Experimental and numerical investigations into the transient multi-wafer batch atomic layer deposition process with vertical and horizontal wafer arrangements

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Abstract

This paper investigates two types of wafer arrangements, vertical and horizontal, in a multi-wafer atomic layer deposition (ALD) reactor. The growth rate of ALD deposited alumina thin film is characterized and compared experimentally and numerically. It's found that the wafer layout influences the deposition process significantly. Vertical multi-wafer arrangement is shown superior to the horizontal arrangement in terms of film deposition rate because of the enhanced collisions between precursor molecules and wafer surfaces in vertical arrangement. Studies using three-dimensional transient numerical model of fluid dynamics and surface reaction kinetics in multi-wafer batch ALD reveal the self-limiting details on the physical and chemical nature of ALD process. First, the deposition process is shown highly “self-limited”: surface reactions in ALD are completely terminated once surface species conversion comes to the end. Second, deposition process is found under a joint influence of precursor concentration and surface site saturation status. Before deposition rate reaches its peak, the precursor concentration is dominant in determining the deposition rate, but it is largely confined by the available surface reactive sites after the peak. Position dependence of deposition rate as shown by both experiments and simulations is weak and negligible.

Keywords: Atomic layer deposition; Multi-wafer batch ALD; Alumina ALD; Experimental investigation; Simulations

Nomenclature

A	pre-exponential factor in the Arrhenius equation
b'	stoichiometric coefficient for reactant bulk species
b''	stoichiometric coefficient for product bulk species
B	bulk (solid) species
c	local molar fraction
E	total energy (J)
E_r	reaction activation energy (J mol^{-1})
F	external body forces (N)
g'	stoichiometric coefficient for reactant gaseous species
g''	stoichiometric coefficient for product gaseous species
G	gaseous species
h	enthalpy (J kg^{-1})
J	mass diffusive flux ($\text{kg m}^{-2} \text{s}^{-1}$)
J_h	energy diffusive flux (W m^{-2})
k	material thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)
k_r	rate constant of reaction r
M	molecular weight (kg mol^{-1})
N_b	total number of bulk species
N_g	total number of gaseous species
N_R	total number of surface reactions
N_s	total number of surface species
P	static pressure (Pa)
R	the gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
R_i	Arrhenius molar rate of production of the i th species ($\text{mol m}^{-3} \text{s}^{-1}$)

$\hat{R}$	net rate of production of species by chemical reaction ($\text{mol m}^{-3} \text{s}^{-1}$)
$\mathfrak{R}$	Mass reaction rate ($\text{kg m}^{-3} \text{s}^{-1}$)
s'	stoichiometric coefficient for reactant surface species
s''	stoichiometric coefficient for product surface species
S	surface species
t	time (s)
V	velocity (m s^{-1})
u_n	normal velocity to the wafer surface (m s^{-1})
X	X direction in Cartesian coordinate
Y	Y direction in Cartesian coordinate
Z	Z direction in Cartesian coordinate

Greek symbols

ρ	mixture density (kg m^{-3})
ρ_p	precursor density (kg m^{-3})
$\tilde{\tau}$	stress tensor (N m^{-2})
β_r	temperature exponent in the Arrhenius equation

Subscript

b	bulk species
g	gaseous species
i	the i th species
s	surface species
r	the r th reaction
(s)	surface sites

<s> solid (or bulk) species

w wall surfaces

Superscript

* surface site species

1. Introduction

With more than three decades' development, atomic layer deposition (ALD) has been developed into one of the well-established nano-manufacturing techniques to fabricate ultra-thin films of various materials with excellent uniformity and conformity in surface geometry [1, 2]. ALD has been adopted extensively in microelectronics industries and is on the expansion to a wide range of industrial applications [2]. However, one of the main limitations of ALD is still the throughput [1]. Because of the one-atomic-layer growth pattern per cycle in ALD process, the low deposition efficiency remains an inherent challenge for the ALD community, especially for the single wafer reactors [3]. On the other hand, choice of process parameters, e.g., pulsing time, purging time, temperature, etc., may also have a crucial influence on the overall ALD deposition process [4].

