ALD Precursor Delivery & Debugging: A Case Study in Polymer Development

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Mentors: J Provine & Michelle Rincon

EE 412
12/5/2014

ALD = “High-Quality” Films

Ultratech/CambridgeNanoTech
Simply ALD

We simplify ALD by designing affordable turnkey systems for university researchers and industry worldwide so they can deposit high-quality thin films on a variety of substrates.

Ultratech/CambridgeNanoTech
Simply ALD

- Organic Chemistry
- Surface Science
- Solid State Physics
- Plasma Physics
- Materials Science
- Mechanical Engineering
- Electrical Engineering
- Industrial Engineering

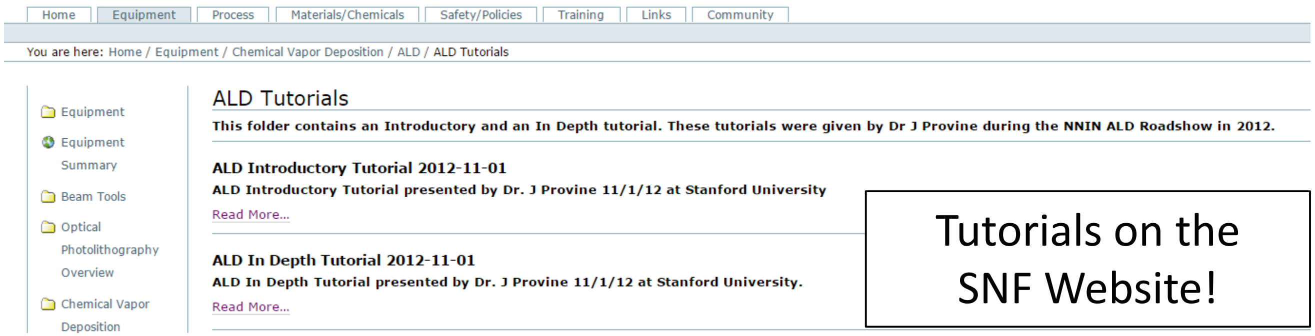
Atomic Layer Deposition Features?

- Digital Thickness Control
- Pinhole Free & Dense Films
- Low Temperature Processing
- High Aspect Ratio (> 1,000:1)
- High Uniformity (wafer-scale)
- Adhesion to Alternative Substrates
  - Polymers, Plastics, Glass, Metals
- Roll-to-Roll Scalability
- Flexible Substrates

Precursor & Recipe Development ↔ Atomic Structure ↔ Engineering Properties ↔ Device Performance

Molecular Layer Deposition

- Leverages the benefits of an ALD process for organic films


Home | Equipment | Process | Materials/Chemicals | Safety/Policies | Training | Links | Community

You are here: Home / Equipment / Chemical Vapor Deposition / ALD / ALD Tutorials

Equipment
Equipment Summary
Beam Tools
Optical Photolithography Overview
Chemical Vapor Deposition

ALD Tutorials

This folder contains an Introductory and an In Depth tutorial. These tutorials were given by Dr J Provine during the NNIN ALD Roadshow in 2012.

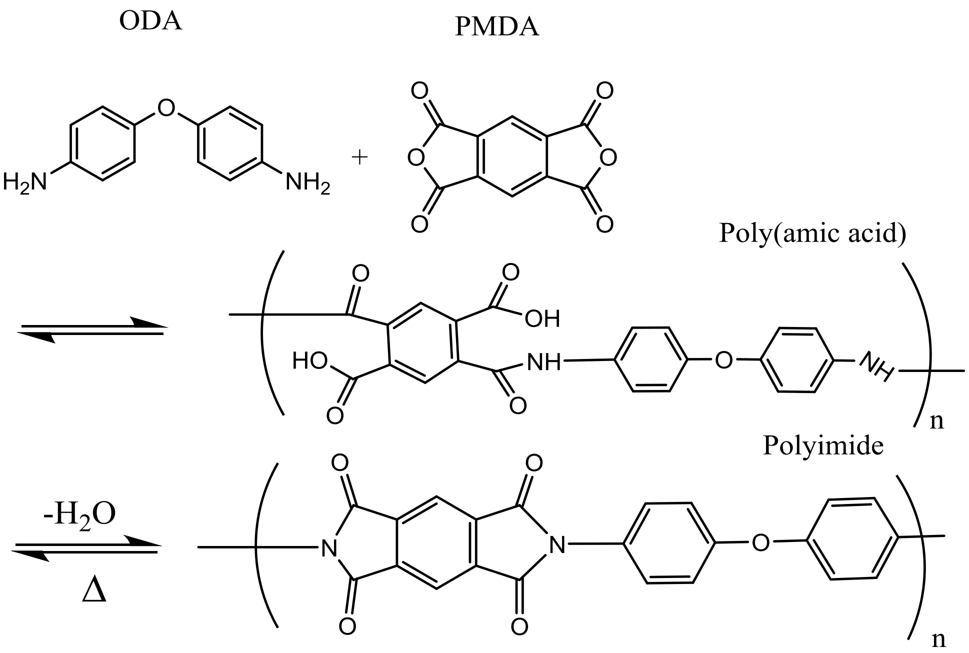
ALD Introductory Tutorial 2012-11-01
ALD Introductory Tutorial presented by Dr. J Provine 11/1/12 at Stanford University
Read More...

