# Area-Selective ALD of $HfO_2$

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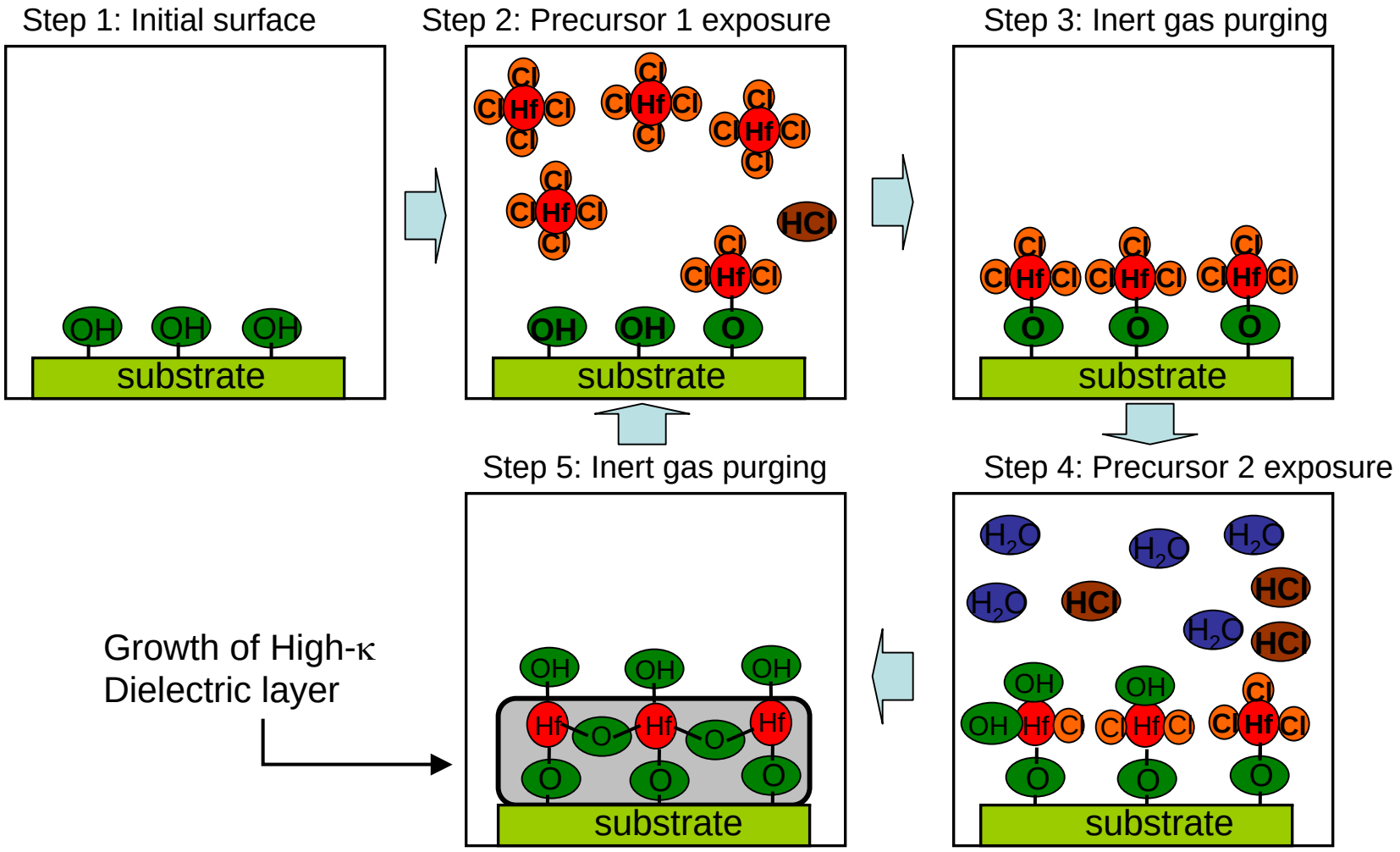
ERC Teleseminar, July 29, 2004

# Outline

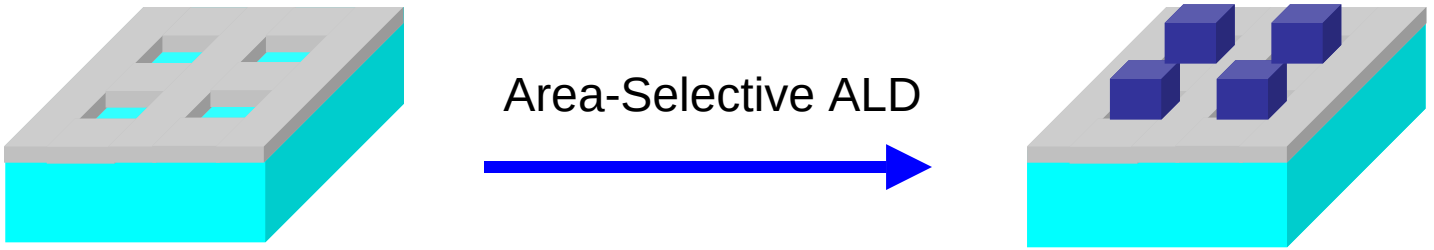
- Introduction to Area Selective ALD
- Development of Monolayer Resists for ALD
- Patterning and Area Selectivity


# The ALD Process

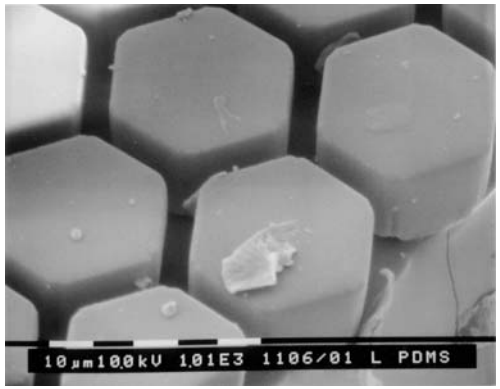



- Self-saturating surface reaction cycles: thickness control

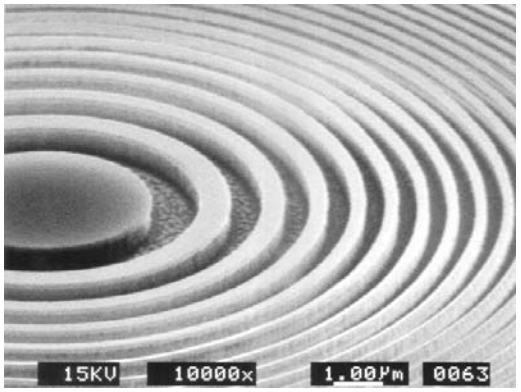
# Generate 3-D Pattern from 2-D Template




Microcontact printing

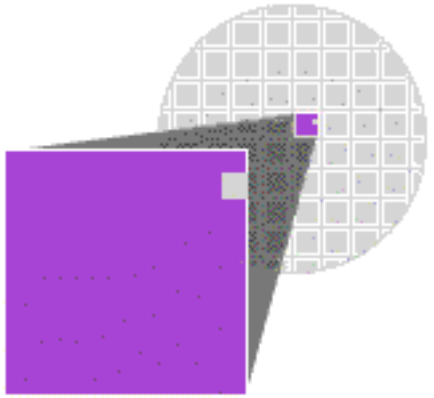



E-beam lithography (direct writing)




Source: Paul Scherrer Institut

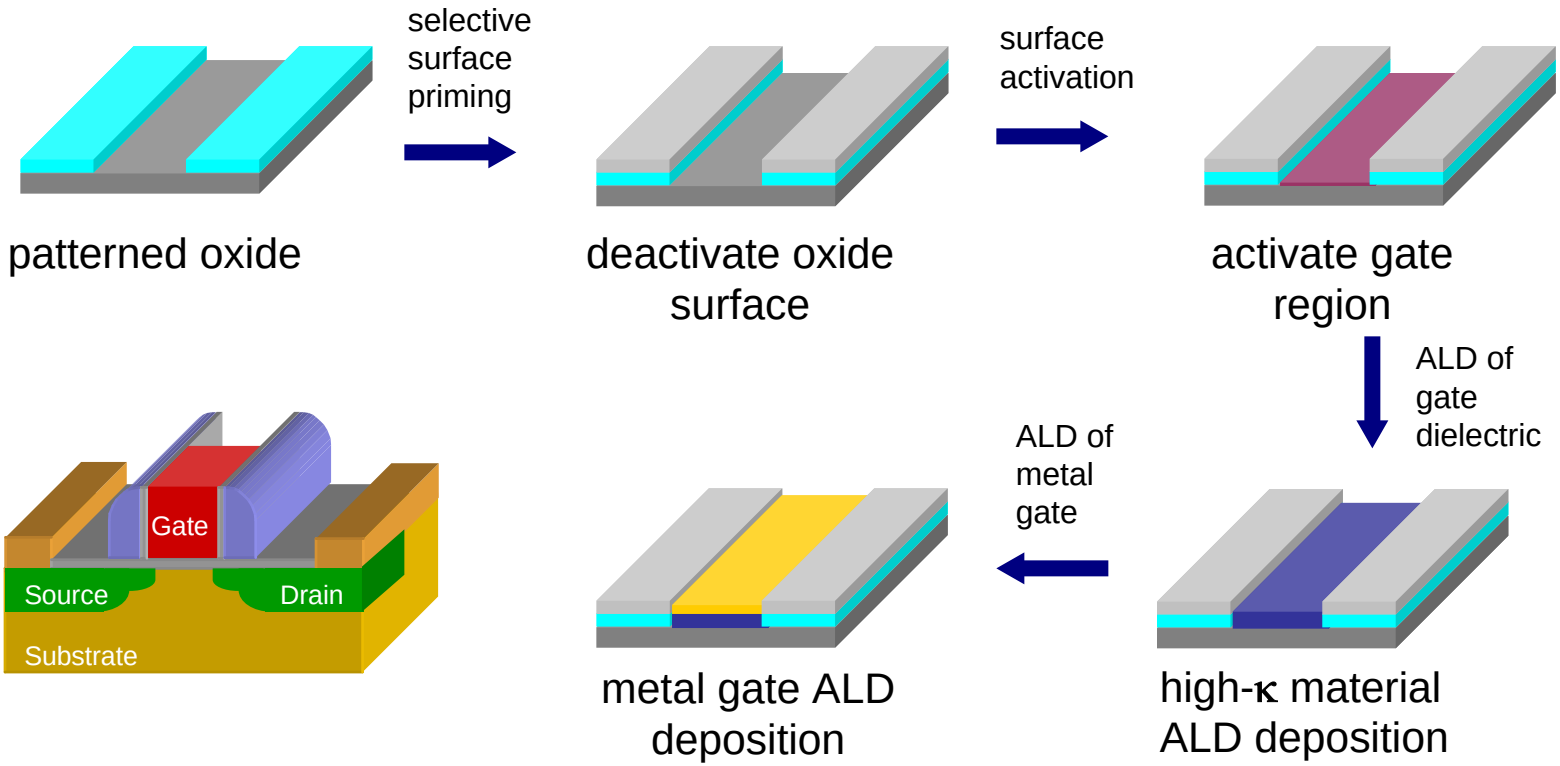
Photolithography patterned $SiO_2$/Si



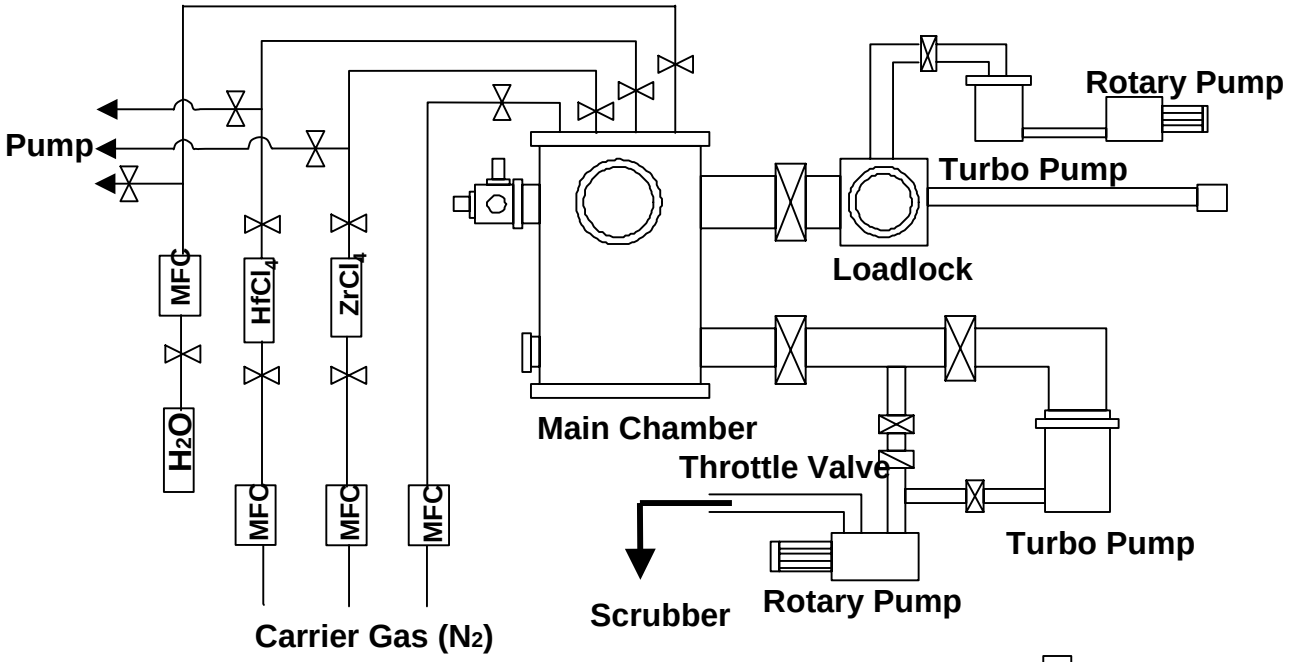
Source: Intel

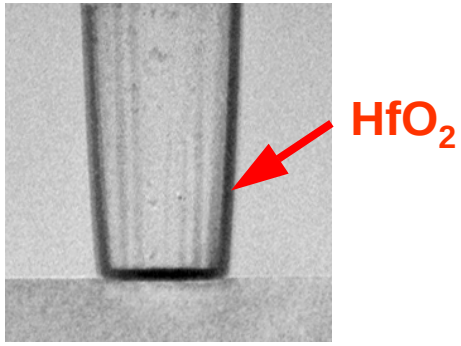
# Process Flow for Area-Selective ALD for Gate Stack

- Goal: Self-aligned deposition process for gate dielectrics and gate metal

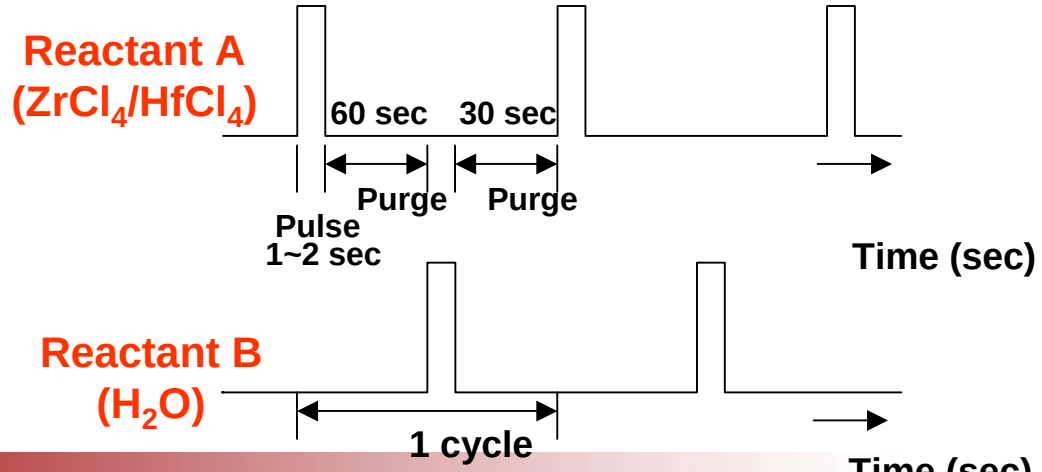


# Schematic Diagram of McIntyre ALD System

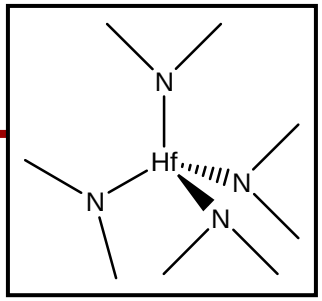



- Base pressure = $5*10^{-8}$ Torr
- Process temperature : 300°C
- Process pressure : 0.5 Torr
- Source temperature :
  - $H_2O$ (liquid) = 20°C
  - $HfCl_4$ /$ZrCl_4$(solid) = 150°C



