

Atomic Layer Deposition: Introduction to the Theory and Cambridge Nanotech Savannah & Fiji

J Provine & Michelle Rincon November 1, 2012 Stanford University NNIN ALD Roadshow (special thanks to Ganesh Sundaram, Eric Deguns, Prof. H. Brongersma, and Prof. Fritz Prinz)



Methods for Depositing Thin Films

Method	ALD	MBE	CVD	Sputter	Evapor	PLD
Thickness Uniformity	good	fair	good	good	fair	fair
Film Density	good	good	good	good	fair	good
Step Coverage	good	varies	varies	poor	poor	poor
Interface Quality	good	good	varies	poor	good	varies
Low Temp. Deposition	good	good	varies	good	good	good
Deposition Rate	fair	fair	good	good	good	good
Industrial Applicability	varies	varies	good	good	good	poor



What is ALD? aka How does it work?

- Originally called Atomic Layer Epitaxy
 - Has been around in one form or another for almost 50 years
- A chemical vapor deposition method
 - However, the reaction is split into two parts
 - Each part is self-limiting and surface only
 - After completion of the two half-reactions the system is stable and a monolayer of film has been deposited



ALD Example Cycle for Al₂O₃ Deposition



In air H_2O vapor is adsorbed on most surfaces, forming a hydroxyl group. With silicon this forms: Si-O-H $_{(s)}$

After placing the substrate in the reactor, Trimethyl Aluminum (TMA) is pulsed into the reaction chamber.





Trimethylaluminum (TMA) reacts with the adsorbed hydroxyl groups, producing methane as the reaction product

 $AI(CH_3)_{3 (g)} + : Si-O-H_{(s)} \rightarrow :Si-O-AI(CH_3)_{2 (s)} + CH_4$





Trimethyl Aluminum (TMA) reacts with the adsorbed hydroxyl groups, until the surface is passivated. TMA does not react with itself, terminating the reaction to one layer. This causes the perfect uniformity of ALD. The excess TMA is pumped away with the methane reaction product.





After the TMA and methane reaction product is pumped away, water vapor (H_2O) is pulsed into the reaction chamber.





H₂O reacts with the dangling methyl groups on the new surface forming aluminumoxygen (Al-O) bridges and hydroxyl surface groups, waiting for a new TMA pulse. Again metane is the reaction product.

$$2 H_2 O_{(g)} + :Si-O-AI(CH_3)_{2 (s)} \rightarrow :Si-O-AI(OH)_{2 (s)} + 2 CH_4$$





The reaction product methane is pumped away. Excess H₂O vapor does not react with the hydroxyl surface groups, again causing perfect passivation to one atomic layer.





One TMA and one H₂O vapor pulse form one cycle. Here three cycles are shown, with approximately 1 Angstrom per cycle. Each cycle including pulsing and pumping takes e.g. 3 sec.

Two reaction steps in each cycle:

 $AI(CH_3)_{3 (g)} + :AI-O-H_{(s)} \longrightarrow :AI-O-AI(CH_3)_{2 (s)} + CH_4$ $2 H_2O_{(g)} + :O-AI(CH_3)_{2 (s)} \longrightarrow :AI-O-AI(OH)_{2 (s)} + 2 CH_4$



Signature Qualities of ALD

• Step One: Linear growth rate





Signature Qualities of ALD?

• Step Two: Self-limiting deposition/cycle

Saturation Curve at 250°C



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ALD "Window"

Each ALD process has an ideal process "window" in which growth is saturated at a monolayer of film.





ALD Window





Advantages of ALD

Unique Chemistry Driven Process

- Self-saturating reactions with surface
- Thermal decomposition of precursor not-allowed
- Low temperature and low stress (molecular self assembly)
- Excellent adhesion
- Conformal Coating
 - Perfect 3D conformality: no line of sight issues
 - Ultra high aspect ratio (>2,000:1)
 - Large area thickness uniformity and scalability
- Challenging Substrates
 - Gentle deposition process for sensitive substrates (i.e. biomaterials, plastics)
 - Coats challenging substrates (teflon, graphene gold)



Typical ALD processes have a growth rate between 0.5-1.5Å per cycle



Disadvantages of ALD

Unique, Chemistry Driven Process

- Not every material possible
- Precursors can limit process due to reactivity / availability
- Process limited by activation energy
- No thermal decomposition of precursor allowed

Conformal Coating

- Deposition can be comparably slow: cycles times of 1 second to >1 minute depending on substrate and temperature
- Removal of excess precursor and by-products is required
- Challenging Substrates
 - Functionalization steps may be required



