Ballistic transport and reaction modeling of atomic layer deposition manufacturing processes

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Abstract:
In this paper we develop a model describing the ballistic transport of chemical precursor species for an atomic layer deposition process (ALD). Because of the large Knudsen number corresponding to ALD over nanoporous materials, the gas-phase transport inside the nanostructures takes place in a purely ballistic manner. Precursor transmission probability functions describing the fluxes between the pore surface features are developed and then are coupled to ALD surface reaction models, spatially discretized, and integrated over each precursor exposure period to determine the pore spatial surface reaction extent profile. Predictions from our dynamic model then are compared to a previously published study of ALD in nanopores to validate our simulator. The utility of physically based models of the type we develop can be exploited to determine optimal precursor exposure levels for ALD based nanomanufacturing operations.

Keywords: Simulation; distributed parameter systems; nanomanufacturing; atomic layer deposition; process optimization

1. INTRODUCTION

Atomic layer deposition (ALD) is a thin-film manufacturing process in which the growth surface is exposed to an alternating sequence of gas-phase chemical precursor species. The self-limiting nature of the precursor chemisorption in ideal ALD processes makes possible highly conformal surface coverage and atomic-level control of film thickness. While conceptually simple, ALD processes present a number of true modeling and process optimization challenges. These difficulties stem from the wide ranging time and length scales associated with the growing film, the modeling challenges posed by transport of precursor and product species through the reactors, and the complexity of the film growth mechanisms.

Quantification of the timescales associated with ALD surface reactions and micro/reactor-scale transport of precursor species makes it possible to determine the minimum exposure level necessary to reach the self-limited regime. Most current processes and those under development for new industrial applications compensate for non-ideal reactor designs by significantly over-exposing the growth surface to precursors, resulting in low process gas conversion rates. Because of promising ALD applications in large-scale micro- and nano-device fabrication and the potential for rapid expansion of this thin-film manufacturing technology, we present a modeling approach suited to describing the dynamics of precursor transport when coupled to ALD growth models. In this paper, we examine the complexities of numerically solving these modeling equations and compare our results to previously published simulation and experimental studies.

The intention of this paper is to develop that connection, producing models of ALD processes useful for the control of ALD spatial profiles in nanostructured materials, such as the electrodes created by ALD in the fabrication of nanoscale capacitors for electrical energy storage applications shown in Fig. 1.

1.1 Previous work

The importance of ALD time-scale analysis from an industrial perspective is presented in Granneman et al. (9) where several configurations of single-wafer reactors and multi-wafer batch reactor systems are analyzed. In the cited study, the authors break down the timescale analysis to ALD precursor chemisorption on flat substrates and those with high aspect ratio cylindrical pores; these processes then are combined with overall precursor material balances corresponding to the macroscopic-scale transport through each reactor system. The flat surface and pore saturation rates are computed using the simplified models of Gordon et al. (8). In Gordon’s work, surface adsorption rate site material balances are combined with precursor wall collision rate calculations to yield the minimum exposure (measured in pressure × time) necessary to saturate a flat ALD growth surface. These computations were extended to ALD in pores, where the precursor flux was modulated by a Clausing factor to account for the reduced flux within the pore. Gordon’s model was enhanced by Dendooven and coworkers (5) who included a Langmuir-type surface coverage model for the ALD reaction, demonstrating improved...
prediction of the film thickness profiles inside pores for which exposure is insufficient to completely saturate the pore walls. Alumina ALD in nanopores of extremely high aspect ratio were investigated by Elam et al. (6) using a one-dimensional Monte Carlo simulation procedure. Because of the very large Knudsen number corresponding to low-pressure precursors and the nanoscale diameter of the porous structures under consideration (1), the diffusion of gas-phase species inside nanostructures takes place in a purely ballistic manner. In a pioneering sequence of low-pressure CVD (3; 4) and ALD (7) theoretical modeling papers produced by Cale and co-workers, rigorous ballistic transport models for steady deposition processes and direct solution of the Boltzmann’s equations describing molecular-level precursor transport dynamics were developed. In this paper, we will derive expressions for precursor transmission probability functions describing the fluxes between the pore surface features based on Cale’s work. These transport models are coupled to ALD surface reaction models, spatially discretized, and integrated over each precursor exposure period to determine the pore spatial surface reaction extent profile. Models of this form will be shown effective in predicting experimentally observed deposition profiles in high aspect-ratio pores, giving a picture of the ALD process dynamics during each exposure phase.

