Spatial Atomic Layer Deposition: A Path to High-Quality Films on Continuous Substrates

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Agenda

- Atomic Layer Deposition (ALD) as a process
- Spatial ALD
  - Approach
  - Performance
- Devices and patterning using Spatial ALD
  - Working demonstrations of film quality
  - Effective film patterning with ALD

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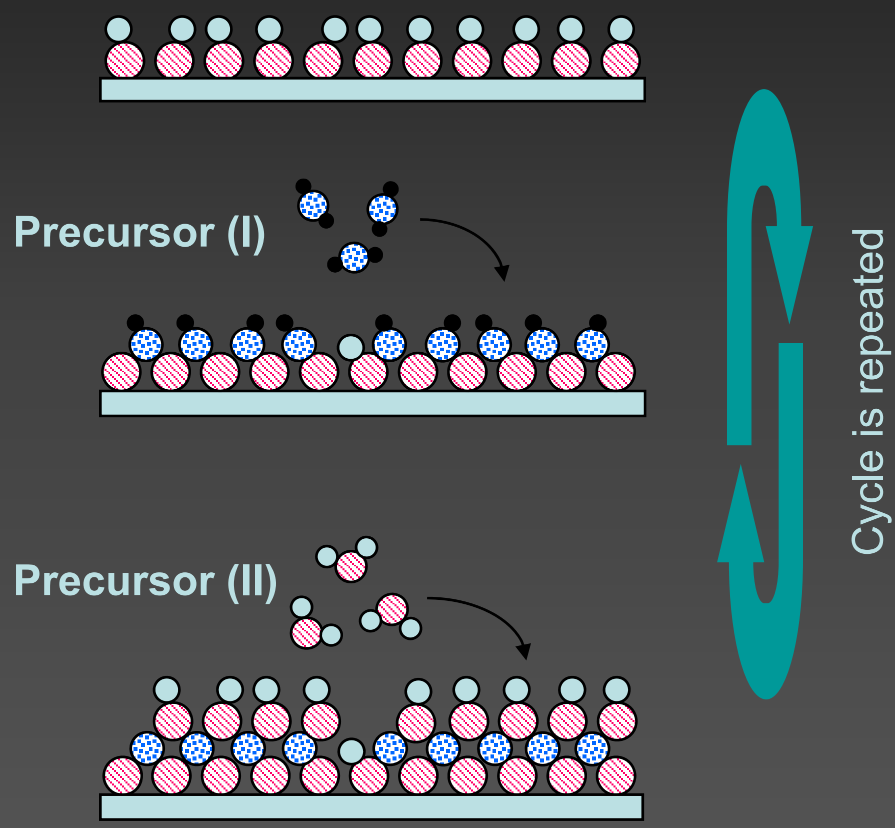
Atomic Layer Depositions (ALD)

ALD: process where a substrate is exposed to reactive gases one by one



Film growth occurs layer by layer

High quality

Conformal

Low temperature

Atomic Layer Deposition Uses

- Barrier layers
  - Very conformal and dense coating
  - Prevent moisture and oxygen transmission
  - Thin layers (100–200 Å) are effective
- Thin, high-performance dielectrics
  - New generation silicon chips: 25 A layers with low electrical leakage
- Many other applications
  - Coating of high aspect ratio structures
  - Transparent conductors
  - Oxide and other binary/ternary semiconductors

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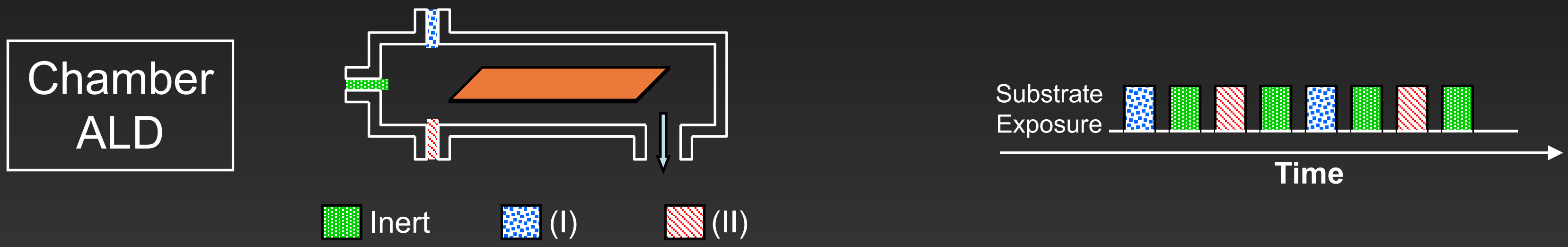
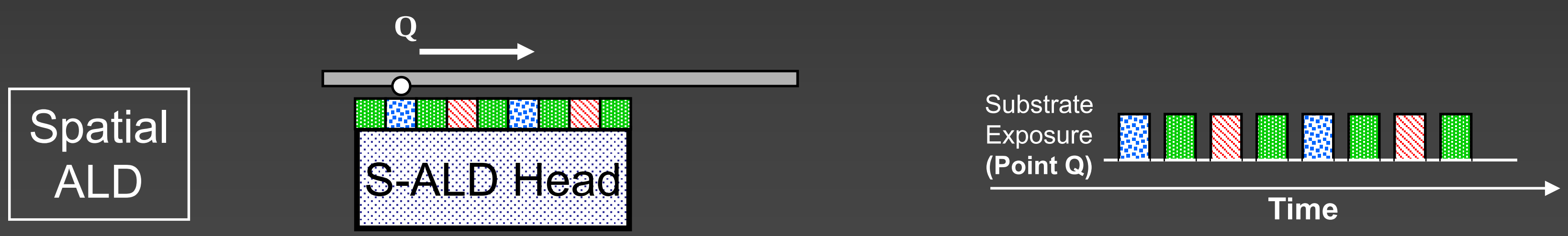
Spatial Atomic Layer Deposition (S-ALD)



