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Reactor scale simulation of an atomic layer deposition process

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ABSTRACT

To simulate an atomic layer deposition (ALD) process in a reactor scale, three-dimensional deposition of Al_2O_3 from trimethylaluminum and ozone inside a viscous flow reactor is investigated. The chemistry mechanism used includes both gas-phase and surface reactions. 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 Navier–Stokes, energy, and species transport equations are discretized through the finite volume method to simulate transient, laminar and multi-component reacting flows. It is found that the larger surface reaction rate constant, and the greater concentrations of gaseous reactants at the substrate result in higher deposition rates on the substrate at 300 °C. At a fixed substrate temperature, the deposition rate distributions are the same among all the cycles that indicate a constant growth rate at each cycle. As a result, Al_2O_3 growth rates of 3.78 angstrom/cycle and 4.52 angstrom/cycle are obtained for the substrate temperatures of 250 °C and 300 °C, respectively.

Keywords: Atomic layer deposition; Multi-component mixture; Finite volume; Gas-phase reaction; Surface reaction; Surface coverage

1. Introduction

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). 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 (Kim et al., 2010). In ALD operations, precursors are alternatively pulsed into a reactor, with a complete purge in between, to produce monolayer-by-monolayer thin films on the substrate in a cyclic manner (Katamreddy et al., 2006). In the process, purging is a crucial step to prevent the CVD type of thin film growth between unreacted precursors in the reactor. ALD operations are typically characterized by a timing-sequence of t_1–t_2–t_3–t_4 for (i) exposure of the first precursor for t_1 s, (ii) purge of the reactor for t_2 s, (iii) exposure of the second precursor for t_3 s, and (iv) purge of the reactor for t_4 s (Tamm et al., 2012). In general, ALD reactors are divided into two groups as viscous flow reactors and molecular flow reactors (Ritala and Leskela, 2002). With a much faster film depositions, viscous flow reactors are often used in ALD processes (Elam et al., 2002).

Generally, an ALD process includes microscopic and macroscopic length scales called feature and reactor scales, respectively. A feature scale corresponds to microscopic trenches on a substrate surface, and a reactor scale relates to reactor geometrical dimensions such as a substrate diameter. Since operating pressures inside a viscous flow reactor range between 1 and 10 torr (133–1330 Pa) (Schuisky et al., 2002), gas mean-free paths may be comparable with microscopic lengths while macroscopic lengths are much larger than mean-free paths. As a result, very large and very small Knudsen numbers

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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 (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
$\bar{g}$	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)
$\bar{K}$	species 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
S^0	standard state entropy (J/mol K)
t	time (s)
T	temperature (K)
ν'	reactant stoichiometric coefficient in a gas-phase reaction
ν''	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)
ε	maximum energy of attraction (J)
η'	rate exponent of a gaseous species in a surface reaction
λ	gas mean-free path (m)
μ	mixture viscosity (kg/m s)
$\bar{\mu}$:	species 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
Ω_D	collision integral for diffusion (dimensionless)
Ω_μ	collision integral for viscosity (dimensionless)

Subscripts

Ar	respect to argon
in	respect to the inlet
i	respect to the ith 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

Superscripts

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

are formed inside the reactor due to feature scales and reactor scales, respectively. In this case, it is a big challenge simulating an ALD process due to the coexistence of molecular and continuum flows inside the reactor.

Depending on simulation goals, an ALD process is computationally studied through a specific scale. A multi-scale simulation provides more comprehensive details about a whole ALD process. Also, a feature scale simulation is used to study film depositions on the substrates including microscopic pores/trenches. However, investigations of flow patterns and species transports inside ALD reactors may be perfectly