Low ESH-impact Gate Stack Fabrication by Selective Surface Chemistry

(*Task Number: 425.026)*

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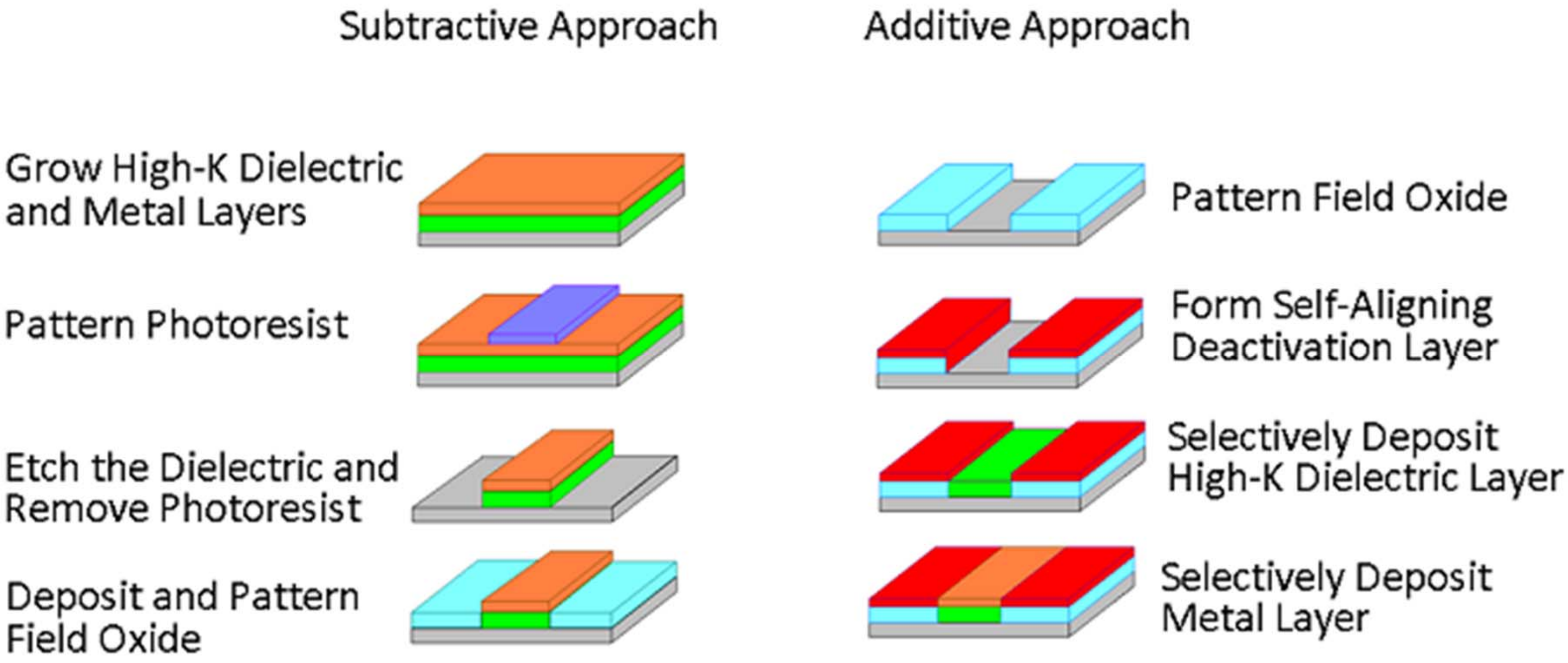
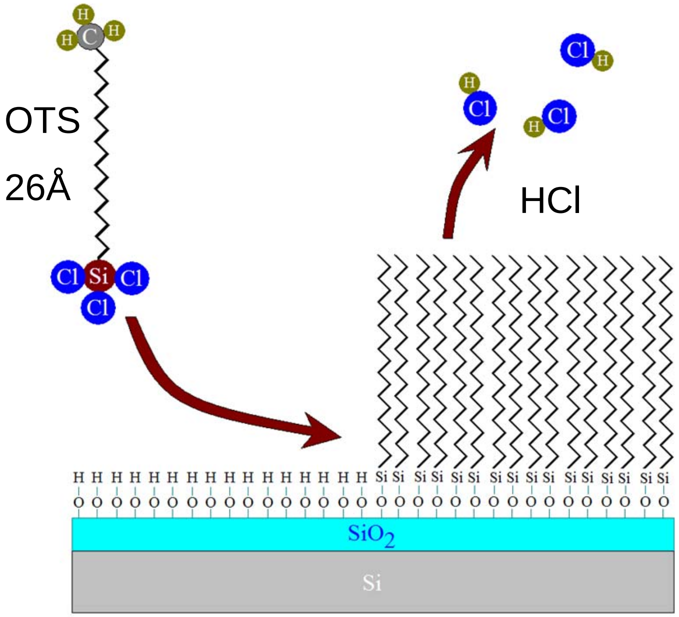
Industrial partners:
SFAZ
ASM

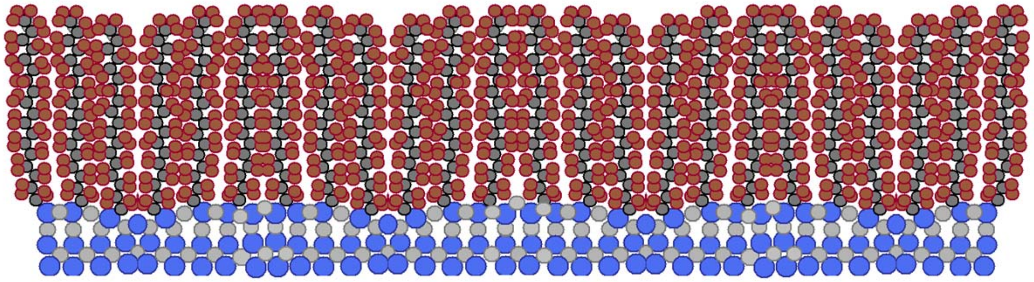
Overall Objectives

- **Simplify multistep subtractive processing used in microelectronic device manufacturing**
  - Develop new additive processes that can be integrated into current devices flows
- **Focus on high-k gate stack testbed**
  - Fabricate low defect high-k/semiconductor interfaces