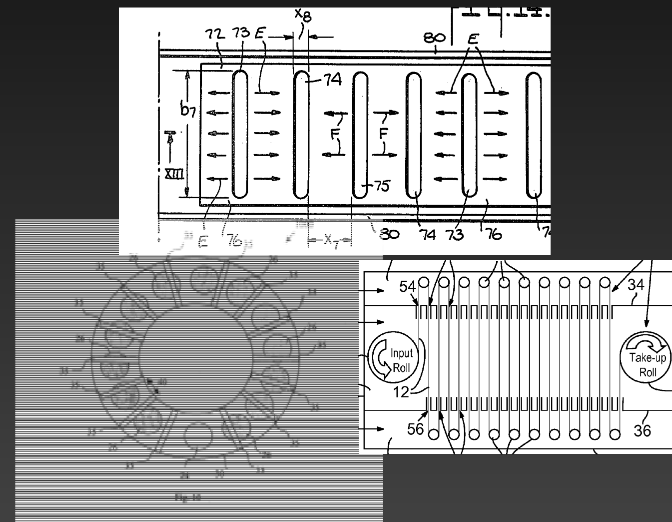


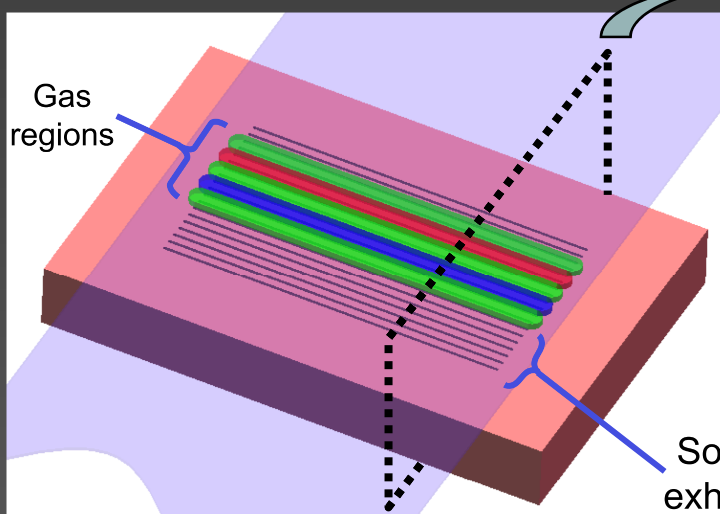
- Spatial Process
  - Steady-state gas flows
  - Can be "open air"
  - Suitable for large or continuous substrates

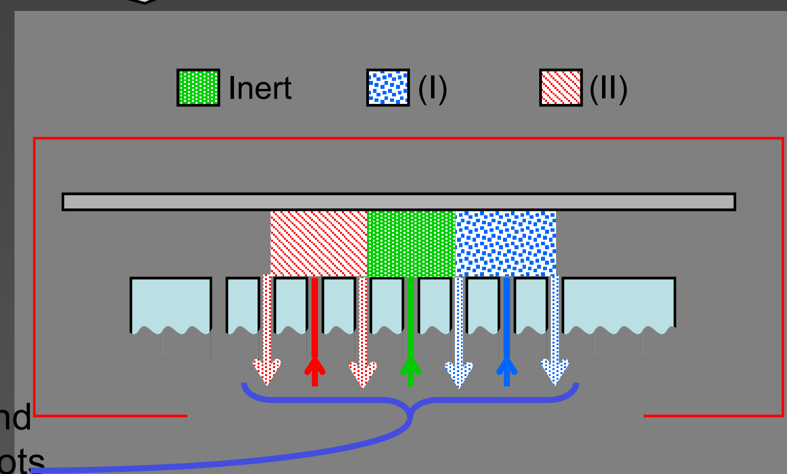
Isolating the Reactive Gases

Gas confinement is key

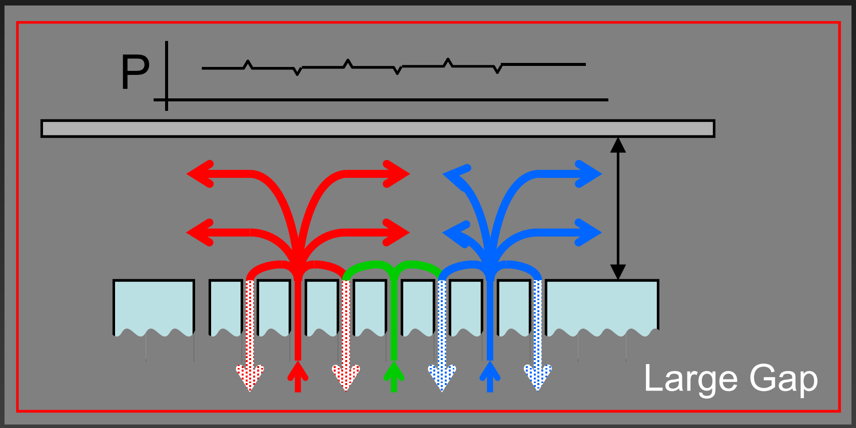
There is a variety of proposed systems for gas confinement

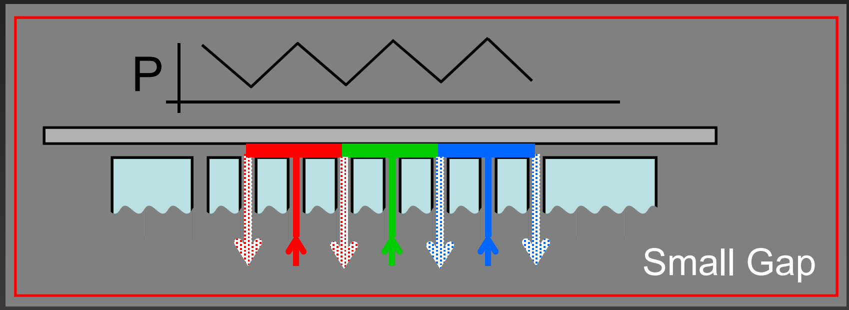






The ALD Coating Head





- Large gap to substrate
  - Low pressure gradients
  - Gas will mix across many channels
- Small gap → Substrate floats (gas bearing)
  - High pressure to drive from source to exhaust: Good Isolation
  - Excellent control of substrate position
  - Very small “chamber”

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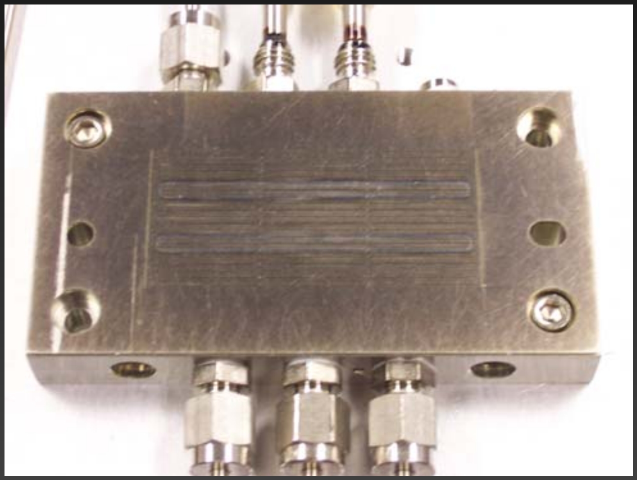
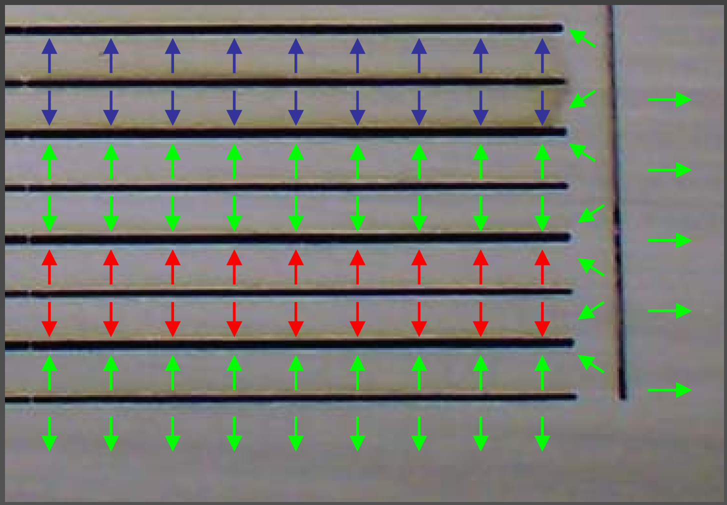
Equipment Design

