

Area Selective Deposition

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Principal Investigator(s): James R. Engstrom

User(s): James T. Jensen

Affiliation: Chemical Engineering, Cornell University

Primary Source(s) of Research Funding: Department of Energy

Contact: jre7@cornell.edu, jtj33@cornell.edu

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

Abstract:

In this work, we aim to further develop the fundamental framework behind area selective deposition (ASD), extending results for blocking Al_2O_3 atomic layer deposition (ALD) on SiO_2 to a new system blocking SiO_2 deposition on Al_2O_3 . We compare results for two Al precursors and two blocking molecules selective to SiO_2 with results for a new Si precursor and a blocking molecule selective to Al_2O_3 .

Summary of Research:

We are extending our previous efforts in ASD by investigating a new Si precursor and a blocking molecule selective to Al_2O_3 . Our earlier work involved depositing Al_2O_3 on metal surfaces while blocking growth on SiO_2 , and we have now moved to depositing SiO_2 on metal surfaces while blocking growth on Al_2O_3 .

We operate a custom-built deposition reactor employing a quartz crystal microbalance (QCM) as a deposition monitor in situ and in real time [1–3]. For the Al_2O_3 deposition results, we prepared 20 nm of SiO_2 on Au QCM crystals in the CNF to create a starting surface for blocking molecules to selectively cover. The two blocking molecules in use in the blocked Al_2O_3 deposition system were (N,N-dimethylamino)trimethylsilane (DMATMS) in the vapor phase and octadecyltrichlorosilane (ODTS) in a liquid solution phase. We confirmed the changes in surface chemistry by taking water contact angle images of SiO_2 surfaces before and after formation of these blocking layers. After forming the layers, we conducted ALD cycles to compare with untreated SiO_2 . For Al_2O_3 deposition, we employed trimethylaluminum (TMA) and bisdimethylamino-diamino-Aluminum (BDMADA-Al) as thin film precursors and H_2O as the co-reactant. Most deposition studies were completed at $T = 120^\circ\text{C}$, with one at $T = 285^\circ\text{C}$. Figure 1 shows QCM data collected during deposition of the Al_2O_3 films from TMA on both unblocked and blocked SiO_2 , while Figure 2 shows similar experiments with the sterically bulkier BDMADA-Al as the thin film precursor. We

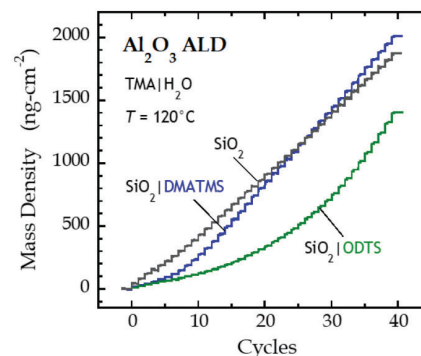


Figure 1: QCM data showing mass densities vs number of cycles for Al_2O_3 using TMA-Al/ H_2O process chemistry at $T = 120^\circ\text{C}$ on SiO_2 crystals passivated with either DMATMS or ODTS.

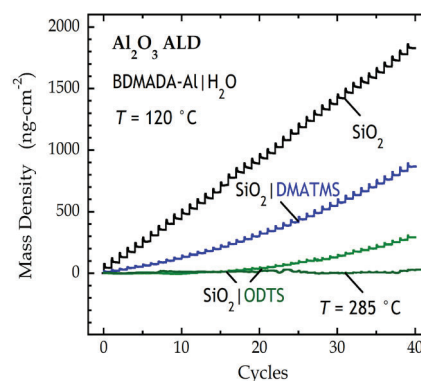


Figure 2: QCM data showing mass densities vs number of cycles for Al_2O_3 using BDMADA-Al/ H_2O process chemistry at $T = 120^\circ\text{C}$ on SiO_2 crystals passivated with either DMATMS or ODTS. One experiment on ODTS was conducted at $T = 285^\circ\text{C}$.

