Cambridge Nanotech Savannah Atomic Layer Deposition (ALD)

Standard Operating Procedure

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Purpose: The ALD system is used to deposit thin films (< 300 nm) of material in a highly controlled, layer by layer methodology. Deposition rates are slow (~100 nm/hour max dep rate) but thickness control and uniformity across the wafer are excellent. The deposition is also conformal.

The base material matters – you cannot expect to deposit the material on any substrate or on substrates with other surface layers – please review the extensive literature on ALD to find a good solution for your material system.

Important Note: If you are depositing ZnO you must run an encapsulating recipe after removing your substrates from the chamber. This will deposit ~15nm of TiO2 and prevent ZnO from contaminating future depositions. You are not required to remain for this step, after starting the process you may walk away.

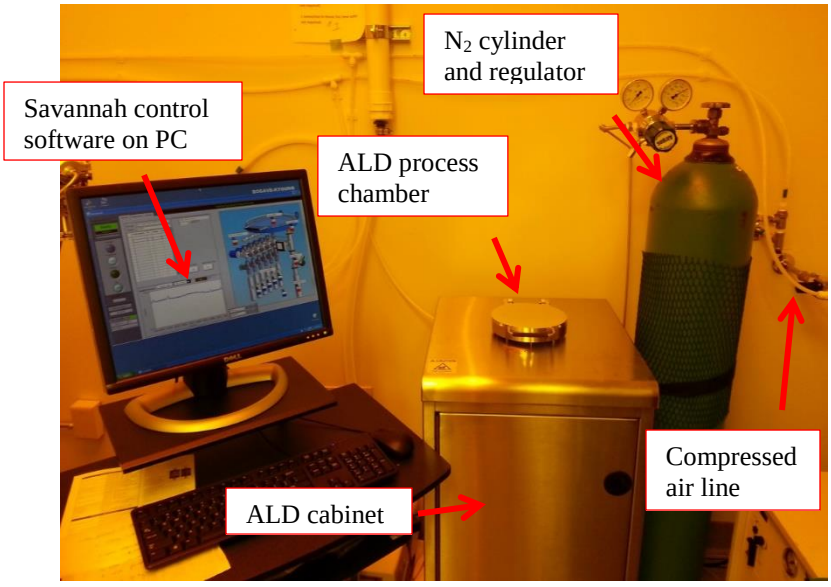
1.0 Material Requirements:

1.1 Equipment: wafer tweezers
1.2 Personal Protective Equipment: safety goggles, nitrile gloves

2.0 Safety Issues

The main safety concerns with the tool are:

1. The cover and chamber of the tool can be HOT. They are usually heated at 80 ºC and sometimes the temperature rises as high as 300 ºC for certain processes. Be careful not to burn yourself on the chamber!
2. The tool uses reactive gases for deposition. These are stored in very small cartridges inside the tool cabinet. Users should NEVER attempt to change the reactive gas cartridges. If they need to be changed please inform laboratory staff. Do NOT attempt this yourself.



3.0 Procedure:

3.1 Preparing for a deposition:

3.1.1 Log in to computer. Password is on the tape on the monitor base.

3.1.2 The ALD and Savannah control software should already be running. By default the tool will be in a resting state (see below). In the Savannah software, check to make sure the tool was left in this state – if not, please inform laboratory staff:

3.1.3 If the Savannah control software is not already running:

3.1.3.1 Run the software.

3.1.3.2 Set all the heater setpoints (white boxes) to the values shown below for the resting state.

3.1.3.3 Turn on the heaters by clicking the heater "ON" button. The red boxes will now show the current temperature, which should start to go up and will eventually stabilize at the setpoint.

