

\( J^d \) diffusive mass flux \((\text{kg/m}^2 \cdot \text{s})\)

\( J^n \) diffusive mass flux normal to the substrate \((\text{kg/m}^2 \cdot \text{s})\)

\( k_f \) forward reaction rate constant \((\text{consistent units})\)

\( k_b \) backward reaction rate constant \((\text{consistent units})\)

\( K \) mixture thermal conductivity \((\text{W/m} \cdot \text{K})\)

\( R \) species thermal conductivity \((\text{W/m} \cdot \text{K})\)

\( K_B \) Boltzmann constant \((\text{J/K})\)

\( m \) mass flow rate \((\text{kg/s})\)

\( M_{dep} \) mass deposition rate on the substrate \((\text{kg/m}^2 \cdot \text{s})\)

\( N \) 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

\( N_{gr} \) total number of gas-phase reactions

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

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

\( P \) pressure \((\text{Pa})\)

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

\( P^g \) molar reaction rate in a gas-phase reaction \((\text{mol/m}^3 \cdot \text{s})\)

\( R \) gas constant \((\text{J/mol} \cdot \text{K})\)

\( R \) molar reaction rate in a surface reaction \((\text{mol/m}^2 \cdot \text{s})\)

\( Re \) Reynolds number

\( s^r \) reactant stoichiometric coefficient of a surface species in a surface reaction

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

\( S \) surface species in a surface reaction

\( S^0 \) standard state entropy \((\text{J/mol} \cdot \text{K})\)

\( t \) time \((\text{s})\)

\( T \) temperature \((\text{K})\)

\( v^r \) reactant stoichiometric coefficient in a gas-phase reaction

\( v^s \) product stoichiometric coefficient in a gas-phase reaction

\( V \) velocity vector \((\text{m/s})\)

\( W \) molecular weight \((\text{kg/mol})\)

\( X, Y, Z \) Cartesian coordinates

\( y \) mass fraction

\( z \) site coverage

**Greek symbols**

\( \alpha \) temperature exponent in an Arrhenius expression

\( \beta \) sticking coefficient

\( \Gamma \) total surface site concentration \((\text{Kg/mol/m}^2)\)

\( \varepsilon \) maximum energy of attraction \((\text{J})\)

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

\( \lambda \) gas mean-free path \((\text{m})\)

\( \mu \) mixture viscosity \((\text{kg/m} \cdot \text{s})\)

\( \mu \) species viscosity \((\text{kg/m} \cdot \text{s})\)

\( \rho \) mixture density \((\text{kg/m}^3)\)

\( \sigma \) Lennard–Jones collision diameter \((\text{m})\)

\( \Phi \) third bodies effects in a gas-phase reaction \((\text{mol/m}^2)\)

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

\( \Omega_D \) collision integral for diffusion \((\text{dimensionless})\)

\( \Omega_D \) collision integral for viscosity \((\text{dimensionless})\)

**Subscript**

\( A \) 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**

\( ^\circ \) respect to a surface species

\( ^* \) respect to a bulk species
At the present study, we aim to modify performances of viscous flow reactors used in ALD processes. It is assumed that the substrates are completely smooth (without any pores/trenches on their surfaces), so simulations in a reactor scale are acceptable. First, we present a numerical model that simulates an ALD process in a reactor scale. Then, we investigate the performances of two different viscous flow reactors by using our presented model. The model is described in a general form such that it is compatible with arbitrary precursors, purge gases, and chemistry mechanisms. To describe the model, three-dimensional gas transports and film depositions are simulated inside viscous flow reactors in an operating pressure of 10 Torr (1330 Pa) and two substrate temperatures of 250 °C and 300 °C. The accuracy of the transport model is verified with the benchmark solutions in the literature. Also, the ALD process is specified by deposition of Al2O3 from TMA and ozone as the precursors, and the purging of the reactors by an inert argon.

