Atomic Layer Deposition on Surfaces Modified with Thin Interfacial Organic Layers

Scott Isaacson

Chemical Engineering, University of Minnesota

NNIN REU Site: Cornell NanoScale Science and Technology Facility, Cornell University, Ithaca, NY

NNIN REU Principal Investigator(s): James R. Engstrom, Chemical and Biomolecular Engr., Cornell University

NNIN REU Mentor(s): Kevin J. Hughes, Chemical and Biomolecular Engineering, Cornell University

Contact: isaac145@umn.edu, jre7@cornell.edu, kjh47@cornell.edu

Abstract:

Atomic layer deposition (ALD) of aluminum oxide (Al_2O_3) has been performed on bare silicon dioxide (SiO_2) and on SiO_2 modified with thin interfacial organic layers. The Al_2O_3 films have been characterized using ellipsometry, atomic force microscopy (AFM), and x-ray photoelectron spectroscopy (XPS). We find that Al_2O_3 films grown on SiO_2 modified with a nitrogen-containing organic layer or a polyethylene glycol based self-assembled monolayer (SAM) grow at a rate of approximately 1 Å per cycle, equal to the deposition rate of Al_2O_3 on bare SiO_2, while a fluorinated hydrocarbon SAM strongly attenuates the rate of growth in the initial ~ 15 cycles. AFM of the Al_2O_3 films indicates a surface roughness of less than 0.5 nm, and XPS analysis confirms the presence of the organic layer at the Al_2O_3/substrate interface after ALD.

Introduction:

In order to continue to increase the performance and decrease the size of integrated circuits, capacitance within the interconnect structure must be reduced [1]. Several porous materials with a low dielectric constant (low-κ materials) have been proposed to address this issue. Unfortunately, the copper used in the interconnects can easily diffuse through these materials, severely shortening their usable lifetime [1].

Atomic layer deposition (ALD) is a technique that enables the deposition of thin, smooth, and conformal films with atomic layer precision [2]. Because of these desirable properties, ALD can be used to create a copper diffusion barrier on low-κ substrates. However, problems arise from infiltration of the gas-phase ALD precursors into the pores of the low-κ material. It has been proposed that an interfacial organic layer (IOL) could be used to seal the surface pores in these materials against gas-phase precursors before ALD is performed. Appropriately designed organic layers may have the added benefit of controlling the kinetics of the early stages of ALD. The objective of the work presented here is to determine how the structure and reactivity of the organic layer affects the growth rate and morphology of an Al_2O_3 film deposited on that layer.

Experimental Procedures:

ALD of Al_2O_3 was performed using an Oxford Instruments FlexAL atomic layer deposition tool. To deposit an Al_2O_3 film, a substrate was sequentially exposed to two alternating precursor gases, trimethylaluminium and water. The deposition chamber was purged with argon gas between precursor exposure. Films were deposited on bare SiO_2 and on SiO_2 modified with thin interfacial organic layers (IOLs).

The IOLs can be separated into two classes, based on whether or not they contain functional groups which are reactive towards the ALD precursors. The reactive IOLs used in this study were a polyethylene glycol (PEG) based SAM and a nitrogen-containing organic layer (referred to as "Layer N" below). (1H,1H,2H,2H-perfluorooctyl) trichlorosilane (FOTS), which contains only CH_2, CF_2, and CF_3 groups, is not expected to be reactive toward the ALD precursors. A cross-sectional view of a generalized sample after modification with an IOL and film deposition by ALD is shown in Figure 1 (thicknesses not to scale).

The thickness of the deposited films and IOLs were measured with a Woollam variable angle spectroscopic ellipsometer. Film morphology was characterized using a Digital Instruments Dimension 3100 atomic force microscope.

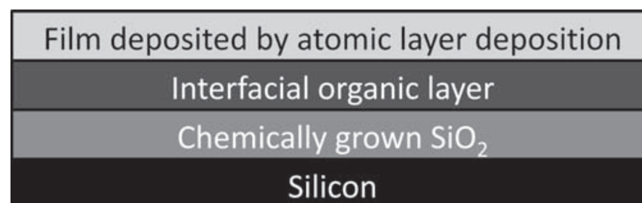

Figure 1: A cross-sectional view of a generalized and idealized sample.

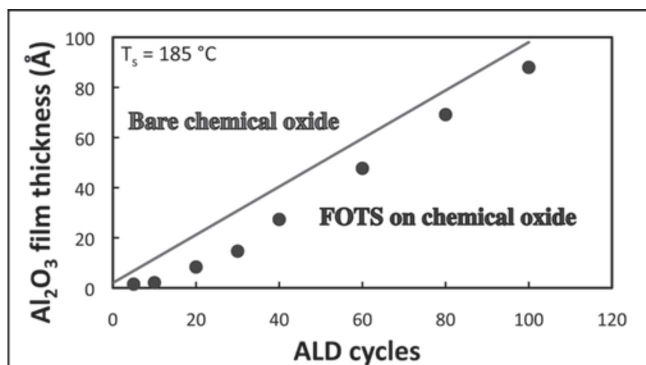

Figure 2: Deposited thickness of Al_2O_3 as a function of the number of ALD cycles for growth on SiO_2 and the FOTS SAM.