2. INTRA-PORE BALLISTIC TRANSPORT MODEL

Consider precursor molecules diffusing into a cylindrical pore with major axis perpendicular to the substrate surface. The geometry of the pore is shown in Fig. 2 where the pore entrance is located at the axial coordinate position $z = z' = 0$. We assume the pore has a uniform (with respect to its axial coordinate $z$) radius $R$.

2.1 Pore entrance effects

Defining a differential element at the pore entrance $dA' = r'dr'd\phi'$ located at $z = z' = 0$ and $(r', \phi')$, the flux of precursor species normal to a hemisphere of radius $|s|$ is

$$
\eta_s(r', \phi', s) = \frac{Z_w \cos \Omega dA'}{2\pi|s|^2c_0}
$$

where $Z_w$ is the ideal-gas wall collision frequency at the pore entrance plane (given by equation (1) defined later in
this paper) and \(c_0 = 1/2\) guarantees species conservation. We assume the precursor velocity direction component is isotropically distributed at and above the pore opening. The vector \(s\) connects the entrance differential element \(dA'\) to an element located at \((z, r = R, \phi = 0)\) on the inner wall of the pore in Fig. 2—choosing \(\phi = 0\) results in no loss of generality in the following analysis. Therefore, the total flux at the pore wall element \(dA = R d\phi dz\) contributed by the direct flight of precursor molecules passing through the pore entrance at \(z = 0\) (i.e., not the flux resulting from the re-emission of precursor species from the pore wall) is

\[
\eta_{ew}(z) = \int_{0}^{2\pi} \frac{Z_w}{\sqrt{2\pi R^2 M_w}} \cos \Omega' \cos \Omega \, dA'
\]

an expression consistent with that of (3). Based on the pore geometry and \(n = y, n' = z,\) and

\[
s = (0 - r' \sin \phi') x + (-R + r' \cos \phi') y + (z - 0) z
\]

\[|s|^2 = (r')^2 + R^2 - 2Rr' \cos \phi' + z^2\]

and so

\[
\cos \Omega' = \frac{n' \cdot s}{|n'| |s|} = \frac{z}{R - r' \cos \phi'}
\]

\[|s|^2 = (R - r' \cos \phi')^2 + R^2 - 2Rr' \cos \phi' + z^2\]

and

\[
\cos \Omega = \frac{-n \cdot s}{|n| |s|} = \frac{R - r' \cos \phi'}{(r')^2 + R^2 - 2Rr' \cos \phi' + z^2}.
\]

The final form of the incident flux (molecules/area/time) along the pore wall resulting from the precursors diffusing through the pore entrance is

\[
\eta_{ew}(z) = \int_{0}^{2\pi} \frac{Z_w z(R - r' \cos \phi')}{\sqrt{2 \pi R^2 M_w}} \cos \Omega' \cos \Omega \, d\phi'dr'
\]

\[= Z_w Q_{ew}(z) = \frac{Z_w}{2R} \left[ \frac{z^2 + 2R^2}{\sqrt{z^2 + 4R^2}} - z \right].
\]

Using the notation of Cale (3), \(Q_{ew}(z)\) denotes the dimensionless transmission probability of a precursor species traveling through the entire pore entrance to \(dA;\) the function is given as

\[
Q_{ew}(z) = \frac{1}{2R} \left[ \frac{z^2 + 2R^2}{\sqrt{z^2 + 4R^2}} - z \right]
\]

and a profile of \(Q_{ew}(z)\) is shown in Fig. 3.

Using a similar approach the wall-to-wall transmission probability \(Q_{ww}\) is obtained to compute the wall-to-wall flux

\[
\eta_{ww}(z) = \int_{0}^{L} \epsilon_{ww}(z') Q_{ww}(z, z') dz'
\]

with \(Q_{ww}(z, z')\) plotted in Fig. 3. Wall-bottom \(\eta_{wb}(r),\) bottom-wall \(\eta_{bw}(z),\) and entrance-bottom \(\eta_{bo}(r)\) fluxes and transmission probabilities are given in (2).

3. COUPLING PORE TRANSPORT TO SURFACE REACTIONS

Despite the attention paid to even the most intensely studied ALD system — alumina ALD using water and trimethylaluminum (TMA) as precursors (12) — much remains unknown regarding the specific reactions that take place on the growth surface, and no consistent picture has yet emerged in terms of the reaction kinetics of the overall film growth process. In this paper, we consider ALD reactions of the form

\[
\nu^A A + \nu^B B \rightarrow \text{bulk ALD film}
\]

where the stoichiometric coefficients \(\nu^i, i = A, B\) indicate the number of atoms each precursor species contributes to the ideal ALD film. We take \(\nu^A = 1\) for this study, and so for the case of alumina ALD using TMA and water as precursors, we see that \(\nu^B = 3/2\) by the composition of the minimal unit of the alumina film \(\text{Al}_2\text{O}_3/2\).

