Area-Selective ALD of HfO_2

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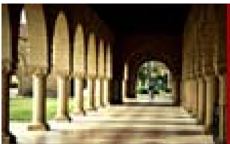
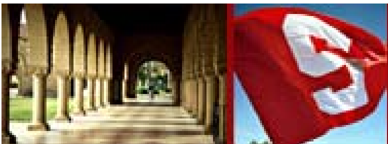
ERC Teleseminar, July 29, 2004



Outline

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



The ALD Process

Step 1: Initial surface

Step 2: Precursor 1 exposure

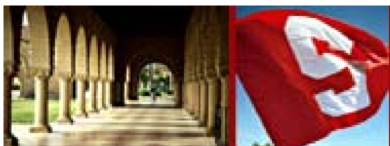
Step 3: Inert gas purging

Step 4: Precursor 2 exposure

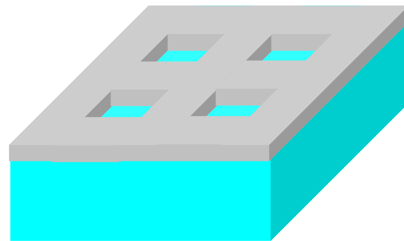
Step 5: Inert gas purging

Growth of High-κ Dielectric layer

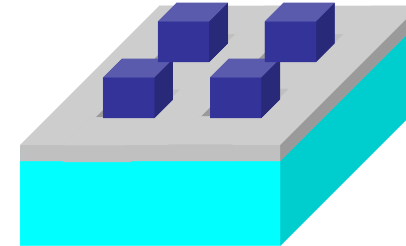
- Self-saturating surface reaction cycles: thickness control



Generate 3-D Pattern from 2-D Template



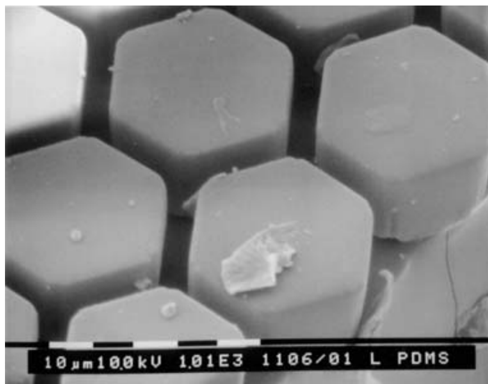
Area-Selective ALD

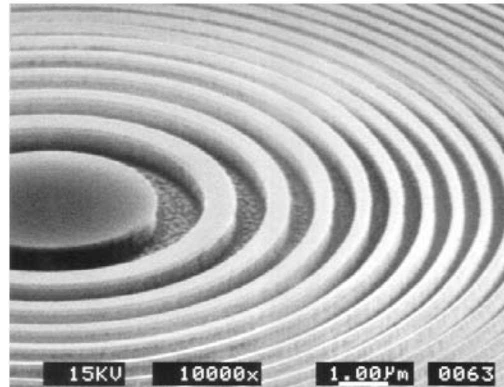


Microcontact printing

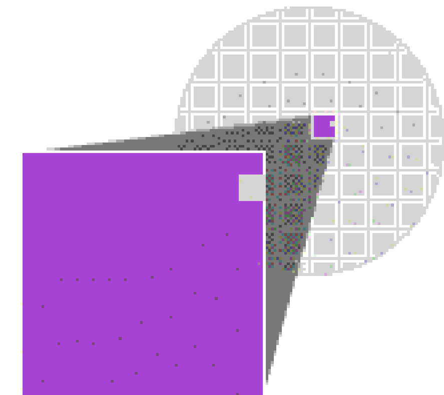
E-beam lithography (direct writing)

Photolithography patterned SiO_2/Si





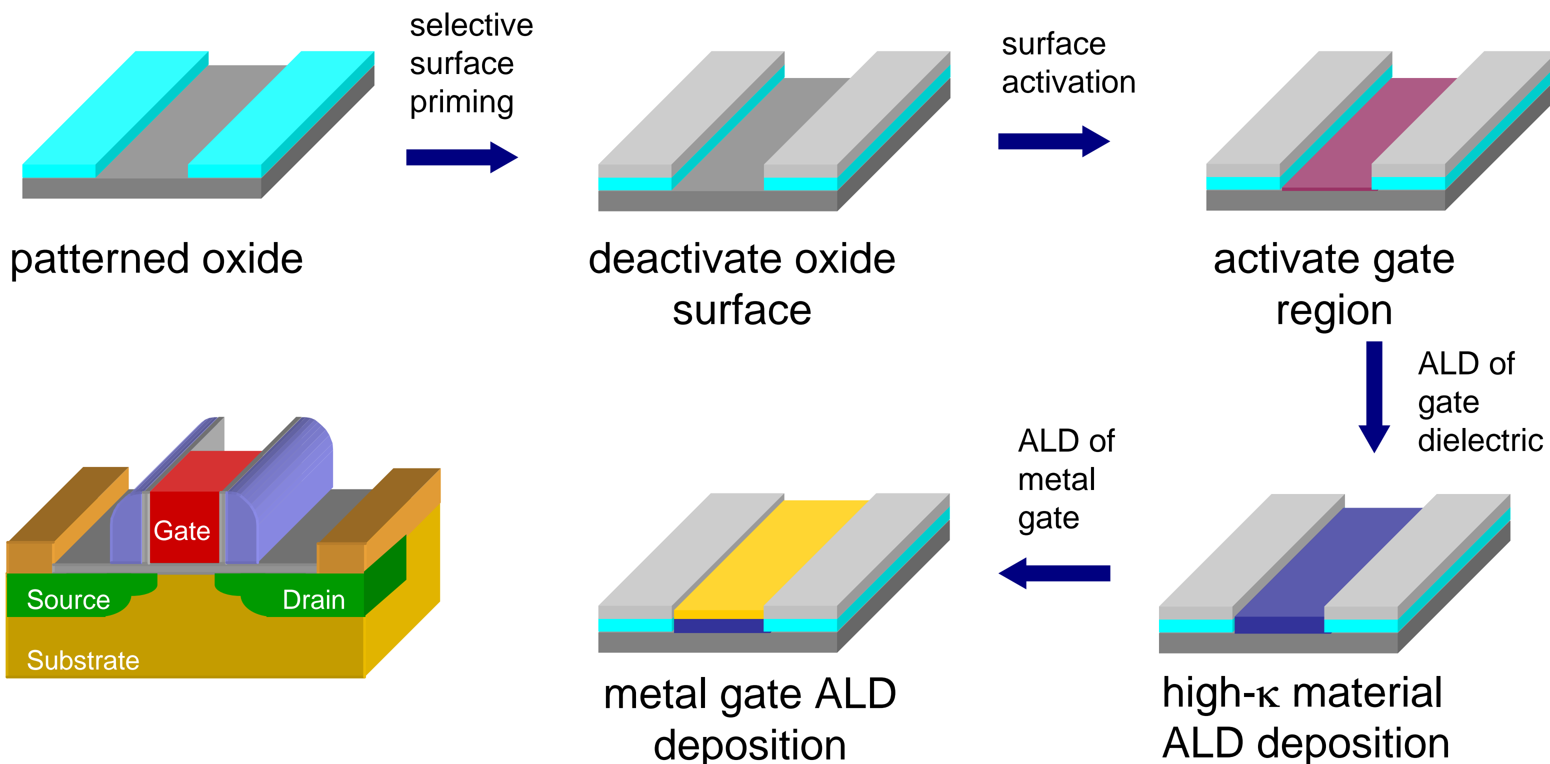
Source: Paul Scherrer Institut

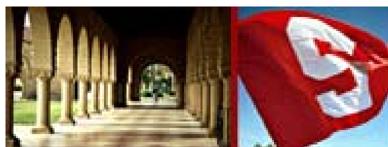


Source: Intel

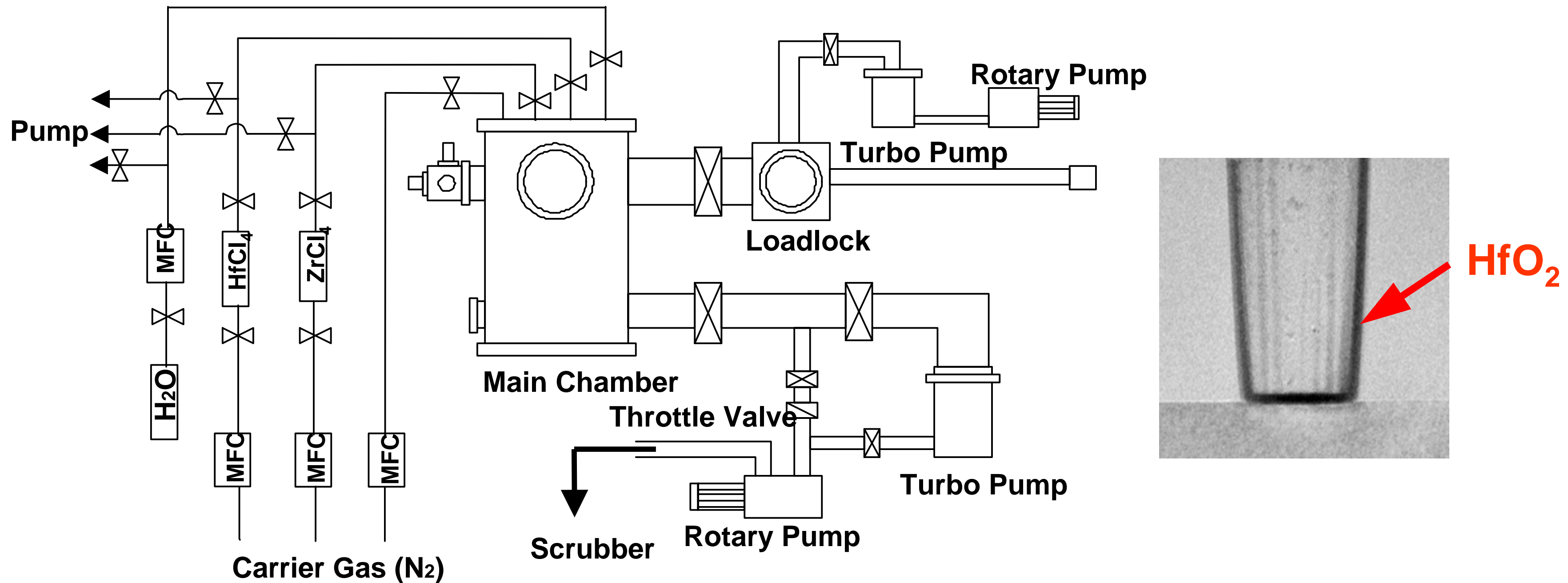
Process Flow for Area-Selective ALD for Gate Stack

