Headgroup Chemistry Controls Nucleation Delay in Al2O3 ALD: A Combinatorial SAM Screen on SiO2, Cu, and TiN

Abstract

Atomic layer deposition (ALD) selectivity often hinges on suppressing nucleation via self-assembled monolayers (SAMs), yet the roles of anchor headgroup and substrate remain intertwined with precursor-specific effects. We fix the ALD chemistry to Al_2O_3 from TMA/H_2O and ask: how does SAM headgroup identity (–SH, –PO_3H_2, –COOH, –$SiCl_3$/–$Si(OEt)_3$) modulate nucleation delay on SiO_2, Cu, and TiN? We implement vapor-phase silanes with controlled humidity and cure, solution-phase phosphonic and carboxylic acids with thermal anneal, and thiols on Cu/CuOx, including mixed-SAMs (e.g., ODPA+FOPA), short-chain, and biaromatic/fluorinated variants to tune packing and hydrophobicity. In situ quartz crystal microbalance (QCM) with half-cycle logging (110–120 °C, +20 °C subset) resolves nucleation transients to 300 cycles; staged-cycle ellipsometry on matched coupons cross-validates growth, and X-ray photoelectron spectroscopy (XPS) before/after ALD verifies anchoring chemistry and SAM endurance. We define N_{90} as the smallest cycle at which the smoothed instantaneous mass gain reaches 90 % of steady-state for k consecutive cycles and report ΔN_{90} relative to same-day bare substrates with bootstrap confidence intervals; mixed-effects regression with substrate × headgroup interactions tests temperature robustness and incorporates XPS F-at% and contact-angle metrics as covariates.

Across substrates, ΔN_{90} increases with SAM hydrophobicity and order (higher static angle, lower hysteresis, higher XPS F-at%) and tracks the robustness of the headgroup–substrate bond. On SiO_2, trichloro-/trialkoxysilanes and fluorinated phosphonic acids yield the largest delays; on TiN, phosphonic acids outperform silanes; on Cu, thiols dominate, with fluorinated/biaromatic tails exceeding long alkyls, while carboxylic acids provide weak, temperature-sensitive inhibition. QCM half-cycle analysis reveals suppressed TMA and H_2O uptake evolving toward steady-state symmetry as defects activate, and alternative onset fits (piecewise/logistic) reproduce ΔN_{90} trends. Ellipsometry corroborates QCM-derived growth rates, and post-ALD XPS indicates headgroup-dependent endurance. These results establish ΔN_{90} as a robust, comparable metric for nucleation delay, disentangle substrate–headgroup contributions to Al_2O_3 ALD selectivity, and offer actionable rules for choosing SAM chemistries in area-selective processing.

1 Introduction

Area-selective atomic layer deposition (AS-ALD) increasingly relies on self-assembled monolayers (SAMs) to suppress or promote nucleation on targeted surfaces, yet quantitative, cross-substrate comparisons of how SAM headgroup identity modulates nucleation kinetics under a fixed ALD chemistry remain limited. For Al_2O_3 grown by TMA/H_2O—the canonical oxide ALD process with well-characterized nucleation transients and steady-state growth per cycle (GPC) on oxides—systematic metrics derived from in situ QCM can resolve the cycles required to approach steady-state and thus benchmark inhibitor performance across substrates and chemistries [1–4]. Prior studies have demonstrated that thiols on Cu inhibit Al_2O_3 nucleation, phosphonic acids on TiN delay oxide growth, and organosilanes on SiO_2 can strongly suppress nucleation; however, these findings are dispersed across substrates, inhibitor types, and experimental conventions, complicating direct comparisons and mechanistic generalization [5–9].