Technical objective

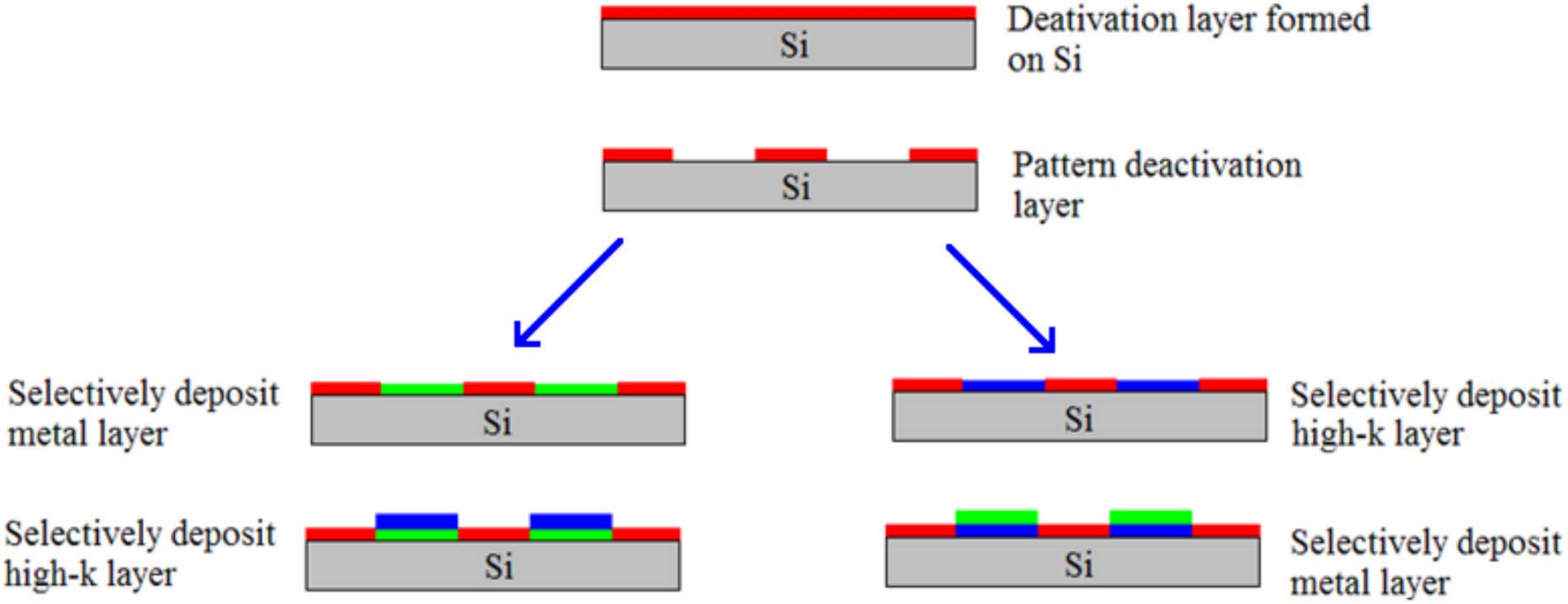




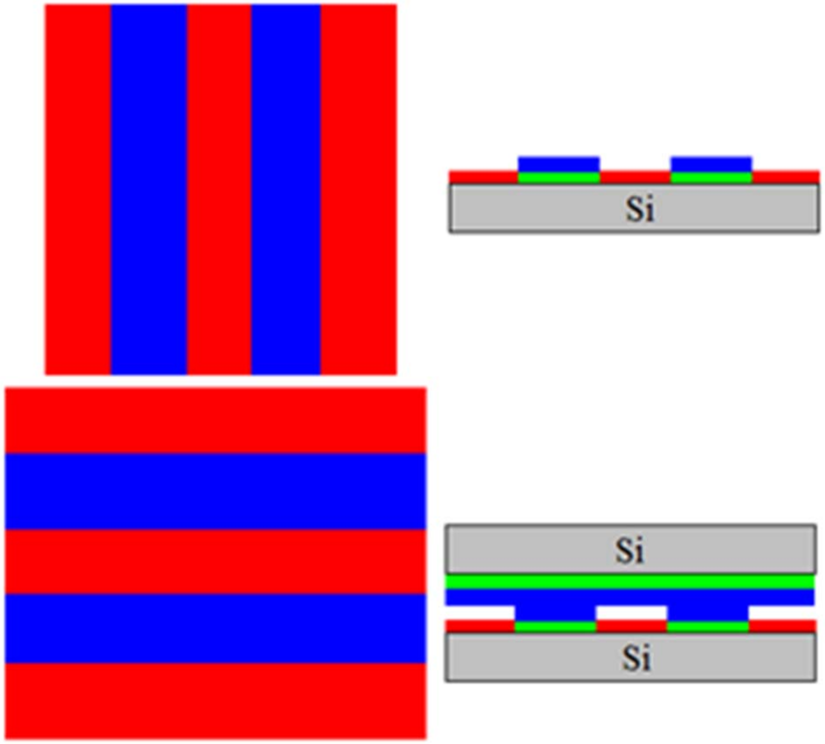
- Use a self-assembled monolayer (SAM) as a chemically inert layer preventing ALD deposition from occurring on surfaces
  - Identify and solve defects in SAM layers which result in deactivation failure (completed)
  - Pattern SAM layer for device manufacturing
  - Vapor phase SAM formation integrated with ALD system

Novel Device Manufacturing

- Single patterning step for deactivation layer
- Use selective ALD of metal and high-k dielectric layer



Novel Device Manufacturing



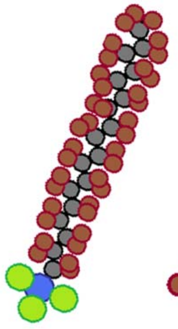
- Reconfigurable logic circuit for CMOS device
- Flip-Chip manufacturing
  - – Selectively create two halves of device

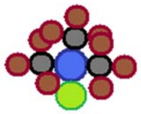
Xia, Q., “Memristor-CMOS Hybrid Integrated Circuits for Reconfigurable Logic”, Nano Letters, Vol.9, No.10, 3640-3645, 2009.