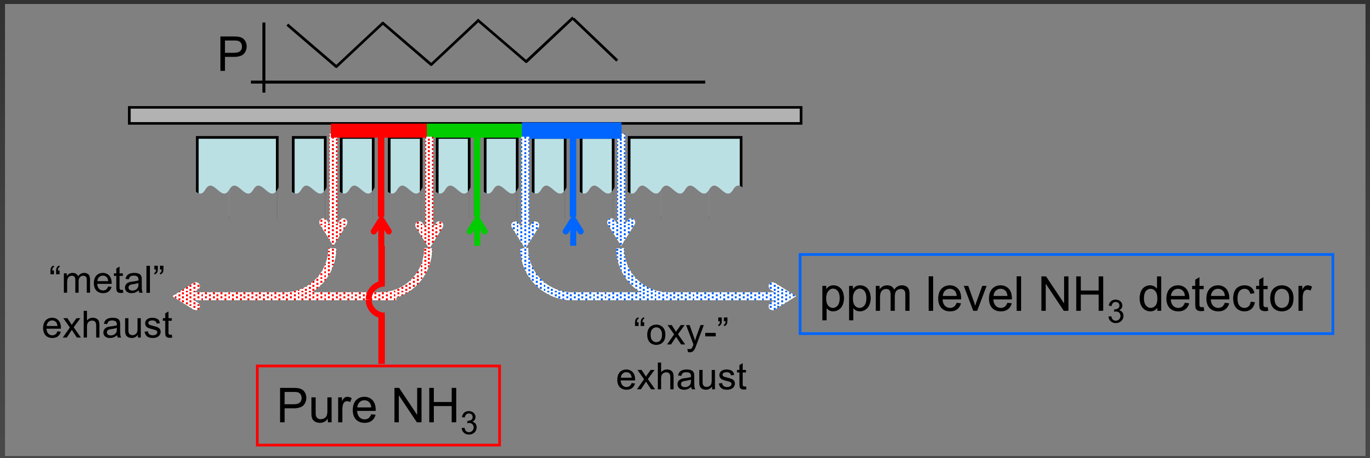
- Current work is on a laboratory scale unit
  - 2" wide coating width
  - Used with discrete 2.5" square substrates
- Process demonstrations
  - Gas isolation
  - ALD film growth and saturation
  - **Open air operation →** extendability to long substrates





Isolation of Precursor Gases

- How good is the gas separation?
  - Measure by using a “tag” gas (NH_3) in the metal channels
  - Look for crossover of this gas to the oxygen channels



- Results
  - Stationary operation: No detectable mixing
  - At our current maximum velocity (0.26 m/s): ~23 ppm mixing
  - Gas phase reaction → minimal factor

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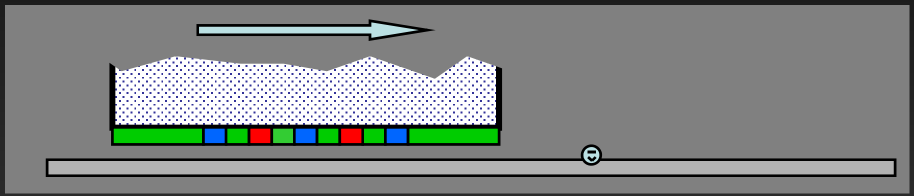
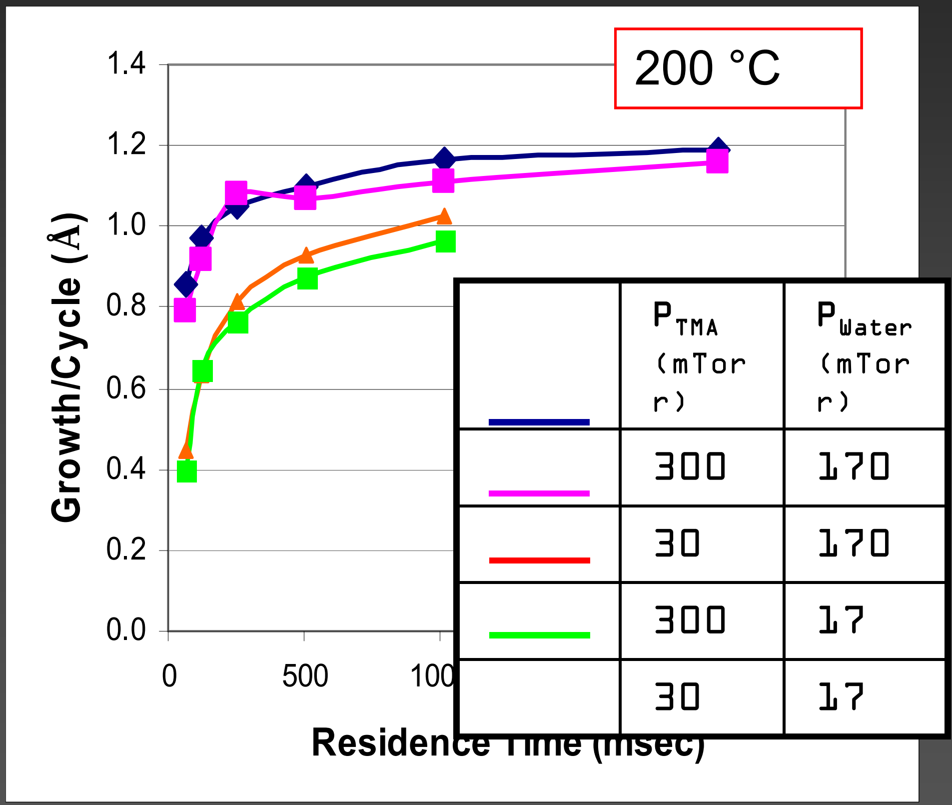
Saturation Behavior for TMA/Water

- Relative residence times hard wired by head design
- However
  - Constant flow: accurate control over chemistry levels
  - Very sharp chemistry changes
- Clear saturation behavior
  - Saturation near 1.2 Å/cycle for TMA/Water