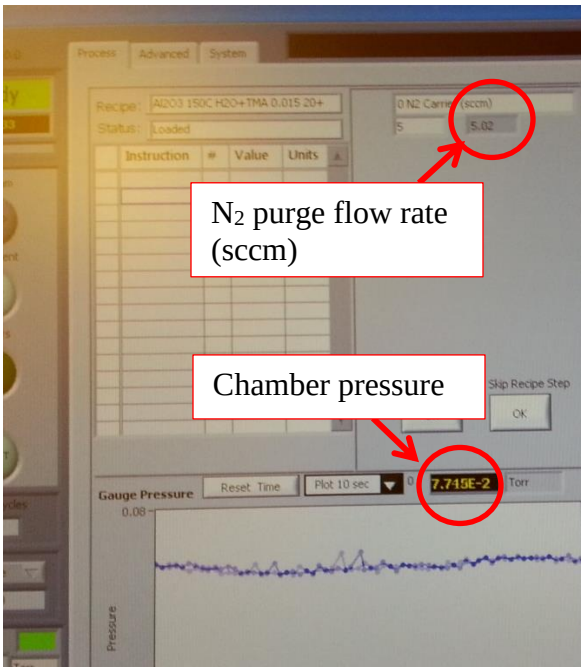
3.1.3.4 Click "PUMP" to pump the chamber down.

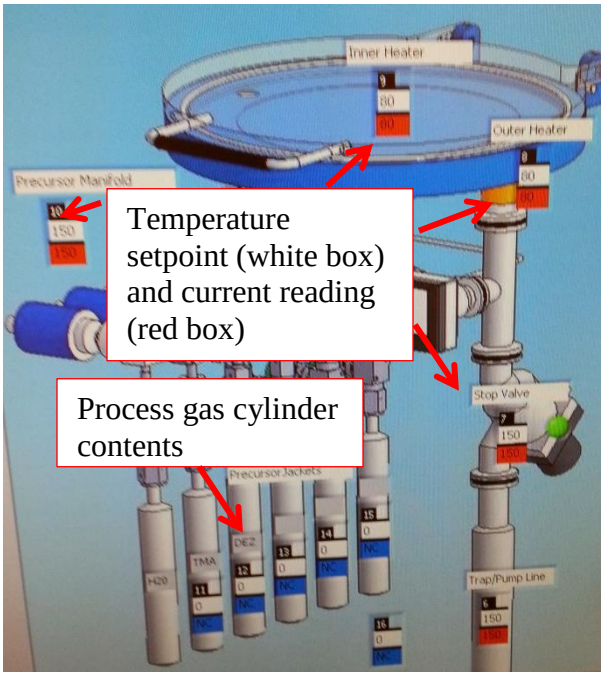
3.1.3.5 Set the N2 Carrier gas rate to 5 sccm.

3.1.3.6 Chamber pressure should stabilize at about 80 mT.

<u>Resting State</u>

80°C inner and outer chamber heaters
150°C precursor manifold, stop valve and trap/pump line
All process gas cylinder heaters at 0 (off).
5 sccm of N_2 carrier flowing in the chamber
chamber pumped down (pressure ≈ 80 mT)





3.1.4 Check that the nitrogen cylinder (see picture on previous page) has sufficient nitrogen remaining.

3.1.4.1 The cylinder pressure inside the cylinder (right hand gauge) should read higher that 300 psi.

3.1.4.2 The nitrogen cylinder should *always be left open* with the pressure regulator set to approximately 20 psi outlet pressure.

3.2 Loading a sample

3.2.1 Click "VENT" to vent the chamber.

3.2.2 Once the chamber pressure reaches atmosphere, open the chamber lid. Be careful! Chamber will be hot!

3.2.3 Place your sample face up in the center of the process chamber using clean tweezers. The **only** materials allowed in the ALD at this time are (this list may be updated in the future as users request additional material options):

silicon, glass (SiO_2 and similar doped glasses), aluminum nitride, silicon nitride, zinc, zinc oxide

3.2.4 Close the chamber lid.

3.2.5 Click "PUMP" to pump down the chamber.

3.2.5.1 N_2 carrier should be set to 5 sccm.

3.2.5.2 The chamber pressure should rapidly drop to about 100 mT.

3.3 Setting up a program

Current precursor canisters that are loaded as of Sept 2019:

V0 = H_2O (Pure Process Water)
V1 = Al_2O_3 (TMA - Tetramethyl Aluminum)
V2 = ZnO (DEZ - Diethyl Zinc)
V3 = damaged fitting, will not hold vacuum, no precursor loaded
V4 = VO_x ([V(dma)$_4$] Tetrakis(dimethylamino)vanadium)
V5 = TiO_2 (TTIP – Titanium Isopropoxide)

Obviously, these will change over time, the sign posted on the ALD or monitor will have the latest configuration.

