Low ESH-impact Gate Stack Fabrication by Selective Surface Chemistry

Project 425.026

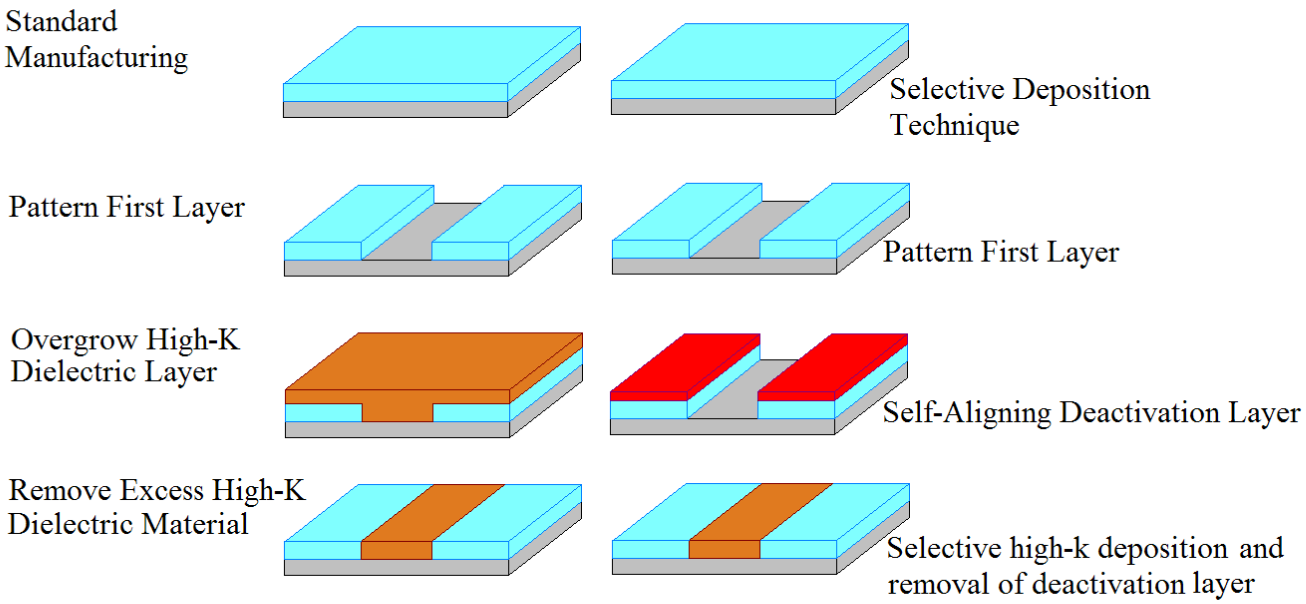
Shawn Miller and Anthony Muscat
Department of Chemical and Environmental Engineering
University of Arizona, Tucson, AZ 85721

