Selective Area Atomic Layer Deposition: Developing Techniques that will Enable Single-nm Technologies

Alicia M. Elliott
Engineering Science, Stony Brook University

NNIN REU Site: Cornell NanoScale Science & Technology Facility, Cornell University, Ithaca, NY
NNIN REU Principal Investigator: Prof. James R. Engstrom, School of Chemical and Biomolecular Engineering, Cornell University
NNIN REU Mentor: Wenyu Zhang, School of Chemical and Biomolecular Engineering, Cornell University
Contact: alicia.elliott@stonybrook.edu, jre7@cornell.edu, wz89@cornell.edu

Abstract:

Atomic layer deposition (ALD) is a chemical vapor deposition process with self-limiting growth, providing atomic level, or "digital," control of thickness. Selective deposition extends this control to three dimensions, so 3D structures can be created without lithography. To deposit selectively, growth is promoted on one surface and prevented on another by varying deposition conditions. This project probes the intrinsic reactivity of two precursors: tetrakis-(ethylmethylamino)hafnium (TEMAH; $Hf(N(CH_3)(C_2H_5)_4)$ and tris(dimethylamino)silane (3DMAS; $SiH(N(CH_3)_2)_3$). Nucleation of each precursor on a metal and dielectric substrate was studied. Saturation curves of film deposited vs. dose time were generated for TEMAH by exposing the substrates to the first half of an ALD cycle. For 3DMAS, thicker films were deposited and the growth rate was estimated using *ex situ* ellipsometry. *Ex situ* x-ray photoelectron spectroscopy (XPS) was used to determine amount of precursor deposited.

MATS

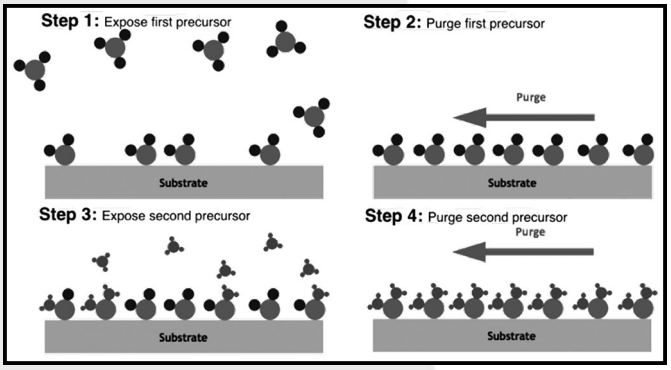

Figure 1: Schematic of the four-step ALD cycle.

Introduction:

Atomic layer deposition (ALD) is a deposition technique with a four step, self-limiting growth process (see Figure 1). Self-limiting growth allows digital control of thickness, creating highly conformal films on high aspect ratio structures.

Semiconductor devices have gone towards three dimensional (3D) features to increase speed and decrease power consumption (e.g., Intel's tri-gate transistor). Selective deposition could be utilized to pattern in 3D using ALD. To achieve this, growth is promoted on one substrate (e.g., a dielectric) and prevented on another (e.g., a metal). If selectivity can be achieved using ALD, this precise control can be extended to three dimensions, creating 3D patterns without lithography.

As a first step to developing a process that is selective, we must first understand the intrinsic reactivity of the thin film precursor with substrates of interest.

The nucleation of each precursor on two substrates, a dielectric (SiO_2 or Al_2O_3) and a metal (Cu), must be studied to determine how to selectively prevent deposition. Precursor dose times and heater temperature should be considered. Dose times can be varied to determine when each substrate becomes saturated with the precursor.

Experimental Procedure:

Two precursors were studied: tetrakis-(ethylmethylamino) hafnium (TEMAH), the precursor for hafnia (HfO_2) films, and tris(dimethylamino)silane (3DMAS), the precursor for silica (SiO_2) films.

TEMAH was deposited onto copper (Cu) and chemical oxide (chemically grown SiO_2) substrates. Chemical oxide (SiO_2) was grown by twice exposing silicon substrates to two minutes of buffered oxide etch 6:1 and 15 minutes of Nano-Strip® heated to 70-80°C. Each sample was exposed to one half-cycle of thermal HfO_2 ALD at a heater temperature (T_s) of ~ 250°C, with the following precursor dose times: 0.0, 0.1, 0.2, 0.4, 0.7, 1.0, 2.0, 3.5, 5.0, and 7.0 seconds. Plasma SiO_2 ALD films were deposited at 200°C onto Cu and ALD-deposited alumina (Al_2O_3) substrates, varying the number of cycles as follows: 0, 10, 20, 50, and 100 cycles. The 3DMAS doses were also varied, with dose times of 0.0, 0.1, 1.0, and 4.0 seconds.