# Bent Group ALD Reactor

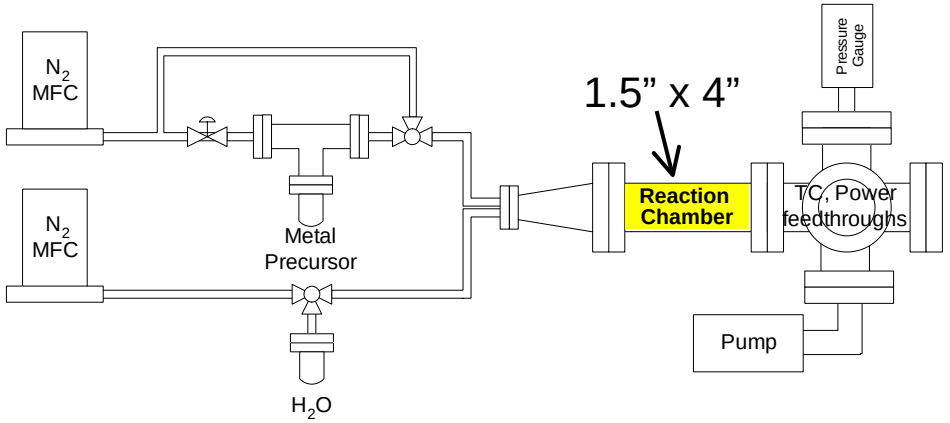


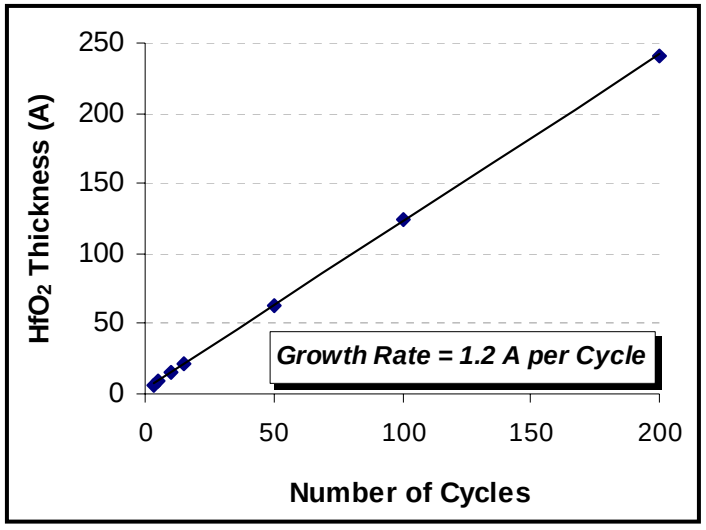

Hf precursor: tetrakis(dimethylamido)hafnium

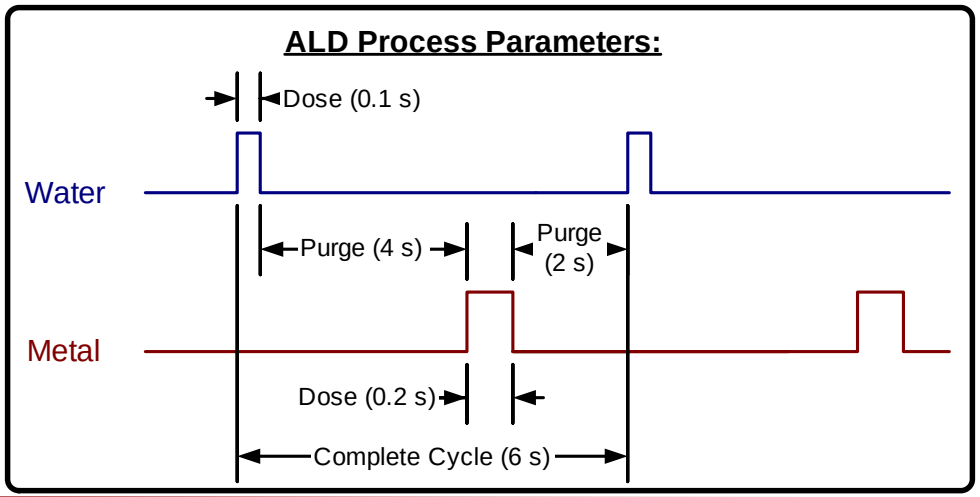
- No HCl; no Cl incorporation
- More uniform growth
- Low deposition temp (250 C)

0.9 -1.2 A/cycle

No impurity incorporation

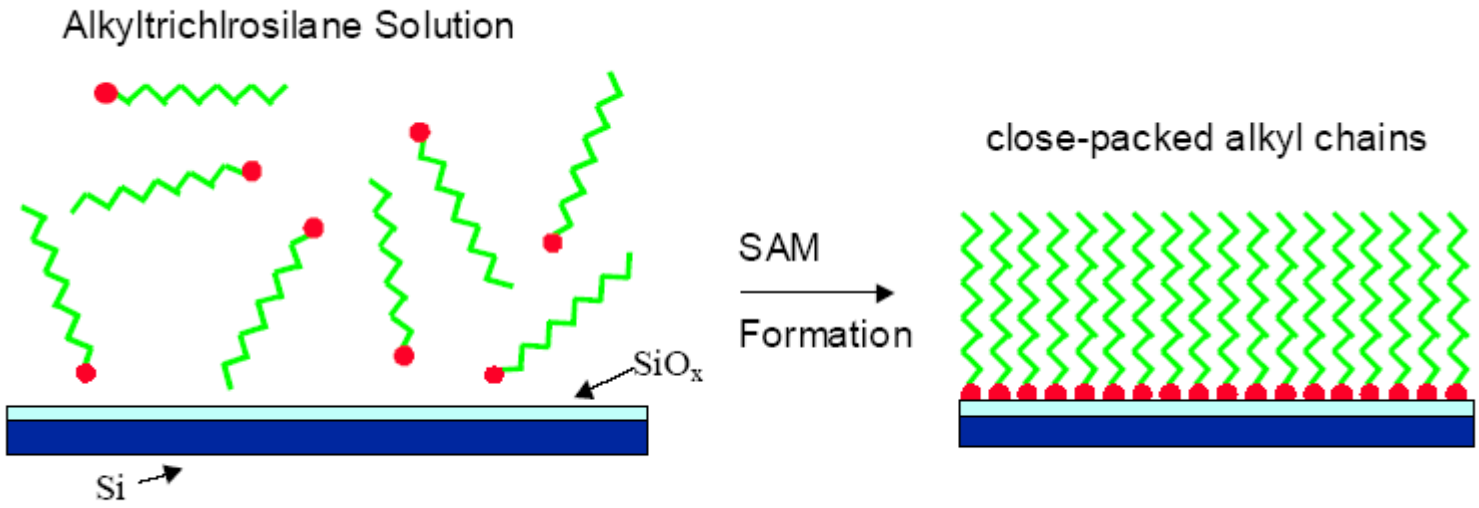


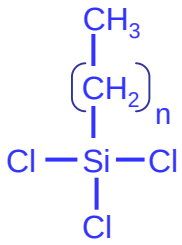
# Self-assembled Monolayers as ALD Resists

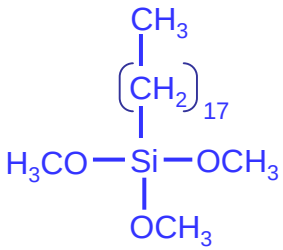
- Self-assembled monolayers (SAMs) are ordered assemblies formed by the adsorption of an active surfactant on a solid face and are well known to modify surface characteristics