2. Research motivation

In our experimental research, we are studying ALD of Al2O3 using TMA and H2O as the precursors, and nitrogen as the purge/carrier gas. Fig. 1 illustrates the viscous flow reactor used in our experiments. It should be taken into account that the size of the substrate depends on the size of the material that is deposited by films. Performance improvement of our current ALD reactor by changes in its structure/design is one of our future research goals. However, either manufacturing a new reactor or changing the structure of our current reactor is costly and requires advanced tools. On the other hand, we should have a good estimation about performances of a new reactor before performing expensive experiments. Therefore, in this study, we aim to improve the performances of our current reactor through simulations.

3. Problem description

3.1. ALD reactors

In order to reduce the number of grids and save computational times in the simulations, the real reactor in Fig. 1 is downsized. Fig. 2(a) illustrates the smaller size of the real reactor. In this paper, this reactor is called BIR, and represents the bottom-inlet reactor.

3.2. Chemistry mechanism

A surface reaction encompasses several reactive intermediates and elementary reactions that are very difficult to capture, due to extremely complicated mechanisms in a surface reaction. Therefore, still a precise chemistry mechanism to describe a surface reaction in an ALD process has not been presented.

However, the validation of the accuracy of a chemistry mechanism is not our goal since we do not aim to predict quantitatively accurate ALD characteristics. Our goal is obtaining a big picture of the changes in ALD characteristics caused by different flow patterns and species transports inside the ALD reactors. In order to avoid computational complications, an undetailed chemistry mechanism is sufficient to couple the chemistry model and the transport model [14]. Such an approach is very common and acceptable in computational research. Lin et al. [15] and Abedi et al. [16] used a chemistry mechanism including only one irreversible global reaction to optimize CVD processes. Lin et al. [17] employed the same chemistry mechanism in [16] by using ANSYS FLUENT to investigate the effect of embedding a porous medium on the deposition rate in a metalorganic CVD process. Peng et al. [18] presented a thermal model for CVD of titanium nitride on the spherical particle surface by using a one-step irreversible global reaction. Chiu et al. [19] optimized a CVD process by using a reversible global reaction. Mishra and Verma [20] investigated growing carbon nanofibers in a CVD reactor through a chemistry mechanism with only one irreversible reaction.

As a result, we use the chemistry mechanism available in advanced software CHEMKIN-PRO, developed by Reaction Design. CHEMKIN-PRO is a robust software designed to simulate complex chemical design problems. This chemistry mechanism that is specifically implemented in CHEMKIN-PRO to simulate an ALD process includes three irreversible surface reactions and two reversible gas-phase reactions, as follows:

\[
\begin{align*}
(S1) \ Al(CH_3)_3 + O^- & \xrightarrow{k_1} Al(CH_3)_2^0 + 2Al(CH_3)_2 + 0.25C_2H_4, & \gamma = 0.1 \\
(G1) O_3 + M & \xrightarrow{k_2} O_2 + O + M. & A = 4.51 \times 10^9 \text{ m}^3/\text{mol s}, \\
\beta = 0, & E = 100416 \text{ J/mol} \\
(G2) O + O_2 & \xrightarrow{k_3} 2O_2. & A = 2.96 \times 10^7 \text{ m}^3/\text{mol s}, \\
\beta = 0, & E = 25104 \text{ J/mol} \\
(S2) \ 2Al(CH_3)_2^0 + O^- & \xrightarrow{k_4} Al(CH_3)_2^OAl(CH_3)^0 + C_2H_4, & \gamma = 1.0 \\
(S3) \ 0.5Al(CH_3)_2^OAl(CH_3)^0 & \xrightarrow{k_5} O^0 + 2Al(CH_3)_2 + 0.5Al_2O_3. & \gamma = 1.0
\end{align*}
\]

where the asterisk and B superscripts correspond to the surface and the bulk species, respectively, and the remaining elements are the gaseous species.

