Understanding Atomic Layer Deposition:
Successes & Limitations and Recipe Development

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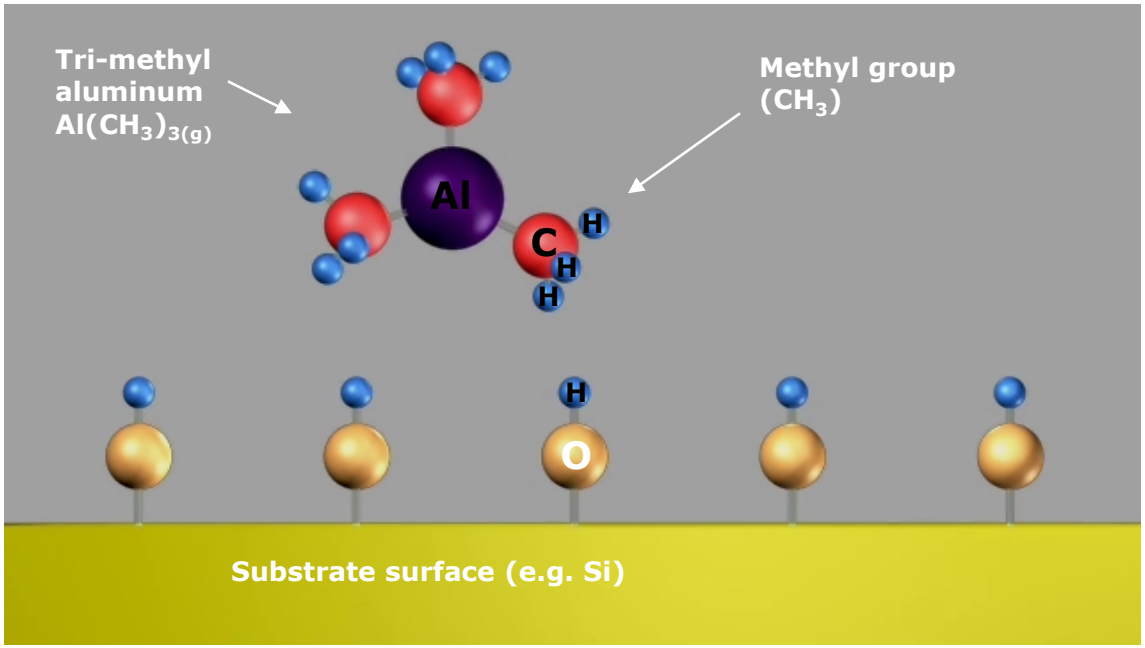
Stanford University
NNIN ALD Roadshow
(special thanks to Ganesh Sundaram, Eric Deguns, Prof. H. Brongersma, and Prof. Fritz Prinz)

What is ALD? aka How does it work?

- First let's look atomistically.
  - A rose by any other name…
- Then we'll look at what that means in ways we can measure.
  - Microscopically? Nanoscopically? *Angstroscopically*?
- Then briefly back at the atomic level to see behind the curtain.

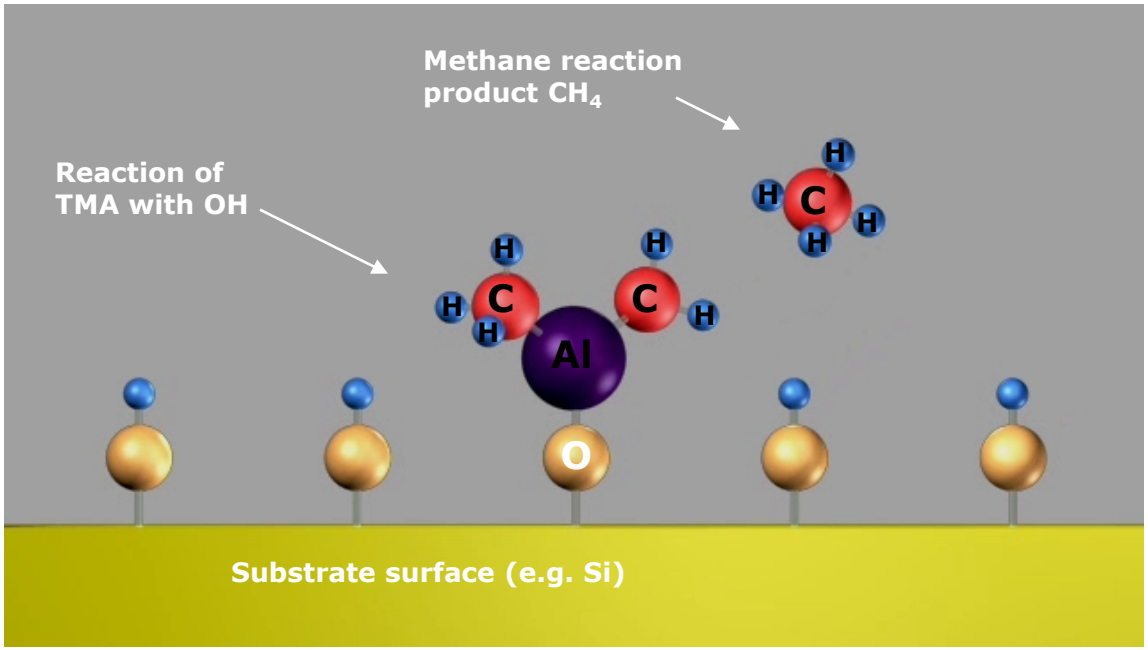
ALD Example Cycle for Al_2O_3 Deposition



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.

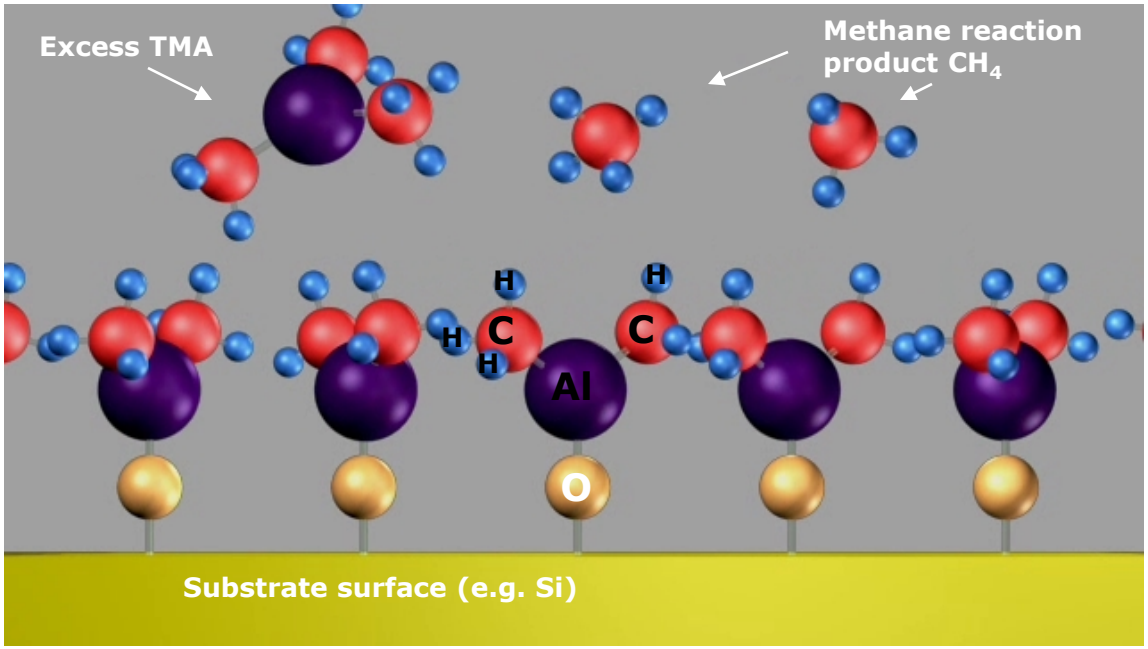
ALD Cycle for Al_2O_3



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

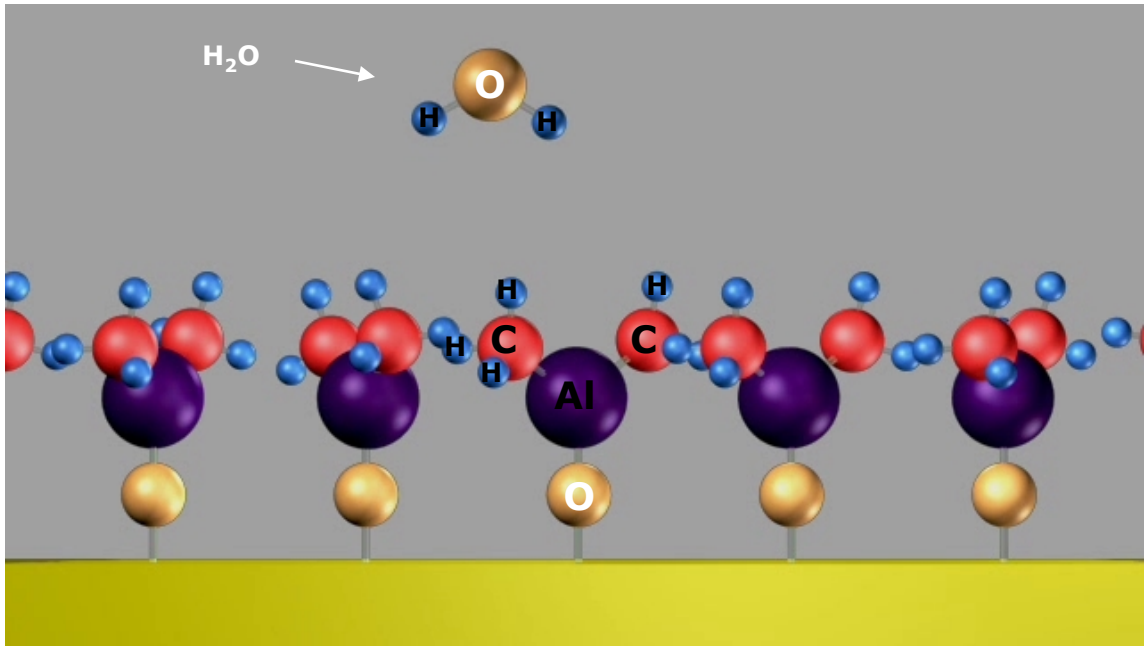
$$Al(CH_3)_{3\,(g)} + :Si\text{-}O\text{-}H_{\,(s)} \longrightarrow :Si\text{-}O\text{-}Al(CH_3)_{2\,(s)} + CH_4$$

ALD Cycle for Al_2O_3



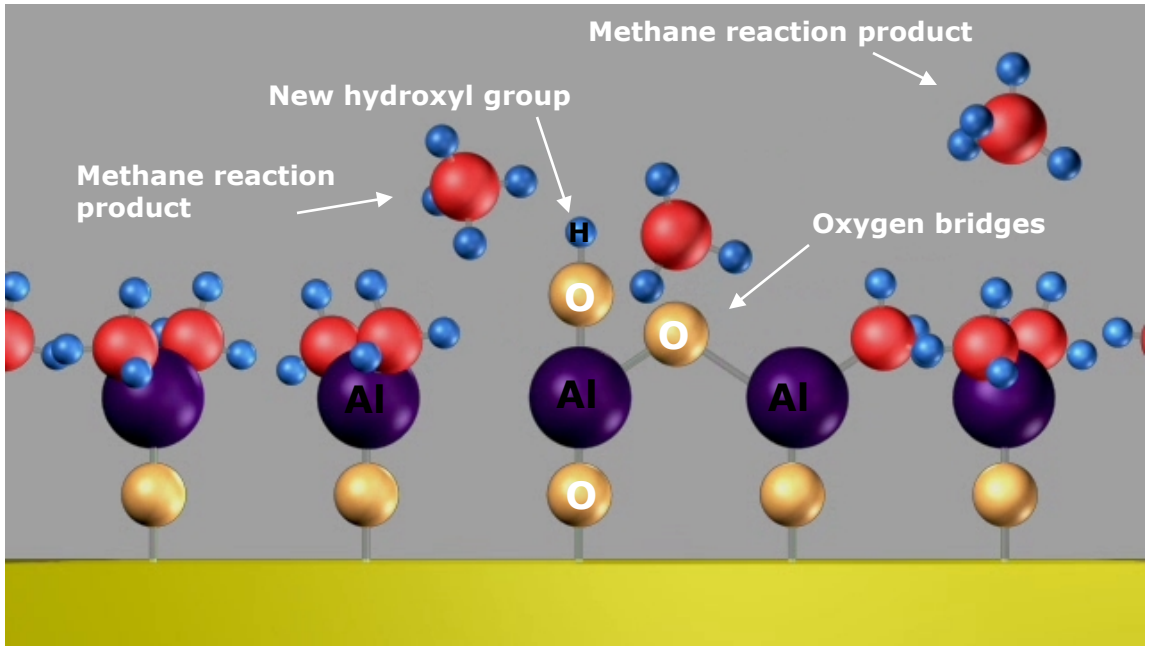
Trimethyl Aluminum (TMA) reacts with the adsorbed hydroxyl groups, until the surface is passivated. TMA does not react with itself, terminating the reaction to one layer. This causes the perfect uniformity of ALD. The excess TMA is pumped away with the methane reaction product.