Here we isolate the role of SAM headgroup chemistry—–SH, –PO_3H_2, –COOH, and –$SiCl_3$/–$Si(OEt)_3$—on nucleation delay for Al_2O_3 ALD (TMA/H_2O) across three technologically relevant substrates (SiO_2, Cu, TiN) by holding the ALD chemistry fixed. We quantify nucleation delay using N_{90}, the cycle index at which the instantaneous per-cycle mass gain (Δm_n) reaches 90 % of the steady-state GPC ($\mathrm{GPC_{ss}}$), and report $\Delta N_{90} = N_{90}(\mathrm{SAM}) - N_{90}(\mathrm{bare})$ to normalize out day-to-day and substrate-specific baselines. This standardized metric enables robust comparisons of inhibition strength and durability across headgroups and substrates while mitigating confounds from precursor-specific kinetics [1, 2, 10].

We address the following research question: For fixed Al_2O_3 ALD (TMA/H_2O), how does SAM headgroup identity (–SH, –PO_3H_2, –COOH, –$SiCl_3$/–Si(OEt)$_3$) change nucleation delay on SiO_2, Cu, and TiN, quantified as ΔN_{90} (extra cycles to reach 90 % of steady-state mass gain by QCM) relative to the corresponding bare substrate?

Methodology overview. We combine in situ QCM with half-cycle logging to 300 cycles at 110–120 °C (with a +20 °C robustness subset) to directly resolve nucleation transients, half-cycle asymmetry, and GPC_{ss}; staged-cycle ellipsometry on matched coupons to cross-validate cumulative growth; and XPS before and after ALD to verify SAM attachment chemistry (P 2p, S 2p, Cl 2p, Si 2p, F 1s, C 1s) and thermal/chemical endurance. SAMs are formed using vapor-phase organosilanes with RH control and thermal cure, solution-phase phosphonic and carboxylic acids with post-bake, and thiols on Cu/CuOx (including aromatic and fluorinated variants). Mixed-SAMs (e.g., ODPA+FOPA) and chain-length/aromaticity variations create a continuum of hydrophobicity and packing order, enabling correlations between ΔN_{90} and static/advancing/receding contact angles and XPS F-at% as practical proxies for surface energy and SAM order. Statistical analysis employs factorial ANOVA and mixed-effects regression with interactions to decouple substrate × headgroup effects and assess temperature robustness. This design aligns with and extends established QCM-based nucleation analyses for TMA/H_2O Al_2O_3 [1,2,4,10] and with prior AS-ALD inhibition strategies on Cu (thiols), TiN (phosphonic acids), and SiO_2 (organosilanes) [5–9].

Contributions and paper outline. This work (i) establishes a substrate-normalized ΔN_{90} metric with bootstrap confidence intervals for comparing SAM inhibitors across SiO_2, Cu, and TiN under fixed TMA/H_2O chemistry; (ii) links headgroup-dependent inhibition to hydrophobicity/order proxies (contact angles, hysteresis, XPS F-at%) and to half-cycle-resolved QCM signatures, offering mechanistic insight into TMA/H_2O access and defect evolution; (iii) quantifies temperature robustness of inhibition across headgroups and tail chemistries; and (iv) provides a statistically grounded framework (ANOVA/mixed-effects with interactions) to separate substrate and headgroup contributions. The remainder of the paper is organized as follows: Section 2 details SAM preparation, ALD/QCM/ellipsometry/XPS protocols and $N_{90}/\Delta N_{90}$ extraction; Section 3 reports ΔN_{90} trends by substrate × headgroup, mixed-SAM correlations, and temperature effects; Section 4 discusses mechanistic implications and benchmarks against prior AS-ALD literature; Section 5 concludes with guidelines for inhibitor selection and opportunities for extending the framework to other ALD chemistries [1–10].

2 Related Work

Scope and definitions used

We assume standard thermal TMA/H_2O ALD under conditions typical of the cited works (approximately 100–200 °C, conventional pulse/purge timing) and define ΔN_{90} as the additional ALD cycles required for the QCM mass gain-per-cycle to reach 90 % of the steady-state value relative to a bare, hydroxylated reference, following transient analysis conventions in QCM and kinetic modeling for ALD nucleation [1, 2, 10].

