Understanding Inherent Substrate Selectivity During Tungsten ALD

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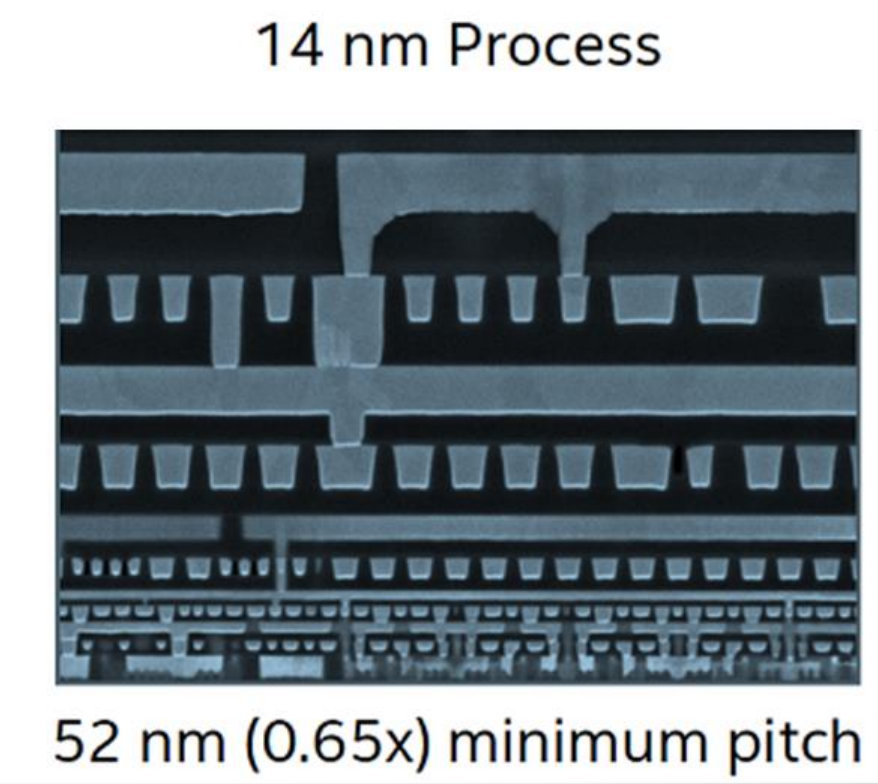
2nd Area Selective Deposition Workshop ASD17

Introduction

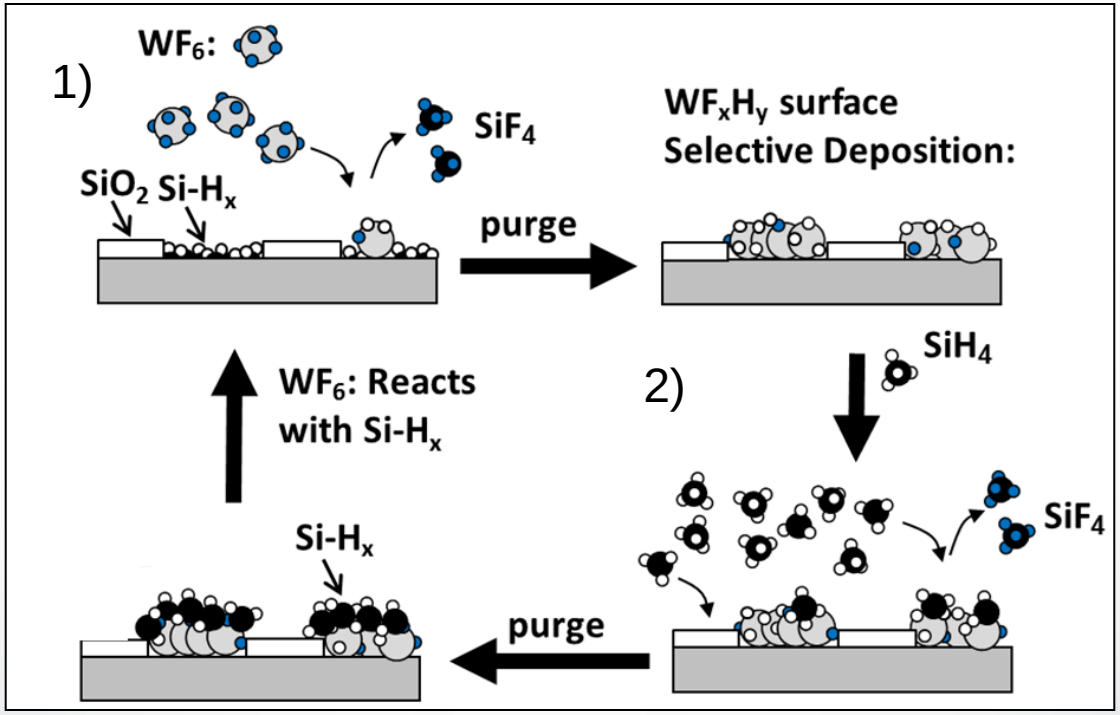
- Transistor devices are becoming smaller with more complex architecture
- Conventional patterning processes are limited:
  - Maintaining edge definition and alignment to underlying features.
  - Small dimensions,
  - High aspect ratio features
  - Use of ultra-low k dielectrics
- Need for selective deposition
  - Blocking layers (SAMs)
  - Competitive adsorption
  - Selective etching
  - Inherent selectivity



Source: Intel (http://www.anandtech.com)

Background: Selective W-ALD

- **Atomic Layer Deposition (ALD)**: deposit conformal films with high thickness control with vapor-phase, self-limiting reactions
- Deposit tungsten with tungsten hexafluoride (WF_6) and dilute silane (SiH_4) at low temperatures (220°C)

