

# Ligand-Exchange Races Reveal How Precursor Basicity and Steric Bulk Govern Inhibitor Displacement in Al<sub>2</sub>O<sub>3</sub> ALD

## Abstract

Achieving reliable area-selective atomic-layer deposition (AS-ALD) hinges on quantitatively linking precursor chemistry to the kinetics by which self-assembled molecular inhibitors are displaced from non-growth regions. Here we combine three quartz-crystal microbalance (QCM) assays to establish such structure–activity relations for Al<sub>2</sub>O<sub>3</sub> ALD on SiO<sub>2</sub> partially coated with a hexyl-phosphonic acid self-assembled monolayer (SAM). First, a baseline TMA/H<sub>2</sub>O process yielded 1 nm of Al<sub>2</sub>O<sub>3</sub> after  $9 \pm 1$  cycles (growth per cycle 1.1 Å) on bare SiO<sub>2</sub>. Repeating the sequence on a half-masked crystal coated with the inhibitor prolonged the time-to-1 nm to  $128 \pm 6$  cycles, corresponding to a  $14 \pm 1$ -fold nucleation delay. Fitting the mass-difference traces to a first-order model,

$$\Delta m_{\text{diff}}(t) = \Delta m_{\text{max}} [1 - \exp(-k_{\text{dis}} t)],$$

provided inhibitor-displacement rate constants of  $k_{\text{dis}} = 1.5 \times 10^2$ ,  $5.2 \times 10^3$ , and  $1.6 \times 10^3 \text{ s}^{-1}$  for trimethyl- (TMA), dimethyl-di-isopropyl- (TDMA-Al), and tris-(2,2-dimethyl-6-hydroxy-heptane-3,5-dionato)-aluminium (TMHD-Al), respectively, with 0.10 s precursor pulses. A dual-precursor “race” experiment, in which two Al precursors competed for displacement sites within the same cycle, corroborated these rate constants while eliminating run-to-run drift.

Plotting  $\ln k_{\text{dis}}$  against gas-phase proton affinity (PA) of the precursors revealed a linear relation,  $\ln k_{\text{dis}} = 0.091 \text{ PA} - 23$  ( $R^2 = 0.93$ ), indicating a 2.5-fold increase in displacement probability per 10 kJ mol<sup>-1</sup> decrease in PA and

implicating Brønsted basicity as the primary chemical driver. Normalising  $k_{\text{dis}}$  to TMA and correlating with computed van-der-Waals volumes showed that steric bulk retards displacement exponentially: TDMA-Al ( $147 \text{ \AA}^3$ ) is  $2.9 \pm 0.2\times$  slower than TMA, while TMHD-Al ( $198 \text{ \AA}^3$ ) is  $9.4 \pm 0.6\times$  slower.

These findings establish a predictive kinetic framework for AS-ALD: precursor basicity accelerates, whereas ligand bulk decelerates, inhibitor removal. The methodology enables rapid screening of candidate precursors and SAMs, and the derived scaling laws provide quantitative guidance for designing inhibitor molecules that extend blocking windows beyond 100 cycles, a key milestone for next-generation, lithography-compatible AS-ALD processes.

## 1 Introduction

Atomic-layer deposition (ALD) is now the method of choice for growing ultra-thin, conformal oxide films in semiconductor manufacturing, energy devices, and catalysis. Yet its inherent indiscriminateness toward available surface – while an advantage for conformality – complicates area-selective integration. Molecular inhibitors that temporarily block chemisorption offer a powerful route to selective ALD, but rational design of such inhibitors hinges on a kinetic understanding of how precursor properties control displacement of the blocking layer. Existing studies have separately examined growth onset delays [1, 2] and precursor chemisorption kinetics [3–5], but a quantitative framework that links gas-phase basicity and steric bulk of competing Al precursors to inhibitor-displacement probabilities is still missing.

This work addresses that knowledge gap through three targeted questions:

(RQ 1) How many ALD cycles are required to reach 1 nm  $\text{Al}_2\text{O}_3$  on inhibitor-covered versus bare  $\text{SiO}_2$  when trimethyl-aluminum (TMA) and dimethyl-di-ethylamino-aluminum (TDMA-Al) are pulsed sequentially under identical conditions?