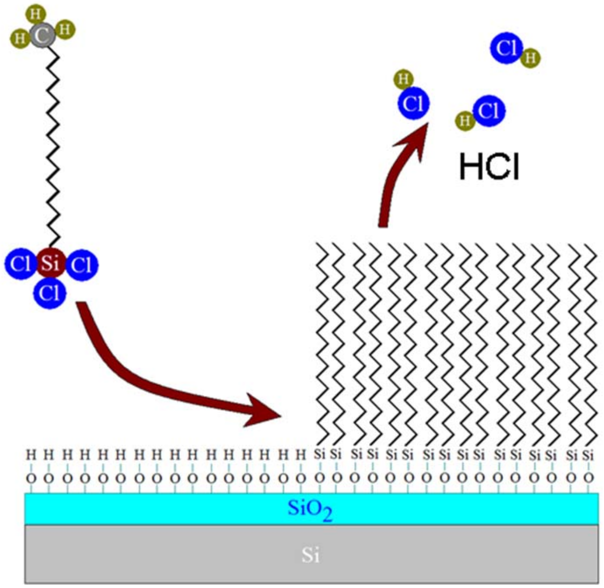
Coll, M., “Formation of Silicon-Based Molecular Electronic Structures Using Flip-Chip Lamination” J. AM. CHEM. SOC., *131*, 12451–12457, 2009

ESH Metrics and Impact: Cost Reduction

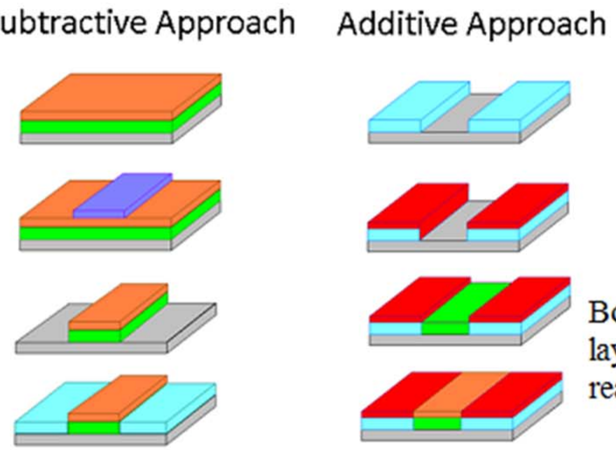
- Safety of SAM solution
  - Chlorosilanes dissolved in toluene
    - Chlorosilanes reacts with water, air sensitive, and combustible
      - OTS (octadecyltrichlorosilane)
      - TMCS (trimethylchlorosilane)
    - **Batch processing must be done in vented environment with controlled humidity and no spark or open flame**
    - **Vapor process could eliminate solvent**
  - Carbon and HCl are only byproducts of the surface reaction


OTS


TMCS



ESH Metrics and Impact: Cost Reduction



Eliminates high-K and metal etching step

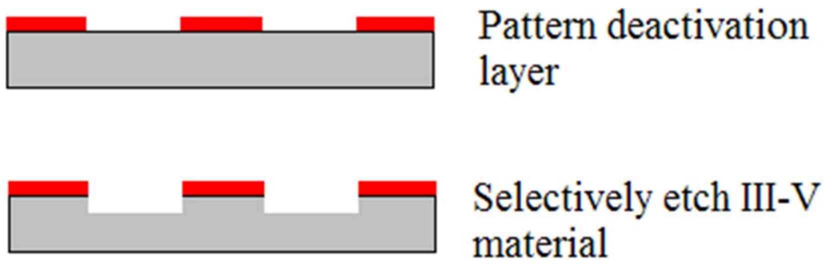
Both high-K and metal layers deposited in same reactor

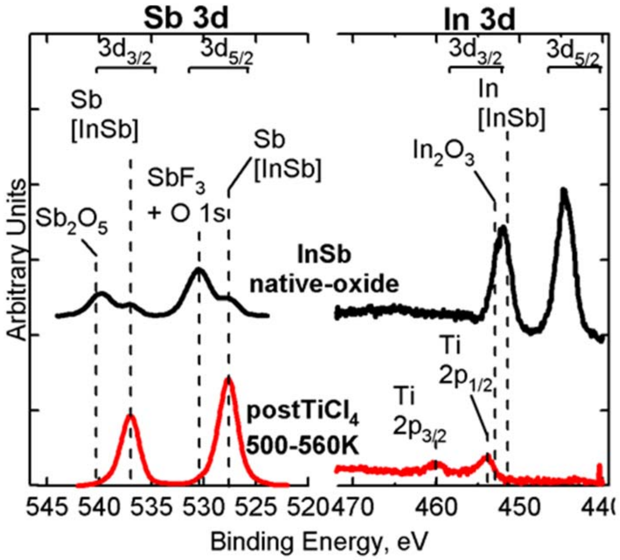
Reduced material use and waste with selective ALD growth

- Additional benefits of hydrophobic surface
  - SAM coating prevents aqueous solutions from interacting with surfaces
    - Coating metal parts or work surfaces which are exposed to water-based solution reduces the need for cleaning such tools/equipment
    - Coat ALD reactor walls with SAM to extend up-time, reduce cleaning, and improve throughput