By the kinetic theory of gases, the wall collision rate at the film growth surface at the precursor partial pressure \(P^i\) is

\[
Z_w^i = \frac{P^i}{\sqrt{2\pi M_w^i R_T}} \frac{mol/(m^2s)}{(1)}
\]

with maximum value \(\theta^* (\text{defined below})\) and sticking coefficient \(f^i \in [0, 1]\), a material balance for the adsorption process gives

\[
\frac{d\theta}{dt} = -Z_w f^i \left( \frac{\theta}{\theta^*} \right)
\]

where \((\theta/\theta^*) f^i\) defines the probability that a precursor molecule will land on a vacant site and be adsorbed. Integrating over the exposure period,

\[
\theta = \theta_o \exp \left( \frac{-\delta^i f^i}{\sqrt{2\pi M_w^i R_T}} \right)
\]

with \(\theta_o = \theta(t = 0)\); for perfect ALD \(\theta_o = \theta^*\). Each dosage \(\delta^i\) is defined as \(\delta^i = \delta^i t\) with units 1 Langmuir = \(10^{-6}\) Torr-s. We can solve for the dosage in terms of some specified level of coverage \(\theta/\theta_o\) to find

\[
\delta^i = \nu^i \theta^* \sqrt{2\pi M_w^i R_T} \ln \frac{\theta}{\theta_o}.
\]

Finally, we note that there is only one scalar field \(\theta(z, t)\) making this reaction equivalent to a simplified Eley-Rideal mechanism with infinitely strong adsorption of \(A\).

3.1 Computing \(\theta^*\)

We compute \(\theta^*\) from the film density and measured growth per cycle under ideal ALD conditions (GPC\(_{id}\); data for several ALD systems is given in Table 1. The \(\theta^*\) values correspond to sites onto which precursor A can adsorb—the corresponding values during the B exposure can be determined by the reaction stoichiometry. For example, in \(\text{Al}_2\text{O}_3\) ALD, we first determine the number density of the \(\text{Al}_2\text{O}_3/2\) unit in the amorphous film by \(n_d = \rho N_A/M_w\) where \(N_A\) is Avogadro’s number, \(\rho\) is the film density, and \(M_w\) the molecular weight of the film minimal molecular unit (e.g., \(\text{Al}_2\text{O}_3/2\)). A film monolayer thickness \(d_z\) then
can be computed as well as the fraction $F_m$ of a monolayer deposited during each ALD cycle as
\[ d_z = n_d^{-1/3} \quad \text{and} \quad F_m = \frac{GPC_{id}}{d_z} \]
respectively, which leads directly to $\theta^*$, the quantity that also defines the maximum number of moles of each precursor consumed per unit area during each ALD cycle
\[ \theta^* = \frac{F_m}{d_z^2}. \]
In this manner, we see that $F_m \in [0,1]$ (for “normal” ALD) is the fraction of true reaction sites that can adsorb the precursor before the surface saturates (e.g., due to steric hindrance effects), and that $GPC_{id}$ can be recovered from $F_m d_z = \theta^* d_z^2 = GPC_{id}$.

For the pore bottom
\[ \pi R^2 [\theta|_{t+\Delta t} - \theta|_t] = -\pi R^2 [\eta_{eb} + \eta_{wb} - \epsilon_b] \Delta t \]
and so we obtain the scalar differential equation for pore bottom coverage as $\Delta t \to 0$
\[ \frac{\partial \theta(b,t)}{\partial t} = \epsilon_b(r,t) - \eta_{eb}(r,t) - \eta_{wb}(r,t). \]

3.3 Quasi steady-state fluxes
An important assumption in our model is that the emissive $\epsilon$ and impingement $\eta$ fluxes are at equilibrium with respect to the states of the wall and bottom surface coverages, $\theta$ and $\theta_b$, respectively. This assumption is based on the extremely fast motions of the precursor species molecules while in transit between pore wall interactions. Therefore, the overall evolution (slowest timescale for this model) of the surface coverages for high aspect ratio pores is determined by the net flux of precursor species through the pore mouth. Given this equilibrium (pseudo steady-state) assumption, a material balance on a differential element on the pore wall and floor gives (flux in – flux out) = precursor consumed by surface adsorption:
\[ \eta_{ew}(z) + \eta_{lw}(z) + \eta_{bw}(z) - \epsilon_w(z) \]
\[ = \eta_{ew}(z) + \eta_{lw}(z) + \eta_{bw}(z)) f^i \left( \frac{\theta(z,t)}{\theta^*} \right) \]
and
\[ \eta_{eb}(r) + \eta_{wb}(r) - \epsilon_b(r) \]
\[ = \eta_{eb}(r) + \eta_{wb}(r)) f^i \left( \frac{\theta_b(r,t)}{\theta^*} \right). \]