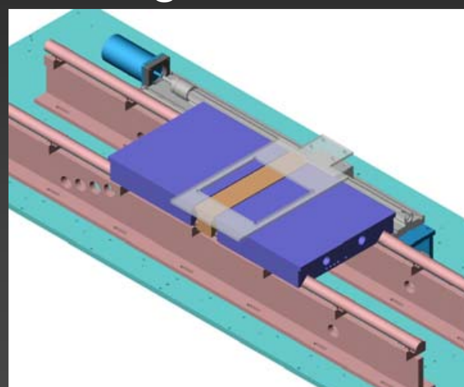




Equipment Development (underway)

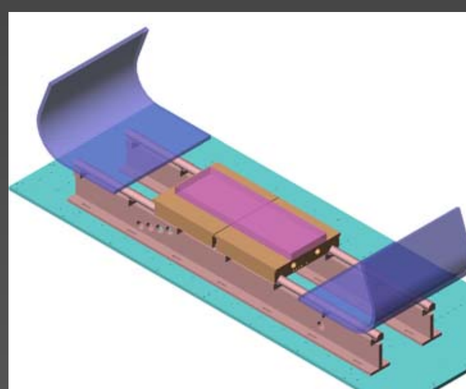
- Objectives
  - Increased coating width
  - Web handling

6 inch rigid



- Phase A
  - Coating head migration to 6” width
  - DEMO: Ability to construct wider heads
  - DEMO: Uniform delivery of gas

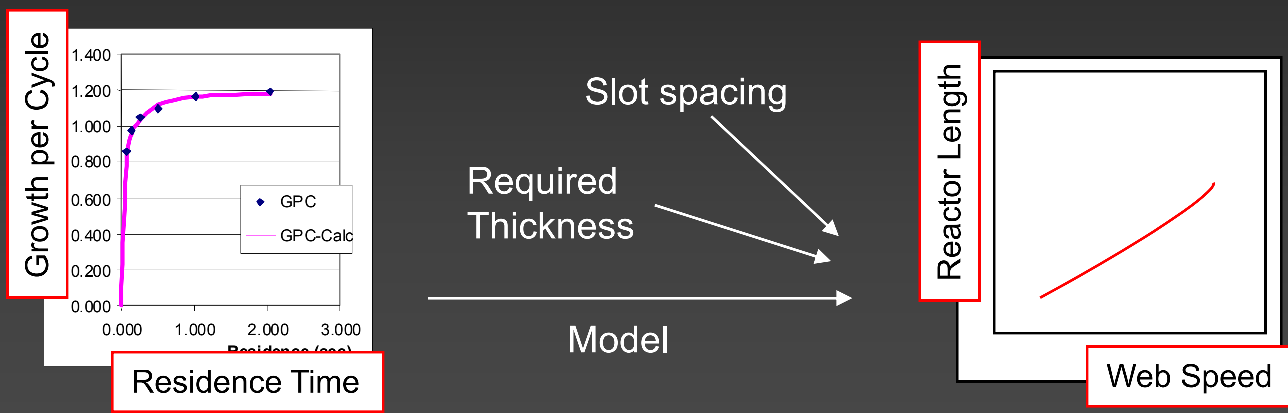
Short Pass Web



- Phase B
  - Short pass 6” web unit
  - DEMO: Ability to handle free standing webs

Throughput

- Empirical model can be constructed for a given reaction system



- Currently have good data on Al_2O_3 and ZnO system

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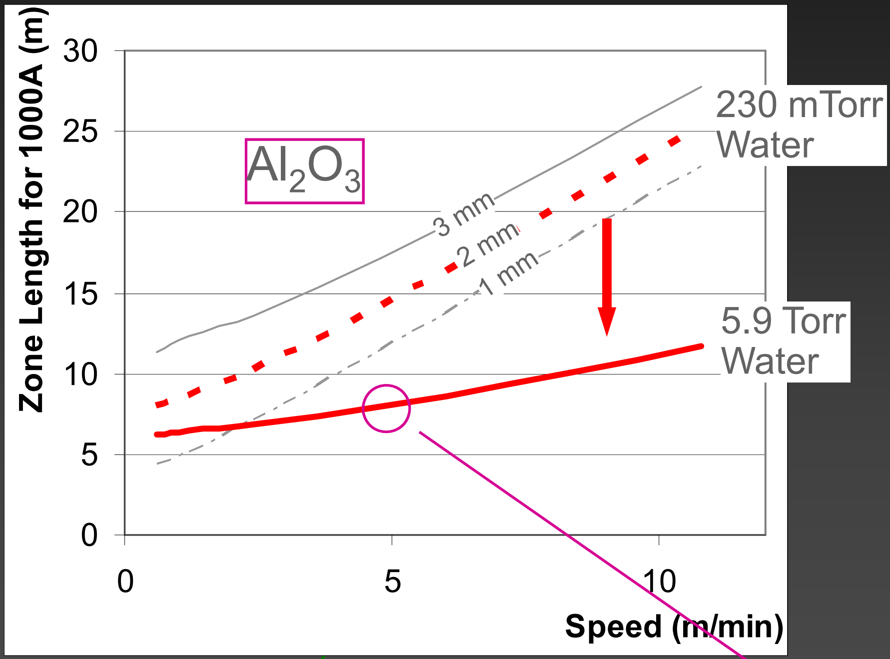
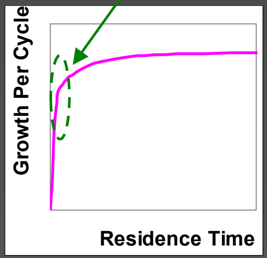
Throughput for Al_2O_3 or ZnO





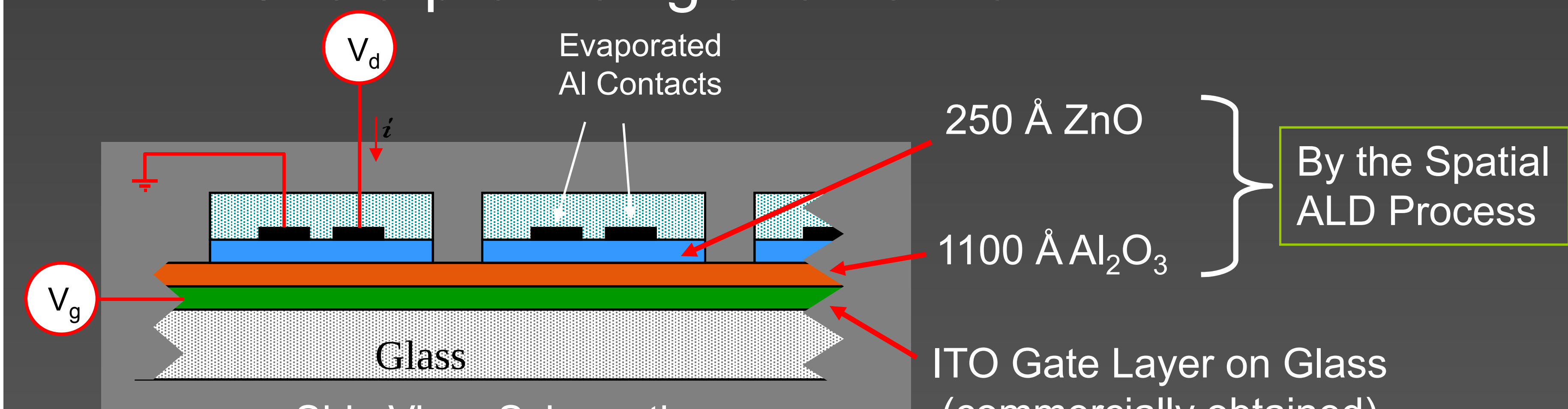
To date: Small to no effects when not in complete saturation