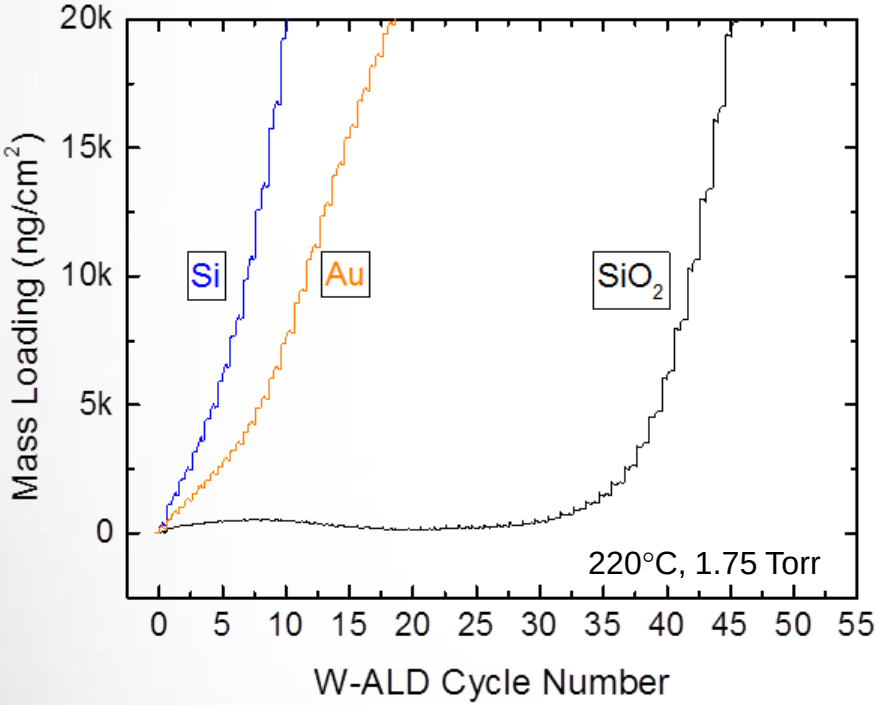


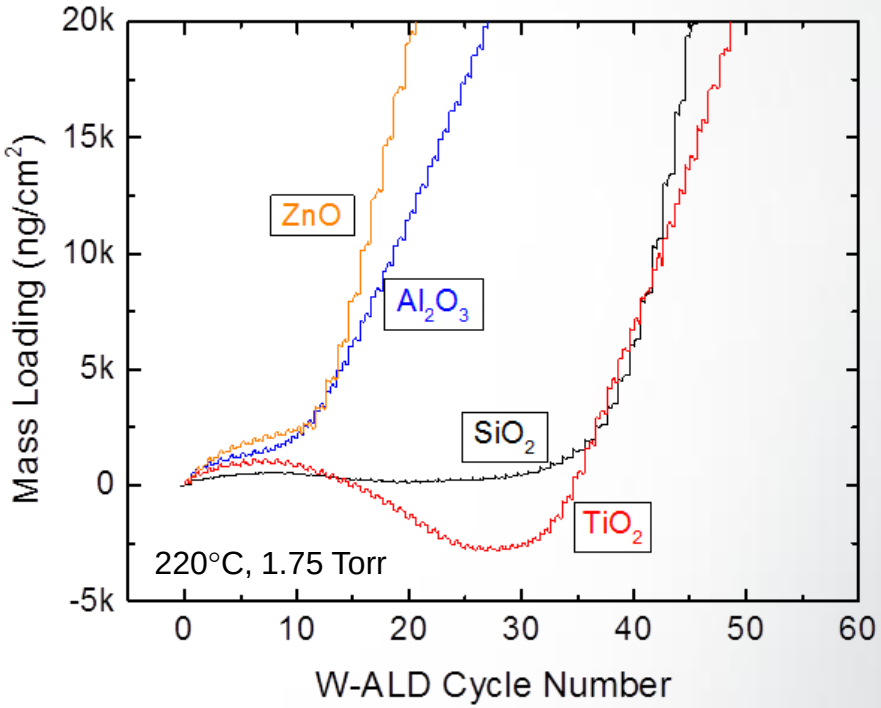
Kalanyan, B.; Lemaire, P. C.; et al. *Chem. Mater.* **2016**.

Inherently Selective W-ALD

- Need to determine:
  1. Substrate surface defects that lead to nucleation
  2. Reactant that initiates undesired deposition
- Study phenomena that either inhibit or promote deposition
  1. Generate and remove nucleation sites via sample prep
  2. Pre-expose substrates to W-ALD precursors
- Improve selectivity by varying temperature and concentration

W-ALD Nucleation (QCM)