ALD Cycle for Al_2O_3



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

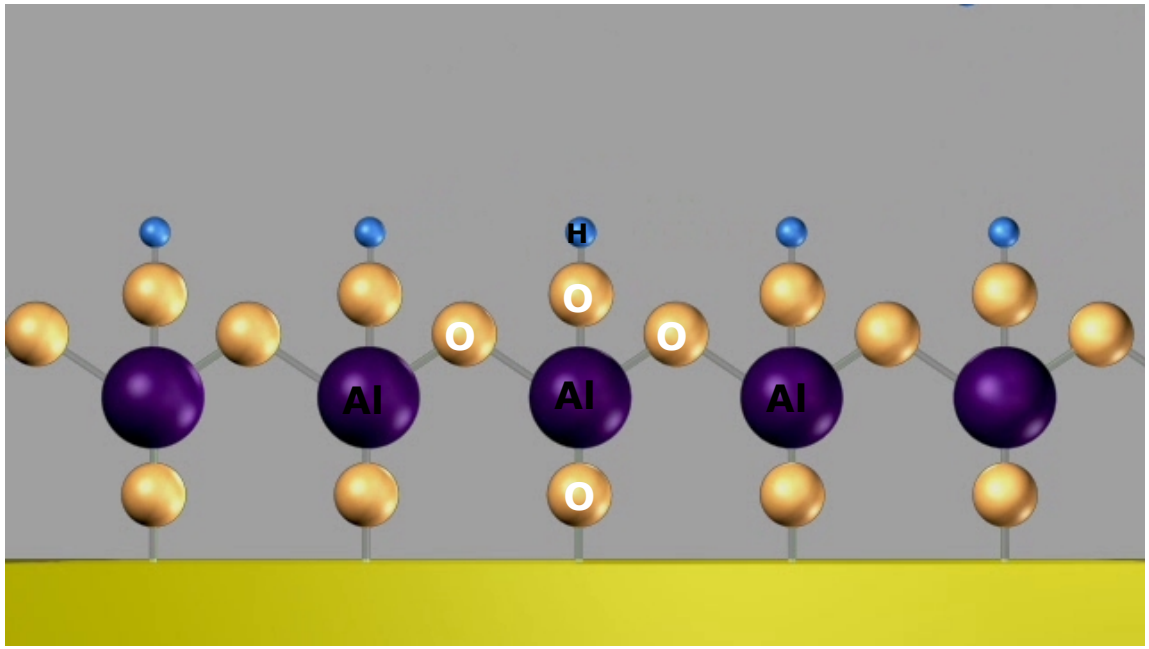
ALD Cycle for Al_2O_3



H_2O reacts with the dangling methyl groups on the new surface forming aluminum-oxygen (Al-O) bridges and hydroxyl surface groups, waiting for a new TMA pulse. Again metane is the reaction product.

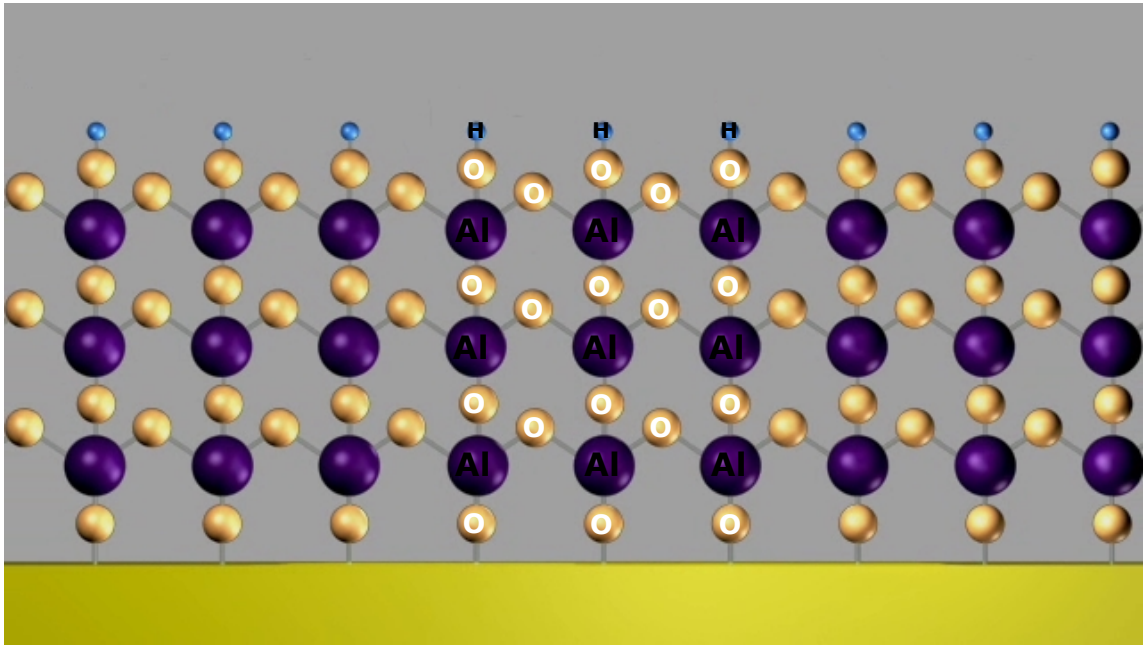
$$2\ H_2O_{(g)} + :Si\text{-}O\text{-}Al(CH_3)_{2\ (s)} \longrightarrow :Si\text{-}O\text{-}Al(OH)_{2\ (s)} + 2\ CH_4$$

ALD Cycle for Al_2O_3



The reaction product methane is pumped away. Excess H_2O vapor does not react with the hydroxyl surface groups, again causing perfect passivation to one atomic layer.

ALD Cycle for Al_2O_3



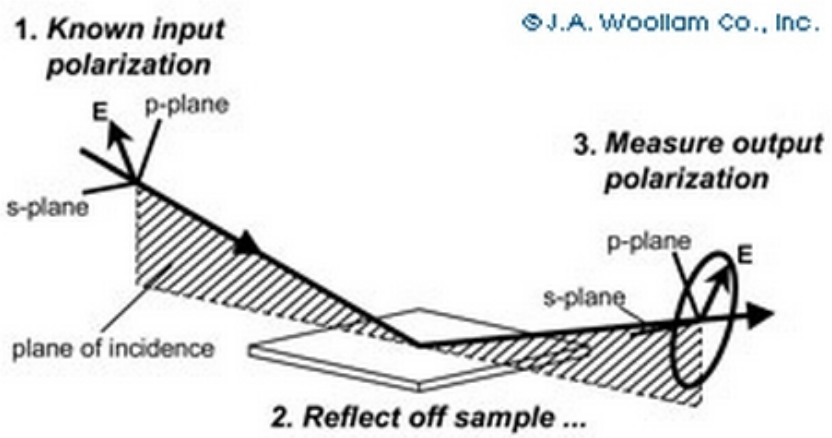
One TMA and one H_2O vapor pulse form one cycle. Here three cycles are shown, with approximately 1 Angstrom per cycle. Each cycle including pulsing and pumping takes e.g. 3 sec.

Two reaction steps in each cycle:

$$Al(CH_3)_{3\,(g)} + :Al\text{-}O\text{-}H_{\,(s)} \longrightarrow :Al\text{-}O\text{-}Al(CH_3)_{2\,(s)} + CH_4$$

$$2\,H_2O_{\,(g)} + :O\text{-}Al(CH_3)_{2\,(s)} \longrightarrow :Al\text{-}O\text{-}Al(OH)_{2\,(s)} + 2\,CH_4$$

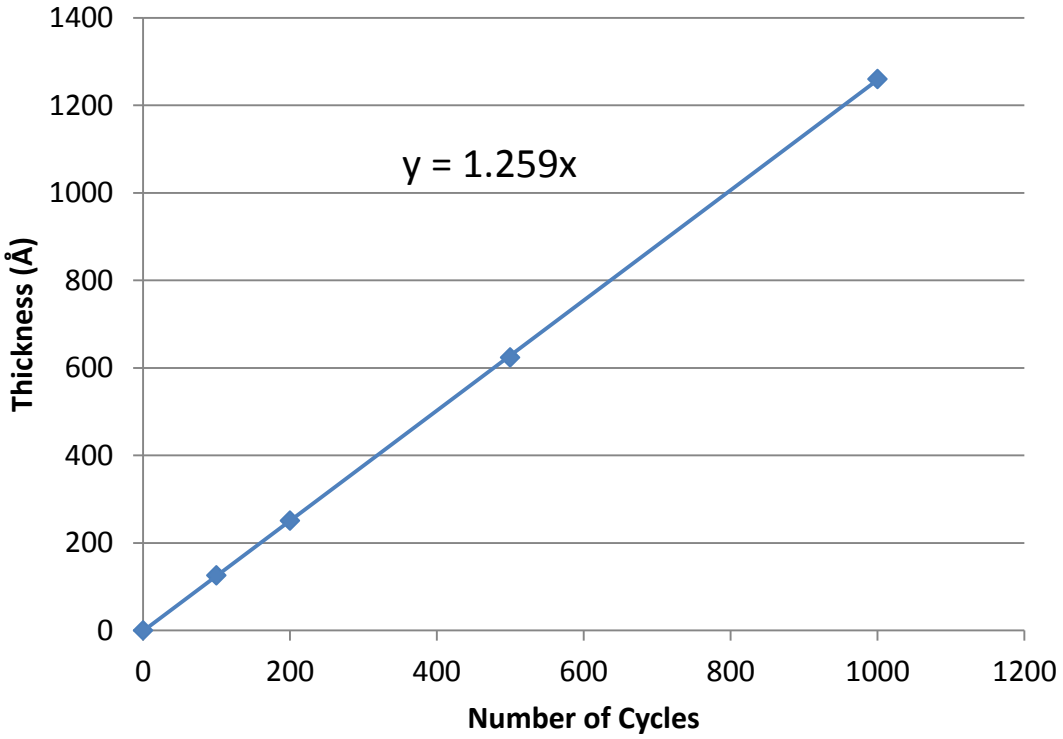
Measurement Technique: Ellipsometry



- Measure change in reflected polarization
- Fast and extremely accurate (<1Å) if material model is known
- Stacks of varying films and absorptive films can cause issues
- Average over a large area

Microscopically (Nanoscopically?) What makes a deposition ALD?

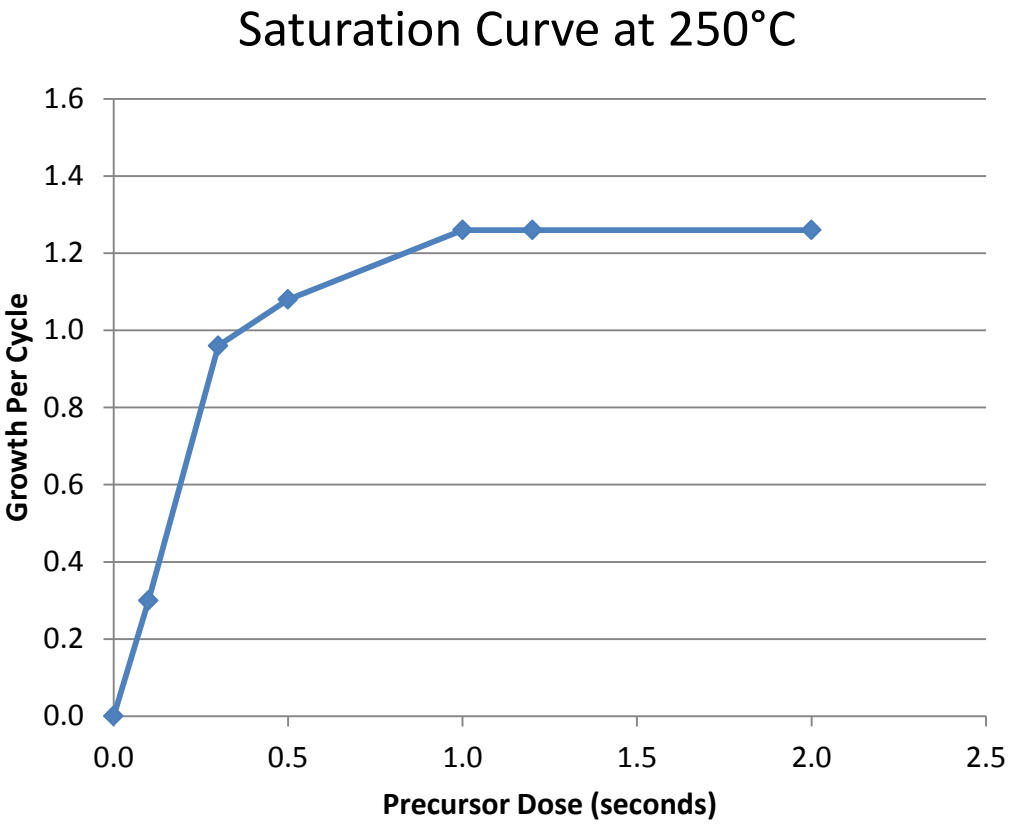
- Step One: Linear growth rate



- Is anything wrong here?

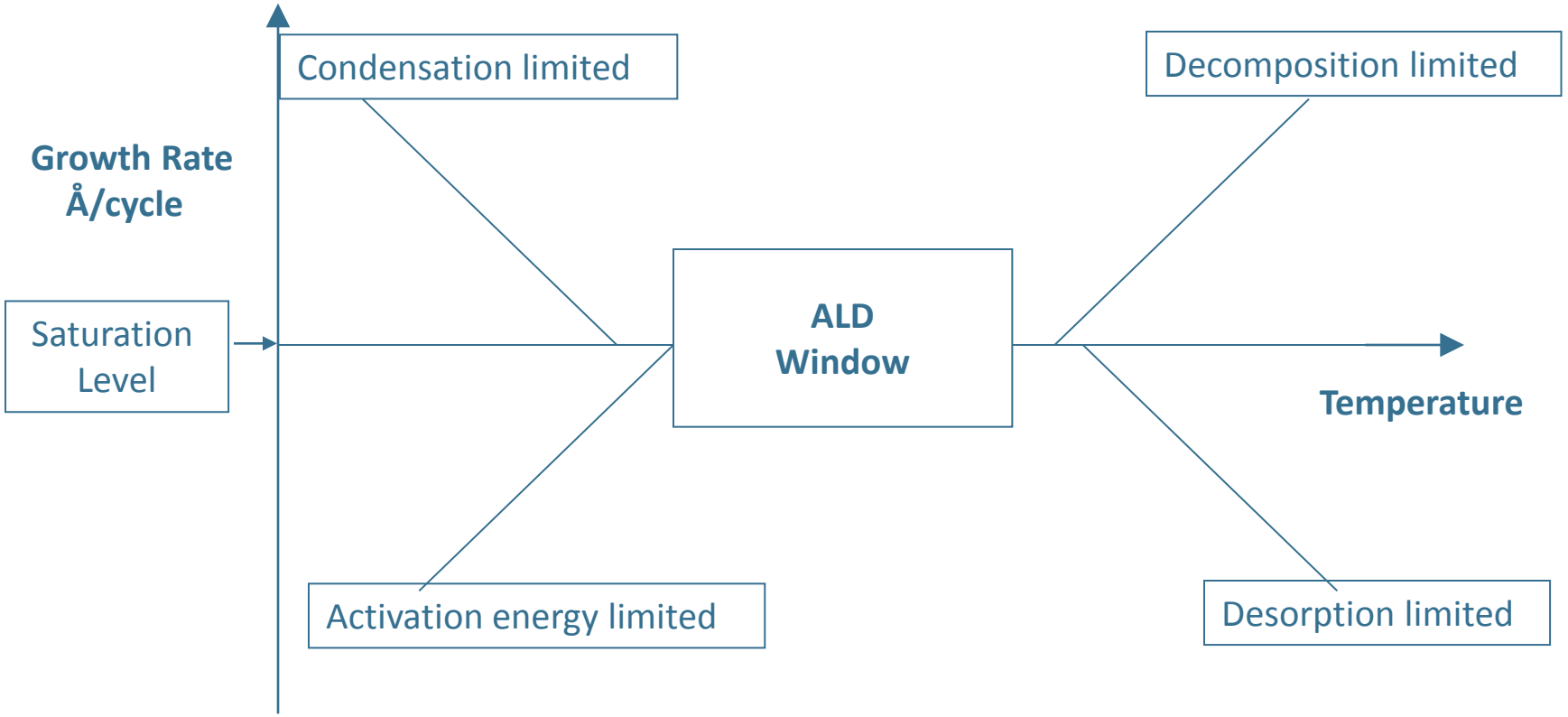
Microscopically (Nanoscopically?) What makes a deposition ALD?