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

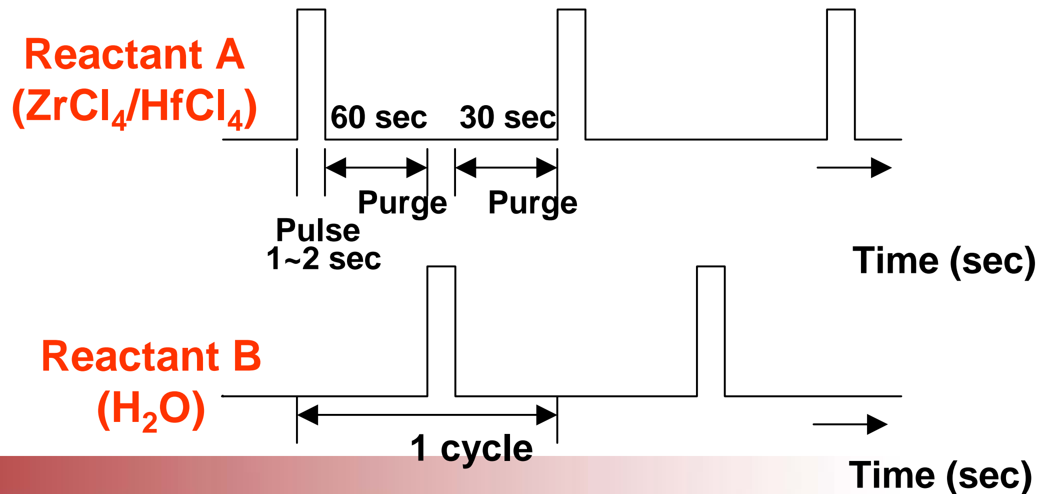


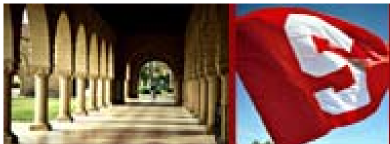


Schematic Diagram of McIntyre ALD System

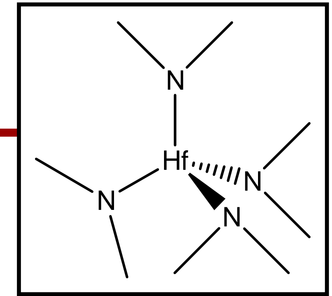


- Base pressure = $5*10^{-8}$ Torr
- Process temperature : 300°C
- Process pressure : 0.5 Torr
- Source temperature :
  - H_2O (liquid) = 20°C
  - $HfCl_4$ /$ZrCl_4$(solid) = 150°C





Bent Group ALD Reactor

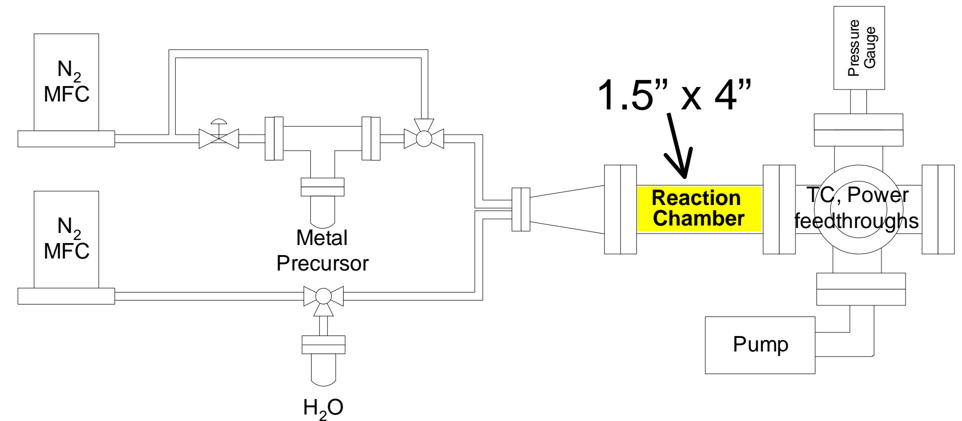


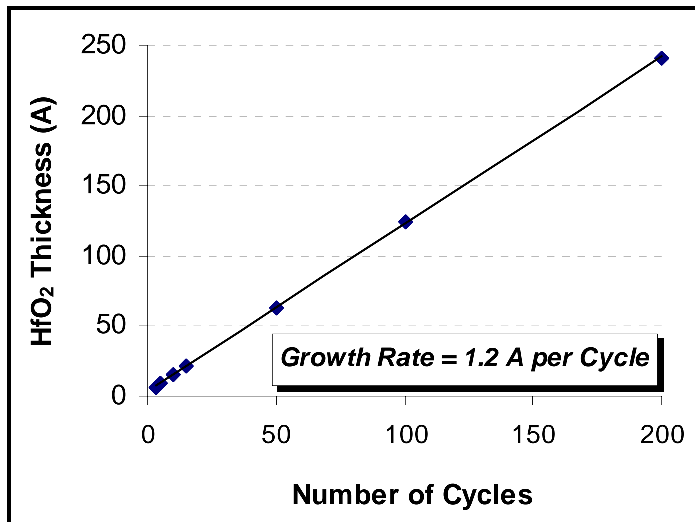
Hf precursor: tetrakis(dimethylamido)hafnium

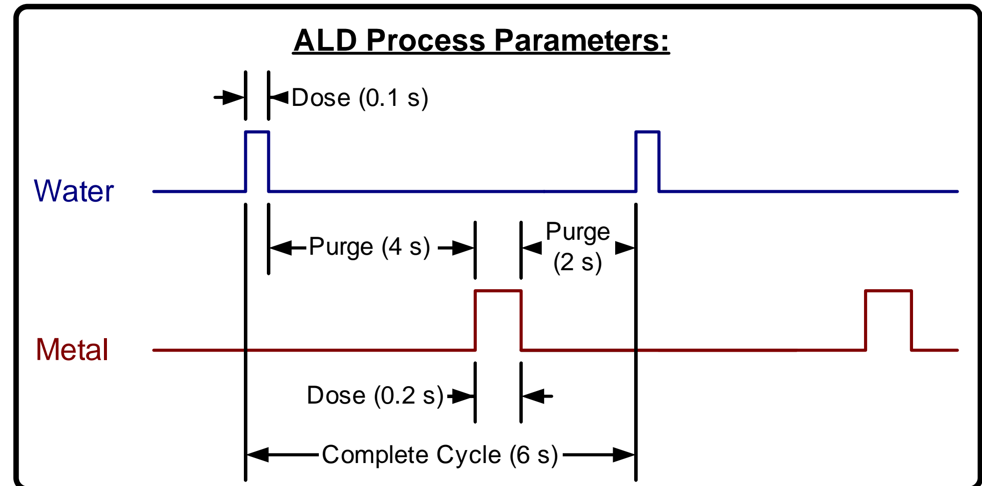
- No HCl; no Cl incorporation
- More uniform growth
- Low deposition temp (250 C)

0.9 -1.2 A/cycle

No impurity incorporation

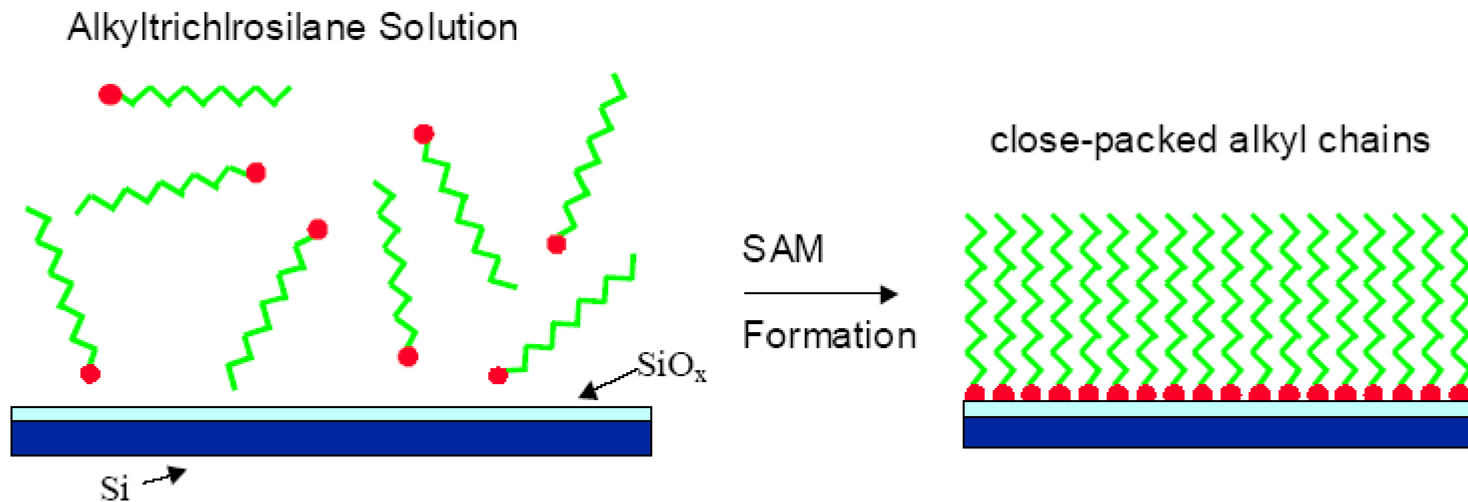






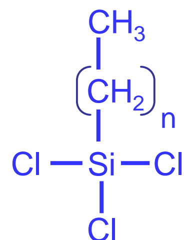
Self-assembled Monolayers as ALD Resists