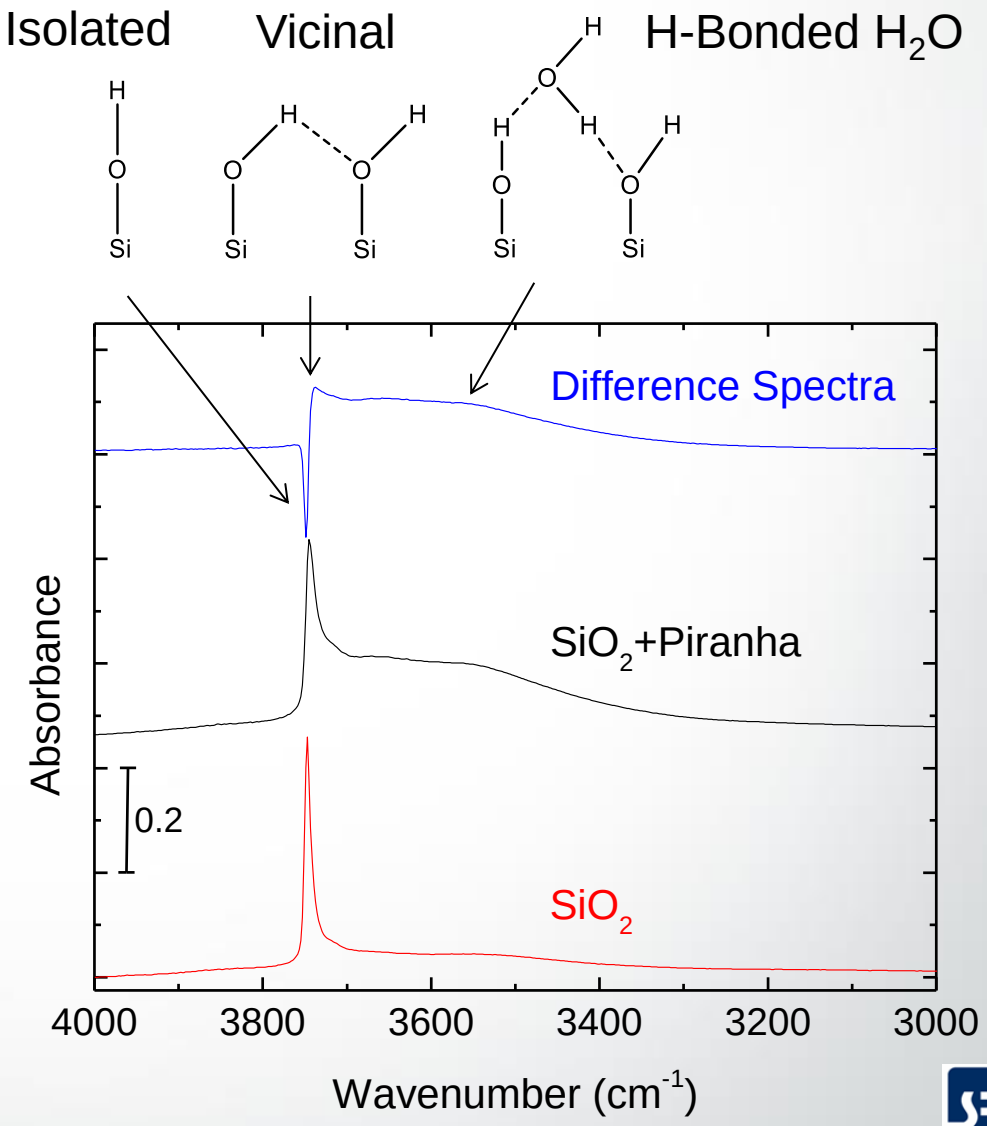




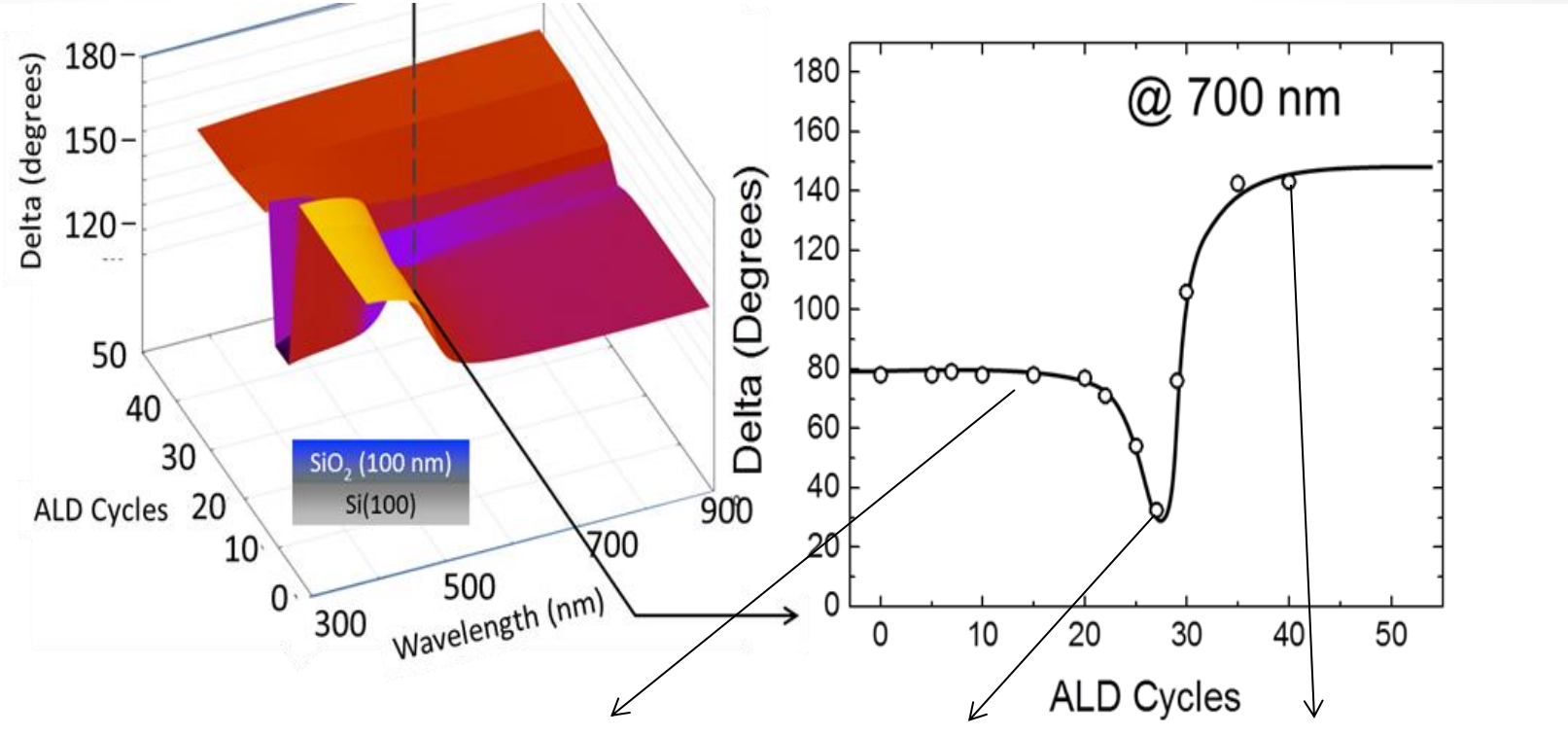
- Little to no tungsten nucleation delay on Si and Au
  - Selectively deposit ~15 nm of W on Si or Au
- Tungsten nucleation delay dependent on oxide composition
- TiO_2 etching during nucleation period

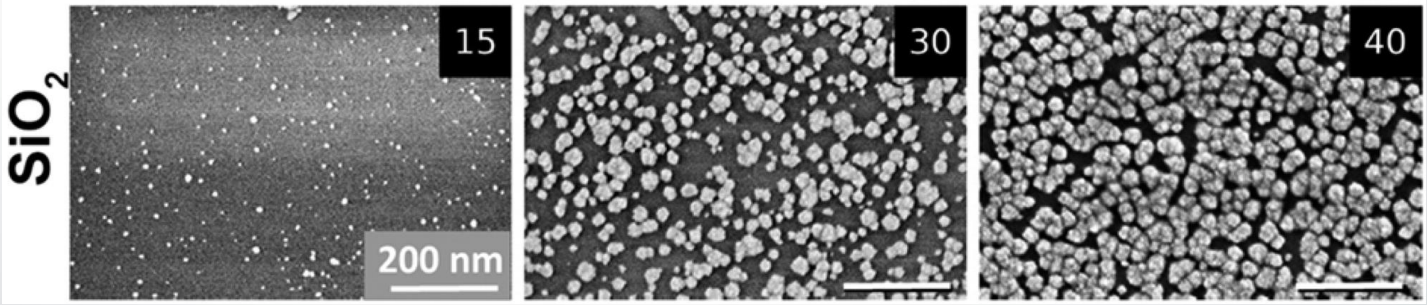
Hydroxyls and Sample Preparation (FTIR)

- Porous SiO_2 substrates
  - Anodization of Si in HF/EtOH
  - Thermal oxidation at 950°C in air
- As-is SiO_2:
  - strong isolated OH peak
- Piranha cleaned SiO_2:
  - Loss of isolated OH
  - generate vicinal OH and H-bonded H_2O



