New Strategies for Area Selective Deposition

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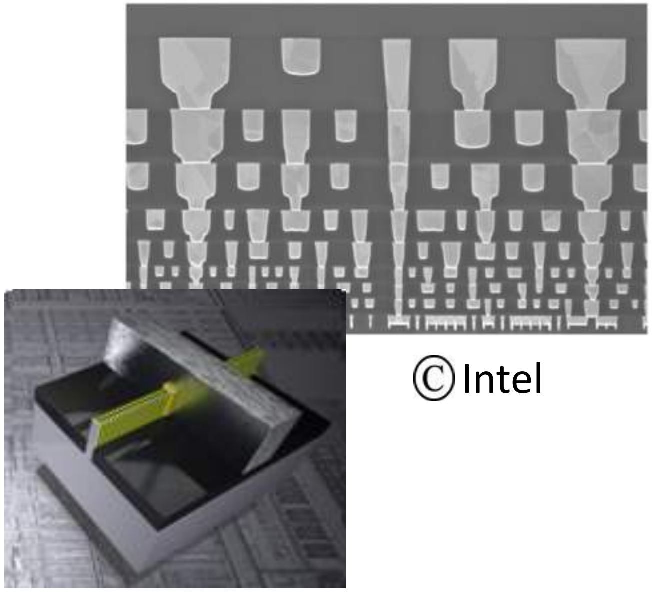
Need for Selective Deposition

New patterning challenges:
- 10 nm-scale structures
- Multiple layers and several different materials
- 3-D structures

Conventional lithographic patterning:
Expensive, time consuming, misalignment errors



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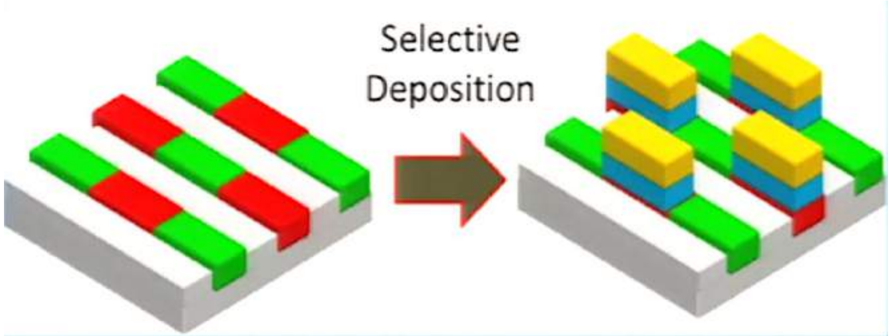
Area Selective Deposition

✓ Direct, additive deposition of materials only where desired
✓ Sub-nanometer control of the growth process, uniform and conformal coating

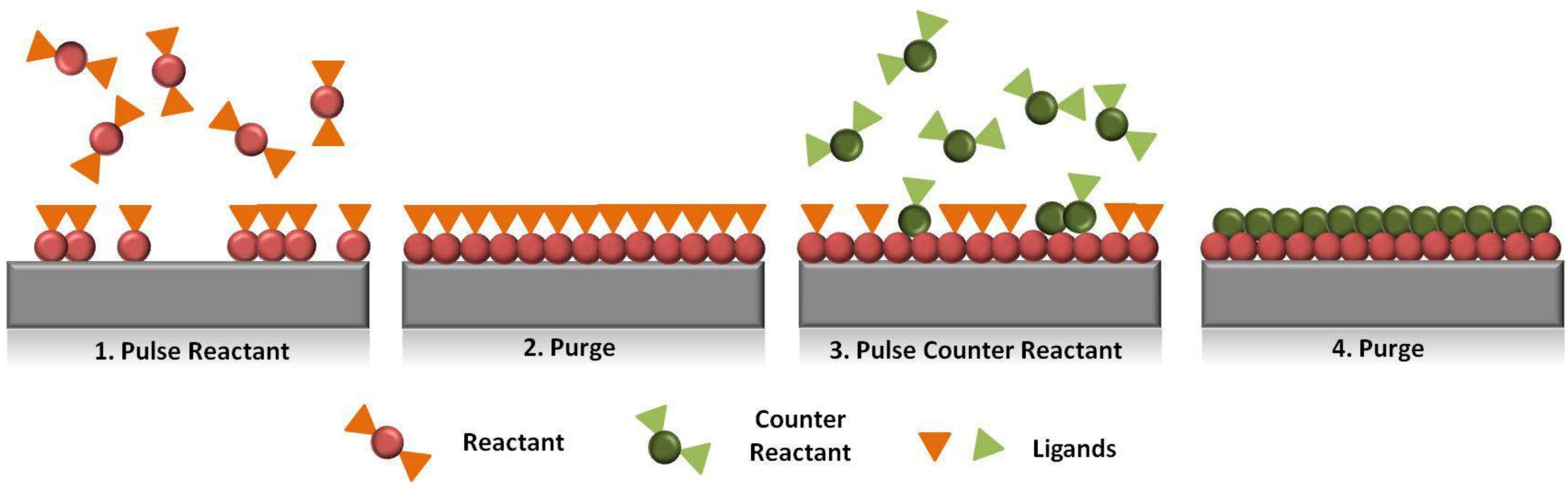


Atomic Layer Deposition (ALD)

- Vapor phase technique for deposition of thin films
- Sequential, self-limiting surface reactions

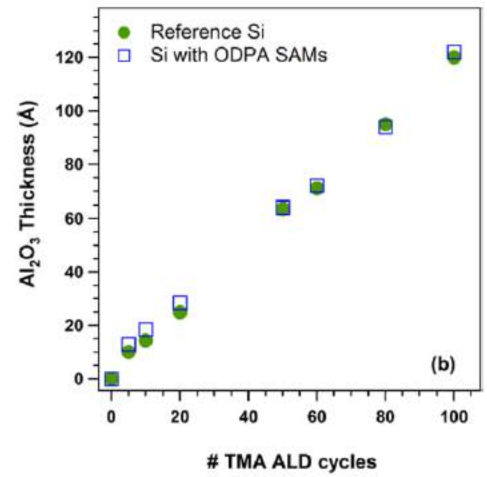
Deposition rate: 100-300 nm/hr
Growth rate: 0.1- 3 Å/cycle
Growth temp.: RT- few 100°C

- Thickness control at sub-nanometer level
- Conformal coating on high-aspect ratio structures
- Tunable film composition
- Deposition of variety of materials (metals, metal oxides,…)

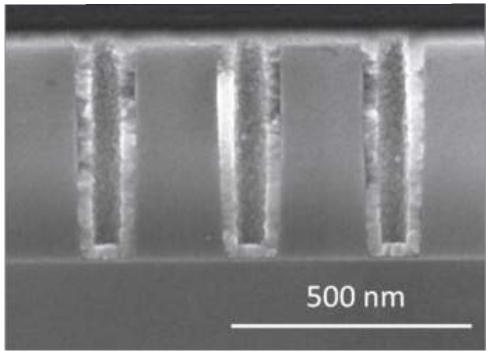


Key features of ALD

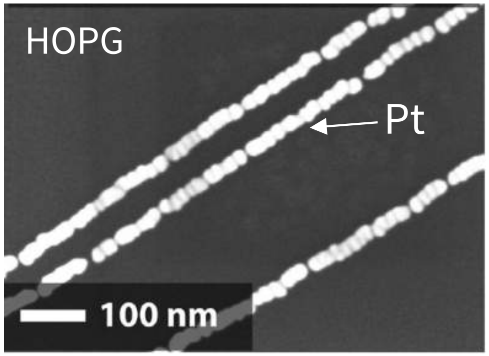
1. **Ultimate control of film thickness**
   sub-monolayer accuracy



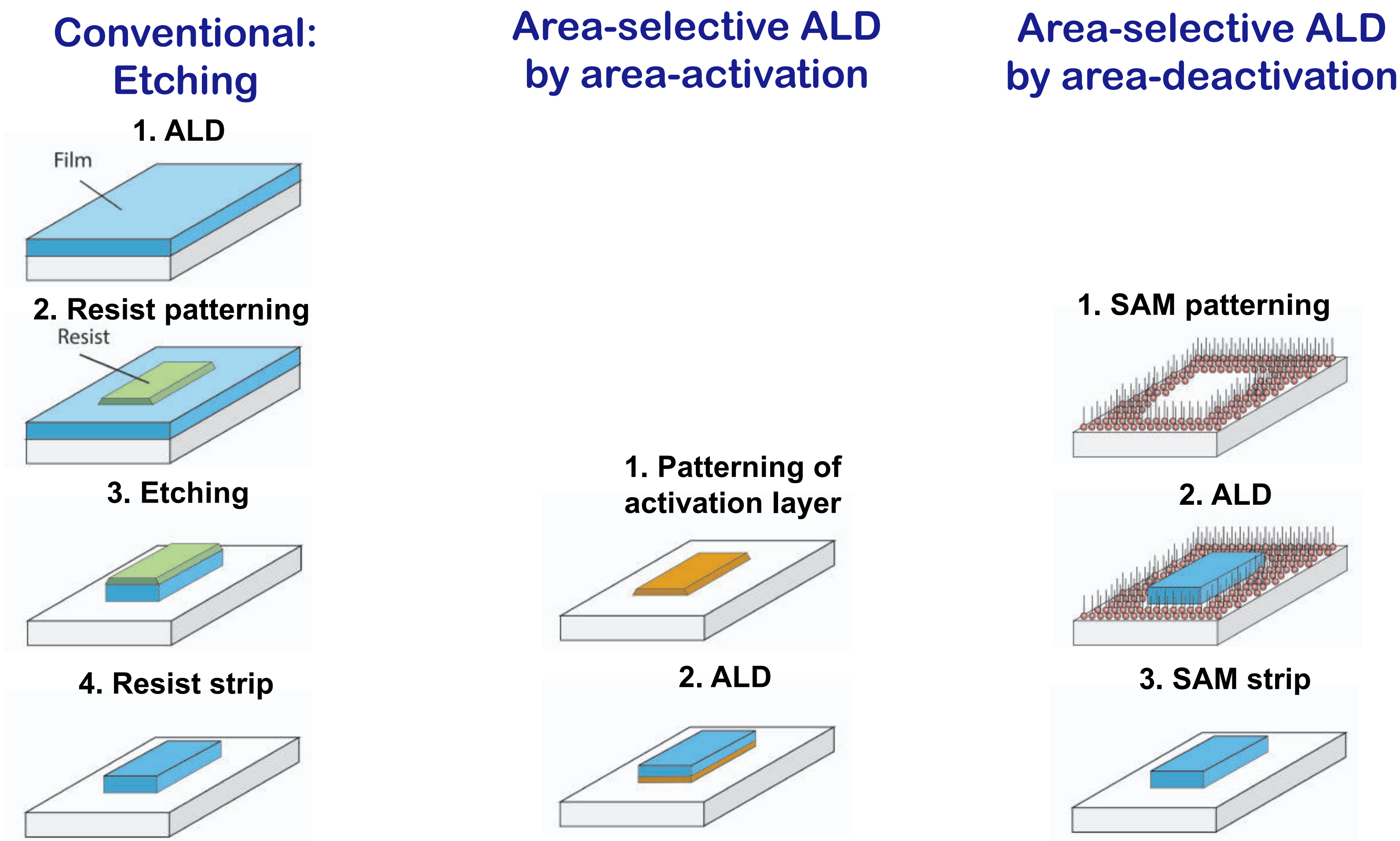
2. **High conformality on nanostructured surfaces**
   due to self-limiting surface reactions



3. **Growth strongly relies on surface chemistry**
   can be exploited for achieve area-selective deposition



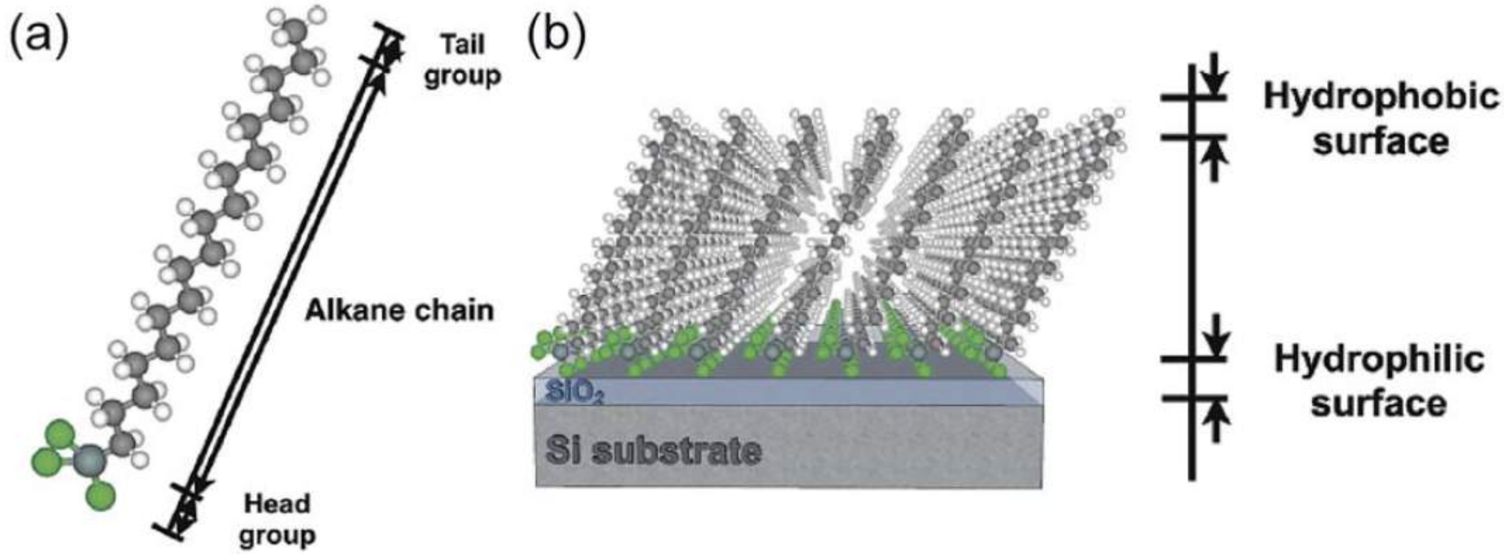
Patterning of ALD-grown films



- Area-selective ALD can be achieved by local **activation** or **de-activation** of the growth.

Mackus *et al.* Nanoscale 6, 10941 (2014)

Area-selective ALD using self-assembled monolayers



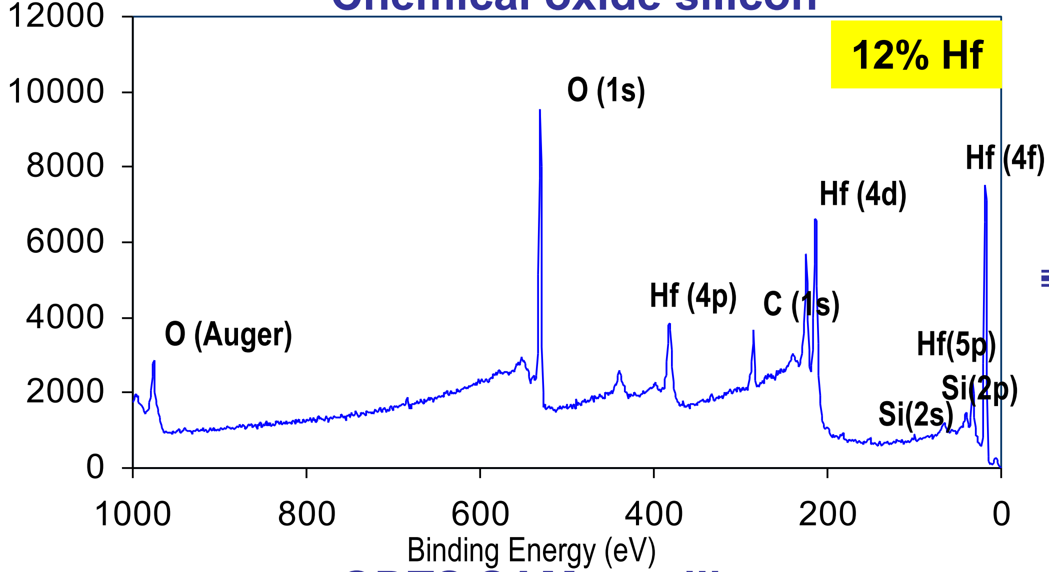
- ALD growth can be de-activated by self-assembled monolayers (SAMs)
- Van der Waals interaction between the alkane chains ensures formation of a ordered monolayer.
- Tail group determines surface functionalization.

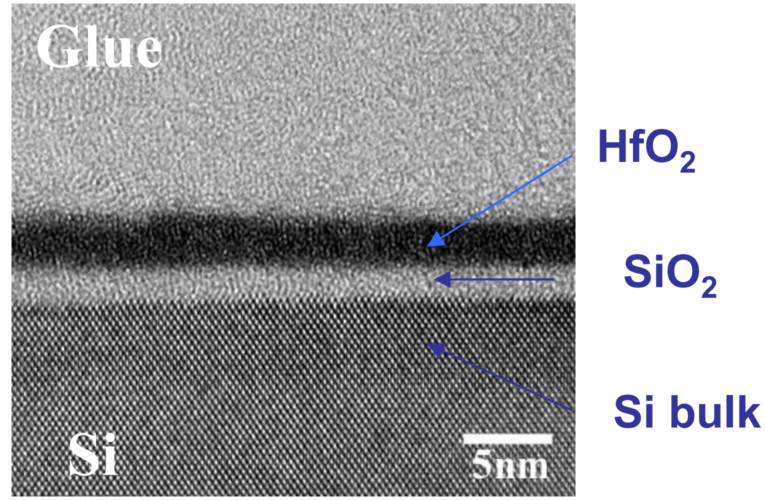
Types of SAMs	
Thiols	R-SH
Silanes	R-$SiCl_3$
Alkenes	R-C=C
Alkanoic acids	R-COOH
Phosphonic acids	R-PO_3H_3