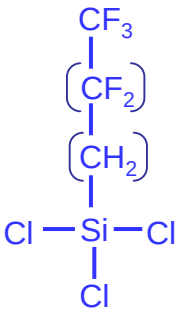


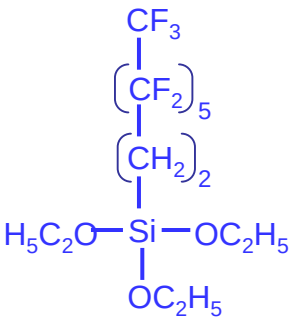
# Deactivating Agents Studied

1. Chain lengths, reactive head groups, and chain monomers



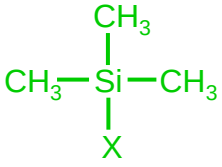




**Alkyltrichlorosilane**
n=0,1,3,5,7,9,11,17

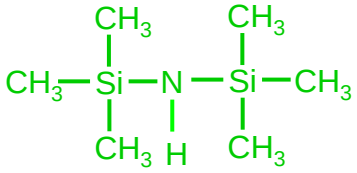
2. Number of halide substituents

$Si(CH_3)_nCl_{4-n}$ n=1,2,3

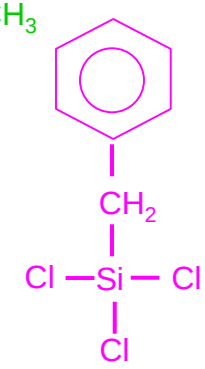
3. Reactive head groups

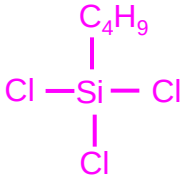


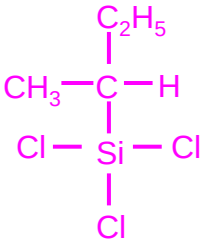

X=Cl, Br, I
**Trimethylhalosilane**

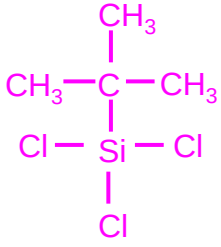



**HMDS**



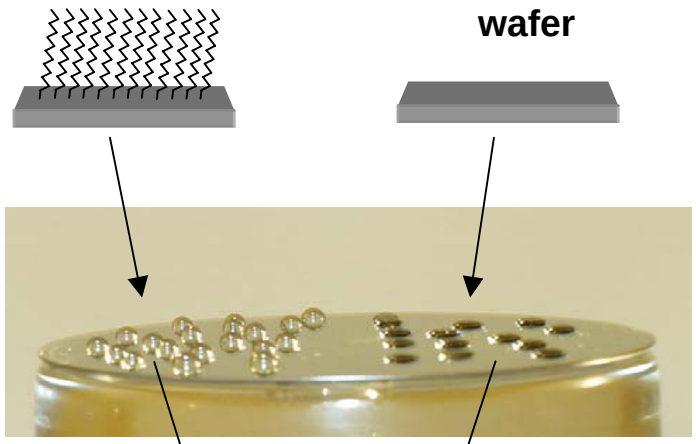




4. Carbon tail structure

# Methodology for Study of Deactivating Agents

A

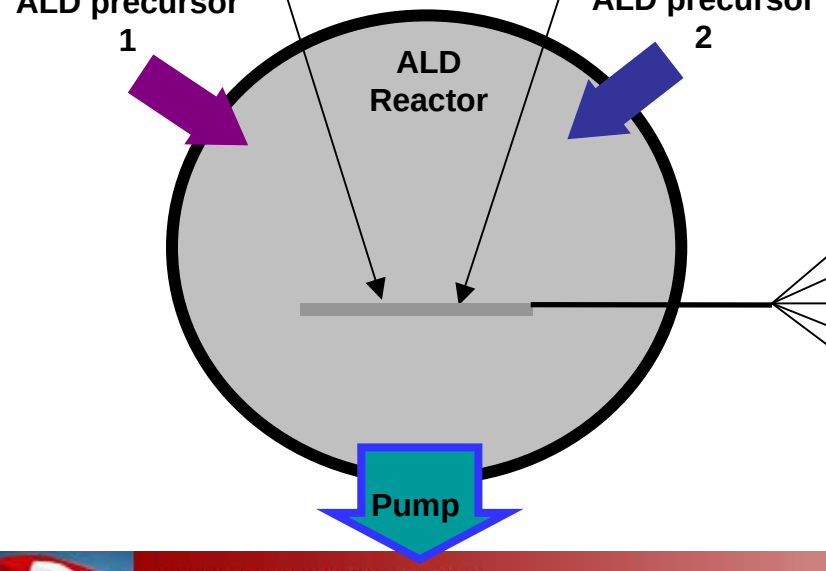



A. Preparation and analysis of deactivating agents

B. ALD growth of $ZrO_2$ & $HfO_2$

C. Sample characterization after deposition

B




C

**XPS:** Film composition

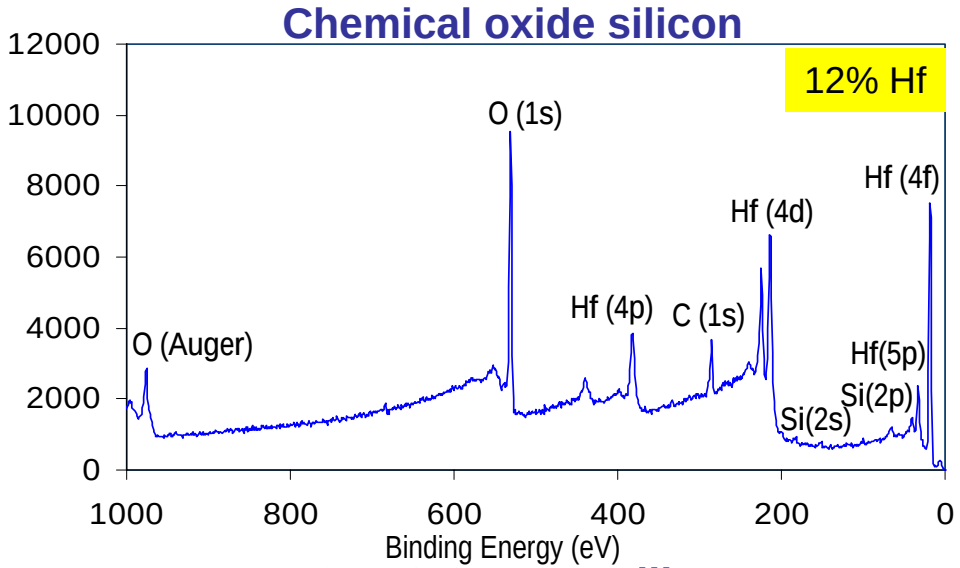
**Ellipsometry:** film thickness

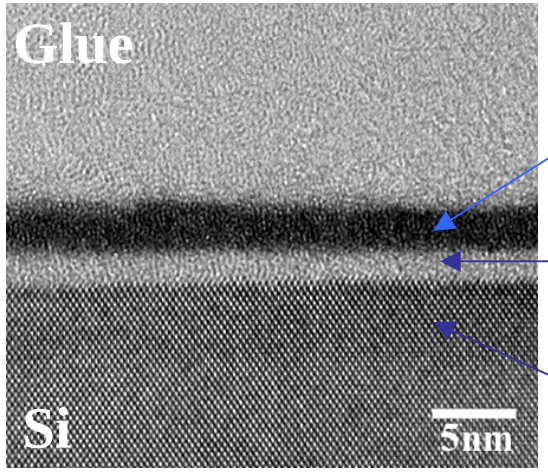
**Contact Angle:** Hydrophobicity

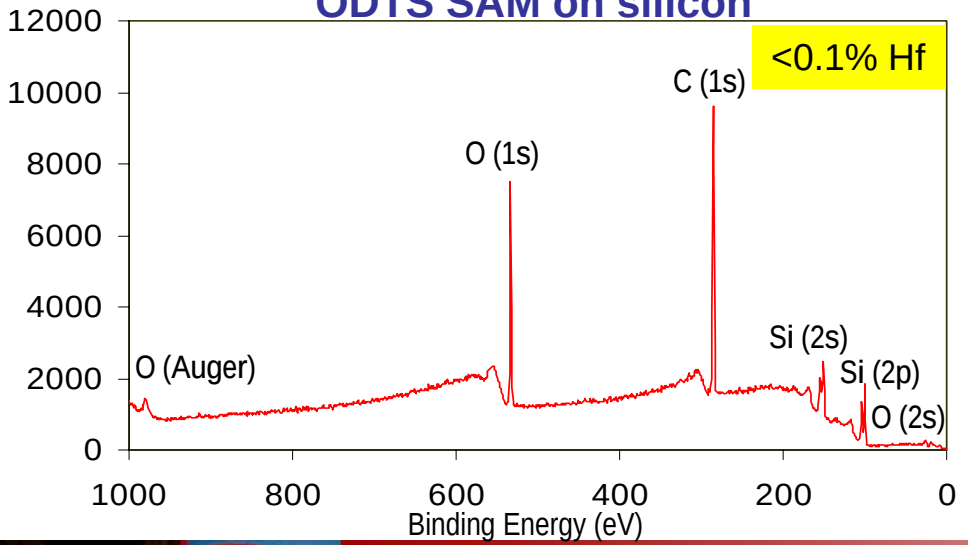
**AFM:** Film morphology

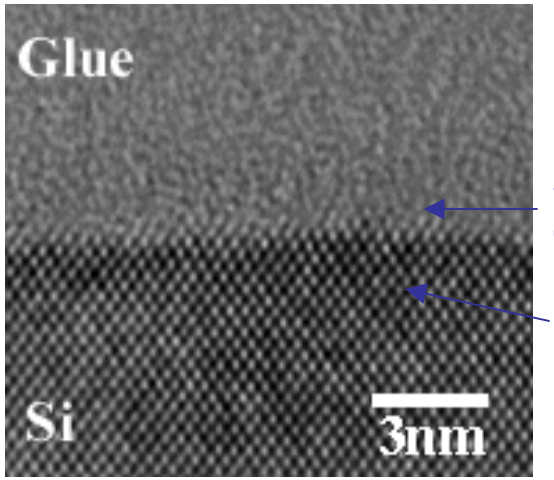
**TEM:** Interfacial properties

# ALD Inhibition by Octadecyltrichlorosilane (ODTS) SAM

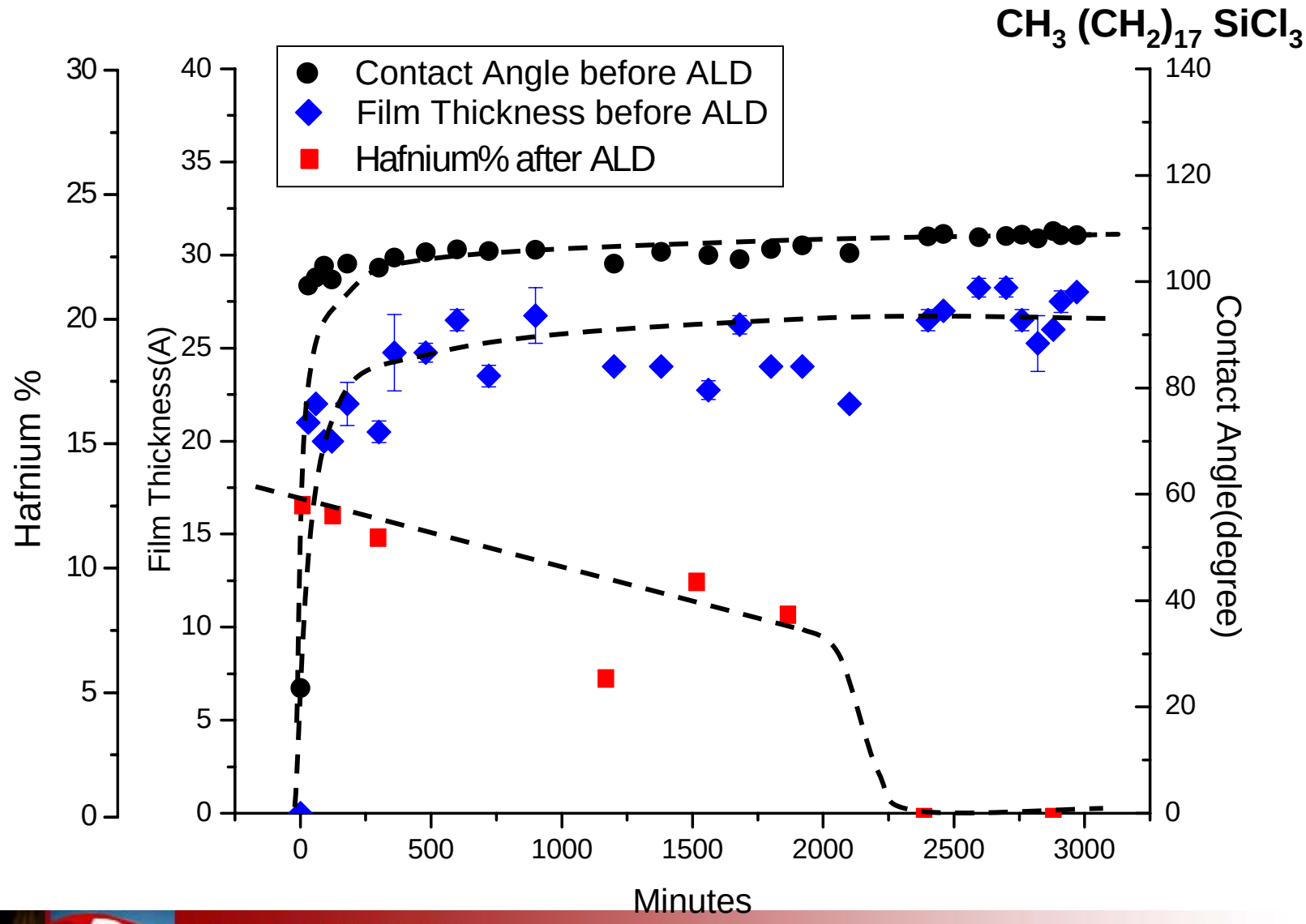


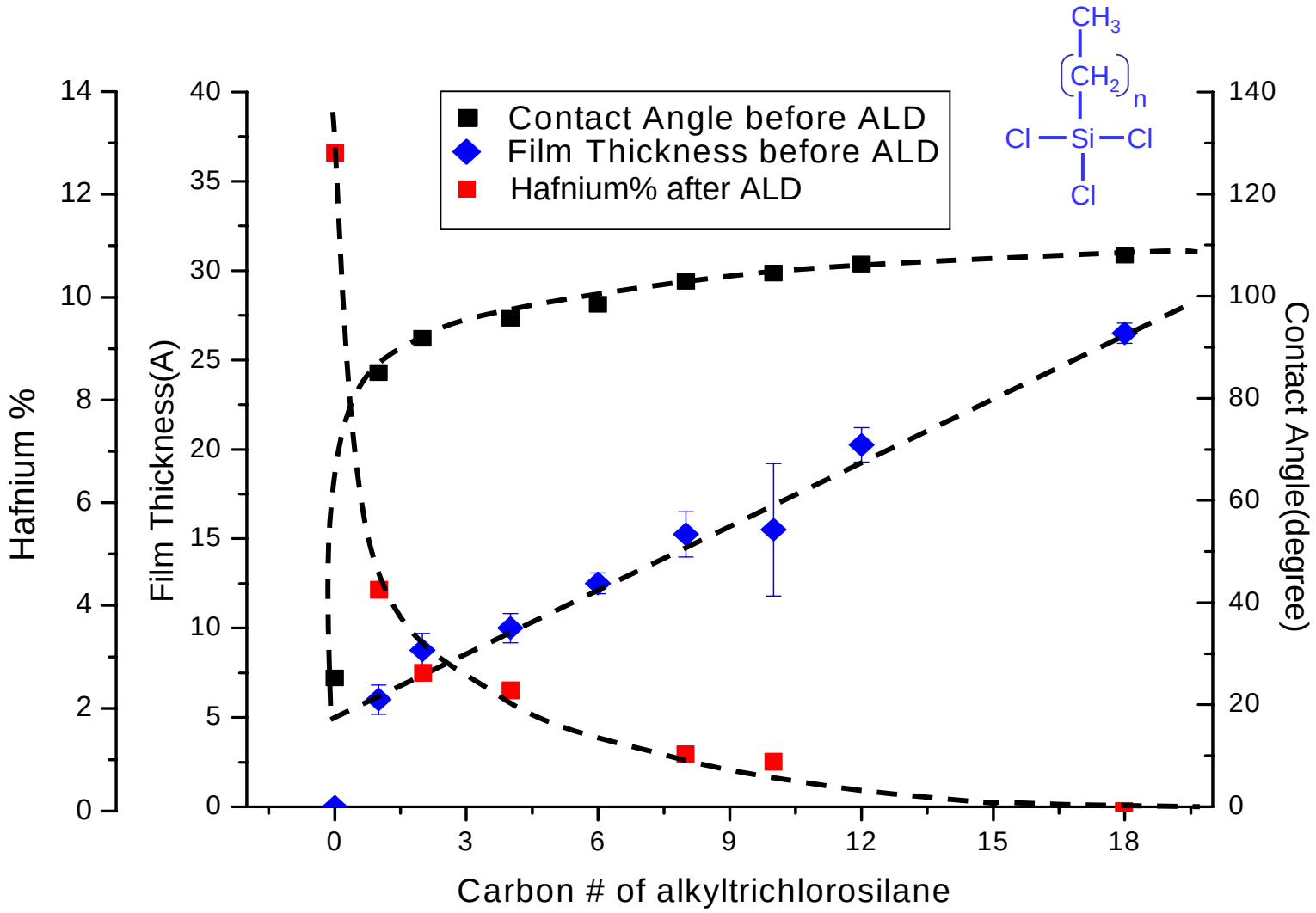



# Silylation Time Dependence for ODTS

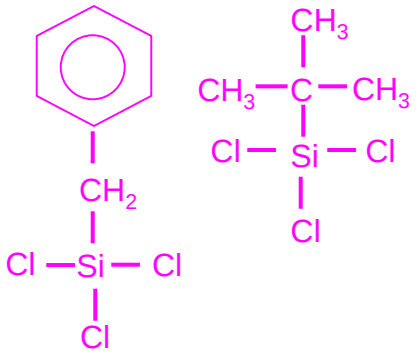


# Alkyltrichlorosilane Chain Length Dependence

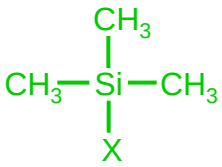


# Other SAMs are less effective than alkyltrichlorosilanes

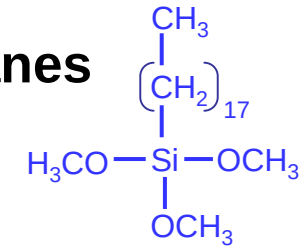
**Less effective SAMs for deactivation include:**



- **Bulky tail groups (including phenyl, t-butyl…)**
- **Monohalosilanes**

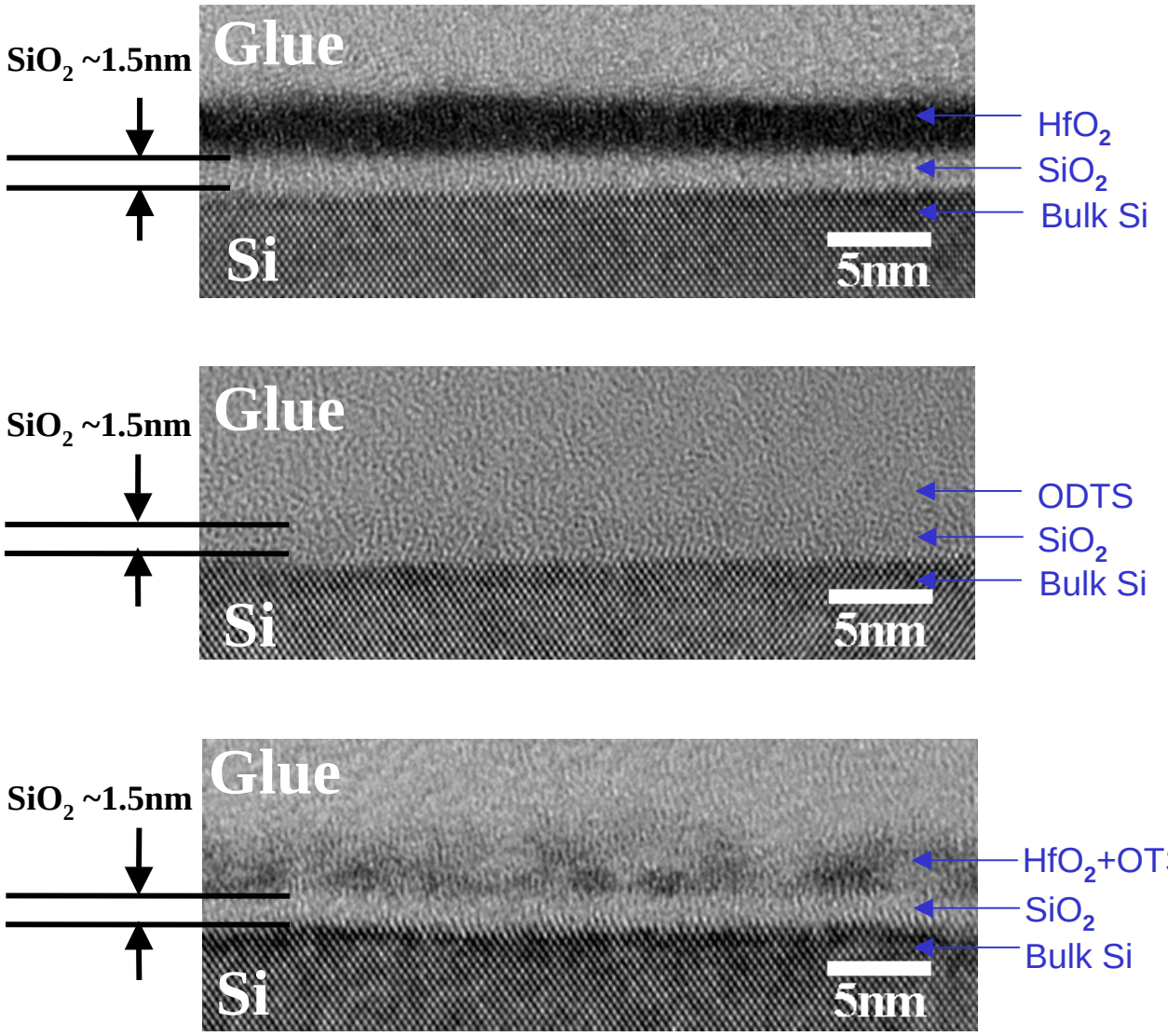


- **n-alkyltrialkoxysilanes**



**Fluorinated alkyltrichlorosilanes do exhibit good blocking**

# Cross-sectional TEM

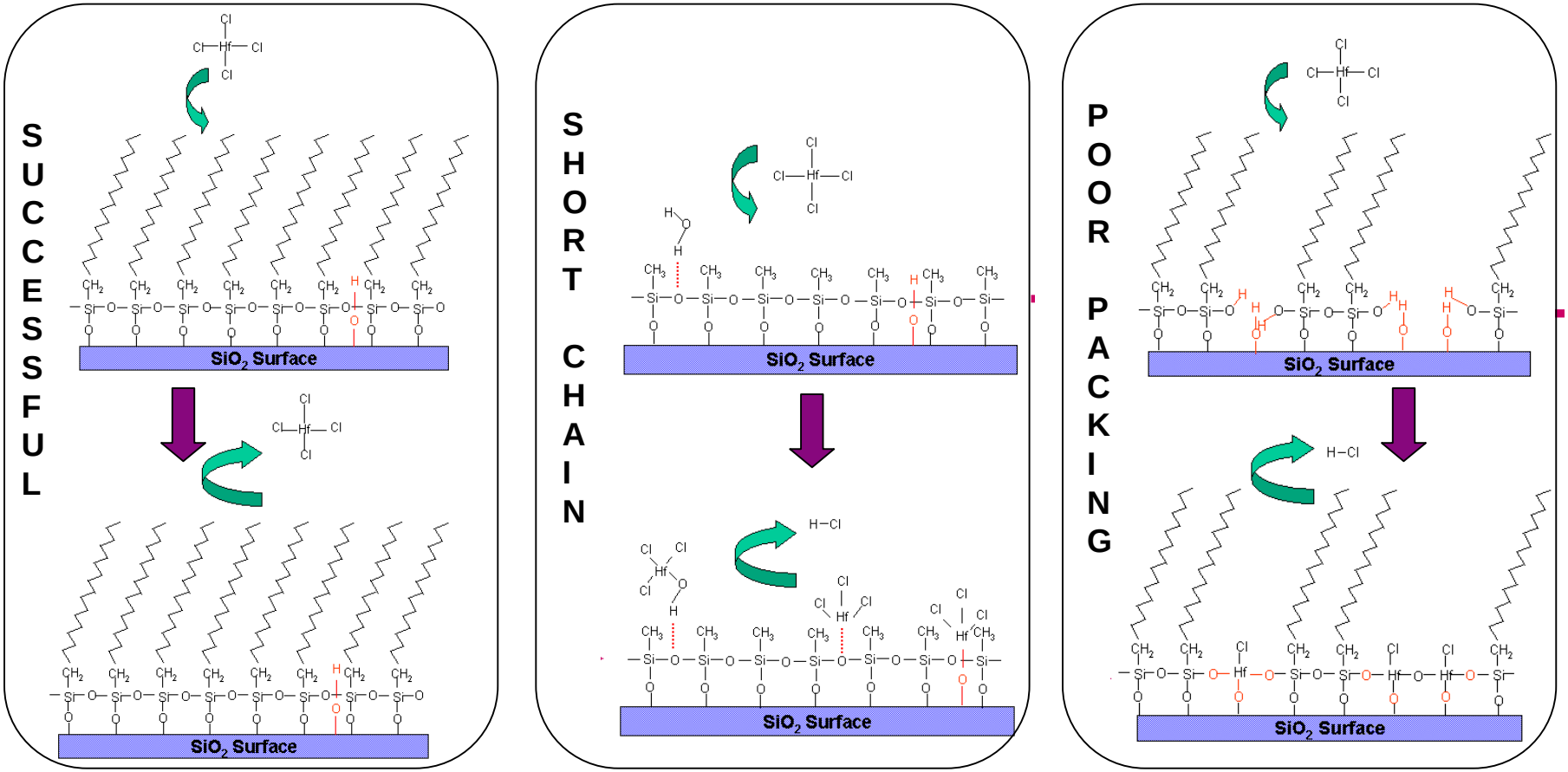


# Proposed Mechanism

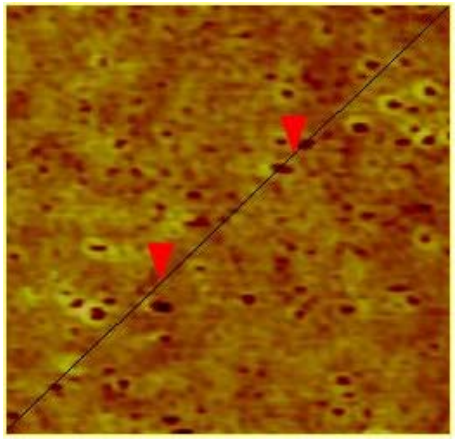
The role of the SAM appears to be twofold:

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

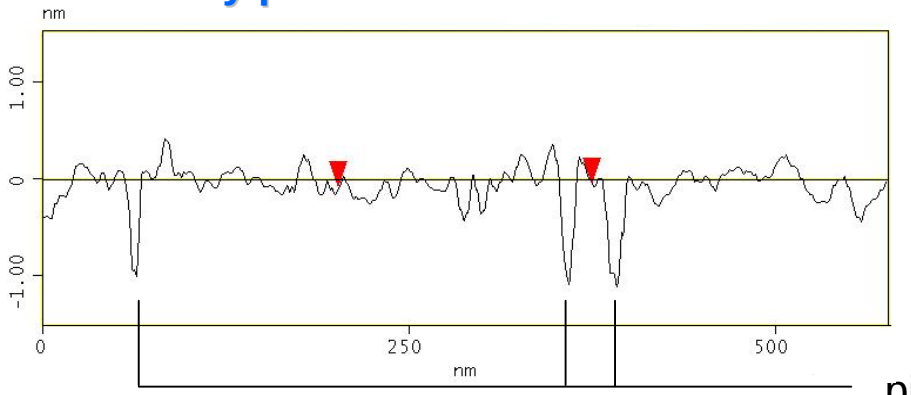
(2) to prevent precursors from reaching the $SiO_2$ surface where they may otherwise react with remaining Si-OH defects and Si-O-Si type bonds.



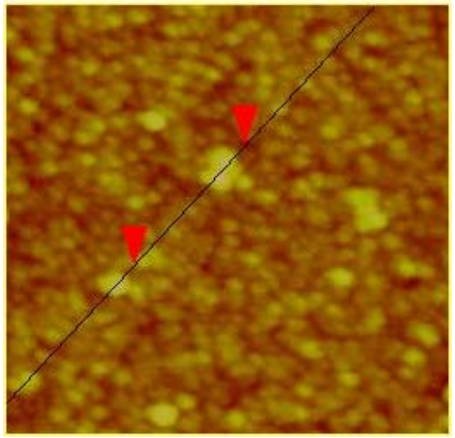
# AFM Analysis of ODTS before & after ALD



**Loosely packed ODTS film before ALD**

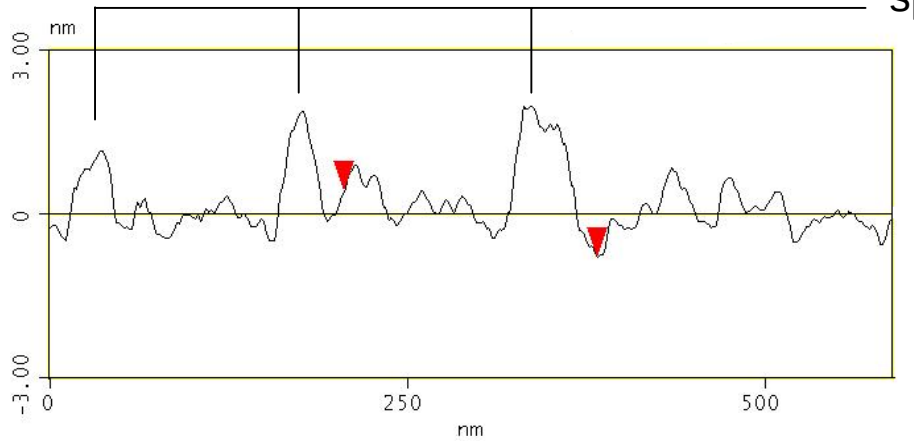



pinholes



**Loosely packed ODTS film after ALD**

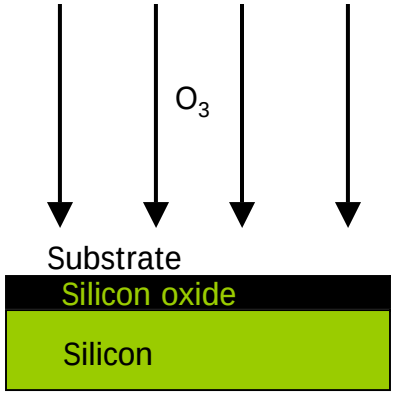
spikes

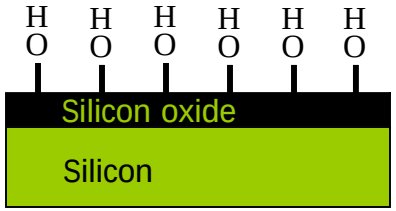



- **AFM and TEM data support the mechanistic model**

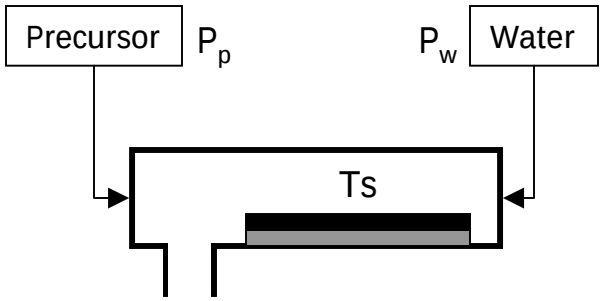
# Experimental Procedure for Vapor Phase Deactivation

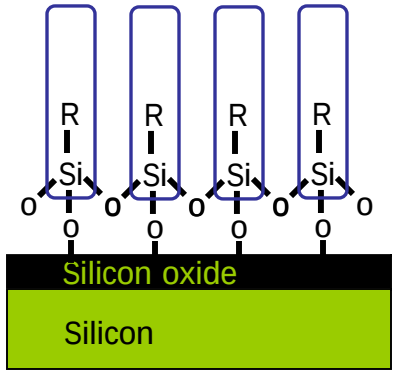
## Pretreatment by ozone cleaner



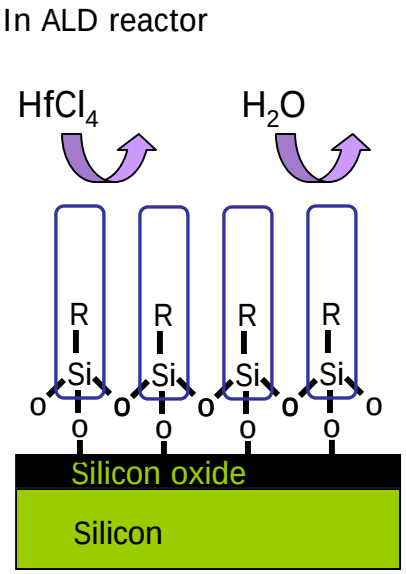




## Preparation of a SAMs by CVD




## Hafnium oxide deposition by ALD

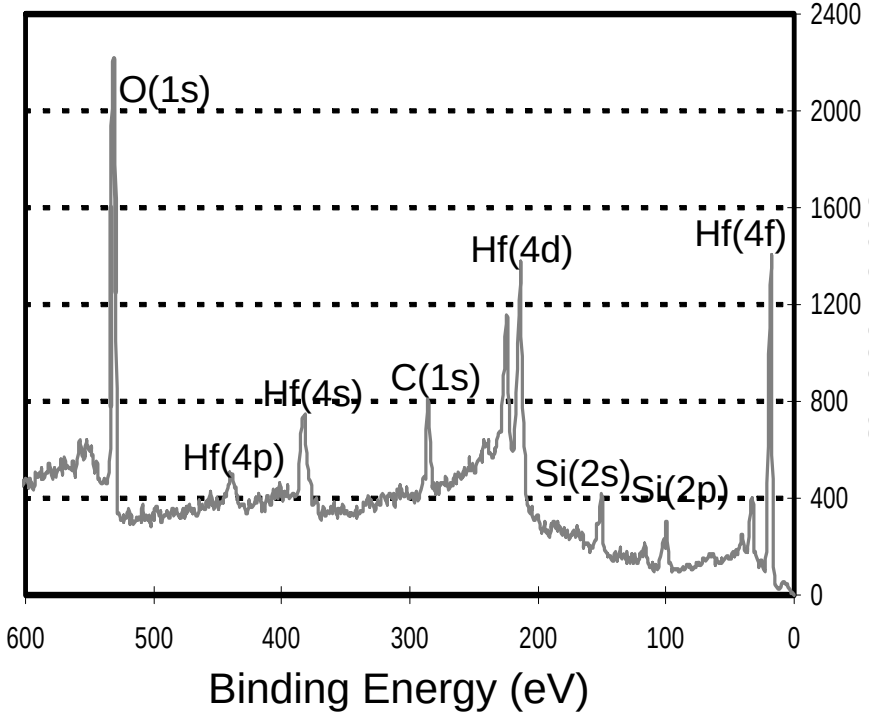



Measure film characteristics by ellipsometer, contact angle measurement

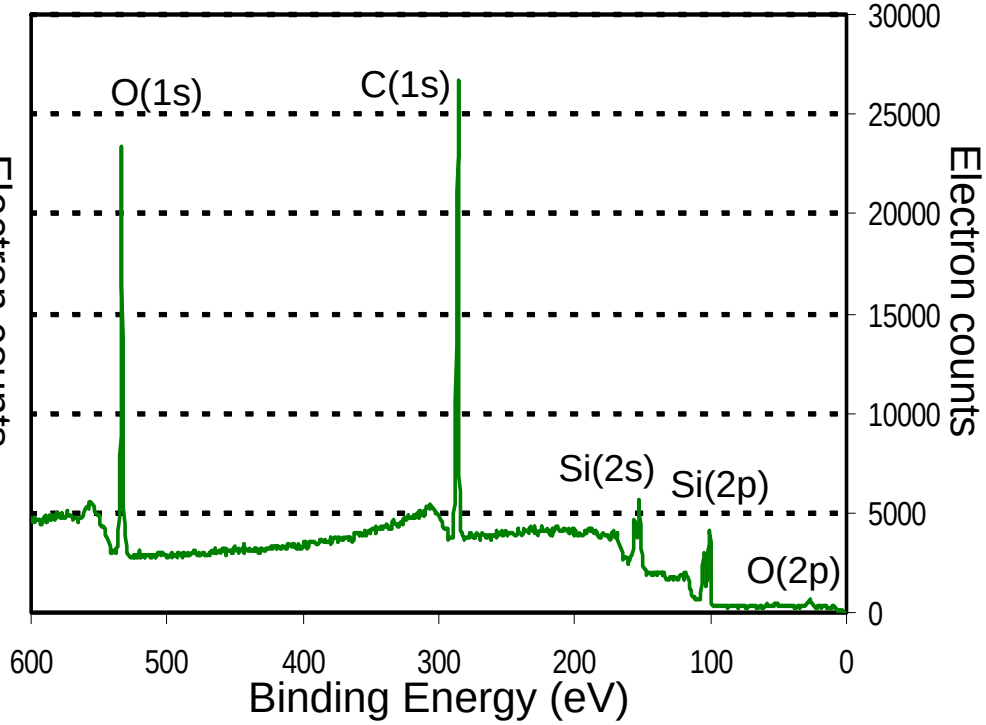
# XPS after Hafnium Oxide Deposition by ALD

