Modeling Non-Ideal Conformality during Atomic Layer Deposition in High Aspect Ratio Structures

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Abstract

Atomic layer deposition allows for precise control over film thickness and conformality. It is a critical enabler of high aspect ratio structures, such as 3D NAND memory, since its self-limiting behavior enables higher conformality than conventional processes. However, as the aspect ratio increases, deviations from ideal conformality frequently occur, requiring comprehensive modeling to aid the development of novel technologies. To that end, we present a model for non-ideal conformality in atomic layer deposition, which augments the existing approaches based on Knudsen diffusion and Langmuir kinetics. Our model expands the state-of-the art by (i) enabling reversible kinetics through an evaporation flux, (ii) including gas-phase diffusivity through the Bosanquet formula, and (iii) being efficiently integrated within level-set topography simulators. The model is calibrated to published results of the prototypical atomic layer deposition of \( \text{Al}_2\text{O}_3 \) from TMA and

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H$_2$O in lateral high aspect ratio structures. We investigate the temperature dependence of the H$_2$O step, thus extracting an activation energy of 0.178 eV which is consistent with recent experiments. In the TMA step, we observe increased accuracy from the Bosanquet formula and we calibrate multiple independent experiments with the same parameter set, highlighting that the model parameters effectively capture the reactor conditions.

**Keywords:** Atomic layer deposition, thin films, high aspect ratio, Langmuir kinetics, topography simulation

1. Introduction

Atomic layer deposition (ALD) is a thin film deposition technique which enables greater control over film thickness and conformity than conventional chemical vapor deposition (CVD) [1]. ALD has become a key technology in semiconductor processing, having found application in, e.g., the deposition of technologically relevant oxides and nitrides [2]. Due to its increased control over conformity, ALD is a key enabler of high aspect ratio (HAR) structures such as dynamic random-access memory (DRAM) capacitors [3] and three-dimensional (3D) NAND flash memory [4].

In contrast to conventional CVD, ALD divides the growth process into at least two sequential, self-limiting processing steps, which repeat in cycles [2]. From the many precursor chemistries enabling ALD, the deposition of aluminum oxide (Al$_2$O$_3$) from trimethylaluminum (TMA, or Al(CH$_3$)$_3$) and water (H$_2$O) has emerged as a paradigmatic system [5]. Even though this process has found application in, e.g., high-$\kappa$ capacitor films for DRAM [3], its main importance stems from the near-ideal aspects of the involved sur-
face chemistry. Thus, a significant body of research has emerged for this process, and it became the de facto standard against which novel approaches are tested.

In an ideal self-limiting reaction with fixed reactor conditions, perfect conformality is theoretically achievable by adapting the step pulse time $t_p$ to the involved HAR structure. Thus, the conformal film thickness could be straightforwardly controlled via the growth per cycle (GPC) parameter, determined by the involved reactants and reactor conditions, and the total number of cycles ($N_{cycles}$). However, in real-world conditions, deviations from ideal conformality in HAR structures are observed [1] since (i) the true surface chemistry is not perfectly self-limiting, and (ii) reactant transport becomes severely constricted. Accordingly, as semiconductor technology advances towards ever higher aspect ratios, the challenge of understanding non-ideal conformality in ALD must be addressed with a combined experimental and modeling approach.

To that end, first-order Langmuir models have been developed and applied to predict saturation times [6], to model growth kinetics [7], and to estimate the clean surface sticking coefficient ($\beta_0$) using either Monte Carlo methods [8] or simplified analytical expressions [9]. Although powerful, these approaches are lacking in at least two fundamental ways. Firstly, the chemical processes are often assumed to be irreversible. In addition, the thickness profiles are not directly evaluated, which is a requirement for the integration of ALD models with additional processing steps and for process-aware device simulation within a design-technology co-optimization (DTCO) framework.

In the past, we addressed this issue in the context of the ALD of tita-
nium compounds by developing a topography simulation combining detailed Langmuir surface models with Monte Carlo ray tracing calculations of local reactant fluxes [10]. Nevertheless, this approach incurs high computational costs and thus is only able to reproduce a few cycles. Therefore, a topography simulation approach for ALD must simultaneously capture the involved surface chemistries and be efficient in calculating the local reactant fluxes.