ALD Inhibition by ODTS SAM

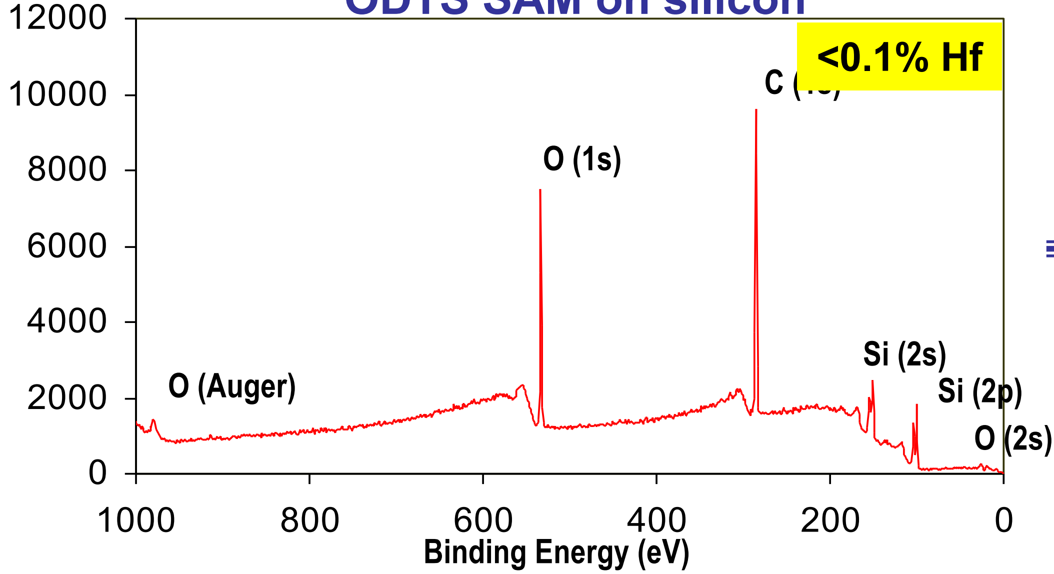
ODTS = Octadecyltrichlorosilane

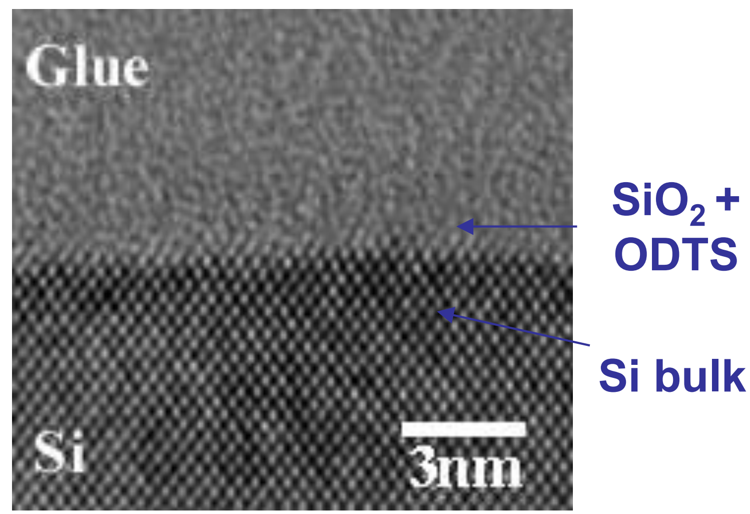
Chemical oxide silicon





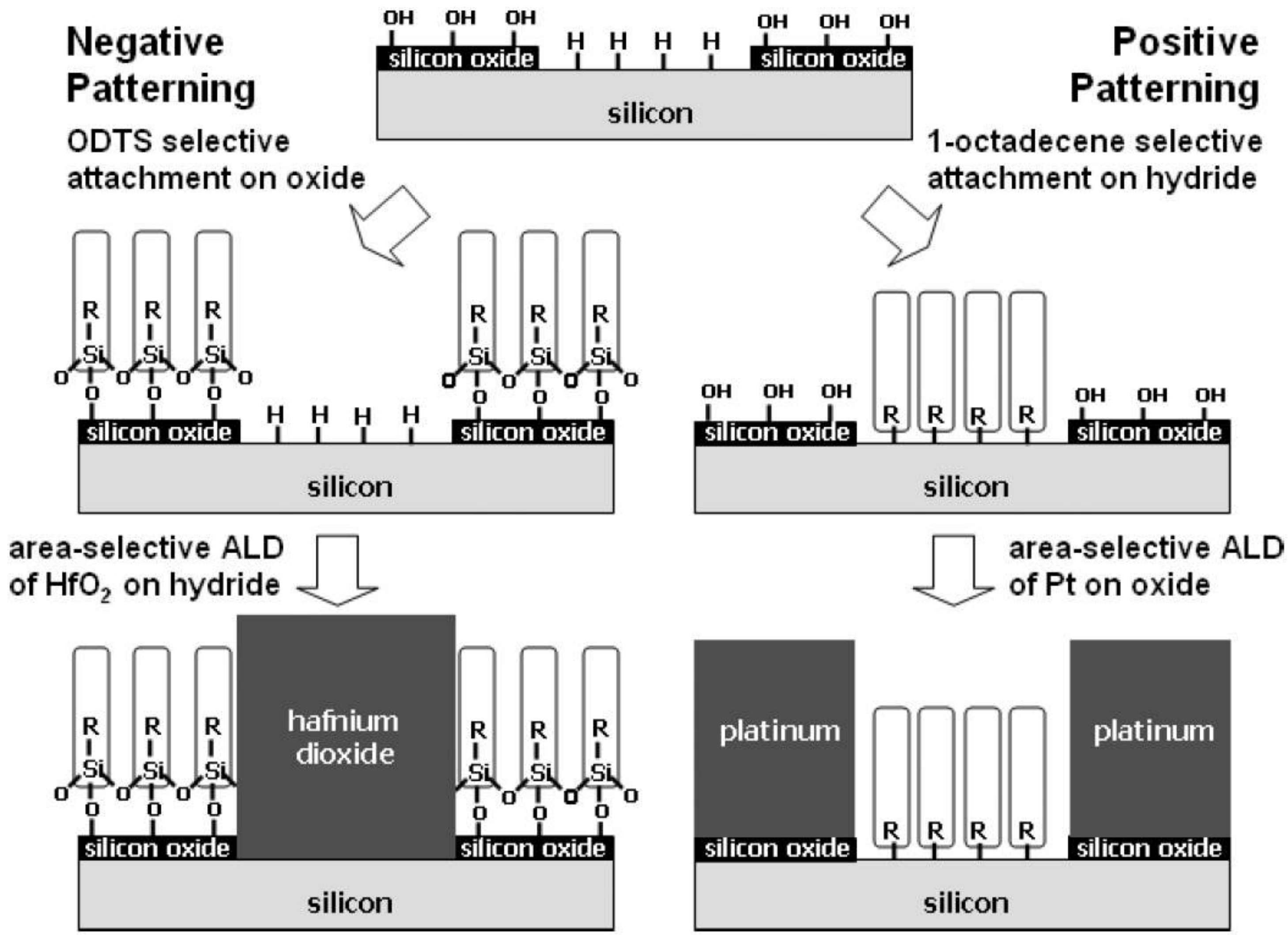
ODTS SAM on silicon





Chen et al. Appl. Phys. Lett. 2004, 84, 4017
Chen et al. Chem. Mater. 2005, 17, 536

Prototypical area selective ALD process

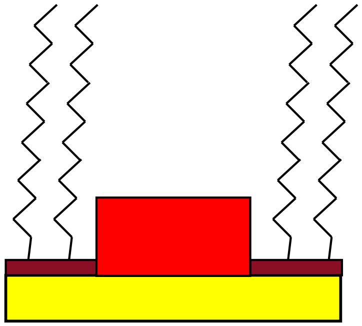


Chen and S. F. Bent, Adv. Mat., 18 (2006) 1086-1090

Area-Selective ALD: Positive and Negative

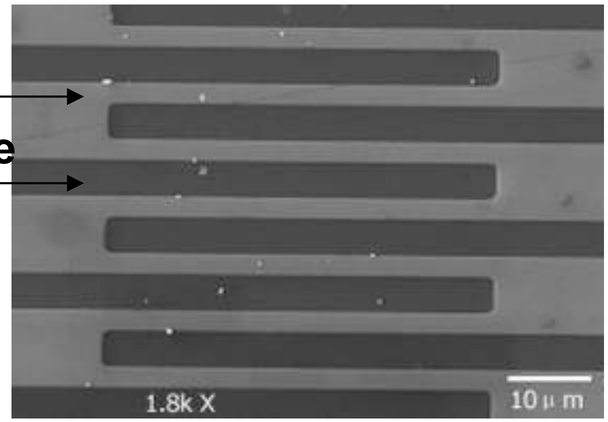
SEM image of representative structure

alkylsilanes

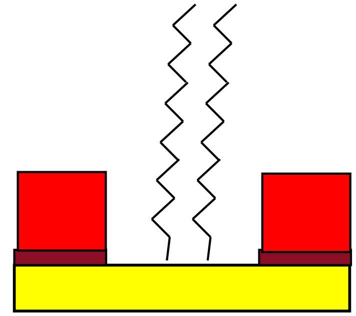


oxide

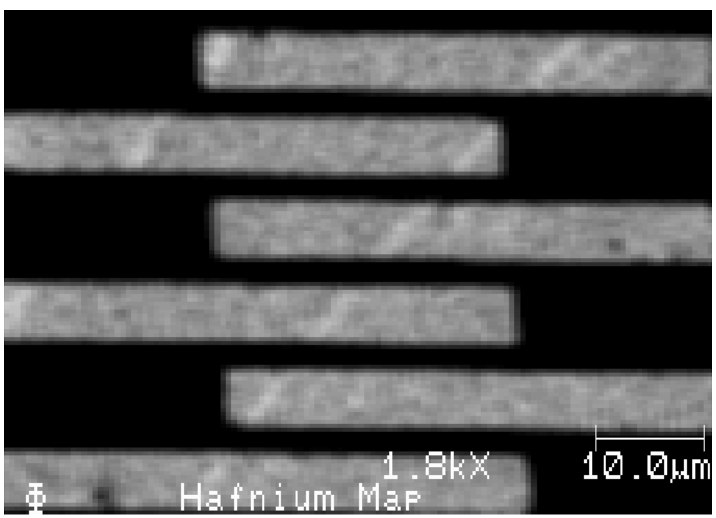
hydride



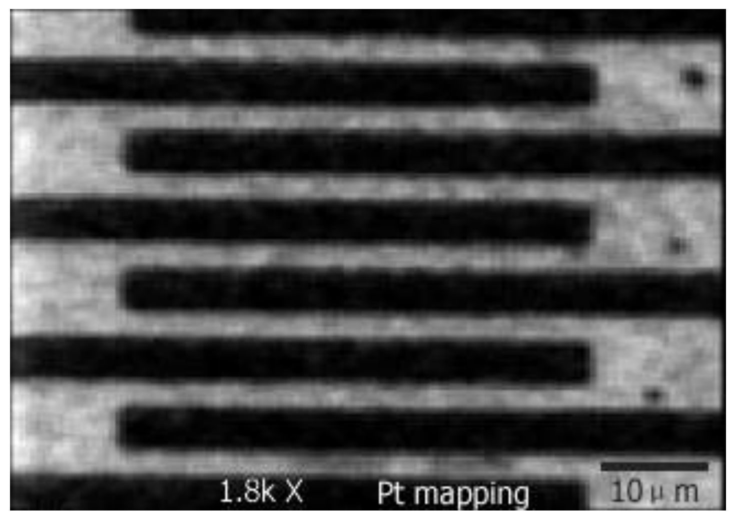
1-alkenes or 1-alkynes



HfO_2 elemental mapping—negative

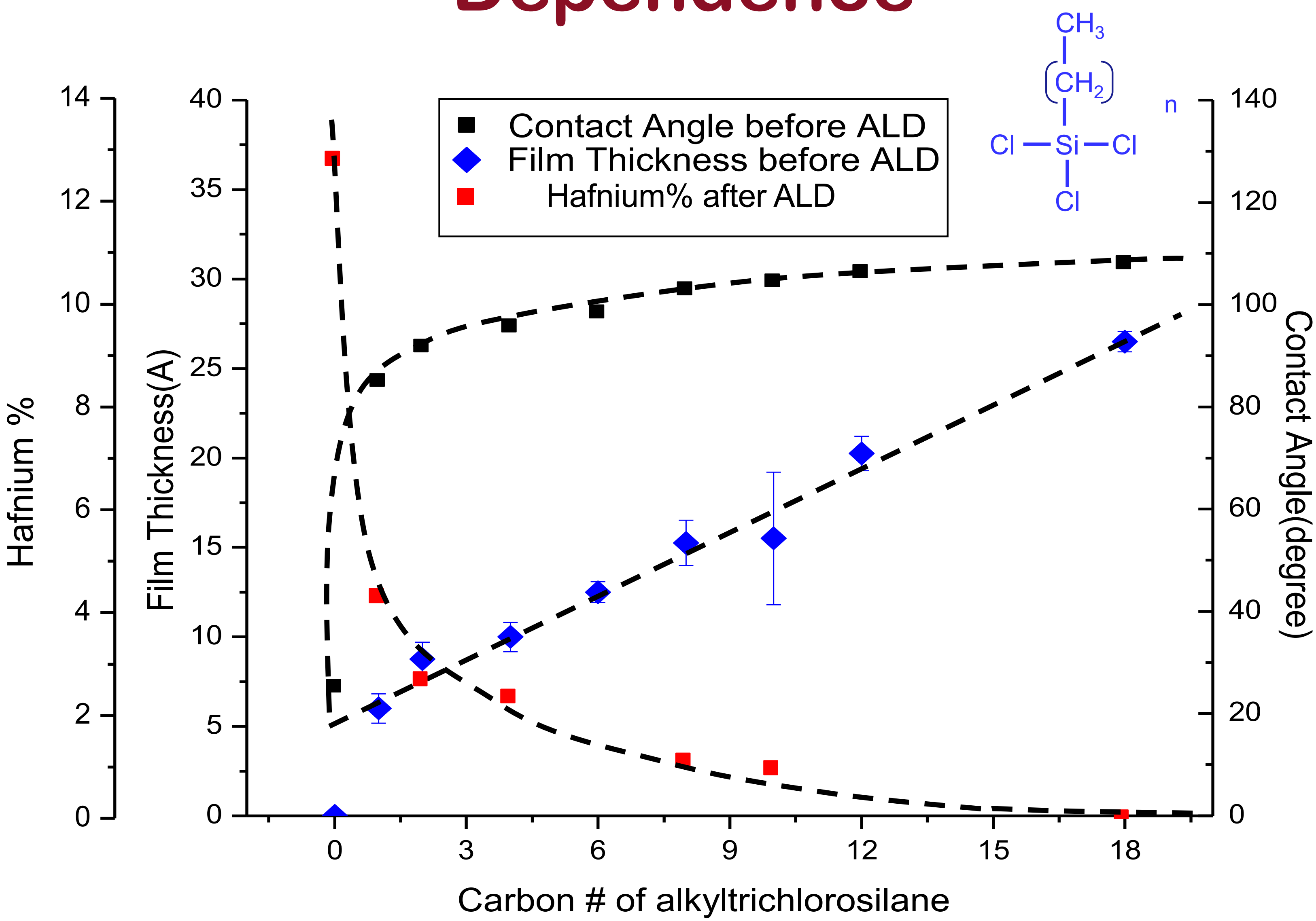


Pt elemental mapping—positive



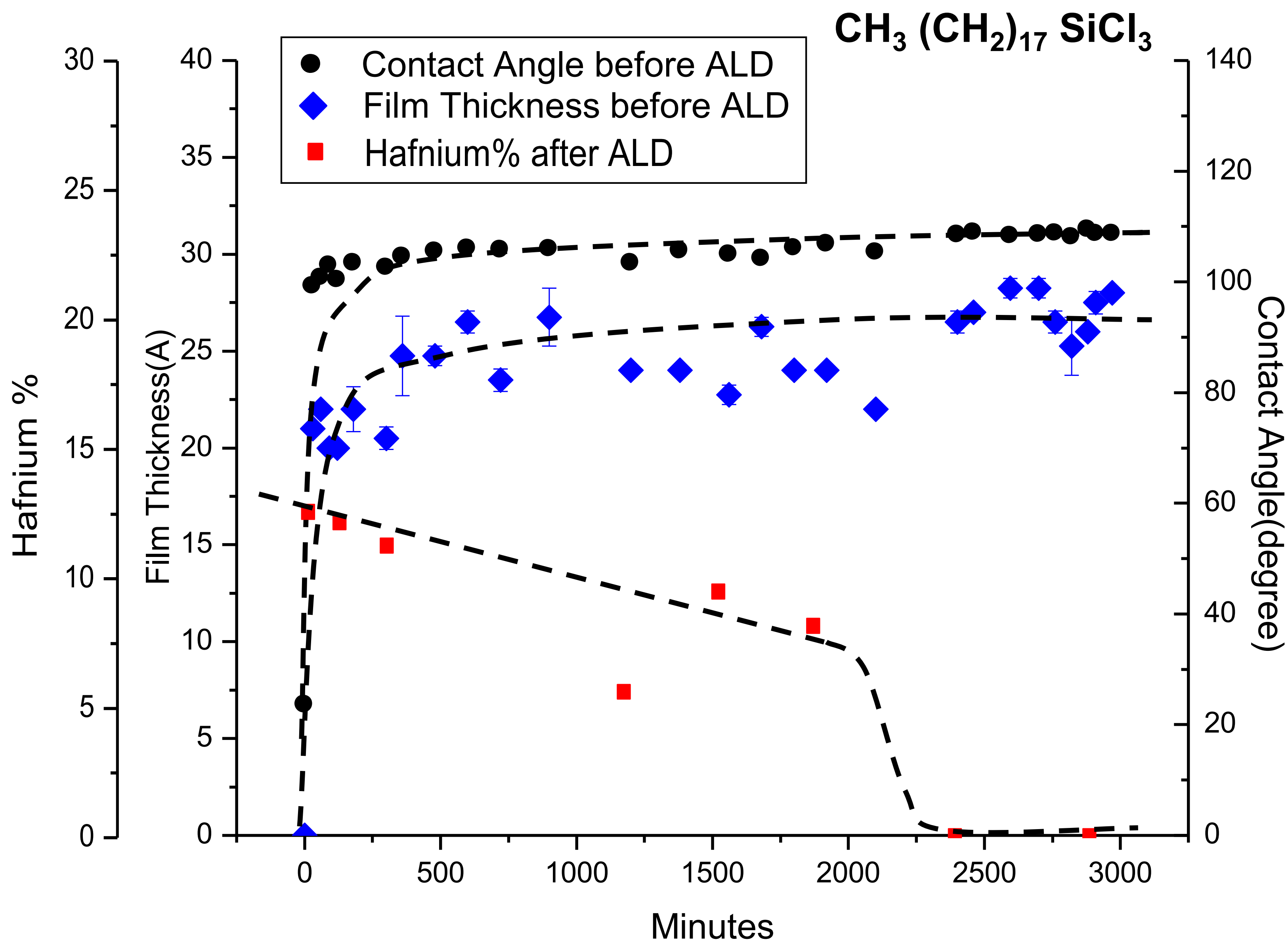
Chen and S. F. Bent, Adv. Mat., 18 (2006) 1086-1090