- Excellent deactivation also achieved with vapor delivery

Bare Si(100) surface

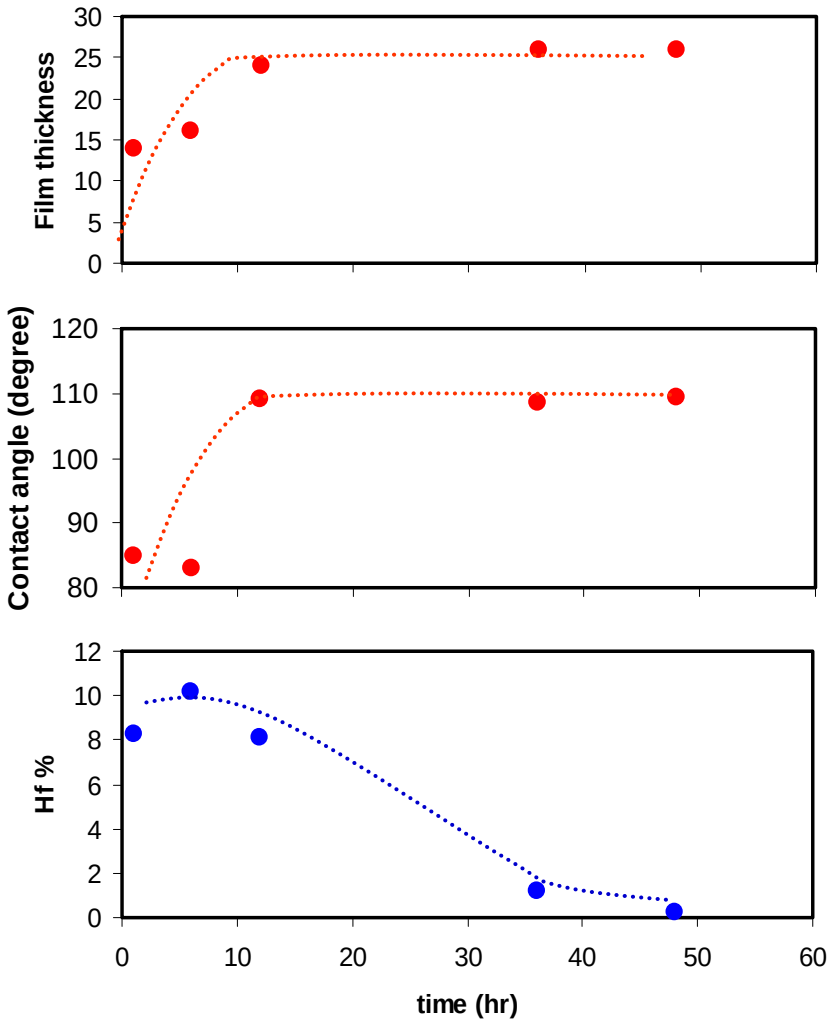



SAMs on Si(100) surface




- Experimental Condition: Precursors (ODTS and water), Ts=170°C, t=2 days

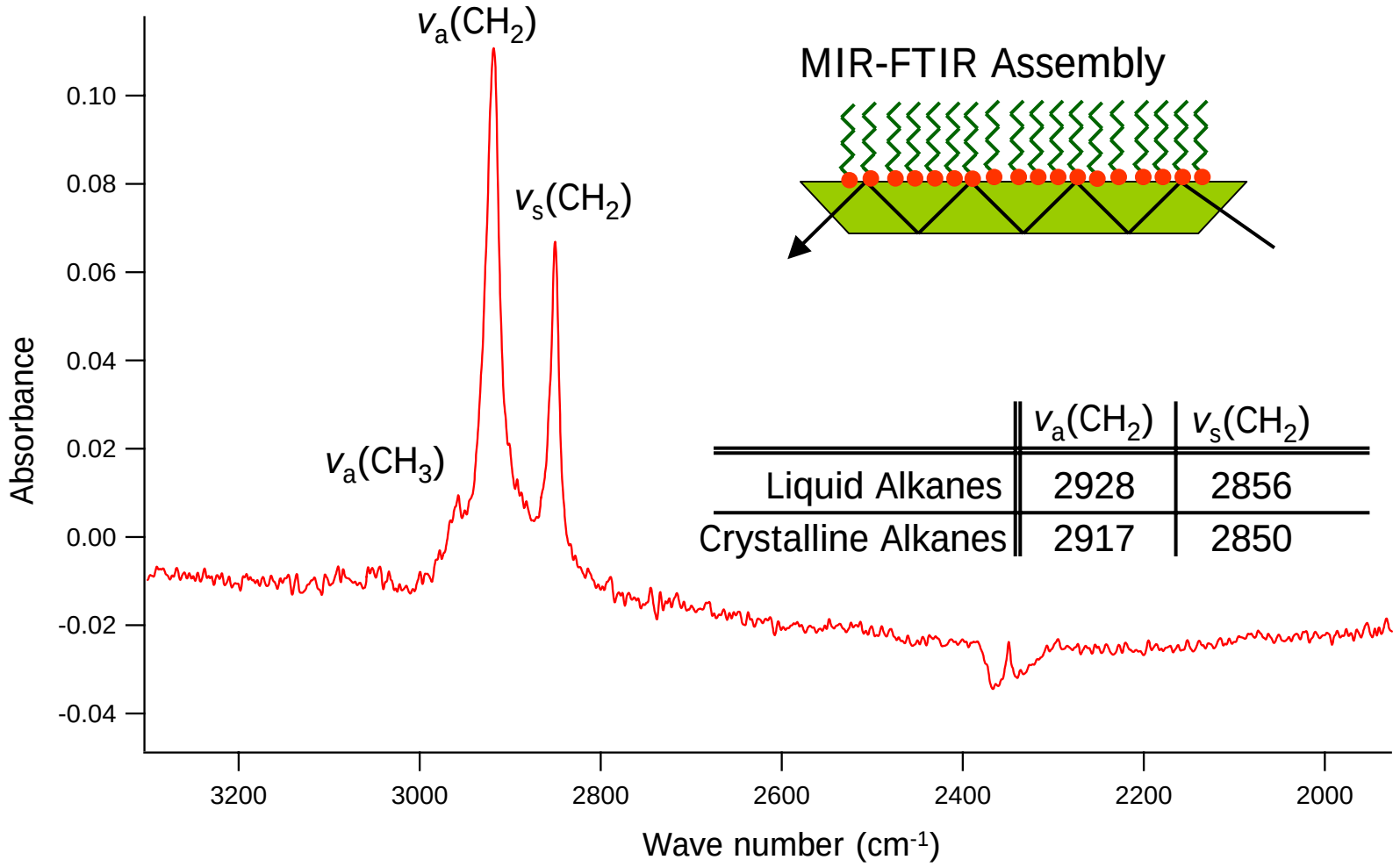
# Formation of SAMs by Vapor Delivery




- Successful ALD resists still require long times for SAM formation from vapor phase

# FTIR spectra of SAMs

- $CH_2$ stretching modes are a sensitive probe of degree of order in SAMs

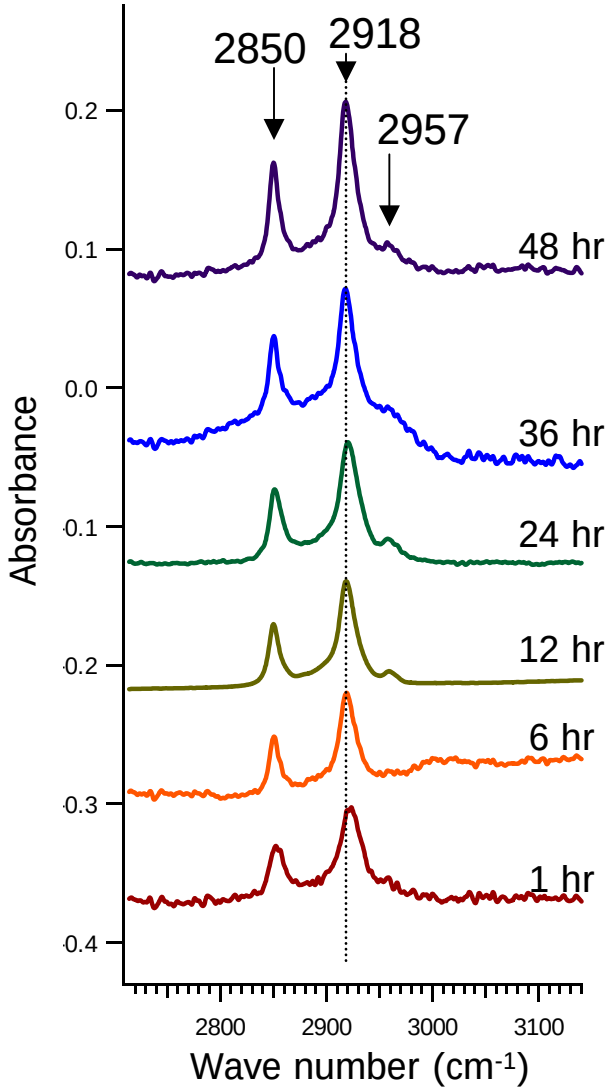


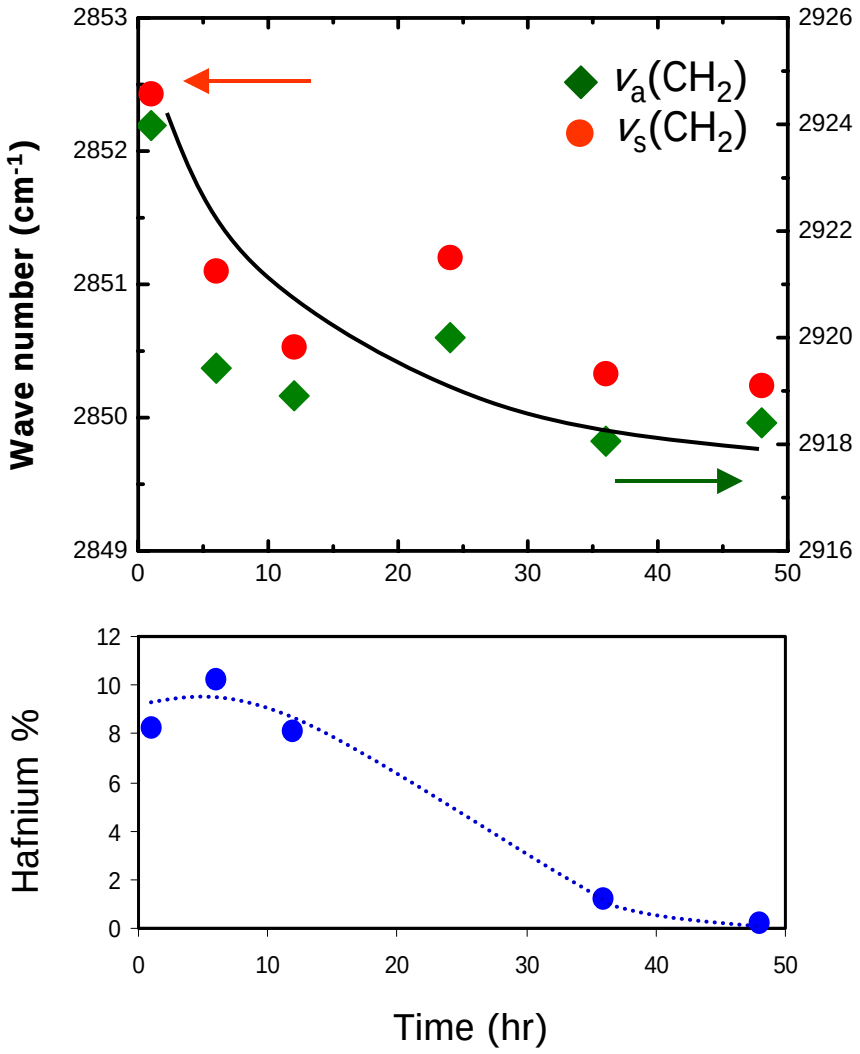

MIR-FTIR Assembly



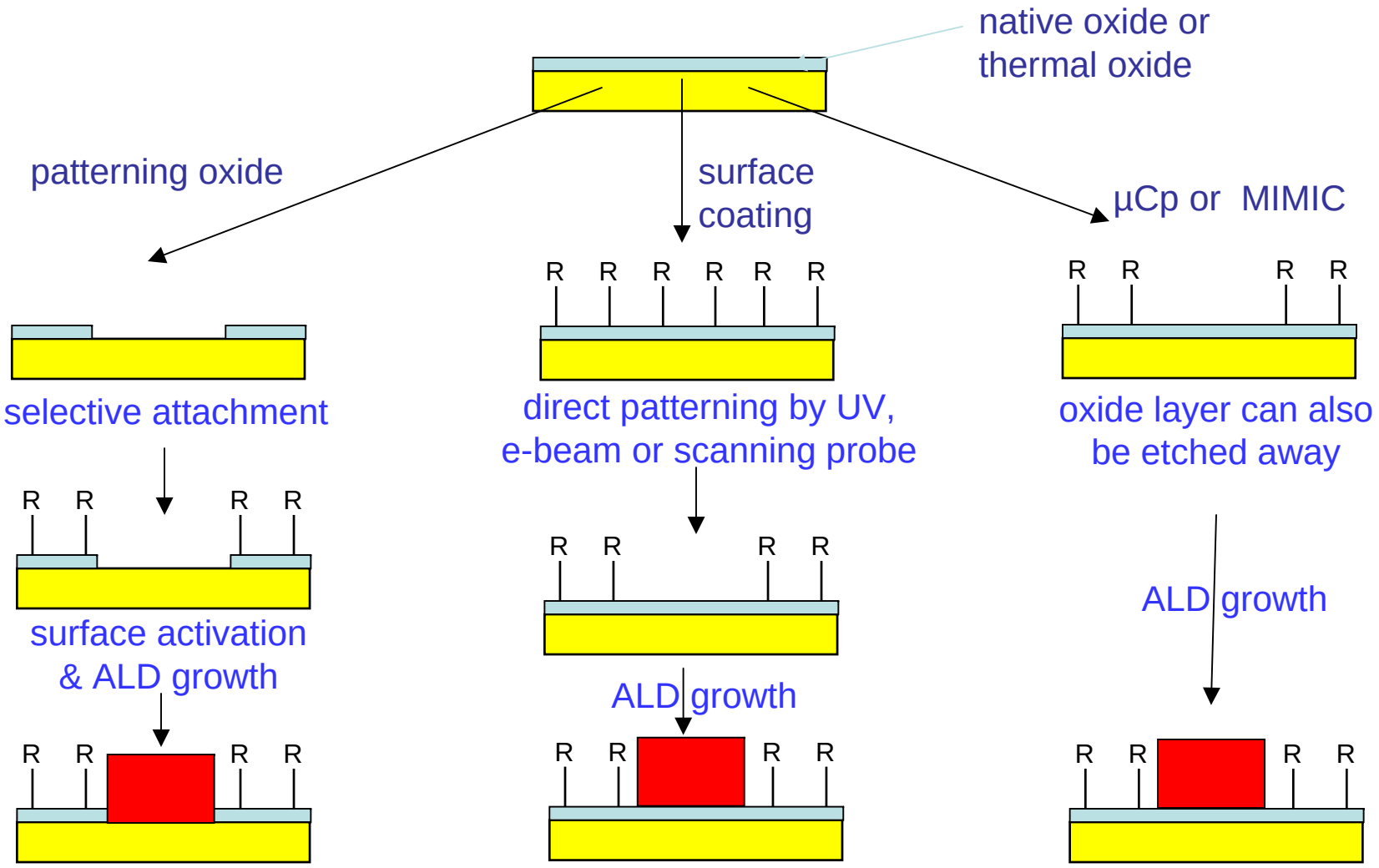
| | $\nu_a(CH_2)$ | $\nu_s(CH_2)$ |
|---|---|---|
| Liquid Alkanes | 2928 | 2856 |
| Crystalline Alkanes | 2917 | 2850 |