ALD In Depth Tutorial 2012-11-01
ALD In Depth Tutorial presented by Dr. J Provine 11/1/12 at Stanford University.
Read More...

Tutorials on the SNF Website!

- MLD of polymer as an enabling process module:
  - Hybrid organic-inorganic thin films and multilayers by combining ALD and MLD
  - Conformal polymer coating for bioencapsulation
  - Pyrolysis and graphitization of MLD polymer to form ultrathin carbon films
  - Solvent resistant, thermally robust, and mechanically compliant passivation enabling microfluidics, operation in harsh operating environments, stress mitigation, and flexible substrate processing
  - Polymer photoresists and masking of high aspect ratio structures

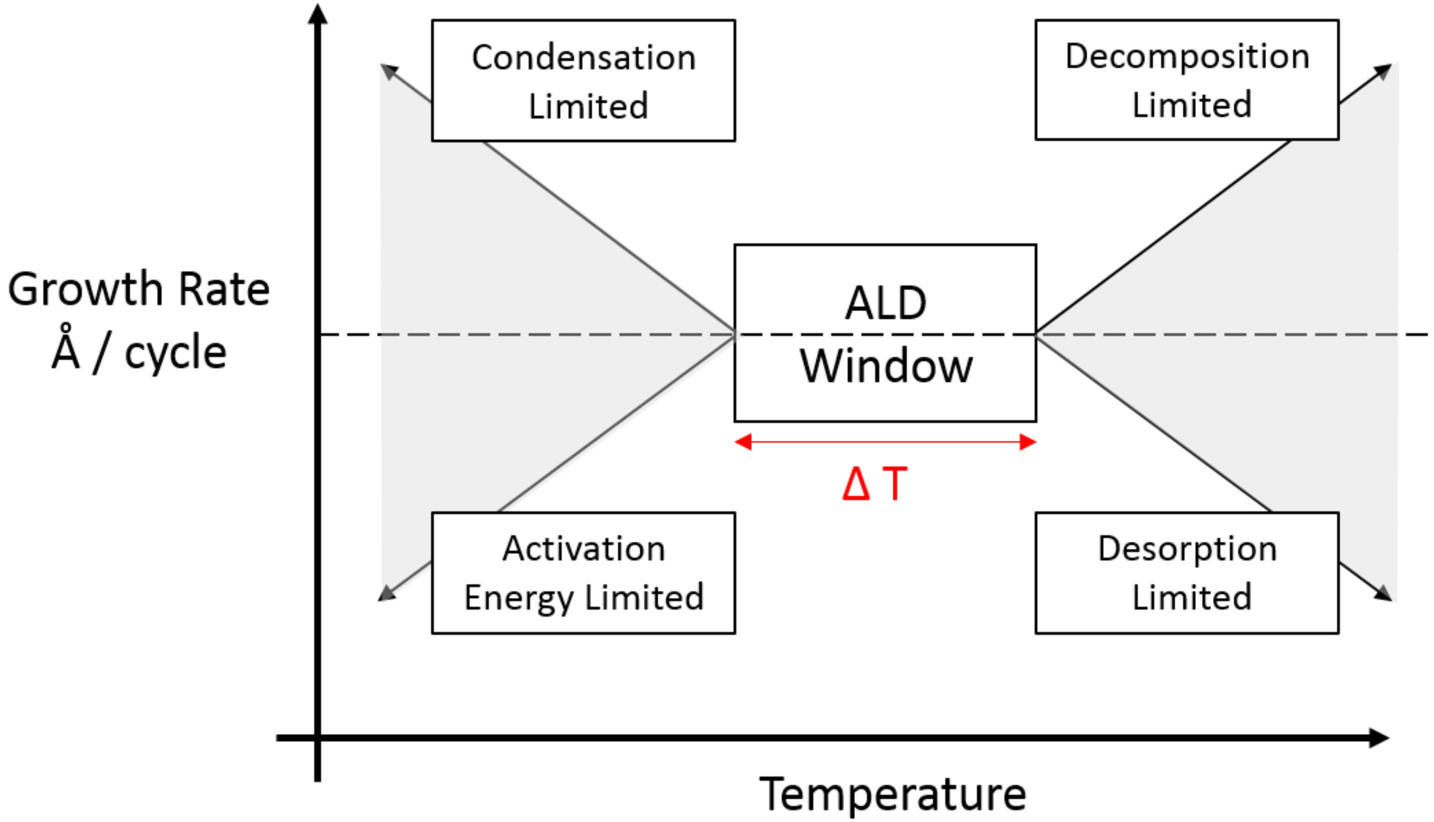
Synthesis of Polyimides



- Dianhydride and a diamine
- Nucleophilic attack by the amine onto the electrophilic carbon
- Forms a poly(amic acid) intermediate
- Reversible process – water is a byproduct

