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Atomic layer deposition process optimization by computational fluid dynamics

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ABSTRACT

This paper presents a computational fluid dynamics model to optimize atomic layer deposition (ALD) process, in which the temperature, precursor mass fraction, mass flow and pressure have been quantitatively analyzed by combining surface chemical reactions with species transport. Simulation results show that the higher temperature increases the growth rate and accelerates the surface deposition process, yet has little impact on precursor distribution in the entire chamber. Both computational and experimental results reveal that precursor concentration is the critical parameter which affects the cycle time and the precursor mass. The gas velocity, depended by the mass flow rate and chamber pressure, is the determinant factor for minimizing the cycle time. Moreover, quicker diffusion and homogeneous distribution resulted from low pressure and high mass flow rate facilitate the optimization of the ALD process. This quantitative model has been verified by experiments under different fluid conditions, which could provide instructive guidance to optimize deposition process in a large pressure range.

1. Introduction

Atomic Layer Deposition (ALD) is a powerful thin film deposition technique based on sequential self-terminating surface reactions [1–3]. The self-limiting nature of the precursor chemisorption in an ideal ALD process enables precise control of film thickness, as well as nice conformality and uniformity over large areas [4,5]. Recently, ALD has attracted much attention in the fields of microelectronics, optoelectronics, renewable energy, *etc.* [4,6,7]. One drawback of the ALD process, however, is the relatively low growth rate. To speed up the ALD process and lower the cost, it is necessary to reduce ALD cycle time and promote precursor usage by improving reactor structure and developing corresponding processes [8–10].

To date, conventional methods to optimize ALD processes are usually based on massive experiment runs [8,9,11–16]. Although some previous literature [11–13] have discussed the ALD growth among pressure, temperature and precursor materials respectively, the quantitative correlation study of process parameters is limited under particular reactor geometry. On the other hand, numerical modeling is an effective method to study the multiple operational parameters of ALD processes. There are three major types of quantitative simulations on ALD processes: microscopic simulation, theoretical derivation and equipment scale numerical simulation. Microscopic atomic scale simulations such as kinetic Monte Carlo methods have been utilized to calculate precursor transport and surface deposition on high aspect ratio substrates [17]. These microscopic methods, nevertheless, are restricted to small scales of space and time (usually within several micrometers/microseconds), and need a rather long time to complete calculations. Mathematical methods from theoretical derivations primarily focus on the calculation of the thermodynamic equilibrium states [18,19]. The computational fluid dynamic (CFD) simulations have been explored in equipment scale to analyze steady flow information of temperature distribution, pressure gradient, precursor concentration, *etc.* [20–25]. The quantitative optimizations of these process parameters require a comprehensive dynamic model that combines microscopic surface reactions in the reactor scale. Yuan's group has developed a quantitative numerical model with detailed

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surface reaction mechanisms to study the influences of temperature and precursor distributions on deposition rate at low pressure (0.1 Torr) [26,27]. The wide range of chamber pressures from vacuum (0.1 Torr) to atmospheric (760 Torr) conditions is chosen, yet the analysis on quantitative relationships between process parameters and the deposition efficiency is rarely reported. Exploring process operated under ambient pressure conditions will further expand the cognition of ALD processes in engineering.

In the present work, the influences of the temperature, precursor mass fraction, mass flow rate and pressure on the dynamic process optimization have been explored with a quantitative numerical model. The connection of process parameters with the deposition efficiency has been quantitatively discussed. The precursor concentration and gas velocity are the determinant factors for process optimizations. Experiments with different fluid conditions (precursor mass fraction, mass flow rate and pressure) have been conducted to support the model simulation results. This quantitative model combining surface chemistry and fluid dynamics would be instructive for both process optimization and reactor designs.