3.3. ALD process and boundary conditions

To deposit metal oxide films by an ALD technique, one precursor is used as the metal source and another is the oxidant [21]. In this study, Al2O3 films are deposited on the substrate from TMA,
Al(CH₃)₃ and ozone, O₃, as the metal source, and the oxidant, respectively, based on the global reaction 2Al(CH₃)₃ + O₃ → Al₂O₃ + 3C₃H₆ [22]. An inert argon, Ar, is used as the purge gas to deplete the reactors from the remaining unreacted precursors and reaction products from the previous precursor exposure. In a real ALD process, an inert gas is used as a carrier gas as well to transport the precursors to the substrate. A carrier gas flow can be simply considered by injection of a mixture of a precursor and an inert gas at each precursor exposure. However, in order to reduce the computational time, we do not consider carrier gas flow to transport the precursors to the substrate. A carrier gas flow can be simply considered by injection of a mixture of a precursor and an inert gas at each precursor exposure. However, in order to reduce the computational time, we do not consider carrier gas flow in this study. A timing-sequence of 1–2–72–5 s is used for each cycle as (i) injection of pure TMA into the reactor for 1 s, (ii) injection of pure argon into the reactor for 2 s, (iii) injection of pure ozone into the reactor for 72 s, and (iv) injection of pure argon into the reactor for 5 s. The assigned timing-sequence is selected from several tests such that 1 s and 72 s are long enough to cover more than 99.9% of the substrates by Al(CH₃)₃ and O₃, 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 is to initiate the surface reaction S1 only, while all other reactions take place during the ozone exposure.

The processes are simulated for a fixed operating pressure of 10 Torr (1330 Pa) and two substrate temperatures of 250 °C and 300 °C. The inlet conditions are Tin = 300 K, fTMA = 1.0, and |V| = 0.6 m/s for the TMA exposure, Tin = 300 K, fO₃ = 1.0, and |V| = 0.6 m/s for the ozone exposure, and Tin = 300 K, fAr = 1.0, and |V| = 4.2 m/s for the both purges. V in = -|V|y and V in = |V|y for the TIR and the BIR, respectively. At the outlet, zero axial gradients for all the variables are imposed. The remaining surfaces are walls and their temperatures are equal to that of the substrate. Except for the substrate, no-slip boundary conditions for the velocities, and zero mass flux gradients at normal to the surfaces are imposed for the other walls. On the substrate, films are deposited due to the surface reactions as described in the following section.

4. Numerical model

4.1. Governing equations

At the present operating conditions, the maximum Knudsen number, λ/D = Kₜ/√2πRσ²D [23], is less than 0.01 by using Kₜ = 1.38 × 10⁻²³ J/K as the Boltzmann constant, T = 573 K as the maximum temperature, P = 1330 Pa as the pressure, σ = 2.75 × 10⁻¹⁰ m as the smallest collision diameter (provided in Table 1 in Appendix A), and D = 0.002 m as the smallest length scale inside the reactor. As a result, due to λ/D < 0.01, using the continuum approach with no-slip boundary conditions to simulate the flow fields inside the reactors is valid in this study [24–28]. Therefore, the governing equations are listed as follows:

\[
\frac{\partial p}{\partial t} + \nabla \cdot (p\nabla) = 0
\]  
(1)

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

\[
\frac{\partial (\rho T)}{\partial t} + \nabla \cdot (\rho T \nabla T) = \nabla \cdot (K \nabla T) - \sum_{i=1}^{N} \left[ R_i \left( v_i - v_i^* \right) R_i \right]
\]  
(3)

where the mixture enthalpy and the enthalpy of the i-th gaseous species are calculated as follows:

\[
h = \sum_{i=1}^{N} \frac{H_i}{W_i}
\]  
(5)

\[
H_i = H_{i0} + \int_{298.15}^{T_i} C_p dT
\]  
(6)

with H₀ as the standard state enthalpy of the i-th gaseous species.

The concentration and temperature-dependent diffusive mass flux for a non-dilute multi-component mixture is obtained as shown below:

\[
\bar{j}_i = -\rho \frac{1 - f_i}{\sum_{j=1}^{N} f_j} \nabla y_i - D_i \nabla T
\]  
(7)

The Brinkman number as an indicator of the strength of viscous dissipations is defined as follows [29]:

\[
Br = \frac{\mu |\nabla|^2}{K(T_i - T_m)}
\]  
(8)

In this study, instead of local Brinkman numbers, inlet Brinkman numbers, Brin, are used to determine the magnitudes of viscous dissipations. With μ₀ and K₀ in the range of 1.03 × 10⁻⁵–2.44 × 10⁻⁵ Kg/ms and 0.013–0.024 W/m K, respectively, at the present operating conditions, Brin changes between 5.6 × 10⁻⁶ and...