2. Methods

2.1. Surface kinetics and flux modeling

As with most ALD modeling approaches [1], our model assumes that the processes are limited by the reactive transport of a single reactant species. For clarity, our discussion focuses on the H$_2$O-limited regime during ALD of Al$_2$O$_3$. However, the same insights are valid for the TMA-limited case and to similar reactants. We propose a first-order Langmuir surface model, combined with diffusive reactant transport for the calculation of the surface coverage $\theta$, building upon the model first proposed by Yanguas-Gil and Elam [6] by considering reversible kinetics and the impact of gas-phase diffusivity.

The following reaction pathways for an incoming water flux $\Gamma_{\text{H}_2\text{O}}$ are considered, represented in Fig. 1: Adsorption-reflection, mediated by a $\theta$-dependent sticking coefficient $\beta(\theta) = \beta_0(1 - \theta)$, and desorption, given by an evaporation flux $\Gamma_{\text{ev}}$. In the original model [6], irreversible kinetics are assumed, i.e., $\Gamma_{\text{ev}} = 0$. These first-order Langmuir surface reactions are captured by the following equation for the time evolution of $\theta$ at each surface.
Equation (1) describes an empirical model with two phenomenological parameters: $\beta_0$ and $\Gamma_{ev}$. The surface site area $s_0$ can be estimated with a “billiard ball” approximation from the deposited film density $\rho$ and GPC [7]. In contrast to the steady-state assumption applied in, e.g., plasma etching simulations [11], we solve (1) up to the reactor pulse time $t_p$ using the forward Euler method with $N_t$ total time steps.

A requirement for determining $\theta(\vec{r})$ is finding the distribution of the reactant flux $\Gamma_{H_2O}(\vec{r})$. This calculation is challenging given that the $\beta(\theta)$ changes not only across the surface but also after the solution of each step of (1). Although powerful methods such as Monte Carlo ray tracing can be used [8, 10], they require substantial computational resources since $\Gamma_{H_2O}(\vec{r})$ must be calculated $N_t$ times.

To alleviate the computational burden, we assume a preferential transport
direction, i.e., that the flux is equal on all surfaces at the same \( z \) coordinate. This allows to calculate the flux assuming diffusive flow in a cylinder of diameter \( d \) and length \( L \), with adsorption losses, given by a 1D differential equation \([6]\): 

\[
D \frac{d^2 \Gamma_{\text{H}_2\text{O}}(z)}{dz^2} = \bar{v}\beta_0 (1 - \theta(z)) \Gamma_{\text{H}_2\text{O}}(z),
\]

\[
\Gamma_{\text{H}_2\text{O}}(0) = \Gamma_0,
\]

\[
D \frac{d\Gamma_{\text{H}_2\text{O}}}{dz} \bigg|_{z=L} = -\frac{1}{4} \bar{v}\beta_0 (1 - \theta(L)) \Gamma_{\text{H}_2\text{O}}(L)
\]

In \([2]\), \( \bar{v} \) is the thermal speed and \( \Gamma_0 \) is the flux of the reactant species inside the reactor, which can be calculated using the kinetic theory of gases \([12]\) from the reactor temperature \( T \), reactant molar mass \( M_A \), and partial pressure \( p_A \). This equation is solved with a central finite differences scheme for each step of the solution of \([1]\).

The diffusivity \( D \) can be analytically approximated for a long cylinder, when particle-wall collisions are more likely than particle-particle collisions (i.e., Knudsen number \( Kn > 10 \)) as \([13]\)

\[
D \approx D_{Kn} = \frac{1}{3} \bar{v}h_d d,
\]

where \( h_d \) is the hydraulic diameter approximation factor mapping the involved geometry to an equivalent cylinder \([7]\). For example, for a wide rectangular trench with opening \( d \) (c.f. Fig. 3), \( h_d \) is estimated to be 2 \([1, 7]\). Should the rate of particle-particle collisions be comparable, i.e., \( 1 < Kn < 10 \), \( D \) can be approximated with the Bosanquet formula \([13]\)

\[
\frac{1}{D} \approx \frac{1}{D_A} + \frac{1}{D_{Kn}},
\]
where $D_A$ is the conventional Chapman-Enskog gas-phase diffusivity calculated from the particle hard-sphere diameter $d_A$. In this work, we assume only Knudsen diffusivity ($D_A \to \infty$), except when otherwise indicated.