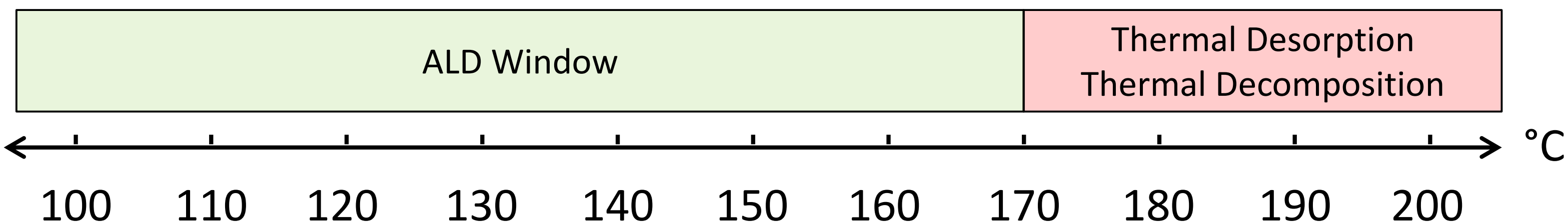
ALD Window

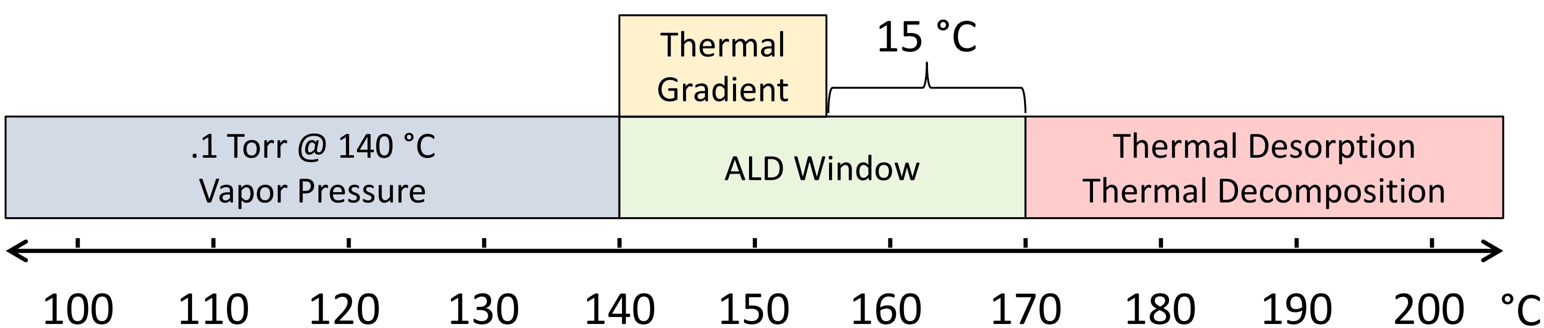
What are the practical issues with a small Δ T ?



Vapor Pressure

VP > 1 Torr	*1 Torr > VP > .1 Torr*	*.1 Torr > VP > .01 Torr*
• Standard Delivery • Ideal	• Inert "boost" gas • Agitate & mix vapor	• Low vapor pressure delivery system