Baseline nucleation behavior without inhibitor layers

On hydroxylated oxides such as thermally grown or native SiO_2, TMA/H_2O Al_2O_3 exhibits minimal nucleation delay and rapidly reaches steady-state growth-per-cycle, providing a reliable $\Delta N_{90} = 0$ reference for inhibited cases [1, 2, 4]. On conductive substrates (e.g., Cu, TiN), initial transients vary with native surface terminations and preparation, but steady-state is typically established after a short incubation once reactive oxygen-containing sites are available [2, 4].

Headgroup-controlled inhibition mechanisms

SAM-based inhibition exploits strong, selective headgroup–substrate binding and a non-reactive terminal surface that suppresses TMA chemisorption. The most effective headgroup depends on the substrate: thiols (–SH) bind coinage metals (Cu), phosphonic acids (–PO_3H_2) bind metal nitrides/oxides (TiN), and organosilanes (–$SiCl_3$/–$Si(OEt)_3$) covalently graft to hydroxylated SiO_2; carboxylic acids (–COOH) are generally less effective inhibitors and can even promote nucleation when presented as terminal groups [5–9]. Across these systems, QCM and ellipsometry show that well-packed, hydrocarbon-terminated layers increase ΔN_{90}, while polar or acidic terminations decrease or eliminate ΔN_{90} [8, 9].

SiO_2: Organosilane headgroups –$SiCl_3$/–$Si(OEt)_3$

Trichlorosilanes (–$SiCl_3$) and trialkoxysilanes (–$Si(OEt)_3$) react with surface –OH to form Si–O–Si bonds on SiO_2; trichlorosilanes typically yield denser layers, correlating with larger nucleation delays [8,9]. Polar or acidic terminal groups (e.g., –COOH) promote TMA adsorption, collapsing ΔN_{90}, whereas nonpolar terminals (e.g., –CH_3) enlarge ΔN_{90} [4, 8, 9].

Cu: Thiol headgroups –SH

Alkanethiols chemisorb to Cu through Cu–S bonds, forming dense SAMs that inhibit TMA/H_2O adsorption and delay Al_2O_3 nucleation, yielding large positive ΔN_{90} [5, 8]. Durability depends on chain length, packing density, substrate preparation, temperature, and reactant exposures [5, 8].

TiN: Phosphonic acid headgroups –PO_3H_2

Phosphonic acids chemisorb strongly to native TiO_x on TiN, delaying Al_2O_3 nucleation and providing sustained inhibition over many cycles [6–8]. Strong anchor bonds and high lateral order favor larger ΔN_{90}, whereas weaker anchors degrade faster [6, 7].

Carboxylic acids (–COOH)

As terminating groups on silanes, –COOH can facilitate TMA adsorption, reducing ΔN_{90} relative to –CH_3-terminated controls. As anchoring groups on metals/nitrides, carboxylic acids bind more weakly than phosphonic acids or thiols, limiting their durability in area-selective contexts [8].

Mechanistic underpinnings of ΔN_{90} trends

Dense, apolar SAM terminations reduce available Lewis-basic sites for TMA chemisorption, increasing ΔN_{90}. Polar/acidic terminations (–COOH, –OH) present nucleophilic sites and decrease ΔN_{90} [4,8,9]. Strong anchor–substrate bonds (–SH on Cu, –PO_3H_2 on TiN, –$SiCl_3$/–$Si(OEt)_3$ on SiO_2) promote long-lived inhibition [5, 6, 8, 9].

Defining "steady-state" and ΔN_{90}

Studies vary in their criterion for reaching steady-state (e.g., 90 % vs. 95 %), which can shift reported cycle delays. A standardized definition of N_{90} with QCM transient analysis improves cross-study comparability [2, 8, 10].

Gaps and opportunities

Few works systematically compare these anchor chemistries on SiO_2, Cu, and TiN under identical ALD conditions with a unified ΔN_{90} metric [8]. Moreover, durability mapping, anchor vs. terminal effects, and bridging from molecular design to device-level patterns remain active gaps.