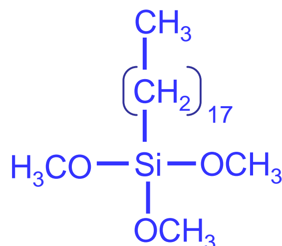
- Self-assembled monolayers (SAMs) are ordered assemblies formed by the adsorption of an active surfactant on a solid face and are well known to modify surface characteristics

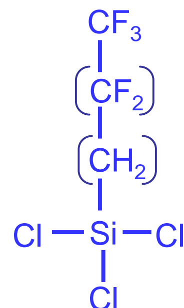


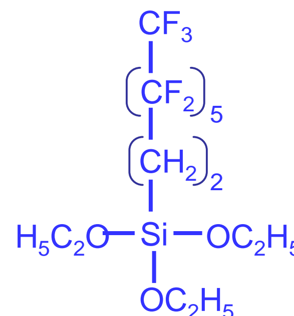
Deactivating Agents Studied

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







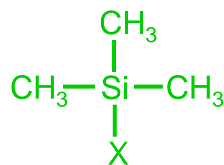


Alkyltrichlorosilane

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

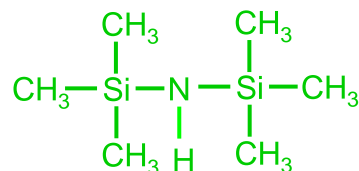
2. Number of halide substituents

3. Reactive head groups



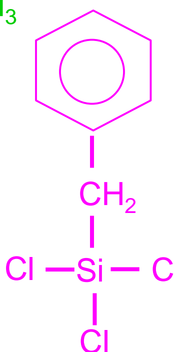
X=Cl, Br, I

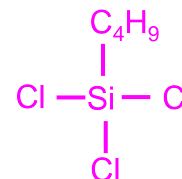
Trimethylhalosilane

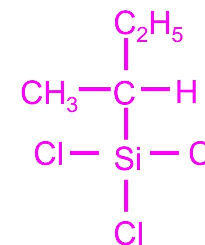


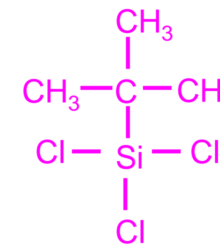
HMDS

4. Carbon tail structure

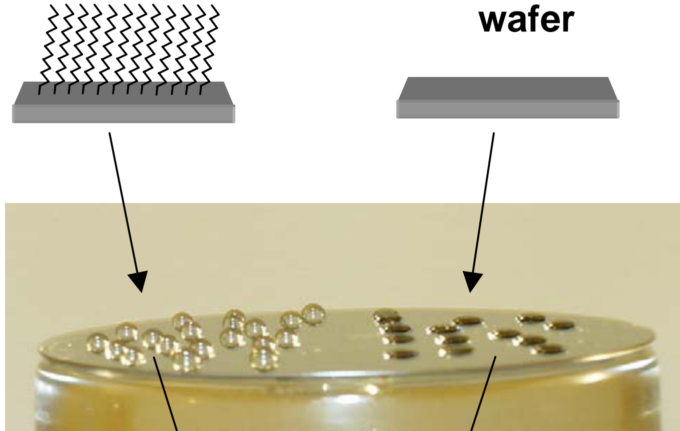








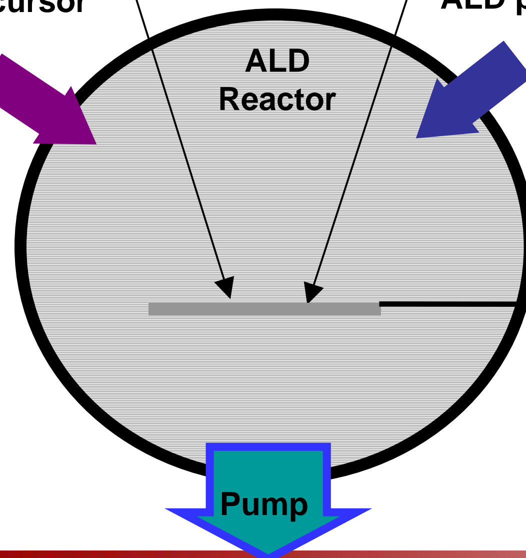
Methodology for Study of Deactivating Agents