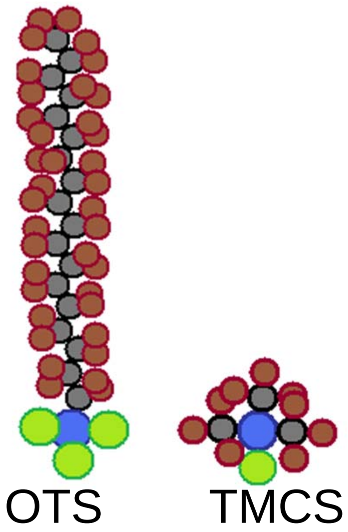
Area Selective Etching III-V

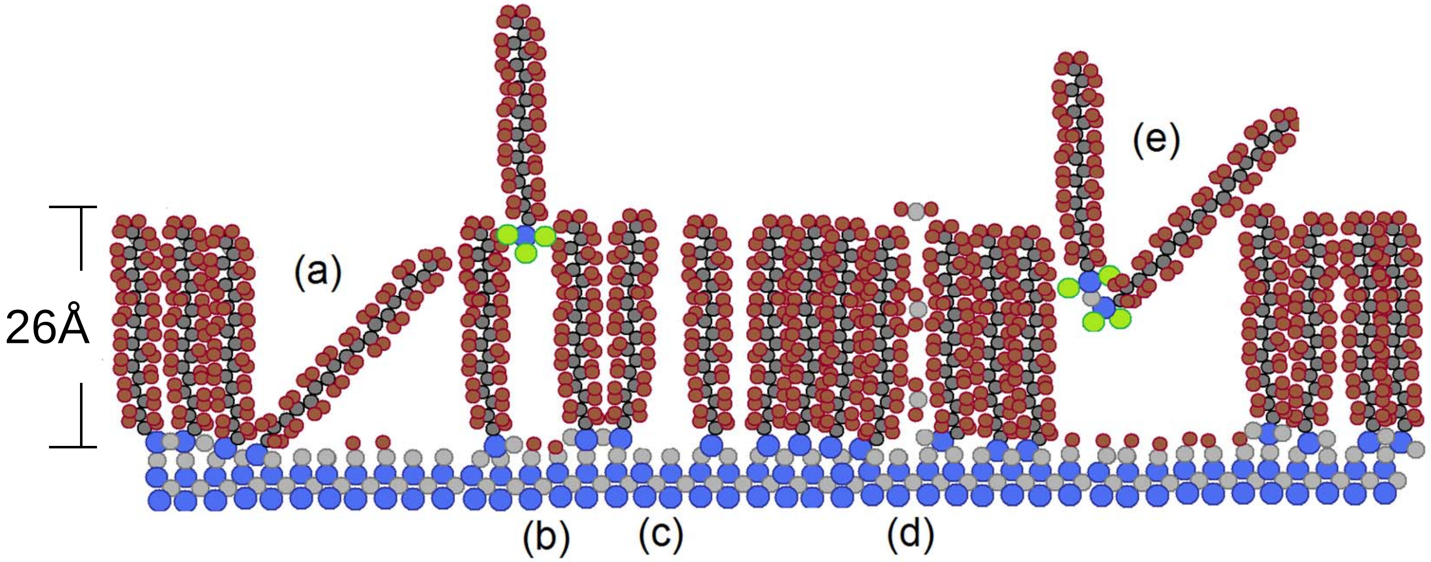
- Deactivation layer can be patterned on III-V semiconductors
  - Controlled chemical etching
  - Deactivation layer resistant to many liquid and vapor phase chemistries