In order to achieve higher throughput for production of ALD films with hundreds of nanometers, in early 1970s batch reactors were already utilized, for example, to manufacture flat panel displays [1]. At the very initial stage of ALD research for semiconductor applications, most ALD studies were conducted on single-wafer ALD systems. In this phase, throughput and other economic considerations were the secondary concern to devise and develop ALD equipment [5]. As the semiconductor industries are seeking higher volume manufacturing techniques to lower the cost of the ALD process which becomes more sensitive in today's business decisions, batch-type ALD systems are being introduced in such cost-sensitive fields as DRAMs and flash memories [5].

Batch ALD reactors can be mainly divided into two categories: multi-wafer and spatial ALD. Figure 1 shows the schematics for the two types of batch ALD systems. Multi-wafer ALD reactor as presented in Fig.1 (a) is a traditional technique in which multiple wafers are coated simultaneously, and the substrates remain stationary in the pulse-purge sequence [5, 6]. Multi-wafer ALD systems have already been made commercially available by a number of ALD manufacturers, such as Cambridge Nanotech (Phoenix series), Picosun (SUNALE P-series), BENEQ (TFS series), etc. Spatial, or continuous ALD system as shown in Fig.1(b), is based on a brand new concept [6]. With the spatial concept, the ALD cycles occur in the spatial domain, and materials are deposited continuously on the wafer [3]. As shown in Fig.1 (b), the wafer is moving under the precursor containers and contacting with the precursors one after another. It's been widely accepted that scaling up from single-wafer ALD to the

batch-type ALD process can largely increase the throughput of ALD cycles [3].

Fig.1. Schematics of the two main categories of batch ALD systems: (a) vertical stack-type multi-wafer ALD reactor [5]; and (b) in-line spatial ALD reactor [6, 7].

Currently, multi-wafer ALD systems are already well devised, but meanwhile most efforts are being made in designing various structures of multi-wafer reactor systems. The complex physical and chemical processes in multi-wafer ALD, however, remain not well understood [5, 6, 8-14]. In fact, ramping-up from single-wafer to multi-wafer system is not straightforward. Due to the larger volume and presence of multiple wafers, the gas flow field in multi-wafer ALD chamber is altered, e.g., in the stack-type multi-wafer reactors as illustrated in Fig.1 (a), the gas flow is blocked by the rows of wafers inside the chamber. Consequently, precursor exposure and purging times may need to be prolonged in multi-wafer ALD reactors [3]. Meanwhile, the process pressure and process temperature need to be re-evaluated for multi-wafer ALD process.

Because of all these issues, process knowledge on the ALD process is crucial to search for the optimal operation parameters to ensure an excellent film deposition uniformity, high deposition rates and high material utilization efficiency. To serve this purpose, experimental trial-and-error methods are always time consuming and expensive. Hence, researchers resort to numerical methods instead of experimental trials to simulate the physical and chemical procedures both in atomic and reactor level. Numerous publications on single-wafer ALD

process are available both in atomic and chamber scale [15-28]. Unfortunately, the literatures regarding multi-wafer ALD process are very limited. Lankhorst *et al.* presented their numerical studies by transient, three-dimensional, multi-scale simulations on the precursor pulse step during the HfO₂ ALD process, and identified several time scales in multi-wafer vertical batch ALD process [4]. Granneman *et al.* analyzed several configurations of single-wafer reactors and multi-wafer batch reactor systems from an industrial perspective [5]. It is worthwhile to be noted that the available numerical models on multi-wafer ALD process lack detailed surface reaction kinetics and mechanism information, or the numerical results are not well validated and correlated with the experimental observations [28].

In our paper, the transient multi-wafer batch ALD process of depositing Al₂O₃ films on silicon wafers using trimethylaluminum (TMA) and water is studied by both experimental and numerical approaches. To find the influence of wafer layout on the deposition process, two types of wafer arrangements, i.e., vertical and horizontal multi-wafer ALD, are specifically investigated. In particular, the two arrangements are compared in terms of alumina thin film growth rate. Further investigation on the detailed knowledge of the precursor transient pulsing process is carried out by 3D numerical simulations.

2. Experiments

Experimental characterizations of the Al₂O₃ film growth rate for vertical and horizontal multi-wafer batch ALD are performed on the Cambridge Nanotech Savannah 100 ALD reactor with a dome lid using TMA+H₂O reactions. The Savannah 100 ALD reactor with a flat lid is shown in Fig.2 (a) and consists of precursor cylinders, precursor delivery manifold, carrier gas manifold, chamber, outlet pipe and a vacuum pump. TMA and water are stored in separate precursor cylinders, and the pulsing (in milliseconds) process of precursors is controlled by ALD stop valves. Nitrogen is flowing through the system continuously as a carrier gas. A vacuum pump is connected with outlet pipe to maintain the low vacuum pressure ($\sim 10^{-1}$ Torr) in chamber. The ALD system can be equipped with a dome lid as presented in Fig.2 (b) to enable multi-wafer batch depositions.