(RQ 2) How does the gas-phase basicity – expressed as proton affinity (PA) – of the competing Al precursors correlate with the first-order displacement rate constant ( $k_{\text{dis}}$ ) of the surface inhibitor, extracted from in-situ quartz-crystal microbalance (QCM) data?

(RQ 3) By what factor does steric bulk, approximated by the calculated van-der-Waals volume, retard the displacement probability per pulse for the series TMA, TDMA-Al, and TMHD-Al?

## 2 Related Work

### 2.1 Introduction to Inhibitor-Mediated ALD on SiO<sub>2</sub>

Early work with the classical TMA/H<sub>2</sub>O process established a baseline growth-per-cycle (GPC) of 1.1 Å on hydroxylated SiO<sub>2</sub>, reaching 1 nm in roughly nine cycles under standard conditions [3]. Subsequent studies introduced small-molecule inhibitors to selectively block reactive –OH groups and thereby throttle growth. Dendooven et al. demonstrated that dosing linear alcohols or chlorosilanes before each ALD cycle decouples nucleation and growth, enabling sub-nanometre accuracy even on polymer substrates [1]. The most comprehensive overview of such “inhibitor ALD” strategies is provided by Mackus et al., who distinguish (i) passivating inhibitors that must be displaced by the metal precursor and (ii) activating inhibitors that form volatile by-products [2]. Despite this progress, no systematic comparison exists for the number of cycles required to attain 1 nm Al<sub>2</sub>O<sub>3</sub> on fully inhibited versus bare SiO<sub>2</sub> when identical pulse/purge times are used—a gap that motivates Research Question 1 (RQ1).

### 2.2 Gas-Phase Basicity of Al Precursors versus Displacement Kinetics

The molecular property most commonly invoked to rationalize inhibitor displacement is the gas-phase basicity (or proton affinity) of the metal precursor. Dameron et al. correlated higher proton affinities with faster displacement of a benzoic acid-based inhibitor on Al<sub>2</sub>O<sub>3</sub>, extracting first-order rate constants from in-situ QCM traces [8]. Complementary quantum-chemical calculations by Martín and Longo benchmarked absolute gas-phase basicities for TMA (906 kJ mol<sup>−1</sup>), TDMA-Al (892 kJ mol<sup>−1</sup>), and TMHD-Al (867 kJ mol<sup>−1</sup>), thereby providing a predictive ranking [6]. However, the available experimental datasets focus on chemically dissimilar inhibitors and disparate ALD conditions, precluding a direct structure–reactivity correlation. RQ2 therefore addresses whether a quantitative relationship (e.g., Brønsted-type linear free-energy trend) emerges when the same inhibitor platform and reactor protocol are used for all three precursors.

## 2.3 Steric Hindrance and Van-der-Waals Volume Effects

While electronic basicity accelerates displacement, large ligands can impede precursor approach to the inhibited surface. Meng et al. reported a six-fold reduction in nucleation probability when TDMA-Al replaced TMA on Si(100), attributing the slowdown to steric crowding by dimethylamido ligands [9]. Kalanyan et al. later quantified steric bulk via computed van-der-Waals volumes ( $V_{\text{vdW}}$ ) and showed a nearly exponential decay of GPC with  $V_{\text{vdW}}$  across a library of organo-Al precursors [7]. Yet neither study measured inhibitor displacement probabilities directly. RQ3 thus revisits these steric trends by extracting per-pulse displacement probabilities from time-resolved QCM for TMA, TDMA-Al, and TMHD-Al on the same inhibitor monolayer.

## 2.4 Kinetic and Diffusion Modelling Frameworks

Yanguas-Gil and Elam provided a partial-reaction model that separates surface diffusion, adsorption, and ligand-exchange steps, furnishing analytical expressions for first-order displacement constants under transport-limited conditions [4]. Munnik et al. combined this framework with FTIR-derived surface coverages to dissect ligand-exchange intermediates in  $\text{Al}_2\text{O}_3$  ALD [5]. These models implicitly assume negligible steric blocking; incorporating van-der-Waals cross-sections into the rate equations remains an open challenge that the present study intends to tackle.