Results and Conclusions:

To establish an ideal growth rate, Al_2O_3 was deposited on bare, chemically grown SiO_2. Film growth on SiO_2 is considered to be ideal because this substrate is smooth and has an excess of active sites on which the Al_2O_3 film may nucleate. A constant growth rate of 0.96 Å/cycle at a substrate temperature (T_s) of 185 °C was observed, consistent with previous measurements [3].

An FOTS SAM attenuated growth of Al_2O_3 on SiO_2 in the first ~ 15 cycles (Figure 2). However, after about 30 cycles, the film growth rate returned to ~ 1 Å/cycle. This behavior suggests that the unreactive FOTS layer presents relatively few active sites on which the Al_2O_3 film can nucleate. This would lead to the film initially growing in patches, or islands [4]. After about 30 ALD cycles, however, it appears that these islands coalesce into a continuous Al_2O_3 film, masking the attenuating effect of the unreactive FOTS layer and returning the film growth rate to the ideal ~ 1 Å/cycle.

Al_2O_3 films were deposited at a rate of 0.96 Å/cycle on the reactive Layer N material, identical to Al_2O_3 films grown on SiO_2. Films deposited on the reactive PEG layer grew at a rate of 1.14 Å/cycle, slightly faster than on SiO_2. These results suggest that Layer N and PEG have an excess of active sites upon which the Al_2O_3 film can nucleate [4]. These results are summarized in Figure 3.

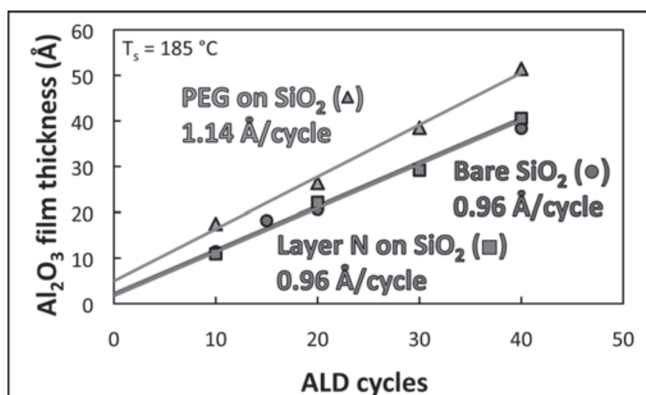

Figure 3: Deposited thickness of Al_2O_3 as a function of ALD cycles for growth on SiO_2 and reactive organic layers.

Ex situ x-ray photoelectron spectroscopy analysis of these films confirmed that, at minimum, some remnant of the Layer N material remained and waws confined to the Al_2O_3/SiO_2 interface after deposition.

Through qualitative analysis of AFM images of these films, we found that films exhibit similar morphology, independent of the reactivity or presence of an interfacial organic layer. In Figure 4, we present an AFM image of a 41 Å thick Al_2O_3 ALD film on Layer N. This film is representative of other Al_2O_3 films deposited on SiO_2 modified with IOLs or SAMs. Quantitatively, we found that all films were very smooth, with root-mean-square roughness values between 2.5 Å and 5.5 Å.

Acknowledgements:

This work was sponsored by the National Nanotechnology Infrastructure Network Research Experience for Undergraduates Program and the National Science Foundation. The author would like to thank Kevin Hughes, James Engstrom, Deirdre Manion-Fischer, and Melanie-Claire Mallison for their guidance and support.

References:

[1] International Technology Roadmap for Semiconductors. http://www.itrs.net, 2007.

[2] Puurunen, R. L. Applied Physics Reviews. 2005, 97, 121301.

[3] George, S. M.; Ott, A. W.; Klaus J. W. J. Phys. Chem. 1996, 100, 13121-13131.

[4] Dube, A.; Sharma, M.; Ma, P. F.; Ercius, P. A.; Muller, D. A.; Engstrom, J. R. J. Phys. Chem. C 2007, 111, 11045-11058.

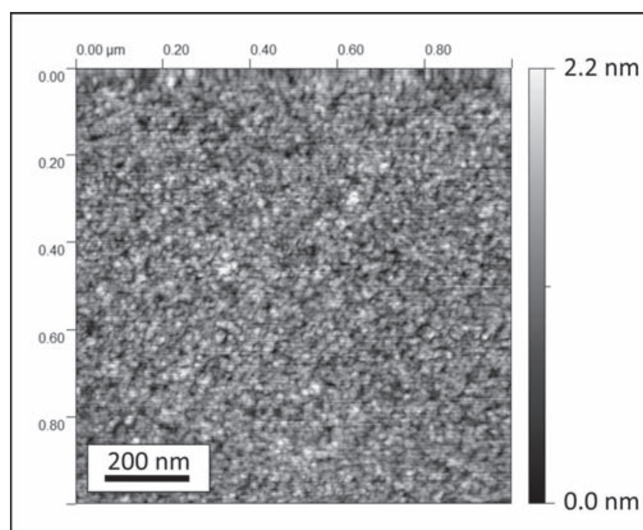

Figure 4: AFM of a 41 Å thick Al_2O_3 film deposited by ALD on Layer N.