Low ESH-impact Gate Stack Fabrication by Selective Surface Chemistry

Project 425.026

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ERC Review Meeting
Feb 19-20, 2010
Tucson, AZ

Industrial partners:
Sematech
ASM

Low ESH-impact Gate Stack Fabrication by Selective Surface Chemistry

(*Task Number: 425.026)*

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Graduate Students:

- **Shawn Miller, MS candidate, Optical Science and Engineering, UA**

Cost Share (other than core ERC funding):

- **ASM**

Industrial Interactions and Technology Transfer

- **Biweekly project updates to ASM**

Mentors

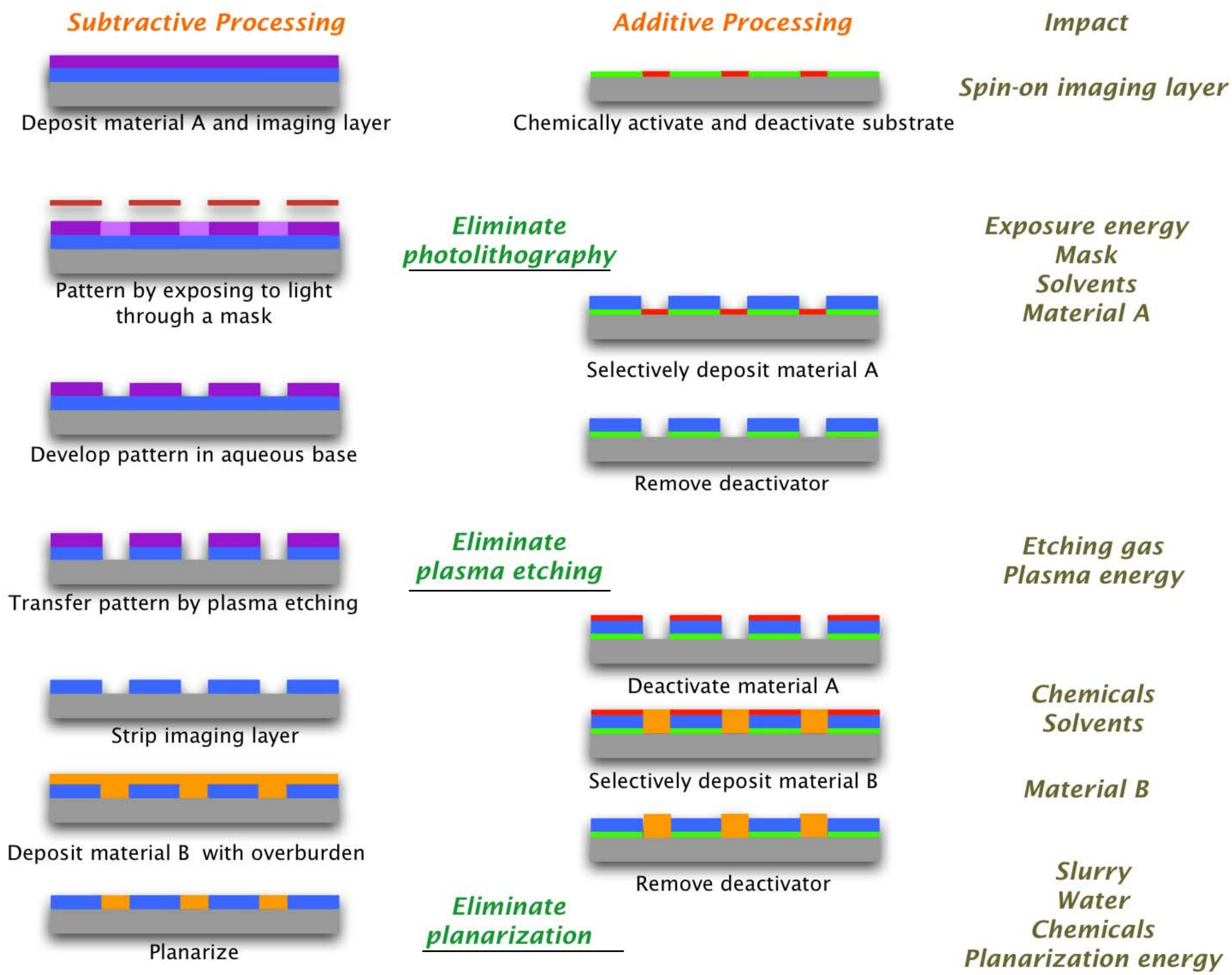
- **Joel M. Barnett, SEMATECH**
- **Willy Rachmady, Intel**

Objectives

- **Simplify multistep subtractive processing used in microelectronic device manufacturing**
  - Develop new processes that can be integrated into current devices flows
  - Minimize water, energy, chemical, and materials consumption
  - Reduce costs

- **Focus on high-k gate stack testbed**
  - Fabricate low defect high-k/semiconductor interfaces

ESH Metrics and Impact: Additive Processing



ESH Metrics and Impact: Cost Reduction

- Integration of selective deposition processes into current front end process flow could reduce ~16% of the processing costs
  - Calculation based on Sematech cost model
  - Eliminate eight processing steps from the gate module
  - Tool depreciation, tool maintenance, direct personnel, indirect personnel, direct space, indirect space, direct material, and indirect material were included
  - Energy, waste disposal, and addition of two selective deposition steps were not included

- There is potential for greater ESH benefit due to minimized cost of raw materials and waste generated