ERC Teleconference
June 17, 2010
Tucson, AZ

Industrial partners:
Sematech
ASM

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



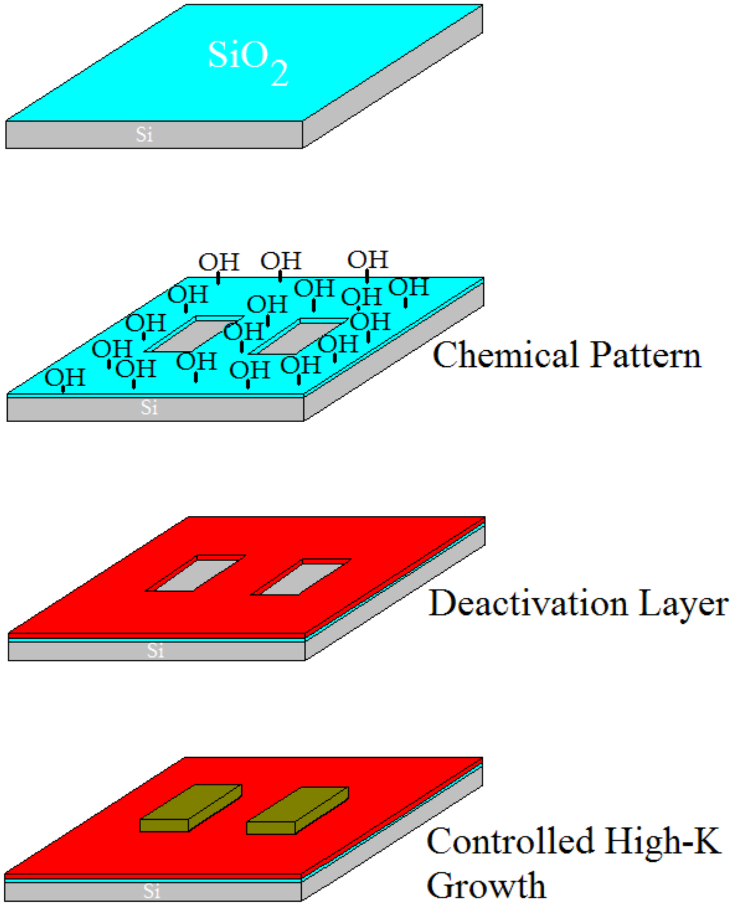
ESH Metrics and Impact: Cost Reduction

- 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

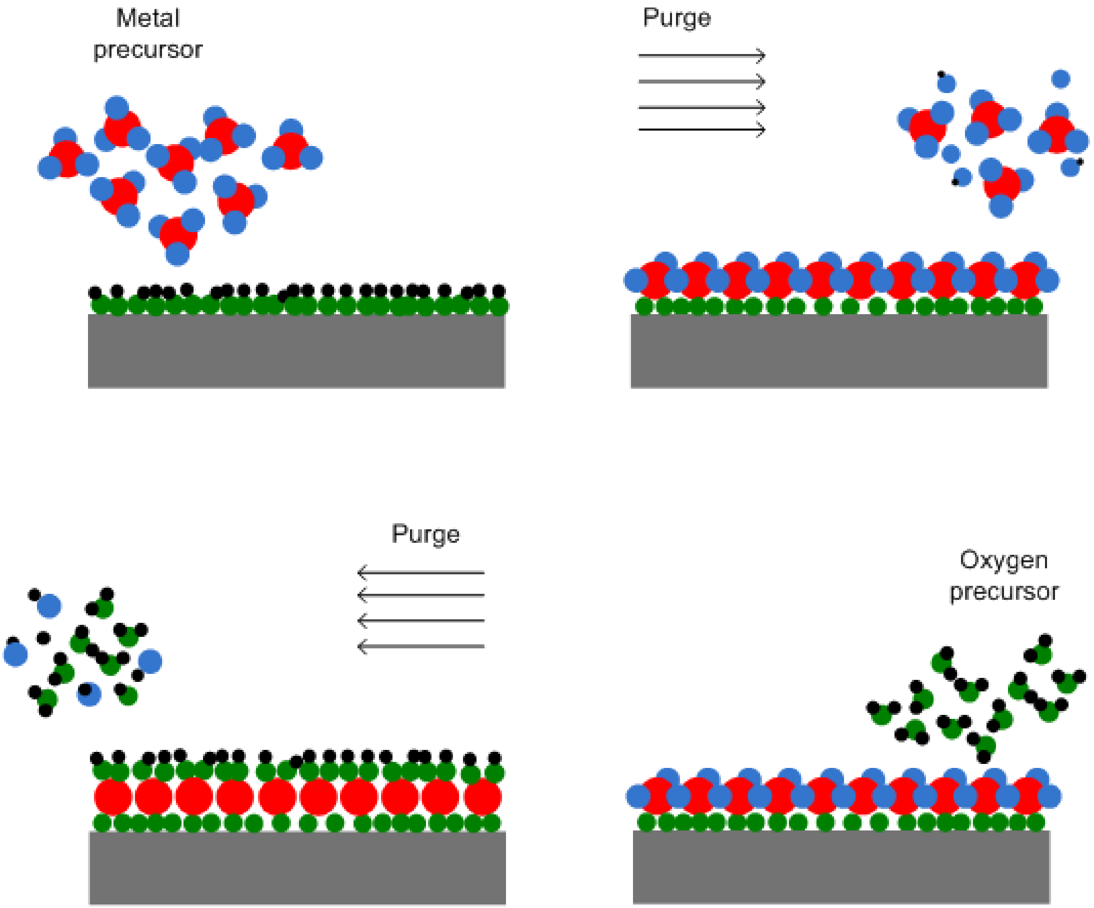
Methods and Approach

- 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
    - Prevents reaction of metal precursor
- Model systems
  - Si, Ge, and III-V substrates
  - High-k films by atomic layer deposition (ALD)
    - Al_2O_3
    - TiO_2