- The material system matters
- Slot spacing is a weaker dependence
- Longer spacing
  - Longer residence → more deposition per cycle
  - Easier head assembly

Example:
- 200 Å Film
- 5 m/min web speed → 1.6 m zone

S-ALD ZnO Thin-Film Transistors (TFT)

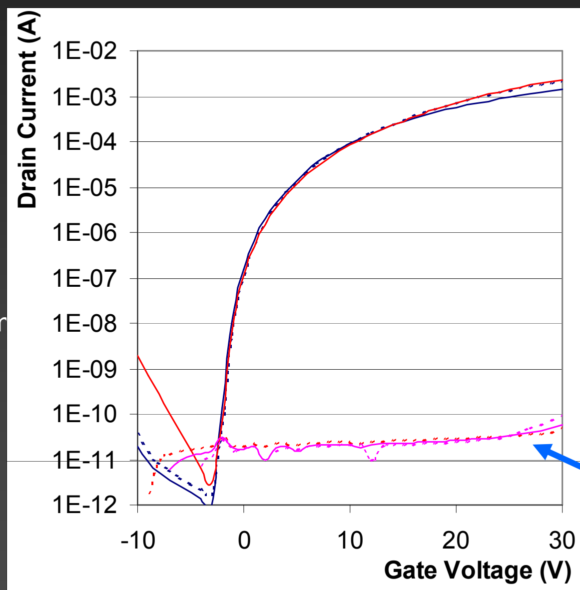
- TFTs: the drive element for flat displays
  - Laptop screen: a-Si TFTs with mobility ~1 $cm^2/V\text{-}s$
- To drive an OLED
  - Higher mobility is needed to handle the pixel current
  - Higher stability is needed to continuously supply the pixel
- ZnO is a promising alternative



Side View, Schematic

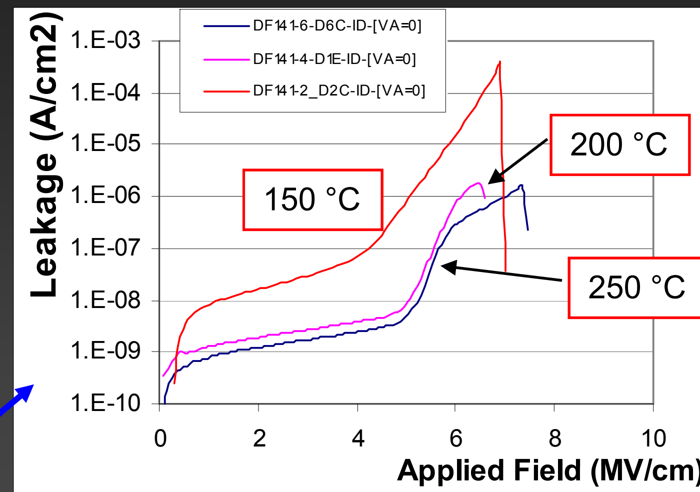
Typical Device Performance

W/L = 600/50 mm
T_{ox}= 1100 Å
ITO Gate
Shadow mask Al contacts



Ig

Al_2O_3 Dielectric Leakage



- High on/off ratio $>10^8$
- Low gate leakage $<2.5 \times 10^{-8}$ A/cm^2
- Mobility: ~15 cm^2/V-s

Additional Characteristics…

- Stability: Comparable to a-Si.
- 2.3 MHz ring oscillator circuits: Fast (J. Sun, et al., IEEE Electron Device Lett.)

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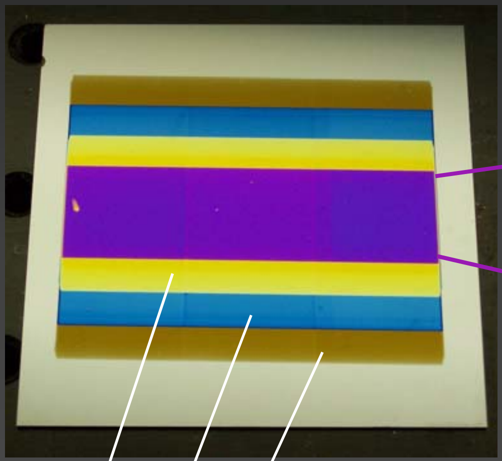
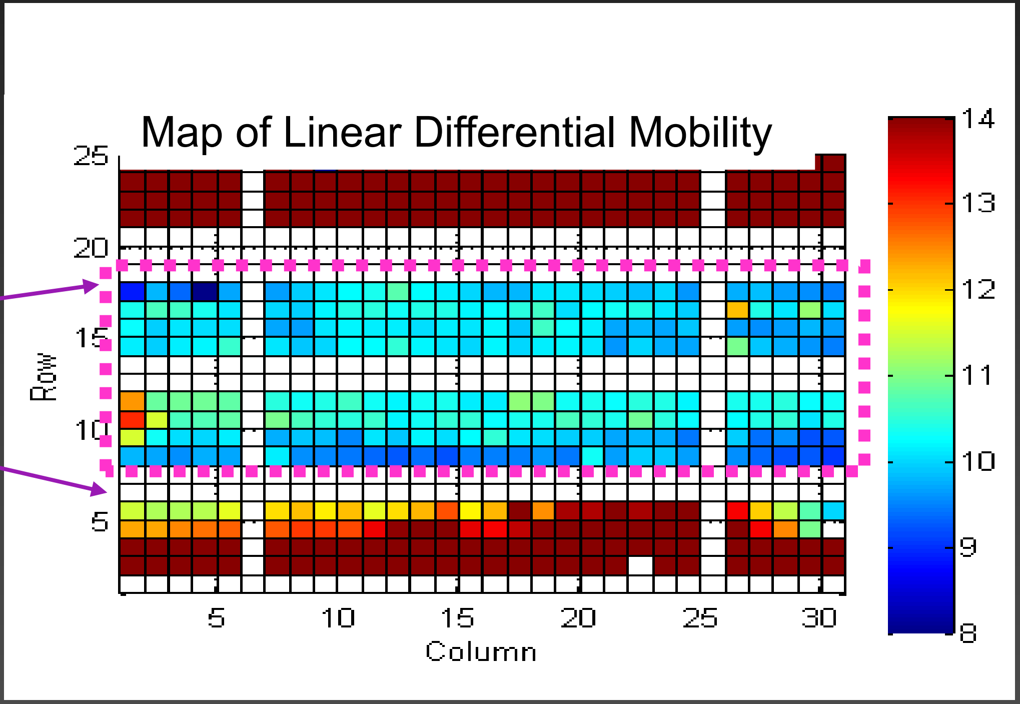
Mapping Electrical Characteristics