Ellipsometric Analysis of W-ALD





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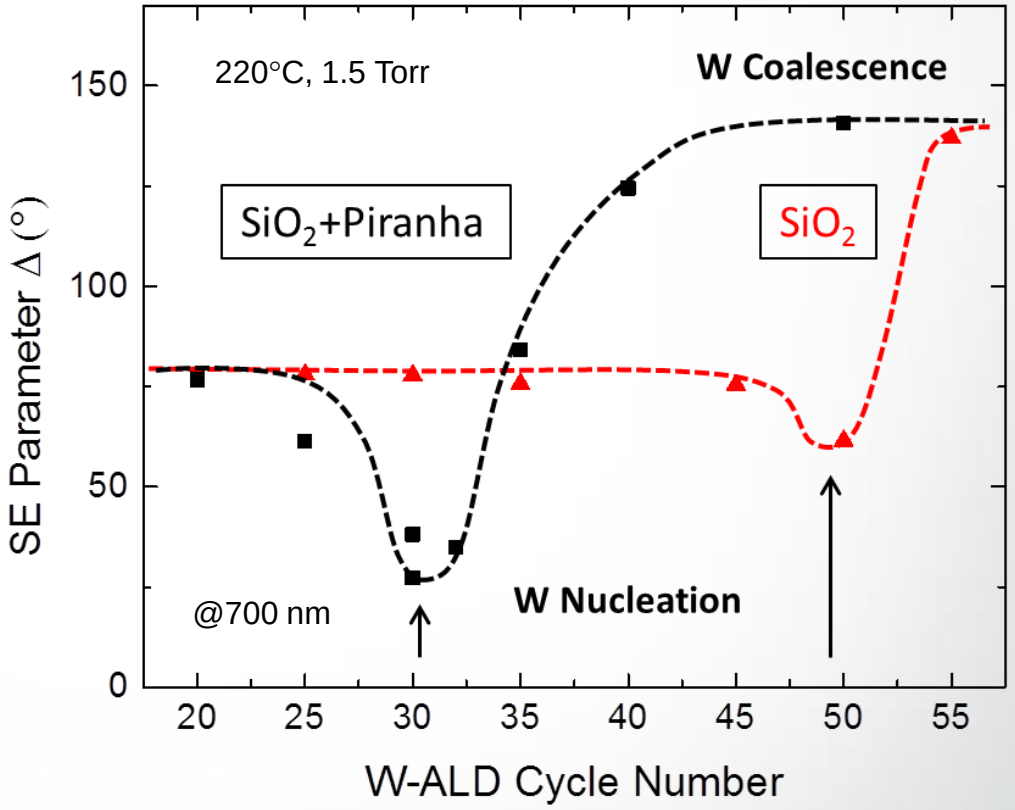
Sample Preparation (Ellipsometry)

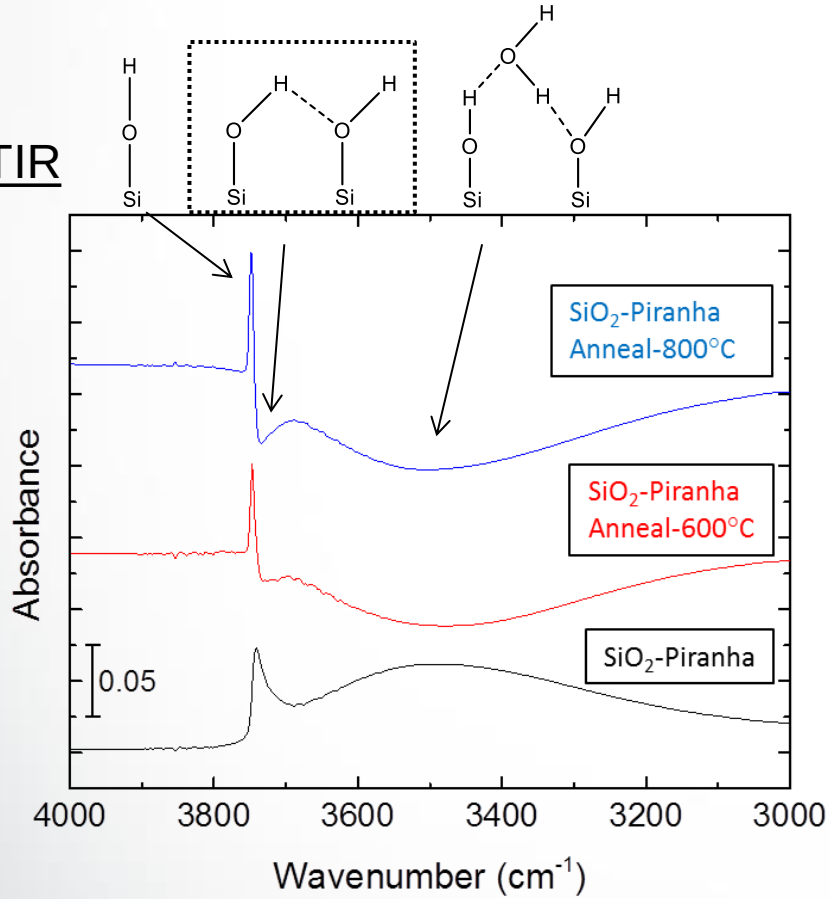
- **Piranha cleaned SiO_2**
  - Increase in vicinal OH
  - H-bonded water
  - Nucleation: 35 cycles
- **As-is SiO_2**
  - Isolated OH
  - Nucleation: 50 cycles



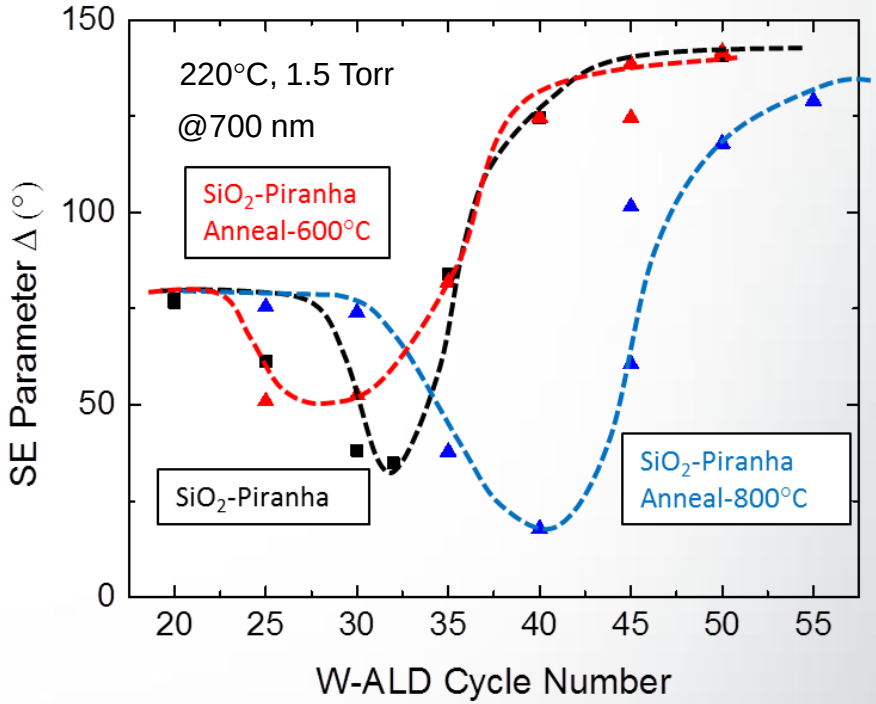
Piranha clean promotes W nucleation by forming vicinal OH sites