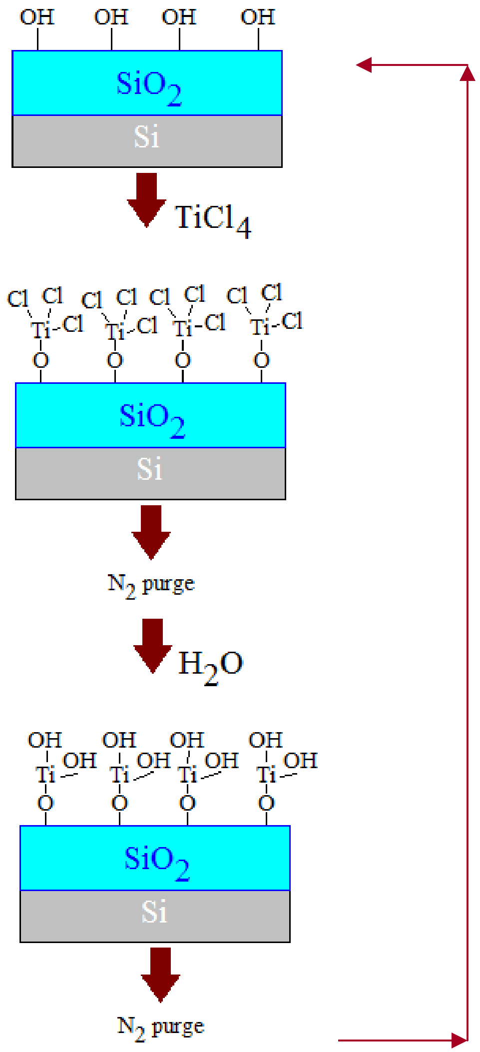


Atomic Layer Deposition of High-k Films

- 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

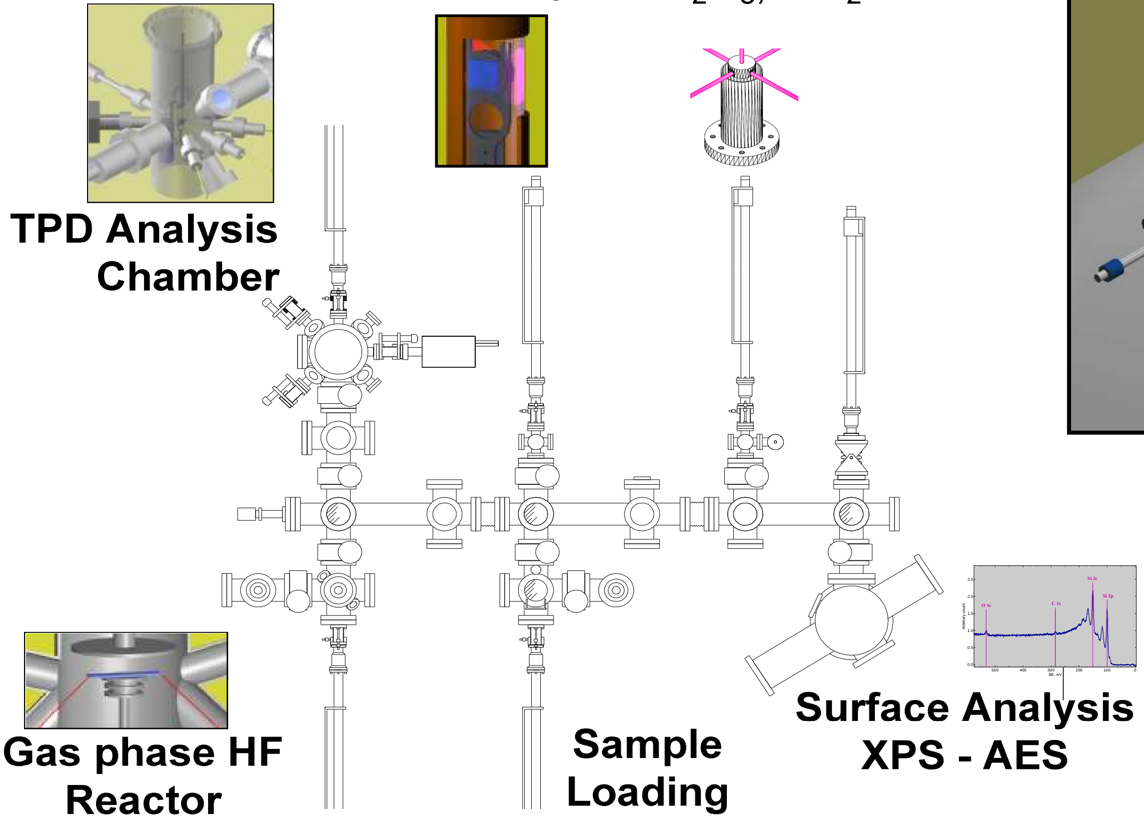
$$TiCl_{4(g)} + -OH \rightarrow -O\text{-}TiCl_3 + HCl_{(g)}$$