Novelty

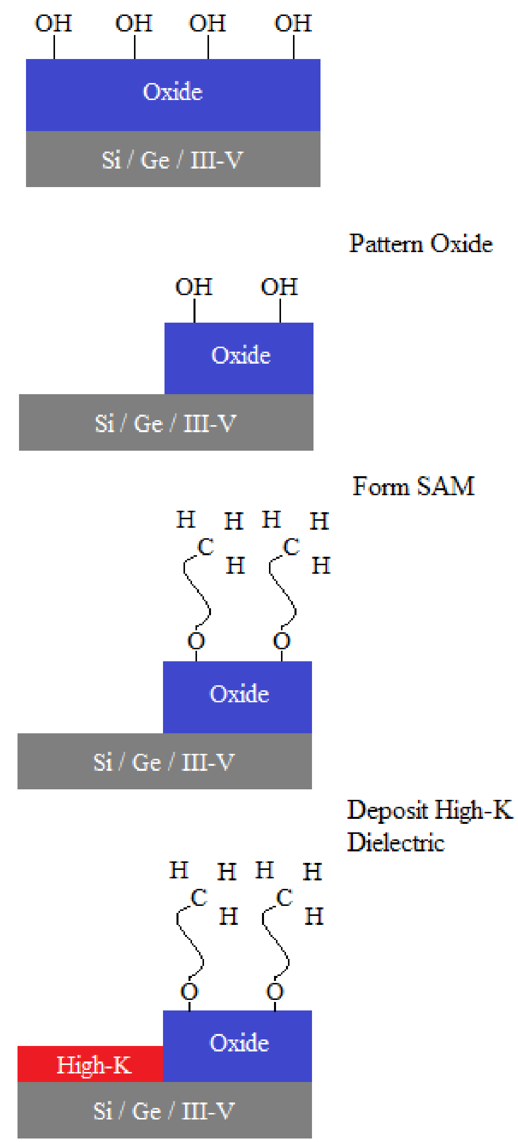
- Develop industrially feasible processes to activate and deactivate surfaces
  - Significantly lower time scale
  - Extend to metal and semiconductor surfaces

- Integrate selective deposition steps at carefully chosen points in the CMOS process flow
  - Realize ESH and technical performance gains

- Quantify costs associated with selective deposition steps to refine industry models
  - Account for energy and waste disposal
  - More accurate prediction of the cost model

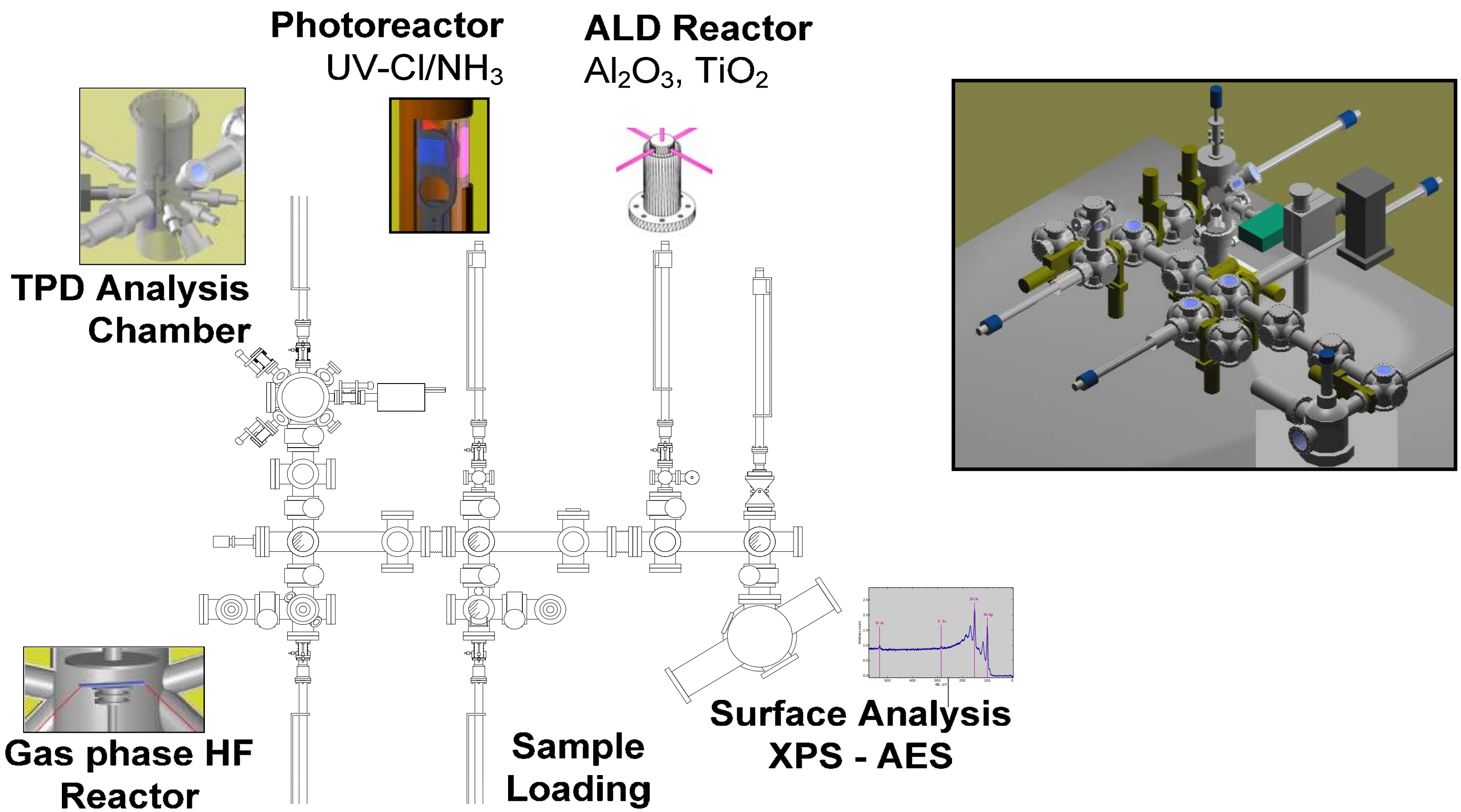
Methods and Approach

- Grow high-k films on semiconductors by activation and deactivation of surface sites
- Activation
  - Utilize surface chemistries to activate substrates for high-k film growth
  - Halogen, amine terminations
- Deactivation
  - Hydrophobic self assembled monolayer (SAM) prevents adsorption of H_2O
- Model systems
  - Si, Ge, and III-V substrates
  - High-k films by atomic layer deposition (ALD)
    - Al_2O_3
    - TiO_2