Sample Preparation: Removing OH Sites

FTIR

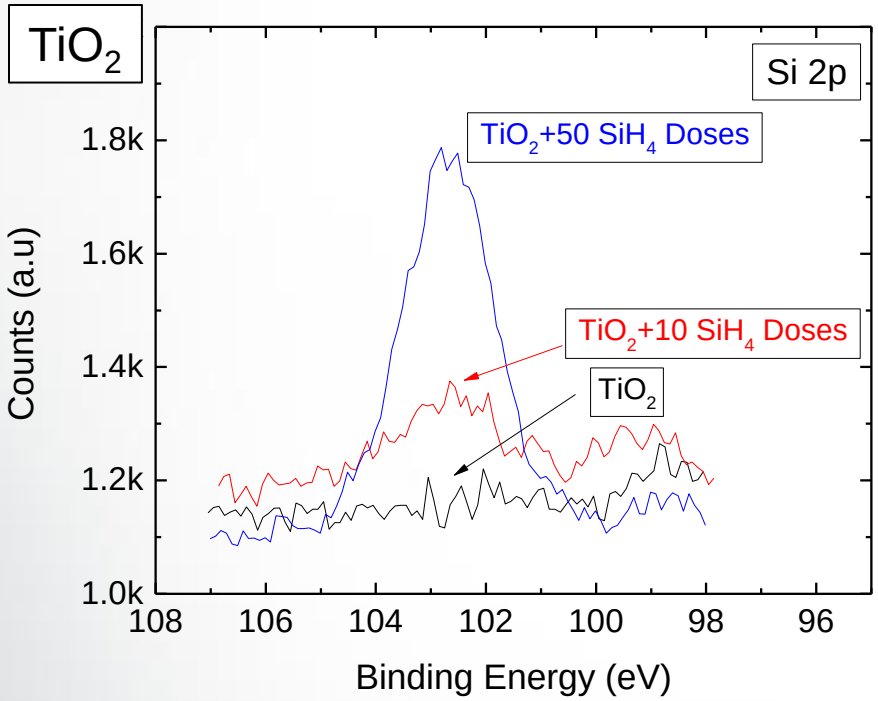


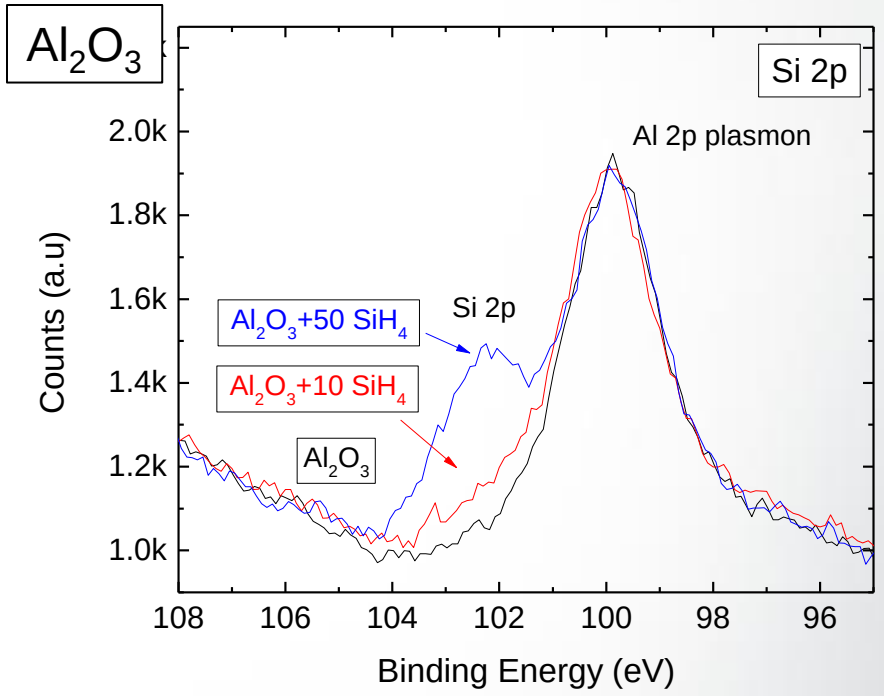
Ellipsometry



- Tungsten nucleation occurs predominantly at vicinal hydroxyl sites

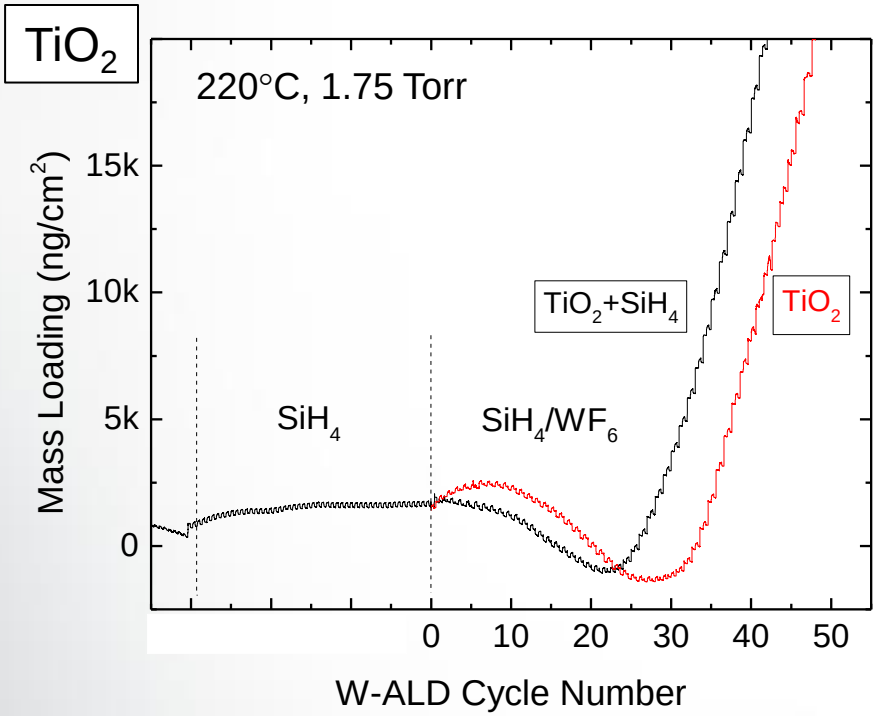
TiO_2/Al_2O_3 + 1) $\underline{SiH_4}$ (XPS)