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

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

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



Photoreactor
UV-Cl/NH_3

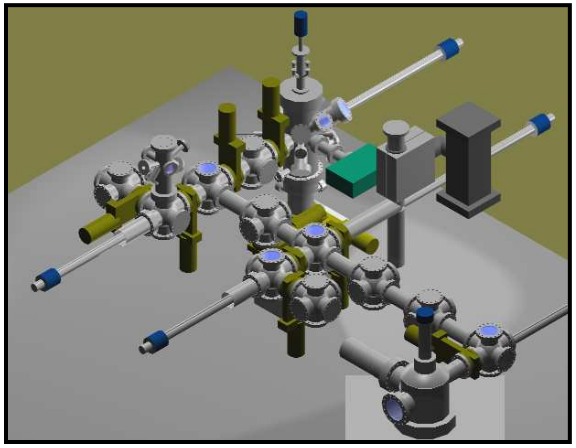
ALD Reactor
Al_2O_3, TiO_2

TPD Analysis Chamber

Gas phase HF Reactor

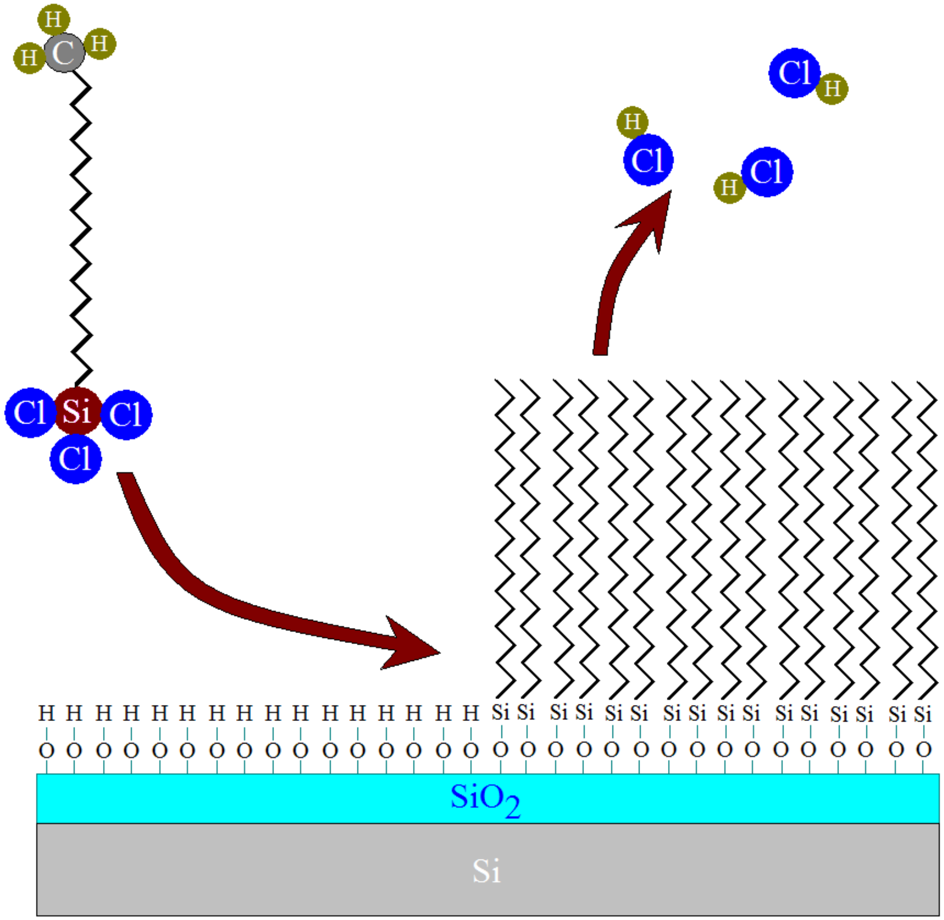
Sample Loading

Surface Analysis
XPS - AES



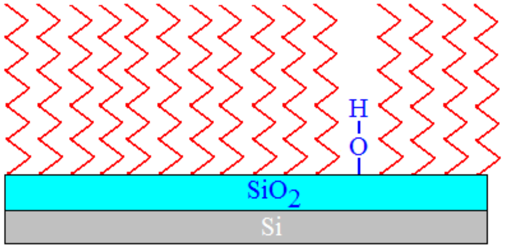
Deactivation using SAM Chemicals

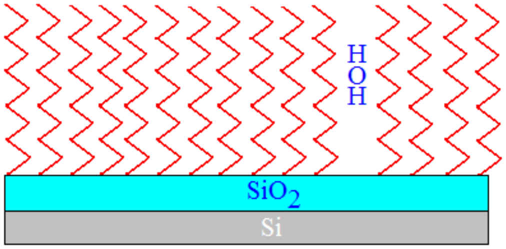
- Octadecyltrichlorosilane
  - OTS
  - $C_{18}H_{37}Cl_3Si$
  - Molecular length 26Å
- OTS SAM layer
  - Formed on piranha etched SiO_2[1-7]
  - 48hrs in 10mM OTS in toluene[2-4,6]
  - 26Å Thickness[1-6]
  - 110° water contact angle [1-6]
  - Deactivates for 50 ALD cycles of $HfCl_4$ or $Hf[N(CH_3)_2]_4$ and H_2O[2-5]