The key hypothesis of our approach is that, given a certain reactor setup, the parameters $\beta_0$ and $\Gamma_{ev}$ are constant. Therefore, we present in Fig. 2 their impact in the required $t_p$ for achieving saturation. We define saturation by first calculating the coverage $\theta_{sat}$ at $z = L$ in the steady-state convergence of (1) followed by calculating the $t_p$ required to achieve 95% of $\theta_{sat}$.

From Fig. 2, we observe that $\beta_0$ has the most influence on the saturation time. Instead of directly impacting $t_p$, $\Gamma_{ev}$ greatly affects the maximum coverage achievable at the trench bottom. Therefore, it strictly limits the maximum aspect ratio achievable by a certain reactor configuration and must be considered in the design of novel technologies.
2.2. Topography simulation

In order to calculate the time evolution of a surface during the fabrication process, we employ the level-set method [11, 14] as implemented in ViennaLS [15] and in Silvaco’s Victory Process [16]. In this method, the surface is described as the zero level-set of a 3D function \( \phi(\vec{r}) \) which evolves in time according to the level-set equation

\[
\frac{\partial \phi(\vec{r}, t)}{\partial t} + V(\vec{r}) |\nabla \phi(\vec{r}, t)| = 0,
\]

where \( V(\vec{r}) \) is a scalar velocity field describing the growth rate. An illustration of a simulated 3D trench geometry after ALD of Al\(_2\)O\(_3\) is shown in Fig. 3.

Figure 3: Illustration of simulated trench after ALD with non-ideal conformality.

The methodology presented in Section 2.1 is limited to calculating \( \theta(\vec{r}) \). However, it is not straightforward to map \( \theta(\vec{r}) \) into \( V(\vec{r}) \). Growth rates can be calculated cycle-by-cycle by evolving the surface by the molecular layer
thickness [10], however, this imposes a performance penalty since the grid resolution must be small enough to capture the individual molecular layer and $\theta(\vec{r})$ must be calculated $N_{\text{cycles}}$ times. This calculation repeats even though the geometry changes minimally between sequential cycles.

In order to capture a realistic ALD process with hundreds or thousands of cycles, a more efficient approach is required, combining multiple cycles into the surface evolution step. For this, we introduce an artificial time $t^* = N_{\text{cycles}}/C$ where $C$ is a numerical constant. In essence, the time unit in our equation are multiples of ALD cycles and the velocity field becomes

$$V(\vec{r}) = V(z) = C \cdot \text{GPC} \cdot \theta(z). \quad (6)$$

The constant $C$ can be chosen by considering the involved number of cycles such that $t^* \approx 1$. In the involved level-set based topography simulators, the velocity field is assumed to be constant during the entire advection step, which is limited to one grid spacing at most [14]. Thus, for (6) to be physically meaningful, the grid size must be small enough such that the variations in the geometry do not significantly impact $\theta(\vec{r})$, since the value of $d$ is updated after each advection step.

3. Results

3.1. The H$_2$O step: Temperature dependence

We calibrate our model to measured thickness profiles of Al$_2$O$_3$ in the H$_2$O-limited regime. Arts et al. [9] report film thicknesses in lateral HAR trench-like structures ($d = 0.5 \mu m$, $L = 5 \text{ mm}$) with an H$_2$O dose of approximately 750 mTorr·s after 400 ALD cycles with a GPC of 1.12 Å at three calibrated substrate temperatures $T$ (150 °C, 220 °C, and 310 °C). We estimate
the unreported $\rho_{\text{Al}_2\text{O}_3}$ to be $1500 \text{ kg/m}^3$ and $t_p$ to be 0.1 s. The calibrated parameters for each $T$ are provided in Table 1 and the model comparison to experimental data is given in Fig. 4. The authors of the original work also estimate $\beta_0$ from the slope at 50% height, and those values are reported in Table 1.