In our study, experiments of two types of multi-wafer arrangements are implemented. Figure 2 (c) presents the vertical multi-wafer experimental setup, in which 27 silicon wafer samples are processed simultaneously. In our experiments, alumina films are deposited on

wafers of crystal silicon 100 with dimensions of 15×20 mm approximately, using 99.9% TMA as the metal provider and 99.0% distilled water as the oxidizer. The wafers are prepared by being washed in 99.9% acetone solution in an ultrasonic cleaning machine for five minutes, and then washed in 99.5% ethanol solution for five minutes. Finally, the wafers are rinsed and cleaned by 99.0% distilled water using the ultrasonic cleaning machine for five minutes. The wafers are attached to the wafer tape frame after cleaned.

Fig.2. (a) Cambridge Nanotech Savannah S100 ALD reactor with a flat lid consists of precursor cylinders, precursor manifold, carrier gas delivery manifold, chamber, outlet manifold and a vacuum pump (not shown in the figure); (b) S100 equipped with dome lid for batch ALD; (c) vertical multi-wafer batch ALD setup with 27 silicon wafer samples; and (d) horizontal multi-wafer batch ALD setup with 27 silicon wafer samples.

By vertical arrangement, it means the wafer surfaces are perpendicular to the flow direction. Similarly, the horizontal multi-wafer arrangement as shown in Fig.2 (d) also process the same number of wafer samples simultaneously. The wafer surfaces in horizontal arrangement are parallel with the gas flows. To compare the two arrangements of wafer configurations in the aspect of film deposition rate, the wafers are placed on the same locations. To be convenient, each wafer is labeled by letters or numbers in three dimensional coordinates, as illustrated in both Fig.2 (a) and (b). Each wafer sample is uniquely marked by a combination of the above three letters or numbers. A, B, and C are used for X direction, a, b, and c for Y direction, and 1, 2, and 3 for Z direction. For instance, the center wafer is labeled

as B-b-2. This labeling method is used through the entire paper.

Before deposition process begins, the ALD system is heated to the targeted temperatures (chamber: 200°C, inlet and outlet manifolds: 150°C) and stabilized for 3600 s. Pulsing time for water is set at 0.015 s, and for TMA is 0.03 s. The purging time for both TMA and water is 30 s. Hence, an ALD cycle in our experiments is TMA/purge/water/purge=0.03/30/0.015/30 s. Nitrogen is flowing through the system at 20 sccm. A total of 100 cycles are deposited for both vertical and horizontal multi-wafer arrangements. The deposited alumina film thickness on the silicon wafers is characterized by a spectroscopic ellipsometer (HORIBA, UVISEL).

3. Model equations

ALD modeling involves decoupling and coupling steps. First, ALD is decoupled into several physical and chemical processes, namely, momentum transport (gas flow), convective heat transfer, species transport, and surface reactions. Each process is represented by corresponding partial differential equations (PDEs). These PDEs can be solved numerically on the defined nodes in meshed domains. Second, to obtain solutions to the entire numerical ALD process, the system of PDEs must be coupled together by taking interactions between each physical and chemical process into account. The mathematical modeling process and assumptions are described in detail in our previous paper [28]. In this paper, we focus on applying the model to simulate the deposition process in the multi-wafer batch ALD system.

The continuum-based model in our study assumes the concerned domain as a continuum. The continuity equation conserves the mass,

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{V}) = 0 \quad (1)$$

where ρ is the density, $\vec{V}$ is the velocity vector.

The process of momentum transport in the laminar flow of ALD system is governed by the Navier-Stokes equations [29, 30],

$$\frac{\partial}{\partial t}(\rho \vec{V}) + \nabla \cdot (\rho \vec{V} \vec{V}) = -\nabla P + \nabla \cdot \tilde{\tau} + \rho \vec{g} + \vec{F} \quad (2)$$

where P is the static pressure, $\rho \vec{g}$ and $\vec{F}$ are the gravitational body force and external body forces, respectively, and $\tilde{\tau}$ is the stress tensor.

