

Geometry-Agnostic Feature-Scale PEALD Model

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Abstract—We present a geometry-agnostic feature-scale model for plasma-enhanced atomic layer deposition (PEALD) that captures radical-recombination-limited conformality and the onset of void formation in high-aspect-ratio (HAR) features. The model combines Monte Carlo ray tracing of radicals with a Langmuir-type surface-coverage equation augmented by an evaporation term, where recombination is treated as a gas-phase loss channel. In contrast to reduced-order diffusion-reaction and ballistic transport-reaction approaches that are typically evaluated on static 1D/lateral HAR (LHAR) channels, the present implementation directly handles evolving 2D/3D process geometries. Validation on LHAR structures reproduces the logarithmic penetration behavior reported for recombination probabilities relevant to oxide deposition. The model is then applied to a gap-fill geometry, where increasing local aspect ratio drives pinch-off and central void formation, consistent with reported cross-sections and motivating an extension to inhibitor-driven area-selective PEALD.

Index Terms—Plasma-enhanced atomic layer deposition, High-aspect-ratio features, Monte-Carlo ray tracing, Surface coverage kinetics, Void formation, Gap-fill process

I. INTRODUCTION

Plasma-enhanced atomic layer deposition (PEALD) is increasingly used to fabricate structures that would degrade at the elevated temperatures required for thermal ALD. Plasma activation enables near-ambient-temperature processing, but it also introduces reduced conformality through the finite recombination probability of reactive plasma species. Existing conformality models are commonly formulated as diffusion-reaction or ballistic transport-reaction descriptions in simplified channel geometries [1], [2]. In this study, we explicitly target

the complementary regime of geometry-agnostic feature-scale topography evolution, where transport, surface kinetics, and shape evolution remain coupled throughout the process flow. We investigate the interplay between recombination, sticking, and evaporation, and demonstrate why inhibitor-based strategies are needed when PEALD is applied to structures with strong aspect-ratio-induced visibility and exposure limitations.

II. MODEL

Radicals launched from the feature entrance are traced through the gas phase. For typical PEALD precursor chemistries, the mean free path is far beyond the characteristic structure length scales; therefore, transport can be treated as ballistic and governed by particle-wall collisions in the Knudsen flow regime. At each surface hit, the particle adsorbs with probability $\beta = \beta_0(1 - \theta)$, recombines with probability $\gamma = \gamma_0(1 - \beta)\theta$, or is diffusely reflected with probability $1 - \gamma - \beta$, based on the intrinsic sticking coefficient β_0 , recombination probability γ_0 , and local coverage $\theta(\vec{r}, t)$. Recombination is treated as a pure gas-phase loss channel. The surface coverage including evaporation flux, following Aginsky *et al.* [3] and Reiter *et al.* [4], therefore evolves as

$$\frac{1}{s_0} \frac{\partial \theta(\vec{r}, t)}{\partial t} = \Gamma(\vec{r}, t) \beta_0 (1 - \theta(\vec{r}, t)) - \Gamma_{\text{ev}} \theta(\vec{r}, t),$$

where $\Gamma(\vec{r}, t)(\text{m}^{-2} \text{s}^{-1})$ is the surface flux obtained by Monte Carlo ray tracing, $s_0(\text{m}^2)$ is the surface site area, and $\Gamma_{\text{ev}}(\text{m}^{-2} \text{s}^{-1})$ is the evaporation flux of adsorbed particles from surface sites. The film growth rate is proportional to coverage, $v(\vec{r}) = \text{GPC} \cdot \theta(\vec{r})$, where GPC is the growth per cycle. The recombination mechanism therefore affects coverage indirectly through the geometry-dependent flux $\Gamma(\vec{r}, t)$. Baseline validation is performed with $\Gamma_{\text{ev}} = 0$ to isolate recombination effects, while additional simulations quantify the impact of finite evaporation.

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A priori, an estimate of whether a given material/geometry combination is recombination-limited can be obtained from the Knoops criterion [5]

$$\text{AR}_{\text{crit}} \approx \frac{1.32}{\sqrt{\gamma_0}}.$$

III. VALIDATION

A. Experimental Lateral HAR Structures

To validate our model, implemented in ViennaPS [6], we reproduce the key experimental benchmark for recombination-limited PEALD conformality from Arts *et al.* [7]. They measured film penetration into lateral high-aspect-ratio (LHAR) PillarHall structures, finding a characteristic logarithmic dependence on plasma exposure time. The slope of this trend is determined by the material-specific recombination probability γ_0 .