Table 1: Model parameters for the H$_2$O step of ALD of Al$_2$O$_3$ calibrated to measurements from [9].

| Parameter       | 150°C | 220°C | 310°C |
|-----------------|-------|-------|-------|
| $\Gamma_{\text{ev}}$ (m$^{-2}$s$^{-1}$) | $6.5 \times 10^{19}$ | $5.5 \times 10^{19}$ | $3.5 \times 10^{19}$ |
| $\beta_0$       | $5.0 \times 10^{-5}$ | $1.2 \times 10^{-4}$ | $1.9 \times 10^{-4}$ |
| $\beta_0$, estimated range from [9] | $1.4 \times 10^{-5}$ | $0.8 \times 10^{-4}$ | $0.9 \times 10^{-4}$ |

Figure 4: Comparison of calibrated simulation to H$_2$O-limited thickness profiles measured by Arts et al. [9]
In Fig. 4 we note a good agreement between our calibrated model and the reported experimental profiles. The estimated values of \( \beta_0 \) are also generally consistent with the estimated ranges from the original work, which is expected since it also relies on first-order Langmuir kinetics. However, we expect that our methodology provides a more accurate estimate, including on the discrepant value at 150°C, since we consider the entire profile and we include \( \Gamma_{ev} \).

Due to the availability of data at different substrate temperatures, we perform an indicative Arrhenius analysis, shown in Fig. 5. In Fig. 5 (a), we observe that the \( \beta_0 \) increases and \( \Gamma_{ev} \) decreases with increasing \( T \), suggesting that chemisorption becomes more thermodynamically favorable. From the linear fit of \( \beta_0 \), we extract an activation energy \( E_A = 0.178 \text{ eV} \) for the reaction. Although this value is lower than first-principle studies suggest \([17]\), it is consistent with a recent experimental analysis exploring a two-stage reaction, where \( E_A \) is estimated as \( 0.166 \pm 0.02 \text{ eV} \) \([18]\).

From the fitted Arrhenius relationships, both model parameters (\( \beta_0 \) and \( \Gamma_{ev} \)) can be expressed as functions of the single physical variable \( T \). Thus, the parameter analysis from Fig. 2 can be reduced from three to two dimensions, as shown in Fig. 5 (b). We observe that the saturation \( t_p \) reduces and \( \theta_{sat} \) increases with higher temperatures, as is expected from a more thermodynamically favorable reaction. However, in many experimental situations \( \theta \) is not easily measurable. Instead, the step coverage \( SC \), which is the ratio between the film thickness at the bottom relative to the fully exposed plane, is measured. We note that the saturation \( SC_{sat} \), defined as \( \theta_{sat}(z = L)/\theta_{sat}(z = 0) \) is high and nearly constant for the entire tested temperature range. Thus,
Figure 5: (a) Arrhenius analysis of $\beta_0$ and $\Gamma_{ev}$ from Table 1. (b) After parameterization to $T$, its effect is investigated in the saturation $t_p$, $\theta_{sat}$ and $SC_{sat}$.

we expect that at low temperatures, even though the SC is high, the film quality could be low due to the presence of defects such as vacancies and voids.

3.2. The TMA step and geometric parameters

Similarly to Section 3.1 the model is calibrated to published thickness profiles of $\text{Al}_2\text{O}_3$ in the TMA-limited regime. Due to the comparatively
higher complexity of TMA, this step has received more research attention, therefore, we are able to simultaneously calibrate our model to multiple independent experiments in similar lateral HAR structures \( d = 0.5 \mu m \) [7, 9, 19]. All available reactor and film parameters were taken directly from the original publications. The unavailable data was estimated as follows: For Yilammi et al. [7], we estimate \( p_A = 325 \) mTorr; for Arts et al. [9], \( t_p = 0.4 \) s and \( \rho_{\text{Al}_2\text{O}_3} = 1500 \) kg/m\(^3\); and for Yim et al. [19], \( p_A = 160 \) mTorr.