Alkyltrichlorosilane Chain Length Dependence



Chen, Kim, McIntyre, and Bent, Chem. Mater. 2005 , 17 , 536

Silylation Time Dependence for ODTS

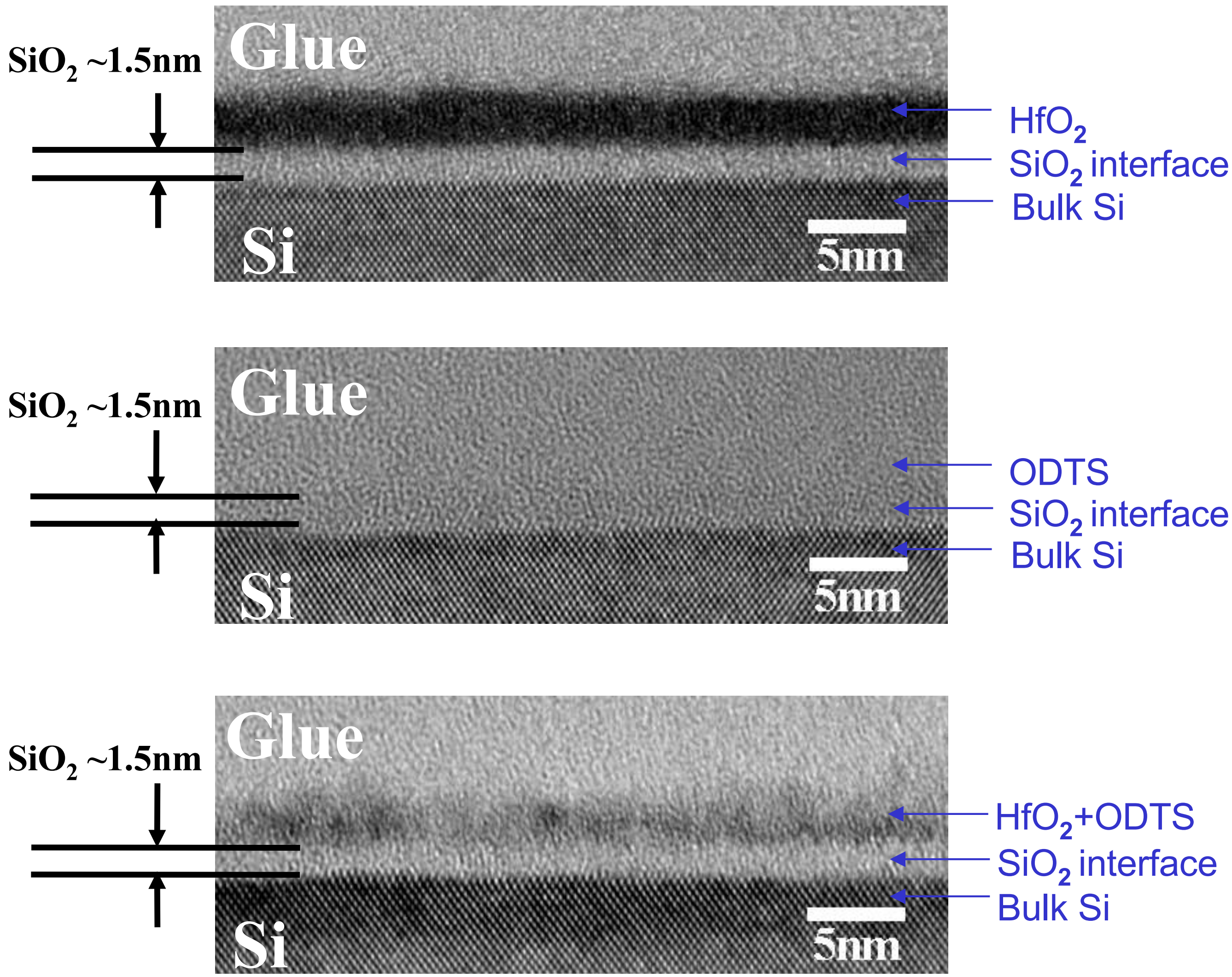


Cross-sectional TEM

Chemical oxide silicon wafer

Densely ODTS coated silicon wafer

Loosely ODTS coated silicon wafer

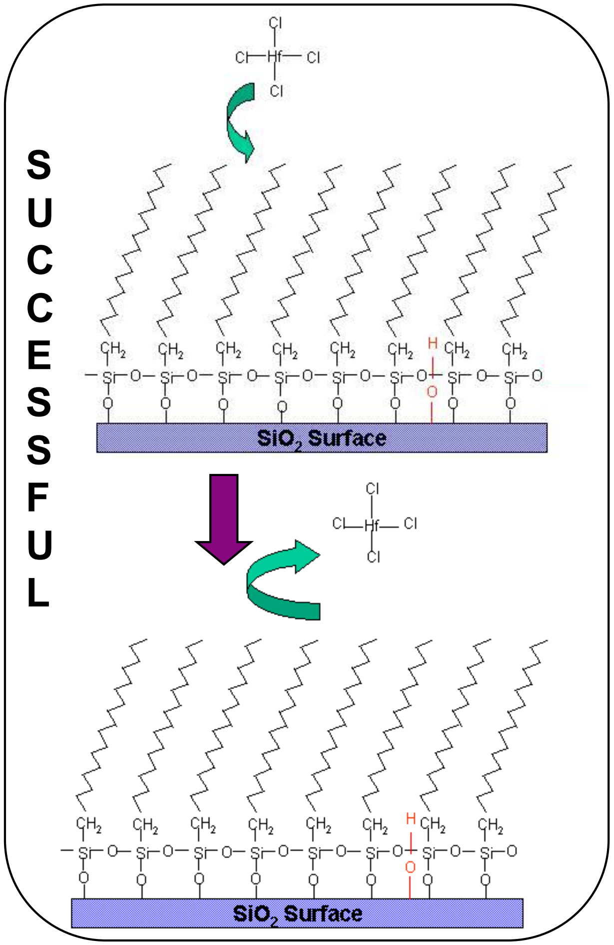


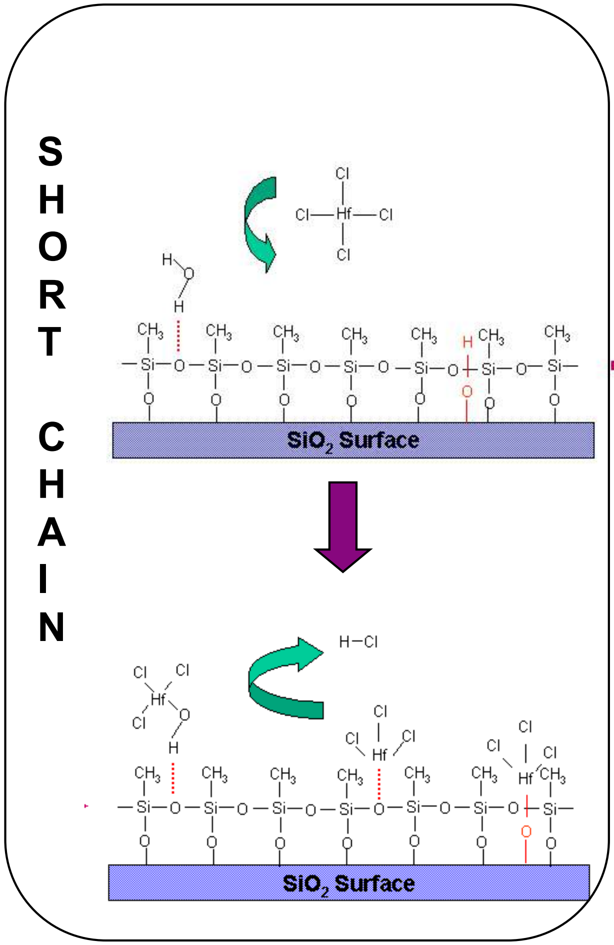
Proposed Mechanism

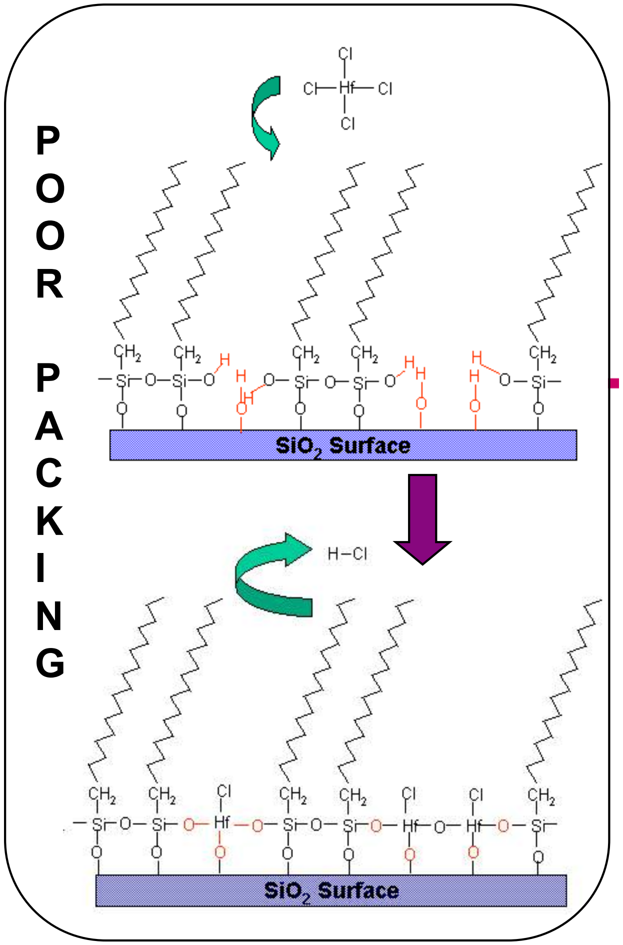
The role of the SAM appears to be twofold:

(1) to remove reactive Si-OH groups at the SiO_2 surface

(2) to prevent precursors from reaching the SiO_2 surface where they may otherwise react with remaining Si-OH defects and Si-O-Si type bonds.

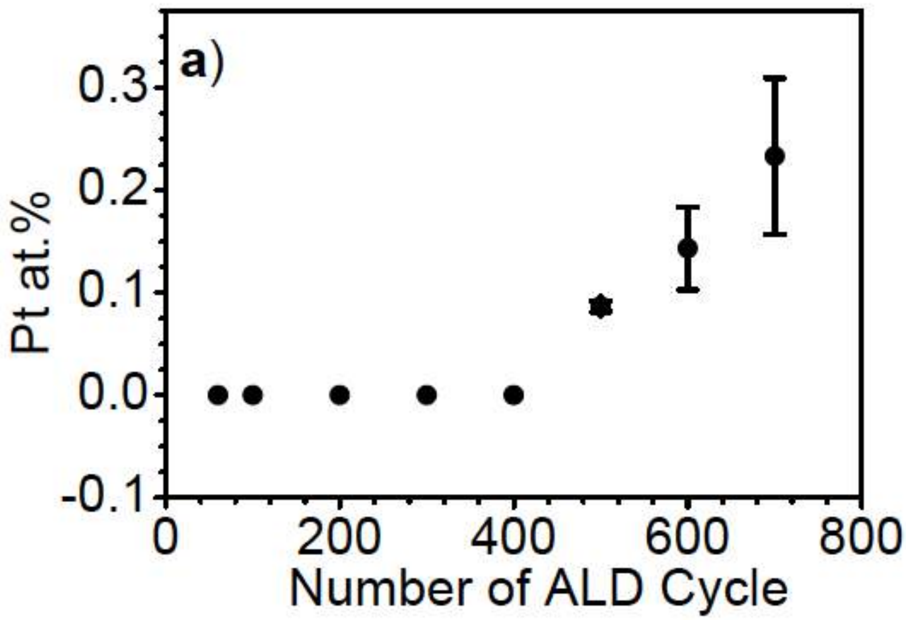




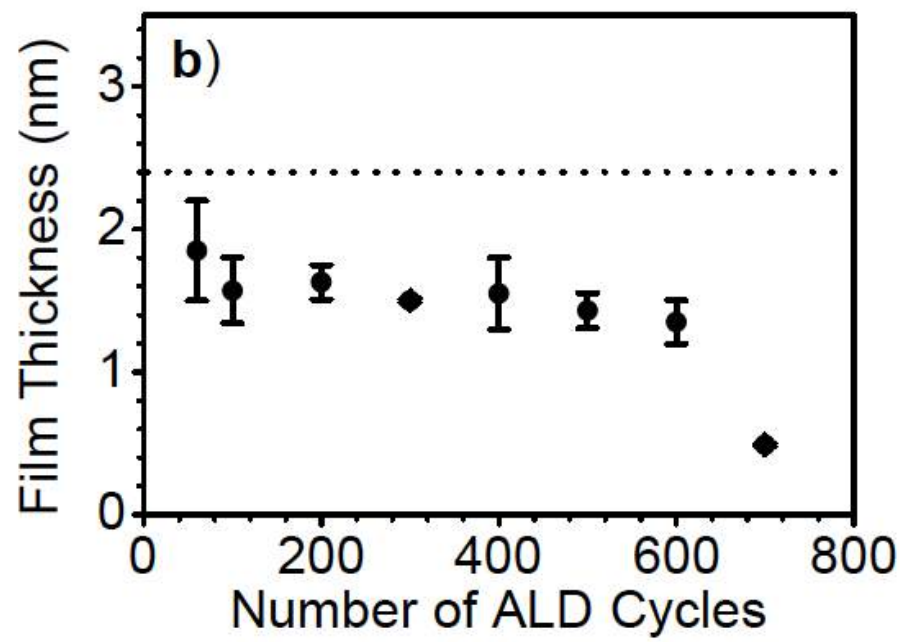


Thickness Limit to AS-ALD

Deactivating limit of ODTS film



ODTS film thickness after ALD

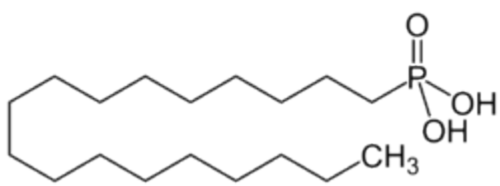


- The Pt ALD reaction is completely deactivated by ODTS at < 400 ALD cycles for the given ALD conditions
- Before ALD process, the ODTS film thickness is ~25 Å; The degradation, indicated by the reduction of the film thickness, of the ODTS film increases with # of ALD cycles
- Despite degradation, ODTS acts as a good resist for Pt ALD

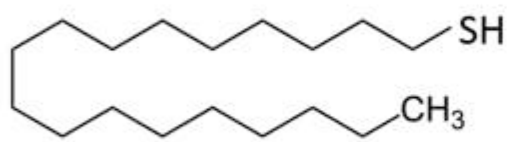
Area Selective ALD on Metal/Dielectric Patterns

- Metal- Dielectric patterns (Cu/ SiO_2)
  - Interconnect layers , transistor level fabrication

- n-alkanethiols (dodecanethiol), aromatic thiols (benzenethiol, …) phosphonic acid (octadecylphosphonic acid), n-alkanoic acid (acetic acid)
- Long chain organic molecules:



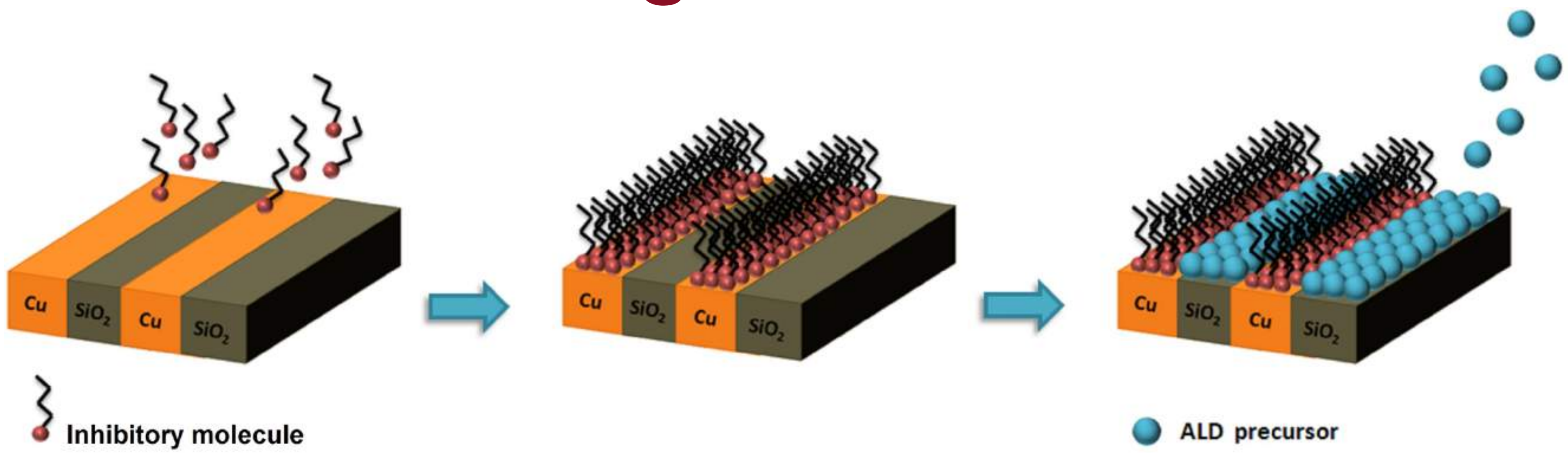
Octadecylphosphonic Acid (ODPA)

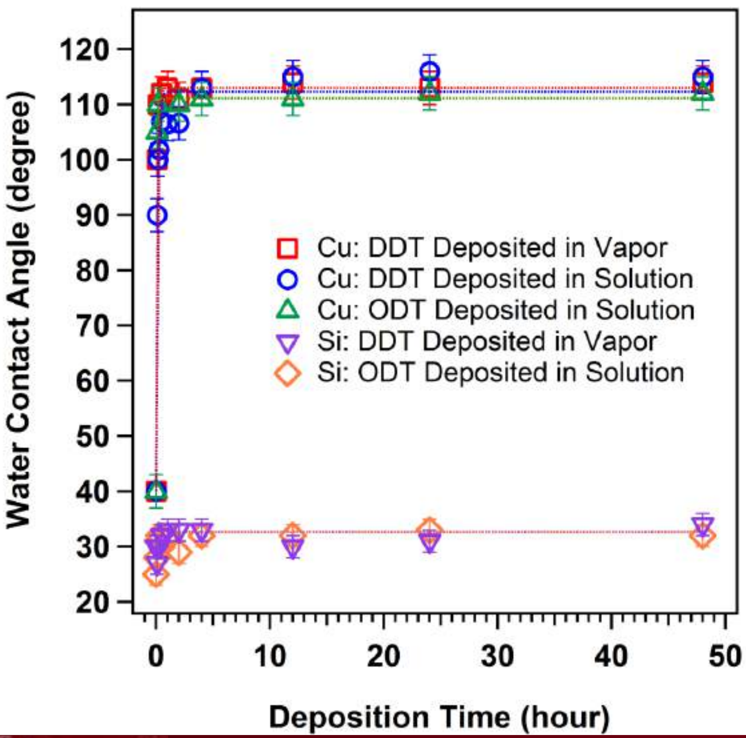


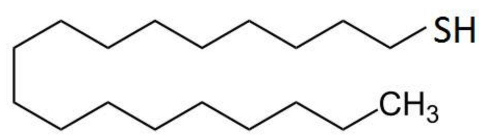
Octadecanethiol (ODT)

Minaye Hashemi et al., J. Phys. Chem. C, 118 (2014)

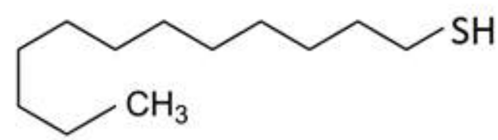
SAM Blocking on Metals: Thiols







Octadecanethiol (ODT)



Dodecanethiol (DDT)

- Substrate cleaning: sonication in acetone and ethanol, 2 min UV/Ozone

- Deposition in solution, 10 mM of ODT/DDT in EtOH
- 40^{o}C,

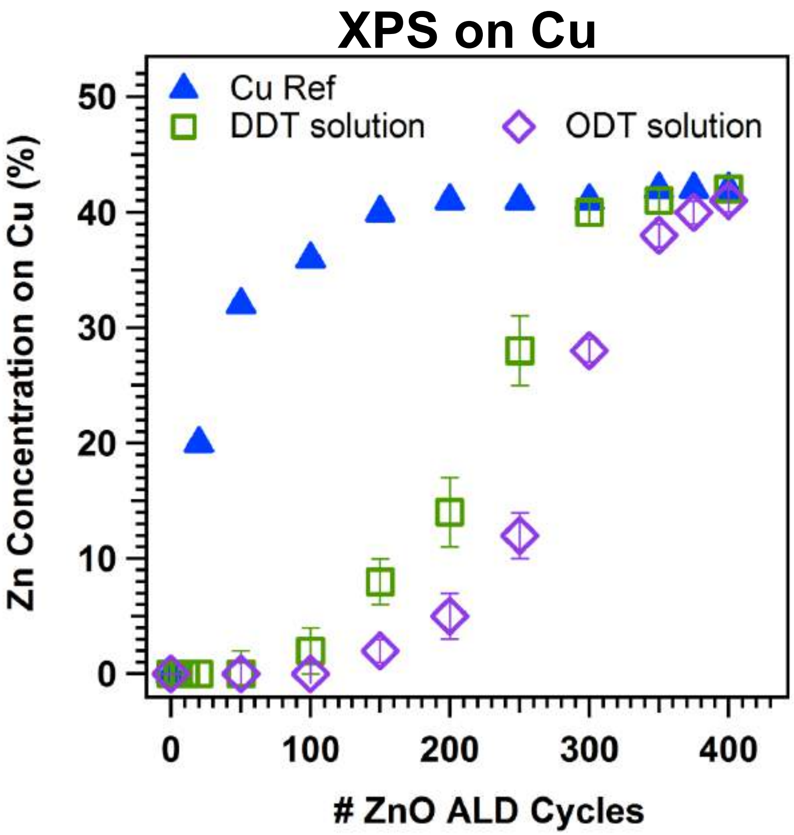
Deposition time: 4 hrs

- DDT Deposition in vapor in vacuum
- 60^{o}C, 60 mTorr

Deposition time: 30 sec

AS-ALD of ZnO Using Thiol SAMs:
Comparison of Chain Length

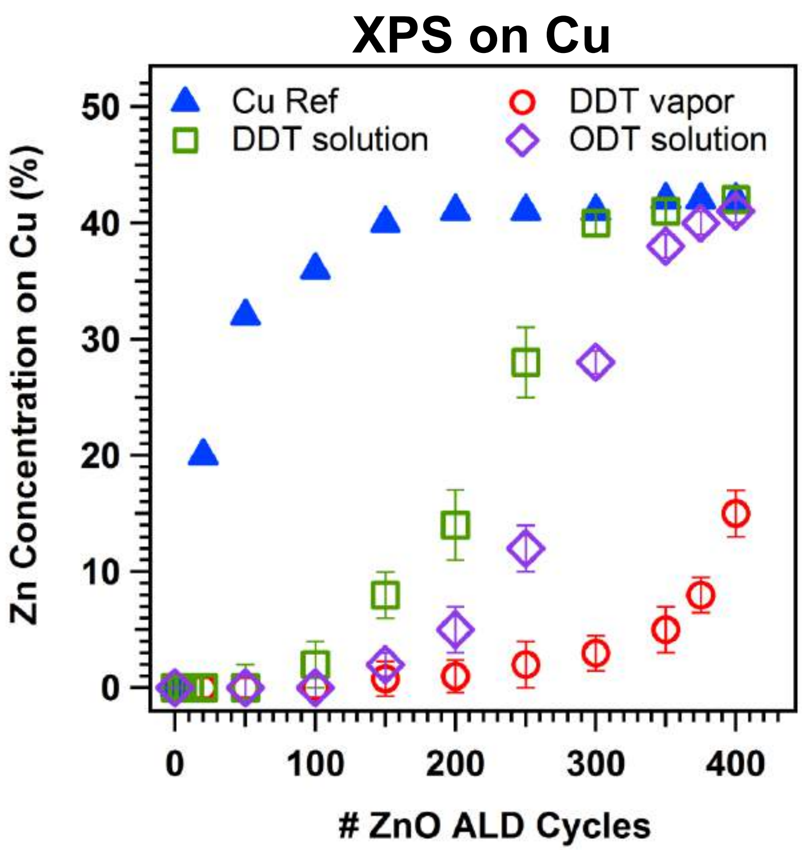
ODT and DDT: solution deposition (4 hrs)
ZnO ALD performed at 120 ° C



F. S. Minaye Hashemi, B. R. Birchansky and S. F. Bent, *ACS Appl. Mat. Interfaces*, 8 (2016) 33264–33272

AS-ALD of ZnO Using Thiol SAMs:
Comparison of Vapor and Solution Deposition

ODT and DDT: solution deposition (4 hrs); DDT: vapor deposition (30 sec)
ZnO ALD performed at 120 ° C



Vapor deposition of thiols: ✓Shorter SAM deposition time required
✓Higher limit for selective deposition of dielectrics

Minaye Hashemi et al.

