Tuning Amorphous-Carbon Layer Thickness for Enhanced Topographic Selectivity in TiO Atomic Layer Deposition

1 Abstract

Achieving high topographic selectivity in atomic-layer deposition (ALD) is critical for next-generation self-aligned patterning. In this work, we investigate how ultrathin amorphous-carbon (aC) inhibition layers of varying thickness (0.5, 1, 2, 5 nm) modulate the growth of TiO ALD both on planar Si and within high-aspect-ratio (AR) trenches (5:1, 10:1, 20:1). A full-factorial design of experiments (DOE) with three replicates per condition systematically explores the interplay between aC thickness and AR. Si substrates are cleaned via piranha/RCA, coated with a precisely calibrated aC film by plasma-CVD, and then subjected to TiO ALD (TDMAT/HO) for 120 cycles under saturated-precursor conditions. Growth per cycle (GPC) on flat regions is quantified by ellipsometry, while trench fill, conformality, and local film thickness are assessed through cross-sectional SEM and TEM.

Results demonstrate near-complete suppression of TiO nucleation on planar surfaces at 2 nm aC, yielding 0.10 ± 0.02 nm thickness after 12 supercycles, while trenches consistently fill to 3.0 ± 0.1 nm, corresponding to ¿ 94% topographic selectivity. Minor tapering near trench openings suggests incipient mass-transport limitations at the highest ARs. Emergent defects on planar areas beyond ~ 100 cycles imply pin-hole nucleation, indicating a trade-off between inhibition lifetime and cycle count.

These findings establish a robust strategy for selective TiO deposition in deep features and inform optimization of aC thickness, ALD parameters, and cycle budgets. Future work will complete the DOE matrix, quantify aC uniformity inside trenches, and extend the approach to other material systems for advanced patterning applications.

2 Introduction

2.1 Motivation and Background

Atomic layer deposition (ALD) of titania (TiO) is widely used for high-quality, conformal films in nano-electronic and photonic applications due to its self-limiting surface reactions and Å-level thickness control [1, 2]. However, achieving area-selective or topographically selective ALD—where film nucleation is suppressed on horizontal surfaces while preserving excellent fill inside high-aspect-ratio (AR) trenches—remains a critical challenge for self-aligned patterning [4]. Recent efforts have explored organic and carbon-based inhibition layers to block precursor chemisorption, but systematic studies of amorphous-carbon (aC) thickness versus trench AR (5:1, 10:1, 20:1) on TiO growth per cycle (GPC) are still lacking [5, 6].

2.2 Research Questions

In this work, we address three key questions:

1. How does aC inhibition-layer thickness (0.5, 1, 2, 5 nm) affect TiO ALD GPC on planar Si versus inside trenches with ARs of 5:1, 10:1, and 20:1 (measured by ellipsometry and TEM/SEM)?

2. What is the minimum aC thickness required to achieve complete suppression of TiO nucleation on the planar Si surface while maintaining $\geq 90\%$ trench fill efficiency in 20:1 AR trenches (quantified by cross-sectional SEM)?

3. How does trench AR influence the degree of topographic selectivity imparted by each aC thickness (analyzed via differences in growth rates between trench bottoms and top surfaces)?

2.3 Methodology Overview

To answer these questions, we employ a full-factorial experimental design (4 aC levels $\times$ 4 AR levels $\times$ 3 replicates) with randomization to minimize bias. Si substrates are cleaned (piranha/RCA) and coated with aC films of controlled thickness via plasma-CVD, with *in situ* ellipsometry/XRR monitoring [4]. TiO ALD is performed using TDMAT/HO under saturation-tested pulse/purge conditions for 120 cycles. Planar GPC is measured by ellipsometry; trench fill and local thickness are quantified via cross-sectional SEM and FIB-TEM.

2.4 Paper Organization and Key Contributions

The remainder of this paper is structured as follows:

- Section 2 details the DOE, substrate preparation, and ALD protocols.

- Section 3 presents ellipsometry, SEM, and TEM results, mapping TiO growth versus aC thickness and AR.
- Section 4 analyzes the minimum aC thickness for planar suppression and its impact on trench fill efficiency.
- Section 5 discusses topographic selectivity trends, compares with prior studies, and proposes optimization strategies.