A. Preparation and analysis of deactivating agents

B. ALD growth of ZrO_2 & HfO_2

C. Sample characterization after deposition



C

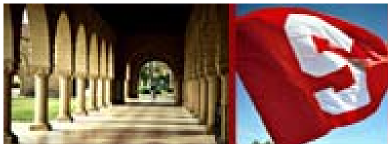
XPS: Film composition

Ellipsometry: film thickness

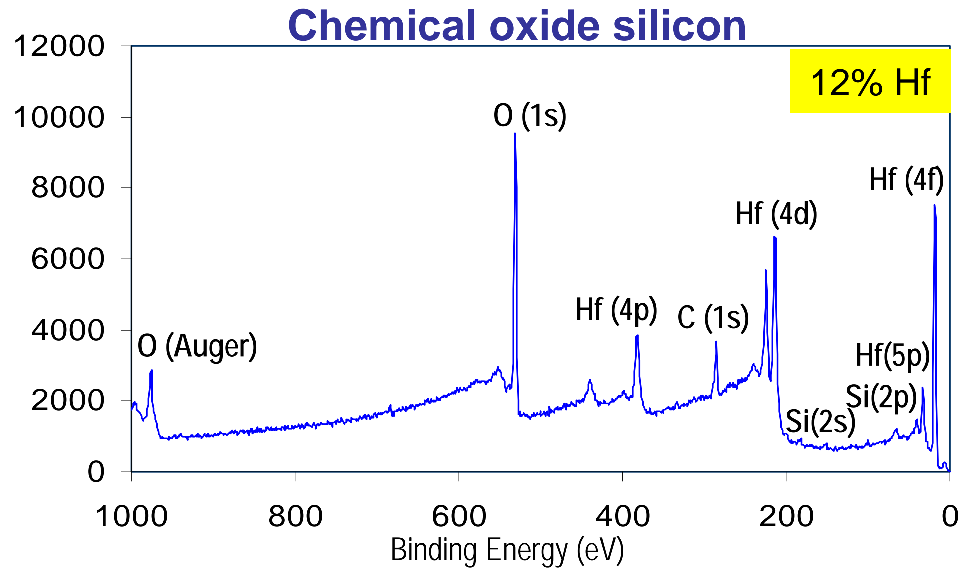
Contact Angle: Hydrophobicity

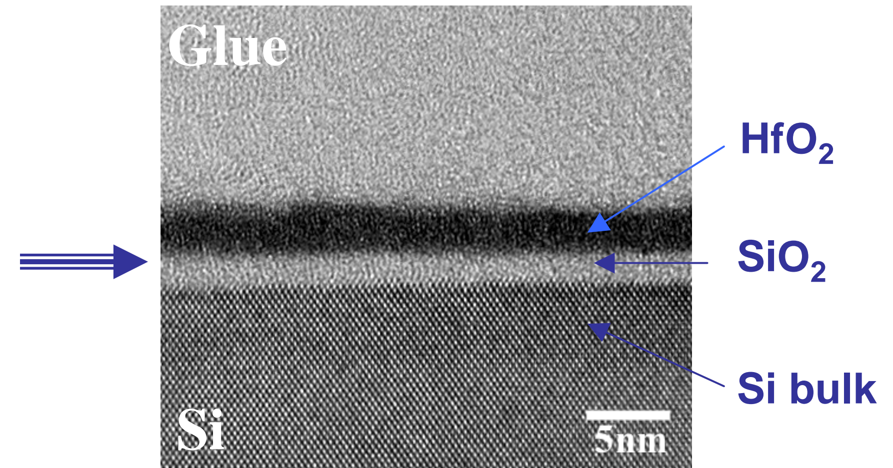
AFM: Film morphology

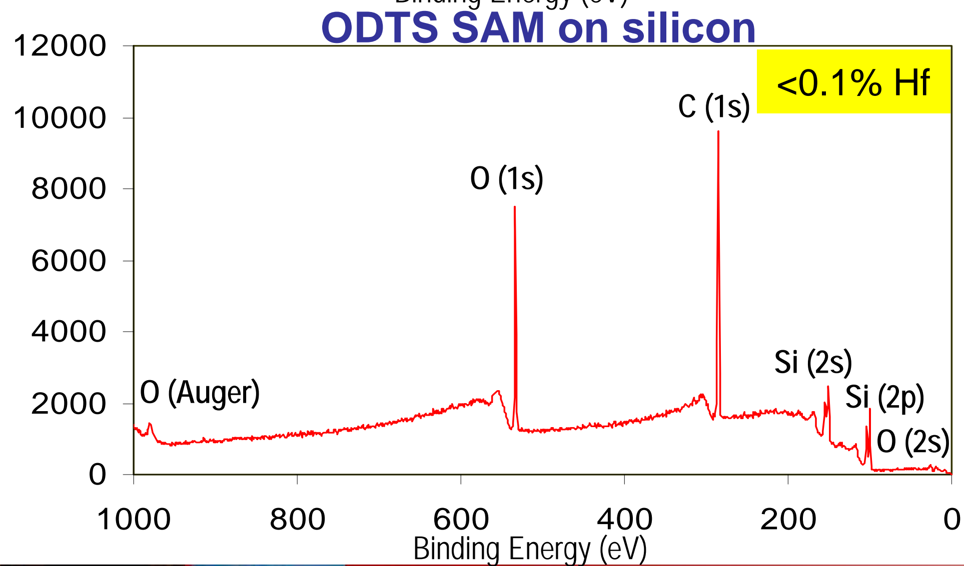
TEM: Interfacial properties

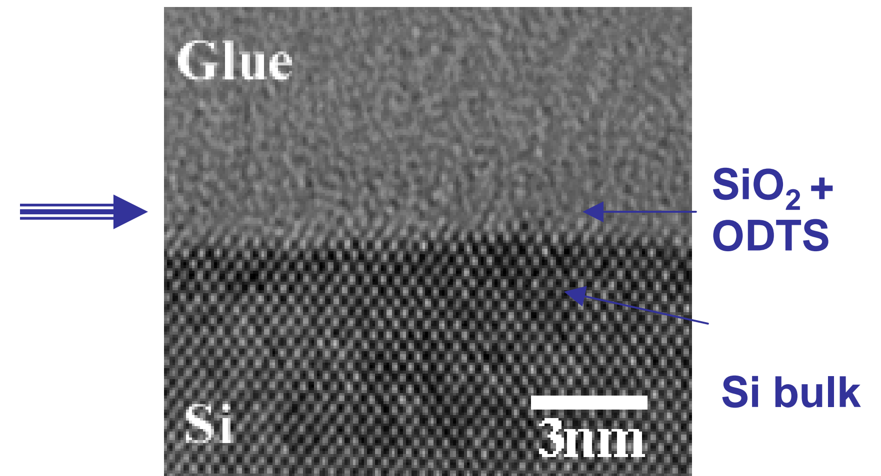


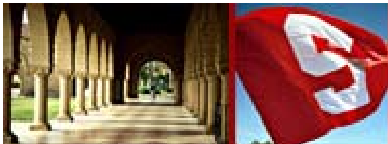
ALD Inhibition by Octadecyltrichlorosilane (ODTS) SAM











Silylation Time Dependence for ODTS

$CH_3 (CH_2)_{17} SiCl_3$

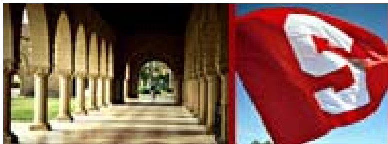
Contact Angle before ALD
Film Thickness before ALD
Hafnium% after ALD

Hafnium %: 0, 5, 10, 15, 20, 25, 30

Film Thickness(A): 0, 5, 10, 15, 20, 25, 30, 35, 40

Contact Angle(degree): 0, 20, 40, 60, 80, 100, 120, 140

Minutes: 0, 500, 1000, 1500, 2000, 2500, 3000



Alkyltrichlorosilane Chain Length Dependence

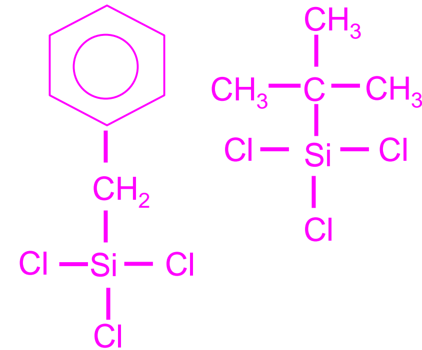
$CH_3-(CH_2)_n-SiCl_3$

Contact Angle before ALD
Film Thickness before ALD
Hafnium% after ALD

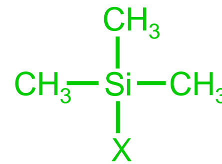
Hafnium %: 0, 2, 4, 6, 8, 10, 12, 14
Film Thickness(A): 0, 5, 10, 15, 20, 25, 30, 35, 40
Contact Angle(degree): 0, 20, 40, 60, 80, 100, 120, 140
Carbon # of alkyltrichlorosilane: 0, 3, 6, 9, 12, 15, 18

Other SAMs are less effective than alkyltrichlorosilanes

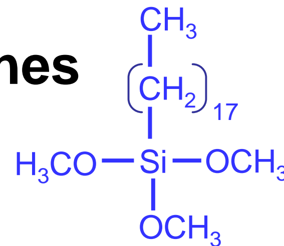
Less effective SAMs for deactivation include:



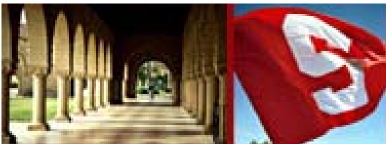
- **Bulky tail groups (including phenyl, t-butyl…)**
- **Monohalosilanes**



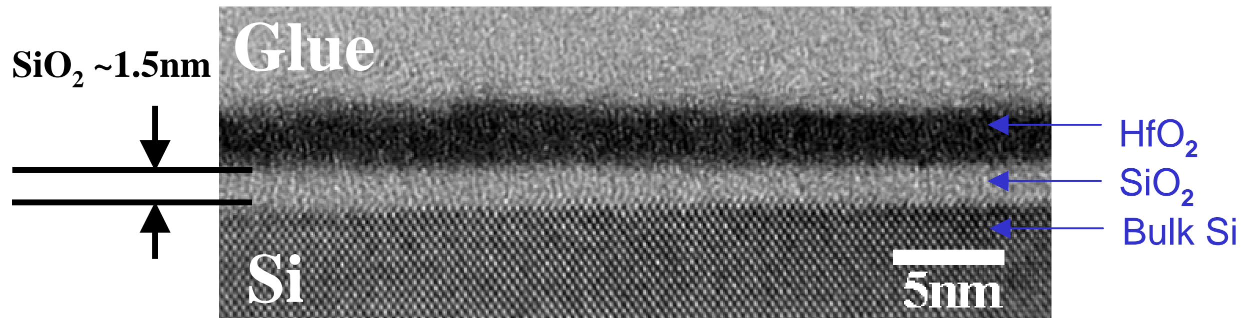
- **n-alkyltrialkoxysilanes**

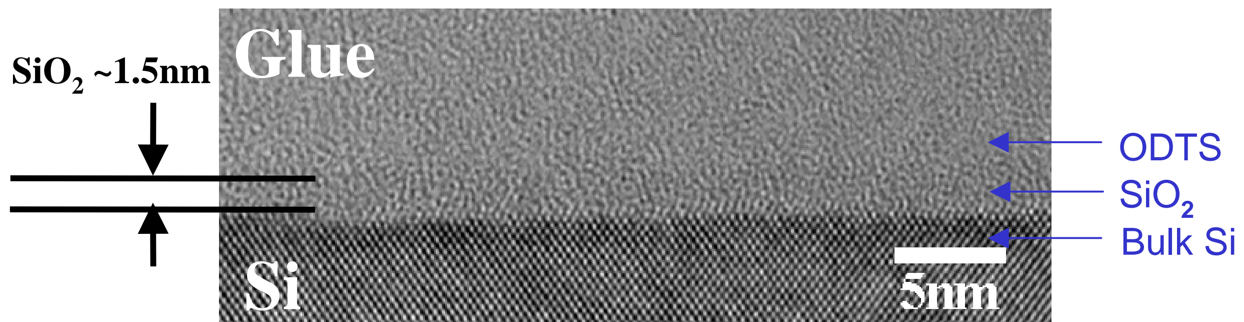


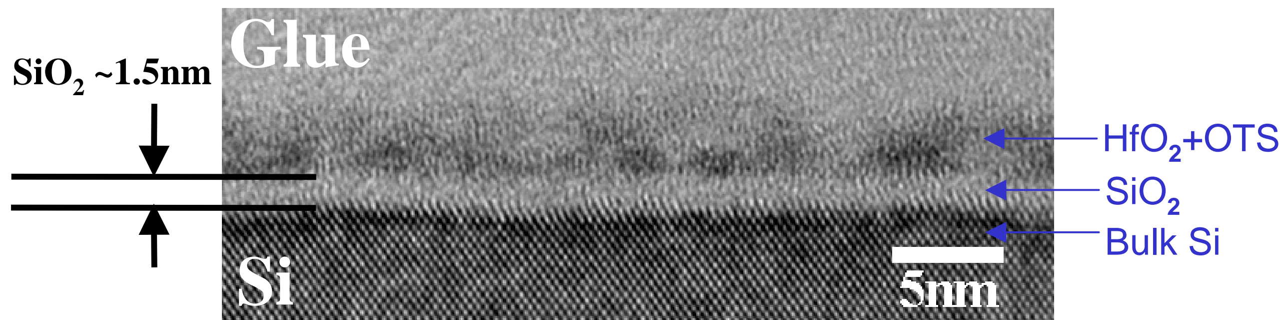
Fluorinated alkyltrichlorosilanes do exhibit good blocking

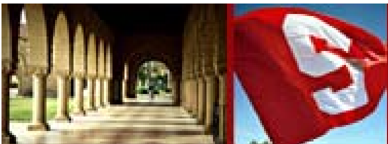


Cross-sectional TEM









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.