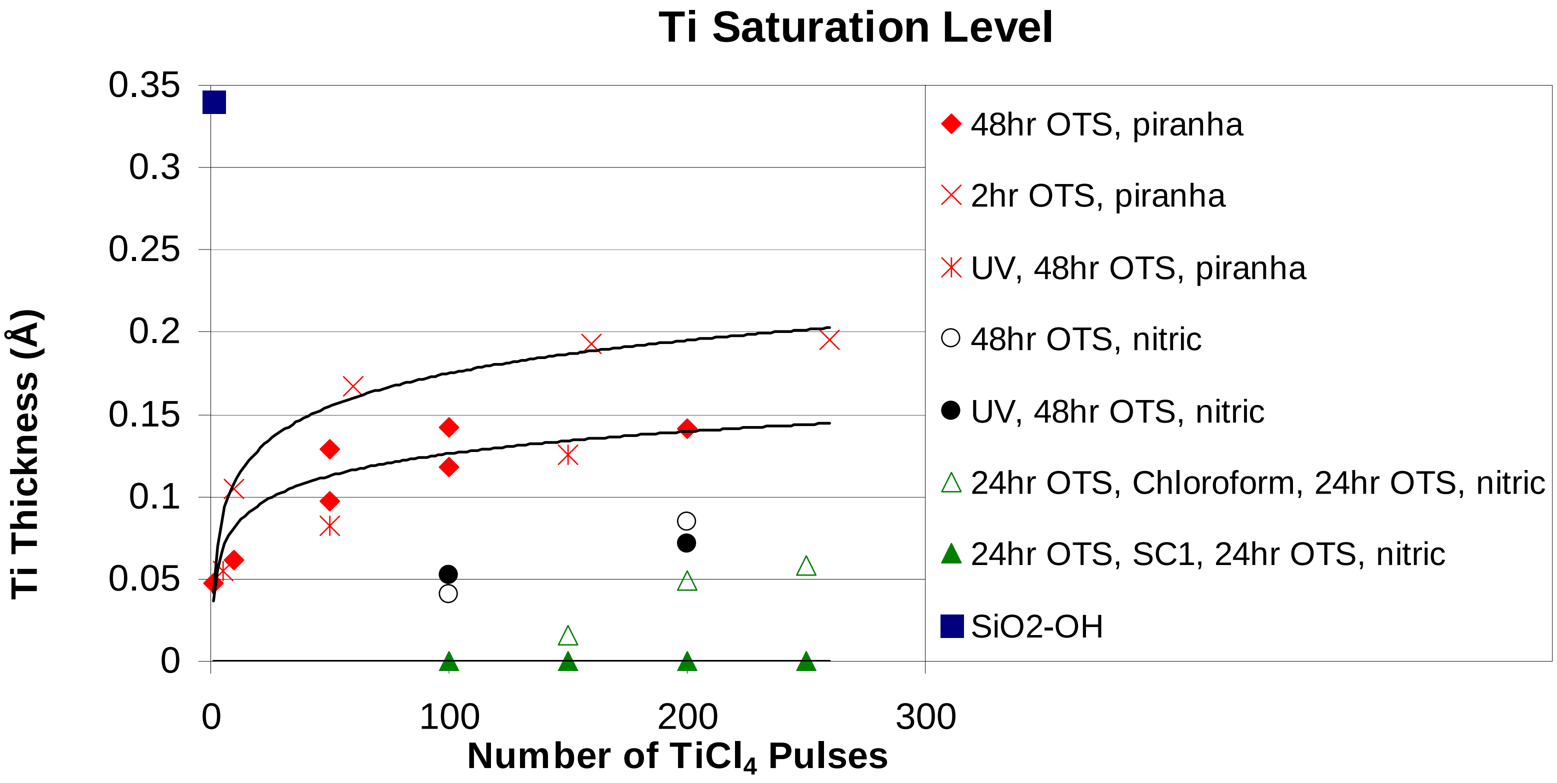
SAM Defects

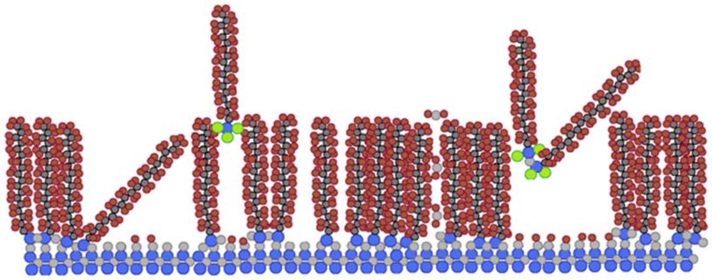




- (A) Poor alignment at island boundaries block surface sites (poor uniformity)
- (B,C) Gaps in SAM too small for primary SAM molecule
- (D) Water absorbed/adsorbed in SAM layer
  - Either during SAM formation or during ALD process
- (E) Polymerized SAM molecules on surface
  - Block surface sites
  - Excess polymer increases thickness and water contact angle
  - Could generate particles

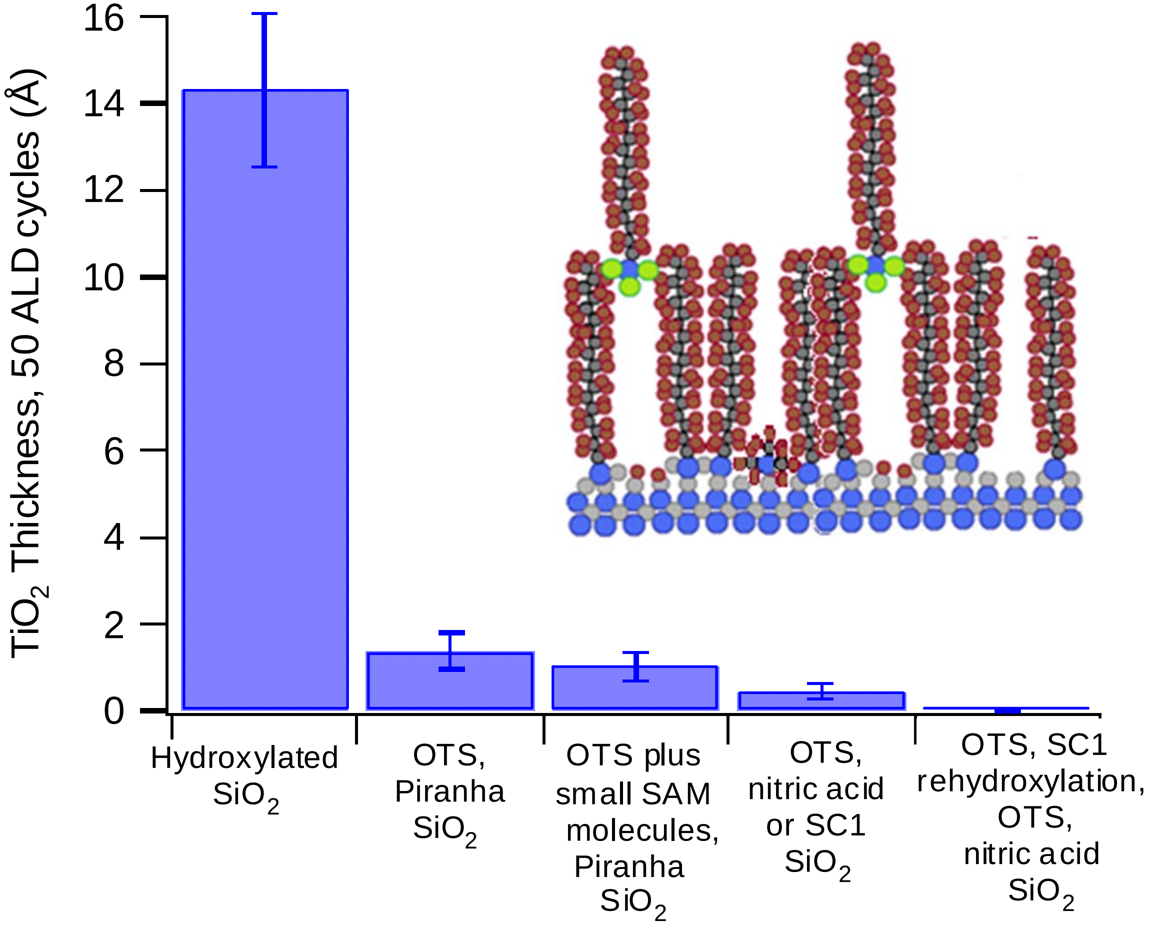
Defect monitoring using $TiCl_4$ pulses



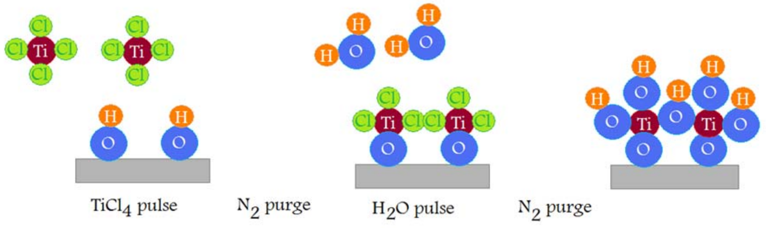


- Defect level in SC1 re-hydroxylated samples was below XPS limit for up to 250 seconds of $TiCl_4$ exposure