The convection-diffusion equation is used to model the species transport in ALD system [31],

$$\frac{\partial}{\partial t}(\rho c_i) + \nabla \cdot (\rho c_i \vec{V}) = -\nabla \cdot \vec{J}_i + R_i \quad (3)$$

where c_i is the local molar fraction of species i , R_i is the net rate of production of species i by chemical reaction, and $\vec{J}_i$ is the mass diffusive flux of mixture species i .

The overall heat transfer in ALD chamber is governed by the energy equation,

$$\frac{\partial}{\partial t}(\rho E) + \nabla \cdot [\vec{V}(\rho E + P)] = \nabla \cdot [k \nabla T - \sum_i h_i \vec{J}_{h,i} + (\vec{\tau} \cdot \vec{V})] \quad (4)$$

where k is the material thermal conductivity, h_i is the enthalpy of mixture species i , and $\vec{J}_h$ is the energy diffusive flux.

The laminar finite-rate method is adopted to couple the surface reactions with species transport. In the method, effect of turbulent fluctuations is ignored and the finite reaction rates are determined by Arrhenius expressions [28]. The production rate of species i by chemical reactions, R_i in Eq.(3) is calculated through the laminar finite-rate model,

$$R_i = M_{w,i} \sum_{r=1}^{N_r} \hat{R}_{i,r} \quad (5)$$

where $M_{w,i}$ is the molecular weight of species i , and $\hat{R}_{i,r}$ is the Arrhenius molar rate of creation or destruction of species i in reaction r .

The general form of the r th irreversible surface reaction in ALD chamber is expressed as,

where G , B , and S denote gaseous species, bulk (solid) species, and surface species, respectively, N_g , N_b and N_s are the total number of the corresponding gaseous, bulk and surface species, $g'_{i,r}$, $b'_{i,r}$ and $s'_{i,r}$ are the stoichiometric coefficients for each reactant species i , $g''_{i,r}$, $b''_{i,r}$ and $s''_{i,r}$ are the stoichiometric coefficients for each product species i , and the rate constant k_r is evaluated by the Arrhenius expression,

$$k_r = A_r T^{\beta_r} \exp\left(\frac{-E_r}{RT}\right) \quad (7)$$

where A_r is the pre-exponential factor, β_r is the temperature exponent, E_r is the activation energy, and R is the universal gas constant.

The reaction rate of surface reaction, $\mathfrak{R}_r$, represented by Eq.(6) is calculated by the kinetic rate law [32],

$$\mathfrak{R}_r = k_{f,r} \prod_{i=1}^{N_g} [G_i]_w^{g_{i,r}} \prod_{j=1}^{N_s} [S_j]_w^{s'_{j,r}} \quad (8)$$

where, for gaseous species, $[]_w$ represents molar concentrations on wall surfaces, and for surface species, $[]_w$ is the surface coverage. The net molar rate of production or consumption of each species i is given by,

$$\begin{aligned} \hat{R}_{i,g} &= \sum_{r=1}^{N_R} (g''_{i,r} - g'_{i,r}) \mathfrak{R}_r, i = 1, 2 \dots N_g \\ \hat{R}_{i,b} &= \sum_{r=1}^{N_R} (b''_{i,r} - b'_{i,r}) \mathfrak{R}_r, i = 1, 2 \dots N_b \\ \hat{R}_{i,s} &= \sum_{r=1}^{N_R} (s''_{i,r} - s'_{i,r}) \mathfrak{R}_r, i = 1, 2 \dots N_s \end{aligned} \quad (9)$$

where N_R represents the total number of surface reactions in ALD chamber.

The chemisorption reaction mechanism is adopted to model the reactions in Al_2O_3 ALD process [17, 28]. The surface reactions are formulated by following two half reactions as:

where $*$ and (s) represent surface site species, $<\text{s}>$ denotes solid (or bulk) species, and g means the species are gaseous. These processes are also illustrated in Fig.3. The first half reaction represents TMA pulse shown by Fig. 3 (a), and the second half reaction for water pulse shown by Fig.3 (b).

The computational procedures are summarized as follows. Precursor distributions throughout the ALD system are obtained by solving the species transport Eq.(3), which is coupled with the momentum conservation Eq.(2) and energy Eq.(4). The chemisorption reaction kinetics is obtained by solving the rate equation Eq.(8) for both TMA pulse and water pulse represented in Eq.(10), and substituting net molar rate of production rate into

Eq.(5) yields the production rate, R_i , as required in Eq.(3).