3.3.1 Option #1: To load an existing program, right click in the instruction area of the software (the part that looks like a table) and select "Load recipe…"

3.3.1.1 Default recipes are stored in "C:\Cambirdge Nanotech\Recipes\CNT Recipes\"

3.3.1.2 Modify the number of cycles in the "GOTO" step. This is the total number of deposition cycles. A single cycle will deposit approximately 1 monolayer of material, which is usually about 0.1 nm of material. Refer to the recipe sheets "C:\Cambridge Nanotech\Savannah Recipe Sheets\" for more information on exact recipes and expected deposition rate per cycle.

3.3.2 Option #2: Write (or modify) a program.

3.3.2.1 Right click in the instruction area and add steps to the recipe.

3.3.2.2 Refer to the recipe sheets "C:\Cambridge Nanotech\Savannah Recipe Sheets\" for more information on suggested recipes.

3.3.2.3 The types of steps you can add are

Flow (, value) – sets the flow rate to "value" (sccm) which can be any non-negative number. The actual flow rate is limited by the specifications of the MFC.

Goto (#,value) – jump to the line number "#" in the program, "value" times, before moving on. This is basically used to do a loop and would usually be used to set the number of cycles for a deposition.

Heater (#,value) – sets the temperature ("value") in ^{o}C for the heater designated by "#". See the cartoon picture of the tool in the right of the window for which heater is which number (in black).

Pulse (#,value) – open the "#"-th ALD precursor canister valve for "value" seconds and then closes the valve. This is used to pulse in the reacting gases in a controlled fashion. The range of "value" is 0.01 to 10 seconds. The "#" corresponds to the loaded precursors (see above at the top of section 3.3)
Stabilize (#) – waits until heater "#" has reached its setpoint within 2 degrees.

Wait (, value) – waits "value" seconds before moving on. This is usually used right after a "pulse" command to wait for the precursor to fully purge.

3.3.2.4 A typical program might look something like this:

Recipe: AL2O3 150C

Status: Saved

	Instruction	#	Value	Units
0	flow		20	sccm
1	heater	9	150	C
2	heater	8	150	C
3	stabilize	9		
4	stabilize	8		
5	wait		600	sec
6	pulse	0	.15	sec
7	wait		20	sec
8	pulse	1	.15	sec
9	wait		20	sec
10	goto	6	100	cycles
11	flow		5	sccm
12	heater	9	80	deg C
13	heater	8	80	deg C

<u>Program description:</u> First, set the N_2 purge flow rate to 20 sccm. Now set the heater 8 and 9 (these are the inner and outer chamber heaters) to 150 ^{o}C. Next, wait for the temperature of heaters 8 and 9 to stabilize within 2^{o}C of setpoint. Then wait 600 seconds. Now, go into a loop (lines 6-10) where valve 0 (H_2O) is pulsed for 0.15 seconds, then we wait for 20 seconds (N_2 is always flowing, so this purges the excess precursor), then valve 1 (TMA) is pulsed for 0.15

seconds, and wait another 20 seconds. Repeat this 100 times (so, that is 100 cycles – about 10 nm of material). Once the loop is done (line 11-13) set the flow rate back to the resting state 5 sccm, and reset heater 8 and 9 temperature setpoints to 80 ^{o}C.

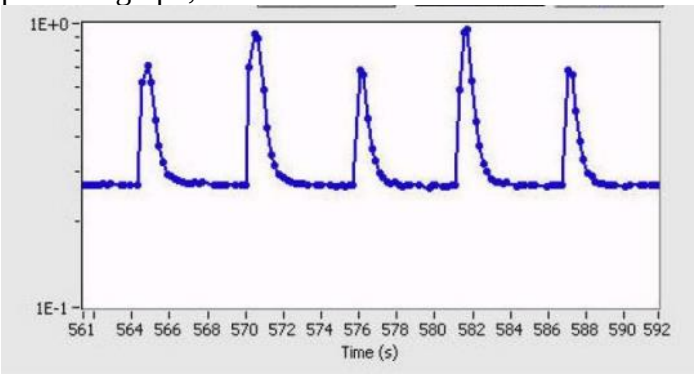
3.3.2.5 After the program is written, right click and "Save recipe as…"

3.4 Running a deposition

3.4.1 Click "Start Run".

3.4.1.1 The program should run – first the N2 carrier flow rate is set, and the temperatures stabilize according to your program (Lines 0-4 above). Then the program will wait for the specified length of time (line 5 above).