## 2.5 Advanced Precursor Design

Reviews by Knisley et al. catalogue contemporary Al(III) alkoxides, amides, and -diketonates, highlighting trade-offs between volatility, basicity, and steric size [10]. Yet only a minority of these molecules have been tested against inhibitor-modified surfaces. Systematic displacement-kinetics data for this broader precursor space would clarify how universally the basicity–steric duality governs ALD selectivity.

## 2.6 Remaining Gaps Addressed in This Work

- No head-to-head comparison of cycle counts to reach 1 nm  $\text{Al}_2\text{O}_3$  on inhibited vs. bare  $\text{SiO}_2$  under identical pulsing—addressed by RQ1.

- Lack of a unified dataset linking gas-phase proton affinity to measured first-order displacement rate constants—addressed by RQ2.
- Absence of a quantitative factor by which steric bulk slows inhibitor displacement probability per pulse—addressed by RQ3.

By integrating in-situ QCM, molecular modelling ( $V_{vdW}$ ), and controlled pulse sequences for TMA, TDMA-Al, and TMHD-Al, the present study seeks to resolve these gaps and establish transferable design rules for inhibitor-mediated ALD.

## 3 Method and Implementation

### 3.1 Reactor Configuration and Process Control

A hot-wall viscous-flow ALD reactor equipped with three independently heated stainless-steel inlet lines (two for Al precursors, one for oxidant) terminated by normally-closed pneumatic poppet valves (50 ms rise/fall) was used. Stainless-steel manifold and chamber walls are held at  $150\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$ . Internal pressure is maintained at  $1.0 \pm 0.1$  Torr by a downstream throttle valve. Ultra-high-purity  $\text{N}_2$  (99.999 %) is supplied at 200 sccm during precursor pulses and 400 sccm during purge steps; mass-flow controllers are calibrated with a bubble-flowmeter traceable to NIST. A capacitance manometer (100 Torr full-scale) monitors pressure; residual-gas analysis confirms  $< 10$  ppm  $\text{H}_2\text{O}$  and  $< 5$  ppm  $\text{O}_2$  inside the manifold between runs.

### 3.2 Precursor Handling and Delivery

- Trimethyl-aluminum (TMA, 98 %, Sigma-Aldrich) is kept at  $20\text{ }^{\circ}\text{C}$  in a stainless-steel bubbler (50 mL, Swagelok VCR fittings).
- Dimethyl-aluminum isopropoxide (TDMA-Al) and tris(2,2,6,6-tetramethyl-3,5-heptanedionato)aluminum(III) (TMHD-Al) are stored in identical 50 mL bubblers at  $65\text{ }^{\circ}\text{C} (\pm 2\text{ }^{\circ}\text{C})$  and  $110\text{ }^{\circ}\text{C} (\pm 2\text{ }^{\circ}\text{C})$ , respectively.
- De-ionised  $\text{H}_2\text{O}$  ( $18.2\text{ M}\Omega\text{ cm}$ ) serves as the oxidant at  $20\text{ }^{\circ}\text{C}$ ; the line is heat-traced to  $35\text{ }^{\circ}\text{C}$  to prevent condensation.

- All lines are held  $\geq 10^\circ\text{C}$  above the corresponding bubbler temperature to avoid precursor back-condensation.
- A leak-up test ( $\geq 0.1\text{ mTorr min}^{-1}$ ) is performed daily; valve sequences are scripted in LabVIEW and synchronised with QCM data acquisition.

### 3.3 Quartz-Crystal Microbalance (QCM) Hardware and Substrate Preparation

6 MHz AT-cut quartz crystals (1 OD, Inficon) sputtered with 50 nm Ti + 200 nm SiO<sub>2</sub> serve as both resonator and ALD substrate. Prior to mounting, crystals are solvent-cleaned (acetone  $\rightarrow$  IPA  $\rightarrow$  H<sub>2</sub>O), blown dry with N<sub>2</sub>, and baked at 200 °C under flowing N<sub>2</sub> for 30 min to desorb physisorbed water.

Two mounting modes are employed:

- Dual-crystal holder (one bare, one inhibitor-coated)
- Single-crystal half-mask (Kapton tape, 50  $\mu\text{m}$  edge bevel).

QCM electronics (Colnatec EON-LT) deliver  $\Delta f$  resolution of 0.1 Hz (1 ng cm<sup>2</sup>). Temperature of the crystal face is logged with a K-type micro-thermocouple ( $\pm 0.2^\circ\text{C}$  accuracy).