- Step Two: Self-limiting deposition/cycle

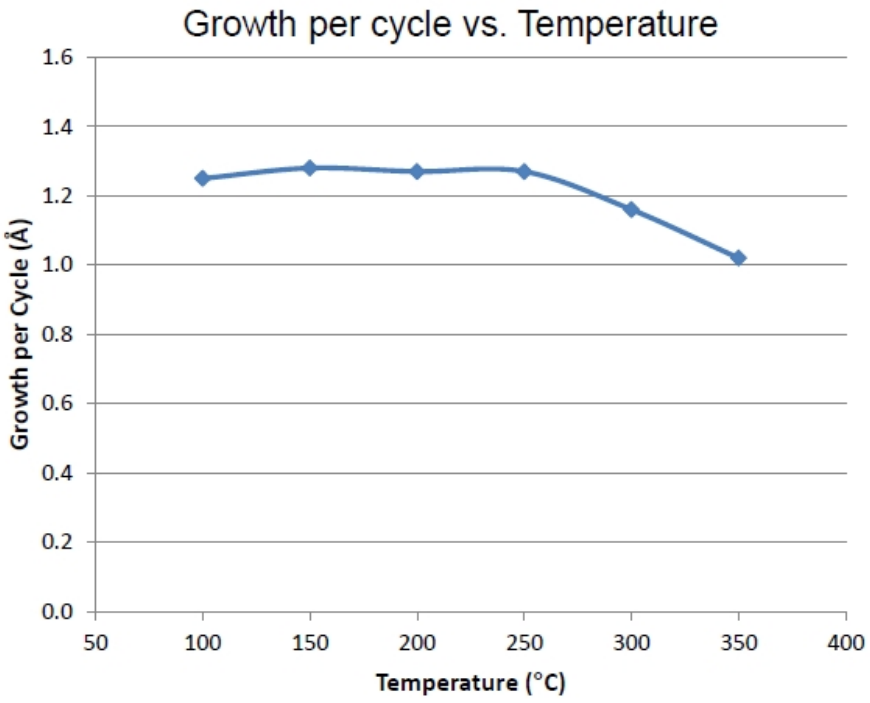


ALD “Window”

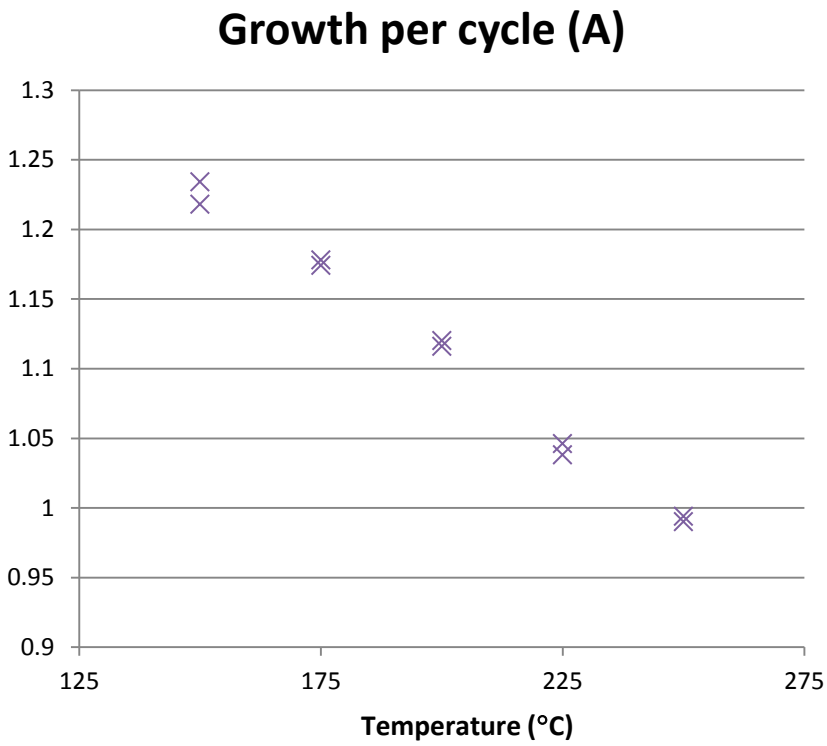
Each ALD process has an ideal process “window” in which growth is saturated at a monolayer of film.



Outside the ALD Window



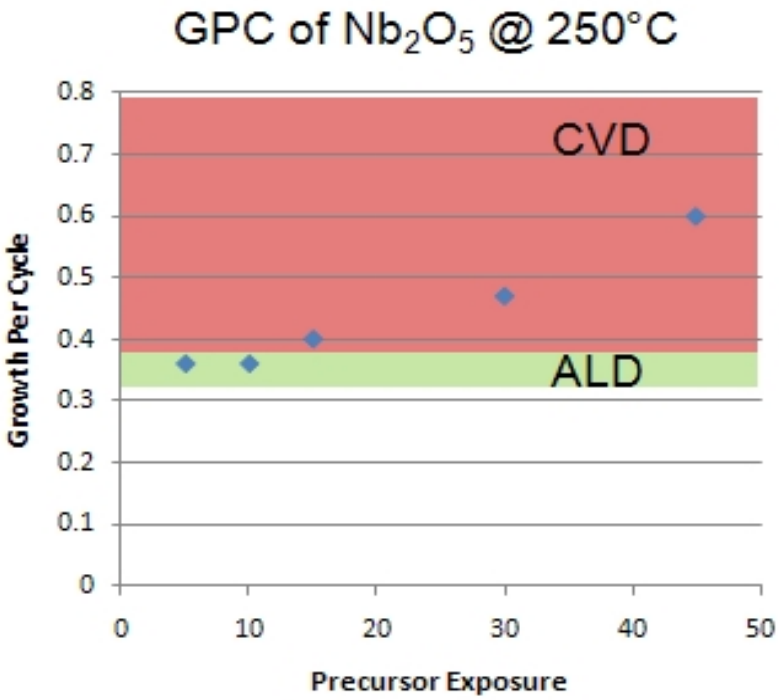
Thermal Alumina



Plasma Hafnia

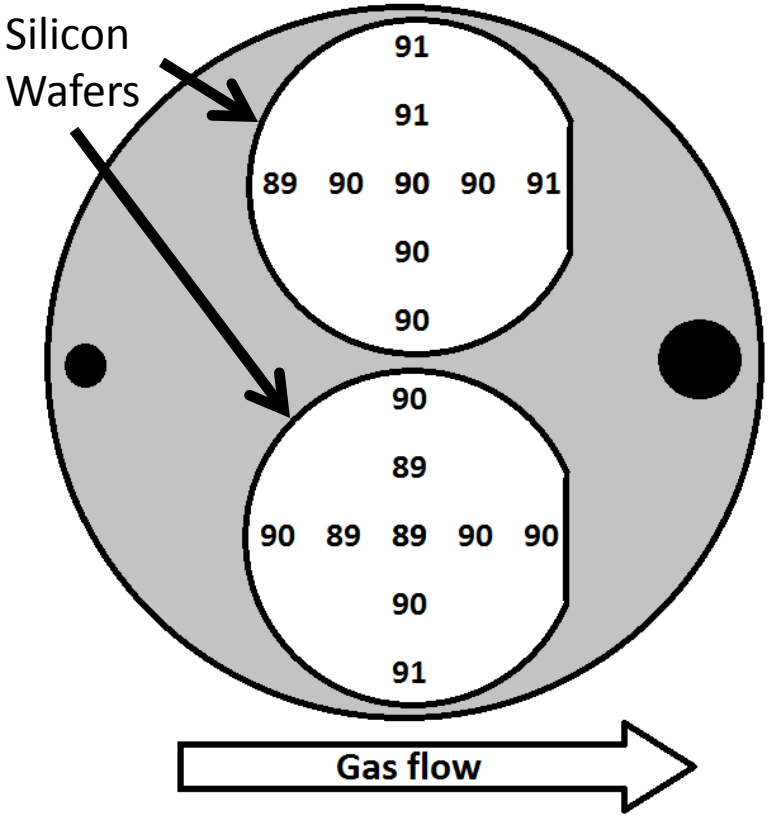
Outside the ALD Window

- If not all of the reactants are removed from the chamber during the purge…
- An easy indication of this is a loss in film uniformity.