SUCCESSFUL

SiO_2 Surface

SiO_2 Surface

SHORT CHAIN

SiO_2 Surface

H–Cl

SiO_2 Surface

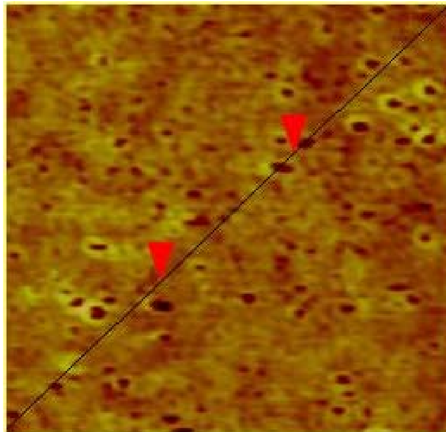
POOR PACKING

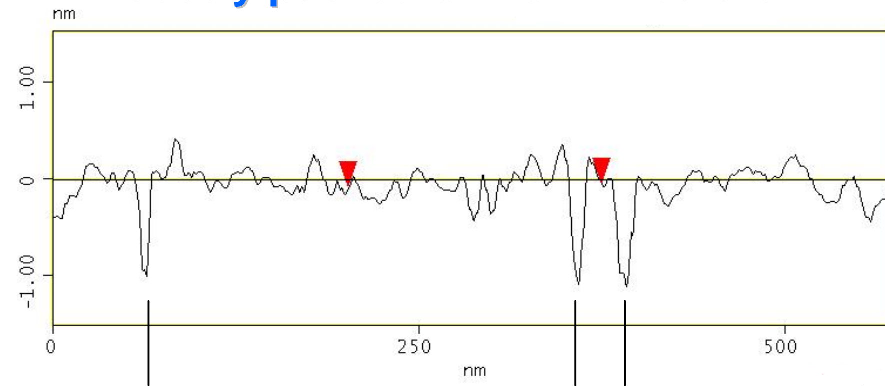
SiO_2 Surface

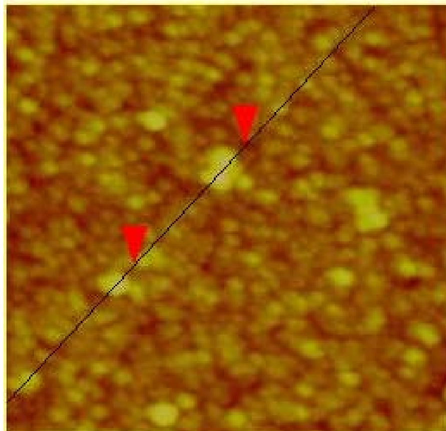
H–Cl

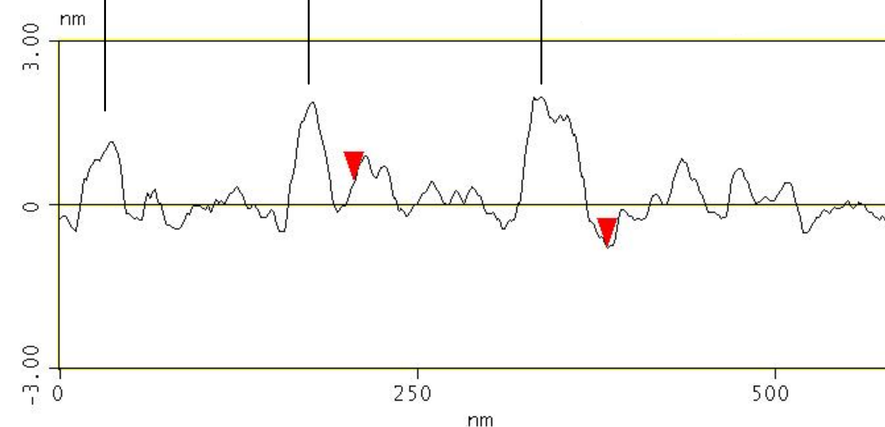
SiO_2 Surface

AFM Analysis of ODTS before & after ALD





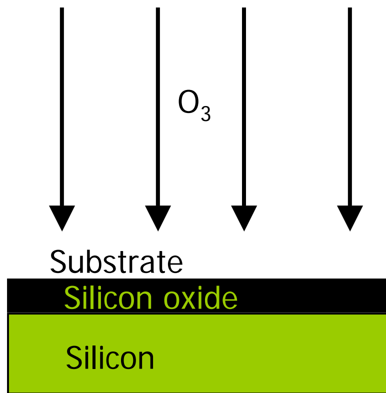


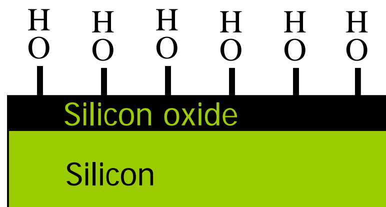


- **AFM and TEM data support the mechanistic model**

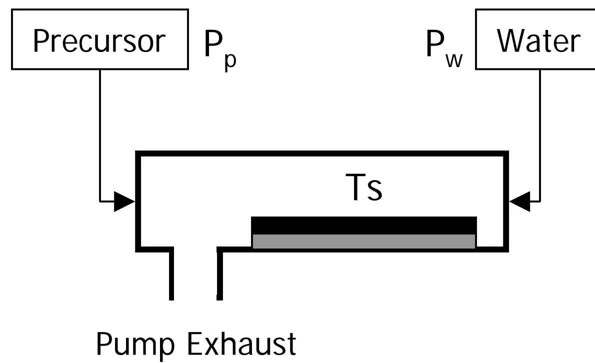
Experimental Procedure for Vapor Phase Deactivation

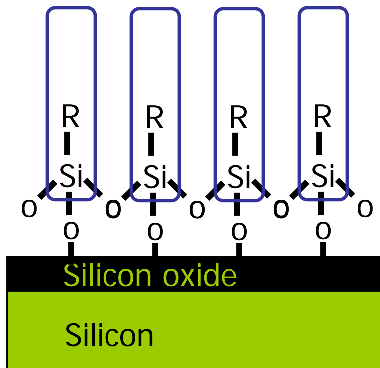
Pretreatment by ozone cleaner



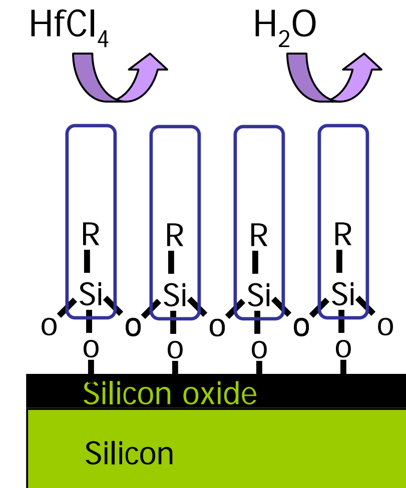


Preparation of a SAMs by CVD

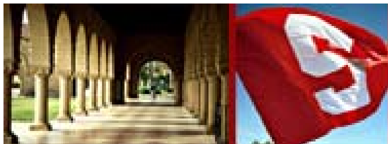




Hafnium oxide deposition by ALD



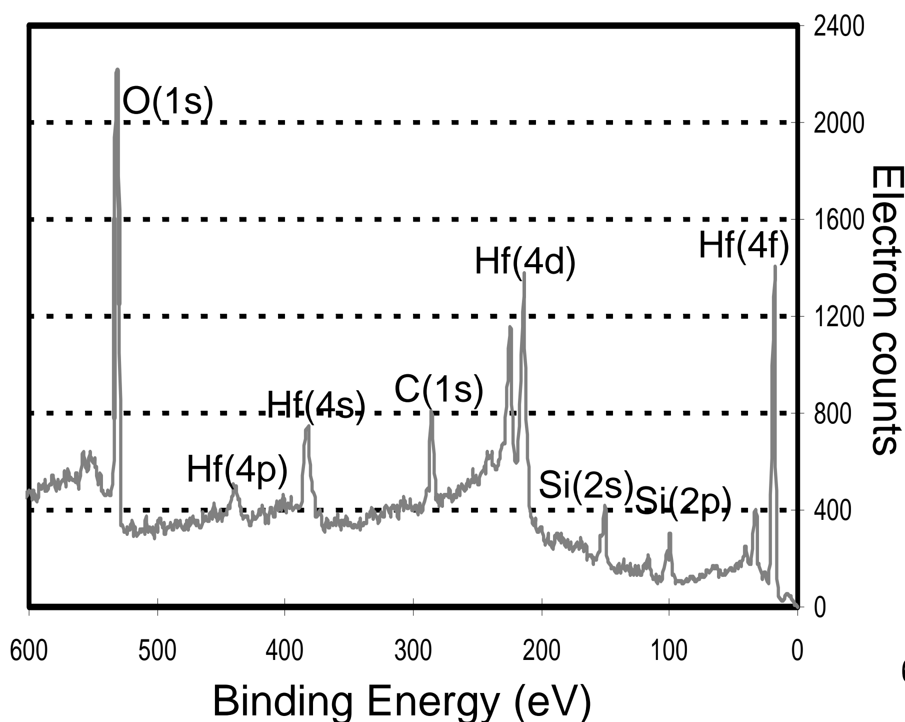
Measure film characteristics by ellipsometer, contact angle measurement



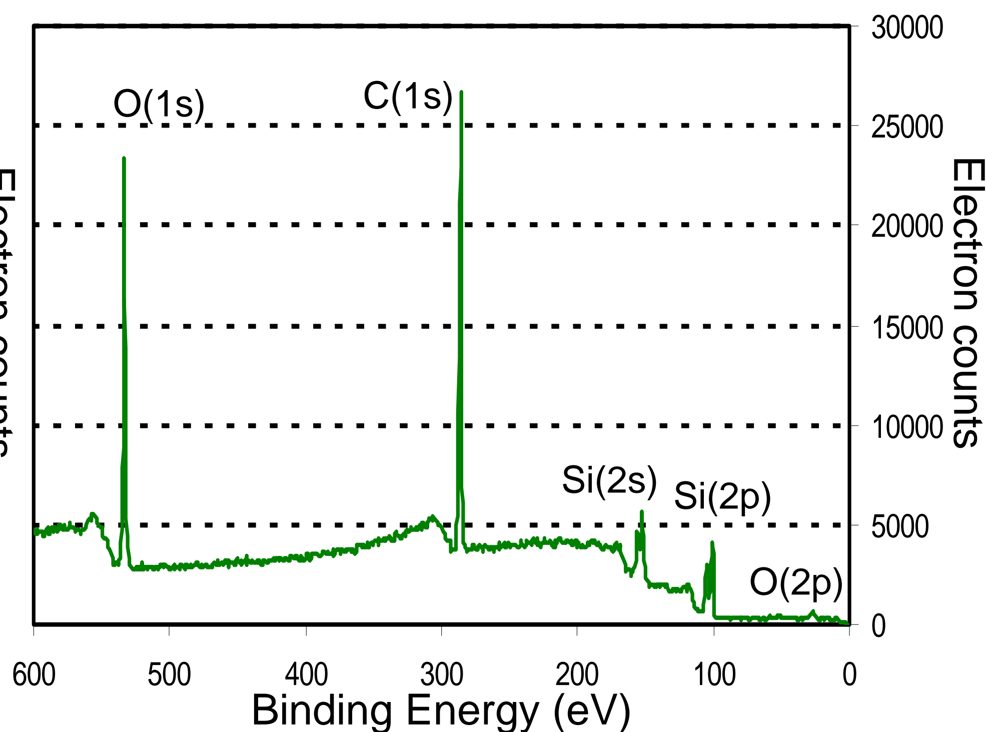
XPS after Hafnium Oxide Deposition by ALD