Deposited film on Si
(shows thickness steps)

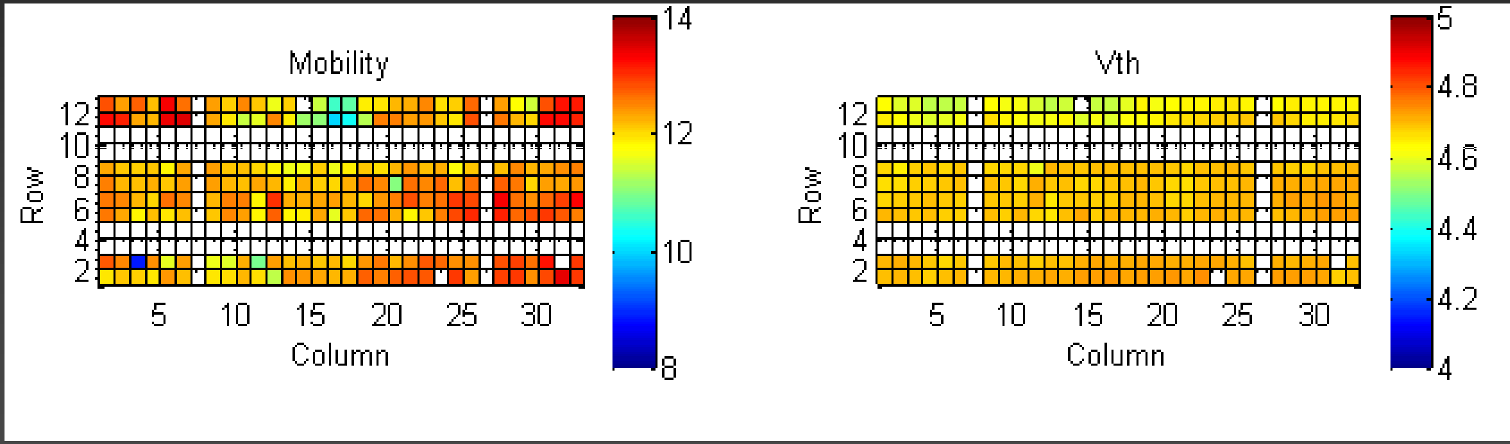


Thinner dielectric and
semiconductor



Measurement region: Central area

TFTs with Shadow-masked Al Contacts



Linear Mobility
12.3 ± 0.6 cm^2/V-s

Vth
4.68 ± 0.04 V

240 devices

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Bias Stability

- Initial observations
  - Stability depends on Gate Bias (not current flow)
  - Mobility shows little change
- Conditions
  - Typically stress time = 10,000 s
  - Bias applied Vg = 10 V (for gate dielectric thickness = 50 nm)
  - Relatively high field (2×10^6 V/cm)
- For W/L = 500/50
  - Linear: Vd = 0.25 V, drain current ~50 μA
  - Saturation: Vd = 10 V, drain current ~0.9 mA

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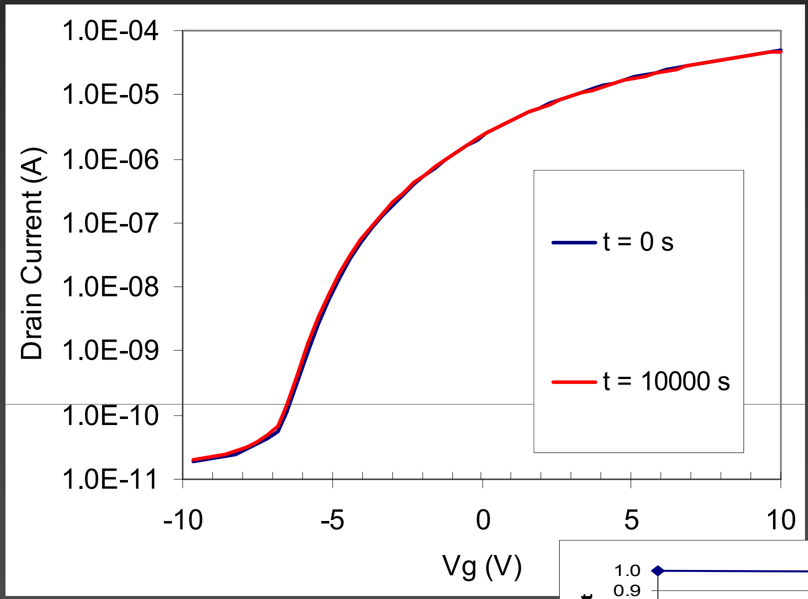
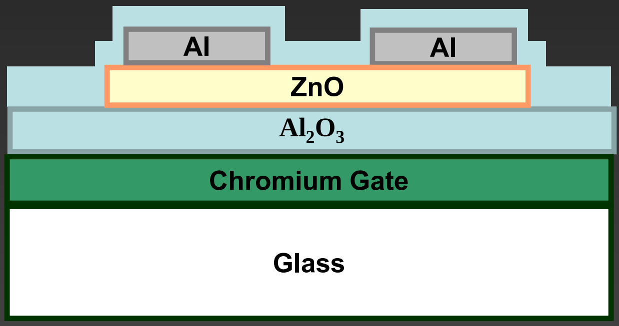
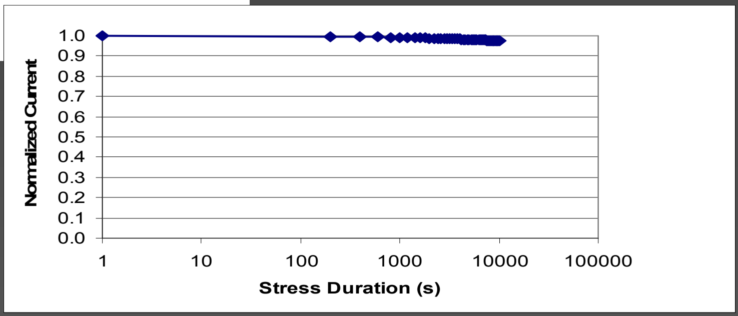
Passivated TFT