AS-ALD of ZnO Using Thiol SAMs:
Comparison of Vapor and Solution Deposition

ODT and DDT: solution deposition (4 hrs); DDT: vapor deposition (30 sec)
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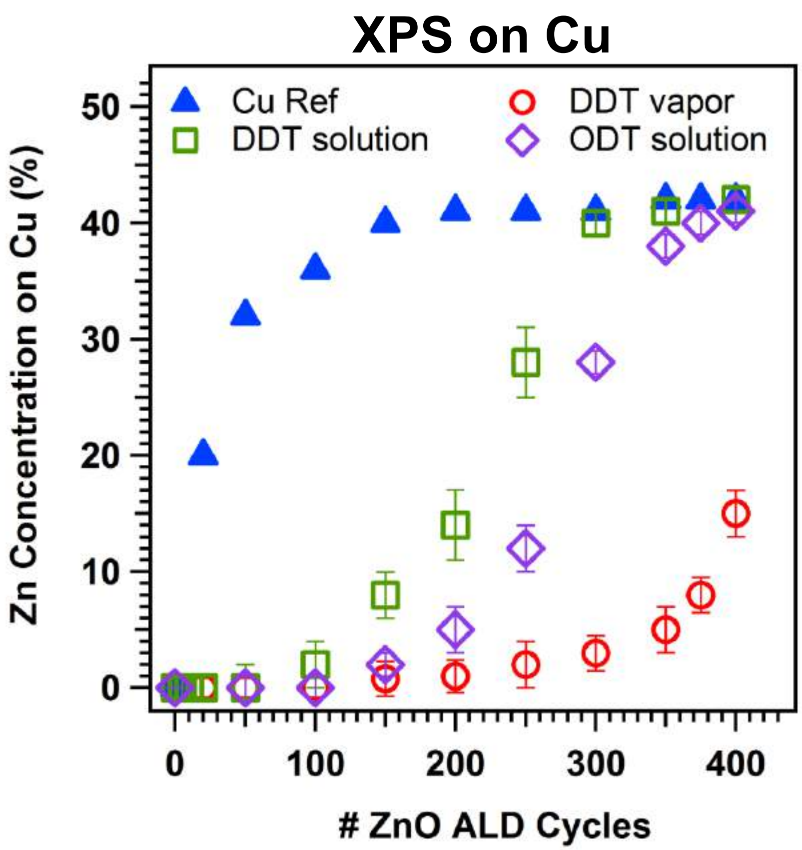
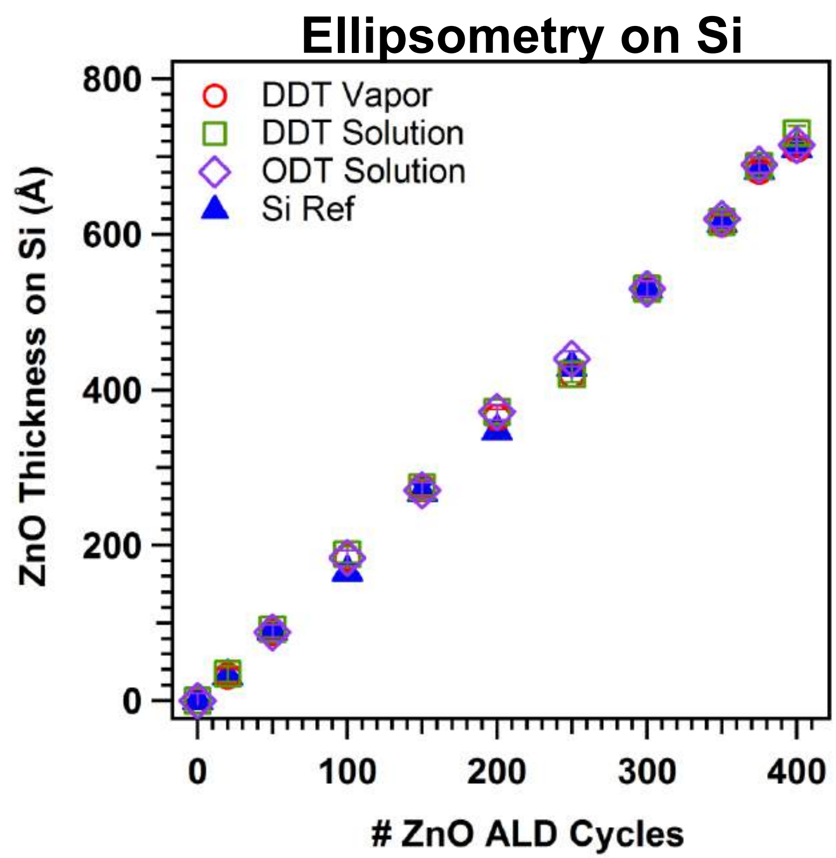




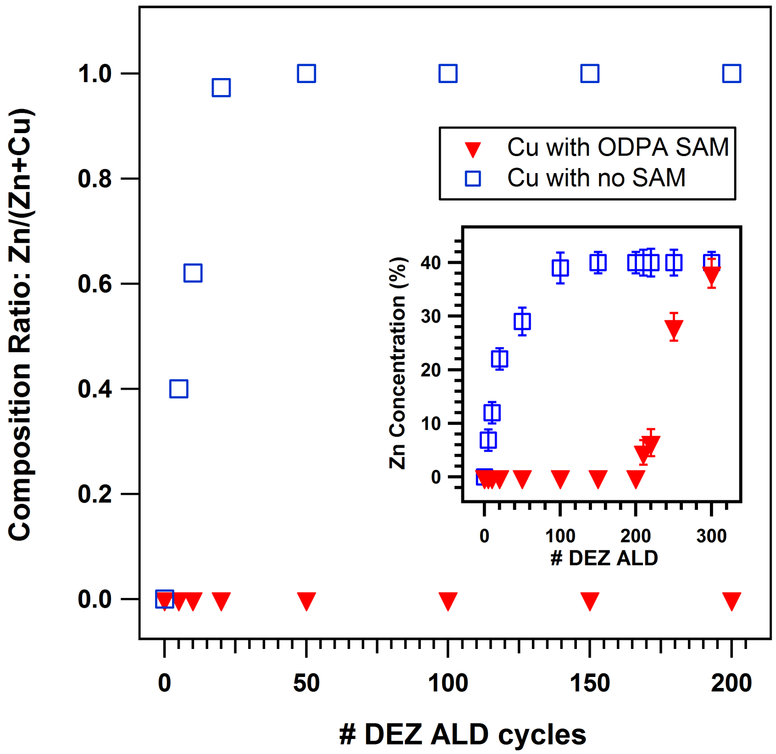
Vapor deposition of thiols: ✓Shorter SAM deposition time required
✓Higher limit for selective deposition of dielectrics

Minaye Hashemi et al.

ODPA blocks ZnO ALD on Cu

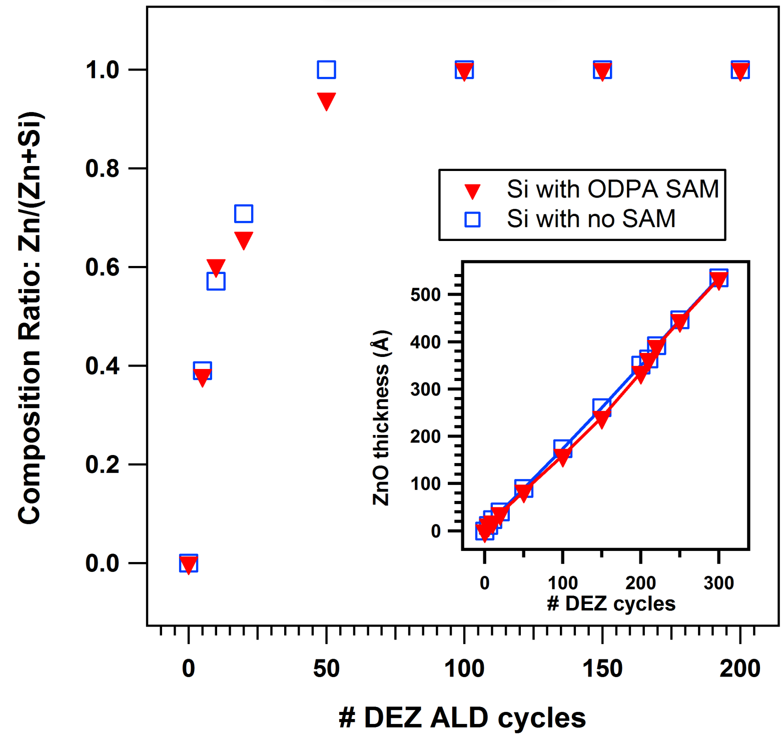
ZnO ALD: Diethylzinc (DEZ) + H_2O
Growth rate: 1.9 Å/cycle
Growth temp.: 150° C

Copper



No growth of ZnO on Cu

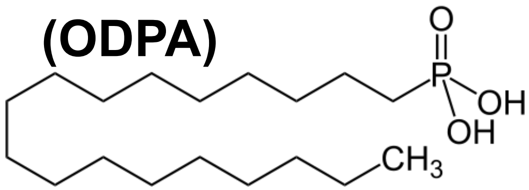
Silicon



Normal ZnO growth on Si

AS-ALD of ZnO using phosphonic acids and thiols

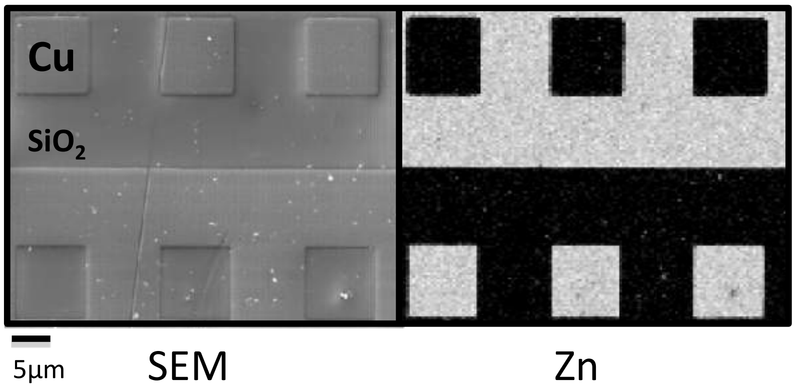
(ODPA)

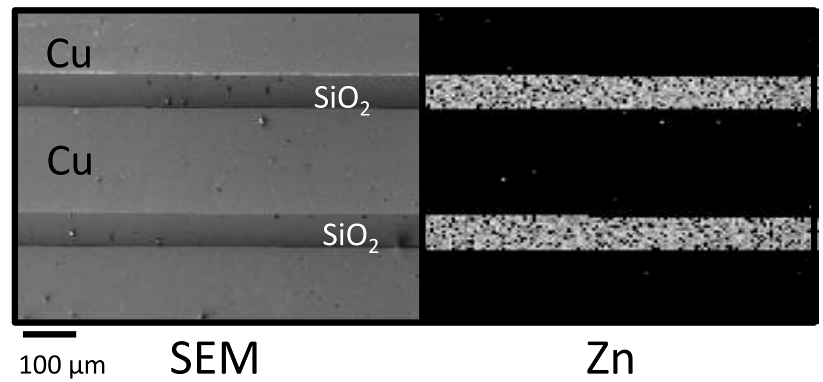


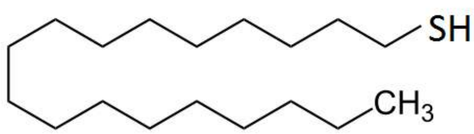
Auger Map

Blocking ZnO ALD for up to 36nm

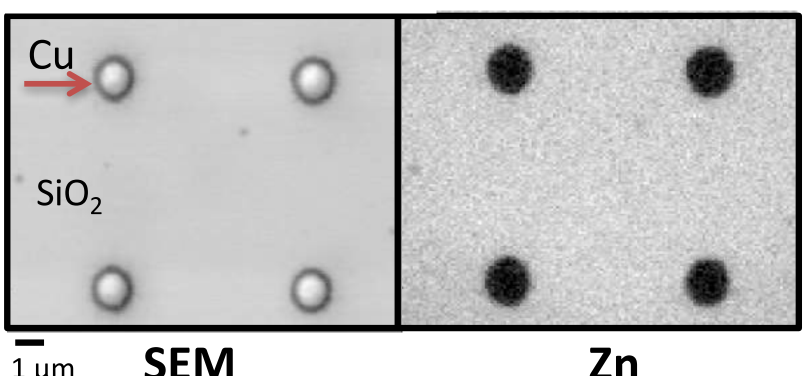
ZnO ALD: Diethylzinc (DEZ) + H_2O
Growth rate: 1.9 Å/cycle
Growth temp.: 150°C

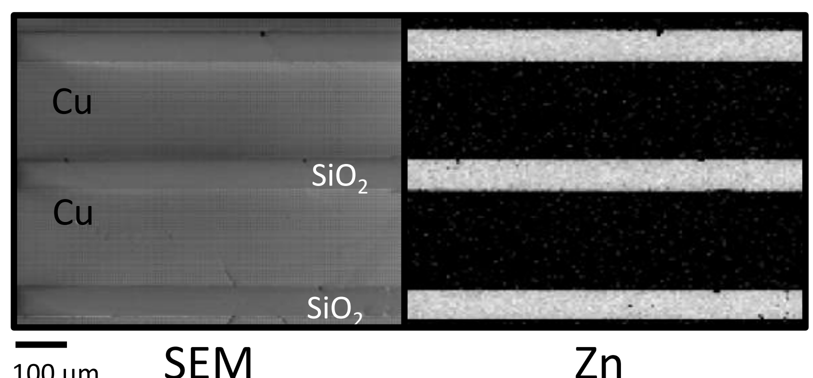






(ODT)





Selectivity varies by material

ODPA blocking agent

Blocking Al_2O_3 (TMA) for 50 cycles (6nm)

SEM **Al** **C**

→ **Selectivity is not as good for Al_2O_3 ALD**

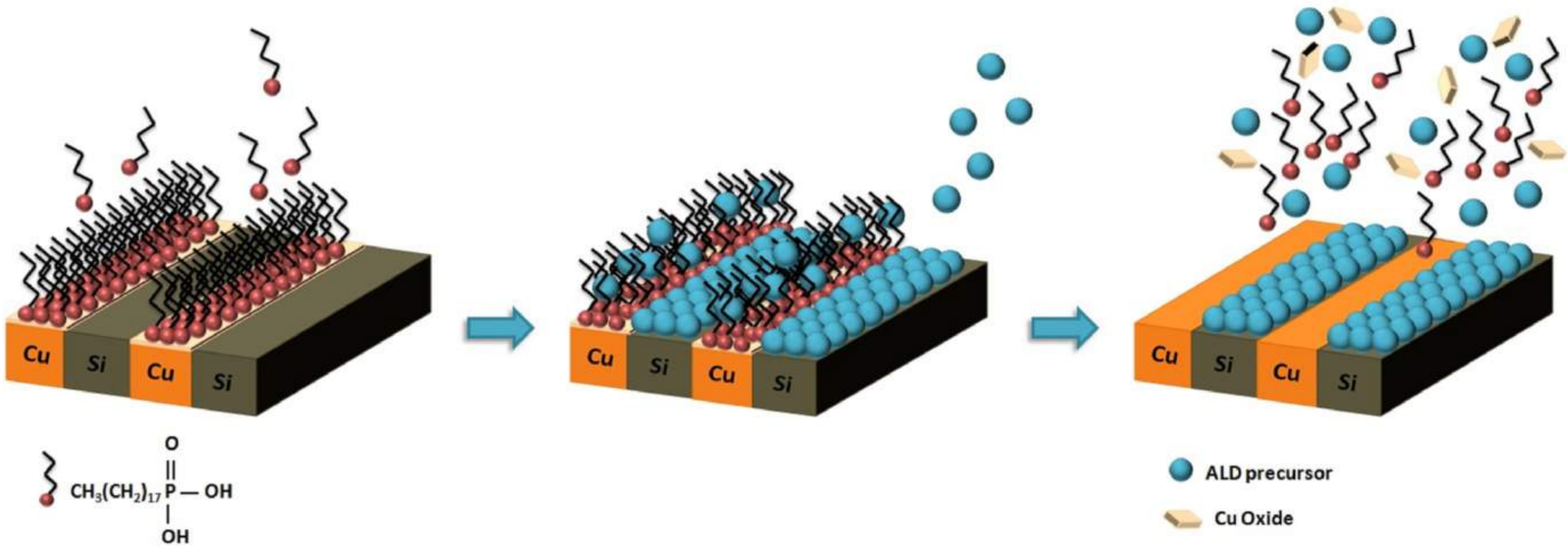
Two Approaches to Improve Selectivity

- Self-correcting process using chemical etching
- Regeneration of the protective SAM

Two Approaches to Improve Selectivity

- Self-correcting process using chemical etching
- Regeneration of the protective SAM

Improve selectivity by chemical etching



- Use an etchant to attack the underlying CuO_x and consequently remove the dielectric layer deposited on top of that
  - CuO_x etchants: acetic acid, hydrochloric acid, nitric acid

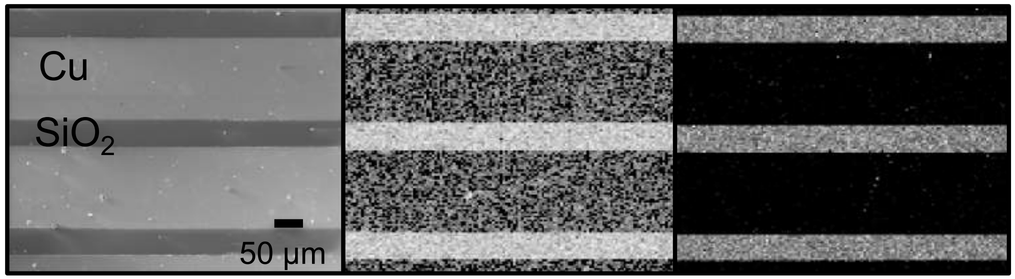
F. S. Minaye Hashemi, C. Prasittichai, and S. F. Bent, ACS Nano 9 (2015) 8710-8717.