Fig.3. Illustrations of surface chemisorption reaction mechanism for: (a) TMA pulse; and (b) water pulse.

4. Numerical solutions

Three-dimensional numerical domains based on the Cambridge Nanotech S100 ALD reactor with the dome lid are presented in Fig.4 (a) and (b). The domains include the main parts of the ALD system, including chamber, wafers, inlet pipes, and outlet. To compare and validate the numerical solutions with experiments, the domains are created accurately according to the two experimental setups shown in Fig.2 (c) and (d).

Fig.4. 3D computational domains in the numerical model are based on S100 ALD reactor with the dome lid: (a) vertical multi-wafer arrangement; and (b) horizontal multi-wafer arrangement.

Numerical solutions to the model equations are obtained under the framework of ANSYS Fluent using the method of Finite Volume Method (FVM). The 3D domains are processed with a non-structural meshing scheme as shown in Fig.4. The model equations are first

discretized in space by the second-order upwind method. By FVM with a pressure-velocity coupled scheme, the values at each domain node are calculated. Second-order implicit method is used for the discretization of time domain. The choice of the implicit method is to ensure computational stability, and the second-order method is for a sufficient computational accuracy.

Boundary conditions are essential in numerical solutions. In our models, the boundary conditions at inlets, outlet, wall and wafer surface sites are specified according to the actual experimental conditions. For carrier gas inlet, volumetric flow rate is set at 20 sccm. The chamber is maintained in low pressure ($\sim 10^{-1}$ Torr) by a vacuum pump which is connected with the outlet pipe. Since precursors are stored in separate cylinders as shown in Fig.2 (a) at room temperature and injected into the system by the pressure difference with the chamber, pressure boundary conditions are enforced on the two precursor inlets. The outlet is connected with the pump and the system background pressure is assigned, which is also the full-load working pressure of the vacuum pump.

In actual process, materials are deposited on the entire inner surface of the ALD system, but in numerical solutions, for computational simplicity without losing its accuracy, we only calculate depositions on the wafers. Any other inner wall surfaces are assumed non-slip, non-flux of mass. At the initial state, full coverage of hydroxyl group on wafer surfaces is assumed for both vertical and horizontal multi-wafer arrangements. Thermal boundary conditions are enforced on the walls. Temperature at wafer surfaces is maintained at 200°C, and other parts of the system are 150°C.

5. Results and discussion

5.1. Experimental and numerical characterizations of film deposition rate

In this section, material deposition rate is characterized by both experimental and numerical approaches. In both vertical and horizontal multi-wafer experiments, Al₂O₃ film thickness is measured using the Horiba UVISEL spectroscopic ellipsometer after 100 cycles of depositions. Since the flow domains are symmetric with respect to the flow direction (X direction), material distributions are similar at the two sides of the center line of chamber. Hence, to simplify our data analysis, 18 wafers from b and c in Y direction labeled as A (B, C)-b (c)-1 (2, 3) are considered. The experimental results are presented in Fig.5, which are

obtained by averaging two measurement data points for each wafer sample.

To obtain bulk Al_2O_3 deposition rate from numerical simulations, mass deposition rates of species $\text{O}_{\langle s \rangle}$ and $\text{Al}_{\langle s \rangle}$ in the two half reactions [Eq.(10)] are integrated over pulsing time, i.e., for TMA pulse, 0.03s, and water pulse, 0.015s. The resulted mass deposition is finally converted to film thickness by introducing alumina film density [33]. The data of film thickness in one cycle for the 18 wafers from both vertical and horizontal simulations are also demonstrated in Fig.5.

Fig.5. Al_2O_3 film growth rate in Å/cycle for vertical and horizontal multi-wafer arrangements obtained from both experiments and simulations. The 18 wafers are labeled in three directions using A, B, C for X direction, b, c for Y direction, and 1, 2, 3 for Z direction.