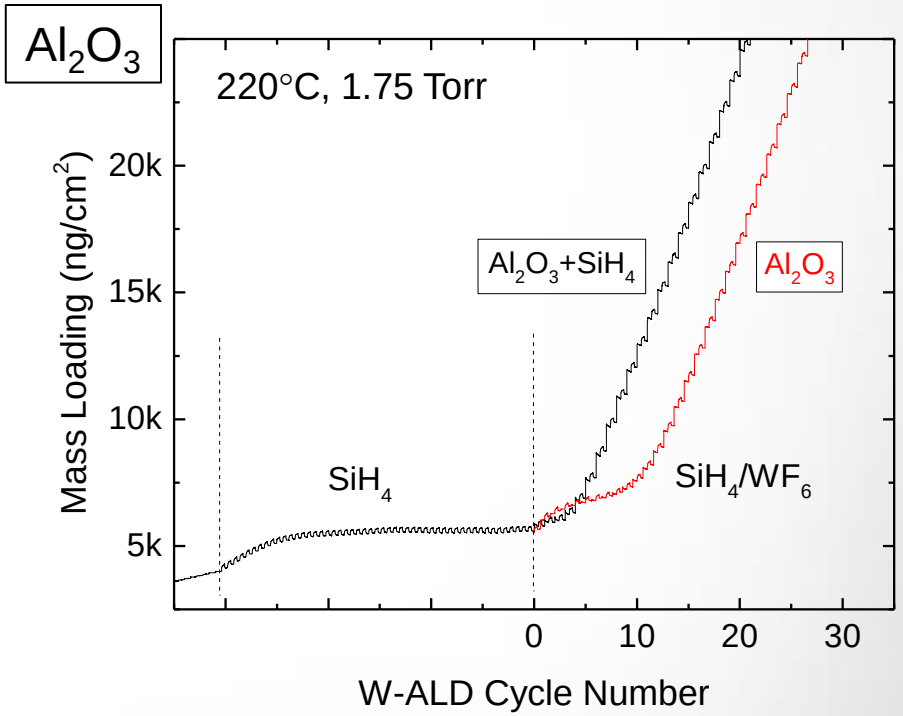




- Increase in Si 2p signal on oxide substrate with SiH_4 exposures
  - Binding energy consistent with oxidized Si

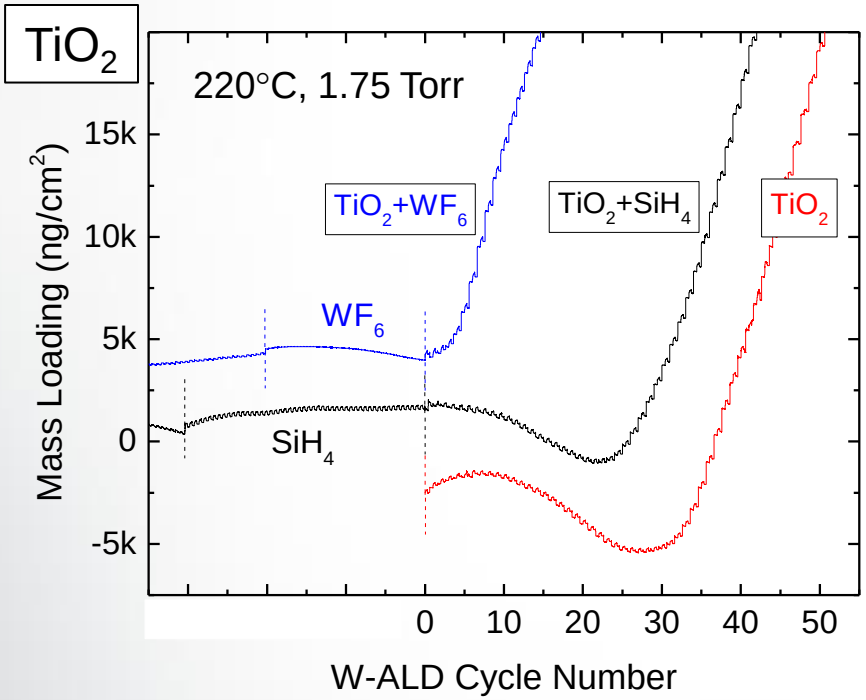
TiO_2/Al_2O_3 + 1) $\underline{SiH_4}$ + 2) W-ALD (QCM)

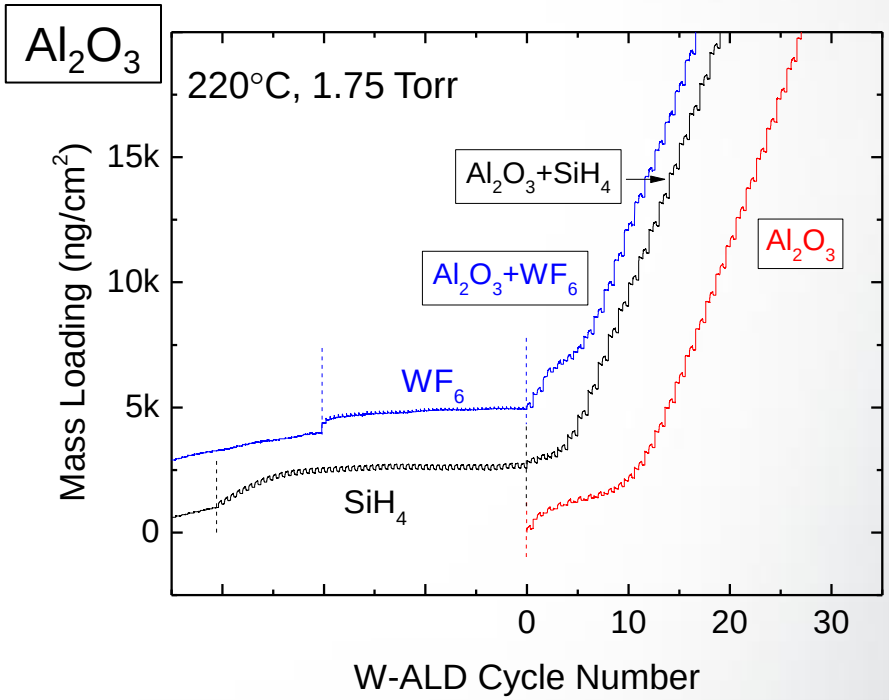




- In-situ QCM assessment of SiH_4 pre-exposures on TiO_2 and Al_2O_3
  - 50 SiH_4 pre-exposures: tungsten nucleation occurs ~10 cycles earlier