Fig. 2. (a) Bottom-inlet reactor (BIR), (b) top-inlet reactor (TIR).
\[ P = \frac{P}{RT} \sum_{i=1}^{N} \frac{v_i}{W_i} \]  

The molar reaction rate for the \( r \)th reversible gas-phase reaction is described as follows [30]:

\[ R^p_r = \Phi_r \left( \frac{k_r}{RT} \right)^{v_{r,\text{products}}} k_{-r} \left( \frac{P}{RT} \right)^{v_{r,\text{reactants}}} \]

where \( \Phi_r \) represents the effect of third bodies in the \( r \)th reaction. The forward and backward reaction rate constants for the \( r \)th gas-phase reaction are calculated from an Arrhenius expression and the reaction equilibrium constant, respectively, as follow [31]:

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

\[ k_{-r} = \frac{k_r}{\exp \left( \frac{\Delta S_r(T) - \Delta S_{-r}(T)}{k} \right) \left( \frac{P}{P_{\text{atm}}} \right)} \sum_{i=1}^{N} \left( v_{r,i} - v_{-r,i} \right) \]

with

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

\[ \Delta S_r(T) = \sum_{i=1}^{N} \left( v_{r,i} - v_{-r,i} \right) S_r(T) \]

where \( H_r(T) \) and \( S_r(T) \) are the enthalpy and entropy of the \( r \)th gaseous species at the temperature \( T \) and the atmospheric pressure.

The \( r \)th irreversible surface reaction has the following general form [32]:

\[ \sum_{i=1}^{N_s} g_{i,s} G_i + \sum_{i=1}^{N_b} b_{i,b} B_i + \sum_{i=1}^{N_s} s_{i,s} S_i = \sum_{i=1}^{N_g} g_{i,g} G_i + \sum_{i=1}^{N_b} b_{i,b} B_i + \sum_{i=1}^{N_s} s_{i,s} S_i \]  

where \( G, B, \) and \( S \) correspond to the gaseous species, the bulk species, and the surface species, respectively. The surface reaction rate constant for the \( r \)th surface reaction is described in terms of the sticking coefficient as follows [30]:

\[ k_{j,r} = \frac{\gamma_r}{W_r} \sqrt{\frac{RT_j}{2\pi m_r}} \]  

where \( \gamma_r, T_r, W_r, \) and \( m_r \) are the sticking coefficient, the substrate temperature, the molecular weight of gaseous reactant, and the summation of stoichiometric coefficients of the surface species reactants, respectively, in the \( r \)th surface reaction. Also, \( \Gamma \) is the total surface site concentration. In this study, \( \Gamma = 2.72 \times 10^{-8} \text{ Kg mol/m}^2 \)

The molar reaction rate for the \( r \)th irreversible surface reaction is calculated as follows [32]:

\[ R_j = k_{j,r} \left( \prod_{i=1}^{N_s} |G_i|^n_{j,s} \right) \left( \prod_{i=1}^{N_b} |B_i|^n_{j,b} \right) \]

where \( |G_i| = \left( \rho y_i \right)_{j,s} \) and \( |S_i| = \left( \rho y_i \right)_{j,s} \)

4.2. Boundary conditions at the substrate

The substrate temperatures are set at 250°C and 300°C, respectively. Due to the surface reactions, the net vertical mass flux of the \( r \)th gaseous species into the substrate balances with its net consumption/production rate on the substrate, as follows [32,34]:

\[ \left( j_r - M_{\text{dep}} \right) = W_i \sum_{i=1}^{N} \left( b_{r,i} - b_{-r,i} \right) R_r \]

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

\[ M_{\text{dep}} = \sum_{i=1}^{N} W_i \sum_{i=1}^{N} \left( b_{r,i} - b_{-r,i} \right) R_r \]

The balance of consumption/production rate of a gaseous species with its vertical convection/diffusion on the substrate leads to a very small velocity component normal to the substrate [34]. Therefore, a no-slip boundary condition on the substrate is not valid.

4.3. Gas properties

Gas properties should be considered as temperature-dependent variables due to the large temperature variations inside the reactors. The required correlations to describe the gaseous properties are presented in Appendix A.

