

Area Selective Deposition

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Primary CNF Tools Used: Woollam RC2 Spectroscopic Ellipsometer, VCA Contact Angle, Oxford FlexAL

Abstract:

In this work, we describe our results aimed at developing the fundamental framework behind the use of small molecules to achieve area selective deposition (ASD), examining the atomic layer deposition (ALD) of Al_2O_3 on SiO_2 . We have examined 2 precursors, and 2 blocking molecules. For ASD, we have determined that the size of the precursor and blocking molecule strongly influence blocking efficacy, with bulkier precursors and long-chain self-assembled monolayers (SAM's) leading to increased blocking on SiO_2 .

Summary of Research:

We are developing the fundamental framework behind the use of small molecules to achieve ASD, examining the deposition of Al_2O_3 on SiO_2 . The overall approach is to examine explicitly the effects of the choice of the precursor and blocking molecules on blocking Al_2O_3 thin film growth on SiO_2 .

We have employed a quartz crystal microbalance (QCM) to monitor thin film deposition in situ and in real-time.^{1,2}

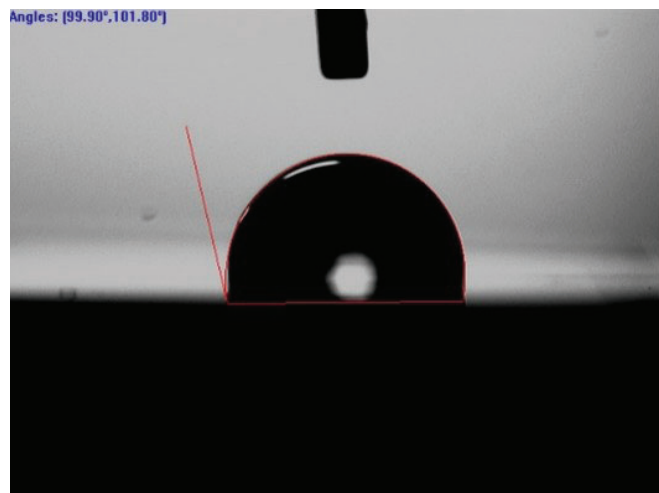


Figure 1: Water contact angle of DMATMS-passivated SiO_2 is $\sim 95^\circ$, which is significantly higher than Bare SiO_2 which is $\sim 15^\circ$.

In CNF, we coated Au QCM crystals with 20 nm of SiO_2 to get a starting surface of SiO_2 for ASD experiments. We exposed the SiO_2 surface to the blocking molecule: (N,N-dimethylamino)trimethylsilane (DMATMS) in vapor phase and octadecyltrichlorosilane (ODTS) in solution phase. Water contact angles were used to assess changes in surface chemistry. The SiO_2 surface becomes hydrophobic upon formation of the blocking molecule, and these changes are shown in Figures 1 and 2. Once the blocking molecule was formed, we performed ALD in our laboratory using 2 different precursors: trimethylaluminum (TMA) and bisdimethylamino-diamino-Aluminum (BDMADA-Al). A key difference between these precursors is that BDMADA-Al is larger and bulkier due to its more complex ligands compared to TMA. In Figure 3 we show QCM data for 40 cycles using BDMADA-Al as the precursor and H_2O as the co-reactant at $T = 120^\circ\text{C}$ on ODTS- and DMATMS- SiO_2 QCM crystals. From the QCM results, the longer-chain ODTS blocking molecule resulted in prolonged attenuation of growth on SiO_2 . In Figure 4 we show a similar set of experiments but using TMA as the precursor. From these results, we again see longer attenuation of growth on ODTS compared to DMATMS, although the growth is larger than what was observed using BDMADA-Al as the precursor under