  - Longer deactivation for larger metal precursors such as $CH_3C_5H_4Pt(CH_3)_3$ or Ir(acac)3[2,7]

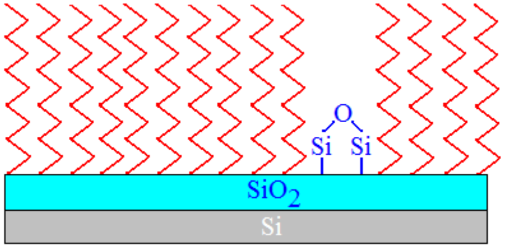


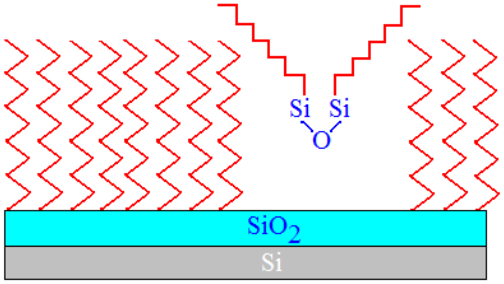
1) J. Hong, D. Porter, R Sreenivasan, P. McIntyre, S. Bent. *Langmuir*, 23, 1160-1165, (2007)
2) X. Jiang, S. Bent. *Journal of the Electrochemical Society*, 154 (12), D648-D656, (2007)
3) X. Jiang, R. Chen, S. Bent. *Surface & Coatings Technology,* 201, 799-8807, (2007)
4) R. Chen, H. Kim, P. McIntyre, D. Porter, S. Bent. *Applied Physics Letters,* 86, 191910, (2005)
5) R. Chen, H. Kim, P. McIntyre, S. Bent. *Chem. Mater.*, 17, 536-544, (2005)
6) Park, J. Doub, T.Gougousi, G. Parsons. *Applied Physics Letters,* 86, 051903, (2005)
7) E. Färm, M. Kemell, M. Ritala, M. Leskelä. Chem. Vap. Deposition, 12, 415-417, (2006)