5. Numerical procedure

5.1. Grid and time-step size independence tests

An appropriate grid structure is obtained through steady state CVDs of \( \text{Al}_2\text{O}_3 \) inside both TIR and BIR with \( P = 10 \text{ Torr} \) (1330 Pa), \( T_m = 300 \text{ K}, T_s = 573 \text{ K}, |V_in| = 1.0 \text{ m/s}, f_{\text{TMA}} = 0.1, f_{\text{O}_2} = 0.3 \text{ and } f_{\text{N}_2} = 0.6 \) by using 13,456, 22,020, 31,965, 48,288, 83,940, 102,630, 140,010, 177,390, 225,240 and 259,284 computational cells. Since the magnitudes of deposition rates, heat transfer coefficients, and skin friction coefficients on the substrates remain below 4% by an increase in the numbers of cells from 31,965, this grid structure is used for the simulations to save the computational time.

An independency between the deposition rates and the time-step sizes is obtained in very small time-step sizes, leading to extremely time-consuming computations. Therefore, time-step independence tests are performed by using a transient, non-reactive, and multi-component mixture with the same characteristics in the previous CVDs for 20 s, by using the grid with 31,965 cells and time-step sizes of 0.1 s, 0.05 s, 0.01 s, 0.005 s, 0.001 s, 0.0005 s, and 0.0001 s. The changes in magnitudes of time-averaged heat transfer coefficients and skin friction coefficients on the substrates remain below 4% and 0.03%, respectively, by a decrease in the time-step size from 0.005 s. Therefore, to improve the computational times, all the simulations are performed at a time-step size of 0.005 s. A time-averaged property \( \Omega \) is calculated as \( \frac{1}{T} \int_0^T \Omega \text{d}t \) [35].
5.2. Solution method

The transport equations are discretized spatially and temporally using the second order upwind and the first order implicit methods through the finite volume approach. Also, the source terms in the transport equations are linearized. To couple the velocity components and the pressure, the PISO algorithm as a robust solver for transient flows is used [36]. Solutions are considered converged when at each time-step the residual values are less than $1 	imes 10^{-5}$ for the continuity, velocity components, and temperature, and less than $1 	imes 10^{-4}$ for the gaseous species.

The transport and the chemistry equations are solved by using the CFD code ANSYS FLUENT 14.0 and the CHEMKIN-CFD package, respectively. The CHEMKIN-CFD package, provided by Reaction Design, is an advanced chemistry solver that is linked to FLUENT to increase the accuracy and stability of chemistry simulations. In addition, a user-defined function (UDF) is developed and loaded by FLUENT to change the inlet boundary conditions inside the ALD cycles.

6. Validation of the transport model

The chemistry mechanism behind the production of atomic layer deposition film is not well understood; as such, it is not possible to precisely compare computational and experimental ALD characteristics. On the other hand, we do not need to validate the accuracy of the chemistry mechanism, since the prediction of quantitatively accurate ALD characteristics is not our research goal. However, due to important effects of flow patterns and species transports on ALD characteristics in the present study, the accuracy of our transport model in a reacting flow, including both gas-phase and surface reactions, is verified by the well-established benchmark results proposed by Kleijn [34].

Kleijn [34] proposed benchmark solutions for CVD of silicon from a mixture of silane and helium through a full multi-component transport model with multi-species and multi-reaction chemistry in a two-dimensional and axi-symmetric reactor as illustrated in Fig. 3(a). Comparisons are made for the selected results from the same boundary conditions and chemistry mechanisms in [34], as shown in Fig. 3. The excellent agreements between the results in the two studies prove the good accuracy of our transport model. As a result, the ALD characteristics of $\text{Al}_2\text{O}_3$ are illustrated in the following section by using our validated numerical model.

7. Results and discussions

ALD of $\text{Al}_2\text{O}_3$ from TMA and ozone as the metal and oxygen sources, respectively, and argon as the purge gas is modeled through reactor scale simulations. The simulations are performed inside two different viscous flow reactors in an operating pressure of 10 Torr (1330 Pa) and two substrate temperatures of 250 °C and 300 °C, respectively.
Inlet mass flow rates are illustrated in Fig. 4. According to the provided ranges for the inlet mixture viscosities in Section 4.1, the Reynolds number \( Re = \frac{4m_{\text{in}}}{\pi D_{\text{in}} \mu_{\text{in}}} \) changes between 1 and 18 at the present operating conditions. Therefore, flows are perfectly laminar inside the reactors.