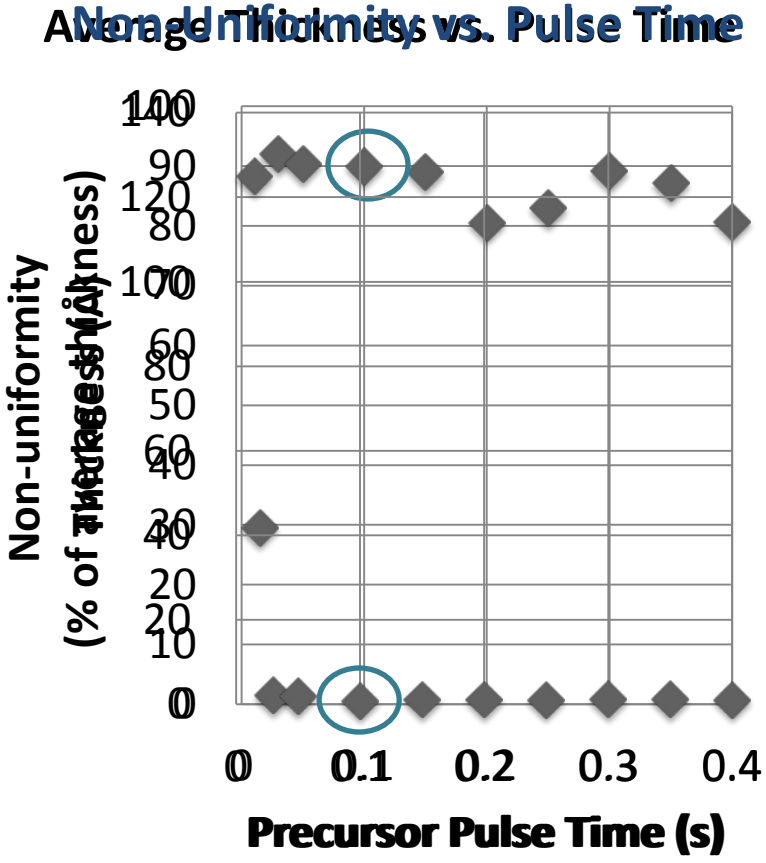


ZrO_2 Uniformity Optimization

Normal Chamber Thickness Map

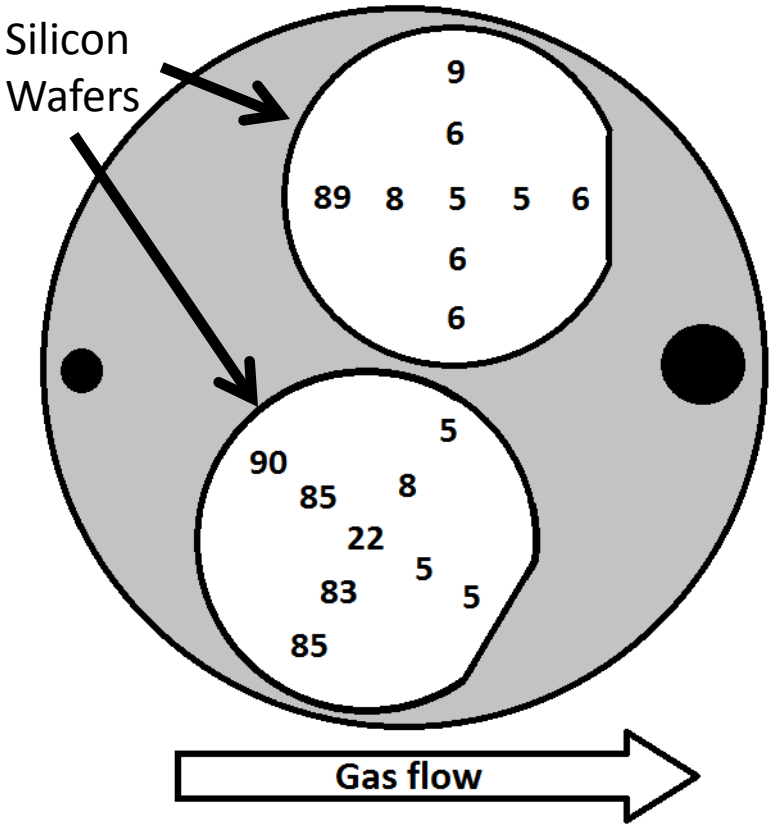


Measurements in Angstroms



ZrO_2 Uniformity Optimization

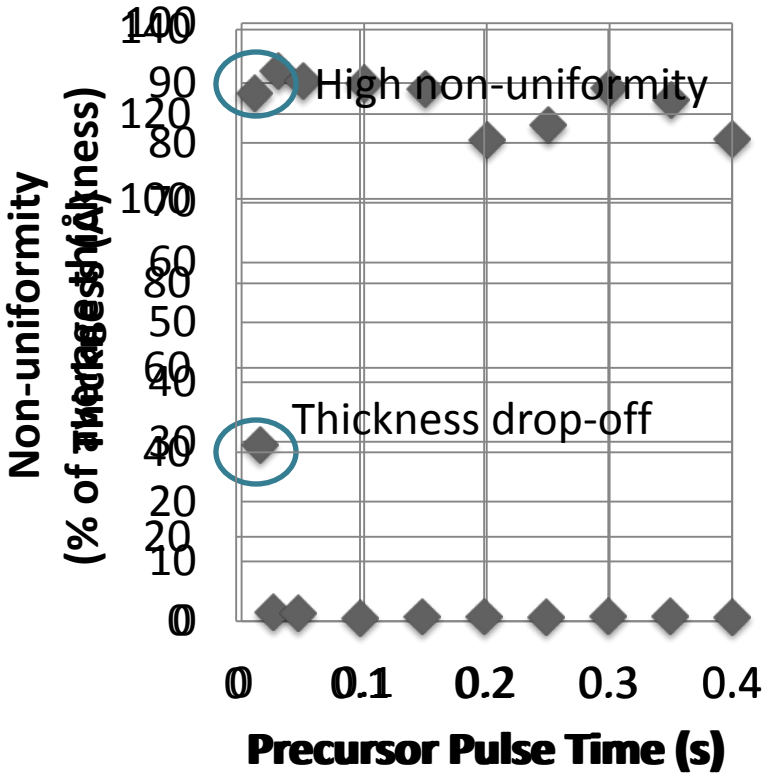
Under-Dosed
Chamber Thickness Map



Measurements in Angstroms

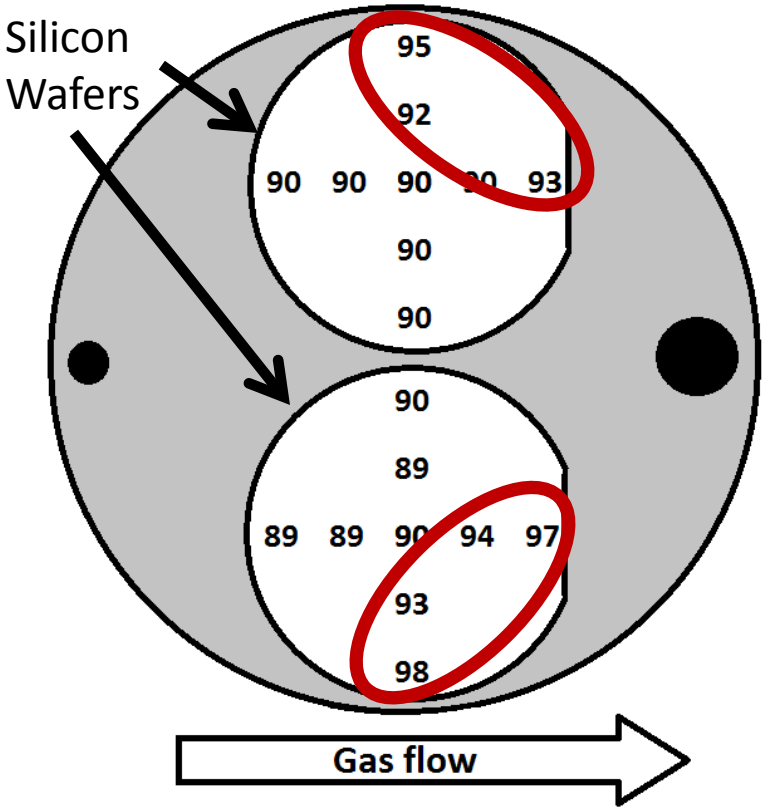
Average Thickness vs. Pulse Time

Non-Uniformity vs. Pulse Time



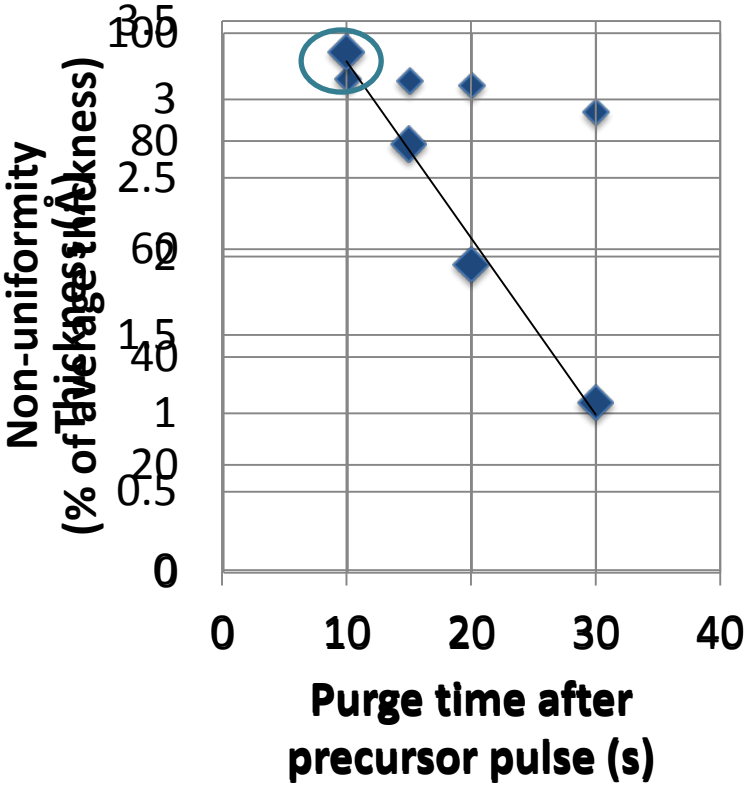
ZrO_2 Uniformity Optimization

Chemical Vapor Deposition (CVD) Chamber Thickness Map



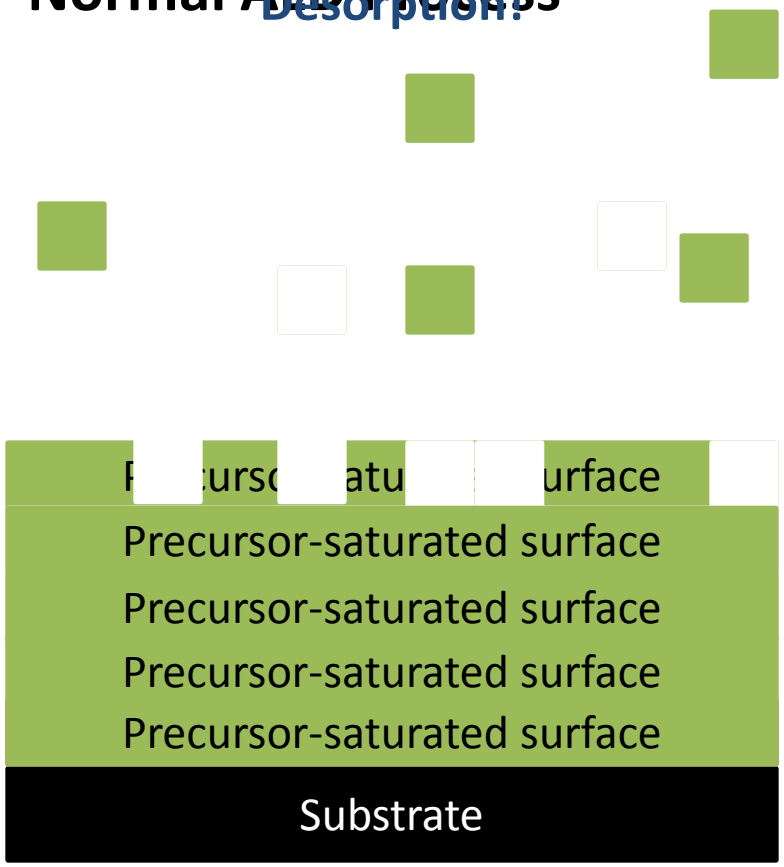
Measurements in Angstroms

Average Thickness vs. Purge Time

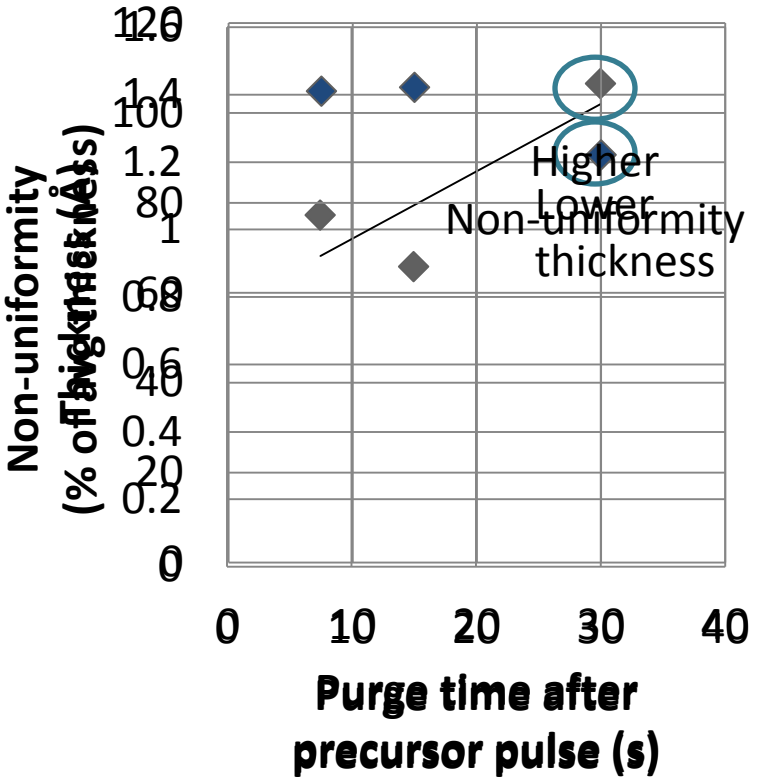


HfO_2 Uniformity Optimization

Normal ALD Process

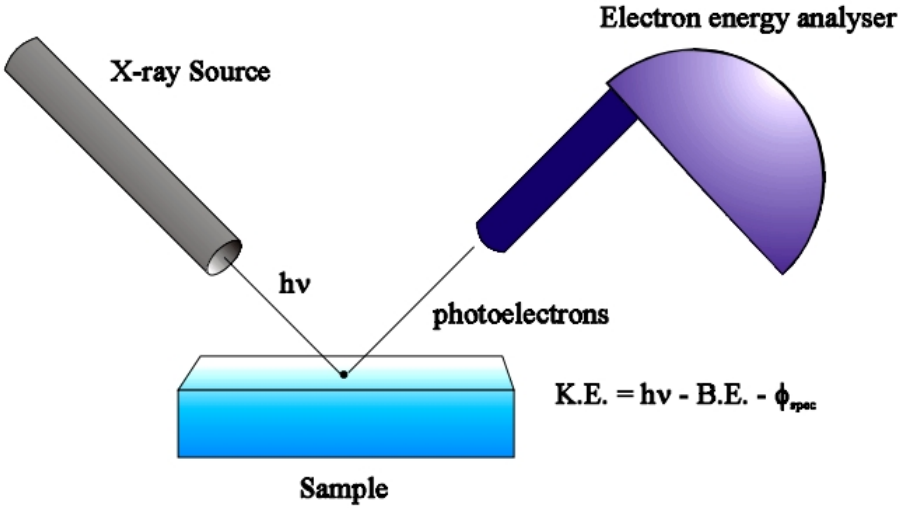


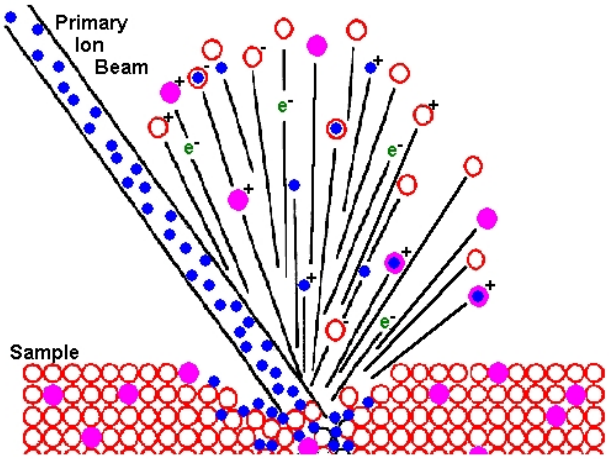
Non-Uniformity vs. Pulse Time



Purge time is too long

What is going on atomistically?



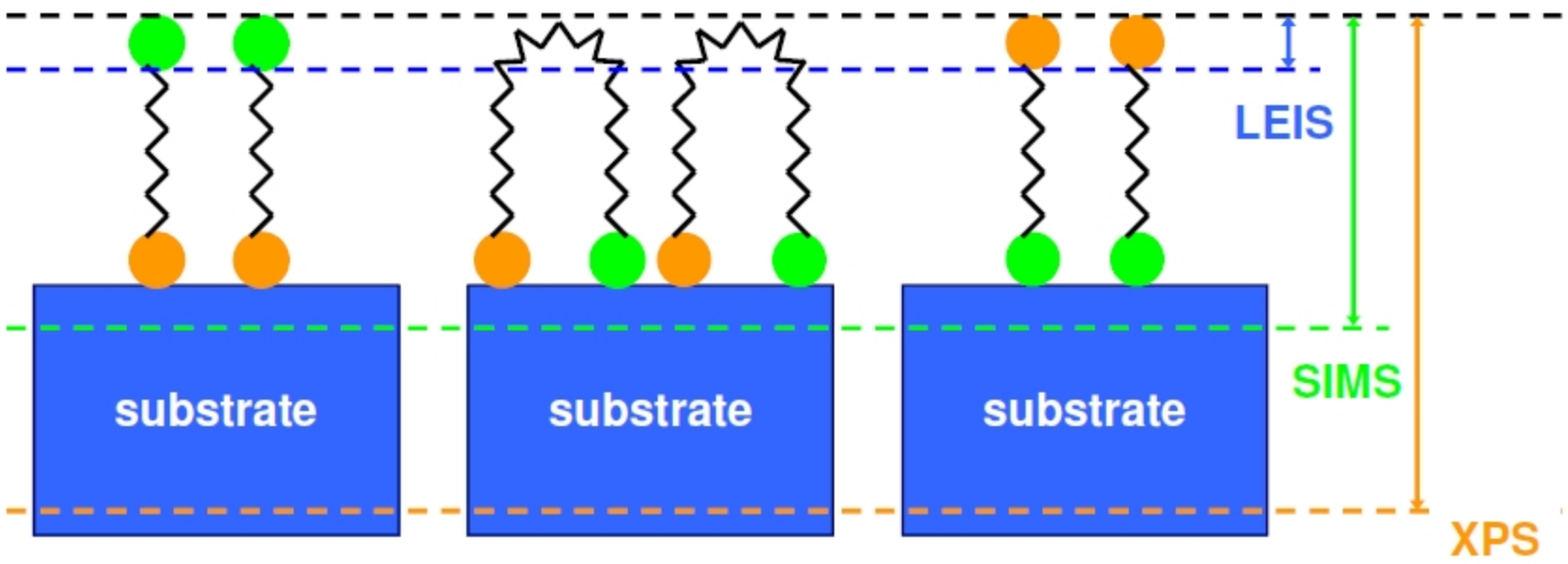


- Compositional analysis
  - Very complete material map
  - Accuracy .1-10% depending on material
- Weighted average over a depth of ~10nm
- Lateral spot size is typically >10µm (system dependent)

- Secondary ions emitted from the surface (and sub-surface)
- Extremely accurate trace contamination
- Depth profiling
- Significant damage to surface
- Interface mixing

What is going on atomistically?