# FTIR spectra of SAMs show evolution of crystallinity

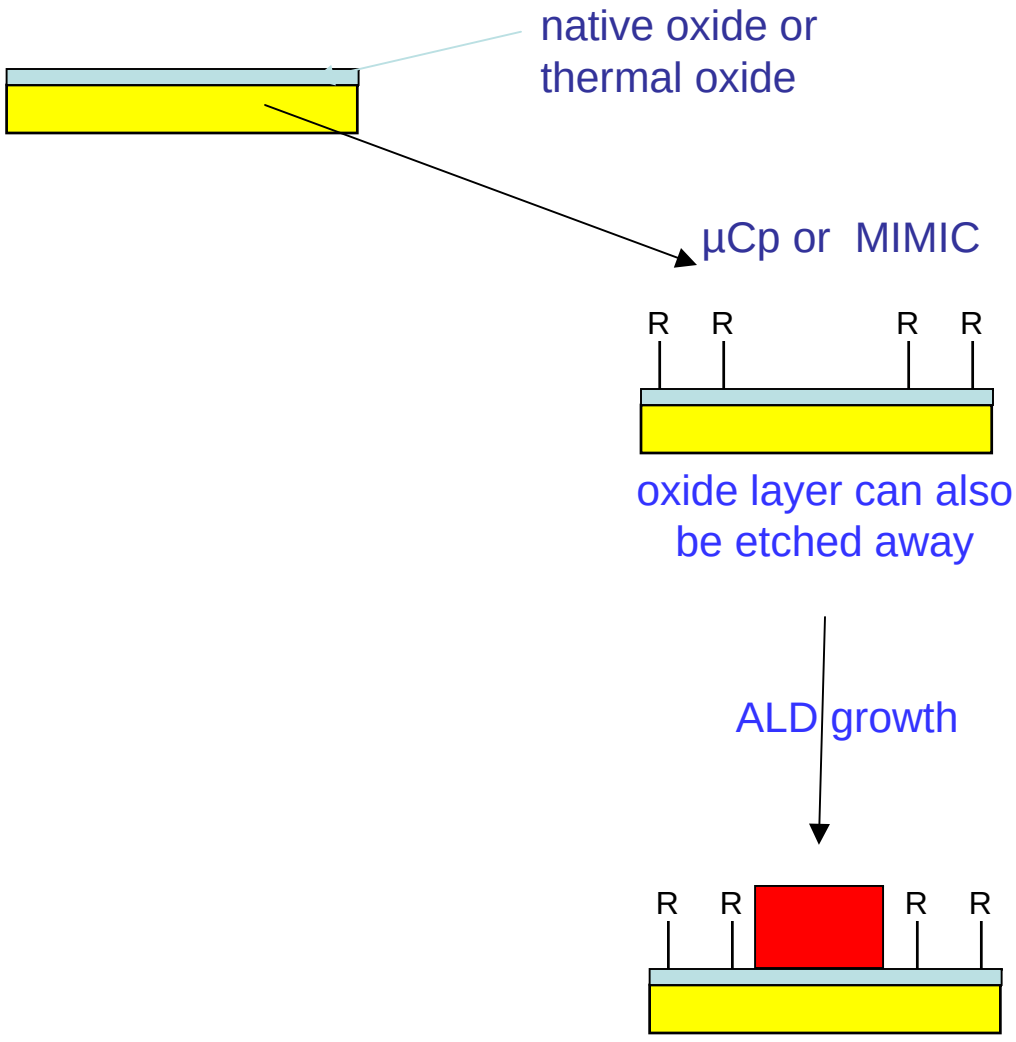


# Patterning Approaches for Area Selective ALD

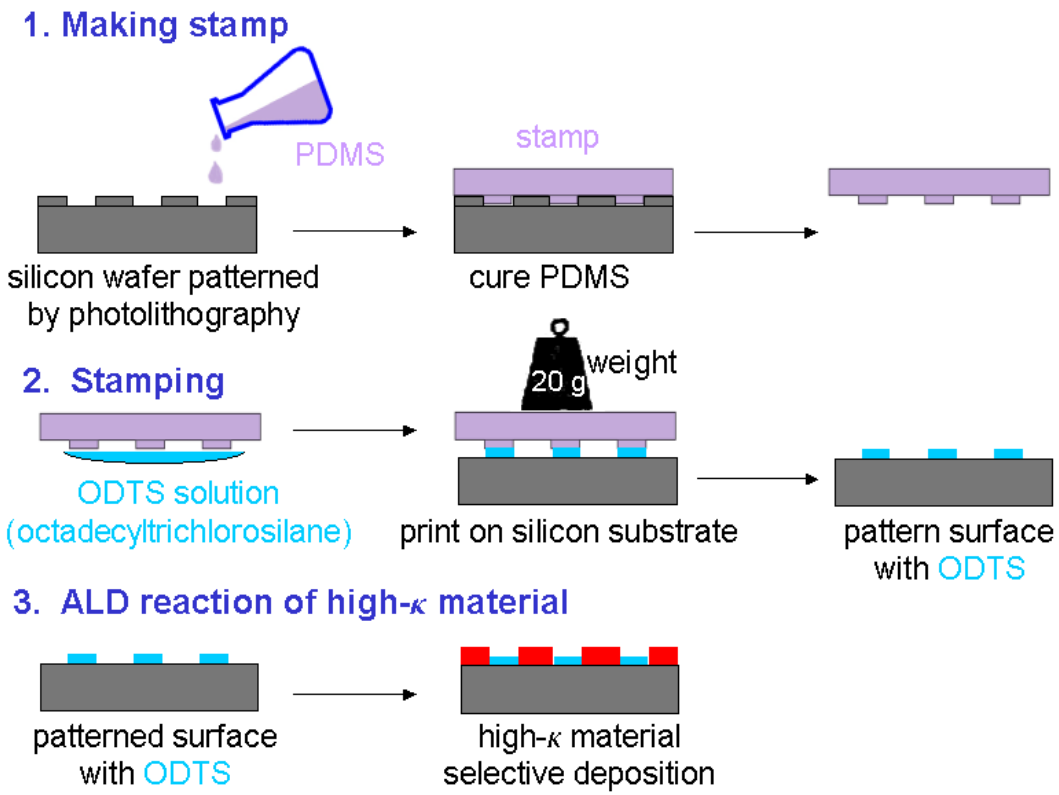


# Patterning by Microcontact Printing

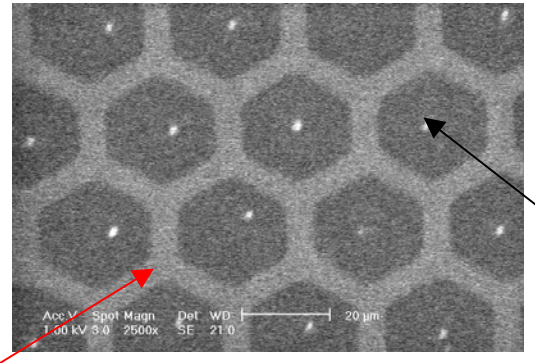


# Micro-contact printing of ODTS for Area-selective ALD

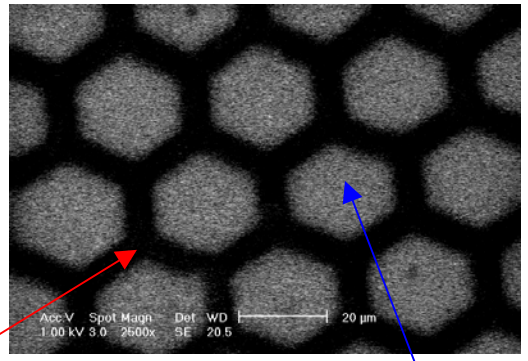
## Strategy:




## SEM image:



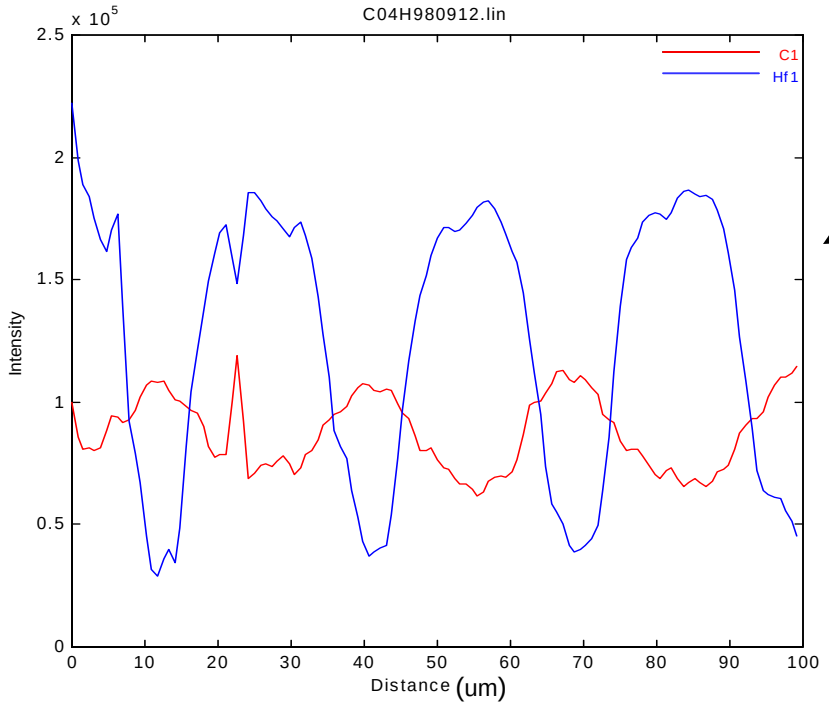

**ODTS** patterned surface before $HfO_2$ deposition

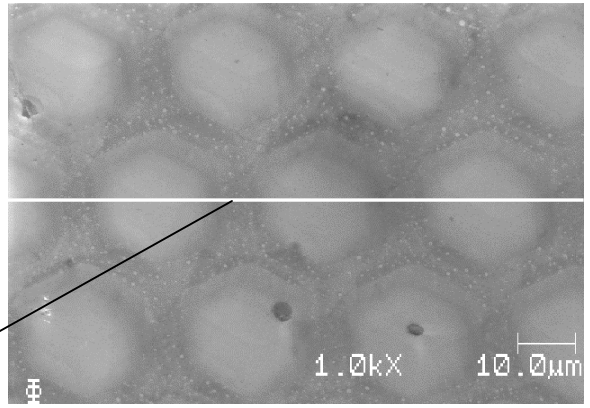


**ODTS** patterned surface after **$HfO_2$** deposition

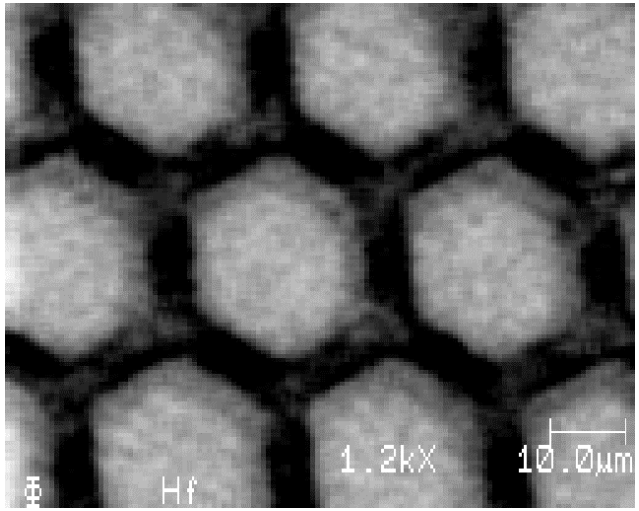
# AES Analysis after ALD Process

## Auger Line Scan



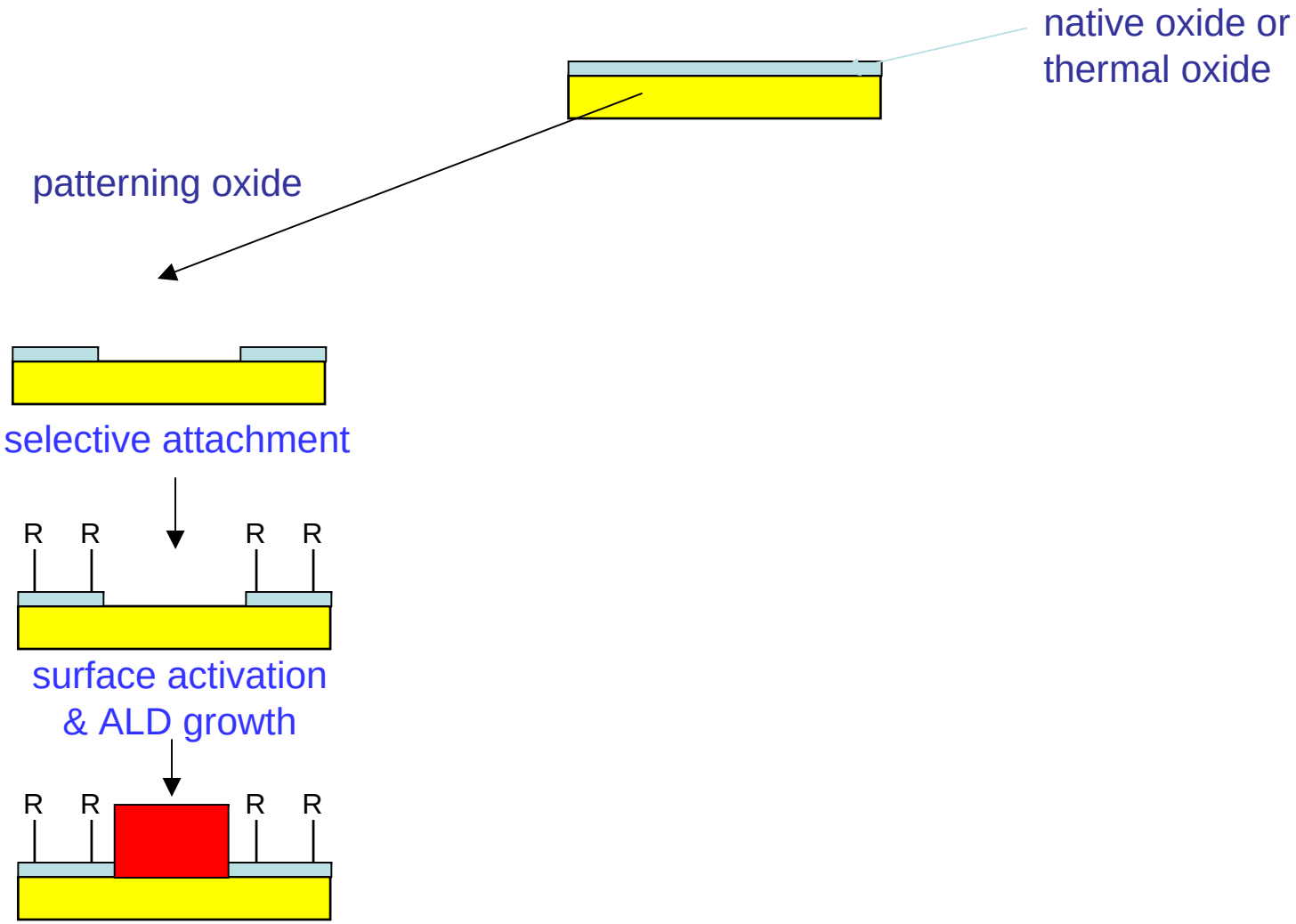




## Hf Auger Mapping

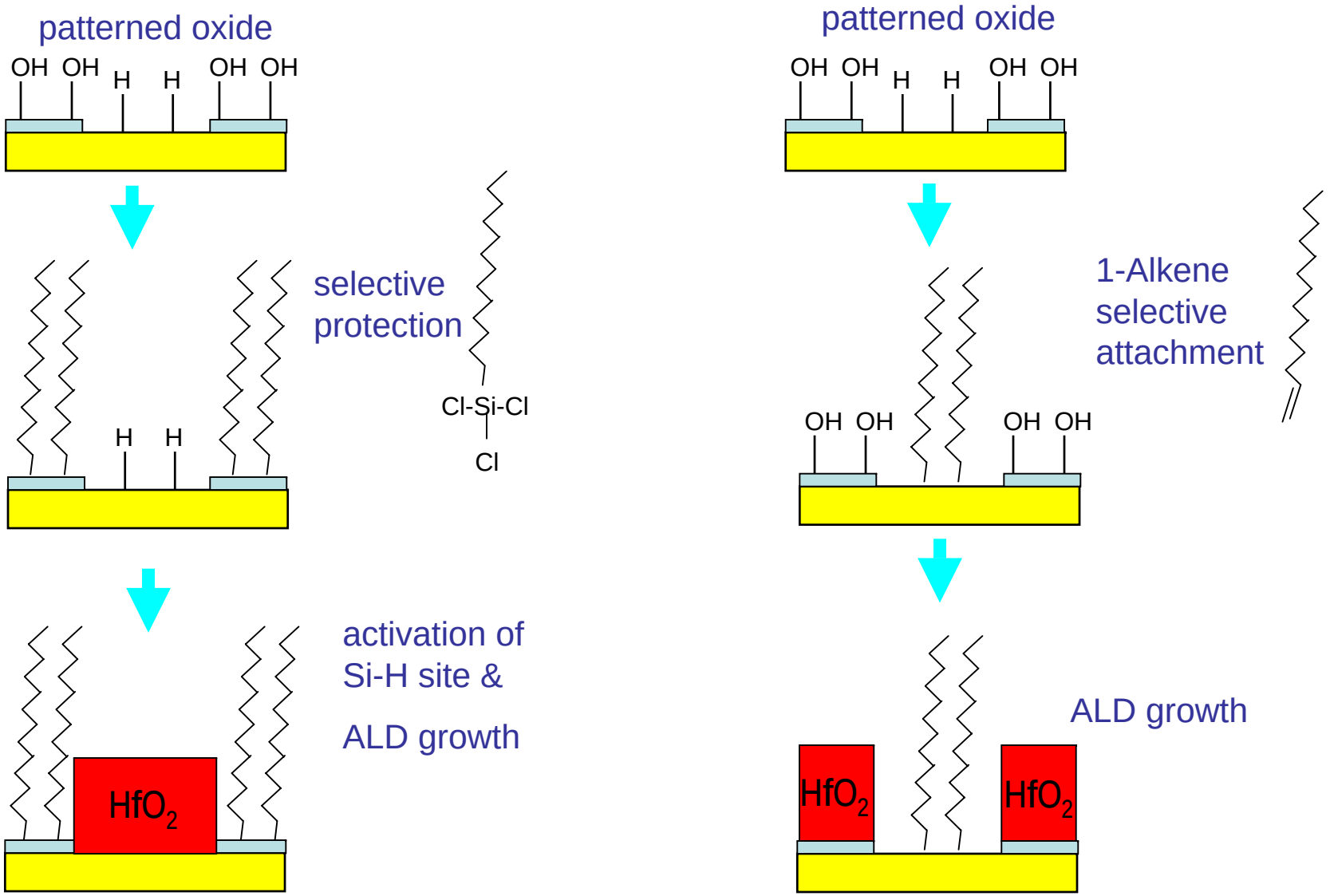



**Data: Charles Evans & Associates**

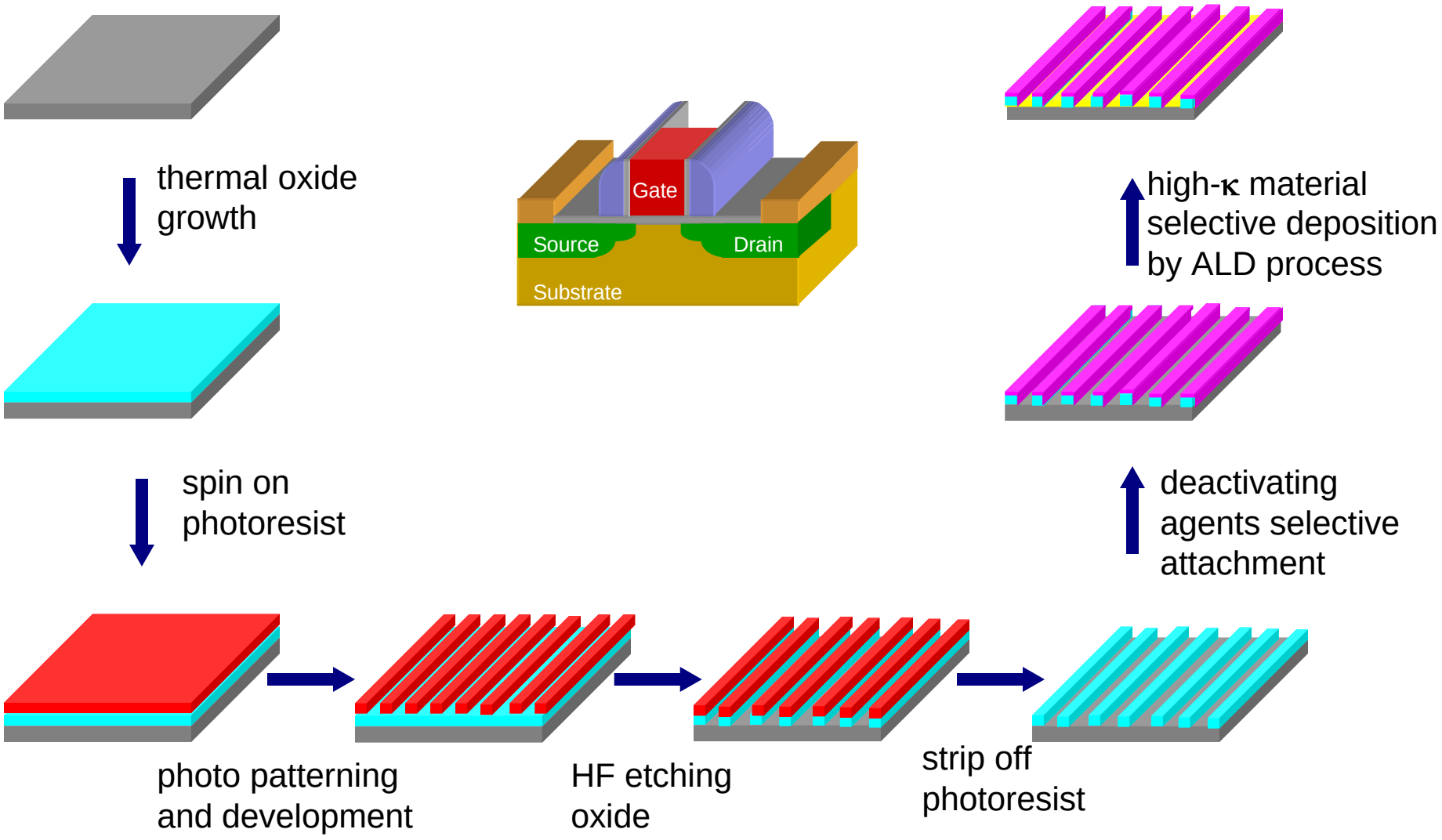
# Oxide Patterning



# Selectivity on Patterned Silicon Oxide



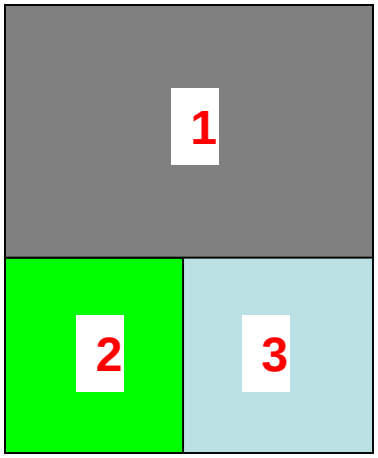
# Area-Selective ALD on Patterned Oxide Sample

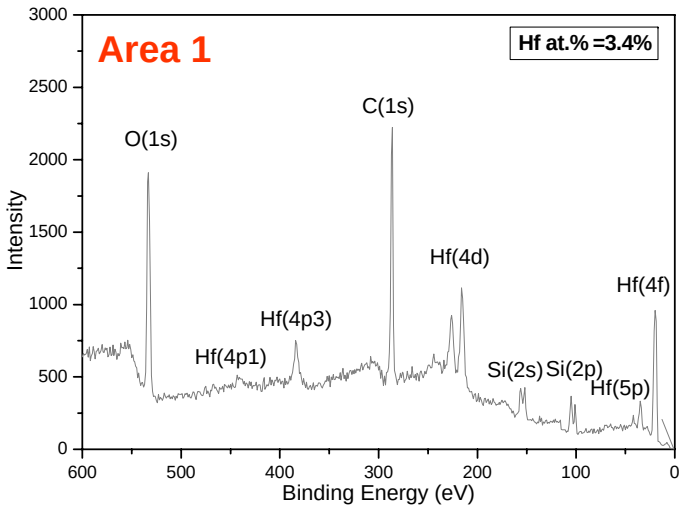


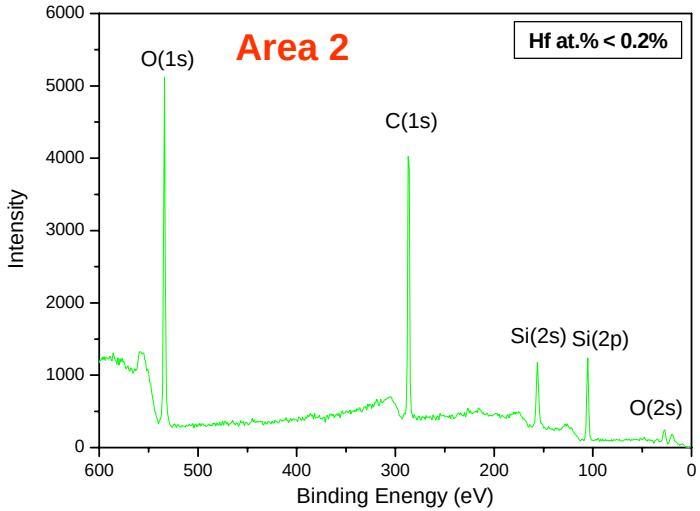
# XPS Analysis on Patterned Oxide Sample after ALD

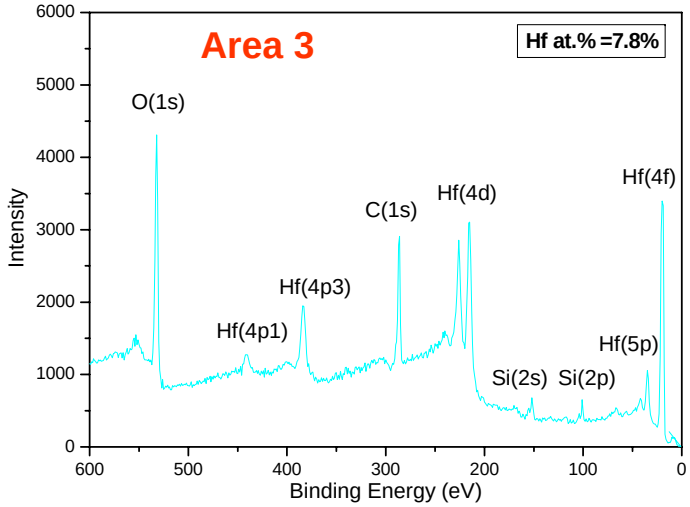
**Samples for Area-Selective ALD**

150μm diameter
X-ray beam



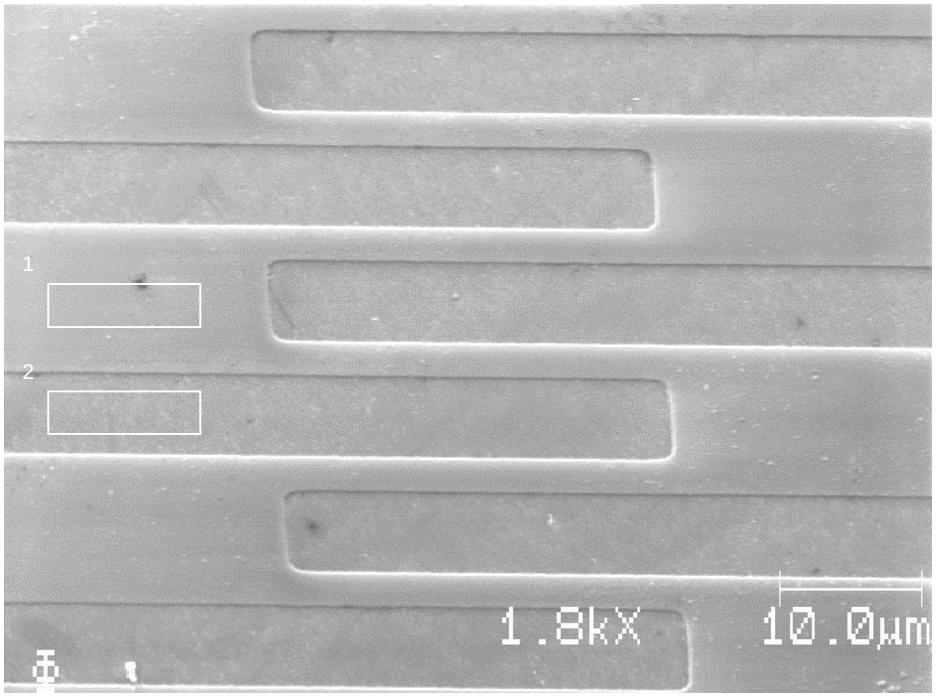



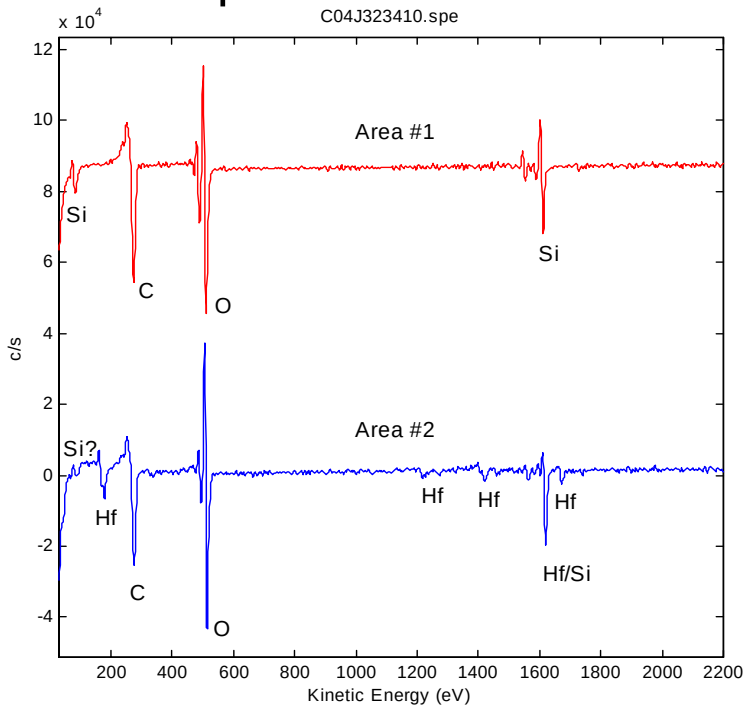

1. Photolithography-patterned area
2. Blanket $SiO_2$ region coated with ODTS
3. Blanket Si-H region reference part

# SEM Image on Patterned Oxide & AES Survey Spectra

SEM image on patterned area




Auger survey spectra on patterned area

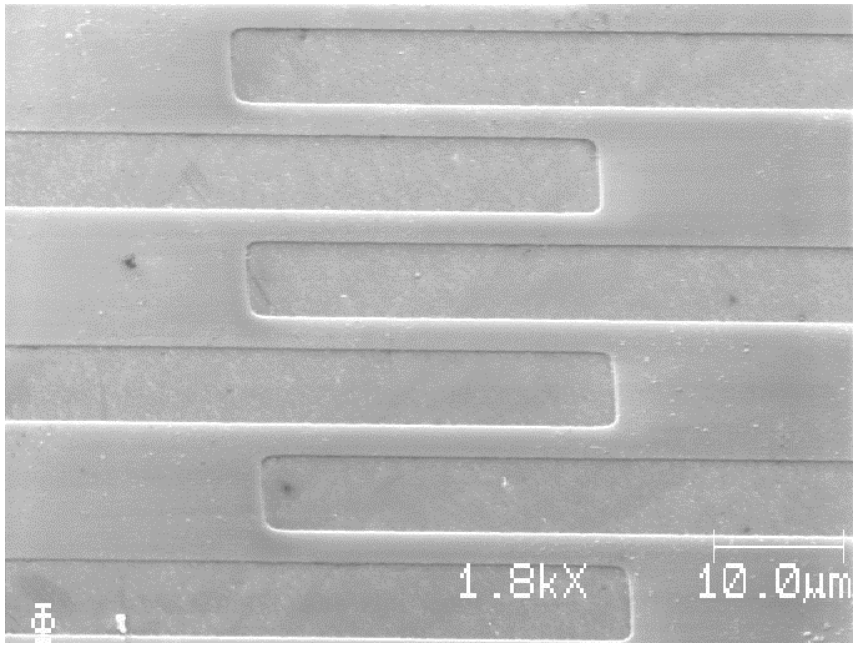



1. **Thermal oxide coated with ODTS**
2. **Activated region for $HfO_2$ ALD process**

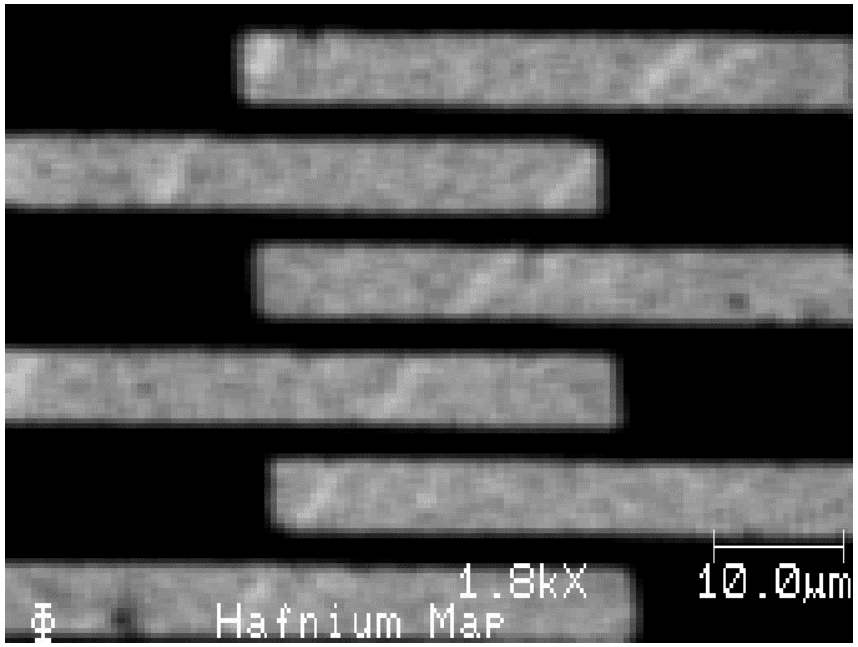
Data: Charles Evans & Associates

# SEM Image vs. Hafnium Elemental Mapping

SEM image on patterned area



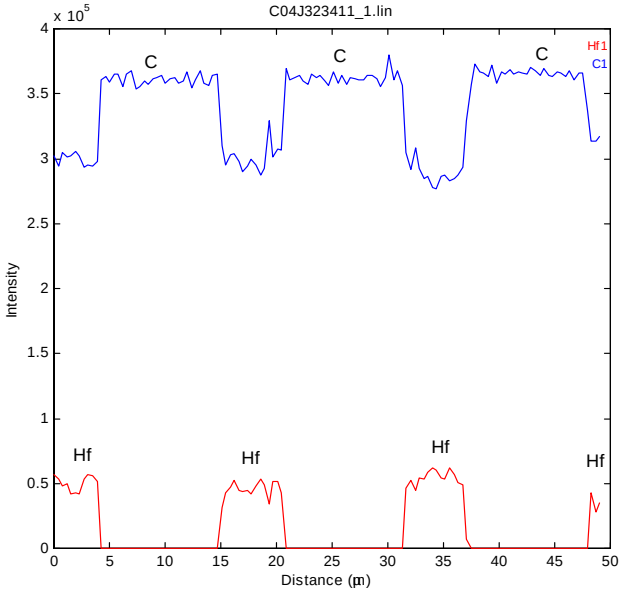

Hafnium elemental mapping on patterned area

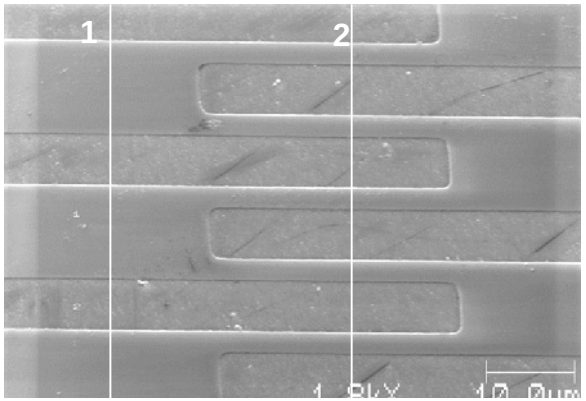



Data: Charles Evans & Associates

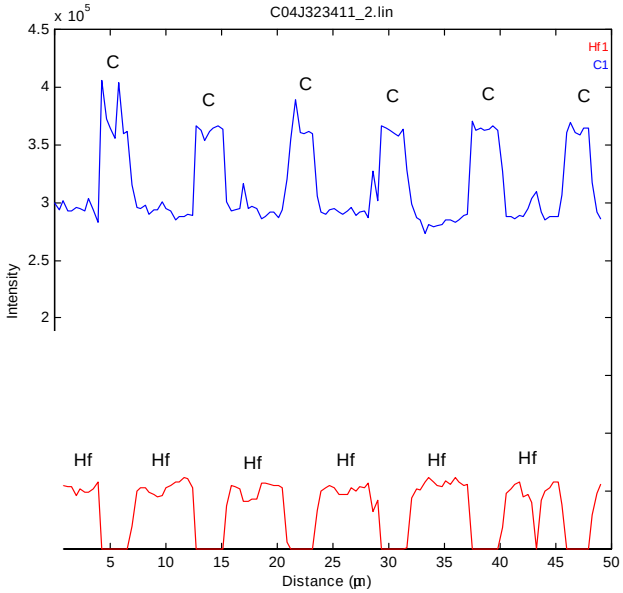
# SEM Image: Defined Lines for Line-Scan