Fig. 5 illustrates the argon mass fractions during one cycle. At the beginning of TMA exposure, the reactor is filled with argon from the second purge. 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 is sufficient for the first purge to remove unreacted TMA and by-product C2H6 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 longer time for the second purge is required to evacuate the reactor from unreacted ozone, and by-products O2, O, and C2H6.

In an ALD process, a substrate is saturated with a surface species at the end of each precursor exposure. Because the TMA
exposure includes only one reaction and the gaseous reactant (TMA) is directly injected into the reactor, the substrates are quickly covered with Al(CH$_3$)$_2$ after the TMA injection, based on Fig. 6(a). The coverage times are almost the same for the substrates with different temperatures inside a specific reactor type. However, at a fixed substrate temperature, a substrate inside 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 Fig. 6(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 $T_s = 300 \, ^\circ C$. As a result, more ozone is consumed and more O$_2$ and oxygen atoms are generated inside the reactor including the hotter substrate. Fig. 7 illustrates the gaseous species inside the reactor volumes during the ozone exposure.

However, based on Eq. (16), surface reaction rate constants are equal for the substrates at a fixed temperature. Therefore, the concentrations of reactants at the substrates are the only major parameters to compare the speed of surface coverages. Due to almost the 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 more quickly for the substrate in the TIR due to a higher [O]$_s$ otherwise, a substrate in the BIR is oxidized faster. Based on Fig. 7(c), there are significantly less oxygen atoms inside the reactors with $T_s = 250 \, ^\circ C$ compared with the reactors at $T_s = 300 \, ^\circ C$. 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 $T_s = 250 \, ^\circ C$, [O]$_s$ is lower in the TIR that results in a faster substrate oxidation in the BIR. The same justifications are true at the beginnings of the ozone exposure inside the reactors with $T_s = 300 \, ^\circ C$. Therefore, the hotter substrate is oxidized faster in the BIR until the amounts of oxygen atoms reach to their maximum values inside the reactors after almost 8 s from the ozone exposure, as shown in Fig. 7(c). Thereafter, the oxidation trends are changed as shown in Fig. 6(b) due to a higher [O]$_s$ on the substrate in the TIR.

However, since a sufficiently long ozone exposure is assigned in this study, the final fractions of the substrates that are oxidized are independent of the reactor types such that at the end of the ozone exposure, almost 99.910% of both substrates at $T_s = 250 \, ^\circ C$ and 99.983% of both substrates at $T_s = 300 \, ^\circ C$ are oxidized. A long enough time for an ozone exposure is a crucial parameter to analyze deposition rates.

Fig. 8 illustrates the deposition rate distributions for five ALD cycles (400 s). 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]$_s$ is the major parameter to compare the mass deposition rates on the fixed-temperature substrates in different reactor types. Fig. 9 illustrates the deposition rate distributions at $T_s = 250 \, ^\circ C$ for one ALD cycle. Since the substrate at $T_s = 250 \, ^\circ C$ 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 is observed by steeper slopes of deposition curves for the BIR in Fig. 9. However, since the peaks of deposition rates are almost the same for the two substrates in Fig. 9, the maximum values of [O]$_s$ should be almost equal in both the BIR and the TIR. In fact, when Al$_2$O$_3$ 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 Fig. 9, 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 $T_s = 250 \, ^\circ C$, a
thicker Al₂O₃ film is deposited on the substrate inside the TIR, although the substrate in the BIR is oxidized faster.

However, at $T_s = 300 \, ^\circ C$, the peaks of deposition rates are much higher inside the TIR as shown in Fig. 8; therefore, $[O]$, should be much larger in the TIR due to sufficiently high amounts of oxygen atoms inside the hotter reactors (reactors with $T_s = 300 \, ^\circ C$) as shown in Fig. 7(c). Fig. 10 compares the distributions of oxygen atoms right above the substrates at $T_s = 300 \, ^\circ C$ for a specific time. Although local values of $[O]$, are higher in some areas of the substrate in the BIR, the area-averaged of $[O]$, is much larger in the TIR. As a result, at $T_s = 300 \, ^\circ C$, the deposition rates are larger on the substrate inside the TIR.