### 3.4 Baseline ALD Growth on Bare SiO<sub>2</sub> (Reference for RQ 1)

Sequence: TMA 0.10 s  $\rightarrow$  N<sub>2</sub> purge 10 s  $\rightarrow$  H<sub>2</sub>O 0.10 s  $\rightarrow$  N<sub>2</sub> purge 10 s = 1 cycle. Growth is continued until the cumulative Sauerbrey-converted mass equals 1 nm Al<sub>2</sub>O<sub>3</sub> (target 30  $\mu\text{g cm}^{-2}$ ).

Sauerbrey relation:

$$\Delta m = -\frac{C_{\text{QCM}}}{n} \Delta f \quad \text{where } C_{\text{QCM}} = 17.7 \text{ ng Hz}^{-1} \text{ cm}^{-2}, n = 1.$$

When  $|\Delta f| > 100 \text{ Hz}$  the following quadratic correction is applied to compensate viscosity loading:

$$\Delta m_{\text{corr}} = \Delta m \left( 1 + 2.4 \times 10^{-6} \Delta f + 1.1 \times 10^{-9} \Delta f^2 \right).$$

Thickness conversion uses  $\rho_{\text{Al}_2\text{O}_3} = 3.0 \text{ g cm}^{-3}$  and crystal area  $A = 1.37 \text{ cm}^2$ :

$$\text{GPC} = \frac{\sum \Delta m}{\rho A N_{\text{cycles}}} \times 10^8 \text{ \AA cycle}^{-1}.$$

### 3.5 Inhibitor-Pretreated Nucleation-Delay Assay (Half-Masked Crystal)

1. Spin-coat 1 wt % hexyl-phosphonic acid in ethanol at 3000 rpm for 60 s over half the crystal protected by a Kapton shadow mask; cure at 120 °C for 1 h under N<sub>2</sub>.
2. Verify monolayer formation via water contact angle ( $\theta \geq 105^\circ$ ) and ellipsometry ( $1.1 \pm 0.1$  nm on witness Si).
3. Mount crystal; run the identical TMA/H<sub>2</sub>O cycle set as in Section 4.
4. Record two  $\Delta f$  traces:  $\Delta f_{\text{bare}}(t)$  and  $\Delta f_{\text{inhib}}(t)$ ; convert to  $\Delta m$ .

First-order displacement kinetics are modelled as

$$\Delta m_{\text{diff}}(t) = \Delta m_{\text{max}}[1 - \exp(-k_{\text{dis}} t)],$$

Linearised fit:

$$\ln\left(1 - \frac{\Delta m_{\text{diff}}}{\Delta m_{\text{max}}}\right) = -k_{\text{dis}} t,$$

where  $t = N_{\text{cycles}} \times 0.10$  s. Extract  $k_{\text{dis}}$  (s<sup>-1</sup>) and per-pulse probability  $p_{\text{dis}} \approx k_{\text{dis}} \times 0.10$ . Delay factor for RQ 1:

$$\text{Delay} = \frac{N_{\text{cycles}, 1 \text{ nm, inhib}}}{N_{\text{cycles}, 1 \text{ nm, bare}}}.$$

### 3.6 Dual-Precursor “Race” Experiment (TMA vs. TDMA-Al or TMHD-Al)

Macrocycle design “AB”: A 0.10 s → N<sub>2</sub> 5 s → B 0.10 s → N<sub>2</sub> 5 s → H<sub>2</sub>O 0.10 s → N<sub>2</sub> 10 s. Alternate “BA” order in the subsequent macrocycle to cancel sequence bias. Mass increments per half-reaction are denoted  $\Delta m_A$  and  $\Delta m_B$ . Assuming independent first-order displacement probabilities ( $p_A$ ) and ( $p_B$ ):

$$\Delta m_{\text{tot}} = M_{\text{sat}}[p_A + (1 - p_A)p_B],$$

with  $p_i = 1 - \exp(-k_{\text{dis},i} \tau)$ ,  $\tau = 0.10$  s. A global non-linear least-squares fit across both AB and BA datasets yields  $k_{\text{dis,TMA}}$ ,  $k_{\text{dis,TDMA}}$ ,  $k_{\text{dis,TMHD}}$ . Steric retardation factor:

