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Investigating atomic layer deposition characteristics in multi-outlet viscous flow reactors through reactor scale simulations

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ABSTRACT

In order to minimize the operational time of atomic layer deposition (ALD) process, flow transports and film depositions are investigated in multi-outlet viscous flow reactors through reactor scale simulations. The simulation process is performed on depositions of Al_2O_3 films using trimethylaluminum and ozone as the precursors, and inert argon as the purge gas. The chemistry mechanism used includes both gas-phase and surface reactions. Simulations are performed at a fixed operating pressure of 10 Torr (1330 Pa) and at two substrate temperatures of 250 °C and 300 °C, respectively. Flows inside the reactors are following the continuum approach; as a result, the Navier–Stokes, energy and species transport equations can be used to simulate transient, laminar and multi-component reacting flows. Based on the chemistry mechanism adopted in this study, the amount of oxygen atoms produced from the ozone decomposition is found to be the major reason for discrepancies in oxidation times and deposition rates at different ALD processes. A reactor with fewer outlets minimizes the ALD operational times by reducing both oxidation time and second purge time. In addition, higher deposition rates at a shorter time are obtained by using a reactor with fewer outlets. However, assigning a long enough time for the ozone exposure results in independency of ALD characteristics from the number of outlets such that the growth rates of around 3.78 angstrom/cycle and 4.52 angstrom/cycle are obtained for the substrate temperatures of 250 °C and 300 °C, respectively.

1. Introduction

Atomic layer deposition (ALD) is an excellent deposition technique based on self-limiting surface chemical reactions to coat substrates with highly uniform and conformal thin films under precise thickness controls in atomic scales [1–4]. ALD is derived from chemical vapor deposition (CVD) where in an ALD each gaseous precursor is alternately pulsed into the reactor; and a binary reaction $a + b \rightarrow c + d$ is split into self-limiting surface reactions between the two gaseous precursors a and b, and the absorbed species on the substrate [5]. Also, to avoid non-uniformity in film depositions due to interactions and gas-phase reactions between the precursors, the reactor is purged by an inert gas between precursor exposures [6].

An ALD process is performed in a cyclic manner, and each cycle includes four steps: (i) pulsing the first precursor into the reactor to form a surface layer on the substrate, (ii) purging the reactor with the inert gas to remove both the unreacted first precursor and reaction products, (iii) pulsing the second precursor into the reactor to form the desired film by self-limiting surface reaction with the first precursor absorbed on the substrate surface, and (iv) purging the reactor with the inert gas to remove both the unreacted second precursor and reaction products, and prepare for the next cycle of deposition [7,8]. 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 to the first and the second precursor exposure times, and t_2 and t_4 represent the first and the second purge times, respectively [9,10]. Since the same deposition thickness is obtained at the end of each cycle, the desired film thickness can be controlled precisely by the number of ALD cycles.

The reactor is an essential component in an ALD process. Among different types of ALD reactors, viscous flow reactors are often used due to their much faster film depositions [11]. In ALD process, the feature and reactor scales are two main length scales. A feature

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Nomenclature

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
C_p	specific heat (J/kg K)
D	inlet, outlet, and substrate diameter (m)
D^T	thermal diffusion coefficient (kg/m s)
$\mathcal{D}_{ij}$	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
$\bar{g}$	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)
$\bar{\bar{I}}$	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)
K_B	Boltzmann constant (J/K)
$\dot{m}$	mass flow rate (kg/s)
$\dot{M}_{dep}$	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_{surf}	total number of surface reactions
P	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)
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
t	time (s)
T	temperature (K)
υ'	reactant stoichiometric coefficient in a gas-phase reaction
υ''	product stoichiometric coefficient in a gas-phase reaction
$\bar{V}$	velocity vector (m/s)
W	molecular weight (kg/mol)
X, Y, Z	Cartesian coordinates
y	mass fraction
z	site coverage

Greek symbols

β	temperature exponent in an Arrhenius expression
γ	sticking coefficient
Γ	total surface site concentration (Kg mol/m^2)
η'	rate exponent of a gaseous species in a surface reaction
λ	gas mean-free path (m)
μ	mixture viscosity (kg/m s)
ρ	mixture density (kg/m^3)
σ	Lennard–Jones collision diameter (m)
Φ	third bodies effects in a gas-phase reaction (mol/m^3)
ψ'	rate exponent of a surface species in a surface reaction

Subscript

Ar	respect to argon
in	respect to the inlet
i	respect to the ith species
j	respect to the jth species
O_3	respect to ozone
r	respect to the rth reaction
s	respect to the substrate
TMA	respect to trimethylaluminum

Superscript

$*$	respect to a surface species
B	respect to a bulk species

scale corresponds to microscopic trenches and pores on a substrate, while a reactor scale represents macroscopic geometrical dimensions such as a substrate diameter or an inlet/outlet diameter of a reactor. Due to low operating pressures inside viscous flow reactors of 1–10 Torr (133–1330 Pa) [12,13], 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. As a result, both large and small Knudsen numbers as representatives of molecular and continuum flows coexist inside an ALD reactor. However, ALD characteristics may be investigated through a specific length scale such as a reactor scale, a feature scale or a multi-scale basis. Although film depositions on a porous substrate should be modeled through a feature scale, species transports inside a reactor may be investigated through a reactor scale simulation. To study both the aforementioned phenomena together, a multi-scale simulation is used. However, employing either a feature scale or a multi-scale simulation usually not only results in time consuming simulations, but also requires advanced computational techniques. For instance, Gobbert et al. [14] used 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. Also, Cheimarios et al. [15] modeled a CVD process through a multi-scale simulation using multi processors and the Message Passing Interface (MPI) technique.

This study aims at investigating the flow and species transports inside the reactors, through reactor scale simulations. Based on our literature review, most ALD simulations were performed on large Knudsen numbers in feature scales [16–23] while reactor scale simulations are rarely investigated. Ho et al. [24] investigated the ALD of Al_2O_3 from trimethylaluminum (TMA) and ozone for different substrate temperatures through both experiments and reactor scale simulations. The deviations between experimental and computational deposition rates in [24] were mainly due to the lack of an accurate chemistry mechanism, as an inevitable limitation due to many unsolved and extremely complicated phenomena in