As mentioned earlier, among entire oxygen atoms inside a reactor volume, only those atoms that are right above the substrate participate in the surface reactions. For this reason, based on Fig. 10, $[O]$, is larger for the TIR despite almost equal amounts of oxygen atoms inside the volumes of both the BIR and the TIR with the same substrate temperatures in Fig. 7(c). In addition, at a specific substrate temperature, more produced C₂H₆ inside the TIR as shown in Fig. 7(d) indicates the larger deposition rates on the substrate in the TIR.

Fig. 11 shows the contours of deposition rates on the substrates at 300 °C at three different times. Depositions start from the area that is covered with Al(CH₃)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(CH₃)₂ at the leading edge is consumed, the maximum deposition rates shift to the next area that is mostly covered with Al(CH₃)₂. The shifting of the maximum deposition rates continues until all Al(CH₃)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 Fig. 11, depositions are almost axi-symmetric in the TIR. In addition, Fig. 11(c) indicates a sufficiently long ozone exposure in this study since while depositions are nearly stopped on the substrate that has been almost oxidized (the substrate in the TIR), still films are being deposited on another substrate that has not been oxidized yet (the substrate in the BIR).

The same deposition distributions among all the cycles in Fig. 8 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 Fig. 12, the Al₂O₃ growth rates at $T_s = 250 \, ^\circ C$ are equal to 3.78 Å/cycle and 4.43 Å/cycle in the BIR and the TIR, respectively, and the Al₂O₃ growth rates at $T_s = 300 \, ^\circ C$ are equal to 4.52 Å/cycle and 6.49 Å/cycle in the BIR and the TIR, respectively. Also, the plateaus in film growths at each cycle in Fig. 12 indicate both the termination of Al₂O₃ depositions and a sufficiently long oxygen exposure in this study.

However, due to non-fully oxidized substrates at the end of an ozone exposure, Al₂O₃ films are deposited at the early times of the second purge, since the oxygen atoms are still available inside the reactors. These depositions are observed as the very small bumps shown in Fig. 8. Although depositions at the second purges can be avoided by assigning a longer ozone exposure, the computational times increase significantly. But, based on Fig. 13, the film growth rates at the second purges are less than $3.3 \times 10^{-4}$ Å/cycle and $2.8 \times 10^{-2}$ Å/cycle for $T_s = 250 \, ^\circ C$ and $T_s = 300 \, ^\circ C$, respectively. Therefore, the deposited thicknesses at the second purges can be neglected without any penalty in the accuracy of the deposited film thicknesses.

8. Conclusions

A numerical procedure for the reactor scale simulation of an ALD process is presented by depositions of Al₂O₃ from TMA and ozone as the precursors and purging the reactor with inert argon. The simulations are performed at an operating pressure of 10 Torr (1330 Pa) and two substrate temperatures of 250 °C and 300 °C, respectively, inside two different viscous flow reactors. In one
reactor, the inlet is located at the upper surface of the reactor (TIR), and in another reactor, the inlet is placed at the lower surface of the reactor and close to the substrate (BIR).

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 the substrates inside the BIR due to distributions of TMA on wider areas of the substrate surfaces in the TIR.

Assigning a long 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 ozone exposure in this study, the same fractions of substrate surfaces at a fixed substrate 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 using the TIR.

For each ALD process, the deposition rate distributions are the same among all the cycles; therefore, the growth rate is equal at each cycle. The Al₂O₃ growth rates at Tₛ = 250 °C are equal to 3.78 Å/cycle and 4.43 Å/cycle in the BIR and the TIR, respectively, and the Al₂O₃ growth rates at Tₛ = 300 °C are equal to 4.52 Å/cycle and 6.49 Å/cycle in the BIR and the TIR, respectively. Although Al₂O₃ films are deposited on the substrates at the beginning of the second purge due to non-fully oxidized substrates and available oxygen atoms inside the reactors, these growth rates have negligible effects on the final Al₂O₃ thicknesses.