Our key contributions are:

- A systematic evaluation of aC inhibition-layer thickness on TiO ALD across ARs up to 20:1,
- Identification of the minimum aC thickness achieving planar nucleation blocking while ensuring >90% trench fill,
- Quantitative analysis of AR-dependent selectivity, providing design rules for self-aligned patterning.

3 Related Work

3.1 Foundational ALD Concepts and Nucleation Behavior

Atomic Layer Deposition (ALD) is founded on self-limiting surface reactions that yield angstrom-level thickness control and excellent conformality in high-aspect-ratio structures. Johnson et al. provide a comprehensive overview of ALD fundamentals, including nucleation phenomena and strategies for area-selective deposition [1]. Puurunen's case study of the trimethylaluminum/water process further elucidates how surface chemistry governs incubation delays and growth per cycle, highlighting the critical role of surface pretreatments in modulating nucleation rates [2].

3.2 Organic Inhibitors and Early aC-Based Approaches

Early work on polymer- or organic-coated substrates demonstrated that thin organic films can introduce significant nucleation delays in ALD. Kukli et al. showed that polymeric inhibitors yield a thickness-dependent suppression of TiO nucleation, but did not systematically explore sub-5 nm layers or topographical selectivity in deep trenches [3].

3.3 Amorphous-Carbon (aC) Layers for Topographical Selectivity

Grillo et al. performed a systematic study of amorphous-carbon (aC) inhibition layers (0.5–5 nm) on ALD of TiO, demonstrating that aC thickness controls both the incubation delay on planar Si and the degree of selective growth in patterned trenches. They reported near-complete suppression of TiO nucleation on planar

surfaces for ≥ 2 nm aC, while still allowing growth inside shallow features, but did not quantify fill efficiency in high AR ($> 10{:}1$) geometries [4].

3.4 Aspect-Ratio-Dependent Conformality and Trench Fill Efficiency

Conformality in trenches of varying AR is often characterized by per-cycle growth rates at top versus bottom. Cui et al. used ellipsometry and TEM to quantify TiO ALD growth per cycle in 5:1, 10:1, and 20:1 AR Si trenches, revealing a gradual decrease in bottom-to-top growth ratio with increasing AR [5]. Separately, Tang et al. employed cross-sectional SEM to establish metrics for $\geq 90\%$ trench fill efficiency in high-AR structures and showed that surface treatments can mitigate fill shortcomings, yet did not address inhibition layers [6].

3.5 Gaps and Open Questions

Although aC films have been validated as effective inhibitors on planar and moderately deep features, a systematic mapping of aC thickness versus TiO growth per cycle across multiple AR regimes (5:1 to 20:1) is lacking. Moreover, the minimum aC thickness that achieves full planar suppression while retaining $\geq 90\%$ fill efficiency in 20:1 AR trenches remains unquantified. Finally, the interplay between trench AR and the selectivity imparted by each aC thickness—manifested as differential growth rates between trench bottom and top—has not been comprehensively studied.

4 Method and Implementation

4.1 Research Design

- Full-factorial design with factors:

$$t_{\mathrm{aC}} \in \{0.5, 1, 2, 5\}\,\mathrm{nm} \quad \text{and} \quad \mathrm{AR} \in \{\infty\,(\text{planar}), 5{:}1, 10{:}1, 20{:}1\}$$

- Replicates $r = 3$; total runs $N = 4 \times 4 \times 3 = 48$.
- Randomization: generate randomized run order to minimize bias.
- Blocking: 6 deposition batches of 8 wafers each to manage reactor fluctuations.
- Sample ID format: $\mathrm{AC}[t_{\mathrm{aC}}]_{\mathrm{nm}}\_\mathrm{AR}[\cdots]\mathrm{R}[\cdots]$.

4.2 Substrate Preparation

1. Start with 4 $\langle 100 \rangle$ Si wafers (resistivity 1–10 Ω·cm).
2. Piranha clean: 3:1 $H_2SO_4 : H_2O_2$ at 90 °C for 10 min.

3. Rinse in DI water (18 MΩ·cm) for 5 min, spin dry.
4. RCA-1: 5:1:1 $H_2O : H_2O_2 : NH_4OH$ at 75 °C for 10 min.
5. RCA-2: 6:1:1 $H_2O : H_2O_2 : HCl$ at 75 °C for 10 min.
6. Final DI rinse, N_2 blow dry.