- Excellent deactivation also achieved with vapor delivery

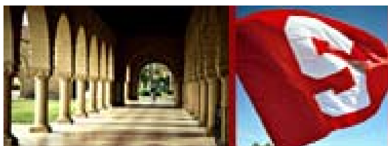
Bare Si(100) surface



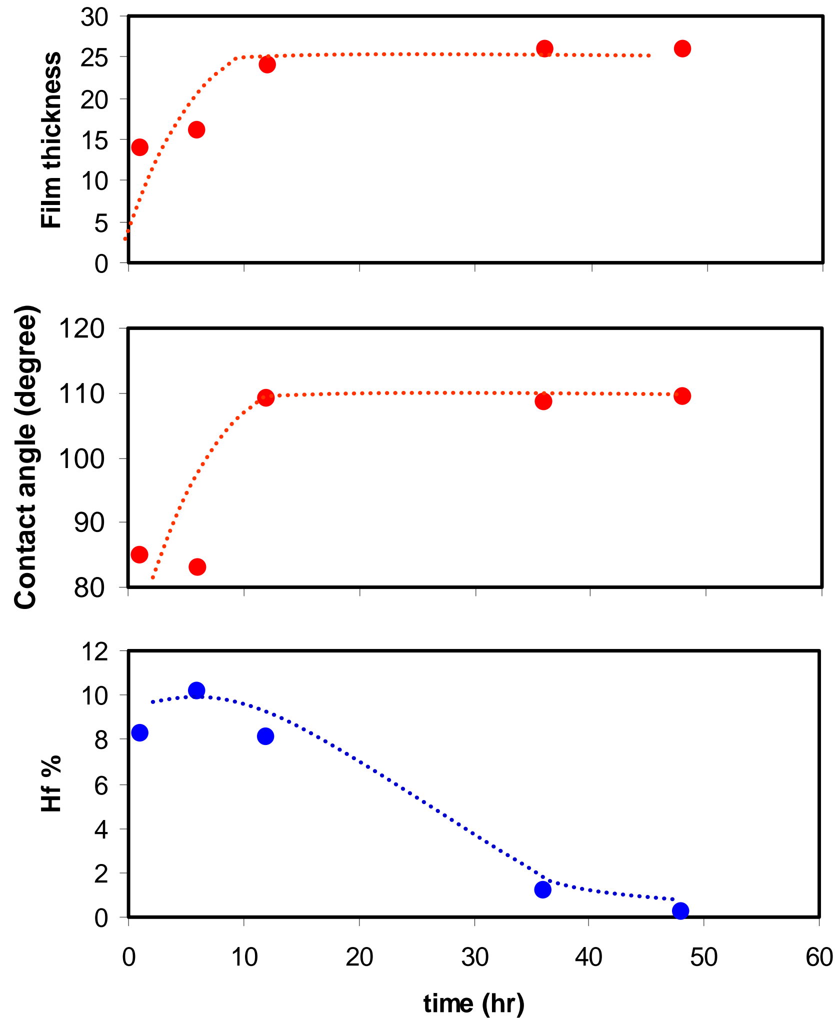
SAMs on Si(100) surface



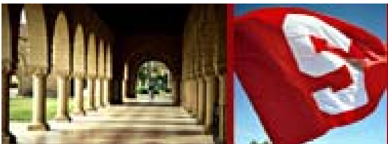
- Experimental Condition: Precursors (ODTS and water), Ts=170ºC, t=2 days



Formation of SAMs by Vapor Delivery



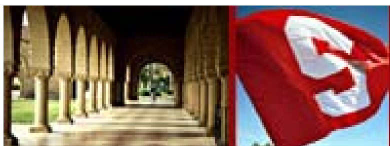
- Successful ALD resists still require long times for SAM formation from vapor phase



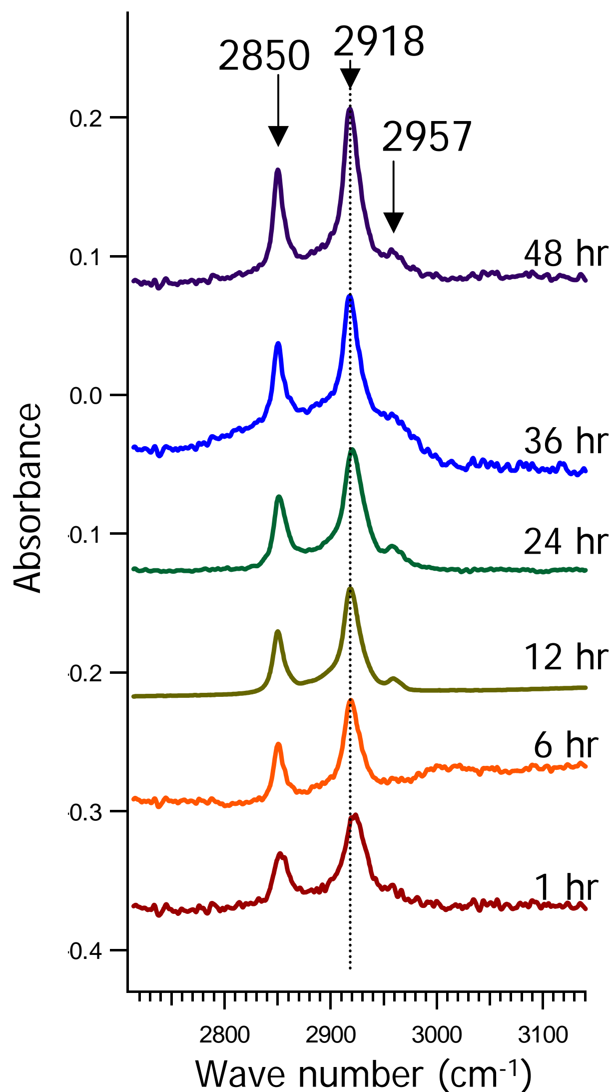
FTIR spectra of SAMs

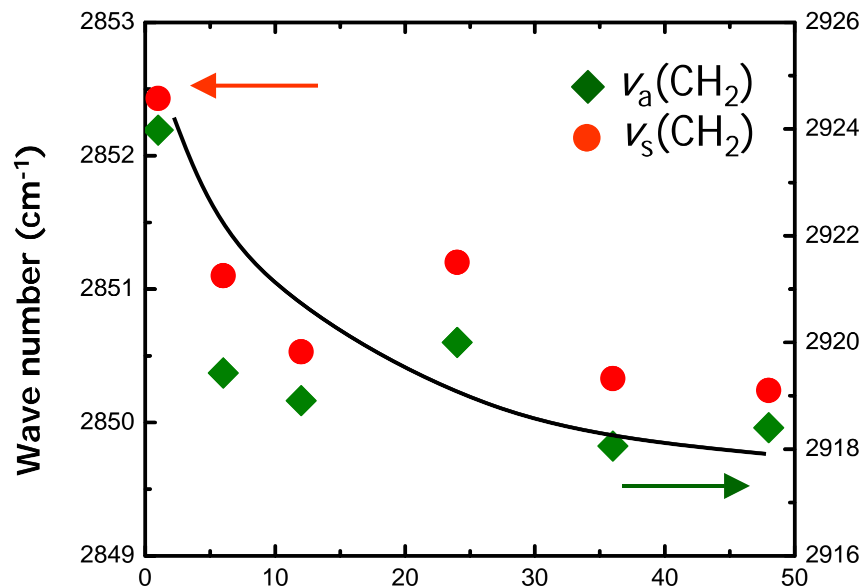
- CH_2 stretching modes are a sensitive probe of degree of order in SAMs

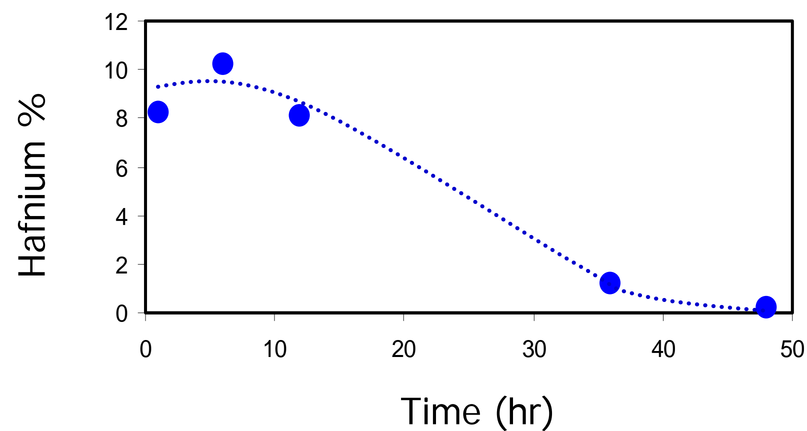
	$\nu_a(CH_2)$	$\nu_s(CH_2)$
Liquid Alkanes	2928	2856
Crystalline Alkanes	2917	2850