Since all reported thickness profiles were obtained on a restricted range of set temperatures (275°C in [9], 300°C otherwise), we calibrate our model to all profiles with the same parameter set presented in Table 2, including the estimates of \( \beta_0 \) from the original works. The disparity is likely due to the effect of \( \Gamma_{\text{ev}} \), which is corroborated by the most similar value being that from [7], whose approach also considers reversible kinetics.

The comparison to the published measured profiles is provided in Fig. 6, showing good agreement. This is strong evidence for the hypothesis discussed in Section 2.1 that the model parameters are determined by the reactor setup, most importantly the reactor \( T \). The peaks shown in the experimental data from [19] are disregarded since they are reported to be spurious interactions with the pillars sustaining the structure.

| \( \Gamma_{\text{ev}} \) (m\(^{-2}\)s\(^{-1}\)) | \( \beta_0 \) | \( \beta_0 \) from [7] | \( \beta_0 \) from [9] | \( \beta_0 \) from [19] |
|--------------------------|----------|----------------|----------------|----------------|
| \( 3.0 \cdot 10^{19} \)  | \( 7.5 \cdot 10^{-3} \) | \( 5.7 \cdot 10^{-3} \) | \( (0.5-2.0) \cdot 10^{-3} \) | \( 4.0 \cdot 10^{-3} \) |

We reproduce additional experiments by Yim et al. [19] in lateral HAR
structures with different initial openings \( d \), shown in Fig. 7. The discrepancy in the structure with \( d = 0.1 \mu m \) is due to the limits of our model, when the opening becomes fully constricted. For the structure with opening \( d = 2.0 \mu m \), pure Knudsen diffusivity is no longer valid, since \( Kn \approx 8.9 \). We recover accuracy by using (4) (marked “Bosanquet”) which is calculated using the hard-sphere diameters of TMA \( d_{TMA} = 591 \) pm and of nitrogen (\( N_2 \), the carrier gas) \( d_{N_2} = 374 \) pm [7].

4. Conclusion

In this work, we present an augmented model for non-ideal conformality during ALD in HAR structures based on diffusive particle transport and reversible first-order Langmuir kinetics. By focusing on the often-disregarded evaporation flux, we achieve a better fit to experimental data and also obtain further chemical insights from the non-ideal saturation behavior. Also, by
approximating the diffusivity with the Bosanquet formula, we are able capture processing conditions with lower Knudsen numbers. Finally, we present an approach for efficiently integrating our model with a level-set topography simulator by combining multiple ALD cycles into an artificial time unit.

We calibrate our model to reported thickness profiles in the prototypical ALD of Al₂O₃ from H₂O and TMA. We study the impact of temperature in H₂O-limited profiles, indicating the strong impact of the evaporation flux at lower temperatures and extracting an activation energy of 0.178 eV which is comparable with recent experimental studies. From calibrating our simulation with a single parameter set to multiple independent experiments in the TMA-limited regime, we strengthen the hypothesis that the parameters are strongly related to the reactor condition, most importantly to its temperature. We also show that the Bosanquet formula recovers accuracy in
conditions where not only particle-wall interactions but also particle-particle collisions are relevant.

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References

[1] V. Cremers, R. L. Puurunen, J. Dendooven, Conformality in atomic layer deposition: Current status overview of analysis and modelling, Appl Phys Rev 6 (2) (2019) 021302. doi:10.1063/1.5060967.

[2] H. Knoops, S. Potts, A. Bol, W. Kessels, 27 - Atomic Layer Deposition, in: T. F. Kuech (Ed.), Handbook of Crystal Growth, Second Edition, North-Holland, 2015, pp. 1101–1134. doi:10.1016/B978-0-444-63304-0.00027-5.

[3] S. Jakschik, U. Schroeder, T. Hecht, G. Dollinger, A. Bergmaier, J. Bartha, Physical properties of ALD-Al_2O_3 in a DRAM-capacitor equivalent structure comparing interfaces and oxygen precursors, Mater Sci Eng B 107 (3) (2004) 251–254. doi:10.1016/j.mseb.2003.09.044.