We need a technique to look 1 atom deep.

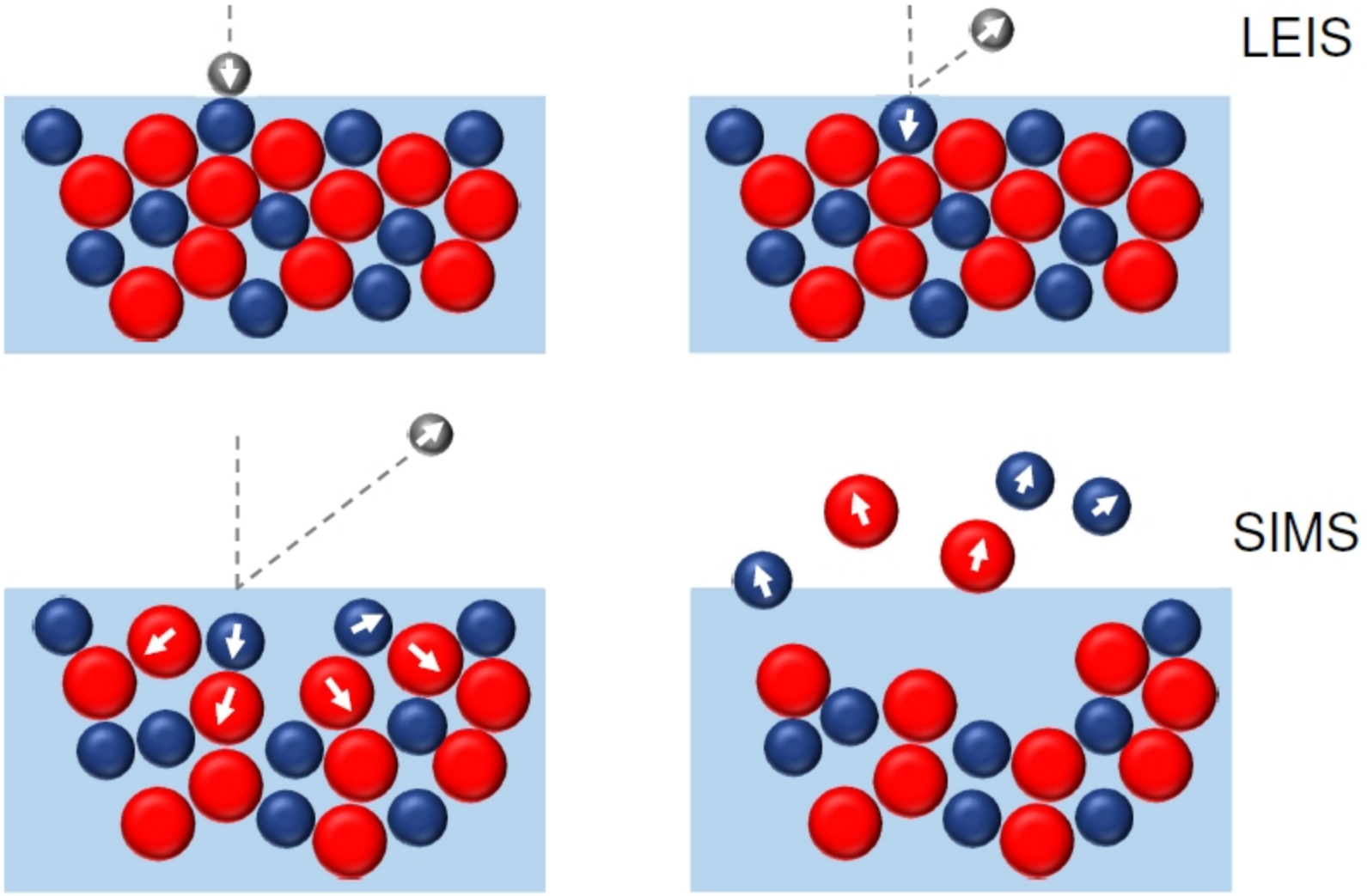


LEIS 1st atom and in-depth; quantitative, sensitive

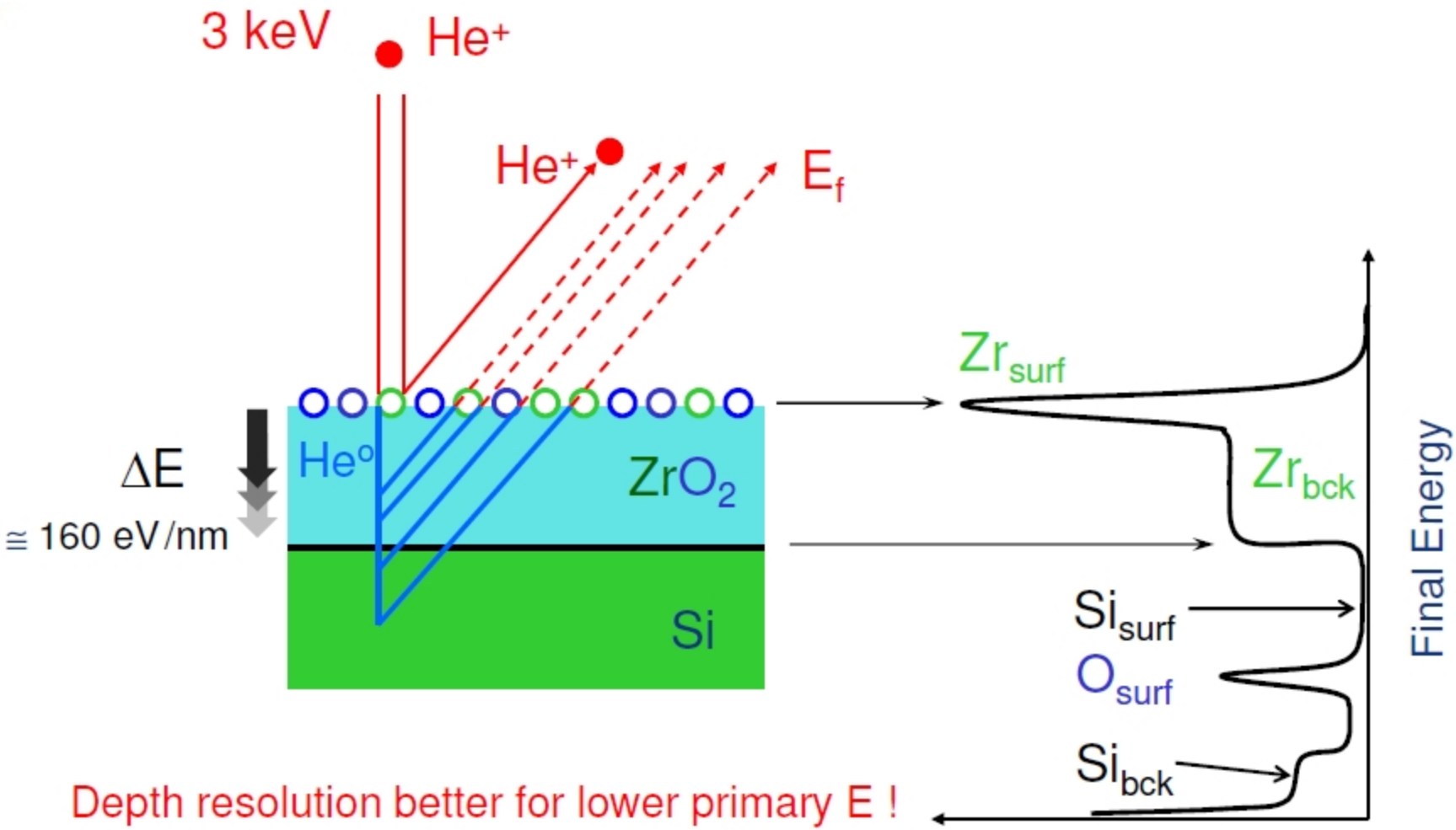
SIMS not quantitative for near-surface / interface