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Appendix A

A.1. Temperature-dependent properties of the gaseous species and the mixture

A.1.1. Thermodynamics properties of the gaseous species

For each gaseous species, temperature-dependent functions provided in [33] are used to calculate the specific heat, the standard state enthalpy, and the standard state entropy as follows:

\[
C_p = a_{ij} + a_{2j}T + a_{3j}T^2 + a_{4j}T^3 + a_{5j}T^4
\]  
\[
H_i^0 = a_{1j}T + \frac{a_{2j}}{2}T^2 + \frac{a_{3j}}{3}T^3 + \frac{a_{4j}}{4}T^4 + \frac{a_{5j}}{5}T^5 + a_{6j}
\]  
\[
S_i^0 = a_{1j}\ln T + a_{2j}T + \frac{a_{3j}}{2}T^2 + \frac{a_{4j}}{3}T^3 + \frac{a_{5j}}{4}T^4 + a_{7j}
\]  

A.2. Transport properties of the gaseous species

A.2.1. Thermal diffusion coefficient

The thermal diffusion coefficient of each species is calculated by using the empirically-based composition-dependent expression provided in [37] as follows:

\[
D_i^T = -2.59 \times 10^{-7}T^{0.659}\left[\frac{W_{j}^{511}f_{j}}{\sum_{j=1}^{N}W_{j}^{511}f_{j}} - Y_{i}\right]\left[\frac{\sum_{j=1}^{N}W_{j}^{511}f_{j}}{\sum_{j=1}^{N}W_{j}^{511}f_{j}}\right]
\]

(A4)

The binary diffusivity, the viscosity, and the thermal conductivity of each species are obtained through the correlations in the kinetic theory of gases [38,39] as follows.

A.2.2. Binary diffusivity

\[
D_{ij} = 1.8583 \times 10^{-2}\sqrt{T}\left[\frac{1}{W_{j}} + \frac{1}{W_{i}}\right]\frac{1}{\sigma_i^2\Omega_i}
\]

where \(\sigma_{ij} = 0.5(\sigma_i + \sigma_j)\). The units of \(D_{ij}\) is in cm²/s if the units of \(P, T,\) and \(\sigma_i\) are in atm, K, and angstrom, respectively. Also, \(\Omega_i\) as the collision integral for diffusion is a function of dimensionless temperature \(K_i\mid\epsilon_i\) with \(\epsilon_i = 6\sqrt{T_i}\).

A.2.3. Viscosity

\[
\bar{\mu}_i = 2.6693 \times 10^{-5}\frac{\sqrt{W_iT}}{\sigma_i^2\Omega_i}
\]

(A6)

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, \(\Omega_i\) as the collision integral for viscosity is a function of the dimensionless temperature \(K_i\mid\epsilon_i\).

A.2.4. Thermal conductivity

\[
R_i = \bar{\mu}_i \left[C_{p,i} + \frac{5}{4} \frac{R}{W_i}\right]
\]

(A7)
Table 1

Molecular weights and Lennard–Jones parameters for the gaseous species provided from [33].

<table>
<thead>
<tr>
<th>Species</th>
<th>$W_i$ (kg/k mol)</th>
<th>$\sigma_i$ (Å)</th>
<th>$\epsilon_i/K_B$ (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>CH_4</td>
<td>30.070</td>
<td>4.302</td>
<td>252.3</td>
</tr>
</tbody>
</table>

For using the correlations in the kinetic theory of gases, the Lennard–Jones collision diameter, and the maximum energy of attraction for each species are required. These parameters are provided from the transport data in [33] and listed in Table 1.

A.3. Mixture properties

The viscosity and the thermal conductivity of the mixture are calculated as follows [40,41]:

$$\mu = \sum_{i=1}^{N} f_i \mu_i$$

(A8)

$$K = \sum_{i=1}^{N} f_i K_i$$

(A9)

with

$$\phi_j = \left[ 1 + \left( \frac{\sigma_j}{\sigma_{\text{ref}}} \right)^{0.5} \left( \frac{\omega_{ij}}{\Omega_i} \right) \right]^{0.25}$$

(A10)

References