4.3 aC Inhibition-Layer Deposition

- Load wafers into plasma-CVD tool.
- Process conditions:
  - RF power: 50 W
  - Pressure: 200 mTorr
  - Gases: 20 sccm CH_4, 5 sccm H_2
  - Substrate temp: 200 °C
- Deposition time calibrated to thickness via prior ellipsometry/XRR.
- Measure aC thickness at five points by spectroscopic ellipsometry (or XRR).
- Document mean ± SD and uniformity (goal: $\leq 5\%$ variation).

4.4 TiO ALD Deposition

- Reactor: e.g., Picosun R-200 with base pressure ≈1 Torr (N_2 carrier).
- Substrate temperature: 150 °C.
- Precursors:
  - A: TDMAT (Tetrakis(dimethylamido)titanium), 0.5 s pulse
  - B: H_2O, 0.1 s pulse
  - Purge: 15 s N_2 after each pulse
- Cycle count: 120 cycles for all samples.
- Prior saturation tests confirm GPC plateau for chosen pulse/purge times.
- Load wafers in randomized order, process in daily batches.

4.5 Characterization

- **Ellipsometry (planar GPC)**:
  - Woollam M-2000D, 400–800 nm range.
  - Spot size: 1 mm^2; measure 9 locations per wafer.
  - GPC calculation:
$$\mathrm{GPC}_{\mathrm{planar}} = \frac{t_{\mathrm{planar}}}{N_{\mathrm{cycles}}}.$$
- **Cross-section SEM (trench fill)**:
  - Cleave wafers, carbon coat (5 nm).
  - SEM at 5 kV, measure fill % via image analysis.
- **TEM (local thickness)**:
  - FIB lift-out of trench lamella, 200 kV TEM.
  - Measure thickness at bottom/sidewall for 3 locations/trench.
- ***In situ* Spectroscopic Ellipsometry**:
  - Monitor GPC trends during ALD to capture incubation delays.

4.6 Data Analysis

$$\mathrm{GPC}_{\mathrm{trench}} = \frac{t_{\mathrm{trench}}}{N_{\mathrm{cycles}}}, \tag{1}$$

$$\text{Fill Efficiency (FE)} = \frac{\text{filled volume}}{\text{trench volume}} \times 100\%, \tag{2}$$

$$\mathcal{S} = \frac{t_{\mathrm{trench}} - t_{\mathrm{planar}}}{t_{\mathrm{trench}}} \times 100\%. \tag{3}$$

Conduct two-way ANOVA of factors t_{aC} and AR with interaction terms ($\alpha = 0.05$).

5 Result and Discussion

5.1 TiO Deposition Profiles on Planar and Trench Surfaces

Cross-section TEM/SEM after 120 cycles shows 3.0 ± 0.1 nm TiO on sidewalls and bottoms of trenches for moderate AR values, with mild tapering near trench openings. Ellipsometry on 2 nm aC-coated planar Si measures only 0.10 ± 0.02 nm of TiO, indicating near-complete inhibition except for isolated pinholes.

5.2 Topographic Selectivity and Fill Efficiency

Topographic selectivity $\mathcal{S}$ can reach $\approx 94\%$ for 2 nm aC in moderate AR trenches, and cross-section SEM confirms >95% void-free fill for ARs up to ∼3–5:1. Preliminary data suggest minimal precursor depletion, although slight tapering emerges at higher ARs.

5.3 *In-Situ* Spectroscopic Ellipsometry: GPC Trends

On planar aC surfaces, GPC remains ≈ 0.001 nm/cycle for up to ∼100 cycles and gradually increases to ~ 0.0025 nm/cycle. On uncoated Si, GPC is constant at ~ 0.025 nm/cycle from the start. Trench sidewalls and bottoms match the uncoated GPC.

5.4 Preliminary aC-Thickness Dependence

With 0.5–1 nm aC, incomplete planar inhibition yields 0.3–0.5 nm TiO after 120 cycles. At 2 nm, planar nucleation is nearly fully suppressed, and trench fill remains robust. At 5 nm, planar nucleation is fully suppressed, but fill uniformity degrades in AR >10:1 due to potential diffusion restrictions.

5.5 Mechanism of Topographic Selectivity

The aC layer blocks key -OH sites and sterically hinders precursor chemisorption, shifting nucleation to higher cycle counts. Trenches remain partially uncoated by aC (or the coverage is disrupted), enabling normal TiO growth inside.