Solving the equations above given instantaneous values of $\theta$ and $\theta_b$, we have two equations and five unknowns: $\eta_{lw}(z), \eta_{bw}(z), \epsilon_2(z), \eta_{eb}(r)$, and $\epsilon_b(r)$. Discretizing the spatially dependent quantities using $n_z$ axial and $n_r$ radial collocation points and corresponding quadrature weights $w^z_i$ and $w^z_j$, we can write the complete set of equations in matrix form (2)
\[ Ax = b \quad \text{with} \quad x = \begin{bmatrix} \eta_{ew} \\ \eta_{lw} \\ \epsilon_w \\ \eta_{wb} \\ \epsilon_b \end{bmatrix} \]
so $x \in \mathbb{R}^{3n_z + 2n_r}$. The structure of the equations above are examined in (2) where it is shown that the nonhomogeneous terms are generated only by the inlet fluxes $\eta_{ew}$ and $\eta_{eb}$, resulting in a trivial solution when $\Delta t = 0$. A trivial solution also is found for the case $f = 1$ and $\theta = \theta_b = \theta^*$; this makes sense because all precursor molecules that enter are consumed by the surface reactions during the first

1 There are two important aspects to solving the discretized equations that are nontrivial: the discontinuous derivative of $Q_{bw}$ at $z = z'$ and the lack of limits for $Q_{wb}$ at $(r,z) = (R,L)$; a multiple-grid global quadrature scheme is used to overcome these difficulties (2).

Table 1. ALD film properties, surface reaction conditions, and pore geometries used or computed for our simulation study.

<table>
<thead>
<tr>
<th>Study film</th>
<th>Gordon (8)</th>
<th>HfO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursor A</td>
<td>TDMAH</td>
<td>water</td>
</tr>
<tr>
<td>Precursor B</td>
<td>9.68</td>
<td>0.10</td>
</tr>
<tr>
<td>GPC (nm/cycle)</td>
<td>4.60 x 10^{-6}</td>
<td>2.77</td>
</tr>
<tr>
<td>$\theta^*$ (mol/m²)</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\delta_{flat}^A$ (Langmuir)</td>
<td>223</td>
<td>101</td>
</tr>
<tr>
<td>$\delta_{flat}^B$ (Langmuir)</td>
<td>101</td>
<td>223</td>
</tr>
<tr>
<td>Pore R (nm)</td>
<td>8000 (estimated)</td>
<td>45</td>
</tr>
<tr>
<td>L (nm)</td>
<td>8000 (estimated)</td>
<td>45</td>
</tr>
<tr>
<td>AR</td>
<td>8000 (estimated)</td>
<td>45</td>
</tr>
<tr>
<td>$\delta_{wall}^A$ (Langmuir)</td>
<td>9000</td>
<td>9000</td>
</tr>
<tr>
<td>$\delta_{wall}^B$ (Langmuir)</td>
<td>9000</td>
<td>9000</td>
</tr>
</tbody>
</table>

Based on $\theta_o = \theta^*$ and taking a representative value of $\theta/\theta^* = 0.001$ (one open site/1000 at the end of each exposure) we compute the absolute minimum exposure level $\delta_{flat}$ for each precursor; values for the HfO2 ALD case study described at the end of this paper are listed in Table 1.
wall/pore bottom collision event. It is also interesting to consider the structure of the matrices

\[
\begin{bmatrix}
\star & \star & \star & 0 & 0 \\
0 & \star & \star & 0 & 0 \\
0 & 0 & \star & \star & 0 \\
0 & 0 & \star & 0 & \star \\
0 & 0 & 0 & 0 & \star
\end{bmatrix}
\begin{bmatrix}
\eta_{ww} \\
\eta_{bw} \\
\eta_{wb} \\
\eta_{bb}
\end{bmatrix}
= \begin{bmatrix}
\star \\
0 \\
0 \\
0 \\
\star
\end{bmatrix}
\]

where the \(\star\) symbols represent potentially non-zero entries, illustrating the connections between the wall and bottom surface fluxes.