Let's take an extra moment on conformality







ALD Precursors

Good ALD precursors need to have the following characteristics:

- 1. Volatility
 - Vapor pressure (> 0.1Torr at T < 200°C)

Liquid at volatilization temperature without decomposition

2. Reactivity

Able to quickly react with substrate in a self-limiting fashion (most precursors are air-sensitive)

3. Stability

Thermal decomposition in the reactor or on the substrate is not allowed

4. Byproducts

Should not etch growing film and/or compete for surface sites

5. Availability



ALD Precursors

The second precursor (Precursor B) must react with adsorbed monolayer (A) in order to form bonds and prepare the surface for another dose of (A)

Some common precursors include:

- Oxidants for oxides
 Water (H₂O), ozone, O₂ plasma, alcohols (ROH), metal alkoxides [M(OR)_x]
- Reductants

<u>Metals</u> Hydrogen gas (H_2), ammonia (NH_3), Silanes (Si_2H_6)

<u>Nitrides</u> Ammonia (NH₃), N₂ plasma, hydrazine (NH₂ NH₂)

<u>Sulfides</u> Hydrogen Sulfide (H₂S)





Al₂O₃ From Beer

Cambridge NanoTech Experiment: replacement of H₂O with beer







Al₂O₃ From Beer



Both 1000 cycles, 1000 Angstrom thick. The results are remarkably similar as the vapor draw allows the water/alcohol vapor to be distilled from the beer precursor cylinder, demonstrating the reduced requirement for high purity precursors if used in certain applications



Two deviations from the perfect ALD model

- Films are typically amorphous
 - Poly or crystalline can be achieved in proper deposition condition or with anneal



- Nucleation
 - Not every self-limiting half-reaction fully occupies every available sight every cycle
 - In fact, at some level this is true for every film deposited
 - Substrate dependence
 - Chemistry dependence
 - Film roughness



A little more about nucleation

Pt from MeCpPtMe₃ and O₂





ALD Processes

Cambridge NanoTech has several standard recipes available as starting points for customers. However, there are many processes which have not been attempted in our applications lab.

Many ALD processes exist:

H		Element included in at least one ALD material															He
Li	Be												С	Ν	0	F	Ne
Na	Mg		Elem	ement not included in any ALD material								Al	Si	Ρ	S	CI	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Мо	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te		Xe
Cs	Ba	La	Hf	Та	W	Re	Os	lr 👘	Pt	Au	Hg	TI	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu	
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	



Oxides made by ALD

Green = ALD process known for an Oxide of the Element

Red = no process known for ALD of any Oxide of the Element





Pure Elements made by ALD

Green = ALD processes known for 16 Pure Elements

Red = no process known for ALD of the Element





Nitrides made by ALD

Green = ALD processes known for a Nitride of the Element

Red = no process known for ALD of a Nitride of the Element





Sulfides made by ALD

Green = ALD processes known for a Sulfide of the Element

Red = no process known for ALD of a Sulfide of the Element





Carbides made by ALD





Fluorides made by ALD

Green = ALD processes known for a Fluoride of the Element																	
Re	d =	no	pro	ces	s kr	10W	n fc	or A	LD (of a	Flu	orio	de c	of th	e E	len	ent
н																	He
Li	Be											B	С	Ν	0	F	Ne
Na	Mg											A	Si	P	5	C	Ar
Κ	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Υ	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Те		Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	TI	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu	
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	