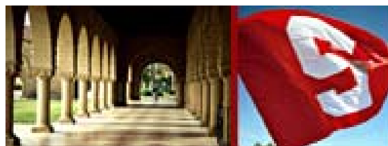


FTIR spectra of SAMs show evolution of crystallinity









Patterning Approaches for Area Selective ALD

native oxide or
thermal oxide

patterning oxide

surface
coating

µCp or MIMIC

R R R R R R

R R R R

selective attachment

direct patterning by UV,
e-beam or scanning probe

oxide layer can also
be etched away

R R R R

R R R R

surface activation
& ALD growth

ALD growth

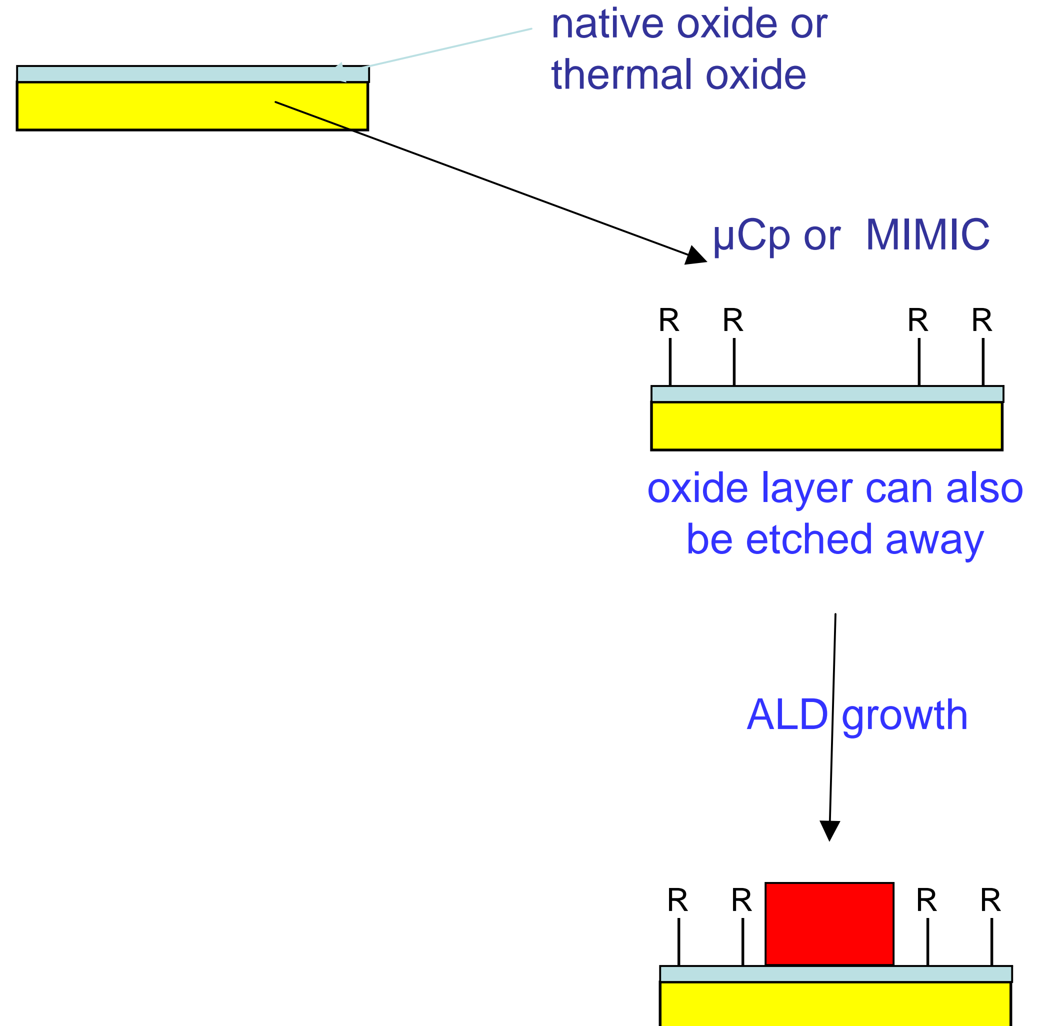
ALD growth

R R R R

R R R R

R R R R

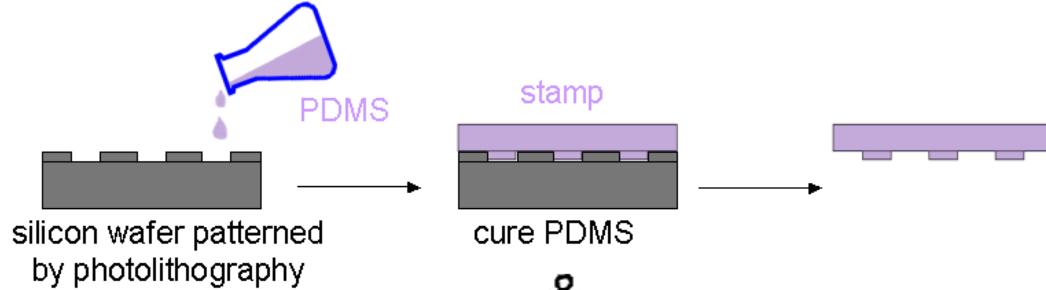
Patterning by Microcontact Printing



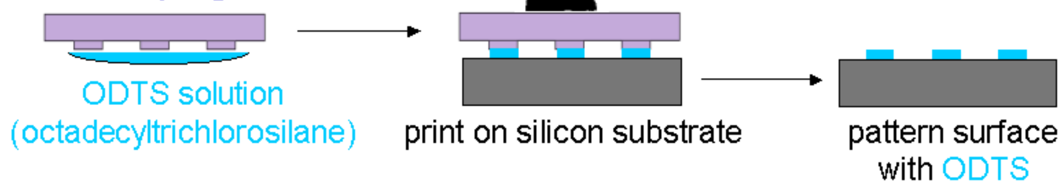
Micro-contact printing of ODTS for Area-selective ALD

Strategy:

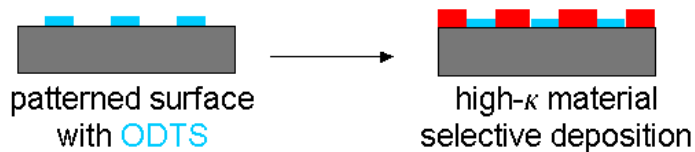
1. Making stamp



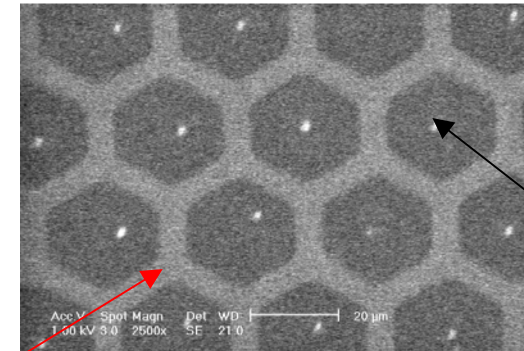
2. Stamping



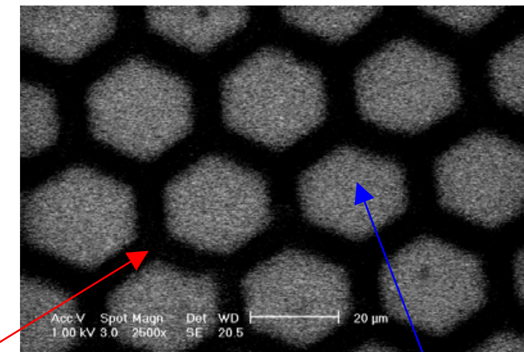
3. ALD reaction of high-κ material



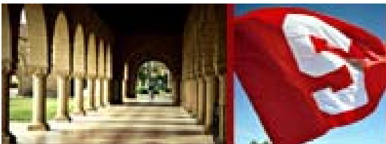
SEM image:



ODTS patterned surface before HfO_2 deposition

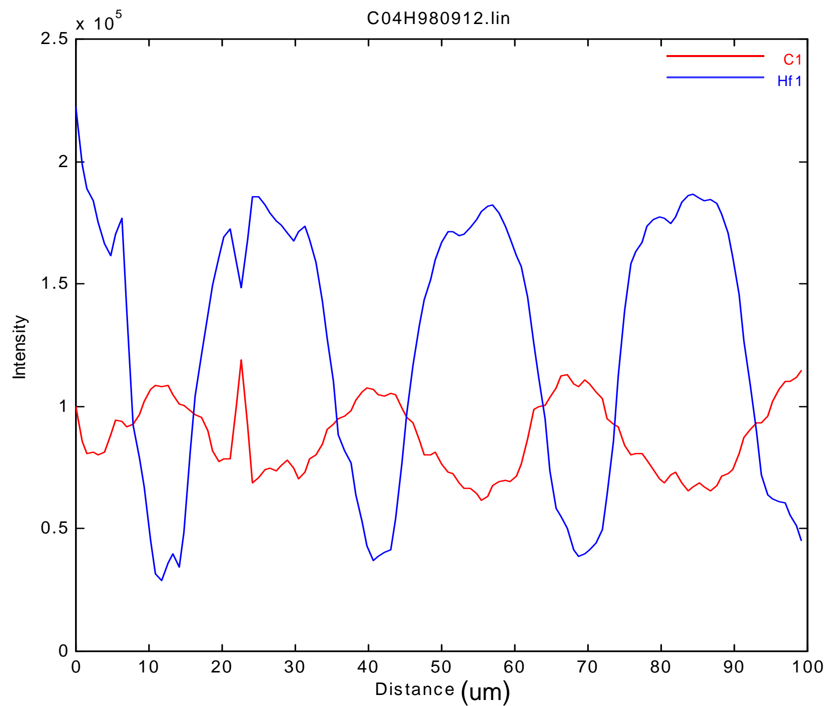


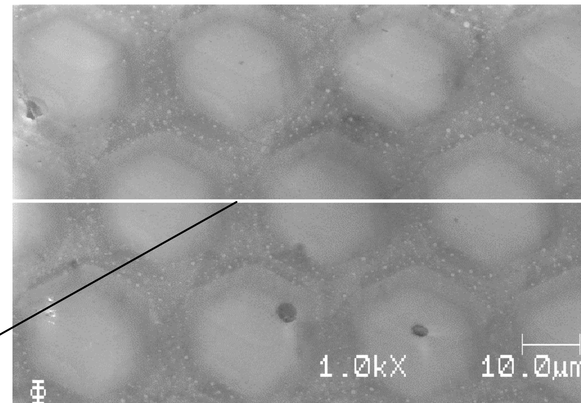
ODTS patterned surface after **HfO_2** deposition