Passivation with alumina in Spatial ALD system
200 °C process
Thickness = 50 nm







Low movement of threshold or current

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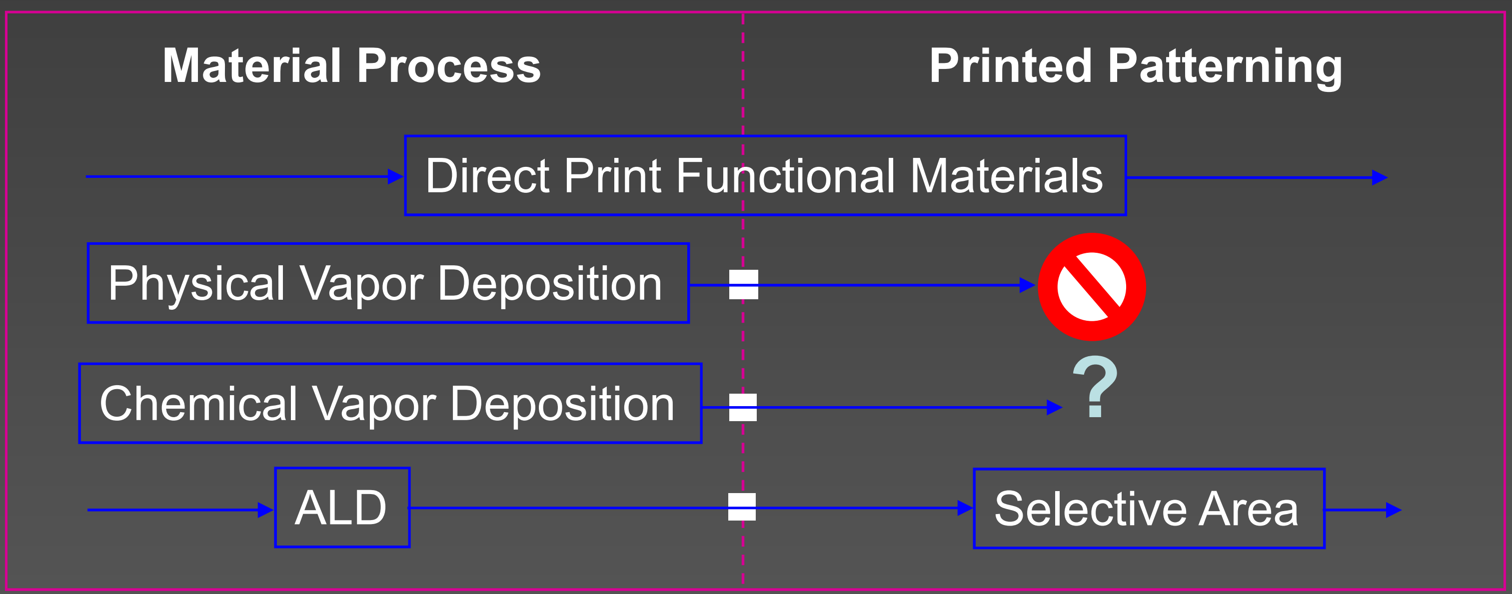
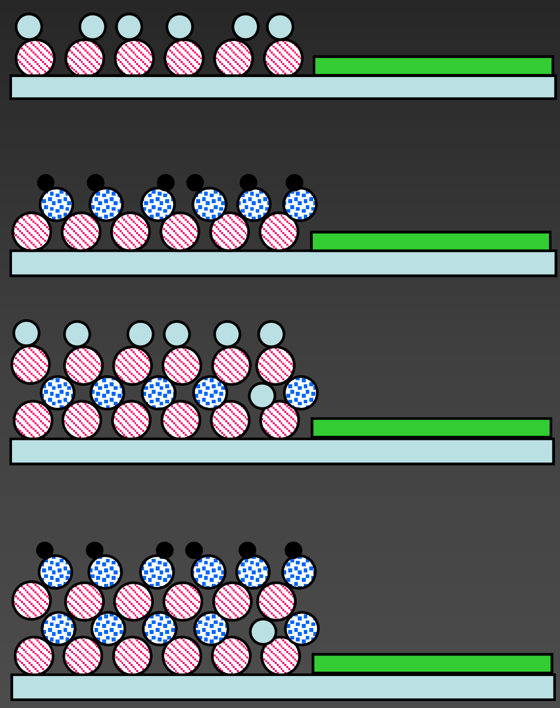
Patterning and R2R ALD

- Typical Semiconductor Processing
  - Photolithographic process
  - Layers applied, then patterned with photoresist + etching
- Large-area processing: A new landscape



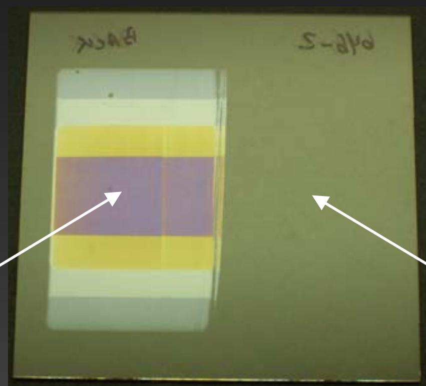
Selective Area Deposition



- Reaction inhibition
  - If precursors cannot react with the substrate, the film does not grow
- Advantages
  - Thin inhibitor layers
  - Inhibitors can be printed
  - After ALD, film is ready for next layer