TiO_2/Al_2O_3 + 1) $\underline{WF_6}$ + 2) W-ALD (QCM)

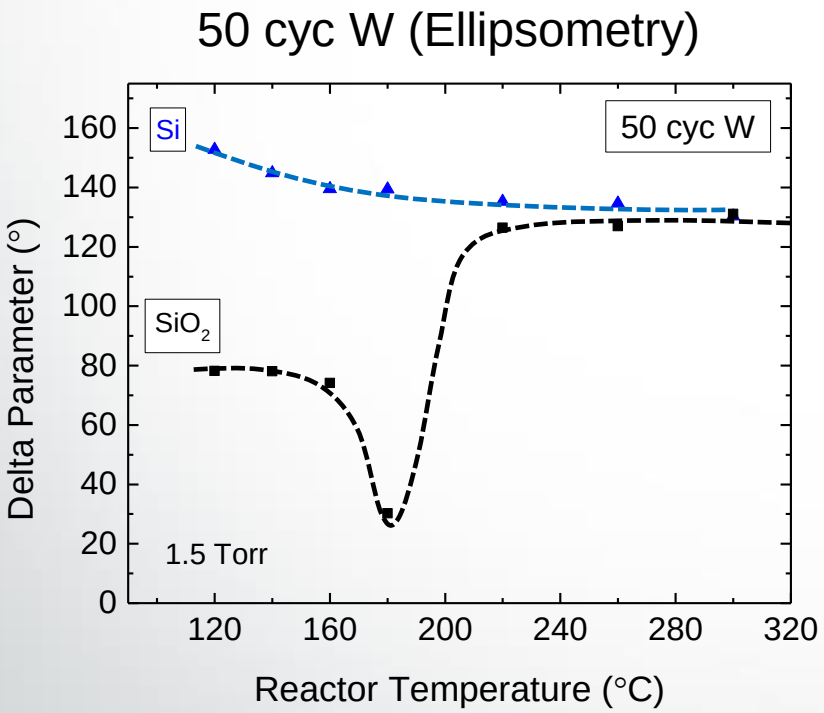


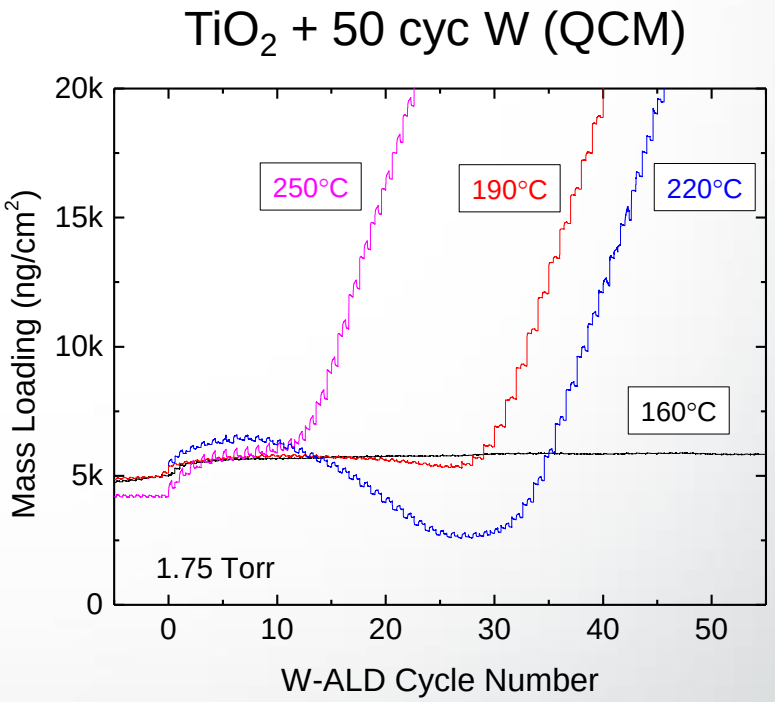


- Minimal nucleation delay on Al_2O_3/TiO_2 following 50 WF_6 pre-exposures
- Tungsten nucleation more dependent on WF_6 than SiH_4 pre-exposures

W-ALD Selectivity: Deposition Temperature

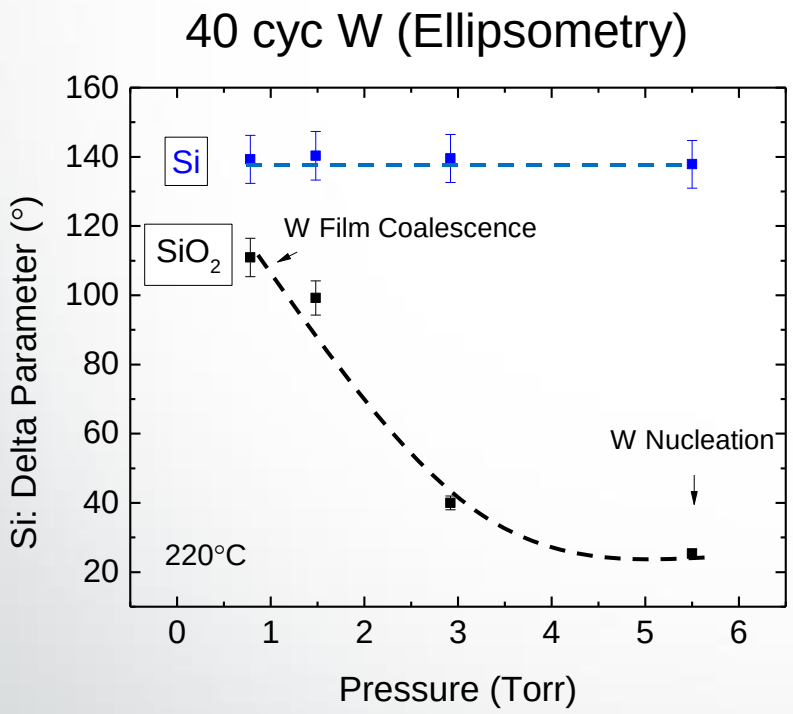
- Reduce tungsten nucleation on SiO_2 and TiO_2 at lower temperatures
  - Unable to overcome activation barrier for adsorption or reaction
  - Also reduces desired W deposition on Si
- Etching occurs in narrow temperature range