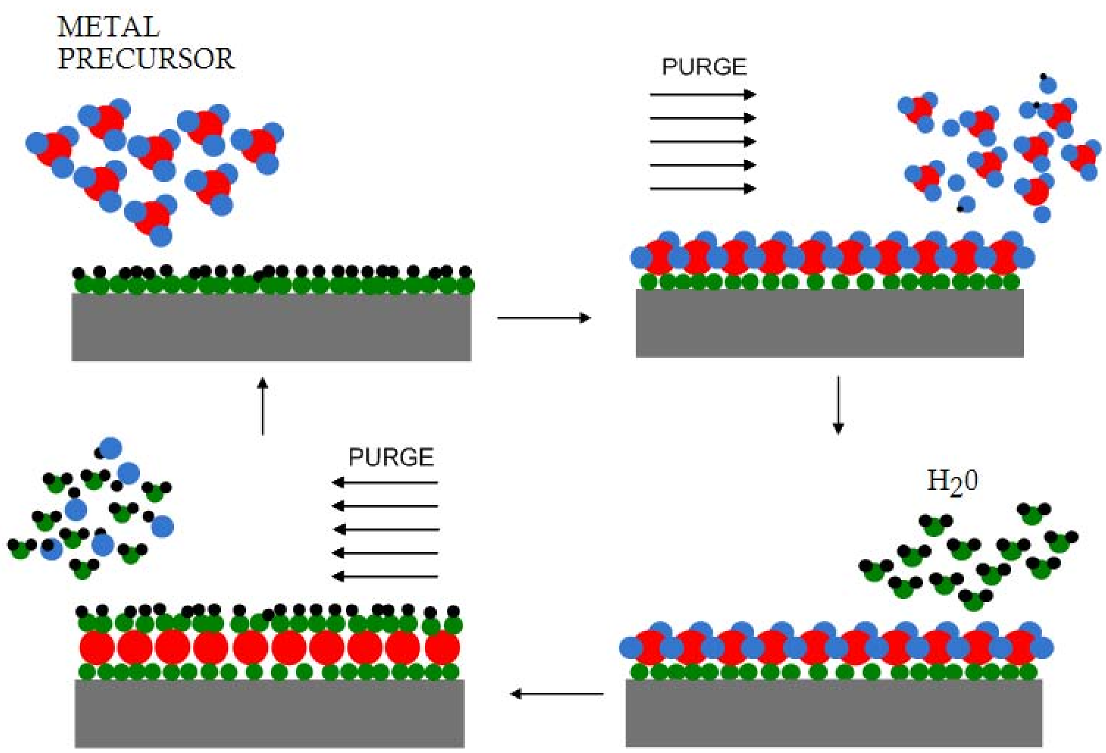
Clustered Reactor Apparatus

- In situ cleaning, high-k deposition, and surface analysis enables studies of surfaces without atmospheric contamination
  - Important for highly reactive substrate such as III-V materials



Atomic Layer Deposition of High-k Films

- Break overall reaction into two half reactions and run one at a time to achieve self-limiting growth
  - Surfaces exposed to sequential pulses of metal and oxygen precursors to deposit oxide



ALD Reaction Mechanism

- Factors governing the selective deposition of high-k film
  - Surface conditioning
  - Precursor selection
  - Deposition conditions

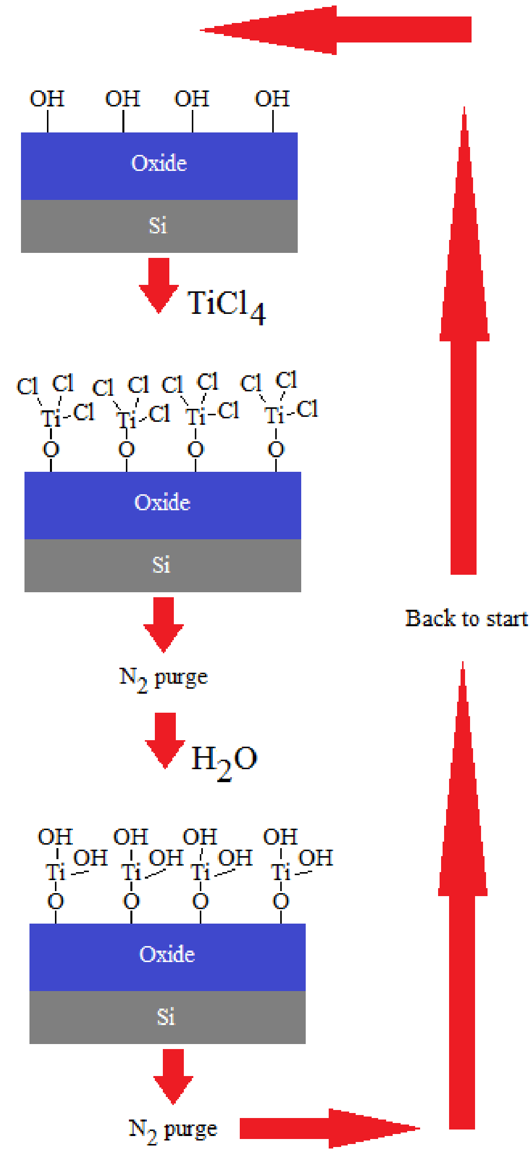
- Hydroxylated surface promotes high-k growth on Si