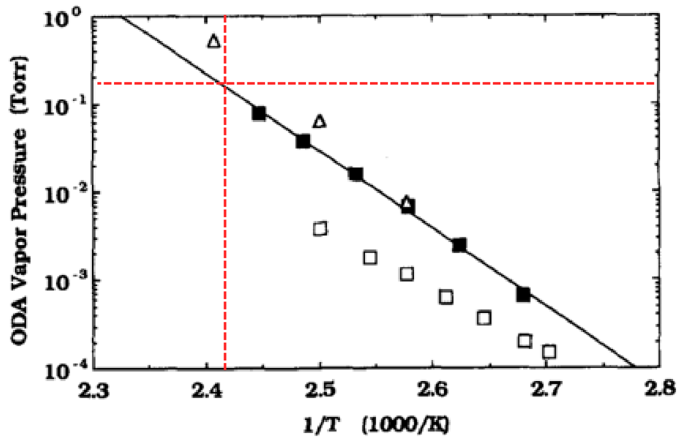




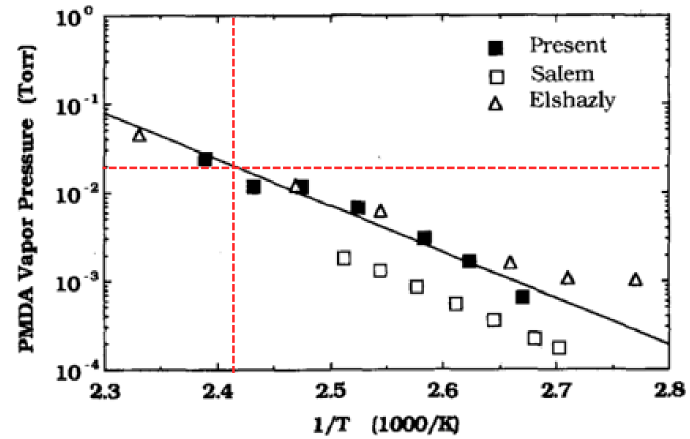
Boost by Ultratech/CambridgeNanotech

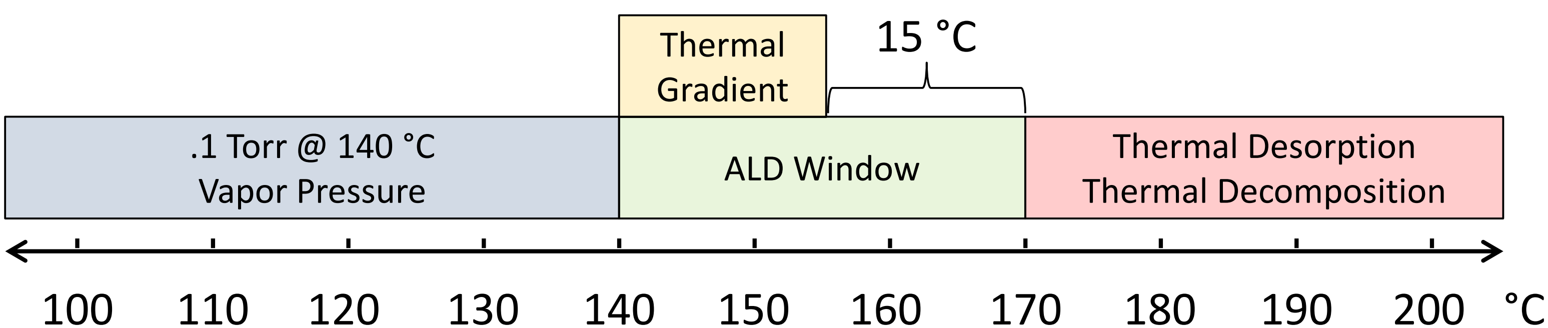
Vapor Pressure

ODA



PMDA

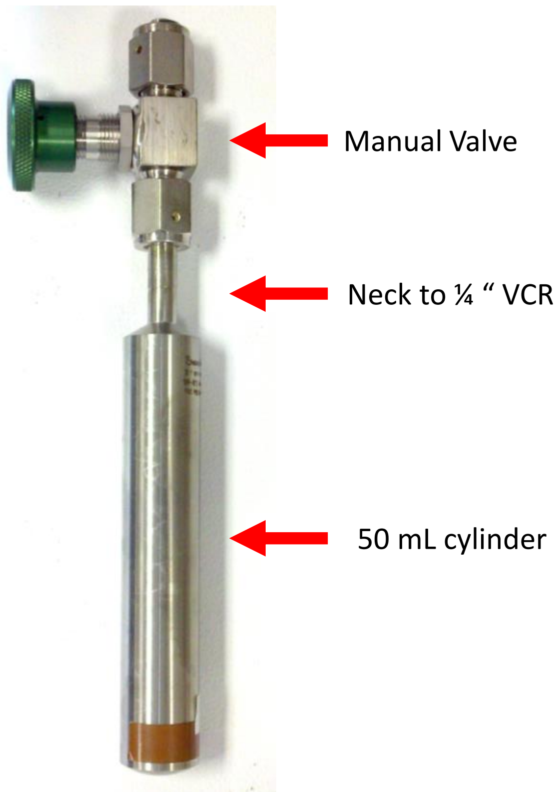




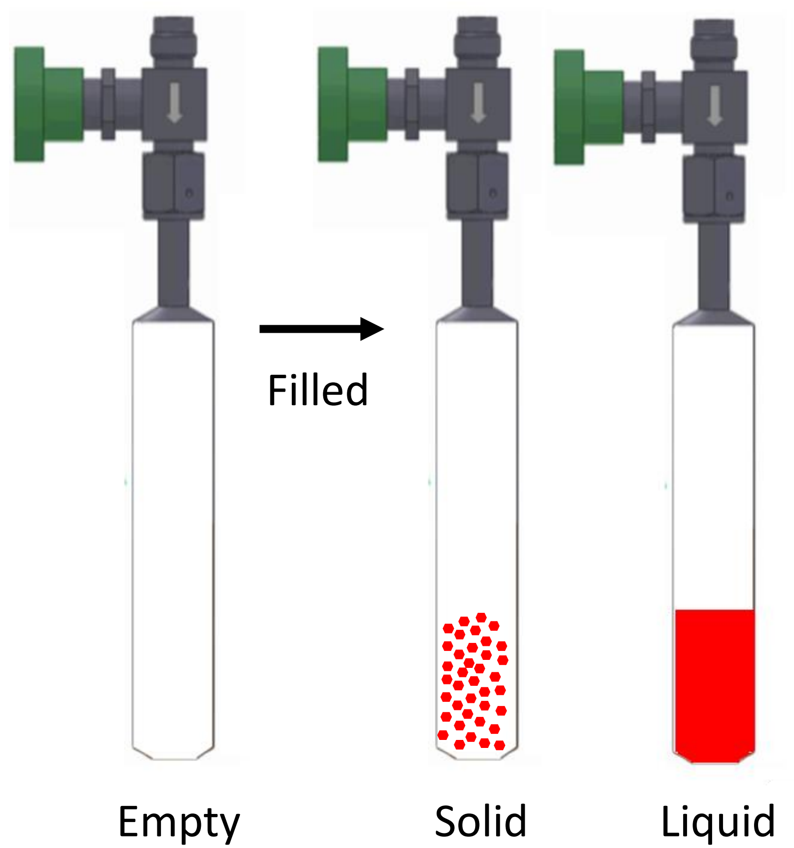
J. Mater. Res., Vol. 8, No. 12, Dec 1993