Periodic table frequently updated at http://www.cambridgenanotech.com/periodic

Periodic Table | ALD Films

H 1			:Oxide :Nitride		C:Cart F:Fluo												He 2
Li 3	Be M:Metal D:Dopant 4 P:Phosphide/Asenide S:Sulphide/Selenide/Telluride											о N В 5 D	<mark>С</mark> 6	N 7	<mark>0</mark> 8	F 9	Ne 10
Na 11	Mg 12 F		Oxide of thi Recipe for					-	se			● N M P AI 13	ОММ <mark>Si</mark> 14 С	<mark>Р</mark> 15	<mark>S</mark> 16	CI 17	Ar 18
<mark>К</mark> 19	O Ca 20 S F	0 SC 21		0 V 23	0 Cr 24	О N M Мп 25 S D	ONM Fe 26	ONM Co 27	○ N M Ni 28	ONM Cu 29 D	2n 30 F	◎ N P Ga 31 D	о м Ge 32	As 33	<mark>Se</mark> 34	Br 35	Kr 36
Rb 37	0 Sr 38 F	0 Y 39	☑ N Zr 40	◎ N Nb 41	о N M Мо 42	TC 43	0 M Ru 44	0 M Rh 45	0 M Pd 46	ом Ад 47	Cd 48 S	© N P <mark> n</mark> 49 S	Sn 50 s	0 M Sb 51 D	Te 52	 53	<mark>Xe</mark> 54
Cs 55	0 Ba 56 s	0 La 57 F	■ N Hf 72 S F	О N М Та 73 С	ONM W 74	0 Re 75	0 0s 76	0 M r 77	0 M Pt 78	Au 79	Hg 80 s	TI 81	0 Pb 82 D	0 Bi 83	Po 84	At 85	Rn 86
Fr 87	Ra 88	Ac 89	Rf 104	Db 105	<mark>Sg</mark> 106	Bh 107	Hs 108	<mark>Mt</mark> 109									

Ce 58	0 Pr 59	Nd 60	Pm 61	0 Sm 62	0 Eu 63		0 Tb 65 D	O Dy 66	0 67	© 68	0 Tm 69 D	0 Yb 70	0 Lu 71
Th	Pa	U	<mark>Np</mark>	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
90	92	93	94	95	96	97	98	100	101	102	104	4	4



The SNF ALD Websites

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https://snf.stanford.edu/SNF/equipment/chemical-vapor-depositio
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ALD. Overall review of the ALD systems in the SNF. Savannah: a gold level contamination, thermal Cambridge Nanotech Savannah S200 system. Operational. Fiji1: a clean, plasma and thermal Cambridge Nanotech Fiji F202 chamber with ozone. Operational. Fiji2: an open material, plasma and thermal Cambridge Nanotech Fiji F202 chamber. Operational. Fiji3: a open material, plasma and thermal Cambridge Nanotech Fiji F200 chamber dedicated to oxide depositions. Arriving November 2011, anticipated online in early 2013. Savannah-mvd: a Cambridge Nanotech Savannah S200 system configured for Molecular Vapor Deposition and with the reaction chamber enclosed in an inert glovebox. Arriving November 2011, anticipated online in early 2013. Current SNF ALD film capabilities car be found on the Fiji1, Fiji2, and Savannah pages. thography. B Sayannah Savannah is a thermal atomic layer deposition (ALD) system. It is a Savannah S200 from Cambridge Nanotech and is categorized as gold contaminated. The system can accommodate pieces up to an 8" wafer al Vapor h Fiii1 Fiji1 is a load-locked, plasma-enabled atomic laver deposition (ALD) system. Coupled with Fiji2, Fiji1 is a Fiji F202 system from Cambridge Nanotech and is capable of both thermal and plasma assisted ALD of various dielectric and metallic films. The system can accommodate pieces up to an 8" wafer. Fijil 1 currently classified as semi-clean. 🗀 Savannah Images

images for the savannah information page

Fiji images

annah Images for the documentation of both Fiji-L and Fiji-R.

a map of fiji-I and fiji-r location in snf

Fiji2 annah

Fiji2 is a load-locked, plasma-enabled atomic layer deposition (ALD) system. Coupled with Fiji1, Fiji2 is a Fiji F202 system from Cambridge Nanotech and is des capable of both thermal and plasma assisted ALD of various dielectric and theraffic films. The system can accommodate pieces up to an 8" wafer. Fiji2 is currently classified as gold contaminated and is open to a wide range of materials.

mages

https://snf.stanford.edu/SNF/equipment/chemical-vapor-deposition/ald

Possible Films

The films available on the Savannah is determined by the precursors installed in the system. The list of available precursors is maintained on this page and also on a file on the desktop of control computer. The file on the computer is the final word on what precursors are installed on the system currently. In the event that this website and the file or the computer disagree - follow the document on the control computer.