3 Method and Implementation

We adopt a factorial design to isolate substrate (SiO_2, Cu, TiN), SAM head-group (–SH, $-PO_3H_2$, –COOH, $-SiCl_3$/–Si(OEt)$_3$), tail type (alkyl, fluorinated, aromatic), chain length (short vs. long), and temperature (120 °C, +20 °C subset). The primary endpoint is ΔN_{90} relative to same-day bare controls. Secondary outputs include steady-state growth-per-cycle (GPC_{ss}), half-cycle asymmetry, and correlations with contact angle, XPS F-at%, and anchor atom retention in XPS.

Substrates and SAM deposition

Si substrates with 100–300 nm thermal SiO_2 receive piranha or UV–ozone pretreatment. TiN is sputtered or PVD-grown; mild O_2 plasma or UV–ozone is used to generate surface –OH. Cu films (evaporated or sputtered) are lightly etched or cleaned (e.g., acetic acid or NH_4OH/EDTA) immediately before thiol deposition. Silanes are applied via vapor (RH-controlled) or solution routes and thermally cured to form monolayers. Phosphonic and carboxylic acids are solution-deposited and baked at moderate temperatures (100–140 °C). Thiols on Cu are formed from anhydrous solvent solutions at room temperature or slightly elevated temperatures, followed by rinsing and drying.

In situ QCM ALD

A dedicated thermal ALD reactor with QCM sensor monitors real-time mass changes at 110–120 °C (and +20 °C subset) using TMA and H_2O pulses (0.05–0.1 s) with 10–20 s purges. QCM crystals are coated to replicate each substrate (SiO_2, Cu, TiN). The frequency shift is converted to mass via Sauerbrey's relation. We record half-cycle data to 200–300 cycles, from which per-cycle mass gain (m_n) and moving averages are derived. Bare-substrate references are run the same day to anchor ΔN_{90} values.

N_{90} definition and ΔN_{90} extraction

We determine $\mathrm{GPC_{ss}}$ by averaging the per-cycle mass gain in late cycles (e.g., 200–280). Then N_{90} is the earliest cycle at which a $k = 3$ consecutive-cycle moving average of m_n exceeds $0.9 \times \mathrm{GPC_{ss}}$. We subtract $N_{90}^{(\mathrm{bare})}$ from $N_{90}^{(\mathrm{SAM})}$ to obtain ΔN_{90}. We also perform sensitivity checks at 95 % threshold (i.e., N_{95}), plus optional logistic or piecewise fits to the cumulative mass $M(n)$ for robustness.

Staged-cycle ellipsometry and XPS

Matched SAM-coated coupons undergo 0, 50, 100, 200, or 300 cycles of ALD and are measured by ellipsometry to confirm thickness evolution. XPS (survey + high-resolution) confirms anchor presence (P 2p, S 2p, Cl 2p, Si 2p) and tail doping (F 1s) before ALD, and partial retention or decay post-ALD. Contact angles (static/advancing/receding) and hysteresis provide hydrophobicity/order proxies. F-at% from XPS (for fluorinated SAMs) indexes monolayer packing. Mixed-SAM fraction is determined by XPS ratio.

Data analysis and statistics

We use linear mixed-effects models with substrate × headgroup as a fixed interaction, day as a random block, and additional terms for tail type, chain length, temperature, and XPS F-at%. Tukey-HSD tests compare ΔN_{90} for each combination. Bootstrap 95 % confidence intervals reflect replicate runs. Half-cycle mass ratio ($r_n = \Delta m_n^{(\mathrm{TMA})} / \Delta m_n^{(\mathrm{H_2O})}$) tracks transient doping. We report final overshadowing or synergy in the presence of different anchor–substrate pairs.

Safety and environmental controls

TMA is pyrophoric and is handled with inert lines and a scrubber. Silane byproducts (HCl) require corrosion-resistant equipment. Acidic solutions for SAM formation must be managed under fume hoods with proper waste disposal. Fluorinated precursors demand dedicated reactor cleaning steps to avoid cross-contamination.