Area selective deposition and etching

Al_2O_3 Dielectric Film

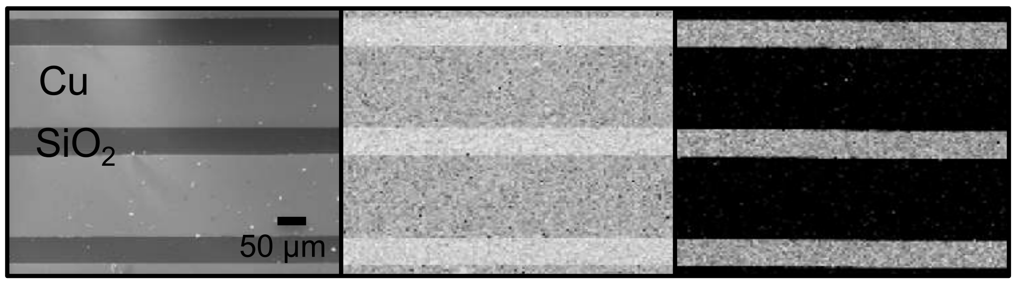
48 hours of ODPA deposition

Al Auger map



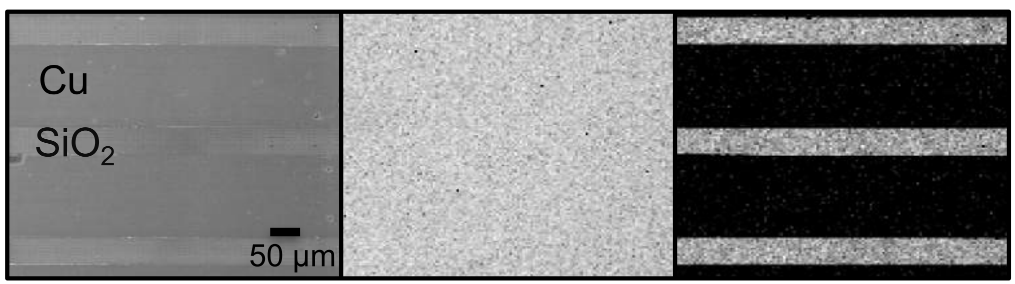
SEM | 60 cycles Al_2O_3 ALD | after etching

6.8 nm Al_2O_3



SEM | 80 cycles Al_2O_3 ALD | after etching

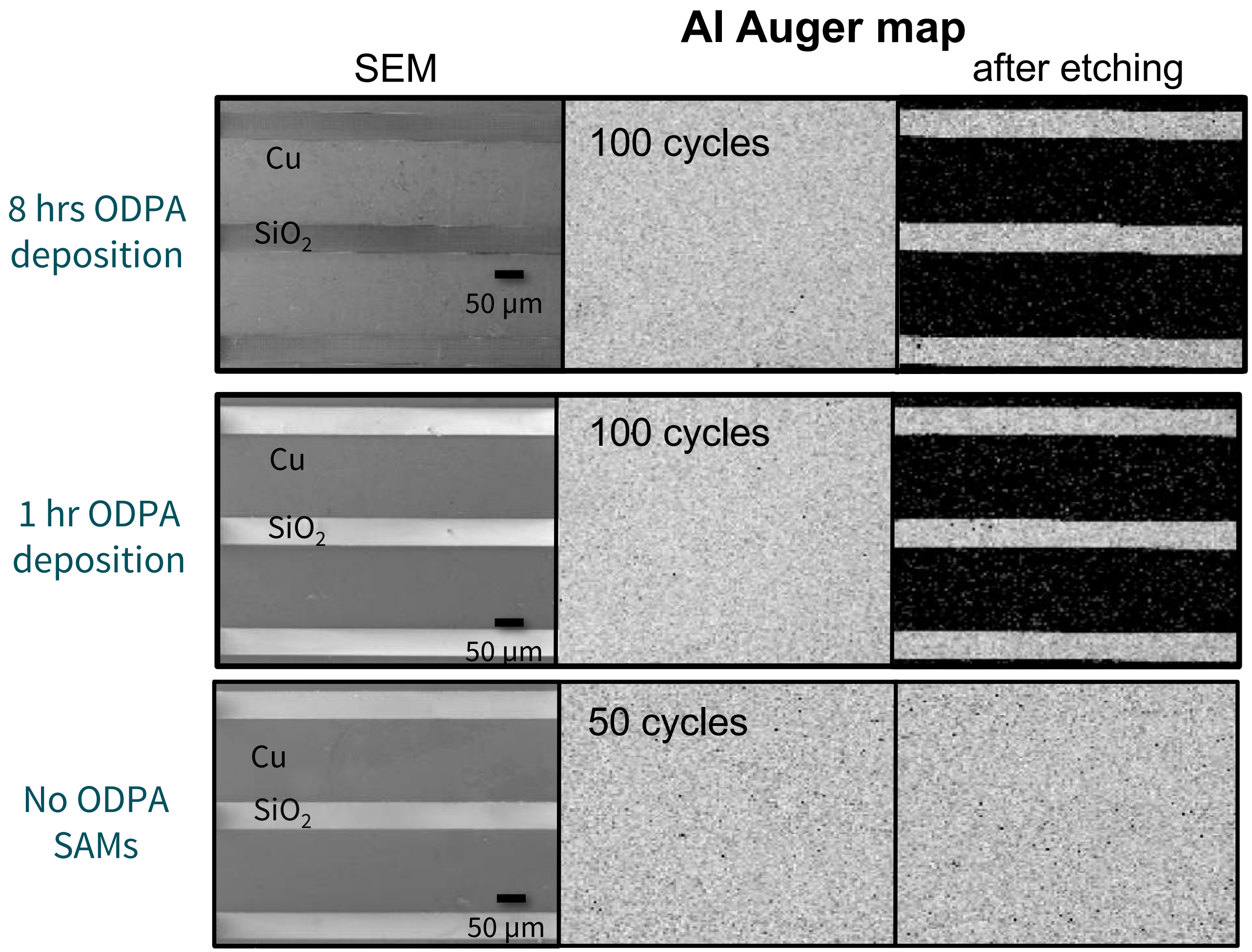
9.4 nm Al_2O_3



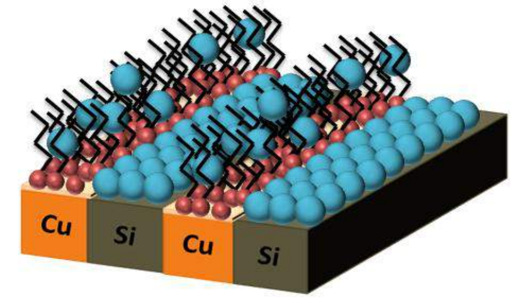
SEM | 100 cycles Al_2O_3 ALD | after etching

12.1 nm Al_2O_3

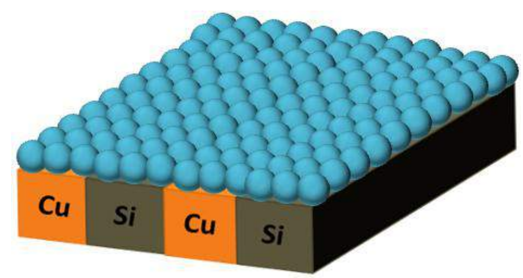
Self-Correcting Procedure Reduces Processing Time



No perfect SAMs needed: Shorter deposition time

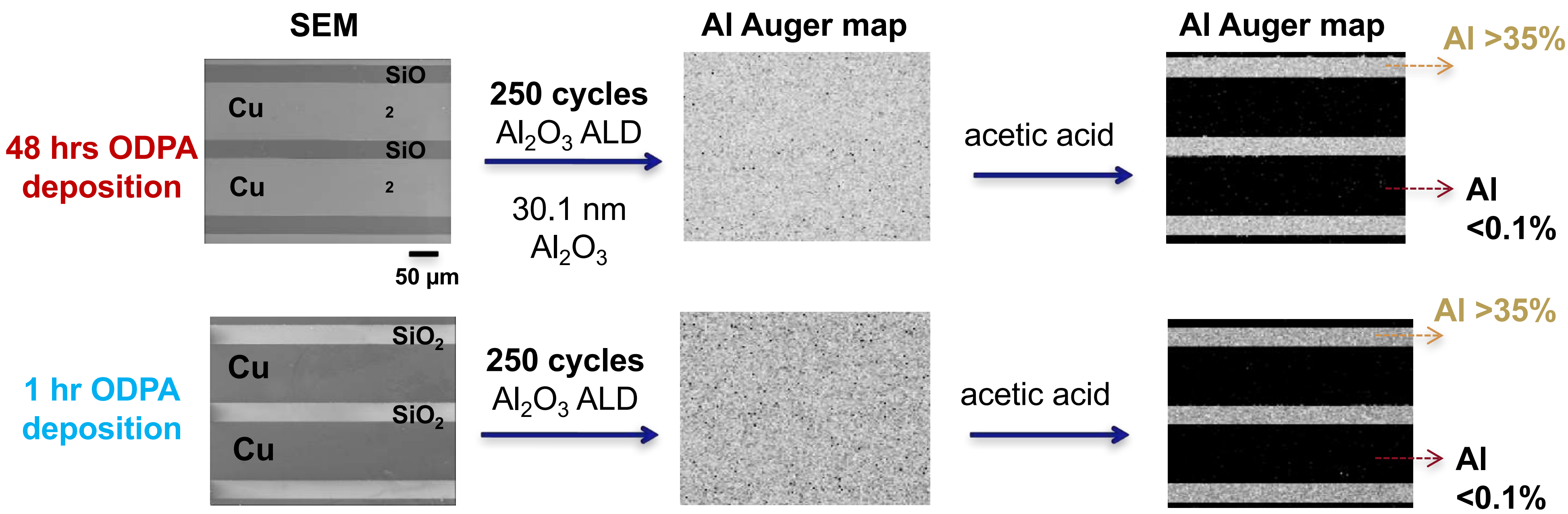


Presence of Cu oxide layer and ODPA SAMs is necessary

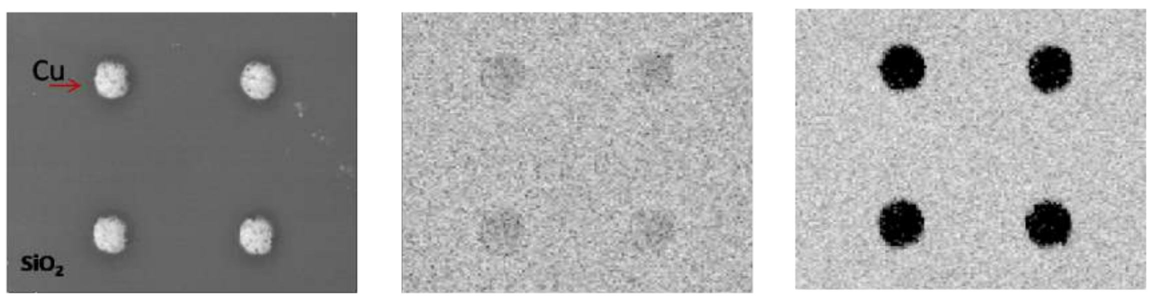


- Poor quality SAM blocks ALD growth sufficiently.
- SAM is however required for lift-off.

Quantification of the selectivity



Selectivity of Al: 350:1



(b) SEM 1 µm

Al map after 1hr ODPA and 80 cycles of TMA ALD

Al map after etching

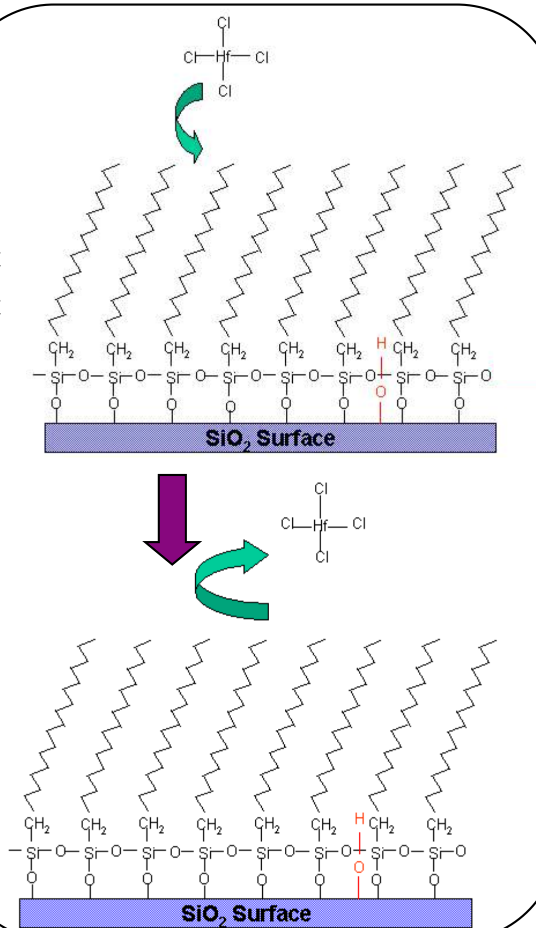
Two Approaches to Improve Selectivity

- Self-correcting process using chemical etching
- Regeneration of the protective SAM

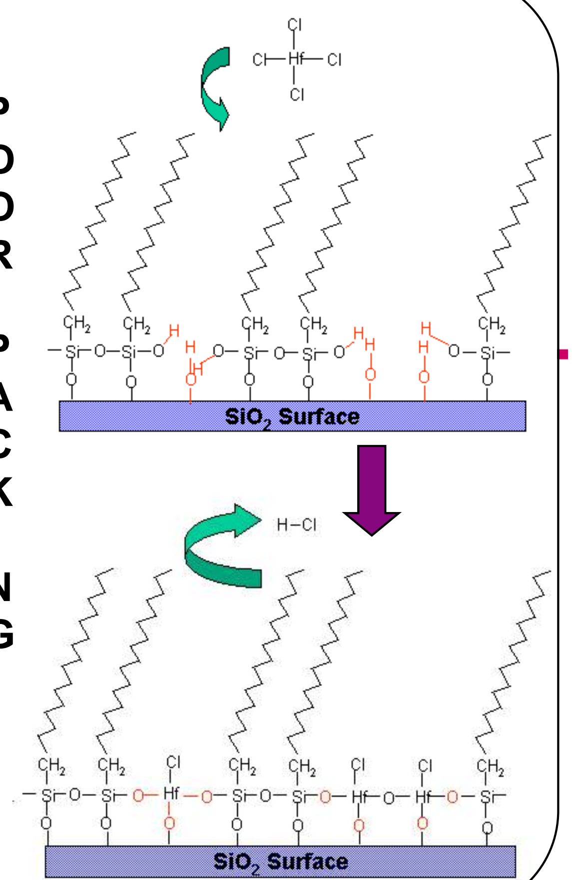
Recall: Proposed Mechanism

A well-packed SAM is required to prevent precursors from reaching the SiO_2 surface where they can react with remaining Si-OH defects and Si-O-Si type bonds.

SUCCESSFUL



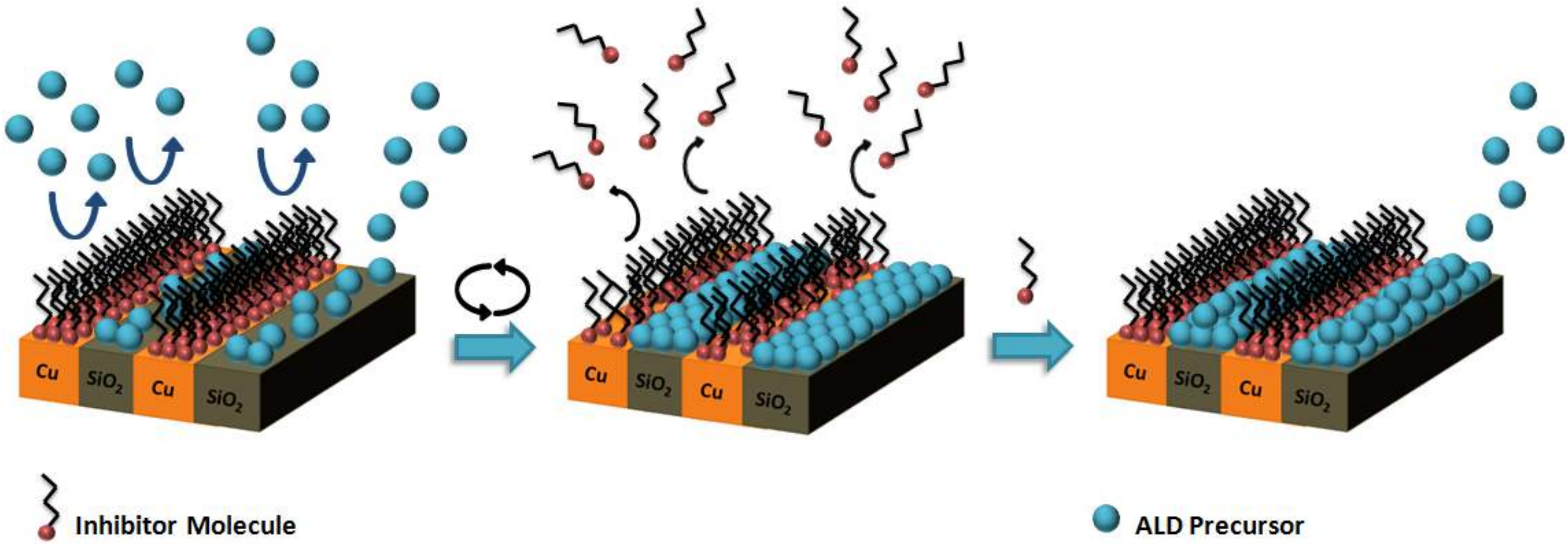
POOR PACKING



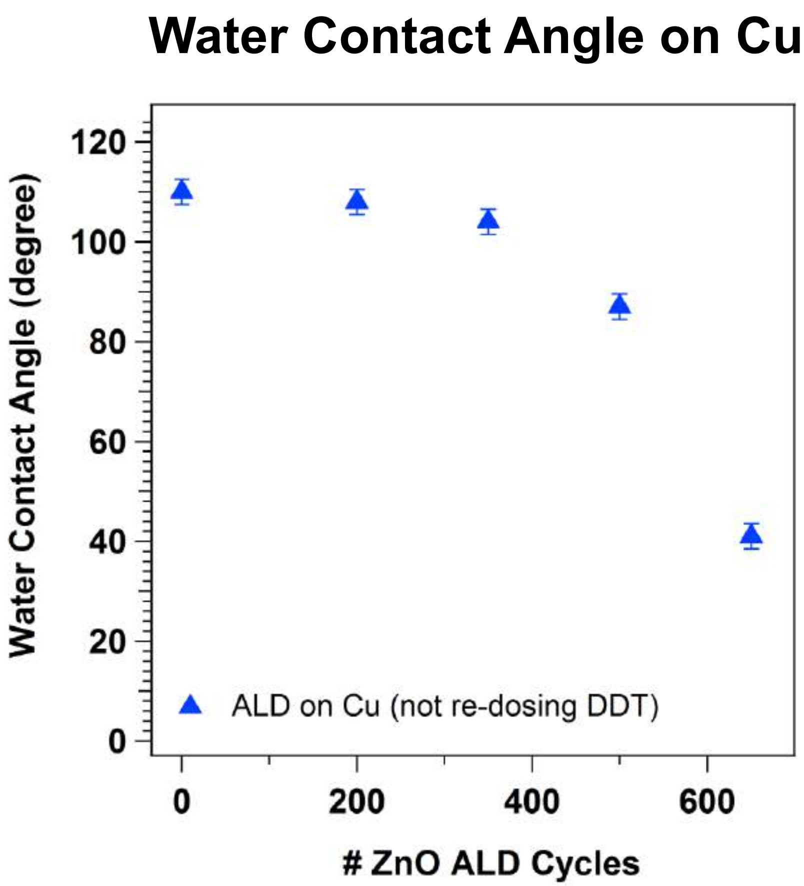
Selective Deposition With Re-Dosing SAMs

- Loss of selectivity due to the damage happening on blocking layer after many cycles of ALD

- Regenerate blocking layer by re-dosing the SAMs
  - SAMs to go down on metal and protect further ALD deposition
  - ALD growth on dielectric to remain unaffected by this re-dosing