Current films available (in stock precursors):

Film	NOTES	Tools	Deposition rate (A/cycle) @ temp)	Thickness Nonuniformity over 2 100mm wafers)	Precursor 1	Precursor 1 temperature	Precursor 2
Thermal Al2O3	Well characterized	Fiji1, Fiji2, Savannah	1 @ 200C	1%	Trimethylaluminum	Unheated	H20
Plasma Al2O3	Well characterized	Fiji1, Fiji2	1 @ 200C	0.50%	Trimethylaluminum	Unheated	O2 plasma
Thermal TiO2	Being characterized	Fiji1, Fiji2, Savannah	0.4	1%	Tetrakis(dimethylamido)titanium(IV)	75C	H20
Plasma TiO2	Being characterized	Fiji1, Fiji2	0.4	2%	Tetrakis(dimethylamido)titanium(IV)	75C	O2 plasma
Plasma TiN	Well characterized	Fiji1, Fiji2	0.5		Tetrakis(dimethylamido)titanium(IV)	75C	N2 plasma
Plasma WN	In development	Fiji1, Fiji2			Bis(ter- butylimino)bis(dimethylamino)tungsten(VI)	60C (TBD)	N2 plasma
Thermal HfO2	Well characterized	Fiji1, Fiji2, Savannah	1.0	1%	Tetrakis(dimethylamido)hafnium	75C	H2O
Plasma HfO2	Well characterized	Fiji1, Fiji2	1.0	1%	Tetrakis(dimethylamido)hafnium(IV)	75C	02
Thermal ZrO2	In development	Fiji1, Fiji2, Savannah	0.8	1%	Tetrakis(dimethylamido)zirconium(IV)	75C	H2O
Disconse							03

https://snf.stanford.edu/SNF/equipment/chemical-vapor-deposition/ald/savannah



SNF ALD Websites

HfO₂ Deposition rate of .99A/cycle for standard recipe

(Thanks to Woo-Shik Jung and for his help with data collection.)



Deposition rate of Hafnia ALD at 200C (note the native oxide of the Si wafer was also tracked and plotted on this graph)



Background Summary

- Atomic Layer Deposition can deliver thin films with
 - Very precise thickness control (~Angstroms)
 - Many materials (metals, dielectrics, magnetics...)
 - Highly conformal
 - Uniform over large areas
 - Engineerable into "meta-materials" with alternating layers
- Downside:
 - Slow slow slow
 - Not all chemistries are created equal
 - Nucleation



Any Questions?



The Cambridge Nanotech Savannah




Main Components of an ALD System

ALD Manifold





Writing a Recipe

- A sequential list of commands
- Basic recipe
 - Length of precursor pulse
 - Length of purge cycle
 - Temperature of reactor and other components
 - # of cycles

Step	command	#	Value	units
0	heater	8	200	С
1	heater	9	200	С
2	Flow		20	sccm
3	Pulse	0	0.02	Sec
4	wait		15	Sec
5	pulse	1	0.015	sec
6	Wait		15	Sec
7	goto	3	100	Cycles
8	flow		5	sccm



Other recipe variables

- Stabilize
 - Select a heater and a temperature
 - The system waits to proceed until the heater maintains that value for a few seconds
 - Allows consistent processing

- Stop-valve
 - Boolean command to control the gate valve to the pump
 - By temporarily valving off the pump you can leave the reactants in the chamber longer
 - This can enhance coverage of extreme aspect ratios (2000:1)



What you can tell from the pulse train



Missing pulses indicate a problem Most likely the precursor is out (should last 1000s of pulses before refilling/replacing)

Height above base pressure should be ~100mTorr for chamber saturation



Plasma Enabled (PE)ALD

• Remote Plasma as a reactant

- Widens ALD window for materials by decreasing activation energy
- Avoids precursor decomposition or damaging substrates with limited thermal budget
- Remote ICP source prevents substrate damage from ions
- Faster deposition cycle times
- Fewer contaminates in films
- Smaller nucleation delay
- Film Examples
 - Low temperature oxides
 - Metal nitrides
 - Metallic films

High-Aspect Ratio Structures

Radical recombination prevents greater than ~20:1



Fiji PE-ALD chamber



Benefits of Plasma

Decreased nucleation for metallic films

- Precursor temp 90°C
- Nucleation is eliminated when using O₂ plasma as reactant
- Constant growth rate per cycle even at low process temp



HARVARD Ex. 2115, p.42



The Cambridge Nanotech Fiji





Main Components of an ALD System





Writing a Recipe

- A sequential list of commands
- Basic recipe
 - Length of precursor pulse
 - Length of purge cycle
 - Temperature of reactors etc
 - Process gas flows
 - Plasma power
 - # of cycles