TiO_2 Deactivation results



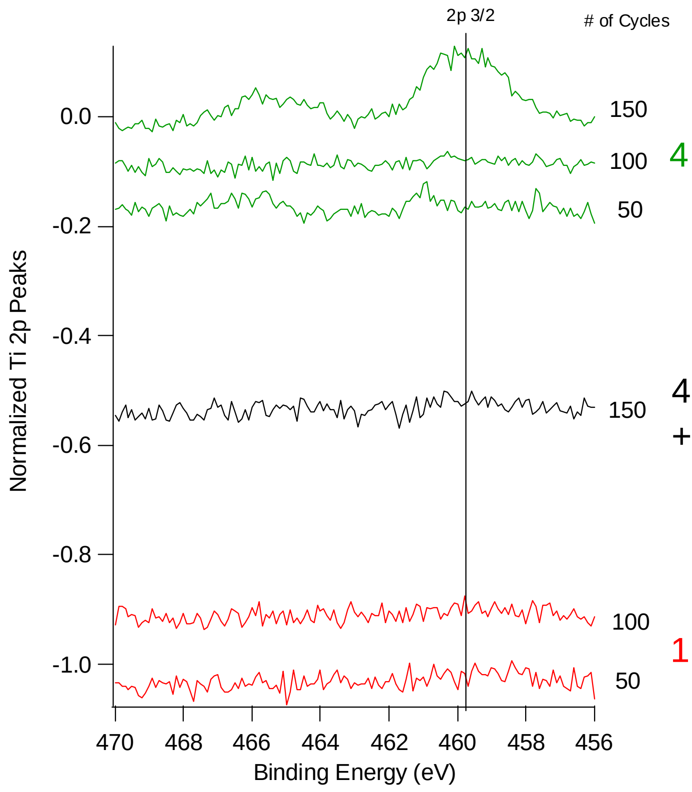
- Up to 200 Cycle deactivation achieved for TiO_2
  - Previous best was 50 cycles for HfO2 after 48hrs
- Providing more hydroxyl groups is key to continuing to increase density



Time scale reduction with re-hydroxylation

- Samples removed from OTS every hour and treated with SC1 re-hydroxylation

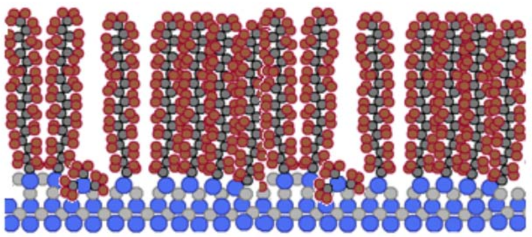
- Deactivation for up to 100 cycles was achieved after only 1hr in OTS solution and 1hr in TMCS (trimethylchlorosilane) solution
  - 1/24th original time scale



4 - 1hr OTS w/3 SC1 re-hydroxylations

4 - 1hr OTS w/4 SC1 re-hydroxylations + 1hr TMCS

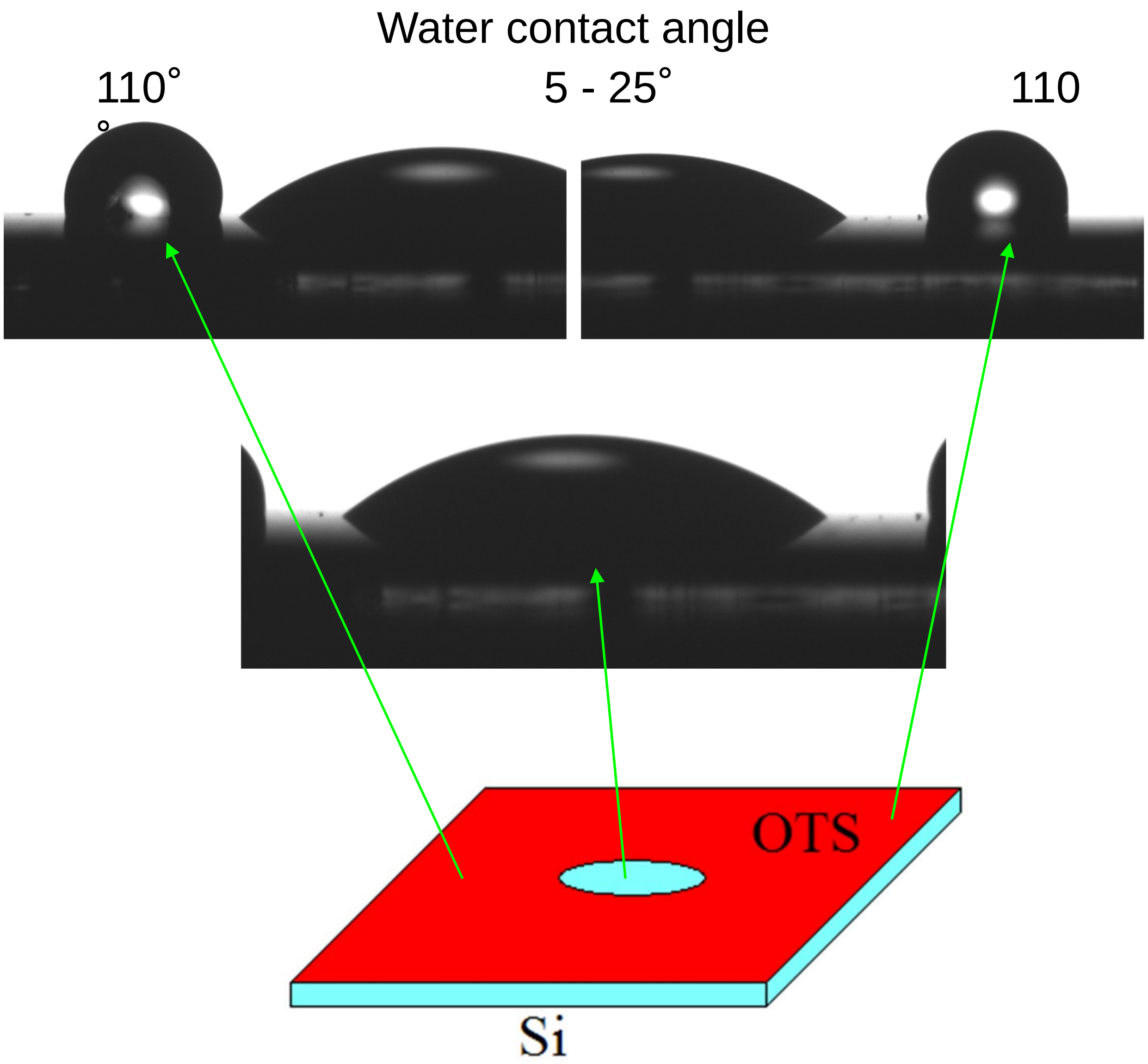
1hr OTS, SC1 re-hydroxylation, 1hr TMCS



Important Learning from Liquid Phase

- Surface hydroxylation proven to be the most important parameter in forming a high quality OTS SAM
  - OTS deposits quickly with abundant hydroxyl groups
    - Primary layer formed in first hour
  - OTS has difficulty finding small gaps once primary layer is formed
    - Same effect achieved with 1 hour TMCS exposure as with 3-1 hour OTS exposures and re-hydroxylations
- Vapor Phase SAM formation will require similar re-hydroxylation