Our simulations, performed in an LHAR trench with $\text{AR} = 1000$ ($0.5\mu\text{m}$ opening, $500\mu\text{m}$ depth), replicate this behavior with high fidelity, as shown in Figure 1 and Figure 2. The model captures the qualitative, exponentially decaying film profiles (Figure 1). More importantly, the 50% penetration depth versus logarithm of plasma exposure time shows good quantitative agreement with the linear trend reported from experiments (Figure 2). Deviations at higher exposure times arise from back-wall loading effects, as visible in Figure 1. Because the experimental structure used a slightly larger AR of 1200 [7], this regime is not entered in the measurements.

The evaporation term Γ_{ev} , omitted here as a simplifying assumption, affects the absolute film profile (Figure 2, $\beta_0 = 10^{-3}$) and is required for full quantitative calibration. The effect of evaporation on obtained profiles is significant already for very low evaporation fluxes ($\Gamma_{\text{ev}} = 0.00125\% - 0.005\% \Gamma$) (Figure 3). Including this term is thus important for reproducing experimental measurements and calibrating the model to different precursor chemistries. Figure 4 shows that finite evaporation flux leads to saturation of the penetration depth, resulting in an evaporation-flux-limited regime.

The overall agreement of our simulations with experimental data validates the model's predictive capability for recombination-limited conformality and its material dependence. The evaporation study further indicates that the experimentally observed penetration behavior can be strongly affected by even weak desorption of adsorbed species.

B. Gap-fill Geometries

The model is then applied to gap-fill geometries with an opening width of 100nm and a depth of $2.5\mu\text{m}$,

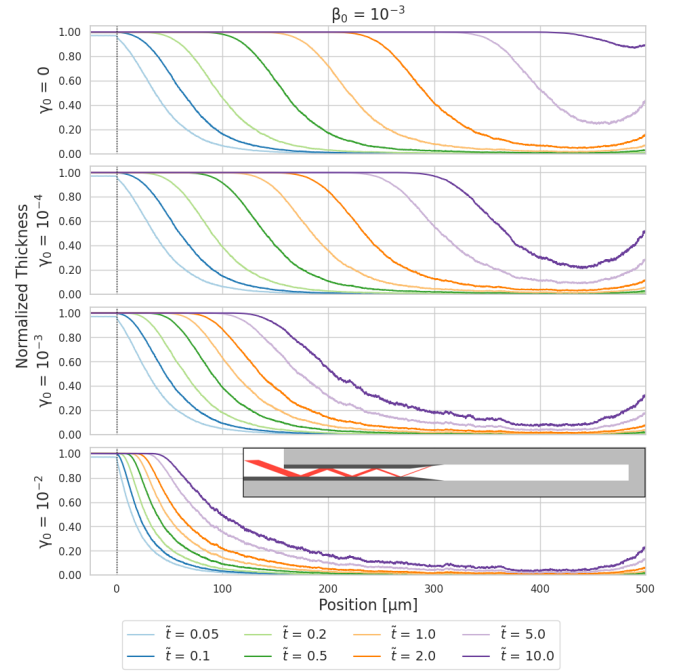


Fig. 1: Simulated film profiles for different recombination probabilities γ_0 with sticking coefficient $\beta_0 = 10^{-3}$, reproducing the experimentally-observed exponential decay. Colors indicate snapshots at different exposure times. The insert shows a schematic of the validation structure and radical transport.

resulting in an initial aspect ratio of $\text{AR} = 25$. Although this lies well below the recombination-limited transition ($\text{AR}_{\text{crit}} \approx 170$ for SiO_2) [5], and far below $\text{AR} \approx 900$ reported for conformal PEALD of SiO_2 [7], the evolving aspect ratio during gap fill eventually leads to profiles that no longer allow conformal deposition. Consequently, the film closes off at the opening before the cavity is filled completely, producing a central void (Figure 5, a-c). This void formation can further be quantified by maximum void width and filling fraction relative to the original structure (Figure 5, d,e). The effect of a side-wall taper angle is investigated in Figure 6 and shows that already very shallow tapering leads to an upwards shift of the void center and that for low recombination probabilities void formation ceases completely. This emphasizes the need to not only model PEALD on ideal structures but rather extract surface profiles from experimental FE-SEM/TEM cross-sections as initial simulation geometries.