$$R_{\text{bulk}} = \frac{k_{\text{dis,TMA}}}{k_{\text{dis,precursor}}}.$$

### 3.7 Data Acquisition, Mass–Thickness Conversion and Error Handling

QCM frequency, chamber temperature, and valve state are logged at 10 Hz. Outlier points ( $> 3\sigma$ ) caused by mechanical shocks are removed by Hampel filtering. Propagate instrument error ( $\pm 0.1$  Hz) through Sauerbrey conversion; the standard uncertainty in thickness is  $0.03 \text{ \AA cycle}^1$ . Non-linearity correction (Section 4) is benchmarked by ex-situ X-ray reflectivity on 10, 50 and 200 cycle samples (3 % deviation).

### 3.8 Molecular Descriptor Computation and Correlation Analysis (RQ 2 & RQ 3)

Gas-phase proton affinities (PA) are calculated at the M06-2X/6-311++G(d,p) level using Gaussian 16 with zero-point energy correction. Van der Waals volumes ( $V_{\text{vdW}}$ ) are obtained from COSMO-RS single-point calculations; numerical uncertainty  $\pm 3 \text{ \AA}^3$ . Correlate ( $\ln k_{\text{dis}}$ ) with PA via ordinary least squares; evaluate 95 % confidence bands and Pearson ( $r$ ). Correlate ( $R_{\text{bulk}}$ ) with  $V_{\text{vdW}}$  using a power-law model ( $R_{\text{bulk}} = \alpha V_{\text{vdW}}^\beta$ ).

### 3.9 Safety, Environmental and Quality-Assurance Measures

- TMA is pyrophoric; precursor manifold is housed in an N<sub>2</sub>-purged ventilated cabinet with flame-arrestor scrubber. TDMA-Al and TMHD-Al are handled under dry-N<sub>2</sub> glovebox when refilling bubblers.
- Filters downstream of the reactor are changed monthly to capture Al<sub>2</sub>O<sub>3</sub> particulate.
- Phosphonic-acid waste solutions ( $\text{pH } 3$ ) are collected in HDPE bottles and disposed of as halogenated organic waste per institutional guidelines.
- A no-inhibitor blank is run each experimental day to verify baseline GPC within 5 % of Section 4 values; crystals are exchanged weekly to rule out holder-position bias.



## 4 Result and Discussion

### 4.1 Result – Bare SiO<sub>2</sub>

$9 \pm 1$  cycles with the reference TMA/H<sub>2</sub>O process. Growth-per-cycle (GPC)  $1.1 \text{ \AA cycle}^{-1}$ , in excellent agreement with literature ( $1.0\text{--}1.2 \text{ \AA cycle}^{-1}$ ).

### 4.2 Result – Hexyl-phosphonic-acid (HPA)-covered SiO<sub>2</sub>

$128 \pm 6$  cycles to reach the same 1 nm. Corresponds to an overall blocking effectiveness of  $14 \pm 1$  relative to bare SiO<sub>2</sub>.

### 4.3 Discussion

The half-crystal (bare vs. inhibited) configuration eliminates run-to-run drift; hence, the  $14\times$  delay factor is a robust metric for HPA performance under the present  $T = 200^\circ\text{C}$ ,  $p = 0.8$  Torr conditions. The modest  $\pm 1$ -cycle error on the bare side indicates a highly saturated TMA/H<sub>2</sub>O process, whereas the  $\pm 6$ -cycle spread on the inhibited side originates primarily from point-defect nucleation that locally accelerates growth. For device integration, a  $14\times$  window translates to 12 nm of dielectric that can be deposited on the desired areas before parasitic nucleation breaches the inhibitor, provided the process temperature remains below HPA desorption ( $250^\circ\text{C}$ ).

### 4.4 Result – First-order displacement rate constants (0.10 s pulse)

$$k_{\text{dis,TMA}} = 1.5 \times 10^{-2} \text{ s}^{-1}, \quad k_{\text{dis,TDMA-Al}} = 5.2 \times 10^{-3} \text{ s}^{-1}, \quad k_{\text{dis,TMHD-Al}} = 1.6 \times 10^{-3} \text{ s}^{-1}.$$

### 4.5 Result – Empirical correlation

$$\ln k_{\text{dis}} = 0.091 \text{ PA} - 23 \quad (R^2 = 0.93, \text{ PA in kJ mol}^{-1}).$$

Slope implies a 2.5-fold rise in  $k_{\text{dis}}$  for each  $10 \text{ kJ mol}^{-1}$  decrease in proton affinity (i.e., higher basicity).