XPS average over 3 – 10 nm; chemical info

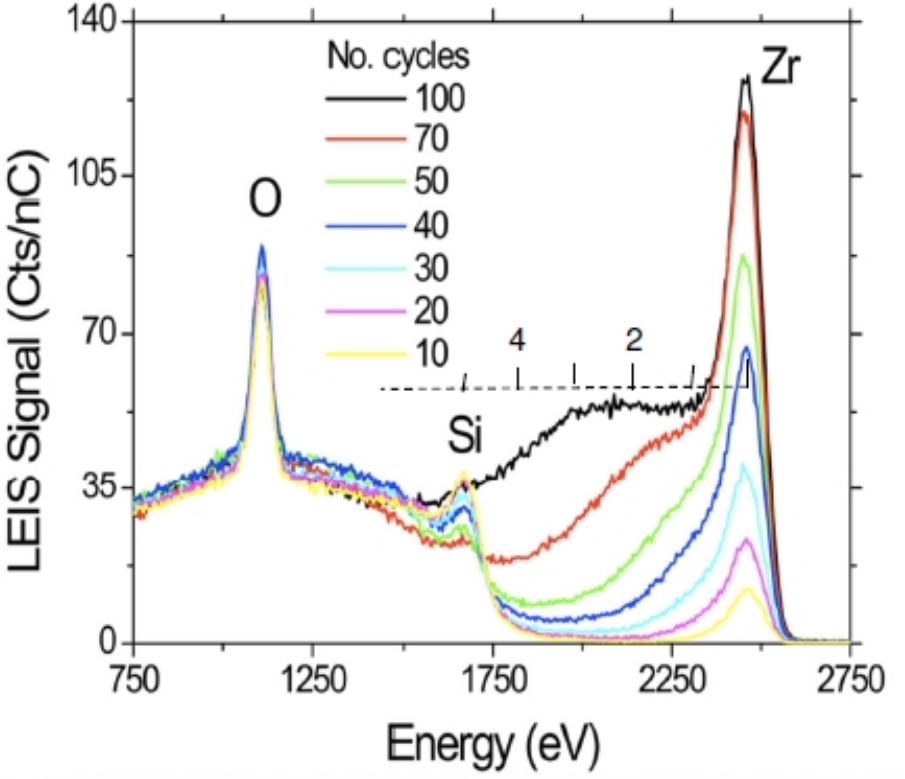
LEIS and The Hypocratic Oath

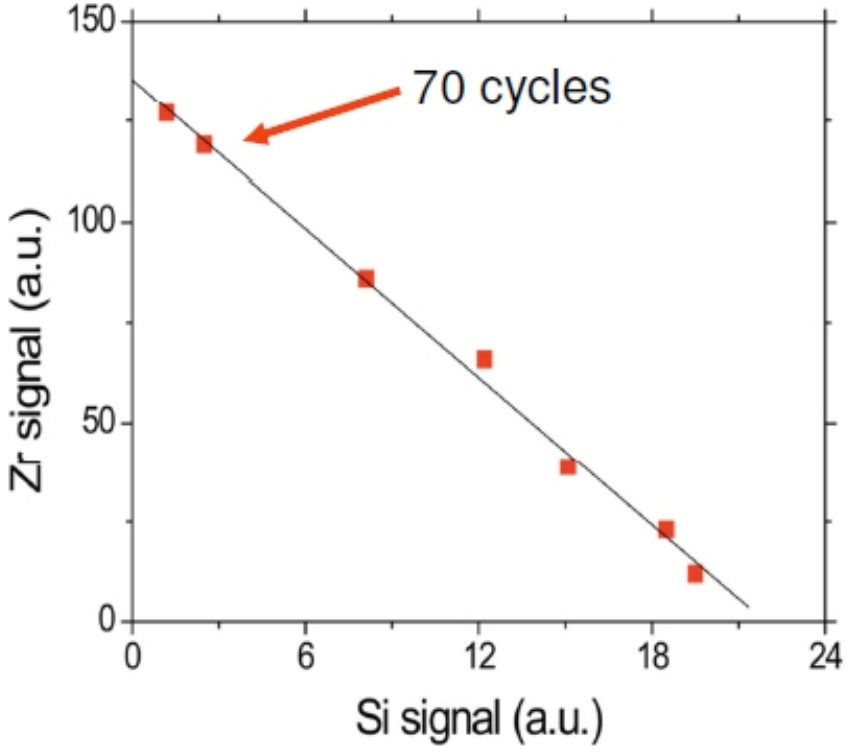


LEIS on an ALD film of ZrO_2



LEIS on an ALD film of ZrO_2

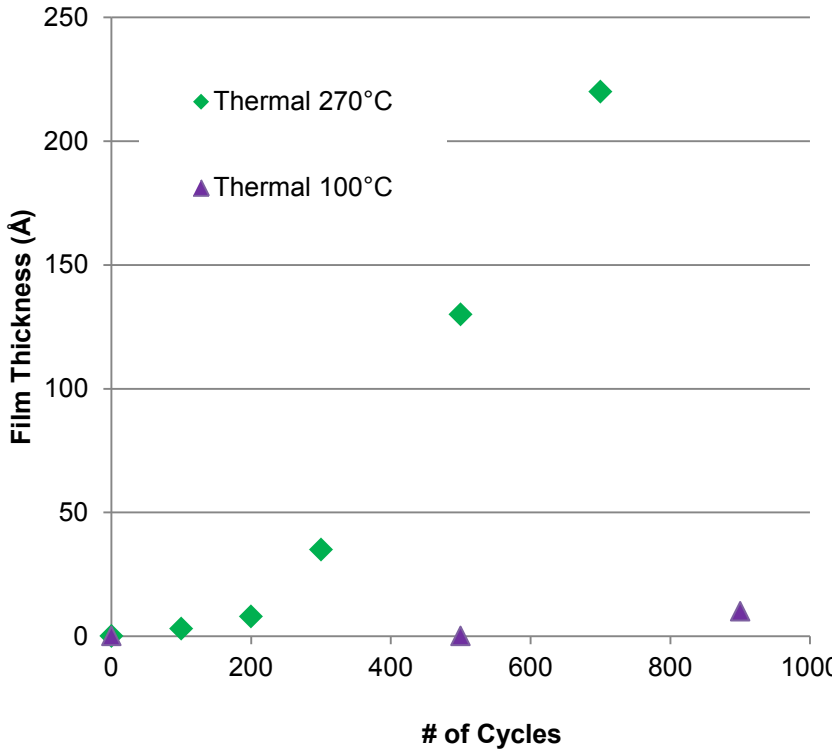


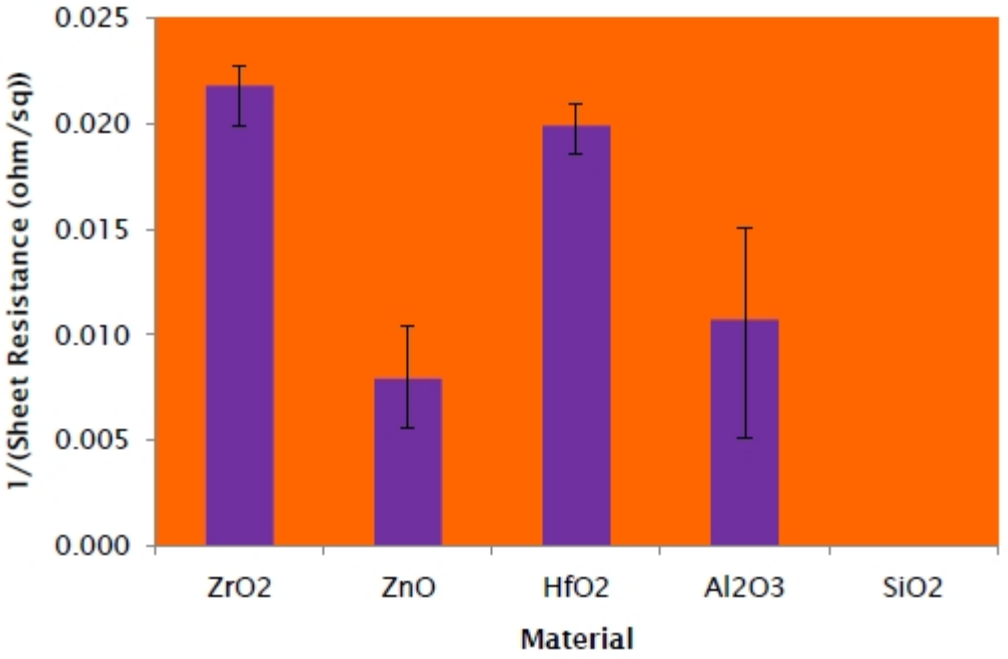


The little secret of ALD…if you know this, you know more than 90% of the people I've talked to about ALD.

Platinum Nucleation

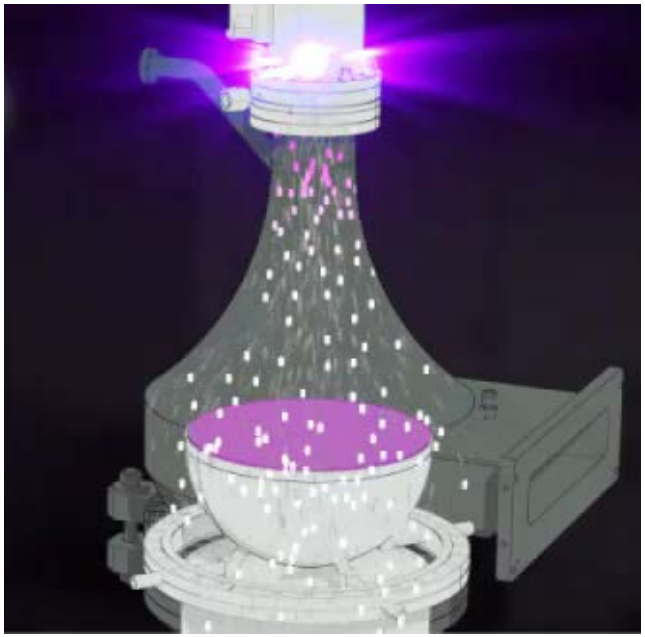
Pt from $MeCpPtMe_3$ and O_2





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

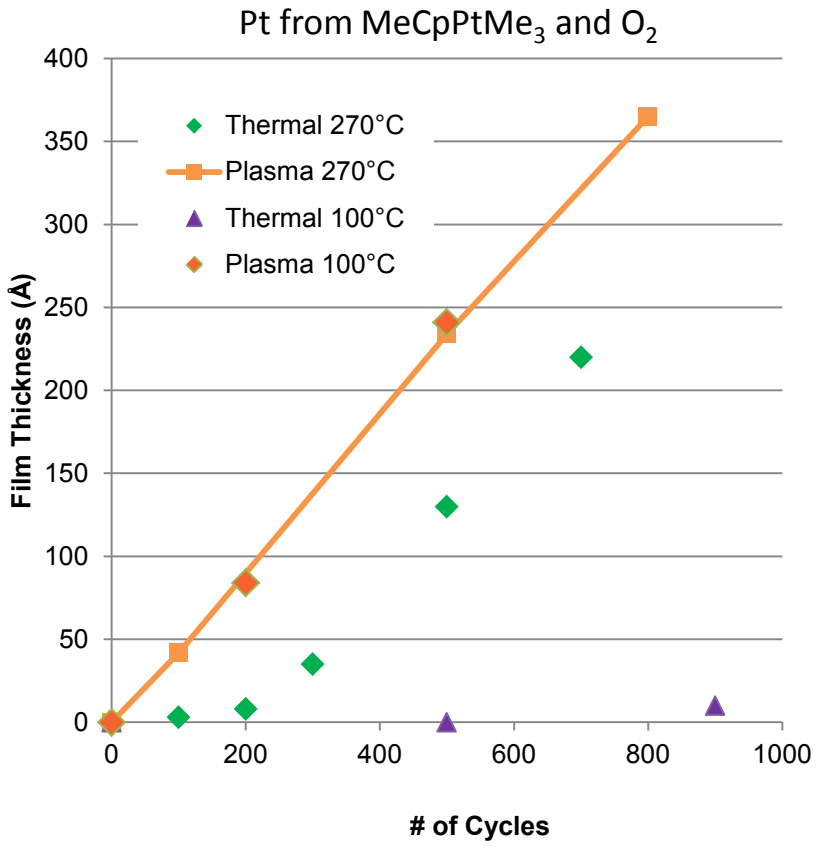


Fiji PE-ALD chamber

Benefits of Plasma

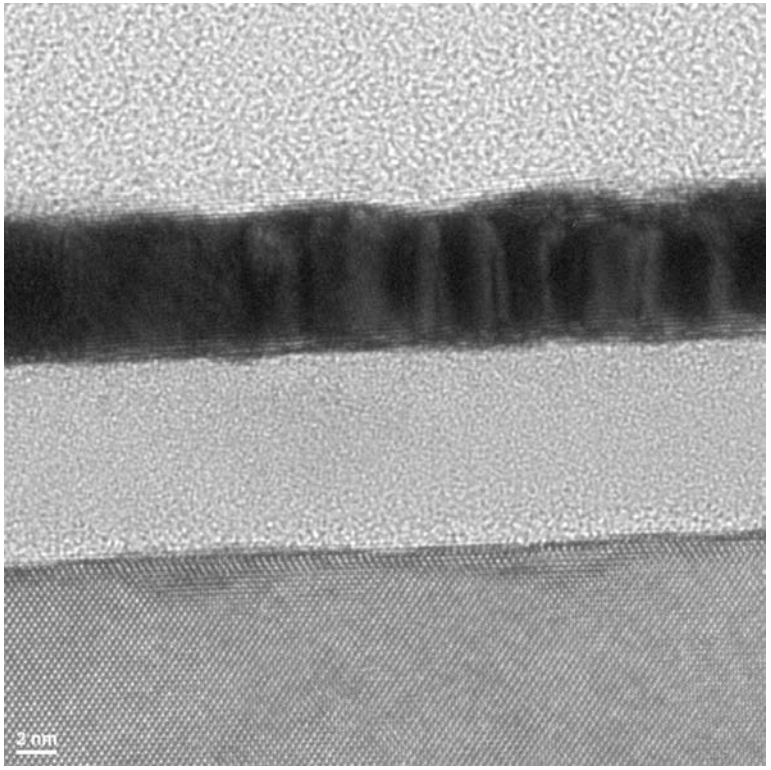
Decreased nucleation for metallic films

- Precursor temp 90°C
- Nucleation is eliminated when using O_2 plasma as reactant
- Constant growth rate per cycle even at low process temp

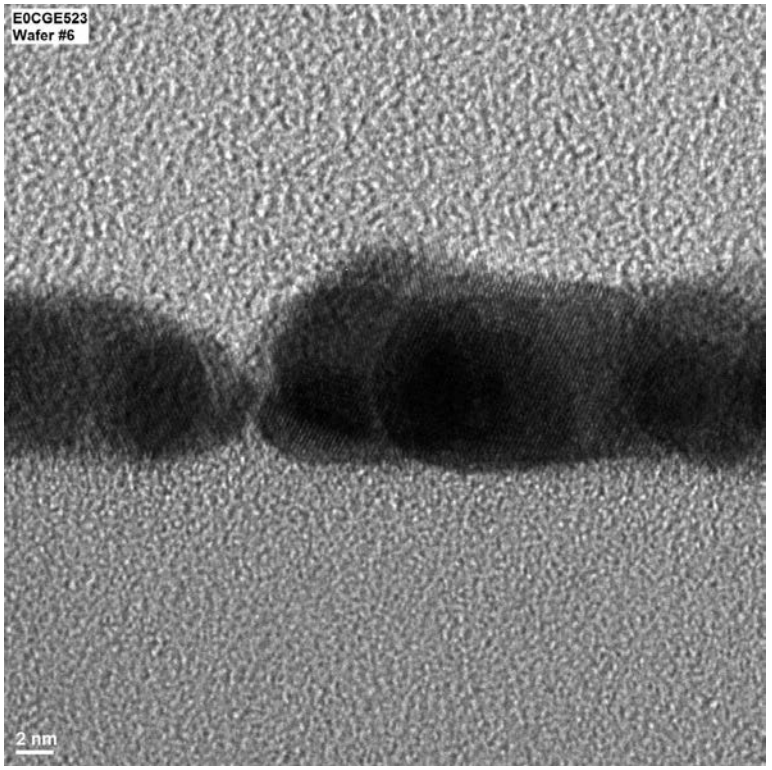


Pt Nucleation

Pt from $MeCpPtMe_3$ and O_2
Thermal vs Plasma ALD



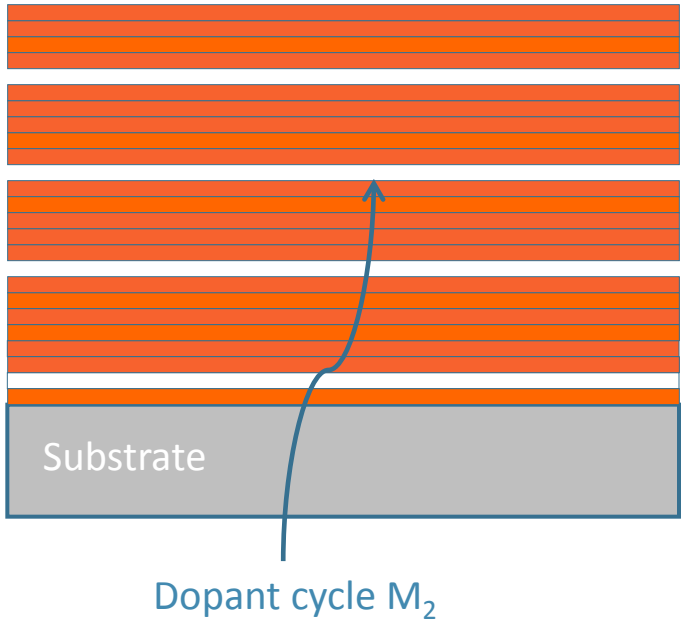
Plasma ALD Pt on Al_2O_3



Plasma ALD Pt on thermal SiO_2

Nanolaminate Formation / Doping

- "Doping" in ALD
  - Doping is carried out by substituting a pulse of precursor M_1 with dopant precursor M_2
  - This allows exploration of a wide concentration window without having to prepare new targets for each concentration (as in sputtered depositions)
  - Grated films with uniform properties possible
  - Annealing films to "activate" dopants is not required