The simulated void onset, position, and final size are consistent with FE-SEM/TEM cross-sections reported for untreated PEALD gap fill [8] (Figure 7, a). Together

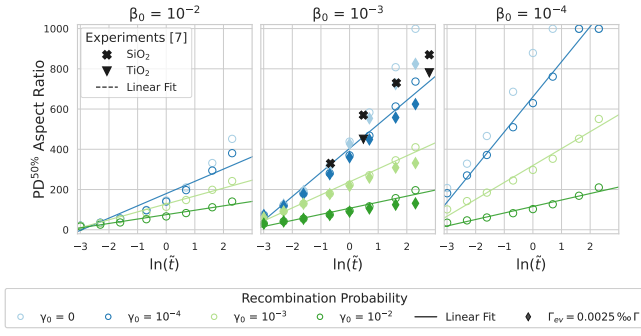


Fig. 2: Simulated 50% penetration depth vs. plasma exposure time $\tilde{t}$ (colored circles), showing good agreement with the logarithmic trend (lines) from experiments [7] (black markers). Colors indicate the recombination probability γ_0 in the columns for fixed sticking coefficient β_0 . For $\beta_0 = 10^{-3}$, colored diamonds show $PD^{50\%}$ values for simulations including $\Gamma_{ev} = 0.0025\% \Gamma$. Exposure times $\tilde{t}$ are normalized by the steady-state time constant $\tau = \frac{1}{s_0 \Gamma \beta_0}$.

with related inhibitor-based studies [9] (Figure 7, c), this comparison shows that conventional PEALD, even when nominally deep in the reaction-limited branch for planar features, is incompatible with seamless gap fill scenarios once the evolving geometry eventually enters a regime that no longer allows conformal deposition.

IV. DISCUSSION AND OUTLOOK

Our results highlight two competing failure modes in PEALD gap-fill. First, radical recombination depletes the reactive flux deep inside features, a mechanism dominant in HAR structures and for high- γ_0 materials. Second, high sticking probability near the feature opening leads to premature pinch-off. While the recombination-limited regime can be partially mitigated by process tuning, the logarithmic dependence on time makes this approach industrially challenging. In contrast, geometric pinch-off cannot be overcome by simply tuning the parameters of a conventional, conformal process.

Overcoming this geometric pinch-off requires reversing the natural flux gradient, which is increasingly achieved through inhibitor-based strategies [8], [9]. Accurately predicting the baseline non-conformality, as demonstrated by our model, is a crucial prerequisite for such approaches. By quantifying reactant depletion and geometric pinch-off, the model establishes the dose and transport profile required of inhibiting species. This work thereby provides the foundational transport and coverage

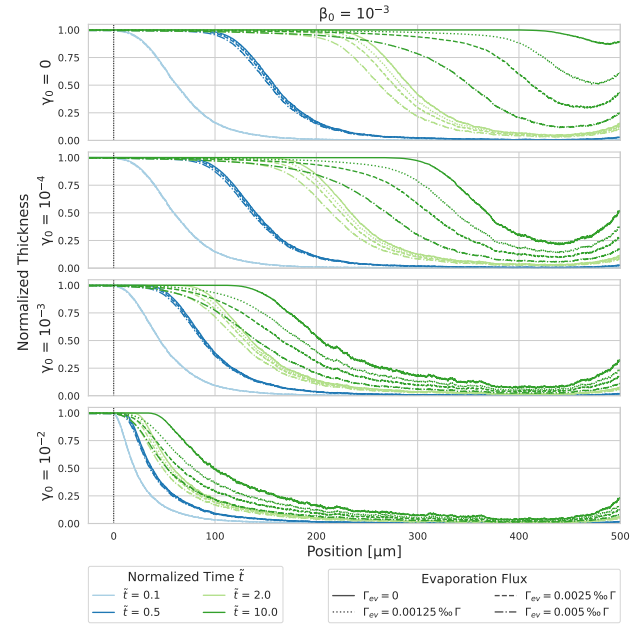


Fig. 3: Simulated film profiles for different recombination probabilities γ_0 with sticking coefficient $\beta_0 = 10^{-3}$. Colors indicate snapshots at different normalized exposure times and line styles represent evaporation flux Γ_{ev} in promille of dosing flux Γ .