As demonstrated in Fig.5, the data of film growth rate from numerical simulations match well with the experiments both in vertical and horizontal multi-wafer ALD processes. This agreement validates our numerical solutions. In Fig.5, vertical arrangement is clearly shown having higher film deposition rate than the horizontal arrangement from both experimental and numerical results. In the horizontal multi-wafer arrangement, the growth rates are ~ 1.1 Å/cycle from both experiments and simulations. The increase of growth per cycle (GPC) in vertical multi-wafer ALD is ~ 0.1 Å/cycle on average. This improvement is significant considering that hundreds of cycles are required to deposit a thin film. The deposition results signify that the wafer layout is a significant influential factor in the deposition process of

multi-wafer batch ALD. Apparently, vertical multi-wafer process is shown superior to the horizontal arrangement in film deposition rate.

This phenomenon is mainly attributed to the collision conditions between precursor molecules and wafer surfaces. In the vertical arrangement, collisions are greatly enhanced, because the wafer surfaces in this case are confronting the material flow directly. By gas flow, precursor material is transferred in the way of convection which results in strong interactions between precursor molecules and wafers.

Fig.6. Numerical velocity contour plots and mass fluxes normal to the wafer (B-b-2) surface during TMA pulsing process: (a) and (b) velocity contour plots for vertical and horizontal arrangement at 0.015 s, respectively; (c) and (d) mass flux normal to the wafer surface for vertical and horizontal arrangement, respectively.

Further information on the flow field verifies the above statement. Figure 6 shows the numerical velocity contour plots and the mass fluxes to the wafer surface during TMA pulsing process on wafer B-b-2. As presented in Fig.6 (a) and (b), the velocity for both vertical and horizontal arrangements are quite similar in magnitude. However, because of the different wafer arrangements, precursor flow velocity normal to the wafer surface varies dramatically

from one to another. This is also confirmed by the mass fluxes to the wafer surface presented in Fig.6 (c) and (d) for vertical and horizontal arrangement, respectively. Mass flux is obtained from the velocity field and precursor density as,

$$J_m = \rho_p u_n \quad (11)$$

where ρ_p is the precursor density, and u_n is the normal component of velocity to the wafer surface.

By comparing Fig.6 (c) and (d), the normal mass flux to B-b-2 wafer surface in vertical arrangement is much larger than in horizontal arrangement during TMA pulsing process. In horizontal arrangement since the wafer surfaces are parallel with the flow direction, material transportation to the surface sites are mainly driven by a diffusive effect, which is much weaker than the convection [31]. On the other hand, due to the larger normal velocity, the mass transfer process to the wafer surface is significantly strengthened by convective flow in vertical arrangement, and thus the contacting and collision probabilities are increased, which leads to more surface reactions on the surfaces, and therefore higher film growth rates as shown in Fig.5.

Fig.7. Transient normal velocity at (a) B-b-2 wafer, and (b) the space between B-b-2 and B-c-2 in TMA pulsing process for the vertical arrangement.

It is also expected that the surface deposition process in vertical arrangement could be further accelerated if the wafers are placed in such an interlined way that the wafers in the second row align to the interspace between the two wafers in the first row. This is verified by the comparison of normal velocity at the B-b-2 wafer and the space between B-b-2 and B-c-2 in the vertical arrangement as shown in Fig.7. It is found that the normal velocity is much higher in the space between the two wafers.

From Fig.5, the wafer position dependence of deposition rates is shown very weak by both experimental and numerical results. Further analysis of this observation is performed by taking average of the deposition rates for the three directions. The results are presented in Fig.8. It is again shown that numerical data agree well with the experimental results. By Fig.8 (a), it is found that wafers located on the middle row (row B in X direction) have higher GPCs than those located on the other two rows. Shown in Fig.8 (b) and (c), wafers located on the side column (c in Y direction) and bottom layer (layer 3 in Z direction) make very little difference in deposition rates.

Fig.8. Averaged Al₂O₃ film growth rates for the three directions from both experimental and numerical investigations: (a) averaged GPCs of the wafers in Y, Z direction; (b) averaged GPCs of the wafers in X, Z direction; and (c) averaged GPCs of the wafers in X, Y direction.

5.2. Numerical investigations of ALD transient deposition process

To further study the physical and chemical details in multi-wafer batch ALD, the transient deposition process is studied using the numerical model. To be specific, TMA and water pulsing processes are simulated with the vertical multi-wafer arrangement. In this part, the pulsing times are doubled in order to observe the entire pulsing processes, i.e., for TMA pulse,

0.06 s, and water pulse, 0.03 s. Precursor concentration, surface species coverage, methane generation and bulk material deposition rate in the transient pulsing processes are correlated in Fig.9. The data are extracted at the center wafer (B-b-2) for both TMA and water pulses.