- Two half reaction in TiO_2 deposition

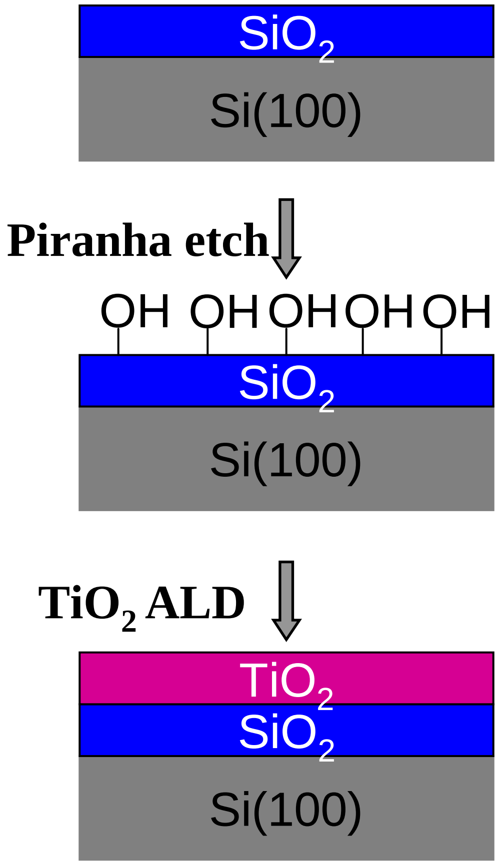
$$TiCl_{4(g)} + -OH \rightarrow -O\text{-}TiCl_3 + HCl_{(g)}$$

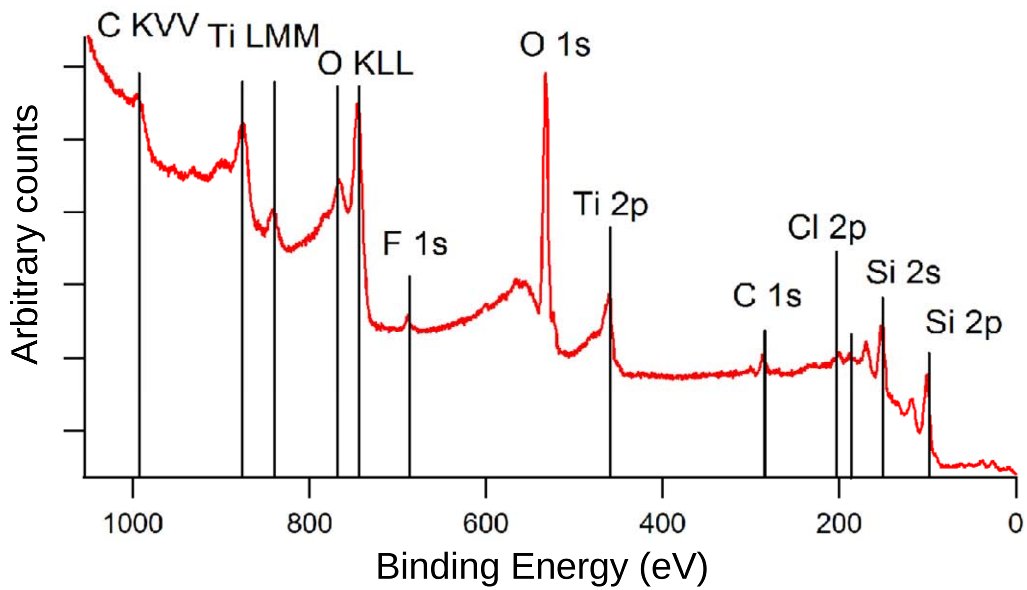
$$2\ H_2O_{(g)} + -O\text{-}TiCl_3 \rightarrow -O\text{-}Ti\text{-}OH + 3\ HCl_{(g)}$$

- Deposition mechanism using $TiCl_4$ precursor could be used as a model for $HfCl_4$ precursor



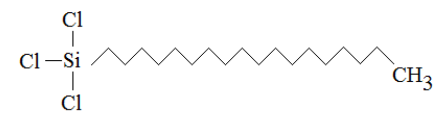
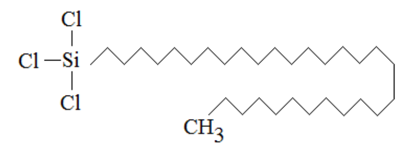
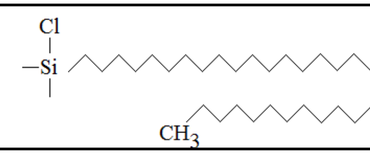
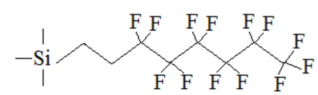
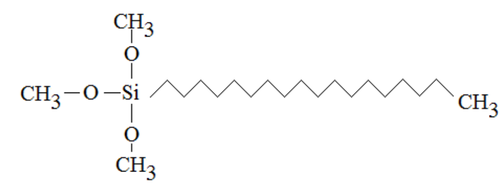
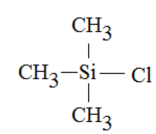
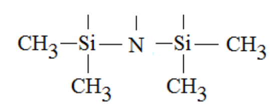
Si(100) high-k deposition: ALD of TiO2