SAM Formation and Defects

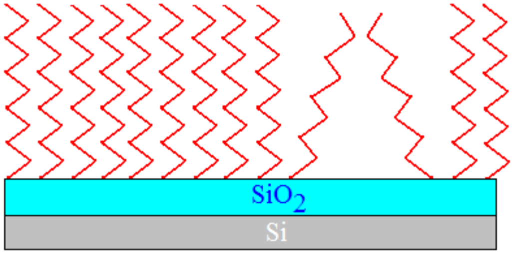




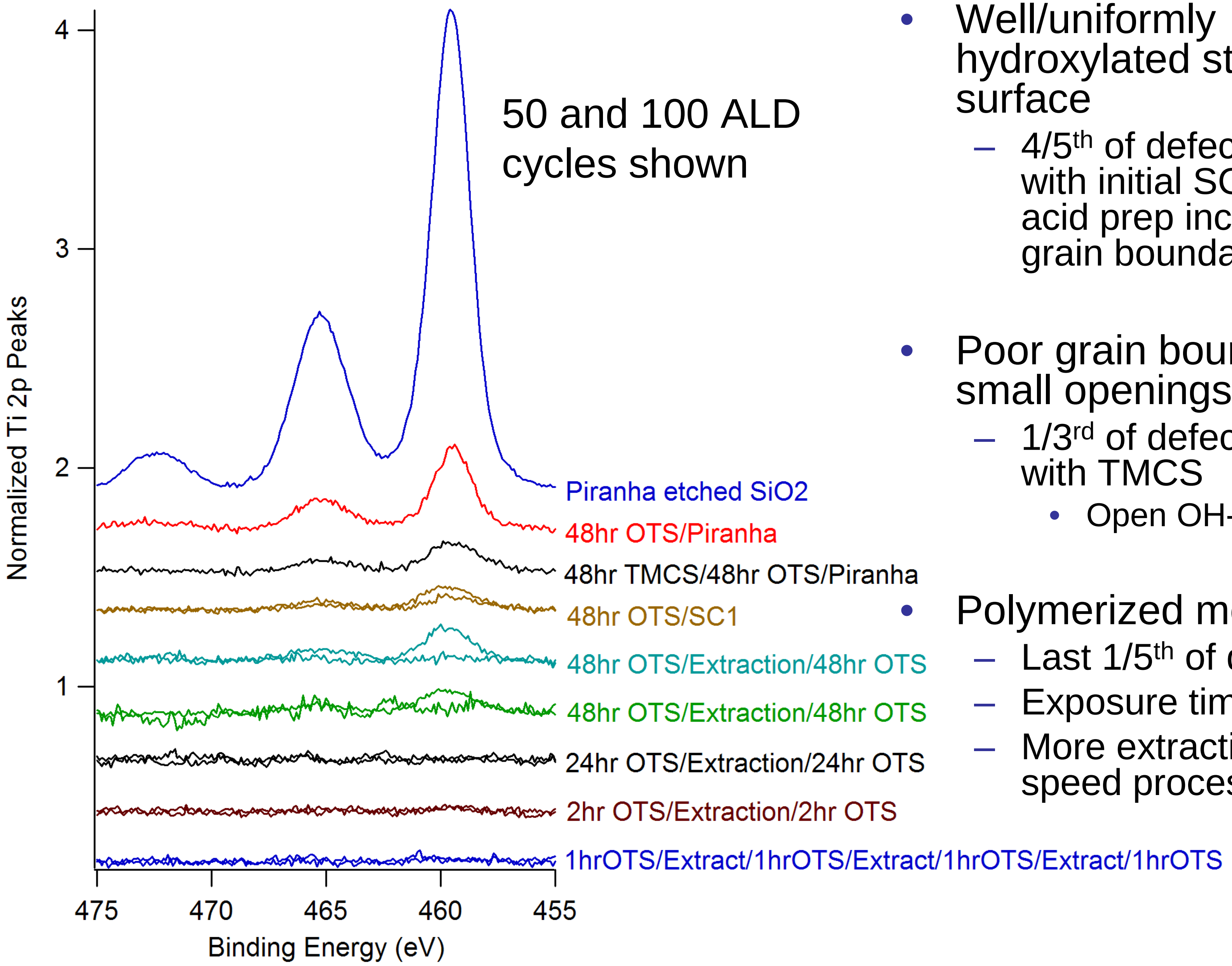




- Unblocked hydroxyl group
  - Difficult to fill in even with small SAM molecules
- Trapped water in SAM
  - ALD water pulse doesn’t stick in SAM
- Open Si-O-Si bond
  - Better (more complete chemical oxidation)
  - Nitric acid etch and SC1 cleaning
- Polymerized SAM molecules laying down on surface
  - Cleaning and re-exposing surface to SAM
- Open grain boundaries between SAM islands