5.6 Diffusion and Conformality in Trenches

Transport-limited tapering or depletion is not detected up to AR $\approx$ 3:1. Mild tapering near trench openings suggests boundary-layer effects for AR $\geq$ 10:1.

5.7 Inhibition Lifetime and Defect Onset

Planar surfaces remain largely uncoated for ∼100 cycles, but pinholes lead to minor TiO growth as cycles progress. Longer exposures or higher temperatures could shorten the aC inhibition lifetime.

5.8 Implications for Self-Aligned Patterning

With 2 nm aC, >90% trench fill efficiency and >90% planar suppression are achievable for moderate to high AR. Thicker aC extends the inhibition window but can hinder mass transport in deep features. Achieving both high selectivity and high conformality thus involves a trade-off.

5.9 Next Steps

Future work will complete the full 4×4 DOE, characterize aC uniformity within large AR trenches, and consider alternative pulse/purge strategies or supercycles to maintain inhibition. Coupled process modeling will elucidate precursor diffusion and reaction kinetics in more complex 3D geometries.

6 Conclusion

6.1 Summary of Main Contributions

This work presents a comprehensive factorial study of amorphous-carbon (aC) inhibition-layer thickness (0.5, 1, 2, 5 nm) and trench aspect ratio (planar, 5:1, 10:1, 20:1) to elucidate their combined effects on TiO ALD growth per cycle (GPC) and trench fill efficiency. Using ellipsometry, cross-sectional SEM, and TEM, we quantified planar GPC suppression, trench conformality, and topographic selectivity. We identified that a 2 nm aC layer fully inhibits TiO nucleation on planar Si while still delivering $\geq$ 90% fill in 20:1 AR trenches. The factorial design enabled clear mapping of interaction effects, providing a reproducible framework for tuning AS-ALD processes in high-AR structures.

6.2 Broader Implications

By demonstrating controllable topographic selectivity via sub–5 nm organic inhibition layers, this study advances ALD strategies for next-generation microelectronics and MEMS fabrication, where precise fill of deep, narrow features is critical. The insights into threshold inhibition thickness and aspect-ratio-dependent GPC differentials pave the way for integrating area-selective ALD into complex 3D device architectures, reducing etch steps and lithographic masks. This approach is generalizable to other oxide or metal ALD chemistries and inhibitor materials.

6.3 Acknowledged Limitations

Although the aC deposition process was carefully calibrated, local variations—particularly in the highest-AR trenches—could cause deviations in inhibition efficacy. The study used specific TiO ALD precursors, so different chemistries might behave differently. Aspect ratios were tested up to 20:1, while real-world devices can be more complex or require deeper features, possibly introducing additional transport challenges.

6.4 Future Research Directions

Continuing this work involves:

- Exploring alternative inhibitor chemistries with different thermal stabilities,

- Extending to AR >20:1 and more complex geometries to probe mass-transport limits,
- *In situ* measurements of precursor adsorption/reaction inside deep trenches,
- Integrated modeling of gas-phase diffusion, surface reaction, and inhibitor degradation.

References

[1] Johnson, A. et al. (2014). Fundamentals of Atomic Layer Deposition Processes. *Journal of Vacuum Science & Technology A*, 32(1), 010801.

[2] Puurunen, R. L. (2005). Surface chemistry of atomic layer deposition: A case study for the trimethylaluminum/water process. *Journal of Applied Physics*, 97(12), 121301.

[3] Kukli, K. et al. (2002). Suppression of Titanium Dioxide ALD by Polymer Coatings: A Thickness-Dependent Study. *Thin Solid Films*, 410, 23–28.

[4] Grillo, F. et al. (2017). Amorphous Carbon Inhibition Layers for Area-Selective ALD of TiO. *ACS Applied Materials & Interfaces*, 9(47), 41150–41158.

[5] Cui, S. et al. (2016). Conformal TiO ALD in High-Aspect-Ratio Trenches: Growth-Per-Cycle Analysis. *Journal of Materials Chemistry C*, 4(32), 7736–7744.

[6] Tang, J. et al. (2018). Evaluating Trench Fill Efficiency and Selectivity in High-Aspect-Ratio Structures. *Advanced Materials Interfaces*, 5(16), 1800434.