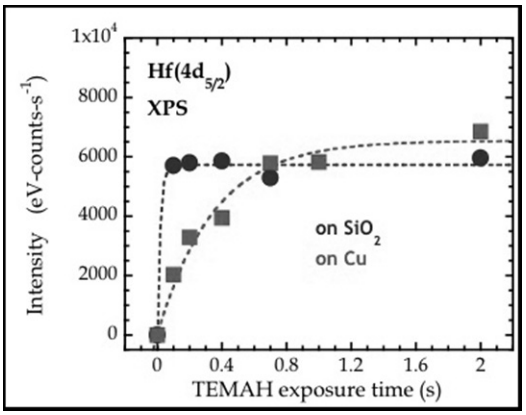

Figure 2: Integrated intensity of the Hf($4d_{5/2}$) peak as a function of TEMAH dose time on SiO_2 and Cu.

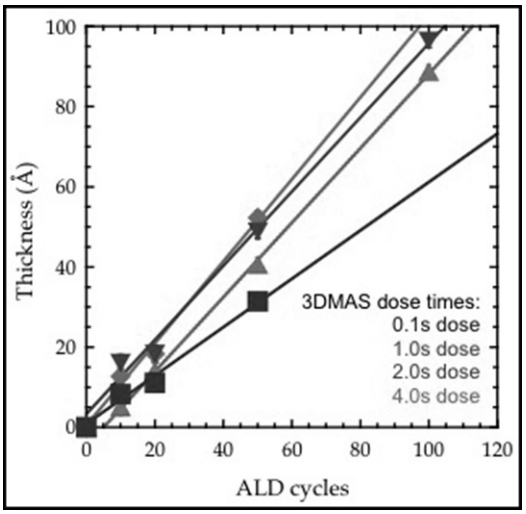

Figure 3: Estimated thicknesses of SiO_2 films (from SE) as a function of ALD cycles for four 3DMAS dose times.

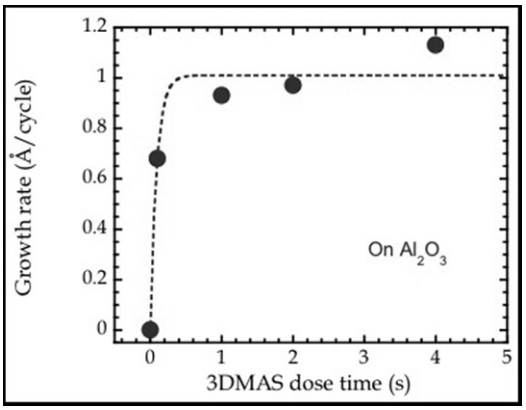

Figure 4: Estimated growth rate of SiO_2 ALD on Al_2O_3 (from SE) as a function of 3DMAS dose time.

Ex situ XPS and spectroscopic ellipsometry (SE) were used to determine how much precursor was deposited. SE was used to estimate film thicknesses for the SiO_2 ALD on Al_2O_3 and estimate growth rates. Saturation curves were generated from these analyses.

Results and Conclusions:

In Figure 2, we present the XPS integrated intensity for Hf($4d_{5/2}$) against TEMAH dose time, generating a saturation curve for each substrate. These results showed that TEMAH saturated on SiO_2 substrates (~ 0.1s - 0.2s TEMAH dose time) much more quickly than on Cu substrates (~ 2s). This is most likely due to the higher concentration of hydroxyl (-OH) groups on SiO_2 surfaces, thus promoting better adsorption of the precursor on the SiO_2.

SiO_2 ALD is a plasma process (using 3DMAS and oxygen plasma), so doing half-cycle ALD like we did for Hf will not capture the important processes occurring in the oxygen plasma half-cycle. A series of thicker films were deposited for each 3DMAS dose time.

In Figure 3, we present the estimated SiO_2 thicknesses on Al_2O_3. Growth rates can be estimated using the slopes of the data points. The growth rate for 0.1s dose time is ~ 0.68 Å/cycle, while 1.0s, 2.0s, and 4.0s dose time growth rates ranged from ~ 0.93 to 1.13 Å/cycle (saturation).

A saturation curve was generated for alumina substrates from this data, as seen in Figure 4. This shows a similar shape to that for TEMAH on SiO_2. Because of the rougher substrate surface for Cu, SE cannot be used to estimate film thickness. XPS analysis will be performed and a saturation curve will be generated.

Acknowledgements:

I would like to thank the National Science Foundation for funding this work, and the NNIN REU Program and the CNF for organization. I would also like to thank Professor James R. Engstrom and Wenyu Zhang for their guidance, teaching, and reassurance. I also thank Melanie-Claire Mallison, Rob Ilic, Vince Genova, and Meredith Metzler. Finally, thanks to all of the CNF staff.

MATS