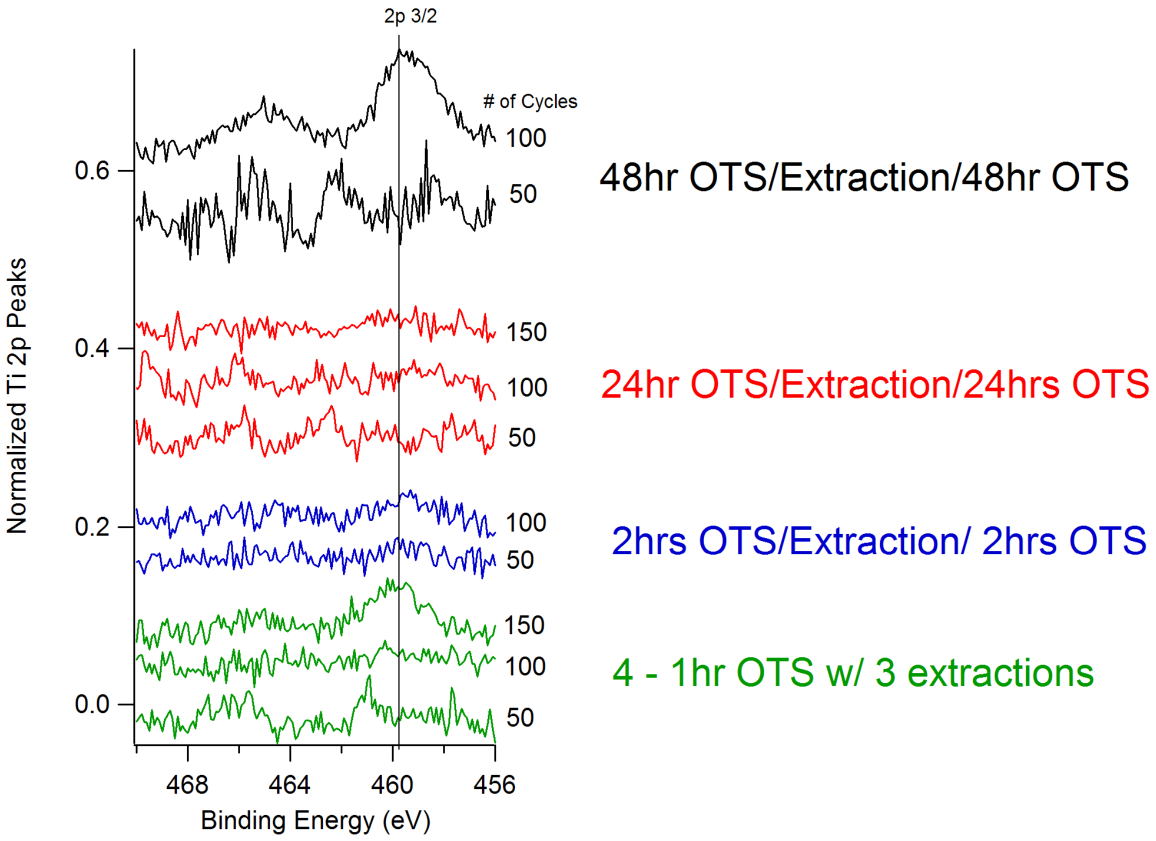
XPS Peak Analysis



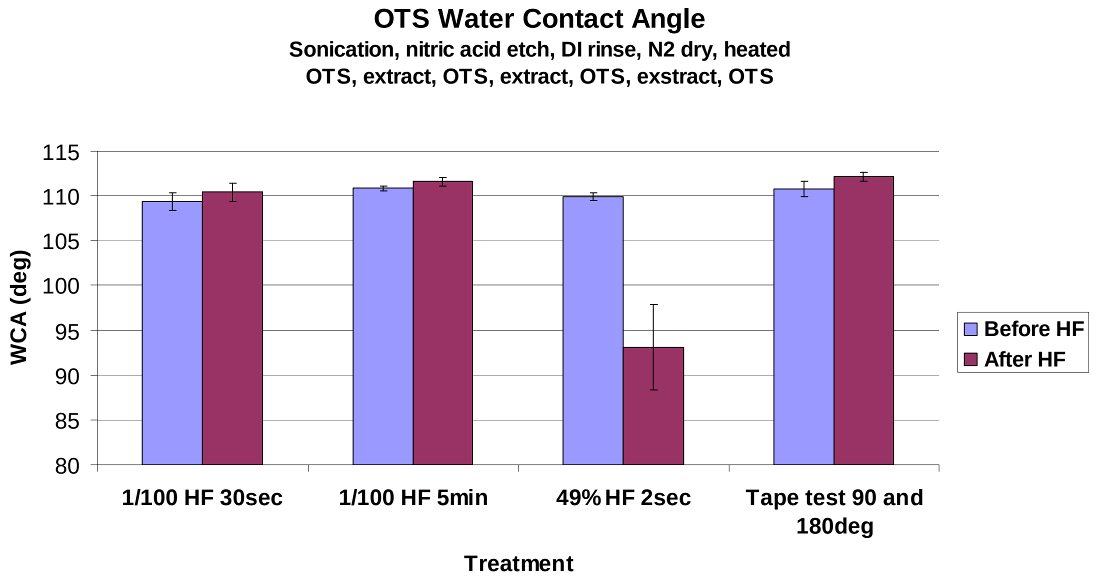
- Well/uniformly hydroxylated starting surface
  - 4/5th of defects removed with initial SC1 or nitric acid prep including most grain boundaries
- Poor grain boundaries or small openings in SAM
  - 1/3rd of defects removed with TMCS
    - Open OH-groups
- Polymerized molecules
  - Last 1/5th of defects
  - Exposure time is critical
  - More extractions helps speed process up