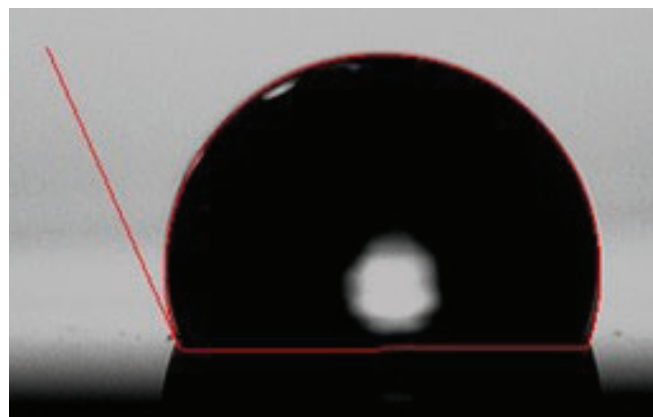


Figure 2: Water contact angle of ODTS-passivated SiO_2 is $\sim 110^\circ$, which is significantly higher than Bare SiO_2 which is $\sim 15^\circ$.

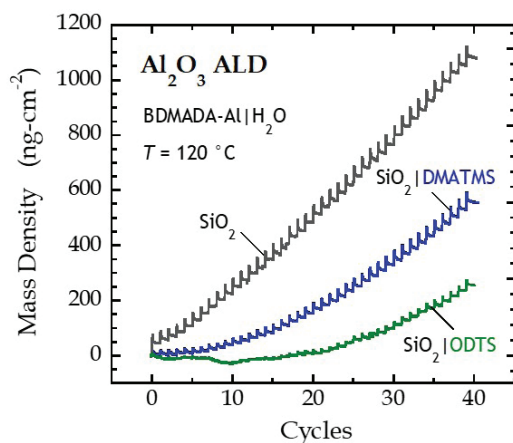


Figure 3: QCM data showing mass densities vs number of cycles for Al_2O_3 using BDMADA- $\text{Al}/\text{H}_2\text{O}$ process chemistry at $T = 120^\circ\text{C}$ on SiO_2 crystals passivated with either DMATMS or ODTS.

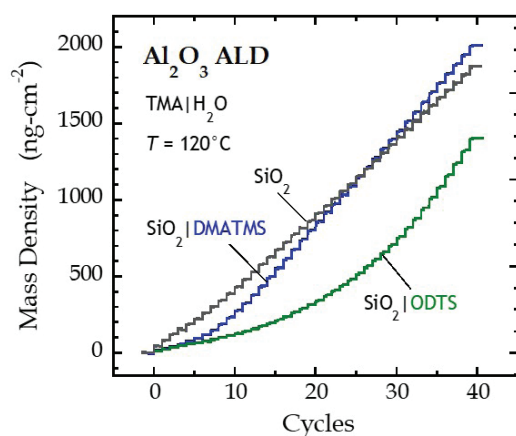


Figure 4: QCM data showing mass densities vs number of cycles for Al_2O_3 using TMA- $\text{Al}/\text{H}_2\text{O}$ process chemistry at $T = 120^\circ\text{C}$ on SiO_2 crystals passivated with either DMATMS or ODTS.

similar reaction conditions.

Conclusions and Future Steps:

We have shown that steric hindrance between the precursor and the blocking molecule plays an important role in blocking ALD growth on non-growth surfaces. Our future steps involve studying alternative precursors and blocking molecules to achieve ASD for a variety of thin films and surfaces.

References:

- [1] Swarup, J. V.; Chuang, H.-R.; You, A. L.; Engstrom, J. R. Effect of Co-Reactants on Interfacial Oxidation in Atomic Layer Deposition of Oxides on Metal Surfaces. *ACS Appl Mater Interfaces* 2024, 16 (13), 16983–16995. <https://doi.org/10.1021/acsami.3c19033>.
- [2] Swarup, J. V.; Chuang, H.-R.; Jensen, J. T.; Gao, J.; You, A. L.; Engstrom, J. R. Nonpyrophoric Alternative to Trimethylaluminum for the Atomic Layer Deposition of Al_2O_3 . *Journal of Vacuum Science & Technology A* 2025, 43 (2), 022404. <https://doi.org/10.1116/6.0004171>.