Fig.9. Correlations of precursor concentration, surface species coverage, methane generation and bulk material deposition rate in the transient pulsing processes by vertical multi-wafer ALD simulation: (a) TMA pulse; and (b) water pulse. Data are extracted from the center wafer (B-b-2) for both TMA and water pulses. The pulsing times are doubled from experiments in order to observe the entire pulsing processes.

It is observed in Fig.9 (a) that surface deposition rate increases with TMA concentration from the very beginning of pulsing step, and as the deposition continues, surface coverage of the initial species, i.e., $*OH$, declines. The gaseous product, methane is generated once the reaction is activated. In the first 0.006 s, deposition rate is increasing slowly, and meanwhile hydroxyl coverage experiences a slow decline. Thereafter, the process is expedited as TMA

concentration is increasing steadily. As a result, methane-terminated species (*AlMe and *AlMe₂) coverage is increasing quickly.

At about 0.015 s, the deposition rate reaches its peak and then declines steadily despite the precursor concentration is still increasing. As the surface reaction continues, the available reactive hydroxyl sites become scarce, and most of the hydroxyl surface species are converted to methane-terminated species. Accompanying this process, more methane is generated. At about 0.034 s, hydroxyl coverage declines to zero, and *OH species is no longer available on wafer surfaces, and consequently surface deposition process is terminated. Nevertheless, it is noted that the precursor concentration is still increasing to higher levels. Methane generation becomes steady as the deposition process is approaching its end, and slightly declines after the reaction is terminated. Finally, *AlMe₂ surface species becomes saturated to 50% (another half is taken by *AlMe). In the process, hydroxyl-terminated surface sites are completely converted to methane-terminated species as described in Fig.9 (a). Precursor pulse, in essence, is a surface species conversion process, during which materials are being deposited.

In comparison with TMA pulse process, similar phenomena are observed in water pulse as presented in Fig.9 (b). In water pulse, however, the deposition process happens much faster. The reaction reaches its peak in only 0.006 s, and is completely terminated at ~0.02 s. This reveals the huge difference of chemical kinetics in the two half deposition processes. By Fig.9 (b), water pulse is shown kinetically faster than TMA pulse. This also validates the choice of shorter pulse time (0.015 s) for water pulse in the experimental treatments. The information of this critical pulse time is essential to improve the sustainability performances, such as deposition efficiency and material utilization in ALD, since any longer precursor pulsing will be a waste of time and materials once the deposition process is terminated. In water pulse process, methane-terminated species are converted to hydroxyl-terminated surface sites, which are prepared for the next TMA pulsing step. Bulk species Al<s> is deposited in water pulse, and since it is heavier than O<s> in mass, the mass deposition rate in water pulse is higher than in TMA pulse as given in Fig.9.

Further data are extracted from various wafers on the middle layer (layer 2 in Z direction) and presented in Fig.10 to study position dependence of the deposition process. Figure 10 shows that in X direction (from A, B to C), precursor concentration at each wafer experiences different process in both TMA and water pulsing processes, and consequently the deposition

process varies differently. The wafers located near the inlet area (row A) gain high precursor concentration first (red and blue curves), and their deposition rates reach peaks much faster than those on the other two rows.

Fig.10. Correlations of precursor concentration, surface species coverage, and bulk material deposition rate in the transient pulsing processes by vertical multi-wafer ALD simulation for the 6 wafers located on the middle layer: (a) and (b) TMA pulse for the 6 wafers; (c) and (d) water pulse for the 6 wafers. Data are extracted from the middle wafers (layer 2 in Z direction), A (B, C)-b (c)-2, for both TMA and water pulses. The pulsing times are doubled from experiments in order to observe the entire pulsing processes.

In Y direction, wafers on column b experience faster deposition processes than those on column c, although this difference decreases from row A, B to C. Nevertheless, faster deposition process does not necessarily result in higher material deposition rate, because the final material deposition rate is achieved by integrating deposition rate over pulse time. Considering that at last all the deposition processes is completed as shown in Fig.10 (a) and (b), the time integration for different wafers exposes little difference on film deposition rate, which is also seen in Fig.5 and Fig.8.