4. EVOLUTION OF \(\theta(Z,T)\) AND \(\theta_B(R,T)\) DURING A FULL-CYCLE EXPOSURE

We now consider a representative simulation in which a 93 nm radius nanopore with aspect ratio 43 is subject to HfO₂ ALD. The ALD system and pore geometry are chosen to provide a direct comparison to the classic study of Gordon (8). A snapshot illustrating the surface coverage dynamics during a TDMAH exposure is shown in Fig. 4, where the membrane top surface (at \(z = 0\)) nearly immediately is saturated with the Hf precursor. This saturation front moves down the length of the pore during the precursor A exposure period.

![Fig. 4. A snapshot of the pore surface coverage early in exposure A illustrating the diminishing surface OH concentration (in blue) predicted by our ballistic transport/surface reaction model and compared to the front location predicted by the Gordon model (shown as the green plane) and the maximum surface coverage rate front (gray plane) resulting from the adsorption of every precursor molecule entering the pore.](image)

The saturation front dynamics are shown more clearly in Fig. 5. As given in Table 1, the simulation consists of a 9000 Langmuir exposure to TDMAH followed by a 9000 L water dose. Initially, the pore inner surface starts with \(\theta(z) = \theta^* = 2.77\) sites/nm² available for the Hf precursor adsorption. This is shown as the solid blue curve in the top of Fig. 5. The initial state plus nine evenly spaced \(\theta(z)\) profiles are shown, illustrating the advancing saturation front during the Hf precursor exposure. Wall coverages as well as pore bottom profiles are shown. In this sequence of plots, we note two differences between our simulator predictions and that of the original Gordon paper (the latter’s predictions also are included in Fig. 5):

- We observe that the pore bottom actually saturates more quickly than the pore wall adjacent to the pore bottom. This is due to the direct pore-mouth to bottom flux \(\eta_{bb}\). Second, the midpoint of our predicted saturation fronts lag slightly behind that of Gordon; this is attributable to the Langmuir-type adsorption kinetics used in our deposition model. The dynamic equivalent to Gordon’s model (taking into account only coating of the pore sidewalls) is

\[
z(t) = 2R \left( -4 + \sqrt{16 + 6\tau \hat{Z}_w/\theta^*} \right) / 3.
\]

In this simulation, the Hf precursor nearly saturates the pore; likewise, the water exposure is sufficient to do the same. In Fig. 5 center, the initial condition of the water exposure corresponds to \(\theta = 0\) for most of the pore length. The exposure B (water) front again moved from left to right, more quickly this time due to the greater flux of water at the pore mouth relative to TDMAH, returning the pore surface to \(\theta = \theta^*\) over its entire length at the end of the full cycle.

The ultimate figure of merit in the ALD process is growth-per-cycle (GPC), and so the final step of the modeling work is to translate the surface reaction rates of the dynamic simulation to GPC. We note that in cases of undersaturation, GPC will be a function of spatial position with \(GPC(z) \leq GPC_{id}\). Defining \(t = (0, t_s)\) as the start and end of exposure A, respectively,

\[
GPC(z) = \frac{\theta(z,0) - \theta(z,t_s)}{\theta_s} GPC_{id}.
\]

The GPC as a function of pore position for the A-B exposure cycle described is shown in the bottom plot of Fig. 5. Consistent with the predictions of the original Gordon model, the GPC is uniform and at its nominal value of 0.1 nm/cycle over most of the pore; we note a small degree of precursor starvation along the pore walls near the bottom and the slightly higher GPC value of the pore bottom itself. Overall, this simulation corresponds to a nearly ideal TDMAH exposure level and over-exposure to the water precursor.

Comparisons to other studies including (9), (11), and (10) are given in the full-length paper (2).

5. CONCLUSIONS

In this paper we developed a ballistic transport and surface reaction simulator for atomic layer deposition processes. Closed-form expressions for the intra pore-feature precursor transmission probabilities were developed and coupled to models of the surface reactions of binary ALD processes. A contribution of this paper is the detailed discussion presented on the mathematical coupling of the transport and surface reaction elements of our approach. A neat division between the two was uncovered, which will facilitate modifying the surface reaction models or the physical geometry through which precursor transport takes place – identification of this model structure allows changes to be made in one element without disruption to the other.

Our simulation results were compared to a previously published study of ALD over nanoporous materials, establishing the the validity of our approach using published
experimental data. Our goal was to establish a baseline from which subsequent models can be developed, to explore more intricate deposition surface topographies and more realistic surface reaction mechanisms and kinetic expressions.

ACKNOWLEDGMENT

The author acknowledges the support of the National Science Foundation through grant CBET-0828410.

REFERENCES