[4] A. Fischer, A. Routzahn, R. J. Gasvoda, J. Sims, T. Lill, Control of etch profiles in high aspect ratio holes via precise reactant dosing in
thermal atomic layer etching, J Vac Sci Technol A 40 (2) (2022) 022603. doi:10.1116/6.0001691.

[5] R. L. Puurunen, Surface chemistry of atomic layer deposition: A case study for the trimethylaluminum/water process, J Appl Phys 97 (12) (2005) 9. doi:10.1063/1.1940727

[6] A. Yanguas-Gil, J. W. Elam, Self-limited reaction-diffusion in nanostructured substrates: Surface coverage dynamics and analytic approximations to ald saturation times, Chem Vap Depos 18 (1-3) (2012) 46–52. doi:10.1002/cvde.201106938

[7] M. Ylilammi, O. M. Ylivaara, R. L. Puurunen, Modeling growth kinetics of thin films made by atomic layer deposition in lateral high-aspect-ratio structures, J Appl Phys 123 (20) (2018) 205301. doi:10.1063/1.5028178

[8] M. C. Schwille, T. Schössler, F. Schön, M. Oettel, J. W. Bartha, Temperature dependence of the sticking coefficients of bis-diethyl aminosilane and trimethylaluminum in atomic layer deposition, J Vac Sci Technol A 35 (1) (2017) 01B119. doi:10.1116/1.4971197

[9] K. Arts, V. Vandalon, R. L. Puurunen, M. Utriainen, F. Gao, W. M. Kessels, H. C. Knoops, Sticking probabilities of h\textsubscript{2}O and Al(CH\textsubscript{3})\textsubscript{3} during atomic layer deposition of Al\textsubscript{2}O\textsubscript{3} extracted from their impact on film conformality, J Vac Sci Technol A 37 (3) (2019) 030908. doi:10.1116/1.5093620
[10] L. Filipovic, Modeling and simulation of atomic layer deposition, in: Proceedings of the International Conference on Simulation of Semiconductor Processes and Devices (SISPAD), IEEE, 2019, pp. 323–326. doi:10.1109/SISPAD.2019.8870462.

[11] X. Klemenschits, S. Selberherr, L. Filipovic, Modeling of gate stack patterning for advanced technology nodes: A review, Micromach 9 (12) (2018) 631. doi:10.3390/mi9120631.

[12] S. Chapman, T. G. Cowling, The mathematical theory of non-uniform gases, Third Edition, Cambridge University Press, 1991.

[13] W. Pollard, R. D. Present, On gaseous self-diffusion in long capillary tubes, Phys Rev 73 (7) (1948) 762. doi:10.1103/PhysRev.73.762.

[14] J. A. Sethian, Level set methods and fast marching methods, Second Edition, Cambridge University Press, 1999.

[15] ViennaLS, Available online: https://viennatools.github.io/ViennaLS (accessed 08 June 2022).

[16] Silvaco, Victory Process, Available online: www.silvaco.com/tcad/victory-process-3d/ (accessed 08 June 2022).

[17] S. Seo, T. Nam, H. Kim, B. Shong, et al., Molecular oxidation of surface–CH$_3$ during atomic layer deposition of Al$_2$O$_3$ with H$_2$O, H$_2$O$_2$, and O$_3$: A theoretical study, Appl Surf Sci 457 (2018) 376–380. doi:10.1016/j.apsusc.2018.06.160.
[18] B. A. Sperling, B. Kalanyan, J. E. Maslar, Atomic layer deposition of Al$_2$O$_3$ using trimethylaluminum and H$_2$O: The kinetics of the H$_2$O half-cycle, J Phys Chem C 124 (5) (2020) 3410–3420. doi:10.1021/acs.jpcc.9b11291

[19] J. Yim, O. M. Ylivaara, M. Ylilammi, V. Korpelainen, E. Haimi, E. Verkama, et al., Saturation profile based conformality analysis for atomic layer deposition: Aluminum oxide in lateral high-aspect-ratio channels, Phys Chem Chem Phys 22 (40) (2020) 23107–23120. doi:10.1039/d0cp03358h