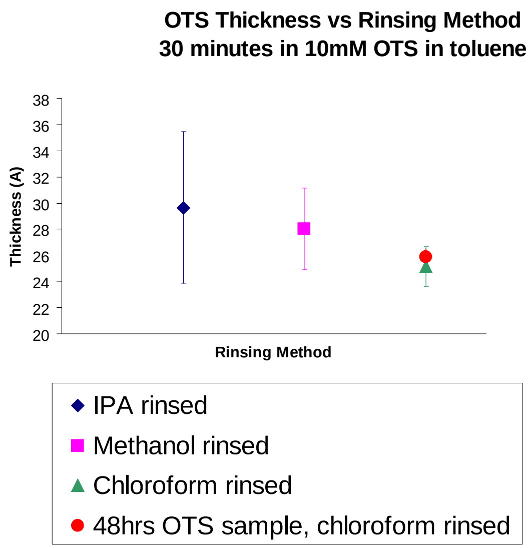


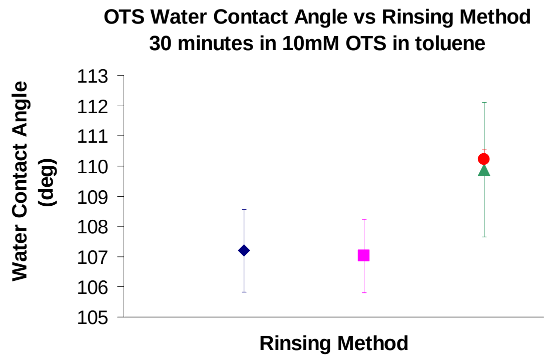
- Demonstrated TiO_2 deposition on hydroxylated Si(100)
  - Residual Cl present on surface
  - Si 2p peak still visible with ~9 Å thick TiO_2 layer

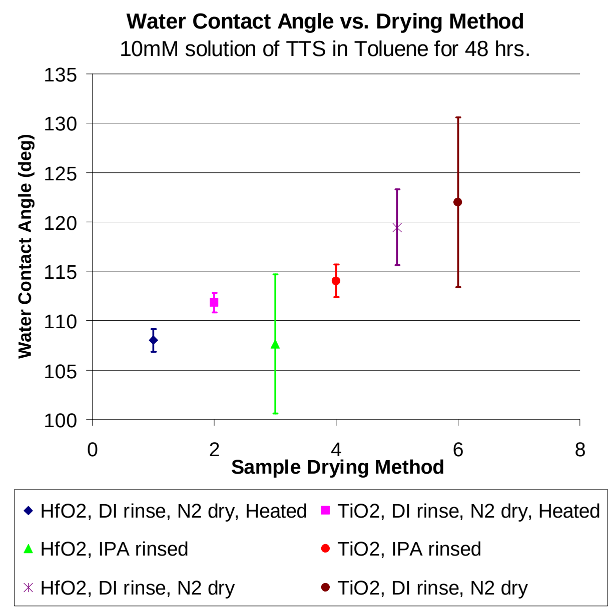
Deactivation using SAM Chemicals

SAM molecules	Formula	Structure
Octadecyltrichlorosilane OTS	$C_{18}H_{37}Cl_3Si$	
Triacontyltrichlorosilane TTS	$C_{30}H_{61}Cl_3Si$	
Triacontyldimethylchlorosilane TDCS	$C_{32}H_{67}ClSi$	
Tridecafluoro-1,1,2,2-tetrahydrooctylsilane FOTS	$C_8H_7F_{13}Si$	
Octadecyldimethoxysilane ODS	$C_{21}H_{43}O_3Si$	
Trimethylchlorosilane TMCS	C_3H_9ClSi	
Tretramethydisilazane TMDS	$C_4H_{14}NSi_2$	

Surface Deactivation: SAM formation

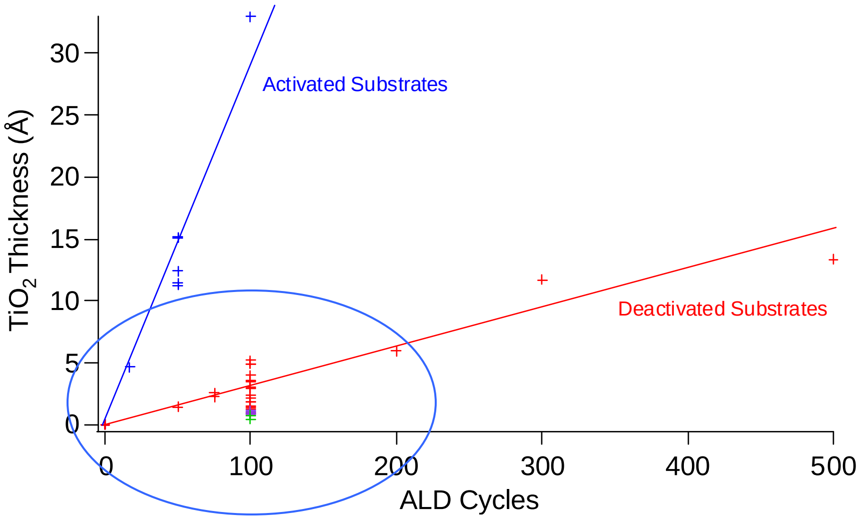


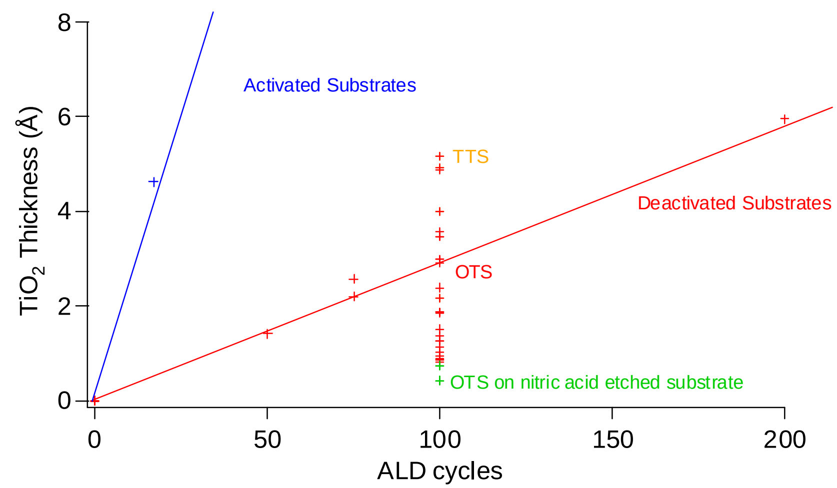




- High quality OTS layer after only 30 minutes (not 2hrs)
  - 26Å
  - 110° water contact angle
  - Smaller standard deviation after 48hrs in OTS than 30min in OTS
- Chloroform rinse was more effective than IPA and Methanol for OTS and TTS
- Polymerization of the SAM molecule was observed due to reaction with adsorbed water producing large deviation in the water contact angle