Vapor Delivery

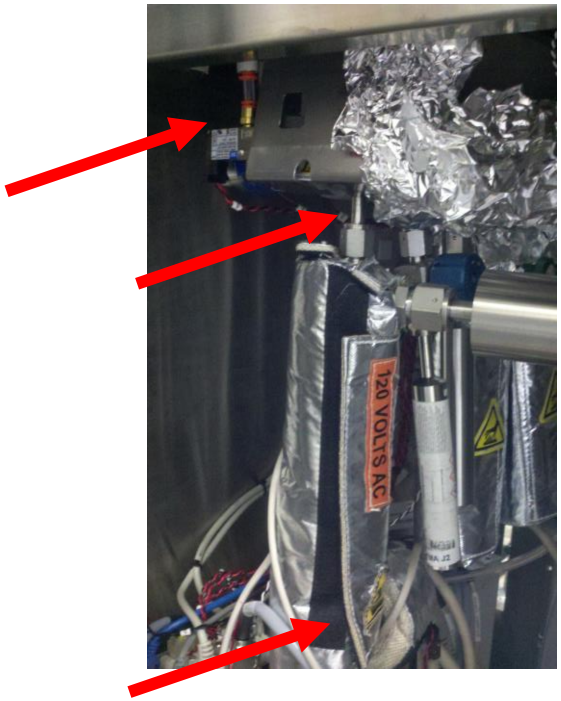
Precursor Assembly

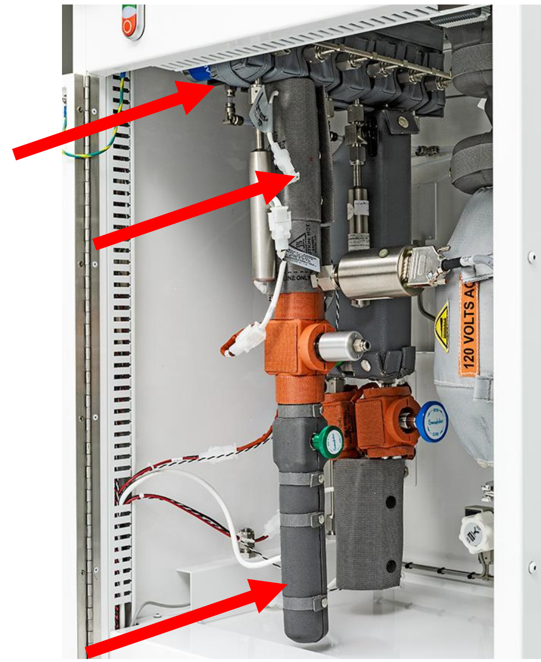


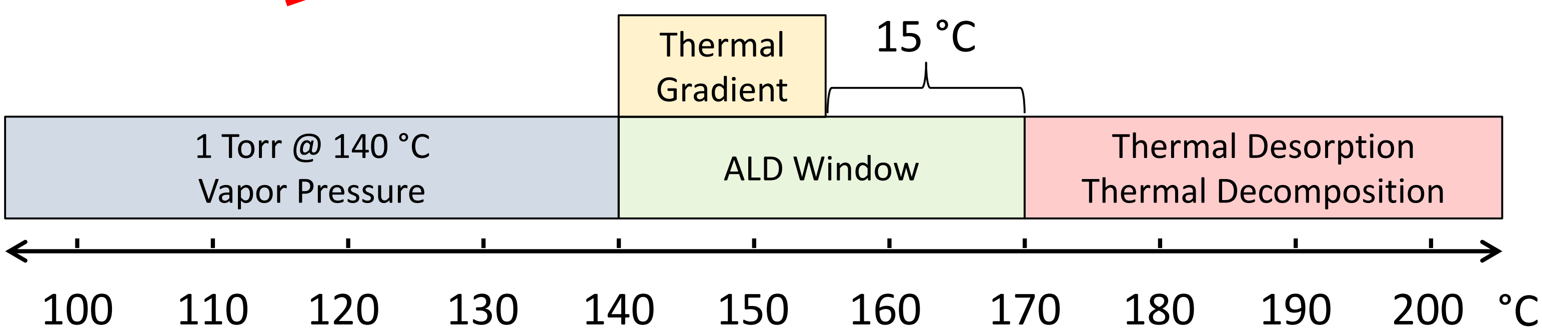
Loading Schematic



Cold Spots & Condensation







Condensation & Clogging

More Clogging

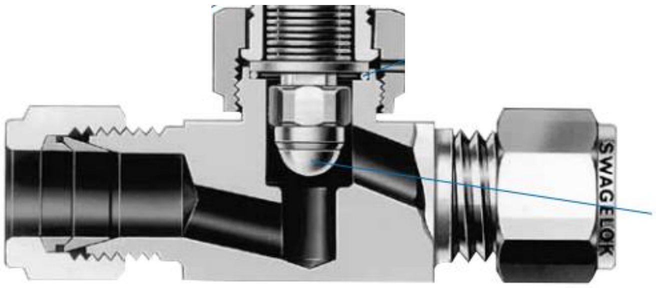
Valve Design & Selection