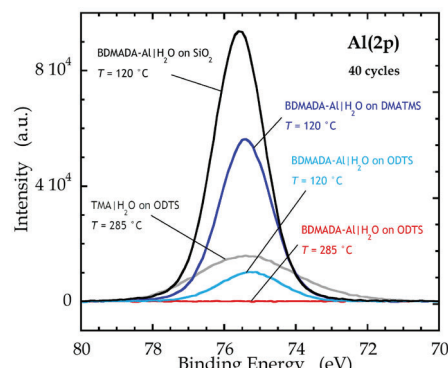


Figure 3: X-ray photoelectron detailed spectra of the Al(2p) region on SiO_2 coupons for a variety of ALD process chemistries and blocking molecules.

have also included data for one experiment at $T = 285^\circ\text{C}$ for BDAMDA-Al deposition on ODTs in Figure 2. We show for both precursors that ODTs blocks deposition more effectively than DMATMS due to enhanced steric hindrance between the larger blocking molecule and the precursor. Similarly, we show that BDMADA-Al provides a deposition system which is easier to block than TMA for Al_2O_3 deposition. We show X-ray photoelectron spectra of the Al(2p) region of samples after different ASD strategies for Al_2O_3 in Figure 3, showing agreement with the QCM traces. Notably, there is no deposition detected with BDMADA-Al on ODTs at $T = 285^\circ\text{C}$.

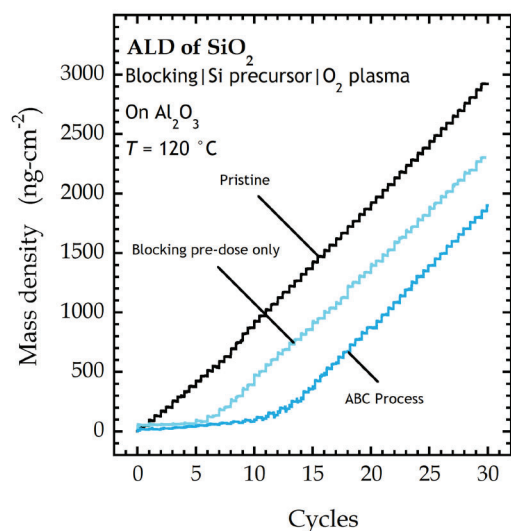


Figure 4: QCM data showing mass densities vs number of cycles for SiO_2 using a new Si precursor and O_2 plasma process chemistry at $T = 120^\circ\text{C}$ on Al_2O_3 crystals passivated with an Al_2O_3 blocking molecule. The ABC process involves a re-dose of the Al_2O_3 blocking molecule for every cycle.

For the SiO_2 deposition system, we started with a CNF-prepared 20 nm thick Al_2O_3 surface and a selective blocking molecule referred to here as the Al_2O_3 blocking molecule. We used a new Si precursor containing only Si-N and Si-H bonds, with no Si-C or Si-Si bonds. The co-reactant was O_2 plasma. Figure 4 shows initial results for SiO_2 deposition blocked on an Al_2O_3 surface. The Al_2O_3 blocking molecule is removed or the layer is damaged by the fifth cycle, after which deposition begins. To extend blocking performance, we show an ABC dosing sequence including a re-dose of the Al_2O_3 blocking molecule after each O_2 plasma dose. As can be seen, blocking is extended to ten cycles. The plasma-activated SiO_2 deposition process exhibits a different type of blocking breakdown than is seen with the thermally activated Al_2O_3 deposition process due to the more aggressive and high-energy nature of plasma processes.

Conclusions and Future Steps:

We show here that steric hindrance serves as a good predictor for blocking performance on non-growth surfaces in ASD systems, considering both Al_2O_3 deposition blocked on SiO_2 surfaces and SiO_2 deposition blocked on Al_2O_3 surfaces. We have exhibited initial results with a new Si precursor, showing blocked growth of the first ten cycles of ALD even in a plasma process. Future work involves tuning reactor conditions, examining new blocking molecules for use with the same Si precursor and O_2 plasma system, and further *ex situ* characterization of the resulting films on both growth and non-growth surfaces.

References:

- [1] J. V. Swarup, H.-R. Chuang, J. T. Jensen, J. Gao, A. L. You, and J. R. Engstrom, "Nonpyrophoric alternative to trimethylaluminum for the atomic layer deposition of Al_2O_3 ," *J. Vac. Sci. Technol. A*, 43(2), 022404 (2025), doi: 10.1116/6.0004171.
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