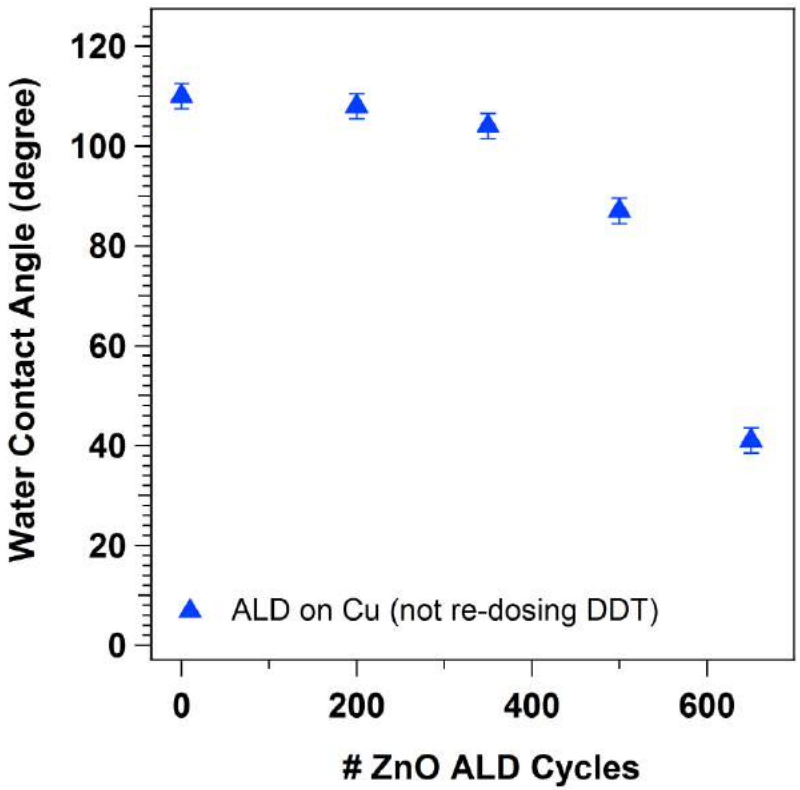
Re-dosing Dodecanethiol in Vapor



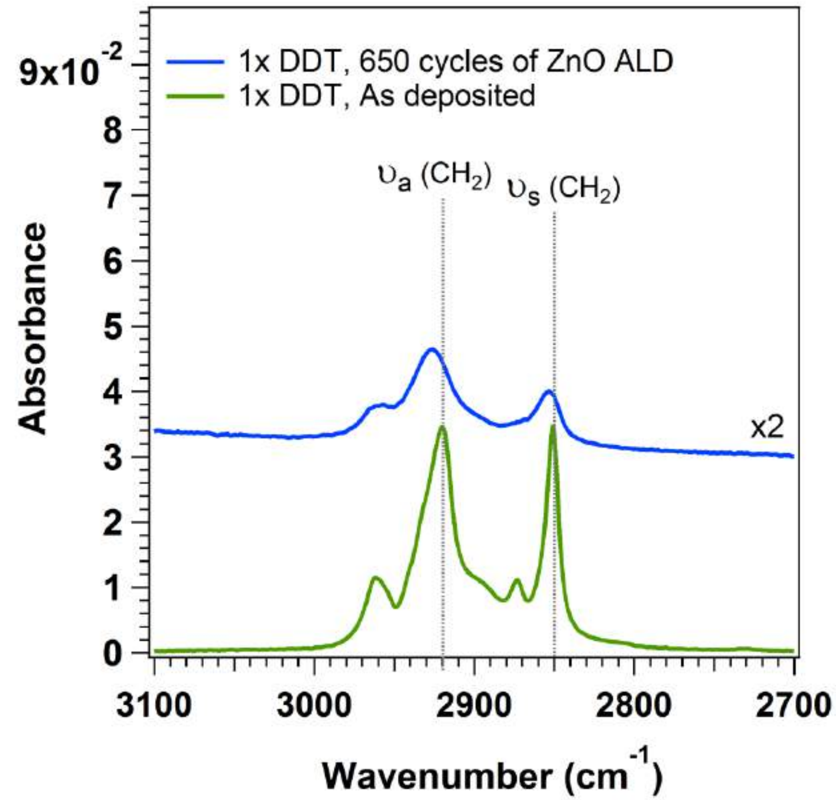
F. S. Minaye Hashemi and S. F. Bent, *Adv. Mater. Interfaces*, 1600464 (2016)

Re-dosing Dodecanethiol in Vapor

Water Contact Angle on Cu



ATR-FTIR on Cu

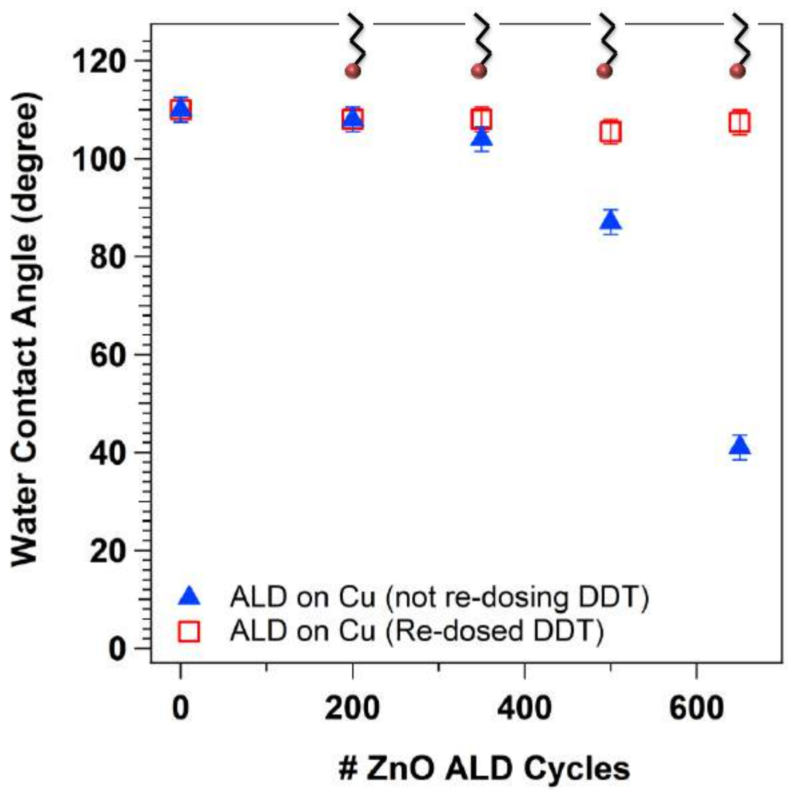


F. S. Minaye Hashemi and S. F. Bent, *Adv. Mater. Interfaces*, 1600464 (2016)

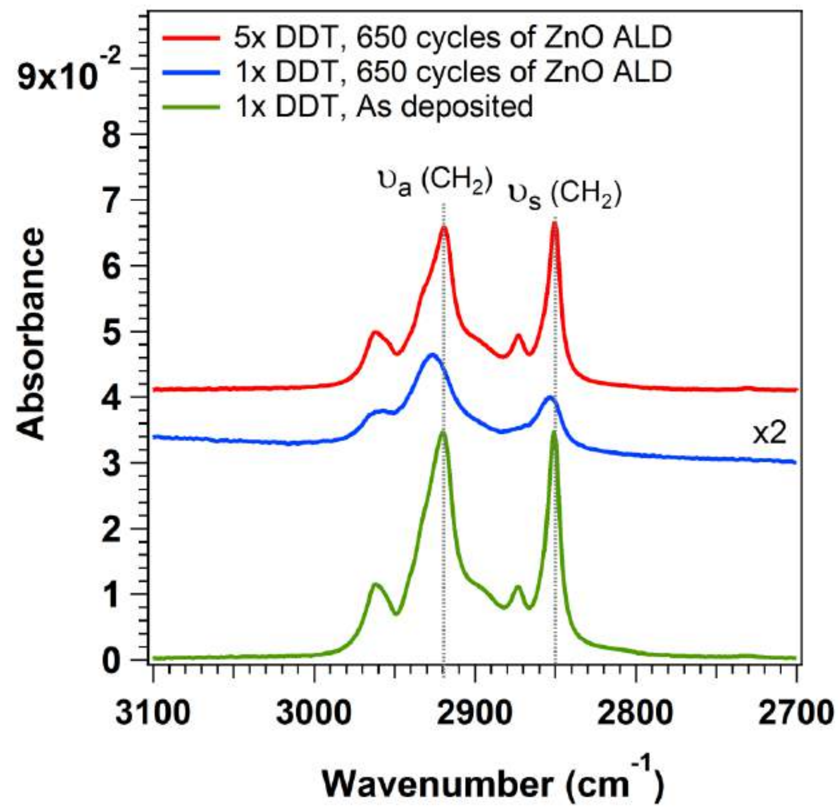
Re-dosing Dodecanethiol in Vapor

- After every 150 cycles of ZnO ALD: Regenerate the thiol in vapor for 30 sec
- Sonicate both Cu and Si in ethanol after deposition of SAM

Water Contact Angle on Cu



ATR-FTIR on Cu



Re-dosing the SAM improves hydrophobicity and order of thiol SAM

F. S. Minaye Hashemi and S. F. Bent, *Adv. Mater. Interfaces*, 1600464 (2016)

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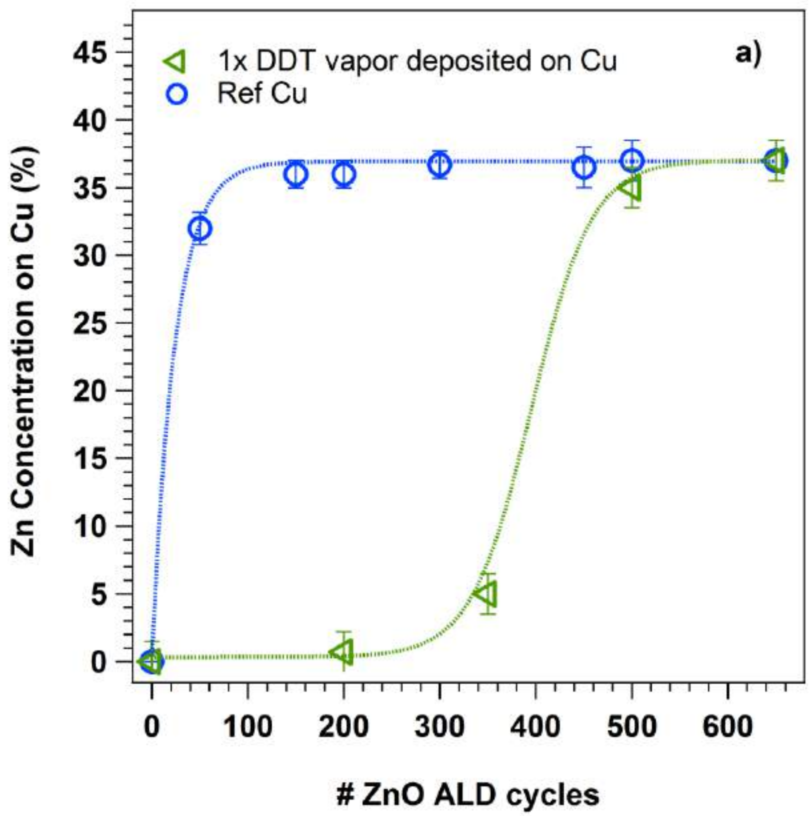
XPS on Cu



F. S. Minaye Hashemi and S. F. Bent, *Adv. Mater. Interfaces*, 1600464 (2016)

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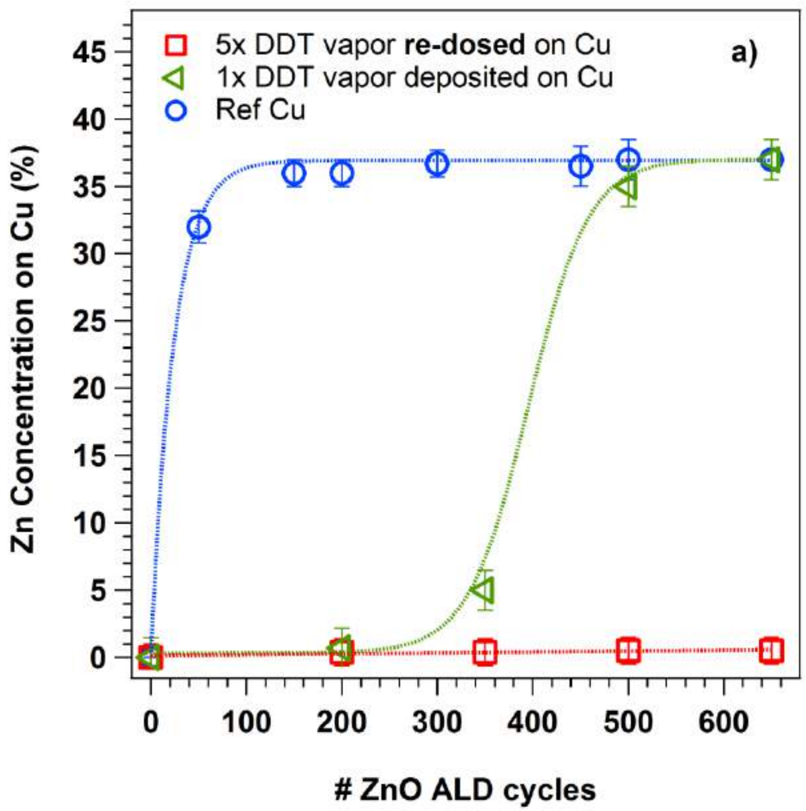

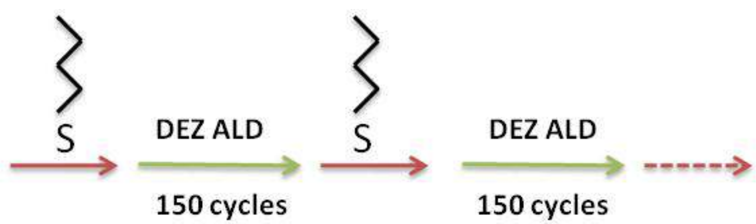

F. S. Minaye Hashemi and S. F. Bent, *Adv. Mater. Interfaces*, 1600464 (2016)

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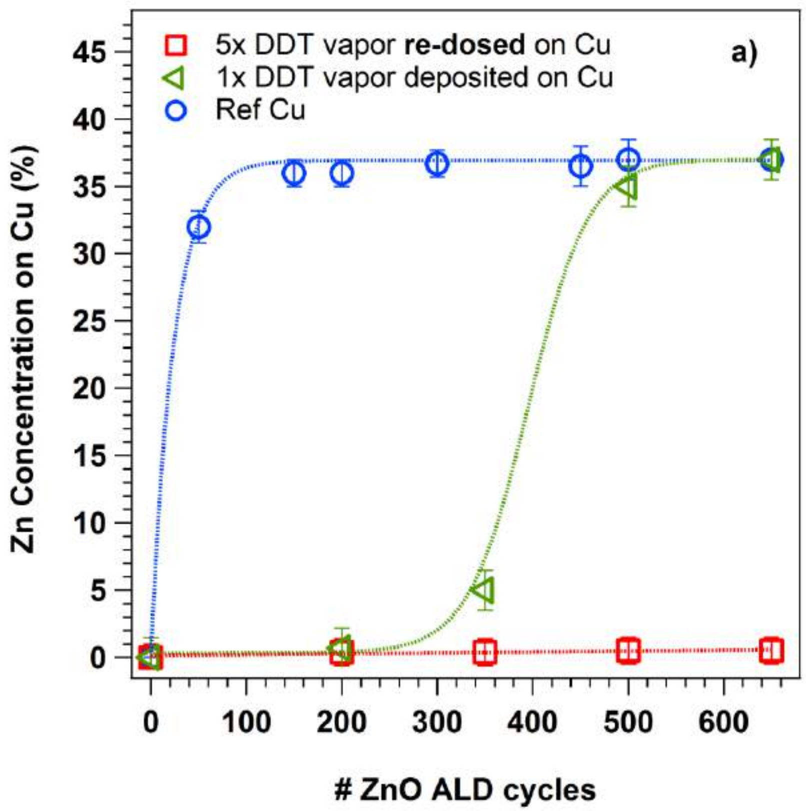
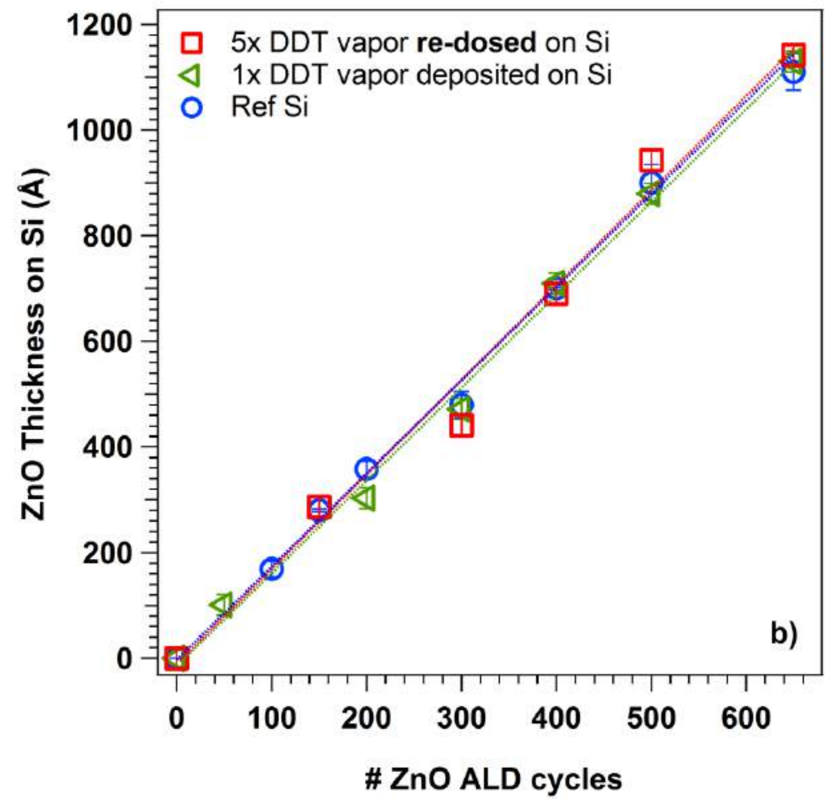