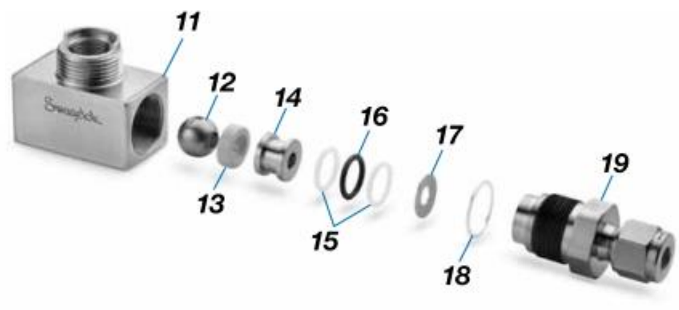
High Temperature

(A) SS-4H-VCR

Low Temperature

(B) SS-42GVCR4





Valve Design & Selection

High Temperature

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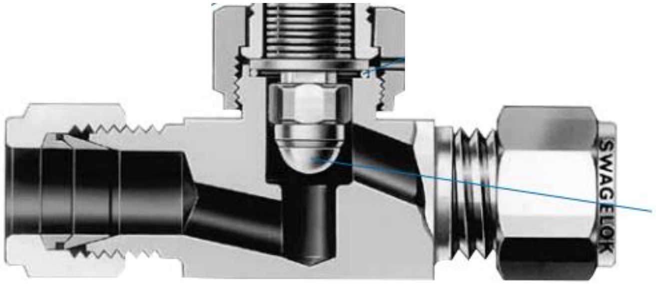
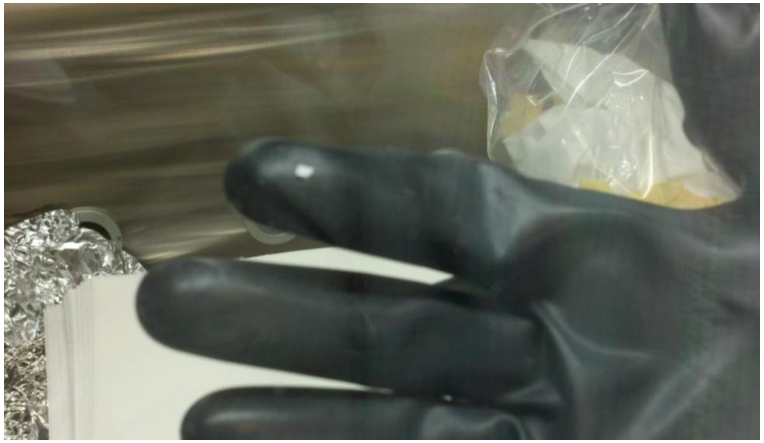
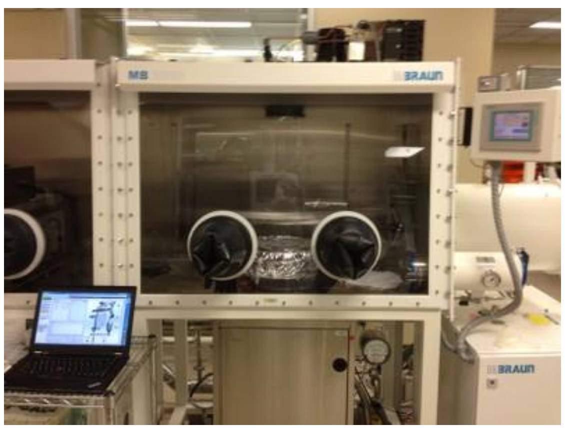