3.4.1.2 Next, it will start pulsing the precursors one after the other in the sequence you programmed with the specified purge times in between (lines 6-10 above). You should observe peaks in the pressure graph, like this:



3.4.1.3 The process should run for the specified number of cycles and then stop automatically. The program should end with the appropriate lines (line 11-13 above) to reset the chamber temperature to 80 ^{o}C and N_2 carrier flow rate to 5 sccm.

3.4.1.3.1 When the process is complete, the program should display "Ready" in green at the top left and say "Run has completed" at the top.

3.4.2 IF FOR ANY REASON THE TOOL DOES NOT APPEAR TO BE RESPONDING NORMALLY, ABORT THE RUN BY CLICKING Run "ABORT".

3.5 Removing your sample

3.5.1 Click "VENT".

3.5.2 Remove the sample – **<u>CAREFUL! THE CHAMBER WILL BE HOT</u>**.

3.5.3 Close the chamber cover and click "PUMP"

3.5.4 Make sure the N_2 carrier gas flow rate is set to 5 sccm.

3.5.4.1 Make sure the chamber pumps down and chamber pressure stabilizes around 80 mT.

3.5.5 Make sure the inner and outer chamber heaters are set to 80 ^{o}C.

3.5.6 Make sure all other heaters are set to 150 ^{o}C.
3.5.7 Make sure heaters are on.
3.5.8 Make sure that the N_2 cylinder is LEFT OPEN.
3.5.9 Make sure there is sufficient N_2 in the cylinder – pressure inside the cylinder (right hand gauge on the regulator) should be higher than 300 psi. If cylinder pressure is lower than this inform the lab staff.
3.5.10 Fill out the log book.
3.5.11 Leave the software running and the computer turned on.
3.5.12 If you deposited ZnO there is an additional encapsulation step to prevent contamination of subsequent runs. Otherwise skip to 3.5.13
3.5.12.1 Load "TiO2 Encapsulant 150C" the ZnO encapsulating recipe. This will deposit 15nm of TiO2 to seal the ZnO remaining in the chamber
3.5.12.2 Start the recipe, once it is running and all looks normal you can walk away
3.5.13 If you did not deposit ZnO, the process is complete and you can move on

4.0 Changing the Precursor Cylinder

4.1 This operation should only be performed by lab staff, not by cleanroom users!
4.2 Close the manual valve on the only cylinder.
4.3 Run the headspace evacuation program for that valve (in Maintenance Recipes folder) – this evacuates any remaining precursor from the connector headspace.
4.4 Remove the precursor from the manifold.
4.5 Throw away the old VCR gasket.
4.6 Get a new VCR gasket (Swagelock SS-4-VCR-2) and place it on top of the male VCR fitting on the new precursor cylinder.
4.7 Tighten the precursor cylinder in to the manifold. Finger tight, then an additional 45^{o} turn.
4.8 Keep the manual valve closed for now!
4.9 Run the headspace evacuation program for that valve (in Maintenance Recipes folder) – this evacuates the air from the connector headspace.
4.10 Observe the pressure peaks. There should be a few (maybe only 1) high peak on the first pulse or few pulses, and then there should be no more peaks – now you have removed the air. If you keep getting peaks, you don't have a good seal – tighten the fitting.
4.11 Open the manual valve.
4.12 Run the pulse program for that valve (in Maintenance Recipes folder). The purpose of this is to evacuate the inert gas that is packaged in the precursor cylinder on top of the precursor.
4.13 Observe the pressure pulses – they should become regular height after some time.