Line 1

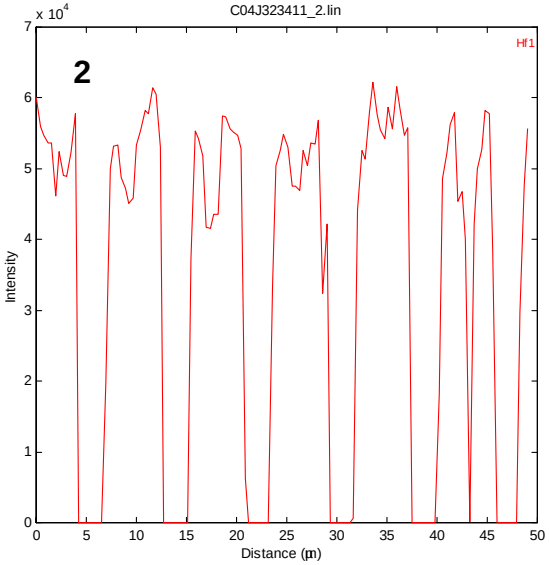



Line 2




Line scan, Area 2:
Intensity vs. Distance,
Hf only

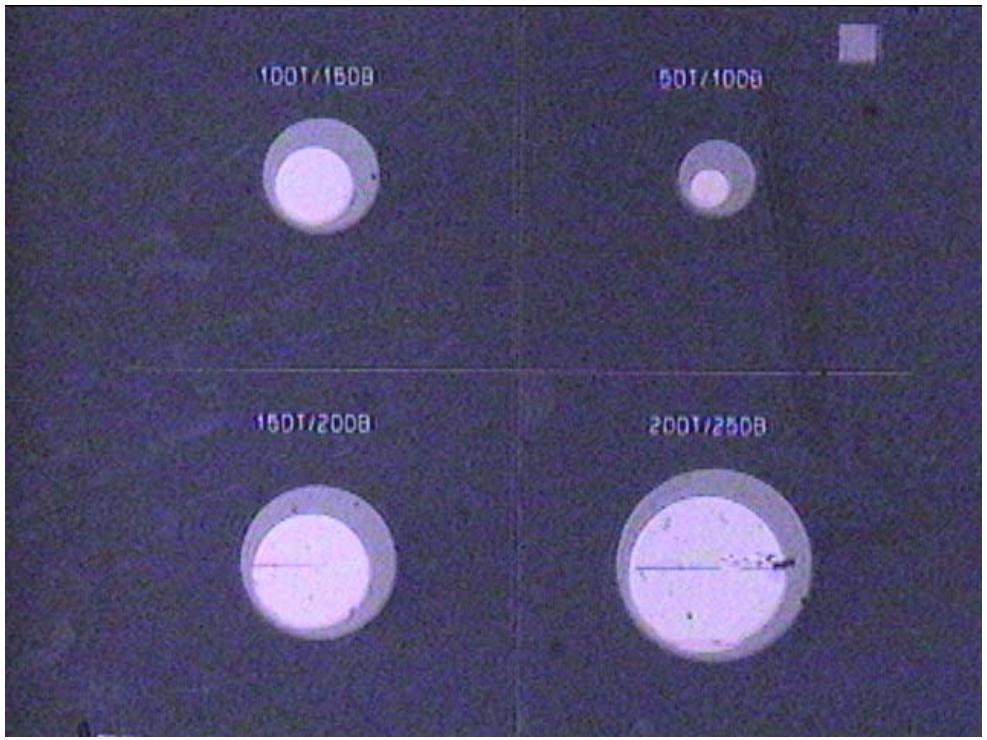


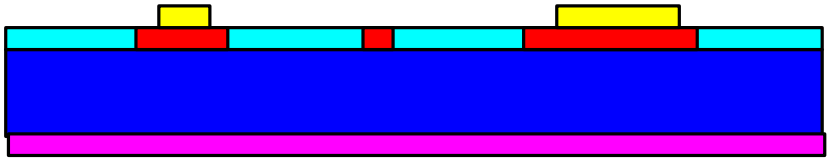


ıta: Charles Evans & Associates

# Initiation of Electrical Measurements

Optical micrograph of capacitor structures:

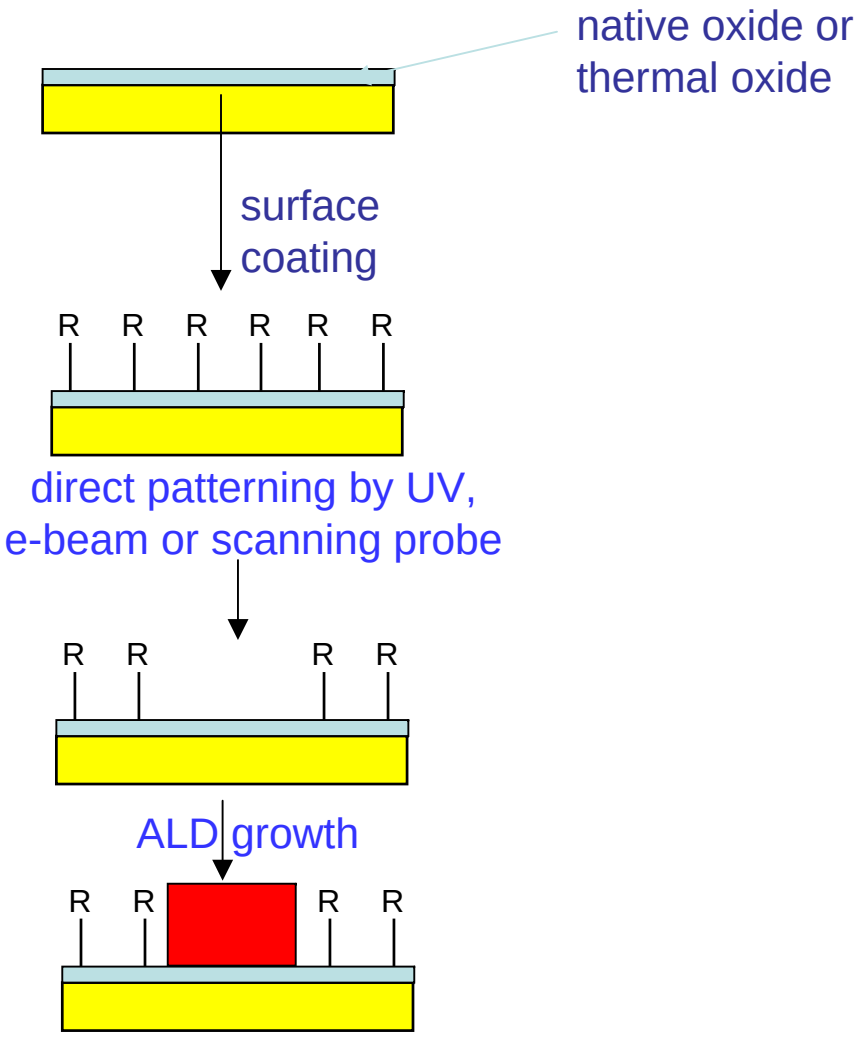


## Capacitor structures fabricated

- Based on Area-Selective ALD process
- $HfO_2$ dielectric
- Pt top electrode
- CV measurements to be carried out

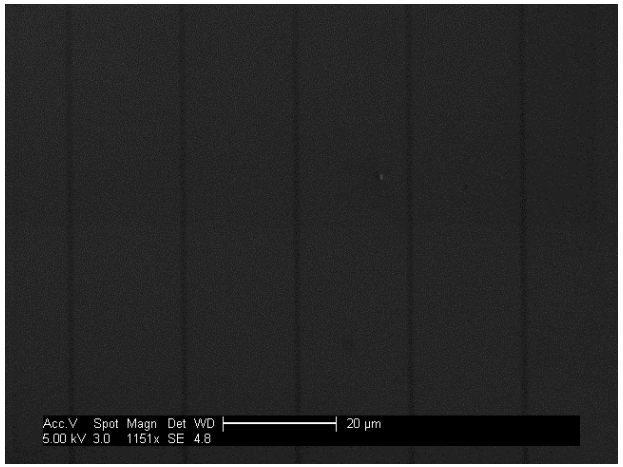
# Direct e-Beam or UV Patterning



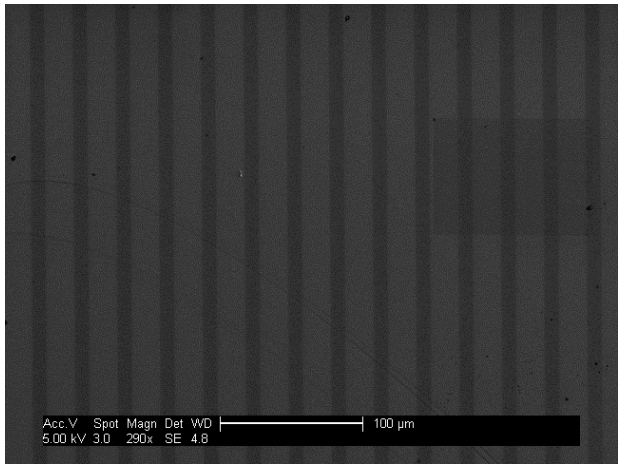
# E-Beam Patterning of ODTS/$SiO_2$

## $SiO_2$ + ODTS

- **Hitachi HL-700F E-beam**
- **Beam voltage = 30 KeV**
- **Pixel size - 0.02 μm or larger in 0.01 μm steps**
- **Pixel rate - variable up to 100 MHz**
- **E-beam Dose = 300 *μC/cm²***




1 *μ*m lines



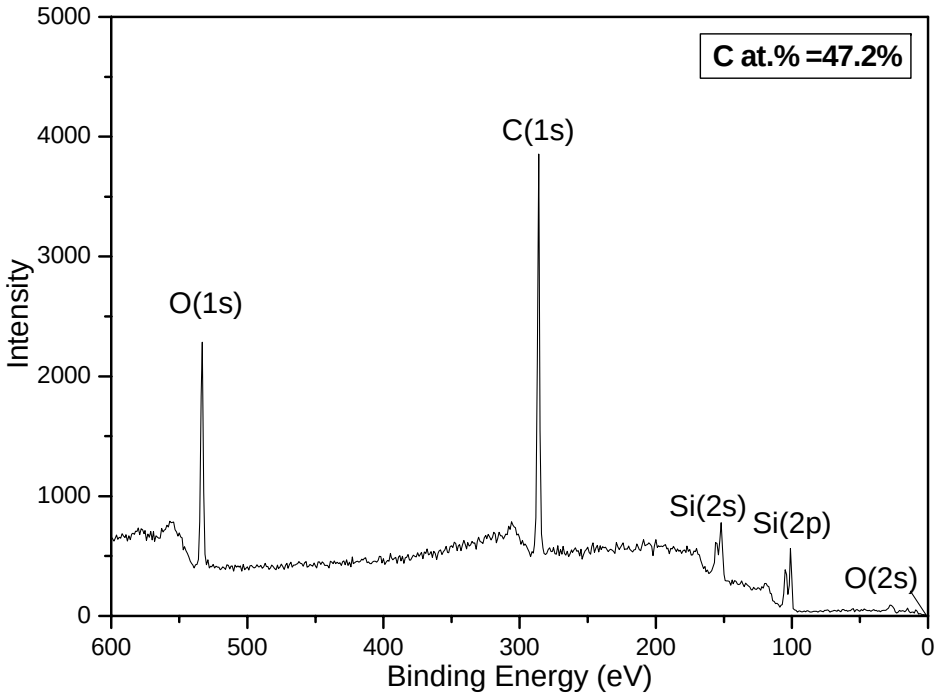

10 *μ*m lines

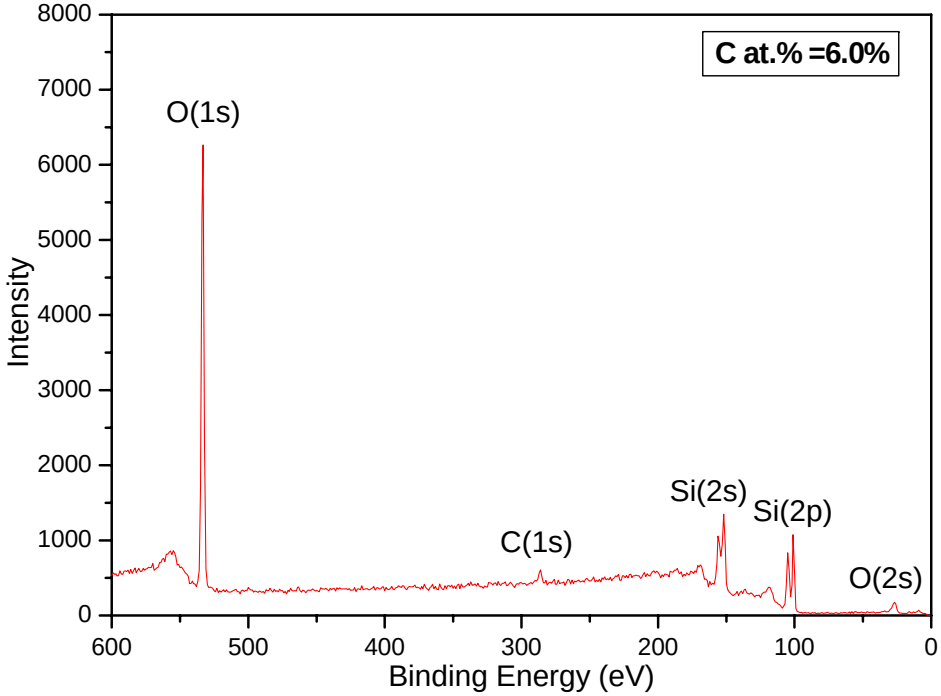
Hemanth Jagannathan

# UV Ozone Direct Exposure on ODTS for Area-selective ALD

**Protected Area**

**Exposed Area to UV Ozone**



# Summary and Acknowledgments

## Conclusions

- Siloxane SAMs have been demonstrated as monolayer resist for $SiO_2$
- Both solution and vapor phase SAM formation is effective
- Properties of SAM required for successful deactivation have been delineated
- Different patterning strategies have been explored
  - Soft lithography
  - Patterned oxide
  - Direct write
- Area selective ALD on patterned oxide has been demonstrated

# Future Work

- Fabrication and testing of capacitor and transistor structures
- Surface activation for high-$\kappa$ growth
- Exploration of other substrates (e.g. nitride)
- Investigation of high-$\kappa$ / substrate interfacial properties
- Study of ALD mechanisms

## Acknowledgments


Funding

**Center for Environmentally Benign Semiconductor Manufacturing**

Facilities