One Hypothesis

Precursor Density

- PDA → 1.15 g/cm^3
- ODA → 1.36 g/cm^3
- PMDA → 1.68 g/cm^3



$P_{cylinder}$ = Atm + 2.25 Torr

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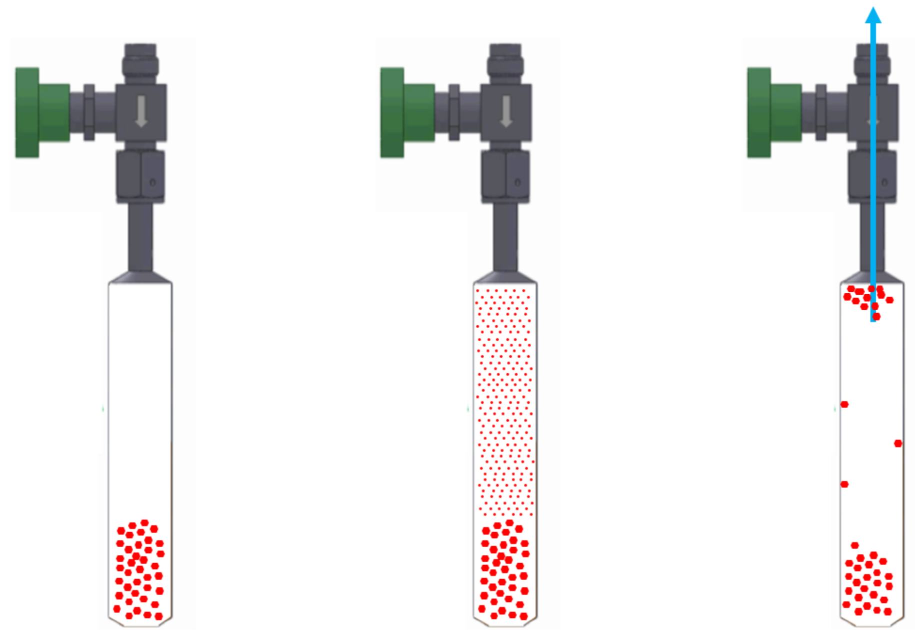
$\frac{P_{cylinder}}{P_{base}} > 5000$



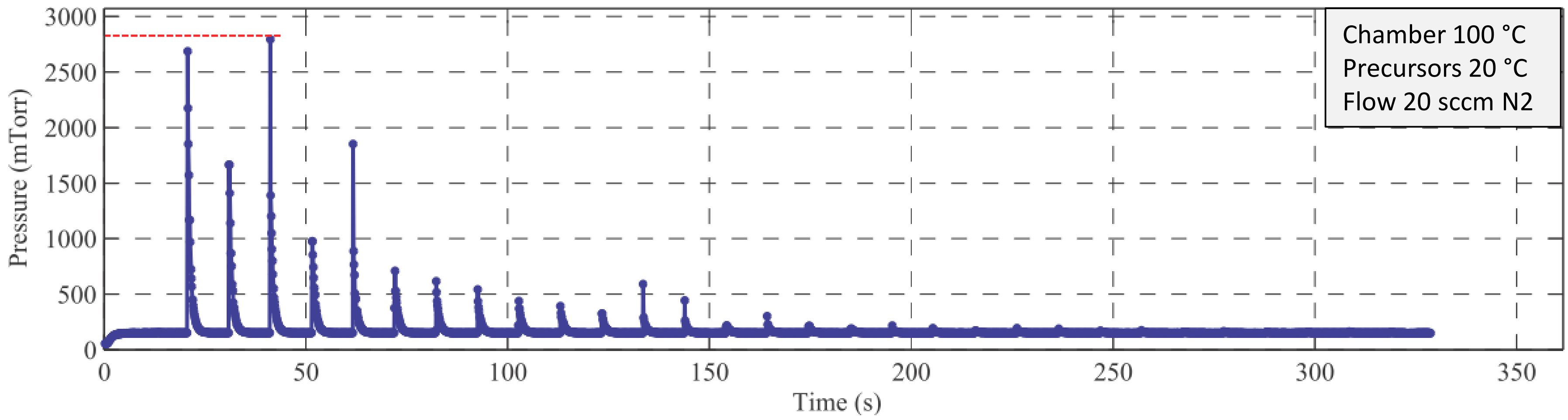
Loaded (20 °C)