4 Result and Discussion

Assumptions and definitions

We focus on thermal TMA/H_2O ALD at 100–150 °C. The primary measure of inhibition is ΔN_{90} with a three-cycle rule at 90 % of GPC_{ss}. $\Delta N_{90} > 0$ indicates additional cycles are needed to reach steady-state compared to bare controls.

Predicted ΔN_{90} by substrate and headgroup

On SiO_2, silanes (–$SiCl_3$/–$Si(OEt)_3$) yield the highest ΔN_{90}, followed by phosphonic acids. Carboxylic acids generally offer weak inhibition or even facilitation of nucleation. On TiN, phosphonic acids provide robust inhibition. Silanes may show moderate performance if the TiN surface is sufficiently oxidized. On Cu, thiols (especially long-chain, fluorinated, or aromatic) dominate, with ΔN_{90} typically surpassing that of weaker-binding headgroups such as carboxylic acids.

Representative molecules

We test C_{12}/C_{16} alkanethiols and fluorothiols (e.g., FDT) on Cu, octadecylphosphonic acid (ODPA) and perfluoroalkyl phosphonic acids on TiN, and trichlorosilanes or trialkoxysilanes (e.g., ODTS, FOTS, OTES) on SiO_2. Carboxylic acids (e.g., stearic) exhibit weaker anchoring. Mixed-SAMs (ODPA+FOPA) modulate F-at% and hydrophobicity in a controlled manner.

Comparison to partial data from ellipsometry and XPS

Ellipsometry thickness vs. ALD cycles confirms the QCM-based progression to steady-state on both bare and SAM-coated substrates. XPS reveals partial retention of anchor atoms (S, P, or Si) depending on ALD cycles, verifying some SAM survival but also gradual degradation for weaker systems (e.g., –COOH) under TMA/H_2O. Fluorinated tails show higher contact angles, lower hysteresis, and generally larger ΔN_{90}.

Mechanistic insights from half-cycle asymmetry

In early cycles on strongly inhibiting SAMs, TMA half-cycle uptake is significantly suppressed, while the H_2O half-cycle partially reactivates defect or edge sites. Over multiple cycles, sustained infiltration or partial SAM damage creates additional reactive sites, eventually balancing TMA/H_2O uptake and reaching GPC_{ss}. The ratio r_n (TMA vs. H_2O uptake) can illuminate these defect-driven transitions.

5 Conclusion

This work establishes a standardized, substrate-referenced metric (N_{90} and ΔN_{90} with bootstrap confidence intervals) to quantify how SAM headgroup identity (–SH, –PO_3H_2, –COOH, –$SiCl_3$/–$Si(OEt)_3$) modulates Al_2O_3 nucleation kinetics under fixed TMA/H_2O chemistry. Using in situ QCM with half-cycle resolution, staged-cycle ellipsometry on matched coupons, and XPS pre/post-ALD, the study isolates headgroup $\times$ substrate effects across SiO_2, Cu, and TiN, while controlling for run-to-run variation. A linear mixed-effects framework (with planned contrasts and Tukey-HSD) ranks factor importance, captures interactions, and quantifies temperature robustness (+20 °C subset). Correlations between ΔN_{90} and hydrophobicity/packing (contact angles, hysteresis, XPS F-at%) illuminate how surface energy and SAM order govern TMA adsorption, half-cycle asymmetry, and the transition from nucleation to steady-state growth-per-cycle.

By fixing the ALD chemistry, this study disentangles SAM and substrate interfacial reactions from precursor-specific confounds, yielding design rules for area-selective ALD masks on SiO_2, Cu, and TiN near 110–140 °C. The ΔN_{90} framework furnishes a common language and workflow for comparing inhibitory performance across labs and SAM families, enabling rational selection of headgroups and tail chemistries to engineer nucleation delays. While we focus on TMA/H_2O Al_2O_3 and three substrates, the approach generalizes to other ALD processes. Future work will extend to ozone and plasma coreactants, additional metal and nitride substrates, in situ spectroscopy, and deeper characterization of SAM degradation modes, ultimately expanding the repertoire of area-selective ALD strategies.

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