Extraction Results

- 48hr exposures create extra polymerized molecules on SAM
- Not seen for 24hr exposures
- Two 2hr OTS exposures with 1 extraction is the minimum time for a dense enough SAM to deactivate TiO_2 ALD
  - At limit of XPS
- Four 1hr OTS exposures with 3 extractions forms a good enough SAM to deactivate TiO_2 ALD deposition for up to 100 cycles

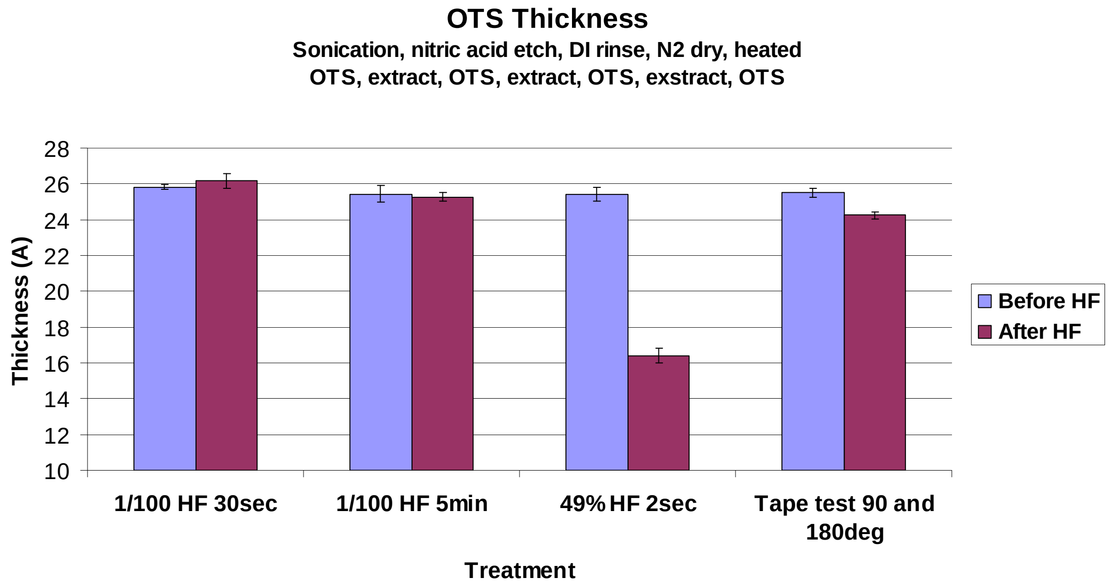


HF dip on OTS



OTS Water Contact Angle

Sonication, nitric acid etch, DI rinse, N2 dry, heated OTS, extract, OTS, extract, OTS, exstract, OTS



OTS Thickness

Sonication, nitric acid etch, DI rinse, N2 dry, heated OTS, extract, OTS, extract, OTS, exstract, OTS

- 4hr OTS SAM formation/extraction process
  - 1/100 HF dip for 30sec
  - 1/100 HF dip for 5min
  - 49% HF dip for 2sec
  - Tape adhesion test

Conclusions

- Achieved deactivation of TiO_2 ALD for 100 cycles with only 4 hours of OTS SAM exposure
  - Shortest timescale for any successful ALD deactivation
  - 1/12th of the typical timescale for ALD deactivation[1-4]
  - Previous shortest time scale was for Pt ALD deposition from $CH_3C_5H_4Pt(CH_3)_3$ and air, which required 12 hours of OTS exposure[1]
- Discovered SAM is stable in dilute HF solutions
  - Any aqueous based solutions will be prevented from reaching the Si-O bonds due to the hydrophobic nature of the SAM, thus preventing etching of the SAM

X. Jiang, S. Bent. *Journal of the Electrochemical Society*, 154 (12), D648-D656, (2007)
X. Jiang, R. Chen, S. Bent. *Surface & Coatings Technology,* 201, 799-8807, (2007)
R. Chen, H. Kim, P. McIntyre, D. Porter, S. Bent. *Applied Physics Letters,* 86, 191910, (2005)
Park, J. Doub, T.Gougousi, G. Parsons. *Applied Physics Letters,* 86, 051903, (2005)

Future Work

- Test TMCS with SAM extraction process
  - Replace OTS with TMCS in last step of extraction
  - Does this extend the number of deactivated cycles?
- Create way of efficiently vaporizing OTS for SAM vapor delivery
- 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
  - Degradation and repair of SAMs layers
    - Can TMCS be used to repair SAM without creating polymer defects?

Acknowledgements

- Special thanks for project funding
  - SRC/Sematech
  - ASM