Ellipsometry on Si



Re-dosing process results in selective deposition of 3x thicker dielectric films

F. S. Minaye Hashemi and S. F. Bent, *Adv. Mater. Interfaces*, 1600464 (2016)

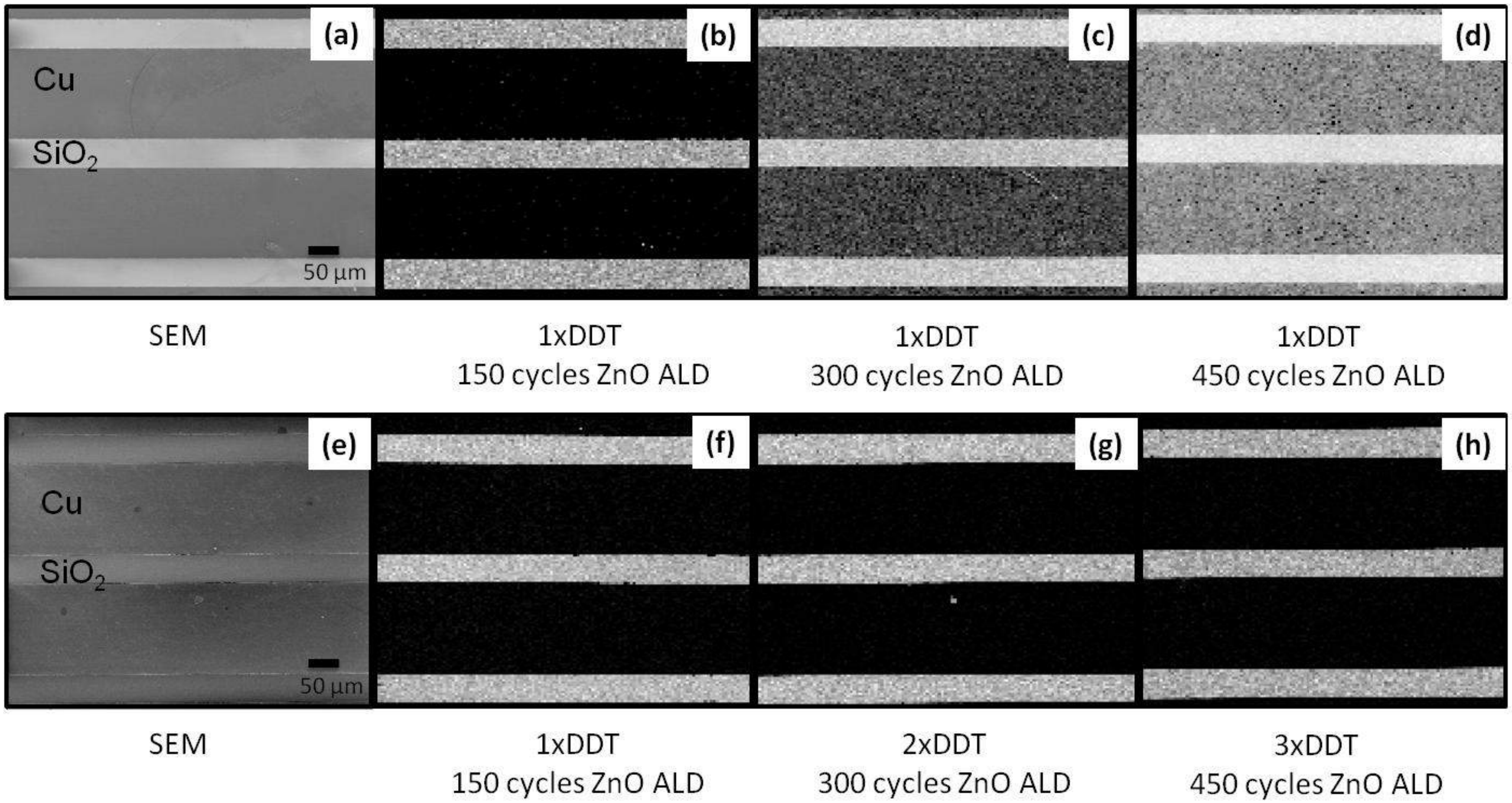
Re-dosing Dodecanethiol Inhibitor Layer

- Regenerate the inhibitor layer in vapor for 30 sec
- Auger Zn map

growth rate: 1.8 Å/cycle

No re-dosing of DDT SAM: Gradual loss of selectivity

Re-dosing of DDT SAM: Maintained selectivity

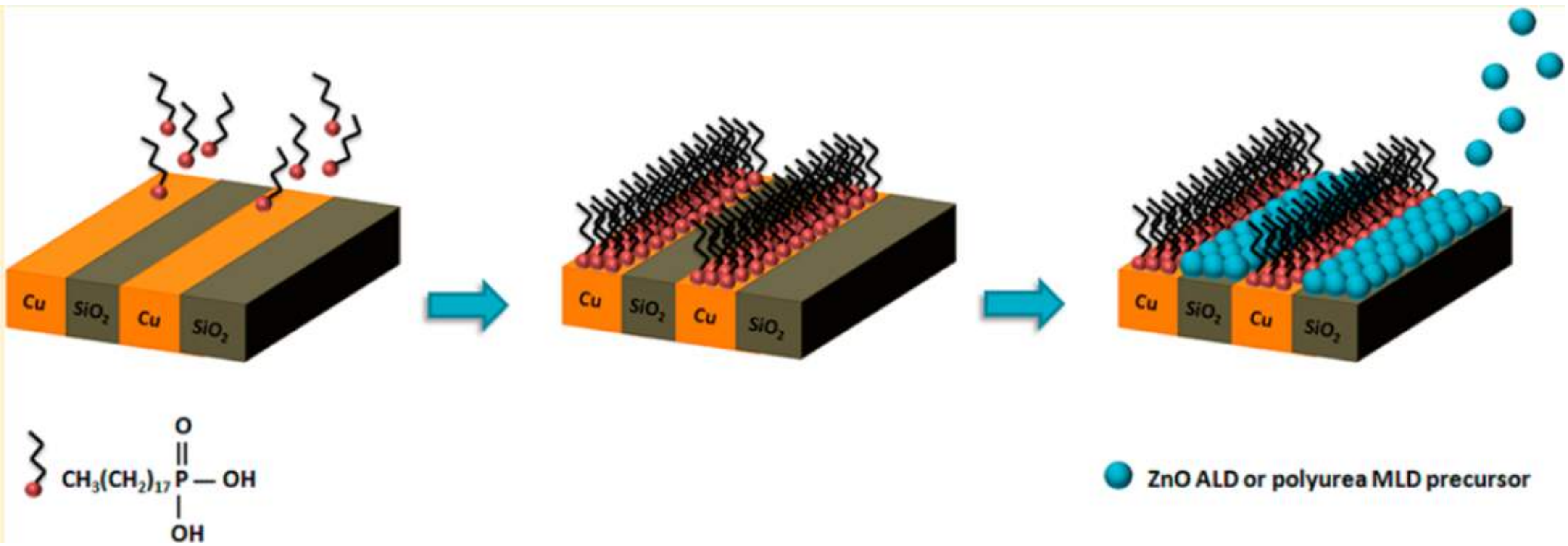


✓Re-dosing process results in selective deposition of 3x thicker dielectric films

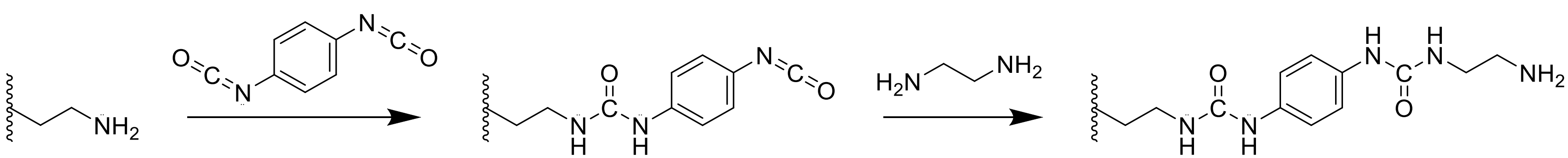
✓Improved selectivity on patterned structures

F. S. Minaye Hashemi and S. F. Bent, *Adv. Mater. Interfaces*, 1600464 (2016)

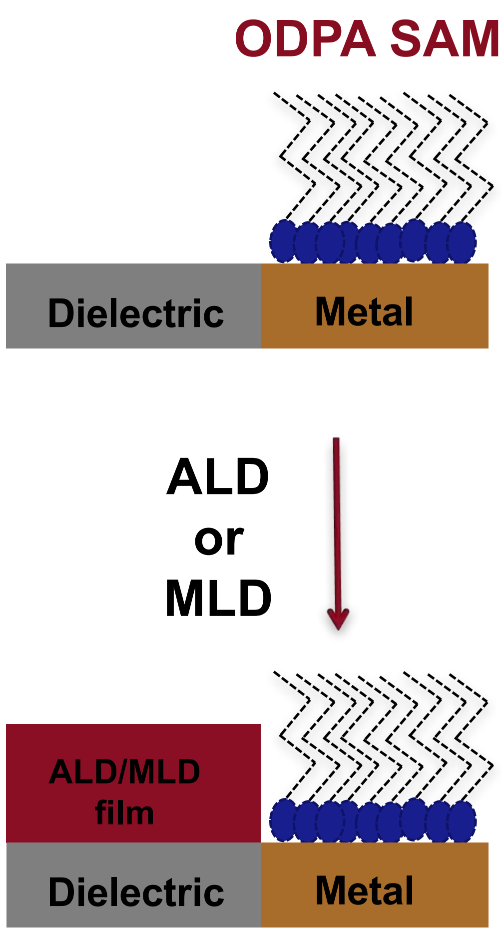
Does area selective deposition work with Molecular Layer Deposition (MLD)?



MLD Process: polyurea

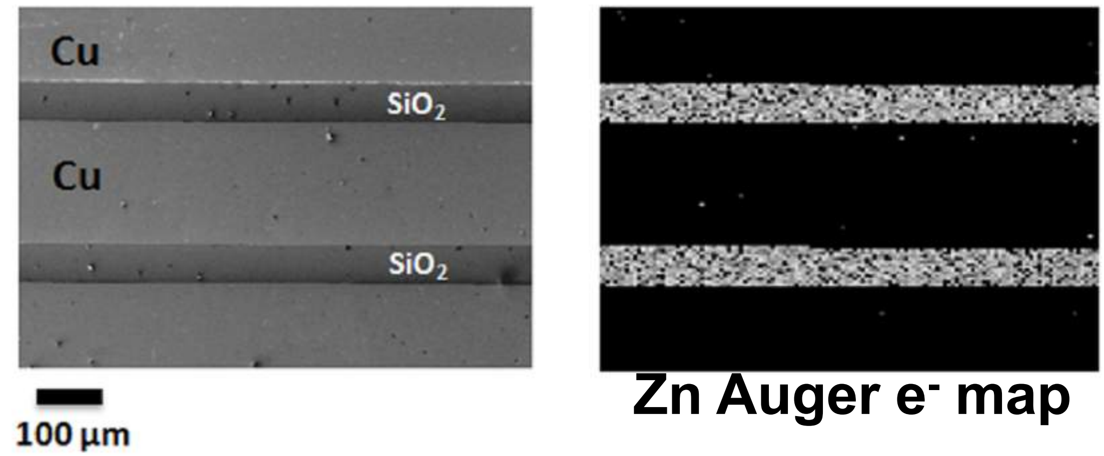


Comparison of ALD vs MLD

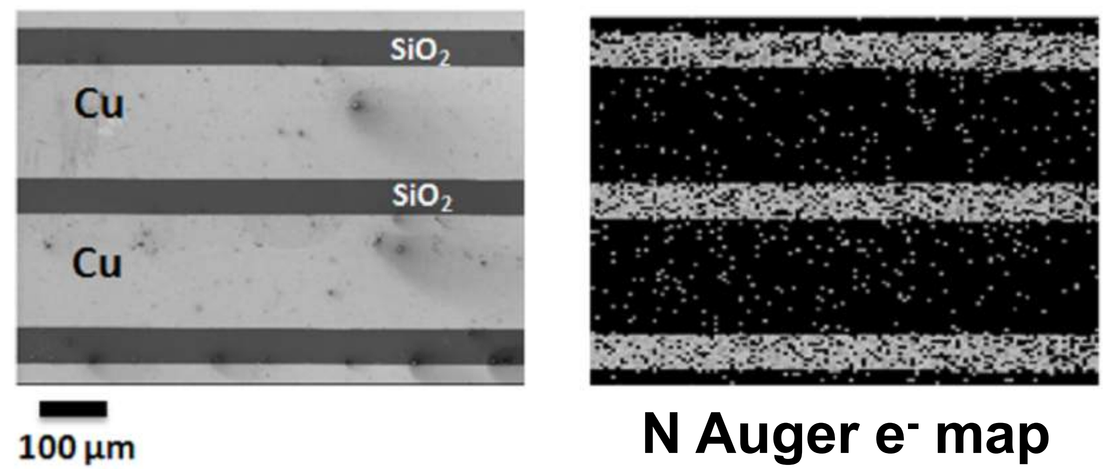


- ❑ Well-packed ODPA SAMs was used to test MLD selectivity

After 19 nm ZnO ALD



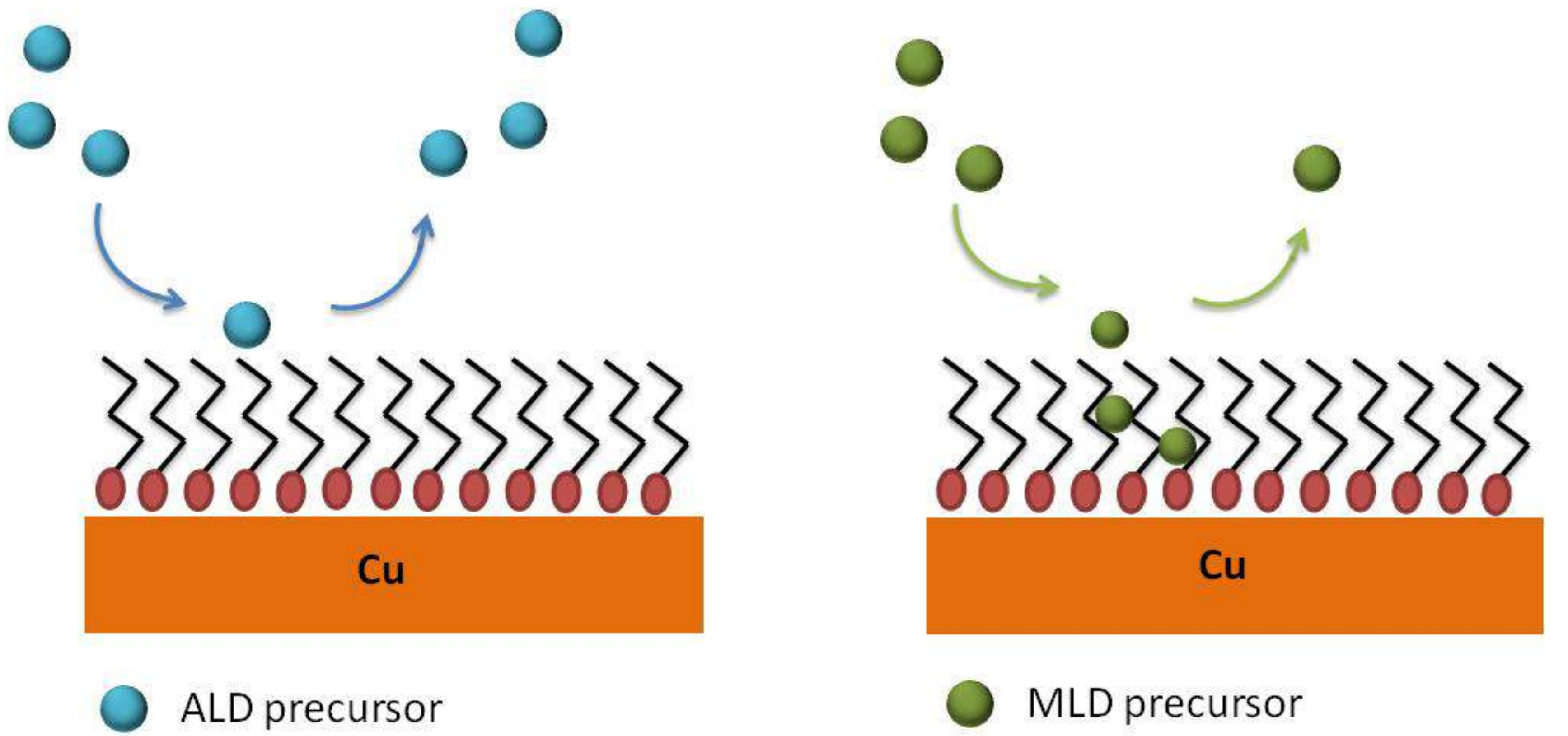
After 6 nm polyurea MLD



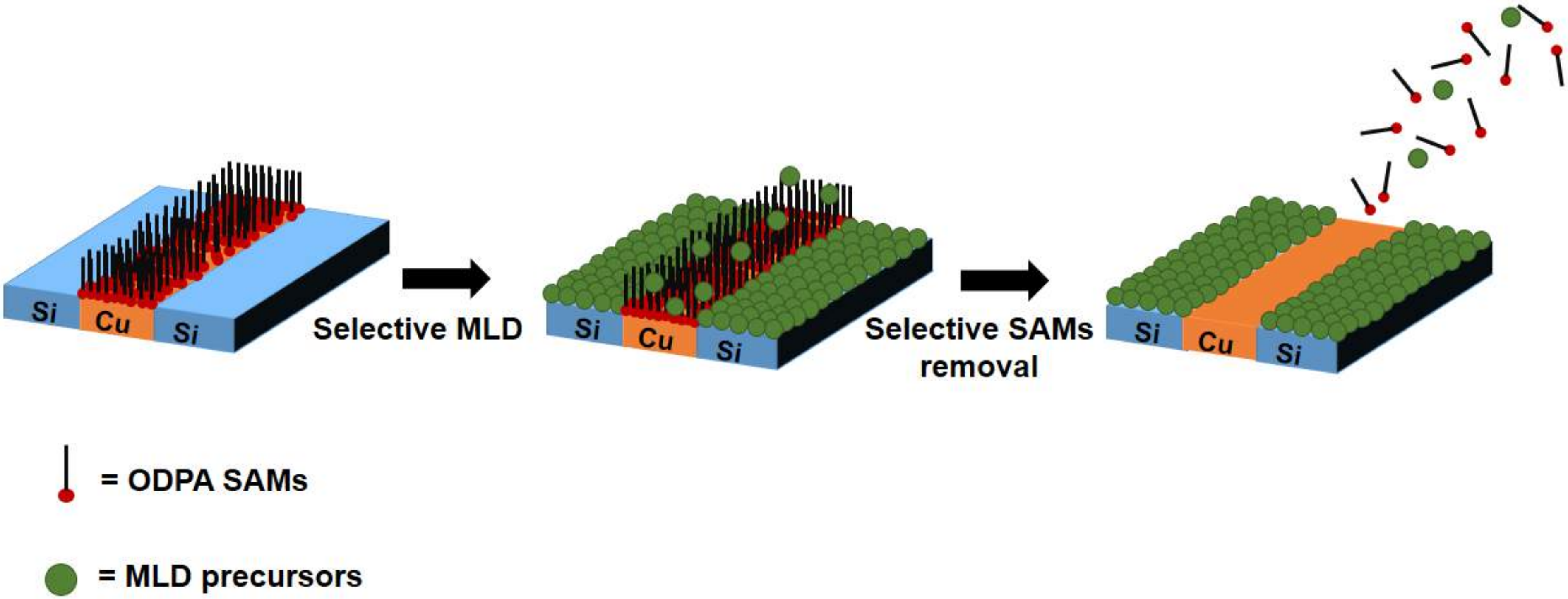
Hashemi, Prasittichai and Bent, *J. Phys. Chem. C* 118 (2014) 10957−10962

Comparison of ALD vs MLD

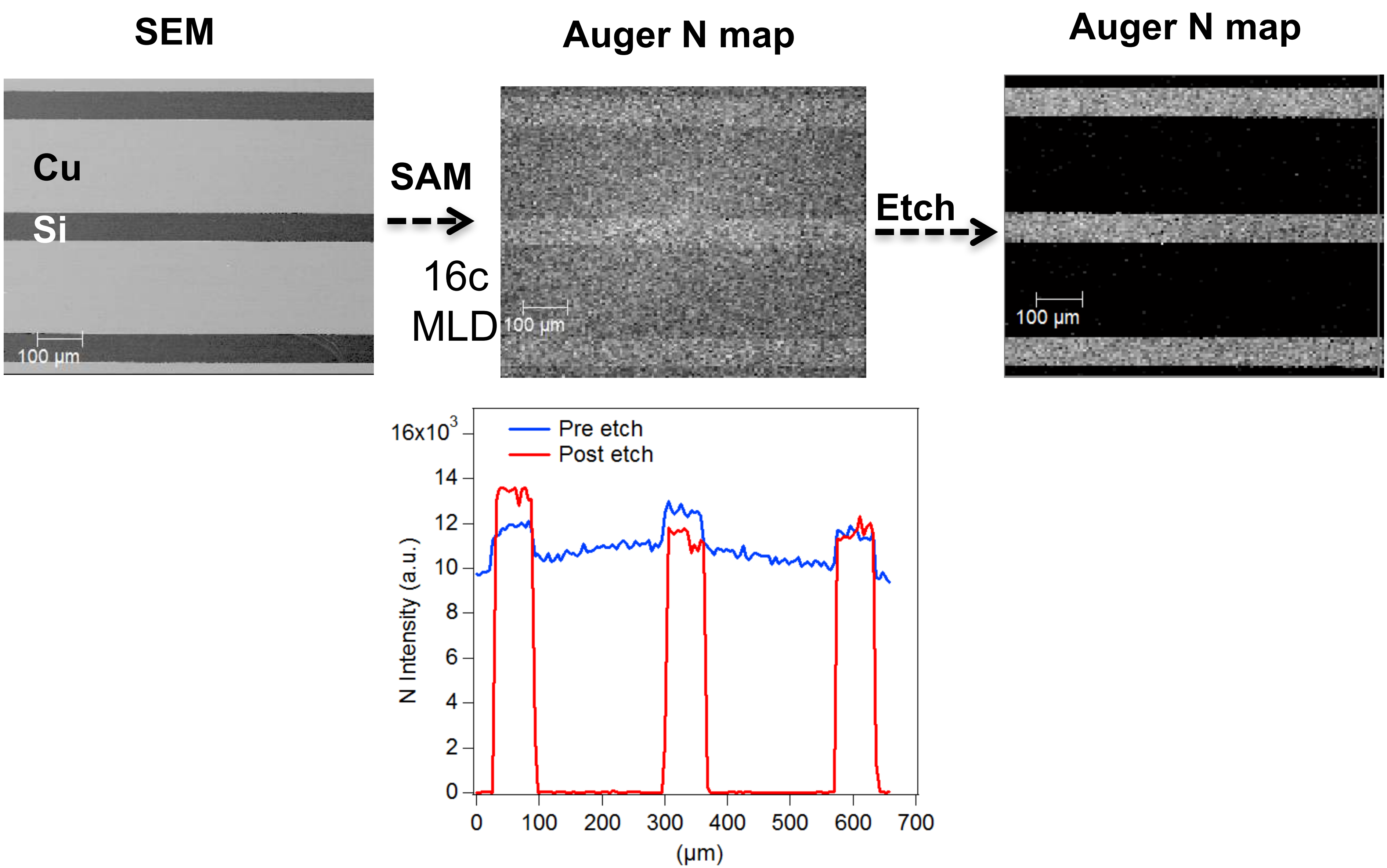
- Results suggests that MLD precursors can absorb in the SAM, leading to nucleation and eventual growth by MLD