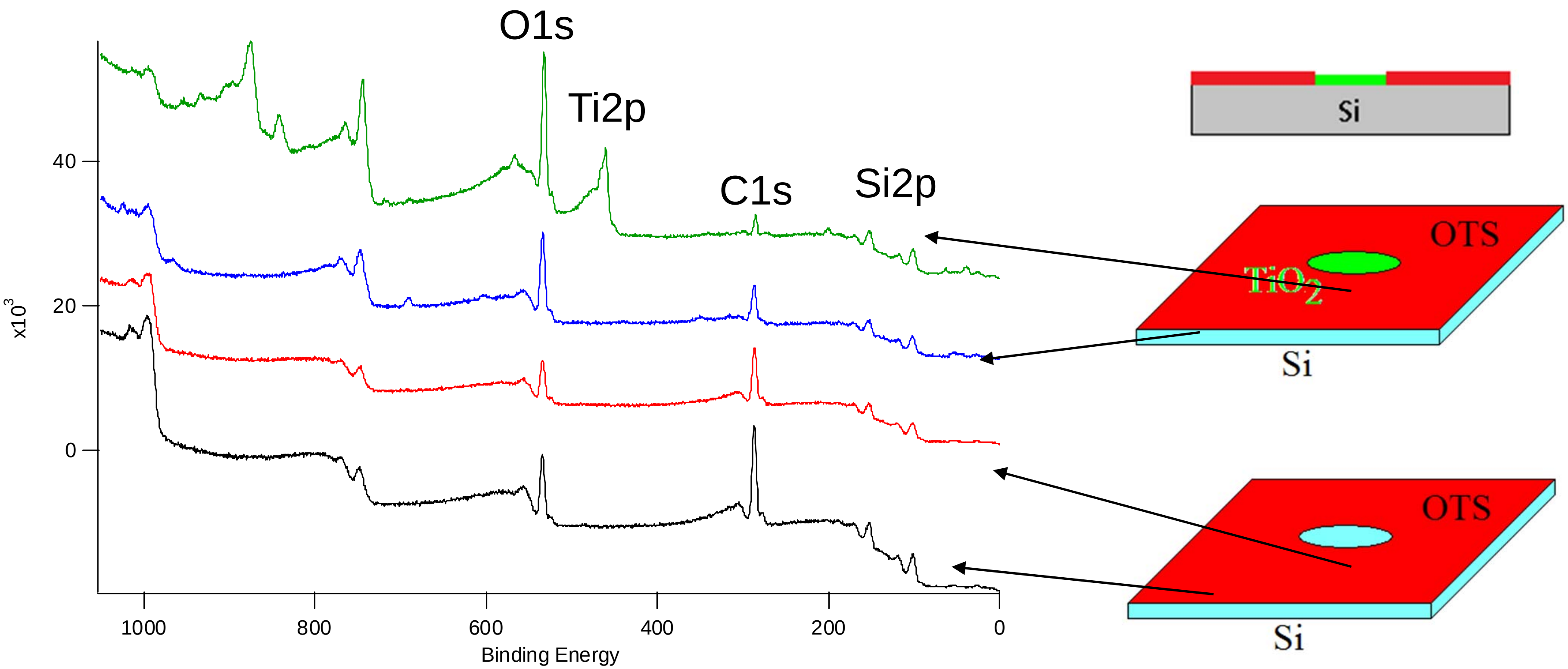
Selective high-k deposition



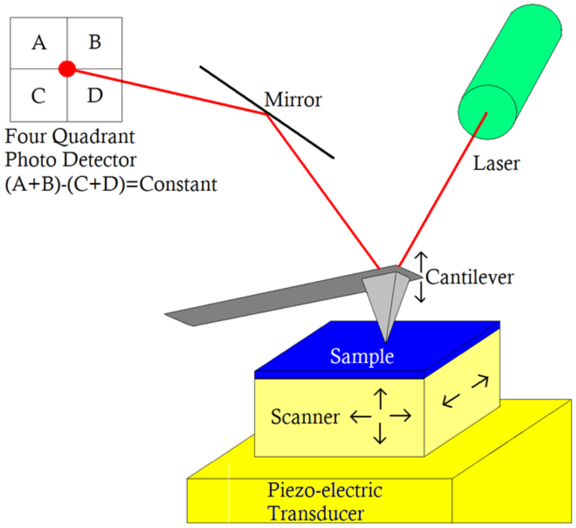
- SAM surfaces exposed to UV in air for 2.5 h through a simple mask
- Removal of SAM occurred only in UV/air exposed areas
- Surface was hydrophilic in UV/air exposed areas and hydrophobic on remaining OTS areas

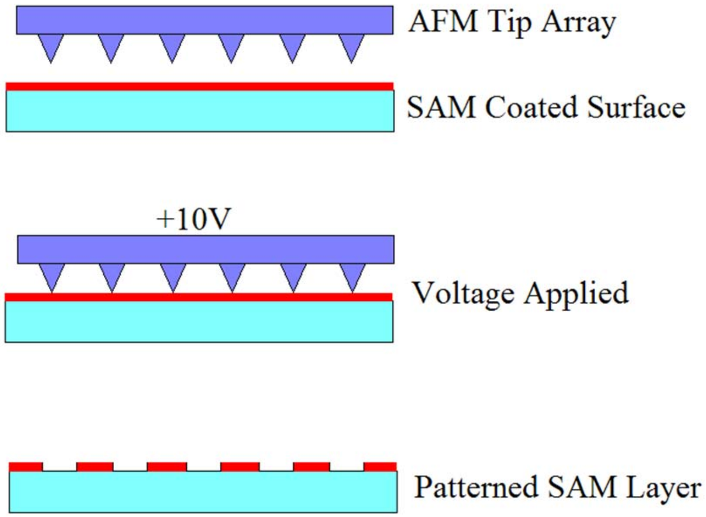
Direct SAM patterning

- Selectively deposited 15Å of TiO_2 only in open areas of OTS coated Si surface
- Pattern formed without photoresist