	Instruction		Value	Units	
0	flow	0	20	scom	Flow carrier gas (0) at 20 sccm
1	flow	1	40	scom	Flow plasma gas (1) at 40 sccm
2	heater	12	250	C	Set heater 12 (Cone heater) to 250°C
3	heater	13	250	C	Set heater 13 (Reactor Heater 1) to 250°C
4	heater	14	250	C	Set heater 14 (Reactor Heater 2) to 250°C
5	heater	15	250	C	Set heater 15 (Chuck heater) to 250°C
6	stabilize	12			Wait for heater 12 to stabilize at setpoint
7	stabilize	13			Wait for heater 13 to stabilize at setpoint
8	stabilize	14			Wait for heater 14 to stabilize at setpoint
9	stabilize	15			Wait for heater 15 to stabilize at setpoint
10	wait		300	sec	Wait 300 seconds (5 minutes for system to stabilize)
11	flow	0	60	scom	Increase carrier gas flow to 60 sccm
12	flow	1	200	scom	Increase plasma gas flow to 200 scom
13	MFCvalve	3	1		Open MIC valve # 3 (oxygen)
14	wait		20	sec	Wait 20 seconds
15	pulse	1	0.06	sec	Pulse ALD 1 for 0.06 seconds
16	wait		5	sec	Wait 5 seconds for carrier gas to flow through system
17	flow	3	20	scom	Flow MFC 3 (oxygen) at 20 sccm
18	wait		5	Sec	Wait 5 seconds
19	plasma		300	Watts	Set plasma power to 300 Watts
20	wait		20	sec	Wait 20 seconds
21	plasma		0	Watts	Turn off plasma power
22	flow	3	0	scom	Turn off MFC 3 (oxygen) gas flow
23	wait		5	sec	Wait 5 seconds
24	goto	15	200	cycles	Goto step 15 (pulse) and repeat steps 15-23. Repeat for a total of 200 time:
25	flow	0	20	scom	Reduce carrier gas to idle flow of 20 sccm
26	flow	1	40	scom	Reduce plasma gas flow to idle flow of 40 scom
27	MFCvalve	3	0		Close MFC valve # 3 (oxygen)

Parameter	Notes
Heater	Each heater has an unique item number and a value given in degrees Celsius. Do not overheat precursors (all precursors should be below 115C and some should not be heated at all - consult with quality circle if unsure). The reaction chamber should always be hotter than the manifold which should always be hotter than the precursor lines. The upper limits on temperature are protected by setpoints internal to the system.
Flow	This controls the flow of through a number of MFC. The plasma process gases are controlled by these MFCs as are the carrier gases. It is defined in sccm. It is not recommended to adjust the standard flow values in recipes. The MFCs for H ₂ , N ₂ , and O ₂ additionally have a hard off state and should be set to zero and then closed. This is already established in all recipes on the tool.
Pulse	This command is for pulsing a precursor line. It requires an ALD valve number and the amount of time you want the valve open in seconds. The fastest these valves can fire is roughly .015 seconds, so note that even if you define a shorter time that is likely the valve open time you will get. (NOTE: when writing a recipe the time in seconds needs a digit to the left of the decimal place; thus you should use "0.015" instead of ".015" for the minimum duration pulse.)
goto	Used to define loops in the recipes. This command takes as an input the step to which the recipe should return. The value for this command defines how many times the loop will run.
stabilize	This command is used to hold a recipe until a heater has reached the desired value. It takes as input a heater ID number and will wait until that heater demonstrates the set temperature with a degree C over a few seconds.
wait	This command takes as input a value in seconds that you would like the system to wait before proceeding to the next command. (NOTE: when writing a recipe the time in seconds needs a digit to the left of the decimal place; thus you should use "0.015" instead of ".015" for the minimum duration pulse.)
plasma	This command indicates the power that should be generated by the RF plasma system in Watts.
stopvalve	This command will close or open the output valve for the reaction chamber depending on a Boolean input. This command is currently not used in any of the standard recipes, but development is beginning for recipes using this feature.
line ac out	Users should not use this command. It changes the heater voltage on precursor heater wraps.



Other recipe variables

- Stabilize
 - Select a heater and a temperature
 - The system waits to proceed until the heater maintains that value for a few seconds
 - Allows consistent processing

- Stop-valve
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What you can tell from the pulse train





Final thoughts

- The field is rapidly changing
 - More precursors
 - More materials
 - More variations
 - More applications
- Like most Nanofabrication...
 - Best chance for success is to get in the lab and push experiments
- Some resources:
 - <u>www.cambridgenanotech.com</u>
 - <u>snf.stanford.edu/SNF/equipment/chemical-vapor-deposition/ald/</u>
 - <u>https://snf.stanford.edu/SNF/equipment/chemical-vapor-deposition/ald/fiji-l</u>
 - jprovine@stanford.edu; mmrincon@stanford.edu



Thank you.

Any Questions?

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