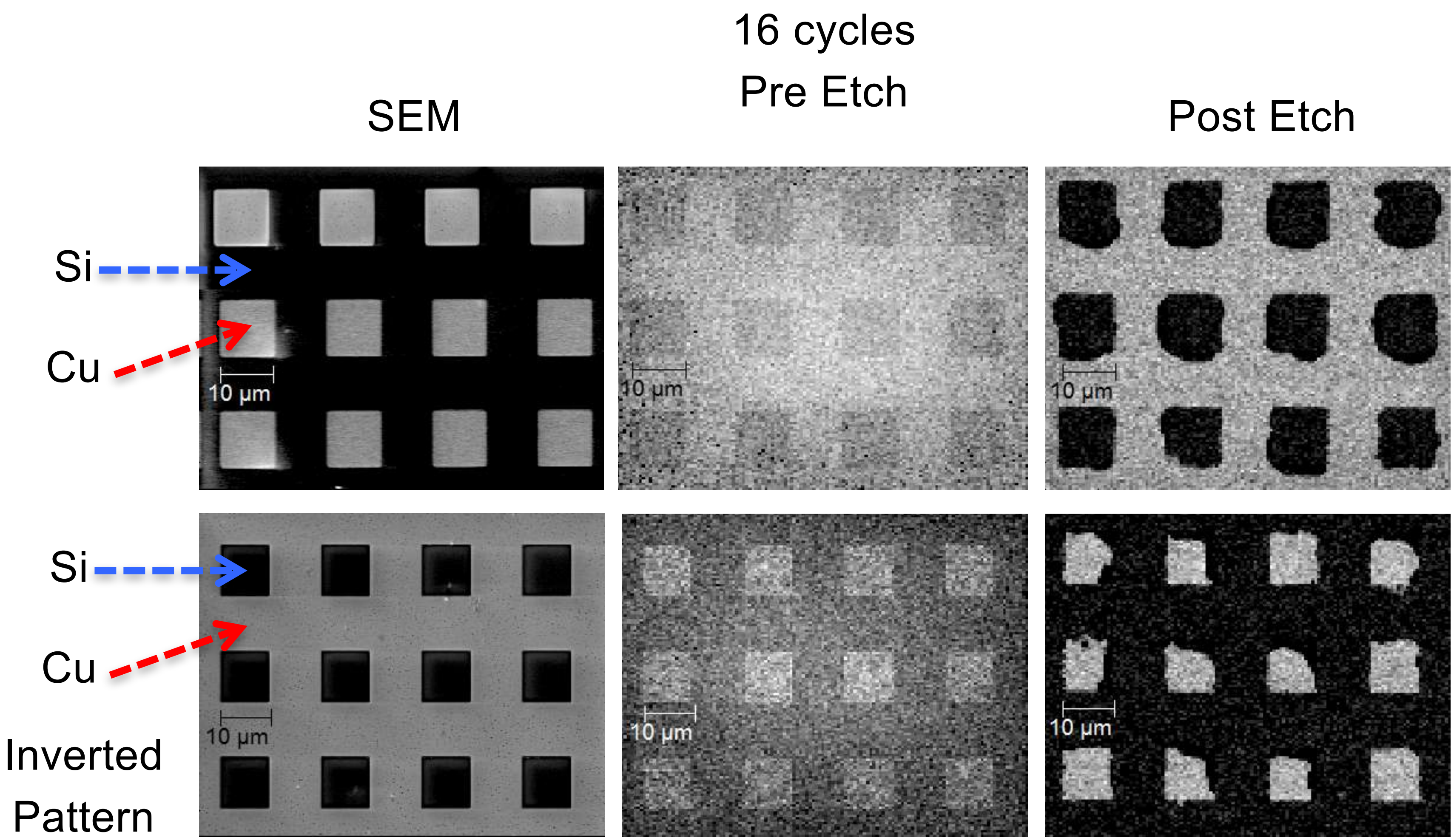
Combine AS-MLD with selective etch



Selective Deposition and Etch using Acetic Acid



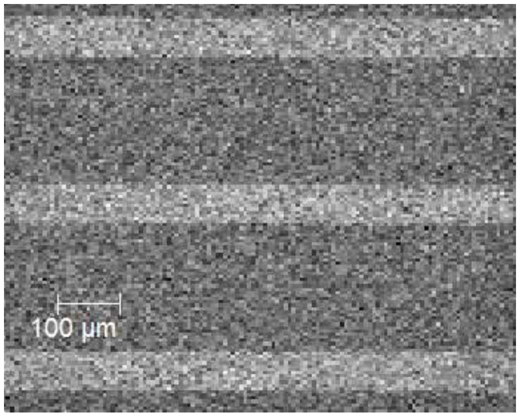
Scale Down Effects



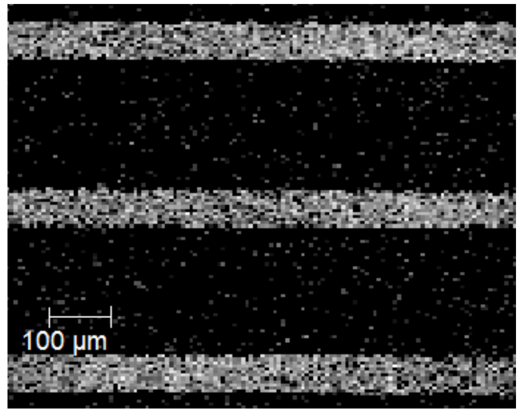
Closser, Bergsman, Ruelas, Minaye Hashemi, and Bent, *J. Vac. Sci. Technol.* A, 35 (2017) 031509

Metal/Dielectric Interface

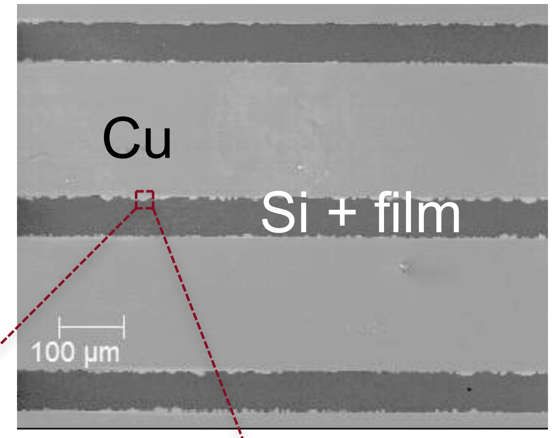
N Map



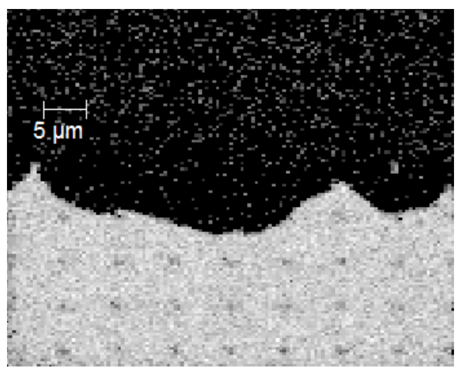
After Etch



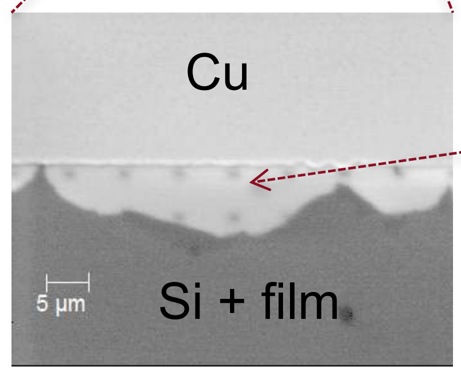
SEM



24 cycles ~ 12.5nm



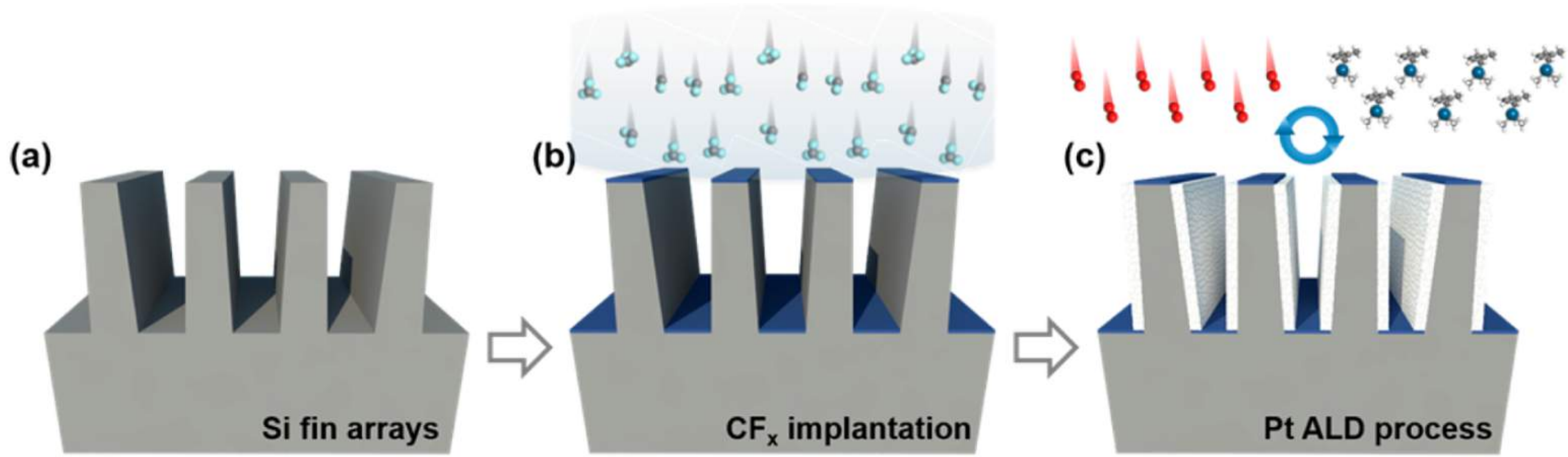
N map



MLD film removed

SEM

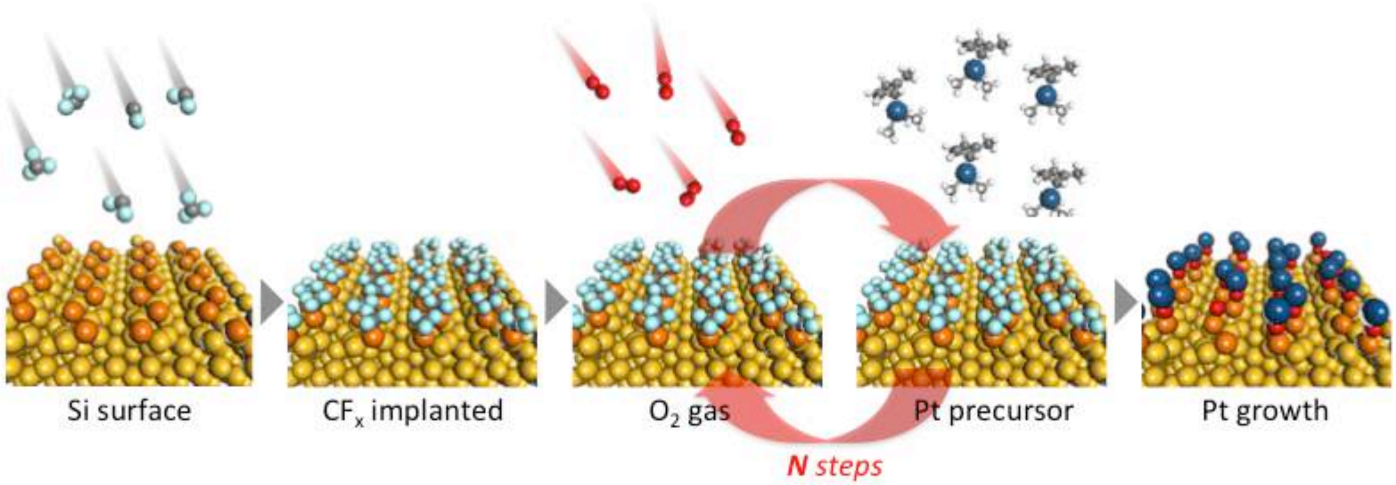
New Process for Topographically-Selective Deposition



Selective ALD by Ion Implantation

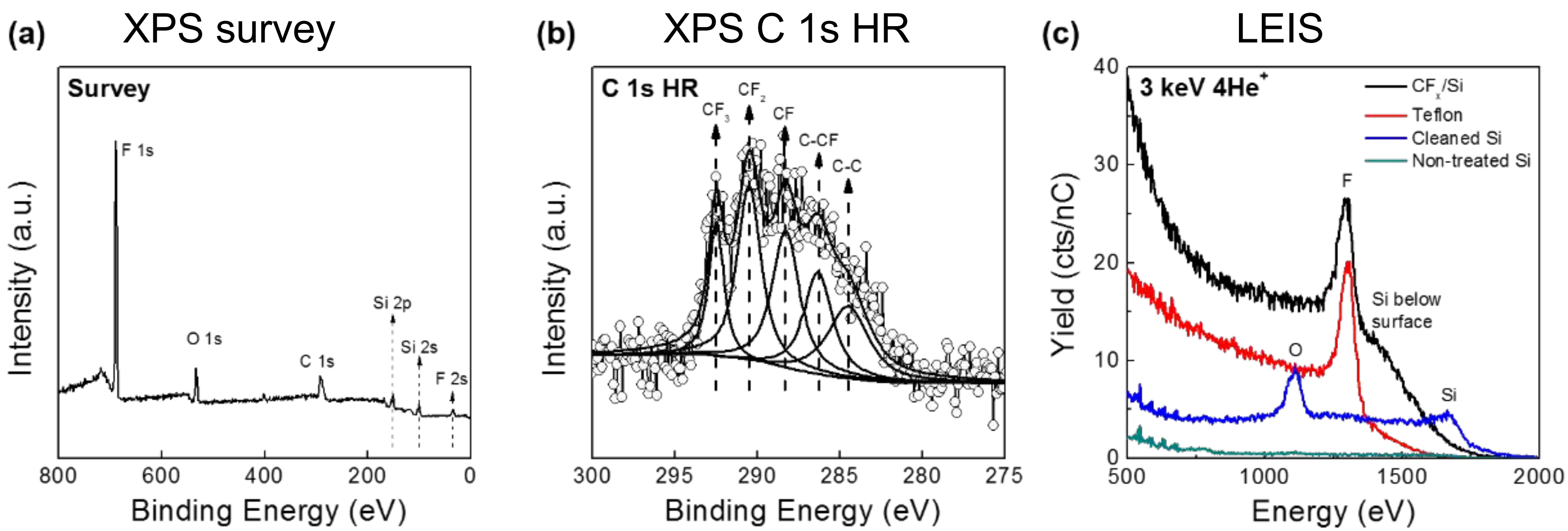
- Alternative to using SAMs:
  - CF_x ion implantation
  - Compatible with semiconductor fabrication

→ **New Methodology of AS-ALD using hydrophobic surface prepared by implantation**

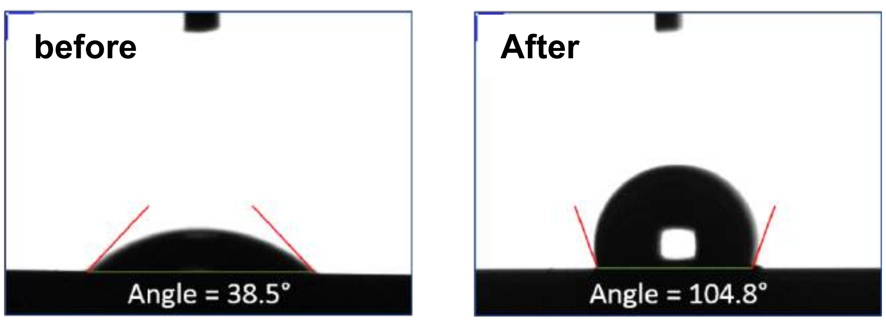


1) Seo et al., Chem. Mater. 16, 1878(2004), 2. Chen et al., Chem. Mater. 17, 536(2005), 3) Hong et al., Langmuir, 23, 1160(2007), 4) Park et al., Appl. Phys. Lett. 86, 051903(2005), 5) Farm et al., Chem. Vap. Depos. 12, 415(2005) 6) Lee et al., J. Electrochem. Soc. 157, D10 (2010) , 7) Kim et al., J. Electrochem. Soc. 158, D1 (2011)

Surface analyses of as-implanted CF_x layer on Si substrate



Water contact angle change

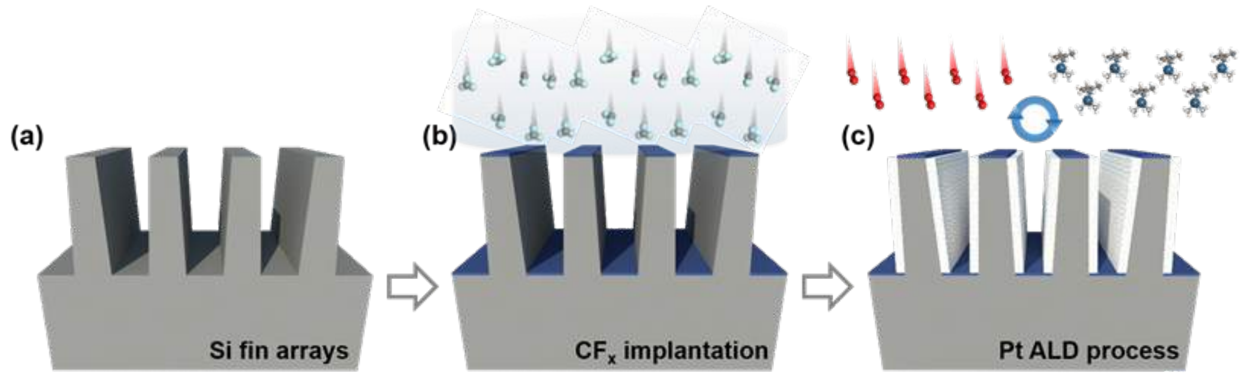


- The surface mainly consists of F and C with F/C ratio = 2.2
- The outermost layer contains a 92% Teflon-like layer (1.5 ± 0.2 nm) and possibly 8% hydrocarbon contamination

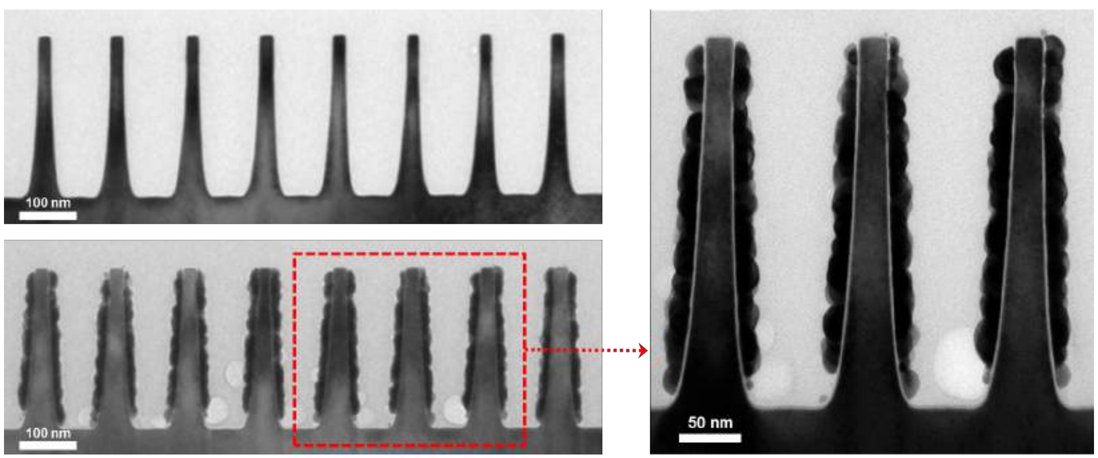
1 KV ion implant energy, $1x10^{16}$ ions/cm^2, CF_x^+ implant

3D AS-ALD of Pt Thin Films on Selectively CF_x-Implanted Si 3D Fins

Schematic illustration of 3D AS-ALD of Pt thin Films on Si Fin Arrays



Cross-sectional TEM images of Si fin arrays with deactivated horizontal surfaces



Successful demonstration of topographically selective growth of Pt thin films along vertical sidewall !!

Woo-Hee Kim et al., *ACS Nano*, 10 (2016) 4451–4458

Summary

- Area selective ALD is a powerful method for fabrication of nanostructures
- Pushing the thickness limits of area selective ALD
  - Self-correcting process
    - *Combine SAM blocking layer and selective etching of SAM and dielectric*
      - *Results in 10x higher selective deposition of Al_2O_3*
      - *SAM deposition time can be decreased from 48 hours to 1 hour*
  - Regeneration of the blocking layer
    - *Improves the selective deposition limit up to nearly 100 nm of ZnO growth*
- Application to area selective MLD
- Demonstration of topographically selective deposition of 3D structures

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- Tzu-Ling Liu
- **Adriaan Mackus**
- Joseph Singh
- **Richard Closser**
- David Bergsman

AMAT Collaborators

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- Dr. Tobin Kaufman-Osborn
- Dr. Ludovic Godet

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- Lam
- Applied Materials