Loaded (20 °C) Installed

1st pulse

Pressure Equilibration

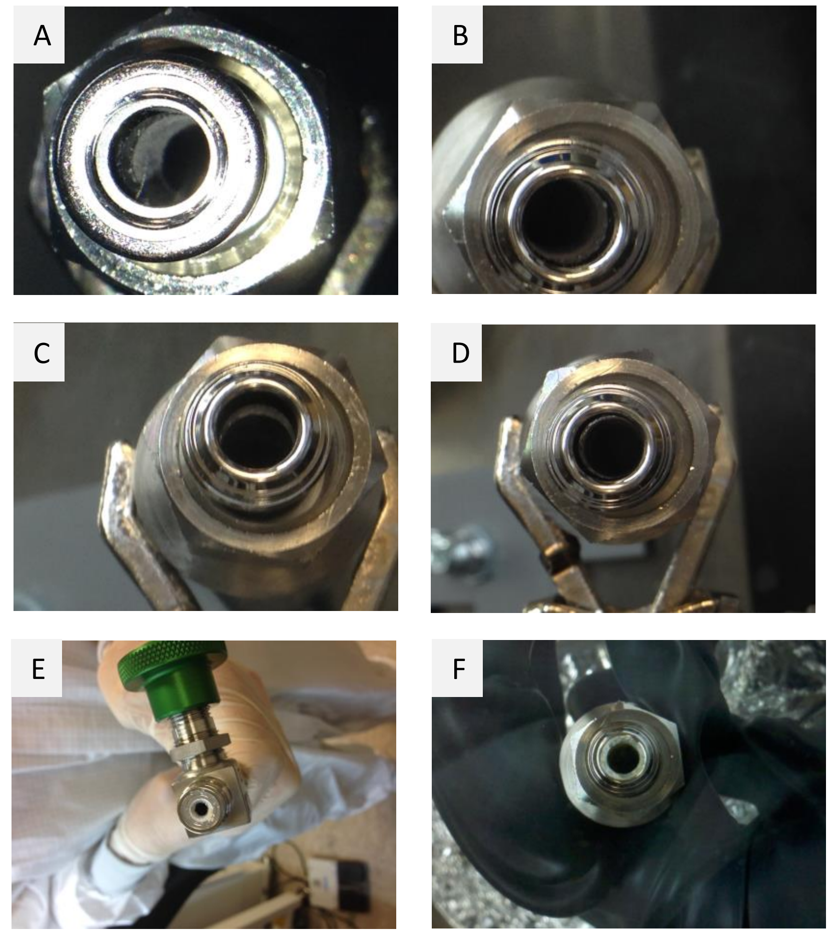
- Precursor sticking coefficient ~ 1
- Fastest pulse time → 15 ms
- After leak check & manual valve opened



Systematic Evaluation

Cylinder Protocol

1. Load cylinder
   ← Inspect A
2. Install precursor
3. Leak check port
4. Open manual valve
   ← Inspect B
5. 15 ms bleed pulses
   ← Inspect C
6. 1 s dose pulses
   ← Inspect D
7. Heat to temperature
8. 15 ms bleed pulses
   ← Inspect E
9. 1 s dose pulses
   ← Inspect F



Best Practices

- What are the properties of your precursor?
  - Melting and decomposition temperatures, vapor pressure
  - Do you have sufficient thermal budget to clear a clog?
- Equilibrate cylinder and tool pressures with small bleed pulses at room temperature
  - Repeat incrementally while elevating precursor temperature
- If the precursor is a solid, monitor the pulses at the desire temperature before running your process.
  - Identify any inconsistency or decrease in the pulses height
  - What is the purity of your precursor (volatile impurities)?
  - Remember, pulses can be deceiving!
- Identify cold spots and address temperature nonuniformity
- Consult with the SNF staff for alternatives diagnostic tools

Conclusions

- Extended operation from 150 →180 C
  - Improved insulation, additional temperature monitoring inside the glove box (lid and glove box seal)
- Best practices to eliminate clogging
  - Protocol for precursor installation and bleeding
  - Molded heater jacket
- Debugging lead to
  - hardware upgrades
    - Insulation (lid, manifold, manual valve)
    - USB Isolator
    - Heater jacket
  - software upgrades
    - N2 MFC control issue
    - Crashing mostly gone

Safety First

- Debugging inside ALD tool enclosure
- Should only be accessed by SNF staff

- Significant Risks:
  – electrical shock
  – burns from heated surfaces
  – exposure to dangerous chemicals

Thank You

- Mentors: Michelle & J
- Organizers: Roger, Mary, Usha
- Classmates: Fun in the lab!