The experimental results given in Fig.5 also indicate that no evident pattern could be identified regarding the position dependence of deposition rate. Considering the fact that the

experiments only take half of the pulsing time in simulations, from Fig.10 the wafers located on row C have a little lower deposition rate than those on the other rows because their deposition processes are not finally terminated within the pulsing step. As a result, deposition rate of wafers on row C is a little lower as indicated in Fig.8 (a). Row B, however, yields the highest deposition rate. This is mainly attributed to the longer time these center wafers have experienced with higher deposition rate, although their peaks are not the highest compared to the first row wafers.

Fig.11. Correlations of precursor concentration, surface species coverage, and bulk material deposition rate in the transient pulsing processes by vertical multi-wafer ALD simulation for the six wafers located on the middle row: (a) and (b) TMA pulse; (c) and (d) water pulse. Data are extracted from the middle wafers (row B in X direction), B-b (c)-1 (2, 3) for both TMA and water pulses.

Figure 11 compares the deposition processes of the six wafers located on the middle row (row B in X direction) for both TMA and water pulses. These wafers are located in the similar distance from the inlet, and thus, they have very similar precursor distributions as shown in Fig.11. Hence, their depositions also experience the similar process from 1, 2 to 3 in Z direction. This is confirmed by the experimental results given in Fig.8 (c) that the differences

of film deposition rate in Z direction are negligible. In fact, as presented in Fig.5, with numerical integration of the deposition rate curves over time, the resultant overall deposition rates make no evident difference.

Therefore, it is concluded that, in general, the position dependence of deposition rate in multi-wafer ALD process is very weak and negligible, and the wafer positions make no evident difference in film growth rate. This makes great sense in large-area wafer ALD coating applications. Even on very large-area wafers, the ALD fabricated films can still be highly uniform [3].

To summarize the information on the transient ALD deposition process, it is concluded that the surface deposition rate is heavily dependent on precursor concentrations in the first half of deposition process, and declines steadily as the surface species conversion approaches its end. In both TMA and water pulsing processes, as the precursor molecules are being introduced into chamber, surface reactions are initiated and then speeded up with more precursor molecules. As the reactions continue, the available reactive species are consumed and converted to the product surface species. In this process, the deposition rate reaches its peak.

After the peak, the surface reaction rate is largely determined by the availability of reactive surface species. Since wafers that are located in different areas of the space, they experience high precursor concentration at different times, resulting in the different deposition processes. To be short, in the first half pulsing process, precursor concentration is dominant in determining the reaction rate, and in the second half, deposition rate depends more on the available reactive surface species. Process deposition is under a joint influence of both precursor concentration and number of reactive surface species.

6. Conclusions

This paper compared the two different wafer arrangements in multi-wafer batch ALD process both experimentally and numerically. It's seen from both experiments and simulations that the wafer layout indeed influences the deposition rates significantly. The vertical multi-wafer arrangement is superior to the horizontal one in film growth rate. An increase of $\sim 0.1 \text{ \AA/cycle}$ in deposition rate is observed from our experimental and numerical results. This is mainly attributed to the enhanced convective effect of chemical species transport to wafer

surfaces in the vertical multi-wafer batch ALD process.

By 3D modeling of multi-wafer batch ALD, the transient deposition process including fluid dynamics and surface reaction kinetics was studied in detail for vertical multi-wafer arrangement. The numerical results revealed the self-limiting details of the flow and surface reaction processes. Deposition process is under a joint influence of precursor concentration and surface site saturation status. In the first half reaction before the deposition rate reaches its peak, precursor distribution is dominant to determine the bulk material deposition rate, whereas film growth rate is largely confined by the available coverage of surface reactive sites in the second half reaction. Finally, the reaction is terminated due to no more presence of reactive surface species. The ALD deposition process is, in essence, a conversion of surface species. This is the basic chemical kinetics behind the ALD process.

By transient simulations, the deposition process is shown highly “self-limited”: surface reactions in ALD are completely terminated once the surface species conversion is finished, even though precursor molecules are still being introduced into the ALD system. This feature confirms the advantages of this thin film fabrication technique: ALD is perfect to produce highly uniform films, and the film thickness can be accurately controlled in an atomic level. Further data from the transient simulations also showed that the deposition rate is not sensitive to the wafer positions, although the time-dependent deposition process varies differently from wafers. The overall position dependence of deposition rate in multi-wafer ALD process is weak and negligible.

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