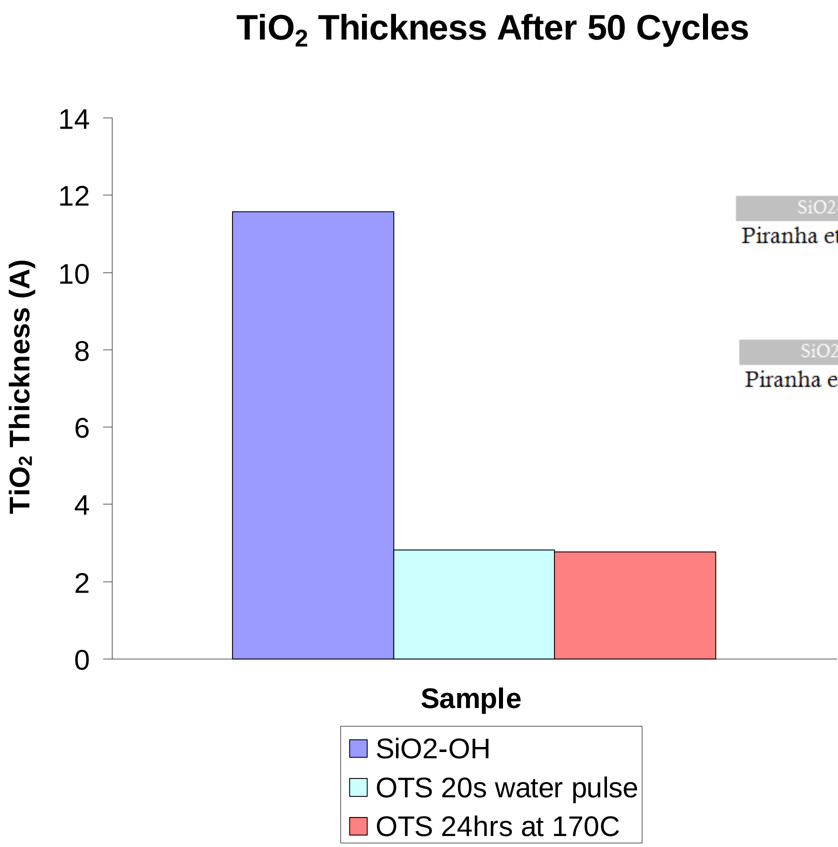
Surface Deactivation: Results

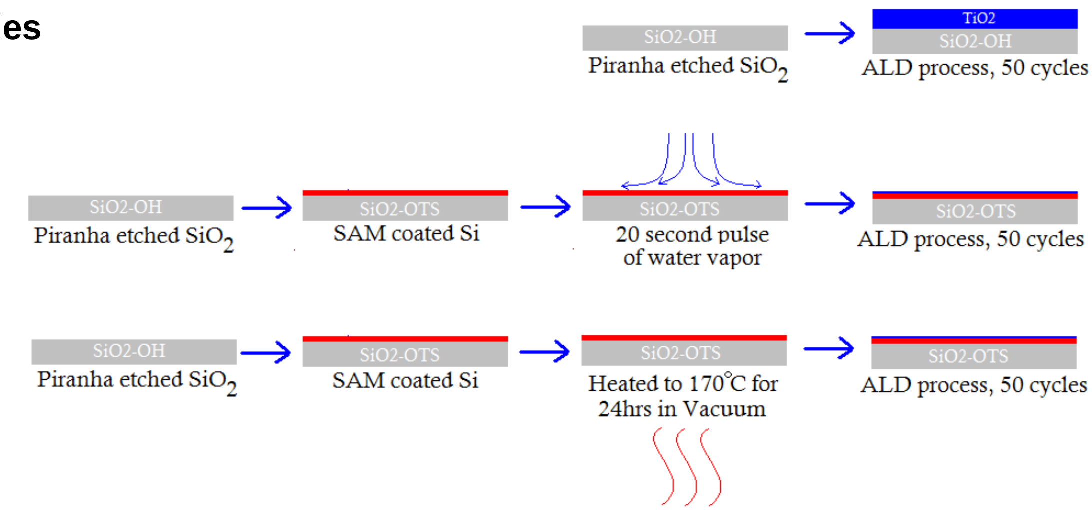




- Reduced TiO_2 growth rate by up to a factor of 50 ± 5
  - Data spread primarily due to sample variation within each solution batch
- Potential SAM defects
  - Water in/on SAM
  - Unblocked hydroxyl groups
  - Exposed Si-O bridges
- Improve deactivation by performing nitric acid etch or SC1 cleaning before SAM formation

