1 SOP Objective

Atomic layer deposition (ALD) is a type of chemical vapor deposition that boasts self-limiting growth, allowing for precise control of film thickness while still yielding conformal growth. While ALD films are typically grown at temperatures exceeding 200oC, growing interest in fragile materials and structures is necessitating the development of low temperature ALD processing. This document contains a standard operating procedure for ALD growth of AlO\textsubscript{x} (alumina) and HfO\textsubscript{x} (hafnia) thin films below 100oC. This document additionally contains standard operating procedures for a slew of structural and electrical film characterization techniques.

2 ALD Process

2.1 Overview

Broadly, the steps to grow an ALD film are as follows:

1) Clean substrate.
2) [If using a seed layer] Deposit seed layer.
3) [If using a seed layer] Clean seeded substrate.
4) ALD growth.

We detail each step below. More generally, these steps should be appropriately situated inside a full process flow, which may include patterning or etching the ALD film. Regarding process steps following ALD growth, we emphasize that photodevelopers can etch ALD films; in particular, TMAH aggressively etches alumina. Film characterization data can be found in the accompanying project report.

2.2 Cleaning

Care must be taken to avoid carbon contamination on substrates, as any carbon adsorbed onto the substrate will be incorporated into the ALD film and degrade film quality. If possible, cleaning should closely precede deposition to limit new carbon adsorbates after cleaning. We used the following cleaning procedure; alternative cleaning procedures may be chosen based on the requirements of the substrate.

1) Rinse with a stream of DI water.
2) Soak in acetone with sonication.
3) Rinse with a stream of acetone.
4) Soak in secondary acetone.
5) Soak in isopropanol.
6) Blow dry with nitrogen.

2.3 Seeding procedure

At low temperatures, generating even nucleation of ALD films can be challenging. If the number of chemically active sites are limited, films may grow in islands for the first few cycles and result in
nonuniform film quality. This issue can be avoided by seeding the ALD film, i.e. depositing a thin layer of a metal oxide prior to ALD growth. These films can then act as sources of nucleation sites and spur uniform film growth. We elected to evaporate pure metallic aluminum layers and allow them to oxidize in atmosphere. The following procedures were chosen to ensure the seed layer oxidizes fully and therefore does not form a parasitic conductive layer.

For alumina seeds:

1) Evaporate 1 nm Al in an electron beam evaporator at 0.4 A/s.
2) Remove from vacuum and expose to ambient atmosphere for 20 min.
3) Repeat steps 1 and 2 until the seed layer reaches desired thickness.

The thickness of the seed layer increases when oxidized in atmosphere. We found that the thickness of the alumina seed layer increased by a factor of 2.9 from the thickness of the deposited Al (see supporting data).

For hafnia seeds:

4) Evaporate 0.6 nm Hf in an electron beam evaporator at 0.4 A/s.
5) Remove from vacuum and expose to ambient atmosphere for 20 min.
6) Repeat steps 1 and 2 until the seed layer reaches desired thickness.

We found that the thickness of the hafnia seed layer increased by a factor of 2.1 from the thickness of the deposited Hf (see supporting data).

2.4 ALD procedure

The standard process for using the SNF Savannah tool can be found at [https://snf.stanford.edu/SNF/equipment/chemical-vapor-deposition/ald/savannah](https://snf.stanford.edu/SNF/equipment/chemical-vapor-deposition/ald/savannah).

To run a deposition at non-default temperatures, the heater setpoints need to be chosen to ensure a positive thermal gradient throughout the system. We here detail processes used for depositing alumina at 60°C and hafnia at 85°C. Hafnia cannot be deposited lower than 85°C because the hafnia precursor must be heated to 75°C to be volatile. Compared to the standard process, there are also additional steps related to cooling the chamber.

1) In the Savannah software, load the standard recipe for the desired film.
2) Adjust heater setpoints in the Savannah software, changing the heater setpoints of the recipe AND on the chamber control (Figure 1).
   a) For alumina at 60°C:
      i) Precursor manifold = 50°C.
      ii) Inner and outer chamber heaters = 60°C.
      iii) Stop valve and trap/pump line =50°C.
      iv) Precursor jacket not heated (default value, do not change).
   b) For hafnia at 85°C:
      i) Precursor manifold = 80°C.
      ii) Inner and outer chamber heaters = 85°C.
      iii) Stop valve and trap/pump line = 80°C.
      iv) Precursor jacket = 75°C (default value, do not change).
3) Vent the chamber.
4) Allow all heaters to reach their designated setpoints.
a) Cooling is fastest if the chamber lid is left sitting open, exposed to air. While the chamber is 
open, however, the user must remain by the tool to ensure the chamber is not contaminated.
b) If you need to step away from the tool during cooling, close the lid and place the heat guard over 
the chamber.
5) Load samples after the chamber temperature reaches the desired setpoint.
a) Place samples in the center of the chamber. Even though growth should be uniform throughout an 
ALD chamber, the center of the chamber will provide the most consistent films when depositing 
at low temperature.
b) If using small chips, or chips coated by resist, place the chips on top of a 4” silicon carrier wafer.
6) Close and evacuate the chamber.
7) Set the software to run the desired number of ALD cycles. Ensure that the precursor pulse steps target 
the valve to the appropriate precursor reservoir (TMA for alumina films; TDMA-Hf for hafnia films).
8) Lengthen the purge times on the software; when depositing alumina at low temperature, we 
recommend a 60 s purge time for both water and TMA precursor, and a 40 s purge time for TDMA- 
Hf.
9) Optional, but recommended for each TDMA-Hf pulse: set up an exposure mode step. The correct 
sequence of commands is as follows:
a) Set the gas flow to 10 sccm.
   i) Savannah command: flow 10
   ii) Note: each cycle should begin with this command.
b) Close the stop valve.
   i) Savannah command: stopvalve 0.
c) Pulse TDMA-Hf.
d) Wait the desired amount of time (we used 5 s).
e) Open the stop valve.
   i) Savannah command: stopvalve 1.
f) Reset the carrier gas flow to 20 sccm.
   i) Savannah command: flow 10.
g) Purge for the usual amount of time.
10) We also recommend changing the wait time before deposition to 15 minutes, as water takes longer to 
pump from the chamber at low temperatures. Begin the ALD process.
11) When the process is complete, vent the chamber and remove your samples.
12) Close and evacuate the chamber, replace the heat guard, and run the “STANDBY” recipe to return the 
heaters to their standard setpoints.
3 Device Design and Fabrication

3.1 MIM Structures

Metal-insulator-metal (MIM) capacitor structures can be used to characterize electrical properties of dielectrics. The simplest devices employ uniformly deposited back metal contact and insulator layers and a patterned top contact layer. It is important to use a noble metal for the back contact because other metals will oxidize between depositing the back contact and the insulator, which will affect the measured capacitance of the device. We chose Pt for the back metal layer because ALD alumina is known to nucleate well on Pt; we chose Pt for the top contact metal layer so that the two metal layers would be identical and the capacitance would therefore be independent of voltage.

3.1.1 Fabrication methods:

1) Clean a silicon wafer with a 300 nm thermal oxide.
   a) Insulating silicon or another insulating substrate may be used instead.
2) Put the wafer into an electron-beam evaporator. Deposit 5 nm Ti as a sticking layer, and then 50 nm Pt as the back metal contact.
   a) We deposited metal at 1 A/s using the KJL evaporator; these details are unimportant.
   b) Cr can be used instead of Ti as a sticking layer.
   c) Au can be used instead of Pt for the back metal contact.
3) Cleave wafer into 10 mm square chips with a diamond scribe.