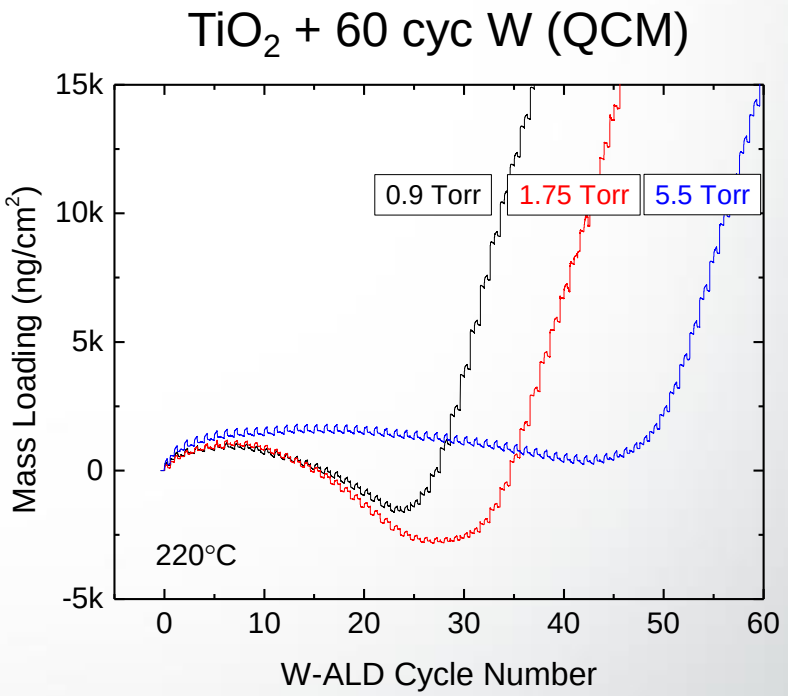




W-ALD Selectivity: Process Pressure/Flowrate

- Tungsten nucleation on oxides delayed at higher carrier flowrate/system pressure
- Lower precursor concentration limits precursor adsorption on oxides



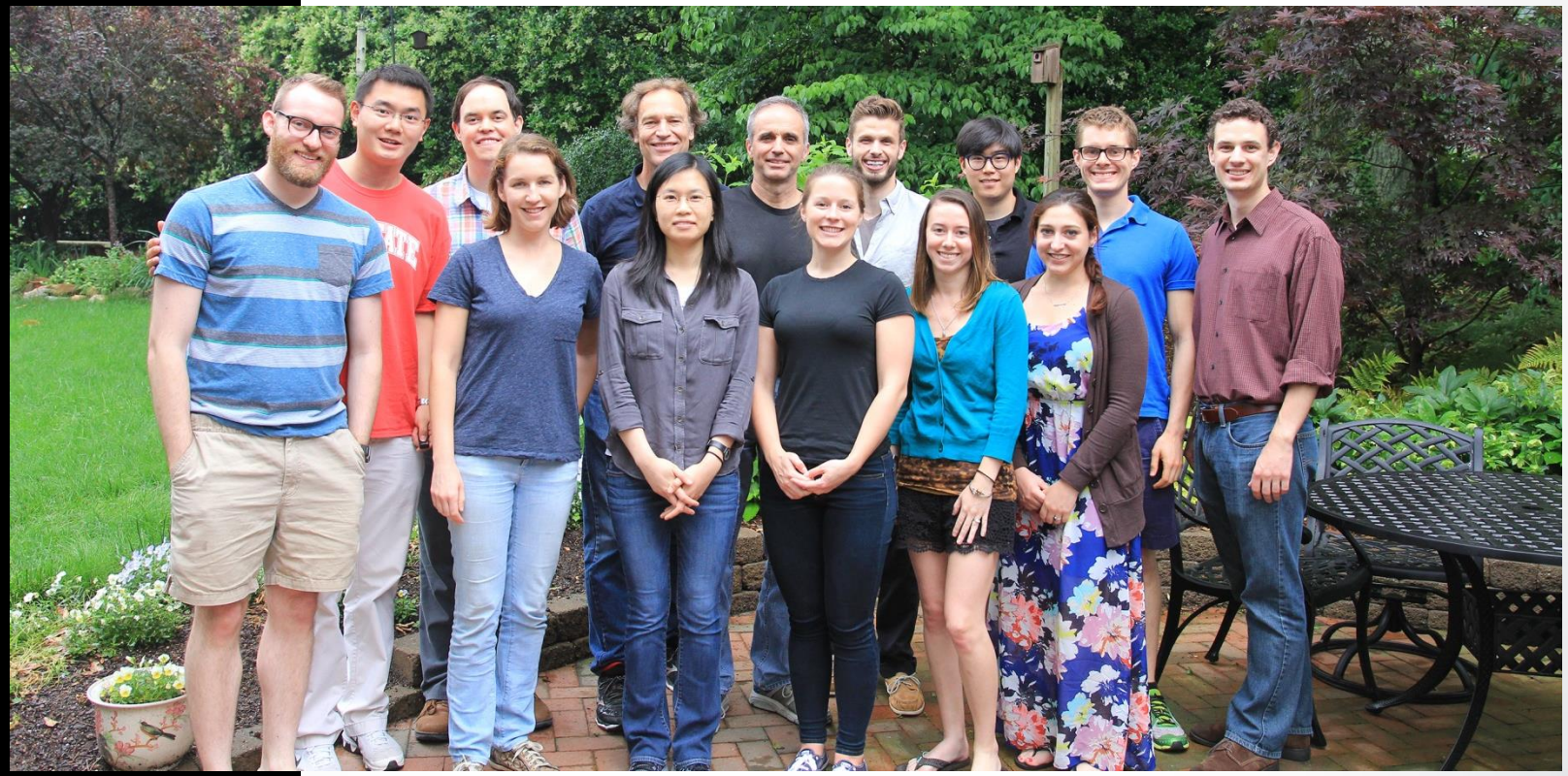


Summary

- Tungsten nucleation delay is substrate dependent: Si>Au>Al_2O_3/ZnO>TiO_2/SiO_2
- Correlation between vicinal hydroxy concentration and W-ALD nucleation
- Surface bound water inhibits W-ALD nucleation
- SiH_4 pre-exposures promote nucleation by forming reducing layer
- Reduce temperature or increase flow rate to limit WF_6 adsorption on oxide surfaces

Lemaire, P. C.; King, M.; Parsons, G. N.
J. Chem. Phys. **2017**.

Acknowledgements



- Gregory N Parsons Research Group
- Funding from Semiconductor Research Corporation (SRC)