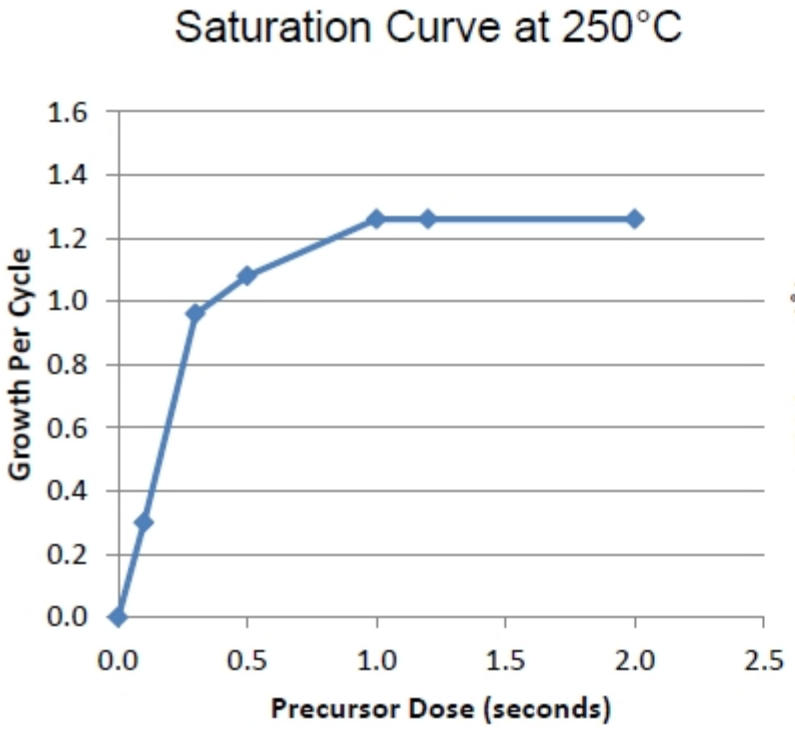
Summary

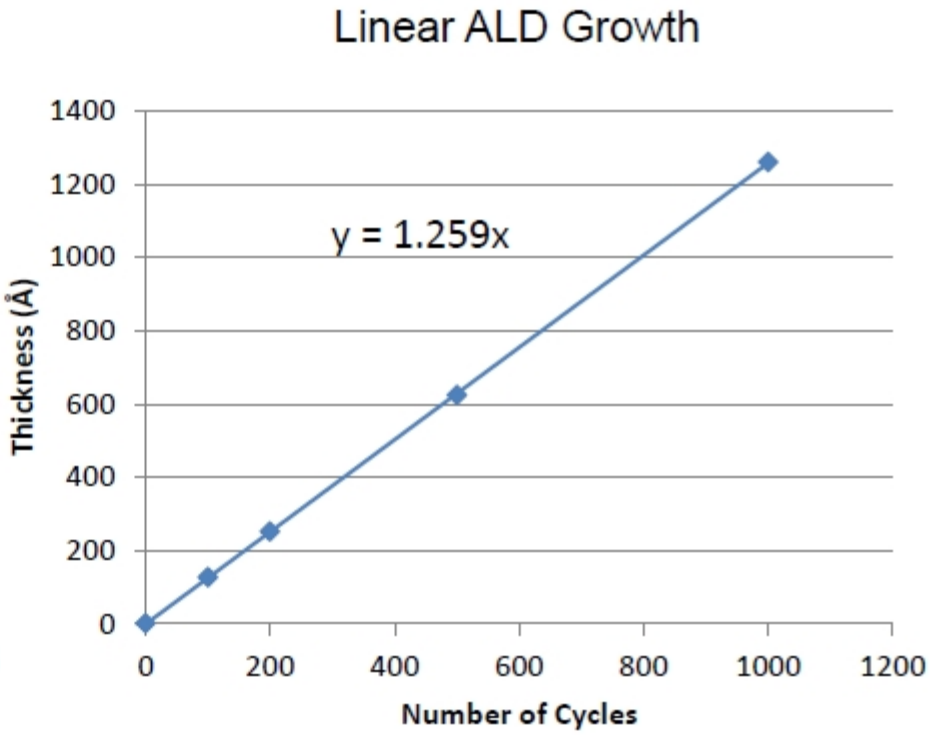
- The Canonical view of ALD is valuable for understanding, but it does not provide full understanding
- A more complete understanding is useful
  - Selective deposition
  - Surface preparation
  - Troubleshooting
- For analysis there is no magic bullet
  - Best to heavily armed
  - The right analysis for your interest

Questions?

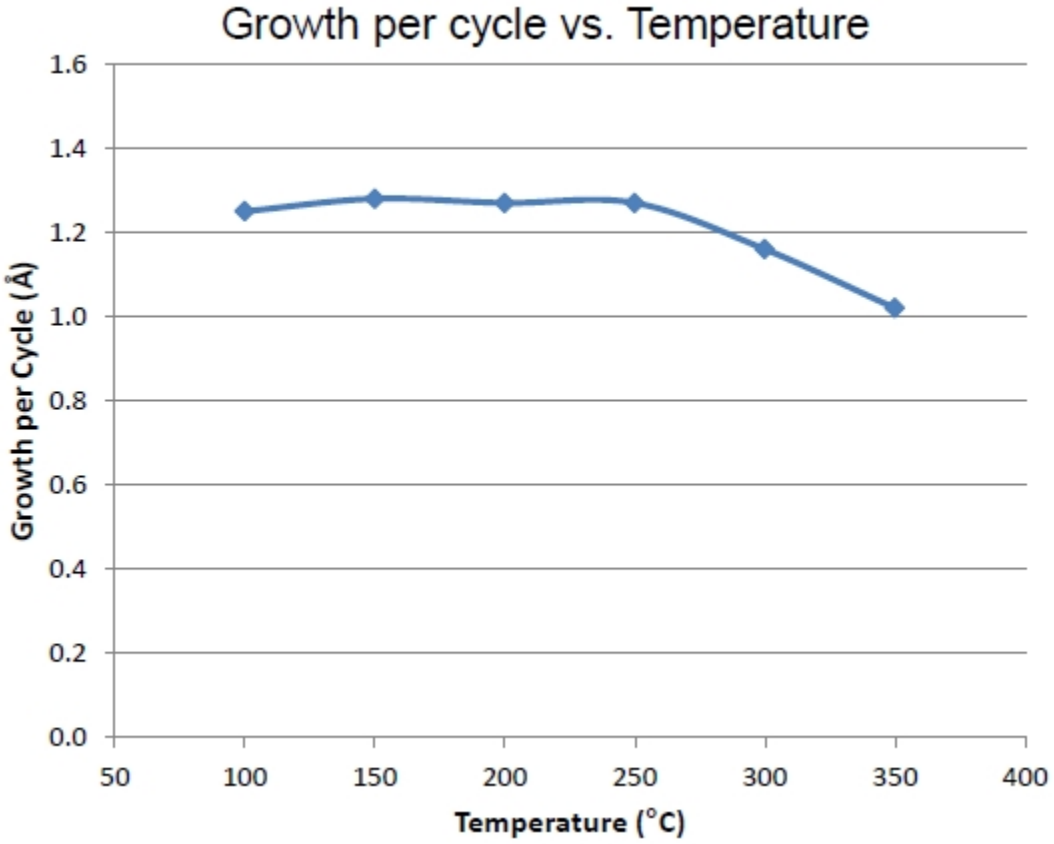
On to Process Development

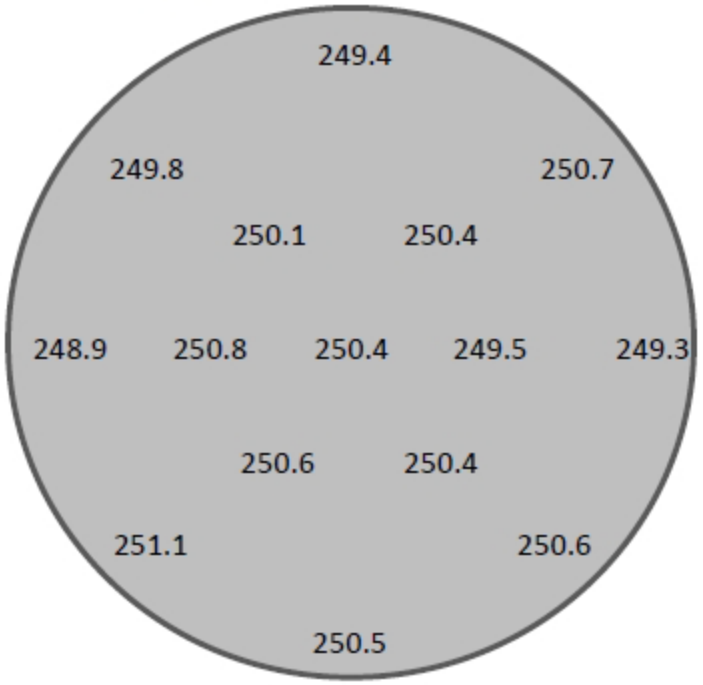
High quality recipe example: MgO





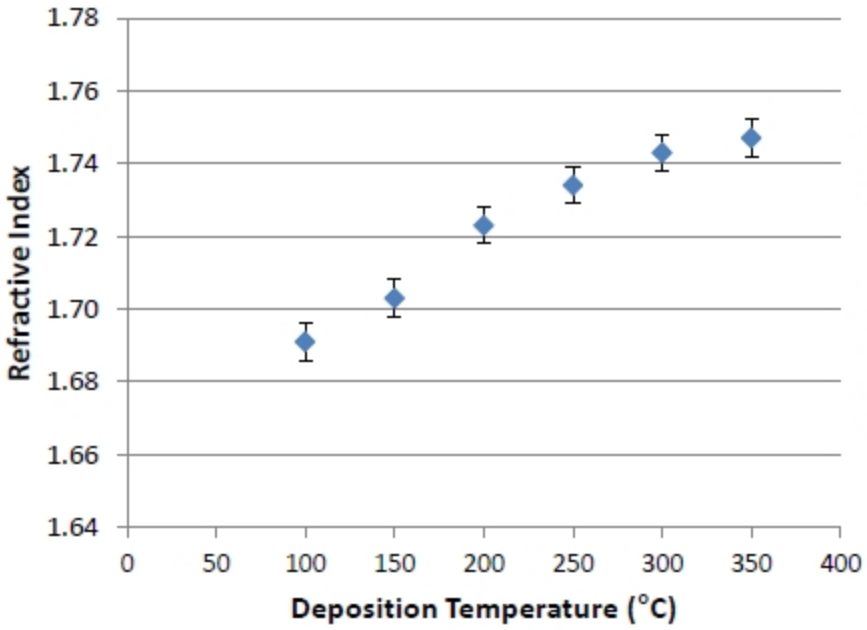
High quality recipe example: MgO

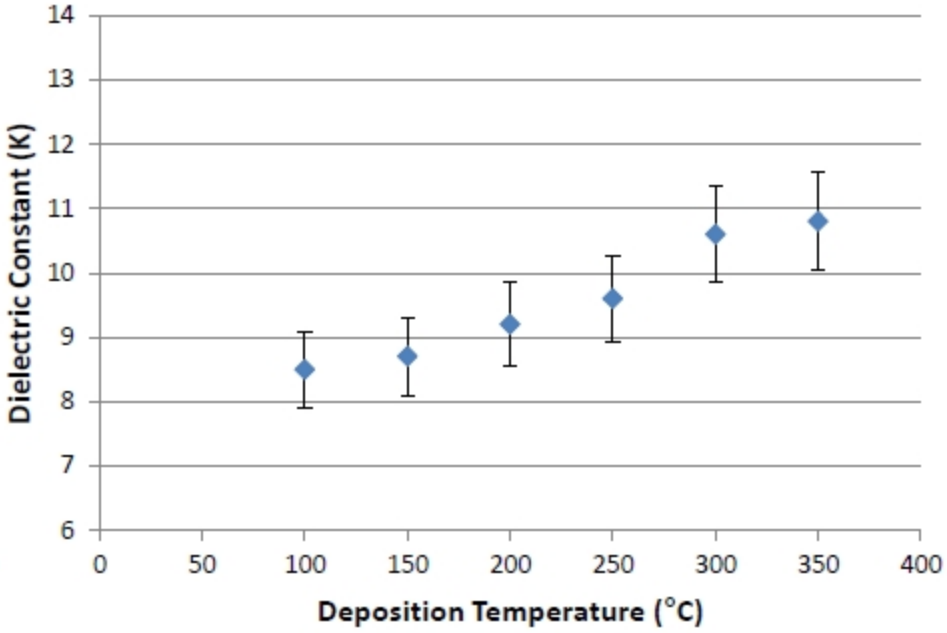




High quality recipe example: MgO

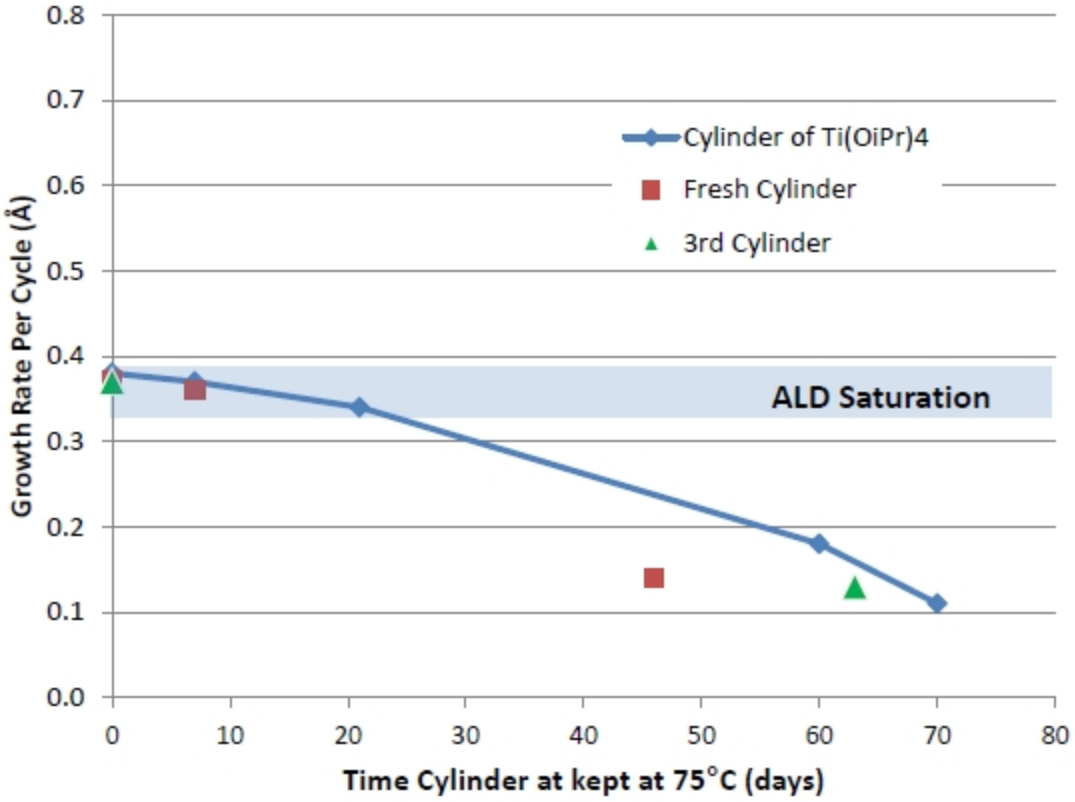
- Refractive index and dielectric constant increase with increasing deposition temperature

