# 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.
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$^{o}$C and hafnia at 85$^{o}$C. Hafnia cannot be deposited lower then 85$^{o}$C because the hafnia precursor must be heated to 75$^{o}$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$^{o}$C:
      i) Precursor manifold = 50$^{o}$C.
      ii) Inner and outer chamber heaters = 60$^{o}$C.
      iii) Stop valve and trap/pump line =50$^{o}$C.
      iv) Precursor jacket not heated (default value, do not change).
   b) For hafnia at 85$^{o}$C:
      i) Precursor manifold = 80$^{o}$C.
      ii) Inner and outer chamber heaters = 85$^{o}$C.
      iii) Stop valve and trap/pump line = 80$^{o}$C.
      iv) Precursor jacket = 75$^{o}$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.

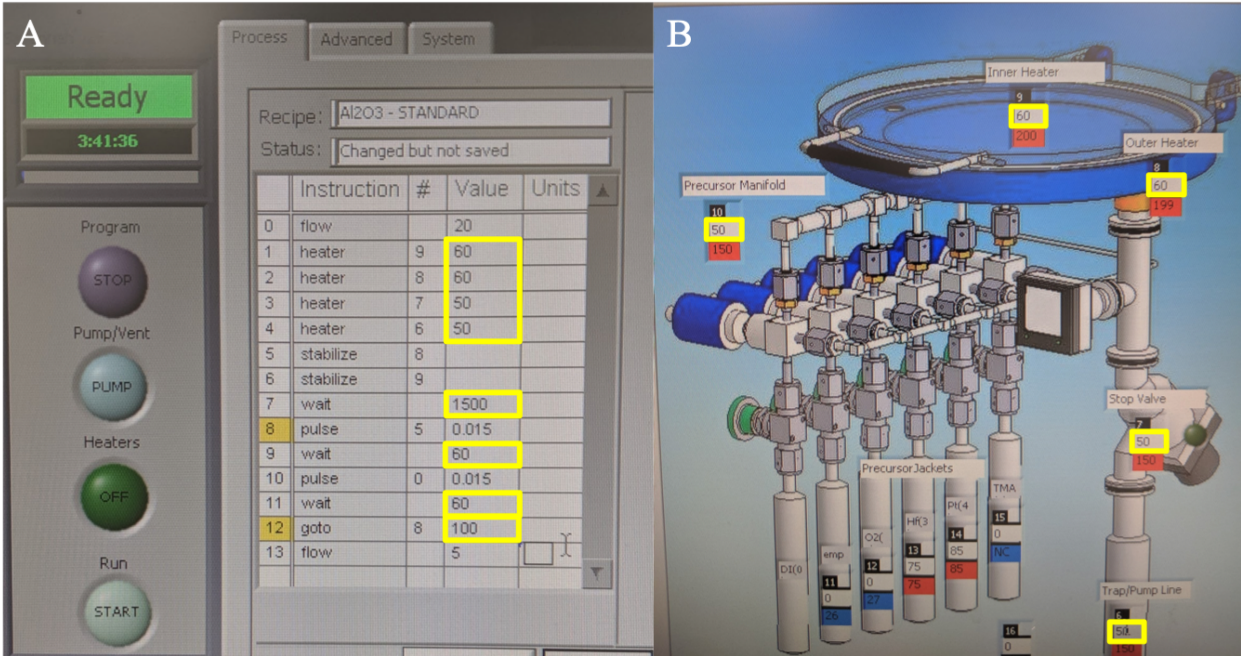


Figure 1. A) Example alumina deposition recipe. Yellow boxes indicate the parameters to adjust for low-temperature depositions, as described in steps 2, 7, 8, and 9 above. B) Heater setpoints can be manually adjusted to immediately begin cooling. Yellow boxes indicate the heaters that should be reset from their default values. Note: never adjust the heater setpoints of the precursor jackets.