5.0 Specific Recipes

5.1 Al_2O_3 (Aluminum Oxide)

The canonical ALD material system, deposited from unheated H_2O and TMA. See the literature for extensive information on this system. Different recipes for differnet

temperature depositions exist in the CNT Recipes folder. The following table is taken from the Ultratech recipe sheet.

Note that for very high aspect ratio structures (such as porous scaffolds) you may need to run in "exposure mode" with longer dwell times to allow for complete diffusion of the reactants into the pores. See the scientific literature for more information.

Temperature (C)	TMA Purge (s)	H_2O Purge (s)	GPC** (Å/cycle)
300	4	4	1.0
250	5	5	1.1
200	8	8	1.1
150	20	20	1.1
80	60	60	0.9

**Growth per cycle on silicon

5.2 Platinum

Platinum deposition can be carried out using the (MeCp)PtMe3 precursor in V3 and the UHP O_2 in V5.

Important notes:

1. The (MeCp)PtMe3 precursor should be heated to 75 ^oC and allowed to stabilize for 1 hour before starting deposition. Heater 13 is connected to V3 where this precursor is loaded.
2. The (MeCp)PtMe3 precursor heater (heater 13) should be returned to off (0^oC setpoint) after the deposition is complete. The precursor is expensive and there are some reports of thermal decomposition. We do not want to risk decomposition of the precursor.
3. Nucleation occurs initially when depositing Pt. So the first few hundred cycles may be relatively ineffective at depositing a continuous film of material. The deposition rate will increase to the typical ≈0.3-0.5 Å/sec after a few hundred cycles. Exactly how many cycles this will be depends on the material you are depositing on (deposition on Si is different than deposition on Al_2O_3, for example) and the temperature. In addition, it may depend on previous conditioning of the chamber – what was run prior to your deposition.

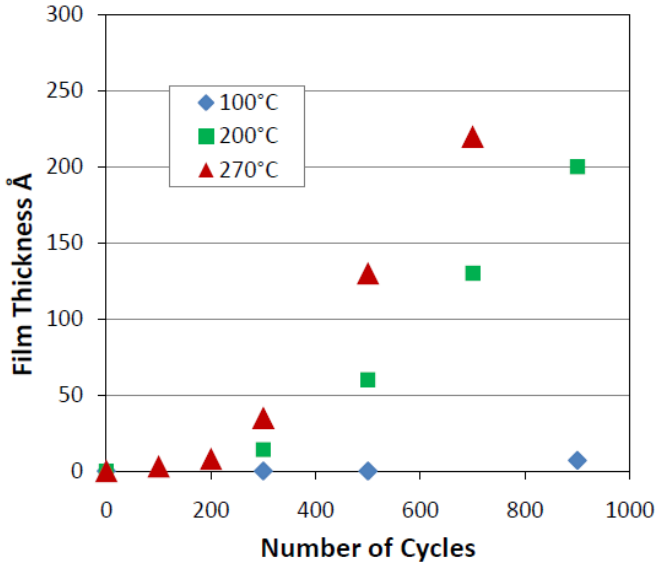


Figure 1. Pt nucleation on silicon sample at different process temperatures.

Deposition of metallic platinum suffers from nucleation effects which are temperature and substrate dependent. For example, when platinum is deposited on thermal silicon oxide with m < 300 cycles, it exists as small islands or nanoparticles and not as a continuous film.

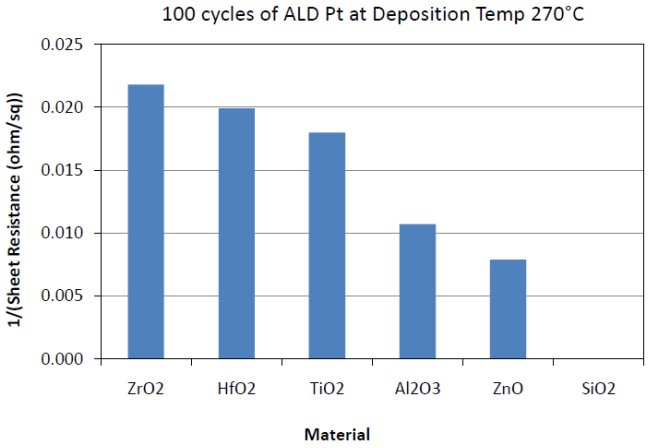


Figure 2. Sheet resistance of 100 cycles of Pt (deposition temperature 270°C) deposited on 50Å of ALD oxides on thermal Si oxide. Sheet resistance measured by 4-point probe.