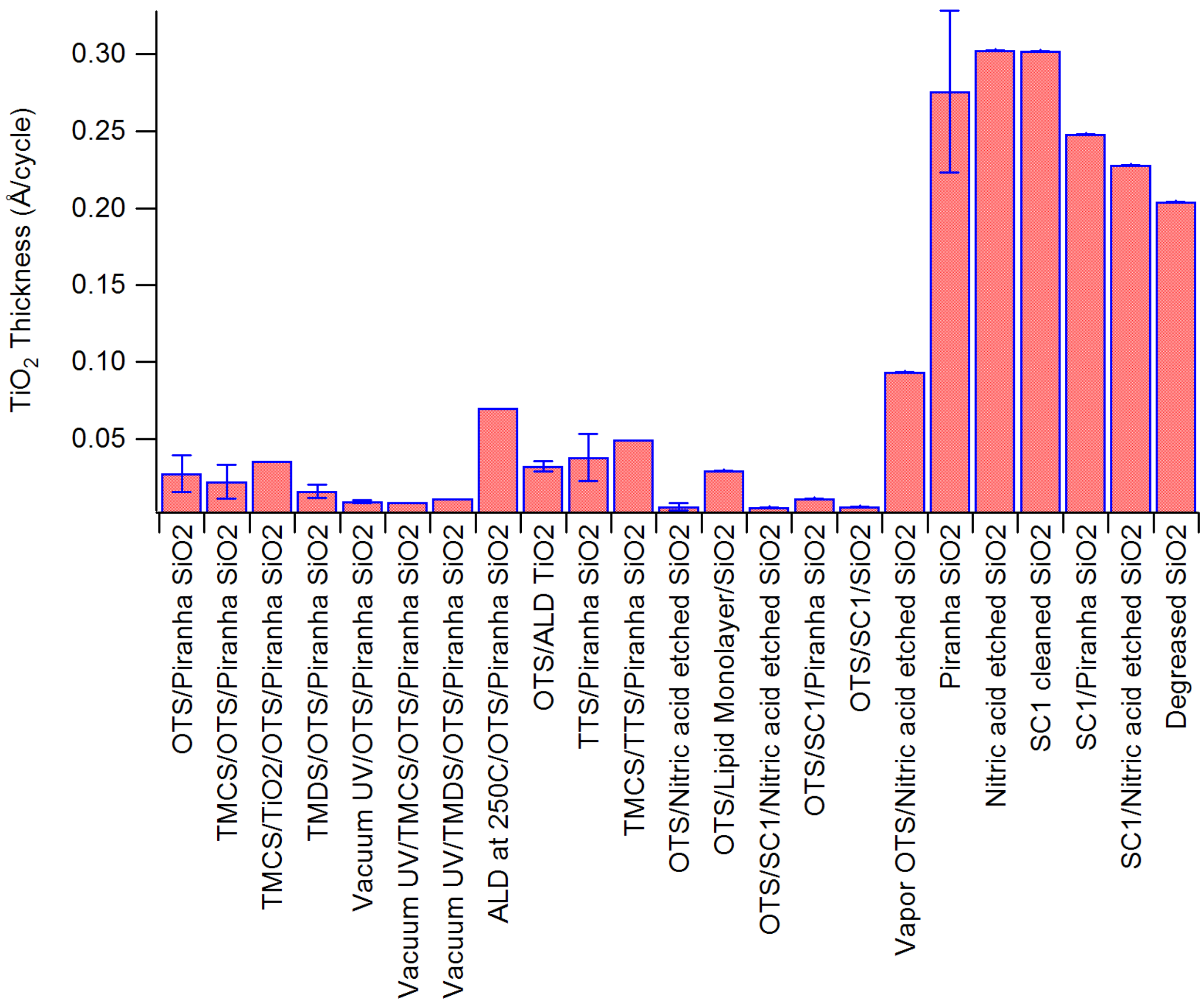
Surface Deactivation: Effect of Water





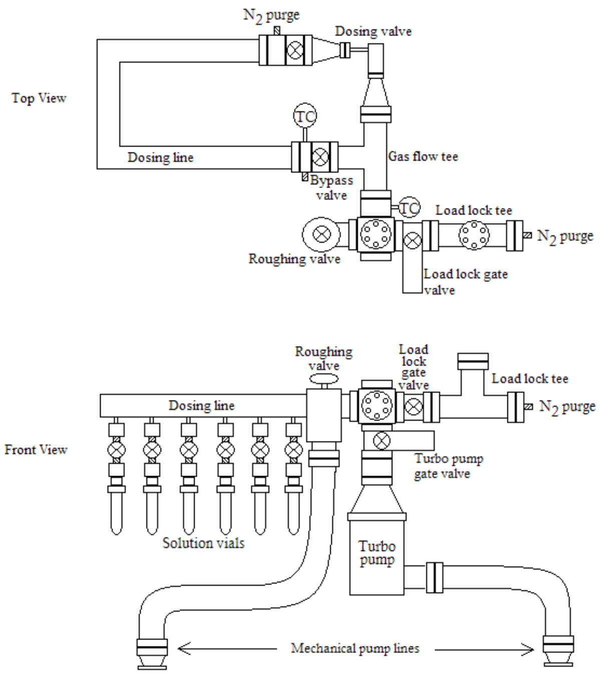
- SAM is equally stable to subsequent water pulses during an ALD process
  - No change in Ti due to additional 20 second water pulse before ALD

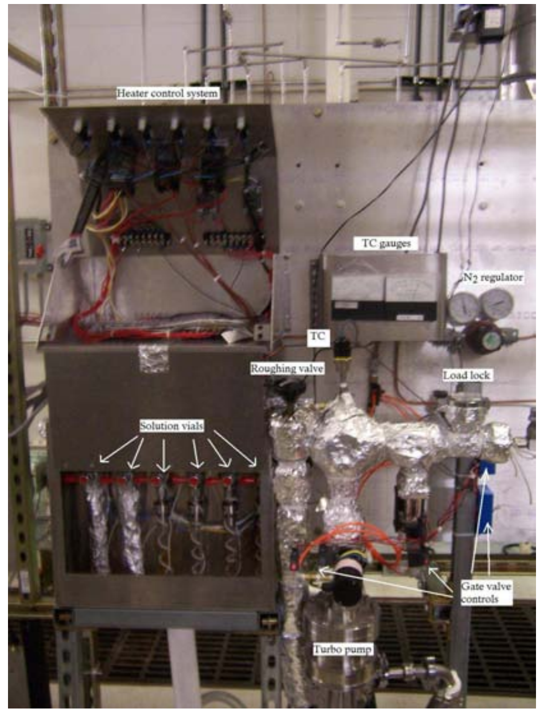
Surface Deactivation / Activation



- Improve SAM deactivation capability by
  - Replacing piranha etch step with a nitric acid or SC1 cleaning