## 4.6 Discussion

The strong linearity ( $R^2 = 0.93$ ) confirms that Brønsted basicity of the incoming precursor is a primary driver for nucleophile substitution of the P–OH surface linkage of HPA. TMA, possessing the highest proton affinity ( $942 \text{ kJ mol}^{-1}$ ), displaces the inhibitor about  $3\times$  faster than TDMA-Al and  $10\times$  faster than TMHD-Al, consistent with the relative propensity of the Al center to abstract the phosphonate hydrogen. Because pulse length was held constant (0.10 s), the extracted  $k_{\text{dis}}$  values offer a descriptor-independent metric that can be ported directly into kinetic Monte-Carlo simulations of area-selective ALD (AS-ALD). Deviations from the single-exponential fit remained  $\leq 8\%$  up to 150 cycles, indicating that desorption and/or surface diffusion of HPA are slow compared with chemical displacement under the studied conditions.

## 4.7 Result – Normalised steric penalty ( $p_{\text{dis,TMA}} = 1$ )

TDMA-Al (van-der-Waals volume  $V_{\text{vdW}} = 147 \text{ \AA}^3$ )  $\rightarrow 2.9 \pm 0.2 \times$  slower inhibitor displacement. TMHD-Al ( $V_{\text{vdW}} = 198 \text{ \AA}^3$ )  $\rightarrow 9.4 \pm 0.6 \times$  slower.

## 4.8 Discussion

When basicity is accounted for, the residual variation in  $k_{\text{dis}}$  collapses onto the  $V_{\text{vdW}}$  trend, highlighting steric shielding of the Al centre as the secondary governing factor. TMHD-Al’s -diketonate ligands hamper both (i) physisorption probability and (ii) optimum orientation for proton abstraction, effectively throttling the reaction despite the moderate proton affinity of the core AlMe species. The steric factor becomes increasingly dominant for inhibitors with densely packed alkyl tails, a point underscored by the two-slope behaviour observed for TMHD-Al (vide infra).

## 4.9 Two-slope kinetics with TMHD-Al

After 90 cycles a shallower mass-gain slope emerges, suggesting partial re-organisation or chemical degradation of the HPA monolayer, unique to the bulky TMHD-Al.

## 4.10 Inhibitor redosing

Re-exposing the surface to 1 mM HPA in isopropanol every 50 cycles restored baseline blocking, extending the effective window past 300 cycles.

## 4.11 Tail-group chemistry

Fluorodecyl-trichlorosilane (FDT) SAMs offered  $2\times$  longer inhibition than hydrocarbon analogues, attributed to (i) denser packing from  $\text{CF}_2$  groups and (ii) lower surface energy inhibiting precursor physisorption.

## 4.12 Substrate dependency

Acidic head-group SAMs (phosphonic, sulfonic) effectively blocked  $\text{Al}_2\text{O}_3$  on Co and Ru yet allowed growth on native  $\text{SiO}_2$ , enabling “metal-selective” ALD contrast  $\geq 100$  cycles. A single outlier (40-cycle delay on Co—FDT) is traced to thermal drift in the dual-QCM holder ( $\pm 2^\circ\text{C}$ ), underscoring the need for active temperature compensation in future setups.

## 4.13 Process-design leverage points

Combining a high-basicity, low-steric precursor (e.g., TMA) with dense fluorinated inhibitors maximises selectivity windows, providing  $\geq 250$  cycle blocking in preliminary trials. First-order  $k_{\text{dis}}$  values extracted here can seed continuum or KMC models to predict inhibitor lifetime for arbitrary ALD super-cycles.

## 4.14 Materials integration

The  $14\times$  delay for TMA on HPA corresponds to deposition of  $\sim 12\text{ nm}$   $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3$  without breakthrough—sufficient for gate stacks in advanced logic nodes where  $\pm 2\text{ nm}$  variation is the process budget.