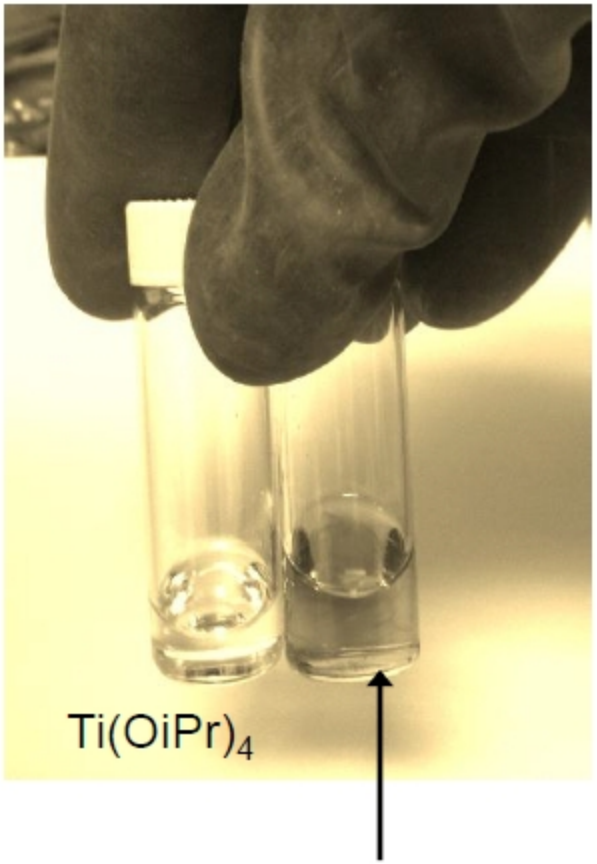




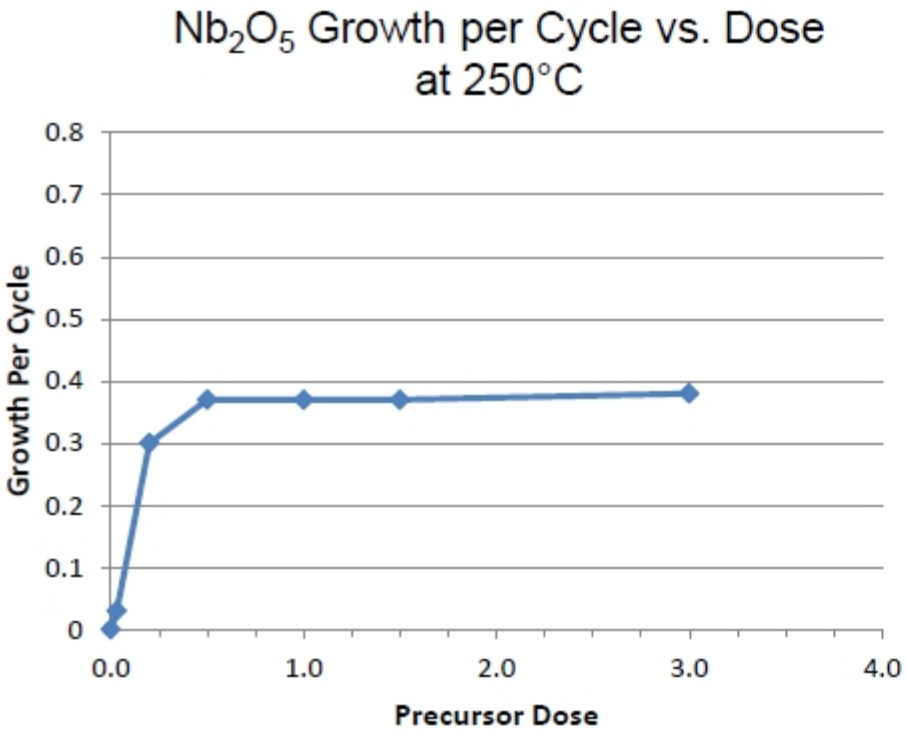
Guard against “unstable” precursors

- Decrease in growth rate occurs after cylinder has “aged”





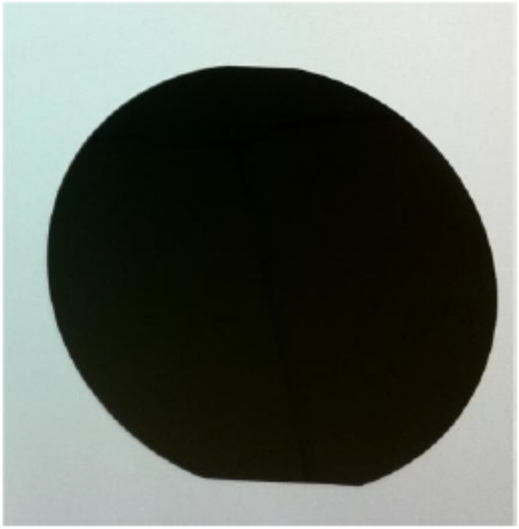
Sufficient dose is needed



- Precursor temperature: 85°C

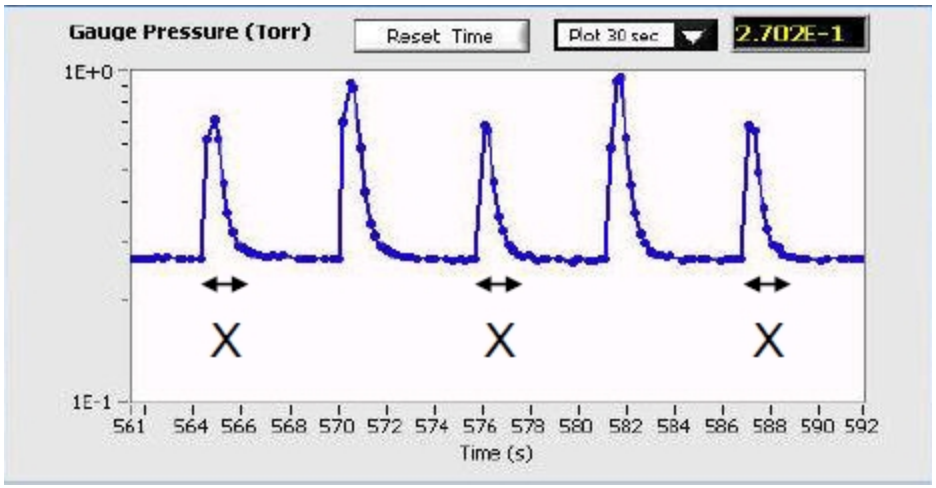
0.25 sec dose

0.5 sec dose



System Purge

- Reactant X must be fully cleared before reactant Y is introduced to the system
  - Otherwise CVD-like growth
- Purge time depends on temperature (and chemical)

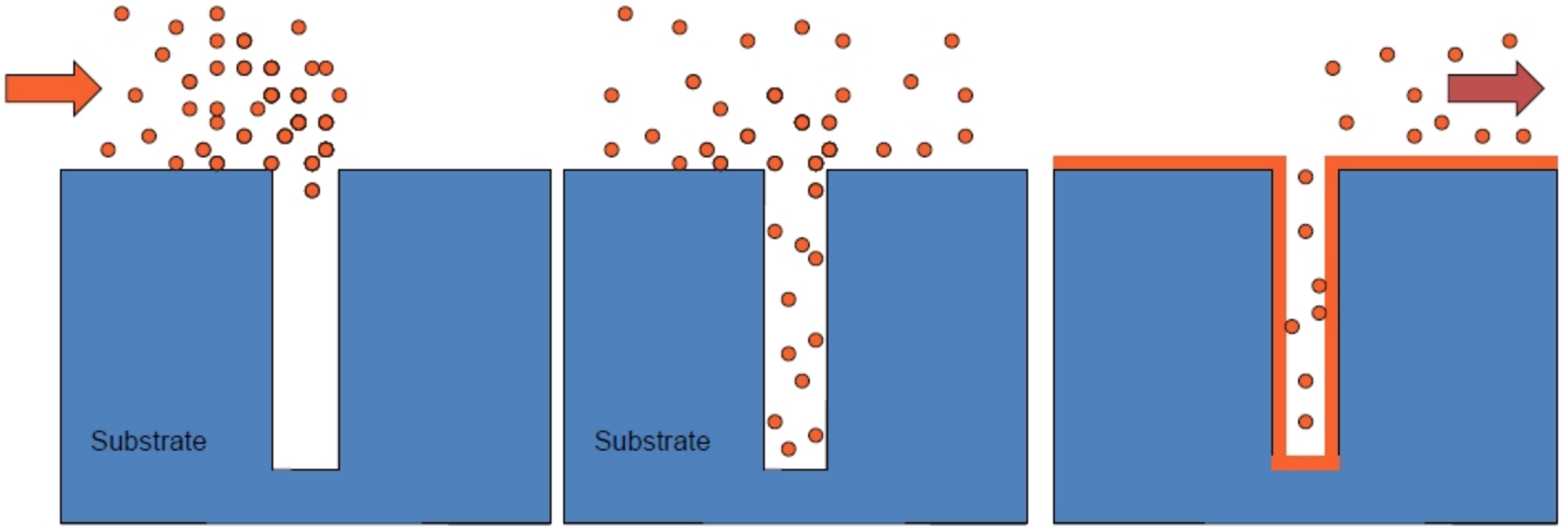


Typical Purge Times - Savannah

Temperature (°C)	Purge Time (s)
300	X + 2
250	X + 5
200	X + 8
150	X + 12
100	X + 30
<100	X + 45

Exposure Mode

- For high aspect ratios or to improve deposition uniformity/consistency
- Close stop valve before pulse and allow saturation time before purge

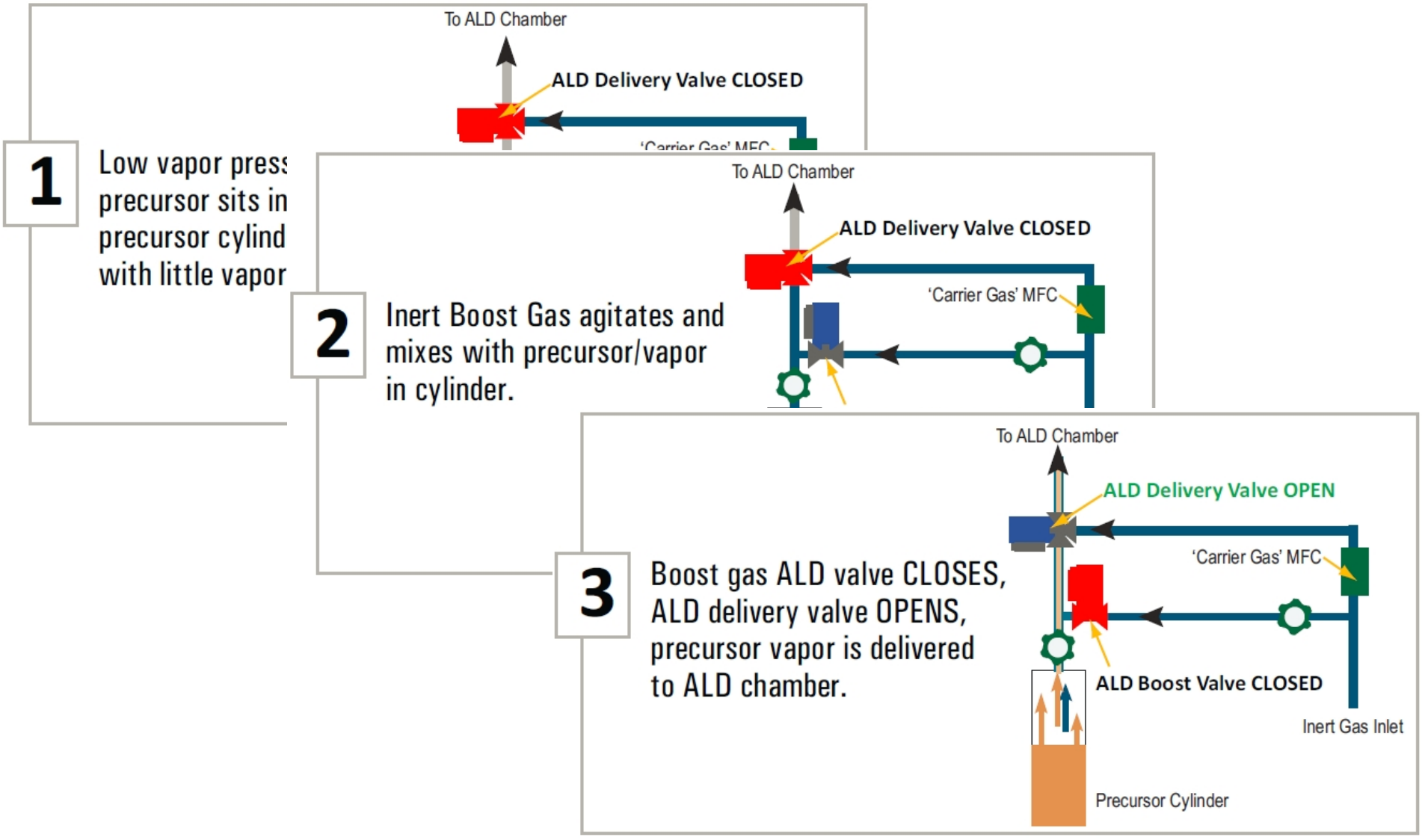


Introduce a dose of precursor

Allow time X for precursor to diffuse into trenches, pores,

Purge for time > X to remove excess precursor. Repeat for second precursor.

Boost for Low Volatility Precursors



Summary

- ALD can be an extremely stable, repeatable, controllable process
- However, good recipe characterization and precursor selection is essential
- Resources
  - Academic literature
  - Cambridge Nanotech (many well established recipes)
  - ALD work at stanford: snf.stanford.edu/SNF/equipment/chemical-vapor-deposition/ald/
  - jprovine@stanford.edu; mmrincon@stanford.edu

Finally: Some Things Learned During Roadshow

- Equipment
  - University of Maryland: Beneq
  - UC Berkeley: Fiji and Picosun
  - UT Austin: Savannah and Fiji (w/ turbo pump)
  - Arizona State: Savannah
  - Cornell: Oxford
  - Washington (Seattle): Oxford
  - GA Tech: Fiji
  - Harvard: Fiji and Savannah
  - Utah: Fiji
- Processes
  - Maryland: thermal vanadium oxide
  - UC Berkeley: thermal Ru
  - UT Austin: thermal BeO_2