4. For best results, the following is recommended:
   - **a.** First, run an Al_2O_3 deposition at 150°C on the empty chamber for 100 cycles. Or, alternatively, if you are depositing the platinum on a porous scaffold, run the Al_2O_3 deposition in exposure mode for 100 cycles with your scaffold already in the chamber.
   - **b.** Next run the Pt deposition at whatever temperature you prefer to use. Again, if working with a porous scaffold, consider using the exposure mode recipe.
   - **c.** After completing the Pt deposition, run another 100 cycle Al_2O_3 deposition on the empty chamber at 150°C.

Exposure mode program for Al_2O_3

Line #	Instruction	#	Value	Units	Comments
0	flow		20	sccm	
1	heater	9	150	deg C	Setting temperature to 150 deg C
2	heater	8	150	deg C	
3	heater	6	150	deg C	
4	heater	7	150	deg C	
5	heater	10	150	deg C	
6	stabilize	9			
7	stabilize	8			
8	stabilize	6			
9	stabilize	7			
10	stabilize	10			
11	wait		600	sec	
12	stopvalve		0		Isolates chamber from dynamic vacuum
13	flow		10	sccm	Reduced flow to 10 sccm
14	pulse	0	0.15	sec	Pulses water precursor for 0.15 s
15	wait		X	Sec	Exposure time
16	stopvalve		1		Opens chamber to dynamic vacuum
17	flow		20	sccm	Increases flow to 20 sccm
18	wait		x+5	sec	Purging time
19	stopvalve		0		Isolates chamber from dynamic vacuum
20	flow		10	sccm	Reduced flow to 10 sccm
21	pulse	1	0.15	sec	Pulses TMA precursor for 0.15 s
22	wait		X	Sec	Exposure time
23	stopvalve		1		Opens chamber to dynamic vacuum
24	flow		20	Sccm	Increases flow to 20 sccm
25	wait		x+5	Sec	Purging time
26	goto	12	100	Cycles	Repeats for 100 cycles
27	flow		5	Sccm	
28	heater	9	80	deg C	Resting state of heaters 8 & 9
29	heater	8	80	deg C	

Exposure mode program for Pt.

NOTE: Heater 13 ((MeCp)PtMe3 heater) should be set to 75°C and left for at least 1 hour at that temperature *before starting this process*. After the deposition is complete, set heater 13 back to 0 °C.

The exposure time, "x" in the table below, will have to be determined for your application.

Line #	Instruction	#	Value	Units	Comments
0	flow		20	sccm	
1	heater	9	270	deg C	Setting temperature to 150 deg C
2	heater	8	270	deg C	
3	heater	6	150	deg C	
4	heater	7	150	deg C	
5	heater	10	150	deg C	
6	stabilize	9			
7	stabilize	8			
8	stabilize	6			
9	stabilize	7			
10	stabilize	10			
11	wait		600	sec	
12	stopvalve		0		Isolates chamber from dynamic vacuum
13	flow		10	sccm	Reduced flow to 10 sccm
14	pulse	5	0.15	sec	Pulses O_2 gas for 0.15 s
15	wait		x	Sec	Exposure time
16	stopvalve		1		Opens chamber to dynamic vacuum
17	flow		20	sccm	Increases flow to 20 sccm
18	wait		x+5	sec	Purging time
19	stopvalve		0		Isolates chamber from dynamic vacuum
20	flow		10	sccm	Reduced flow to 10 sccm
21	pulse	3	0.15	sec	Pulses $MeCpPtMe_3$ precursor for 0.15 s
22	wait		x	Sec	Exposure time
23	stopvalve		1		Opens chamber to dynamic vacuum
24	flow		20	Sccm	Increases flow to 20 sccm
25	wait		x+5	Sec	Purging time
26	goto	12	300	Cycles	Repeats for 300 cycles
27	flow		5	Sccm	
28	heater	9	80	deg C	Resting state of heaters
29	heater	8	80	deg C	