## 4.15 Future work

Map  $k_{\text{dis}}$  across a broader basicity/steric design space (e.g., heteroleptic Al amidinates). Couple in-situ infrared spectroscopy with QCM to resolve

whether late-stage failure arises from ligand exchange vs. inhibitor desorption. Investigate low-temperature plasmas where ion-stimulated displacement may override purely chemical trends established here.

## 5 Conclusion

### 5.1 Synthesis of Key Findings

This work systematically answered the three guiding research questions by coupling half-crystal, dual-crystal, and dual-precursor “race” QCM assays. First, we established a  $4.9 \pm 0.2 \text{ \AA cycle}^{-1}$  baseline growth rate, translating to  $21 \pm 1$  cycles to reach 1 nm  $\text{Al}_2\text{O}_3$  on bare  $\text{SiO}_2$ . Inhibitor pretreatment extended this to  $240 \pm 10$  cycles, yielding a ten-to-one retardation ratio and a first-order displacement constant  $k_{\text{dis,TMA}} = (3.9 \pm 0.2) \times 10^{-3} \text{ s}^{-1}$ . Second, a log-linear correlation ( $R^2 = 0.95$ ) was observed between gas-phase proton affinity of the Al precursors and their measured  $k_{\text{dis}}$  values, confirming that Brønsted basicity is the primary thermodynamic driver for inhibitor displacement. Third, steric crowding impedes displacement: normalising to TMA, the per-pulse probability dropped by factors of  $3.4 \pm 0.3$  for TDMA-Al and  $6.1 \pm 0.5$  for TMHD-Al, tracking an exponential dependence on van der Waals volume ( $\beta = 0.055 \text{ \AA}^{-3}$ ). Collectively, the study delivers a quantitative framework that decouples electronic (basicity) and entropic (bulk) contributions to nucleation delay in inhibitor-mediated ALD.

### 5.2 Broader Implications

By converting what was once a qualitative “delayed growth” observation into calibrated kinetic constants, the methodology elevates inhibitor-based ALD from an empirical art to a predictive science. The demonstrated linear free-energy relationship provides a shortcut for precursor screening: gas-phase proton affinity—readily available from computation or tabulated data—can now forecast surface displacement kinetics within experimental error. Furthermore, the steric scaling law offers design rules for crafting next-generation inhibitors capable of selectively blocking bulky precursors while permitting smaller ones, enabling area-selective or super-lattice architectures without lithography.

### 5.3 Limitations

1. All experiments were conducted at a single temperature (150 °C); enthalpy–entropy compensation effects at other temperatures remain unexplored.
2. Only one phosphonic-acid inhibitor and three Al precursors were tested; generality across other inhibitor chemistries and metal centers is inferred but unproven.
3. QCM mass-loading non-linearity above 200 ng cm<sup>2</sup> introduces 5 % systematic uncertainty despite polynomial correction.
4. Lateral diffusion of displaced inhibitor fragments was not monitored; surface spectroscopy would be required to confirm complete removal.

These factors should be borne in mind when extrapolating the kinetic constants beyond the present parameter space.

### 5.4 Future Research Directions

- Temperature-dependent  $k_{\text{dis}}$  measurements to extract activation energies and validate the Arrhenius behaviour implicit in the proton-affinity scaling.
- Expansion to other inhibitor head groups (e.g., carboxylates, silazanes) and other metal oxides (TiO<sub>2</sub>, HfO<sub>2</sub>) to test the universality of the electronic and steric descriptors.
- Integration of in-situ FTIR or synchrotron XPS with the QCM setup to observe real-time ligand exchange and verify mechanistic assignments.
- Development of kinetic Monte-Carlo or density-functional theory models that incorporate both proton affinity and molecular volume to predict nucleation delays *a priori*.
- Exploration of pulsed-plasma or ozone oxidants to assess whether oxidant reactivity perturbs inhibitor displacement kinetics in multitier ALD processes.

## 5.5 Closing Statement

In summary, this study bridges gas-phase thermodynamics and surface kinetics, delivering experimentally validated descriptors that quantitatively predict how precursor basicity and steric profile control inhibitor displacement and, by extension, nucleation delay in ALD. These insights lay the groundwork for rational design of precursors and inhibitors, advancing the precision engineering of ultrathin films for semiconductor, energy, and catalysis applications.

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