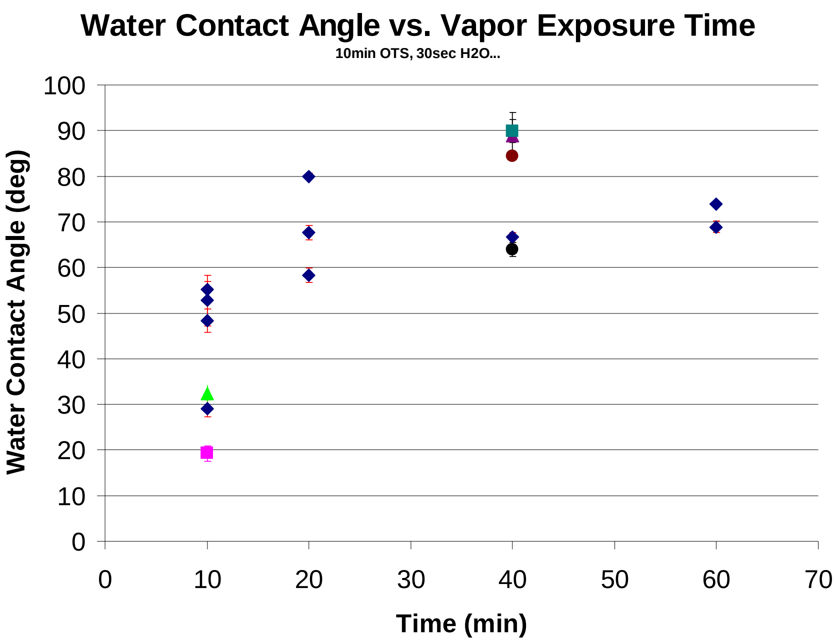
SAM Vapor Phase Delivery: Reactor

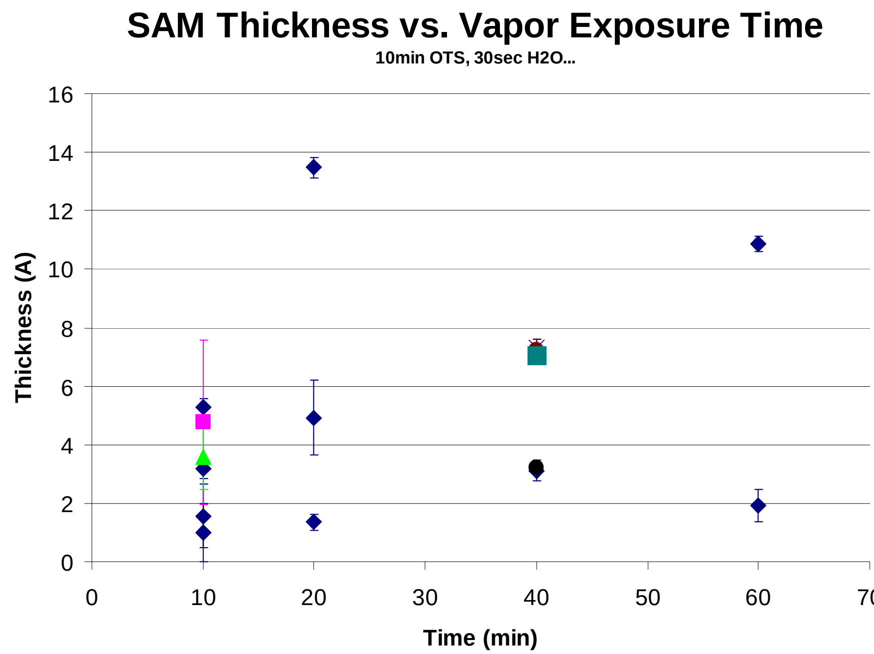


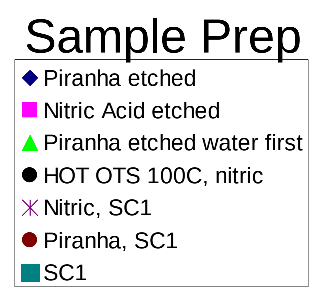


- Vacuum vessel designed to optimize vapor phase delivery of SAM molecules
- Control variables:
  - Vapor pressure
  - Exposure time
  - Temperature of substrate, reactor walls, and SAM solutions
  - SAM and water vapor delivery method
    - Individually
    - Simultaneously
    - Alternately with N_2 purge between pulses

SAM Vapor Phase Delivery: Results







- 95° water contact angle obtained after only 40 min of vapor OTS exposure
  - 1 cycle = 10min OTS/N_2 purge/pump/30s water/N_2 purge/pump
  - Without water pulses maximum water contact angle was only 65°

Conclusions

- Growing the SAM layer on nitric acid etched and SC1 cleaned samples eliminates many of the defects found in SAM layer formed on piranha etch samples

- 95° water contact angle obtained after only 40 min of vapor OTS exposure
  - SC1 cleaning of the chemical oxide layer has aided in SAM attachment to the surface both in vapor phase and liquid phase

- SAM layer is stable during the ALD water pulse process
  - $TiCl_4$ is the nucleating precursor

Future Work

- Investigate vapor phase ozone and gas phase HF/vapor treatment to increase and control hydroxylation of oxide surfaces

- Characterize SAM layers
  - Thermal stability for deactivation
  - Durability for large numbers of ALD cycles
  - Chemical bonding between SAMs and surface
  - Degradation and repair of SAMs layers

- Extend deactivation study to Al_2O_3, TiO_2, HfO_2 surfaces

- Optimize 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

- Investigate optimized selective deposition method on III-V semiconductor surfaces