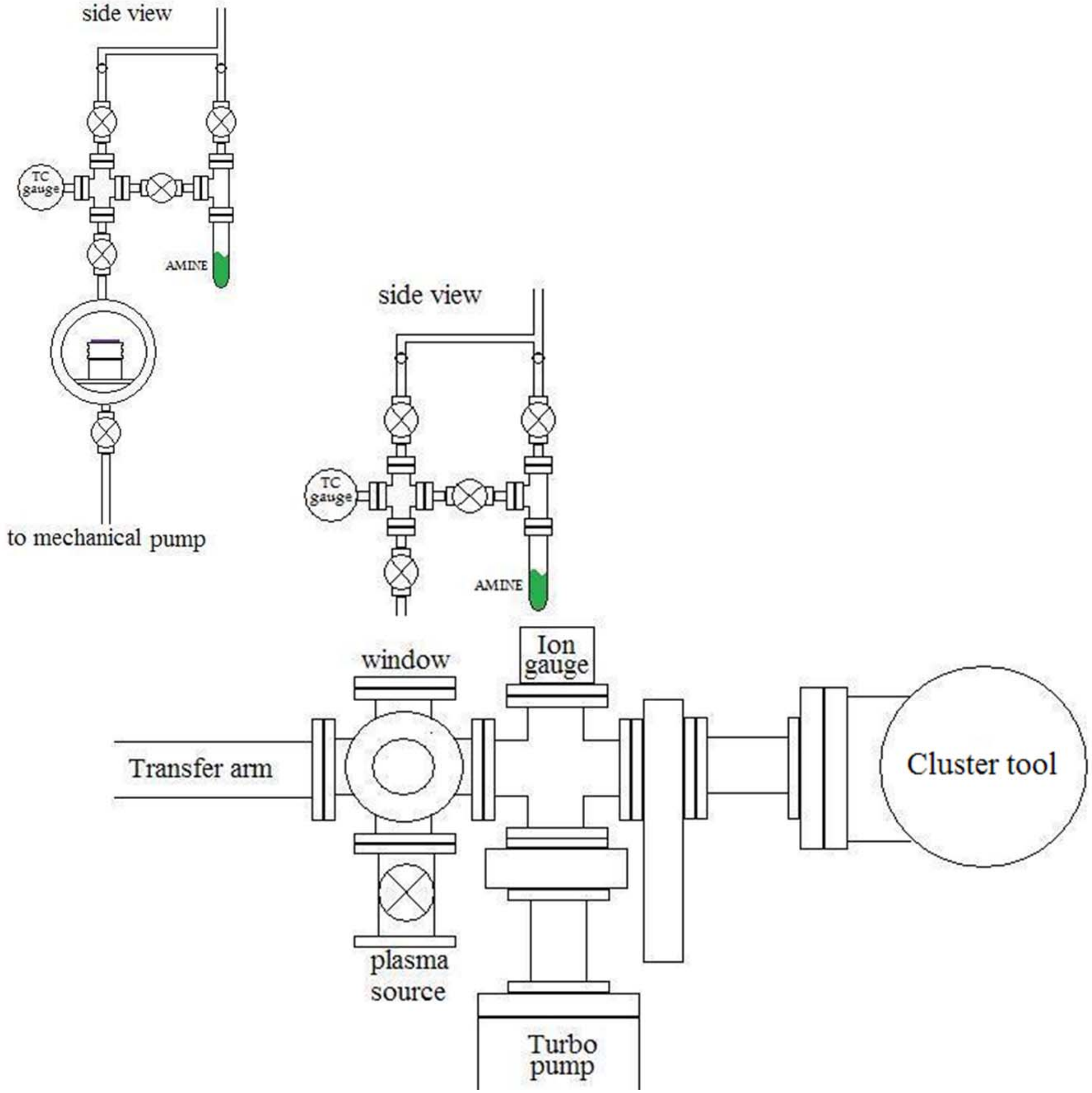
Alternate patterning approach





- Conductive atomic force microscopy (AFM) removes SAM
  - – Multiple tip arrays can be used to make detailed nm scale patterns
- No need for photoresist

New SAM Vapor/In-situ Hydroxylation Reactor



- Safe to install on cluster apparatus
  - Polymerization not seen in previous reactor
- Provides more versatile vapor delivery
- Allows higher temperature testing
  - 300° C
- In-situ hydroxylation
- Connected in-situ to ALD reactor
- Vials are well isolated from other chemicals

Conclusions

- Demonstrated controlled selective deposition of high-k dielectric layer
  - 2 hrs SAM formation time scale
  - Reduced SAM defects (100+ ALD cycles)
  - Only one patterning step required for metal and dielectric deposition (self-aligning high-k growth)
- Simplifies the front end gate stack manufacturing process
  - Reduced cost
  - Reduced material usage
  - Improve environmental performance

Industrial Interactions and Technology Transfer

- Biweekly project updates to ASM
  - Eric Shero
  - Mohith Verghese

Future Work

- Determine the line spreading and line edge roughness for different patterning approaches

- Determine usable lifetime of SAM solution

- Develop an industrially viable method for vapor phase delivery of SAM molecules
  - Pulse and purge both water and SAM molecules as opposed to sealing vapor in a reactor for extended time
  - Extend re-hydroxylation process to vapor phase SAMs

- Characterize SAM layers
  - Thermal stability for deactivation
  - Durability for large numbers of ALD cycles
  - Lifetime of SAM solution

- Investigate selective deposition/etching method on III-V semiconductor surfaces