2. Methods

2.1. System description

Simulations on the study of operational parameters are verified by experiments on a bottom conductive heating reactor (inner diameter: 80 mm, height: 10 mm) as shown in Fig. 1a. The bottom heating reactors of this type are widely used in research laboratories due to their compact size and effective gas delivery. The entire system consists of five parts: precursor dosing hold-cells, the gas manifold, the closed chamber, integrated quadrupole mass spectrometer and pumping system (Fig. 1b). Though the pressure of gas mixture which contains precursor and carrier gas is monitored by a vacuum gauge (Edwards APGX-H-NW25), the precise amount of precursor could not be calculated from this total gauge pressure [8,9]. In order to solve this problem, hold-cells are designed to provide quantitative precursor dose which is very important to perform experimental verification in our equipment. The hold-cells measure the partial pressures of all species with *in-situ* quadrupole mass spectrometer of AMETEK Dycor (LC-D200). The partial pressure difference before and after precursor dosing represents the amount of precursor molecules pulsed into the chamber. The precursor molecules are injected into the reactor by switching off valves in the precursor dosing hold-cells. After the hold cell is pumped down to 1 Torr pressure, the thread valve is opened and other valves are closed, and then precursor molecules diffuse from precursor bottle to the hold cell. Precursor is taken out from the hold cell by a small amount of nitrogen gas (20 sccm), then is diluted with 500 sccm nitrogen again, finally fills into the manifold of the reactor. The amount of precursor molecules could be precisely controlled into the reactor regardless of the chamber pressure. In the experiment, the lowest dose amount is represented by the minimal dose time for the saturated ALD chemical adsorption. The minimal purge time is defined as the shortest time to completely remove the reactant and by product molecules from the reactor without overlap of the other precursor.

2.2. CFD model description

The CFD model is chosen to analyze these quantitative indicators by solving the conservation equations for mass, momentum, and energy [20–22]. The surface reaction is incorporated with the conventional dynamic flow for analyzing the velocity distribution and precursor concentration. The surface coverage represents the percentage of replaced species on the surface. Once the surface coverage reaches 100%, the value of consumed precursor gets the minimum for a completed ALD half reaction. In our study, the minimal dose time is represented by the shortest pulse time during which precursor molecules diffuse from the inlet to the boundary layer and adsorb on the substrate surface. The minimal purge time is defined as time interval in purging stage that the residual precursor mass fraction or molar fraction of gas mixture decrease to lower than 1.0×10^{-6} on the entire reactor. The optimizations of the cycle time are critical to improve the throughput and reduce precursor waste. Static chemical kinetics in surface exchange process is described by the Arrhenius expression. The physical parameters of all the associated chemical species and gas mixtures are listed in Table 1 (in Appendix).

In fluid dynamics theory, species distribution is comprised of the boundary layer and volume distributions [12]. In the boundary layer, the flow stream begins to stagnate and precursors contribute to the surface reaction. Once the gas molecules get into the boundary layer, the velocities decrease sharply and reach zero at the substrate surface. The boundary layer is an important media that links the macroscopic process parameters and the microscopic

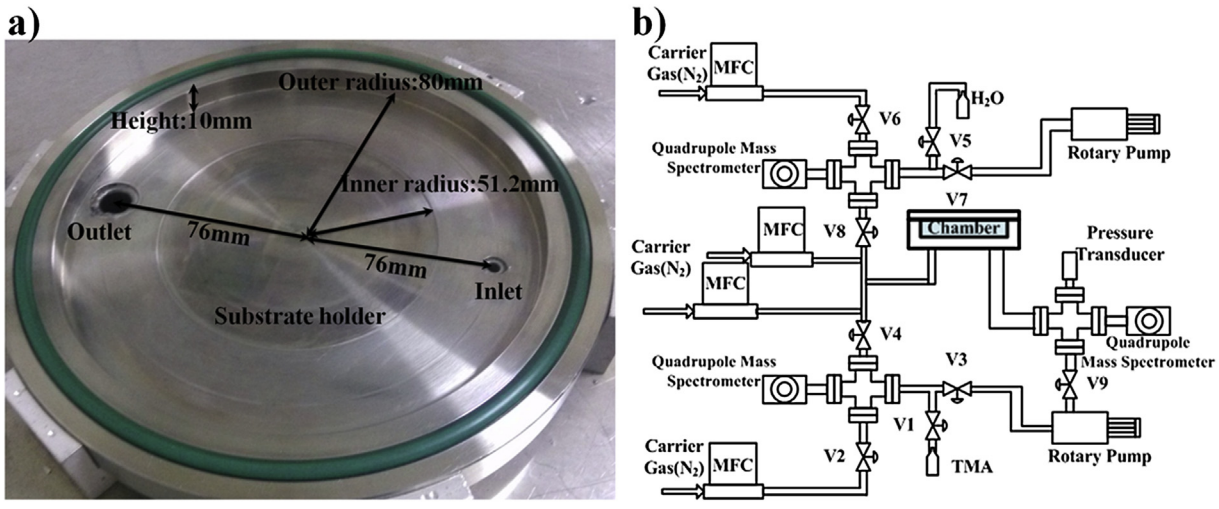

Fig. 1. a) The picture of reaction chamber with actual dimension; b) the schematic of hold-cells integrated ALD system.