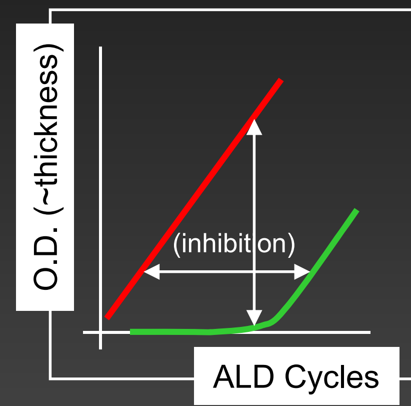
Characterization of Growth Inhibition

½ Sample
No Inhibitor



½ Sample
Inhibitor

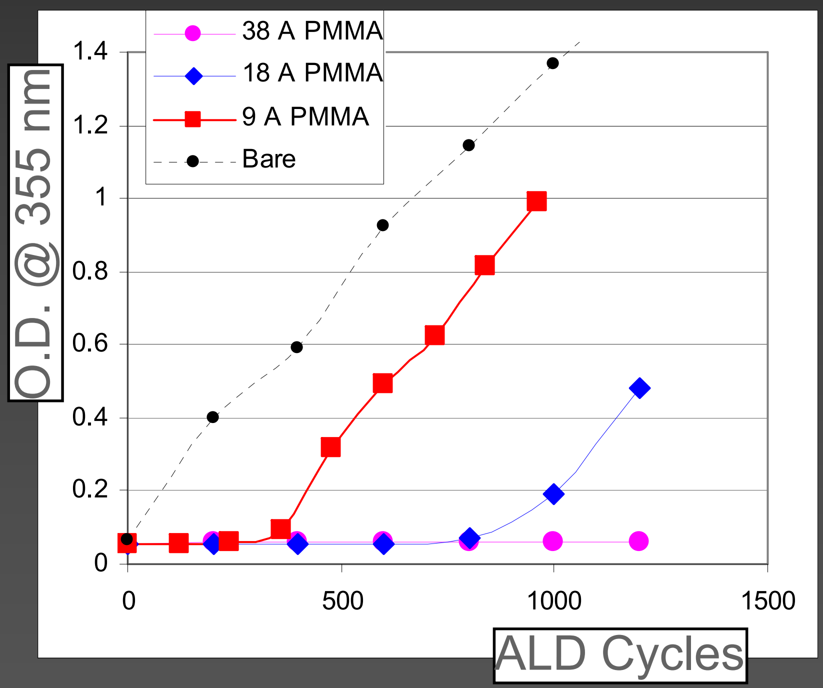
Inhibitor spun on sample



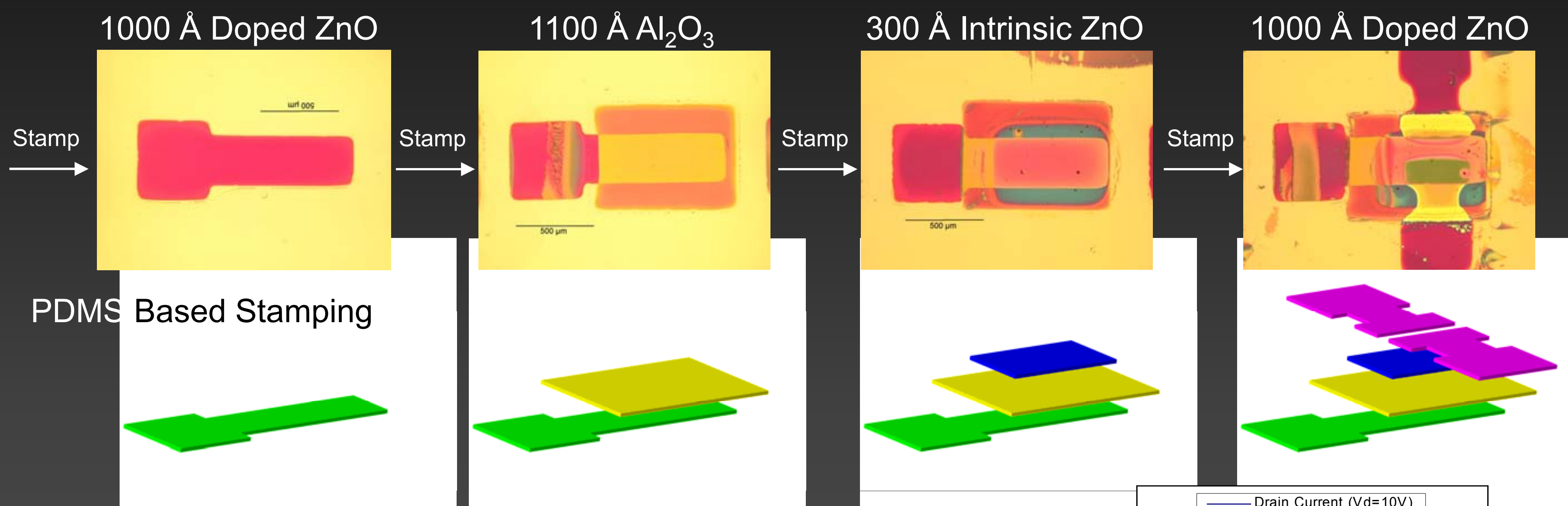
- During ALD growth, sample removed periodically
  - No inhibitor: Normal surface growth
  - Inhibitor side: Reduced/eliminated growth
- Growth of ZnO characterized with 355 nm optical density

PMMA: a Good Inhibitor

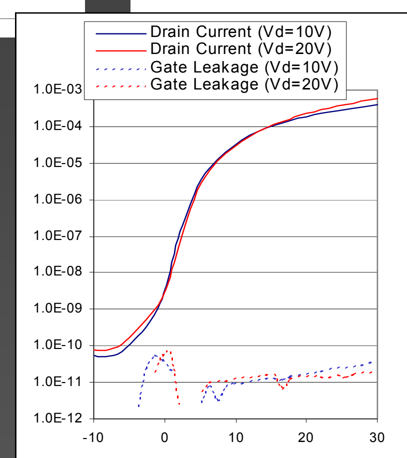
- PMMA solutions spun on borosilicate glass
  - 950,000 MW (Microchem 950-PMMA-A4)
  - Thicknesses by ellipsometry on silicon controls (3000 rpm)
    - 9 Å (0.025% solution)
    - 18 Å (0.05% solution)
    - 38 Å (0.1% solution)
- Inhibition results
  - Strong inhibition even for 9 Å film
  - 40 Å suitable for most applications
  - Thinness: Quick inhibitor removal for inline process



TFT Structure Completely by Selective Area ALD

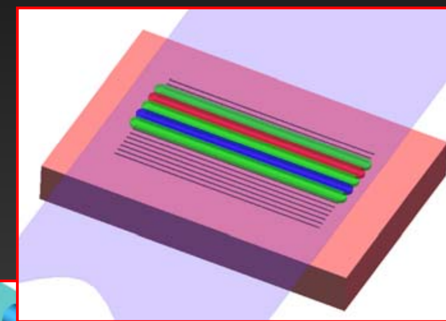


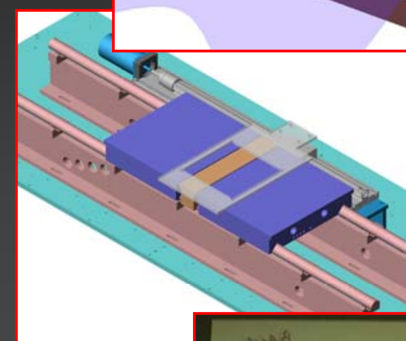
- **Result:** Working transistor with mobility ~3 $cm^2/V\text{-}s$
  - All layers by ALD
  - All patterning by selective area deposition
  - Transparent, too!

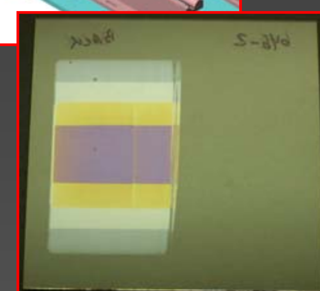


Conclusions

- Spatial ALD Approach
  - Open air performance demonstrated on rigid substrates
  - Scaleup and flexible work underway







- Applications
  - High performance semiconductor / dielectrics
  - Accessible patterning