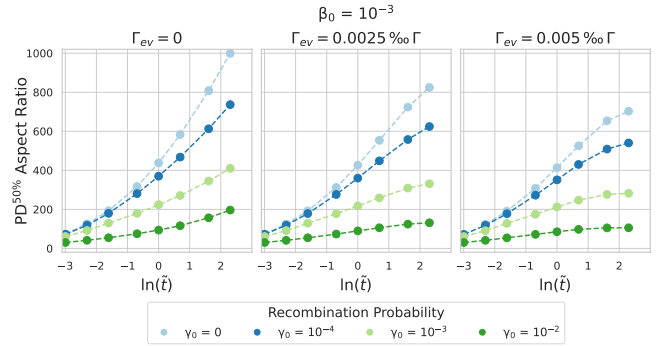


Fig. 4: Simulated 50% penetration depth vs. plasma exposure time $\tilde{t}$ with sticking coefficient $\beta_0 = 10^{-3}$. Colors indicate the recombination probability γ_0 in the columns for different evaporation fluxes Γ_{ev} in promille of dosing flux Γ . Exposure times $\tilde{t}$ are normalized by the steady-state time constant $\tau = \frac{1}{s_0 \Gamma \beta_0}$.

solver required to design and optimize area-selective PEALD processes in complex 3D geometries.

REFERENCES

- [1] V. Cremers, R. L. Puurunen, and J. Dendooven, "Conformality in atomic layer deposition: Current status overview of analysis and modelling," *Applied Physics Reviews*, vol. 6, no. 2, p. 021302, 2019, doi: 10.1063/1.5060967.

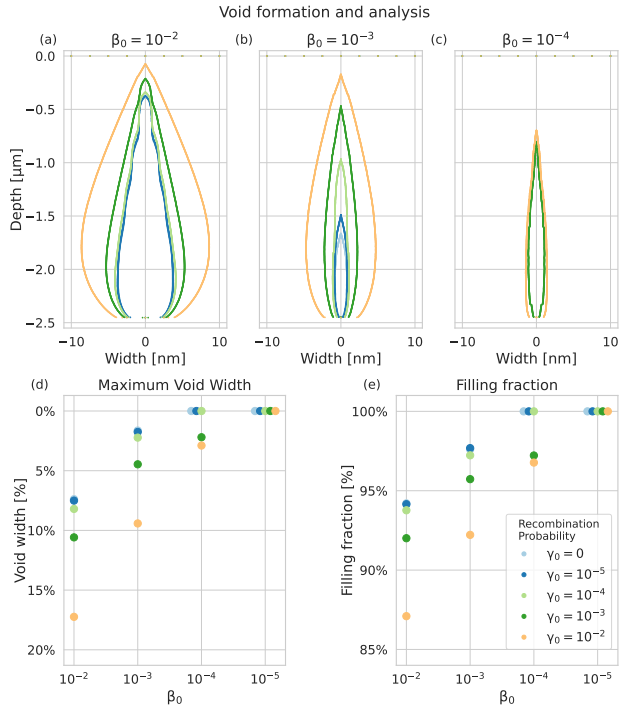


Fig. 5: The onset of void formation in a gap-fill process is visualized in sub-figures (a)-(c). From left to right, surface profiles for sticking coefficients $\beta_0 = 10^{-2}$ – 10^{-4} are shown, while colors represent the range of recombination probabilities γ_0 probed. Sub-figures (d) and (e) quantify void severity by maximum void thickness in % of initial trench width and filling fraction in % of trench area.

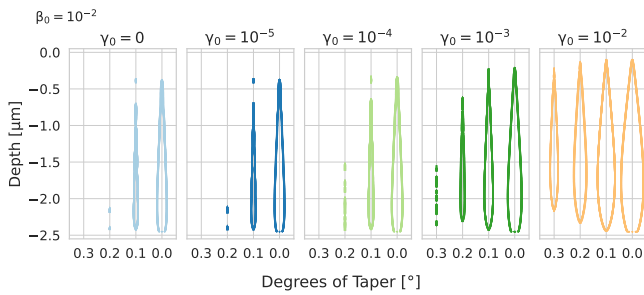


Fig. 6: Evaluation of different side-wall taper angles with sticking coefficient $\beta_0 = 10^{-2}$. Columns and colors indicate recombination probabilities γ_0 . Void formation is visualized for taper angles 0.3° to 0.0° from left to right for each recombination probability.

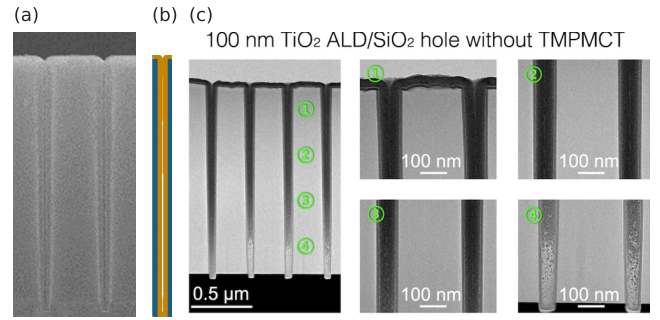


Fig. 7: The simulated pinch-off and central void trends in (b) are consistent with FE-SEM/TEM observations reported for untreated PEALD gap fill in trenches (a) [8] and related inhibitor studies in holes (c) [9].

- [2] J. Järviö, J. A. Velasco, J. Yim, C. Gonsalves, and R. L. Puurunen, “Simulation of conformality of ALD growth inside lateral channels: Comparison between a diffusion-reaction model and a ballistic transport-reaction model,” *Physical Chemistry Chemical Physics*, vol. 25, no. 34, pp. 22952–22964, 2023, doi: 10.1039/D3CP01829F.
- [3] L. F. Aguinis, F. Rodrigues, T. Reiter, X. Klemens, L. Filipovic, A. Hössinger, and J. Weinbub, “Modeling incomplete conformality during atomic layer deposition in high aspect ratio structures,” *Solid-State Electronics*, vol. 201, p. 108584, 2023, doi: 10.1016/j.sse.2022.108584.
- [4] T. Reiter, L. F. Aguinis, F. Rodrigues, J. Weinbub, A. Hössinger, and L. Filipovic, “Modeling the impact of incomplete conformality during atomic layer processing,” *Solid-State Electronics*, vol. 211, p. 108816, 2024, doi: 10.1016/j.sse.2023.108816.
- [5] H. C. M. Knoops, E. Langereis, M. C. M. van de Sanden, and W. M. M. Kessels, “Conformality of plasma-assisted ALD: Physical processes and modeling,” *Journal of The Electrochemical Society*, vol. 157, no. 12, pp. G241–G249, 2010, doi: 10.1149/1.3491381.
- [6] T. Reiter and L. Filipovic, “ViennaPS: A flexible framework for semiconductor process simulation,” *SoftwareX*, vol. 32, p. 102453, 2025, doi: 10.1016/j.softx.2025.102453.
- [7] K. Arts, M. Utriainen, R. L. Puurunen, W. M. M. Kessels, and H. C. M. Knoops, “Film conformality and extracted recombination probabilities of O atoms during plasma-assisted atomic layer deposition of SiO₂, TiO₂, Al₂O₃, and HfO₂,” *The Journal of Physical Chemistry C*, vol. 123, no. 44, pp. 27030–27035, 2019, doi: 10.1021/acs.jpcc.9b08176.
- [8] Y. Choi, T. Kim, H. Lee, J. Park, J. Park, D. Ryu, and W. Jeon, “Bottom-up plasma-enhanced atomic layer deposition of SiO₂ by utilizing growth inhibition using NH₃ plasma pre-treatment for seamless gap-fill process,” *Scientific Reports*, vol. 12, p. 15756, 2022, doi: 10.1038/s41598-022-20201-y.
- [9] C. T. Nguyen, E.-H. Cho, B. Gu, S. Lee, H.-S. Kim, J. Park, N.-K. Yu, S. Shin, B. Shong, J. Y. Lee, and H.-B.-R. Lee, “Gradient area-selective deposition for seamless gap-filling in 3D nanostructures through surface chemical reactivity control,” *Nature Communications*, vol. 13, p. 7597, 2022, doi: 10.1038/s41467-022-35428-6.