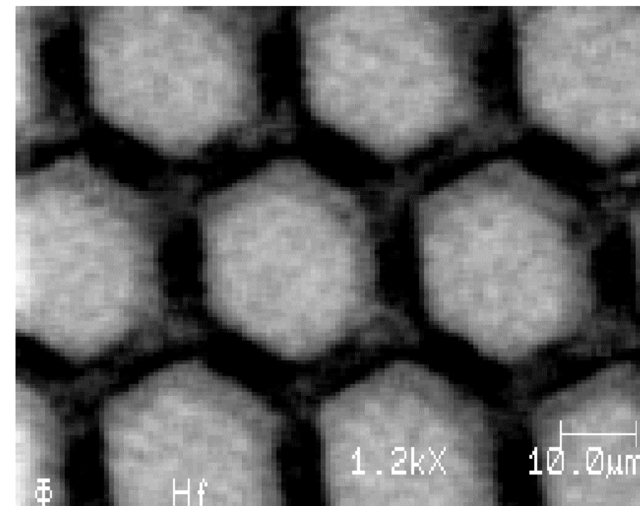
AES Analysis after ALD Process

Auger Line Scan

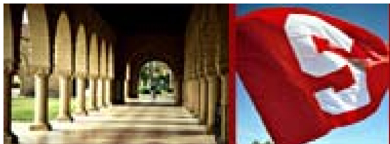




Hf Auger Mapping



Data: Charles Evans & Associates



Oxide Patterning

native oxide or
thermal oxide

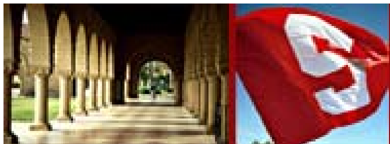
patterning oxide

selective attachment

R R R R

surface activation
& ALD growth

R R R R



Selectivity on Patterned Silicon Oxide

patterned oxide

OH OH H H OH OH

selective protection

Cl-Si-Cl
Cl

H H

activation of Si-H site &

ALD growth

HfO_2

patterned oxide

OH OH H H OH OH

1-Alkene selective attachment

OH OH OH OH

ALD growth

HfO_2 HfO_2

Area-Selective ALD on Patterned Oxide Sample

Gate
Source
Drain
Substrate

thermal oxide growth

spin on photoresist

photo patterning and development

HF etching oxide

strip off photoresist

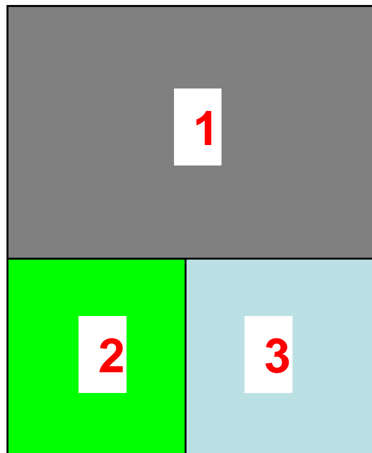
deactivating agents selective attachment

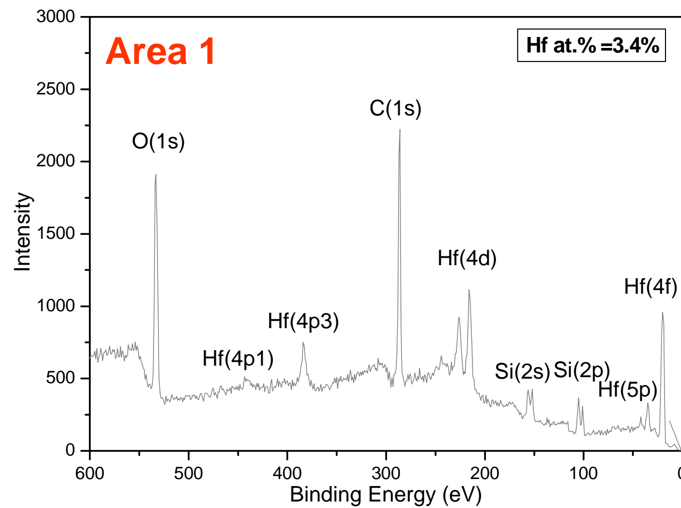
high-κ material selective deposition by ALD process

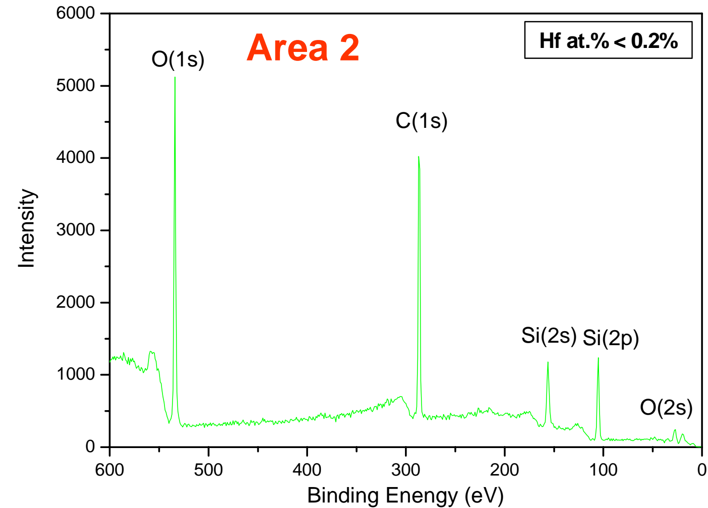
XPS Analysis on Patterned Oxide Sample after ALD

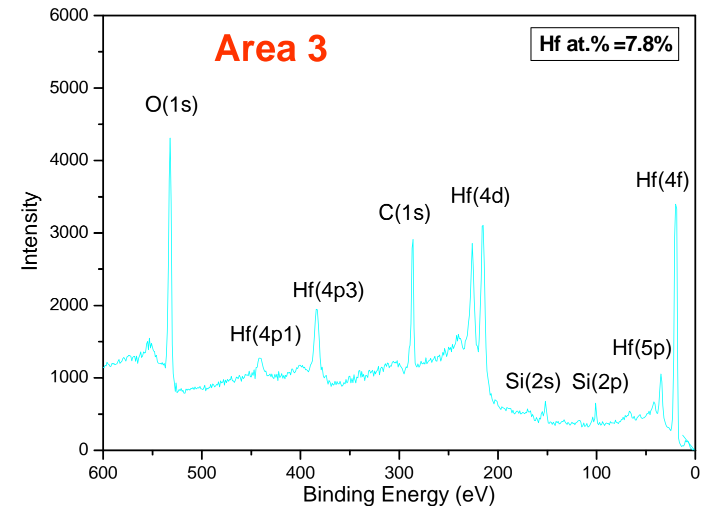
Samples for Area-Selective ALD

150μm diameter
X-ray beam

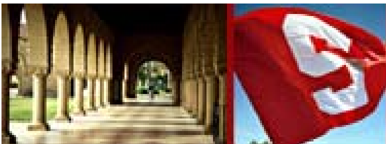






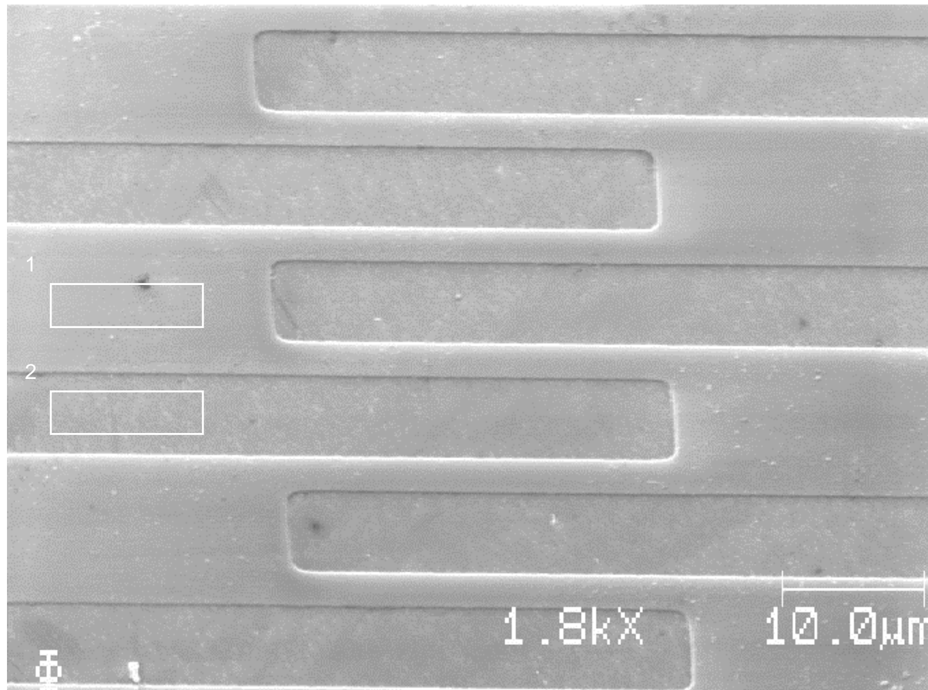


1. **Photolithography-patterned area**
2. **Blanket SiO_2 region coated with ODTS**
3. **Blanket Si-H region reference part**

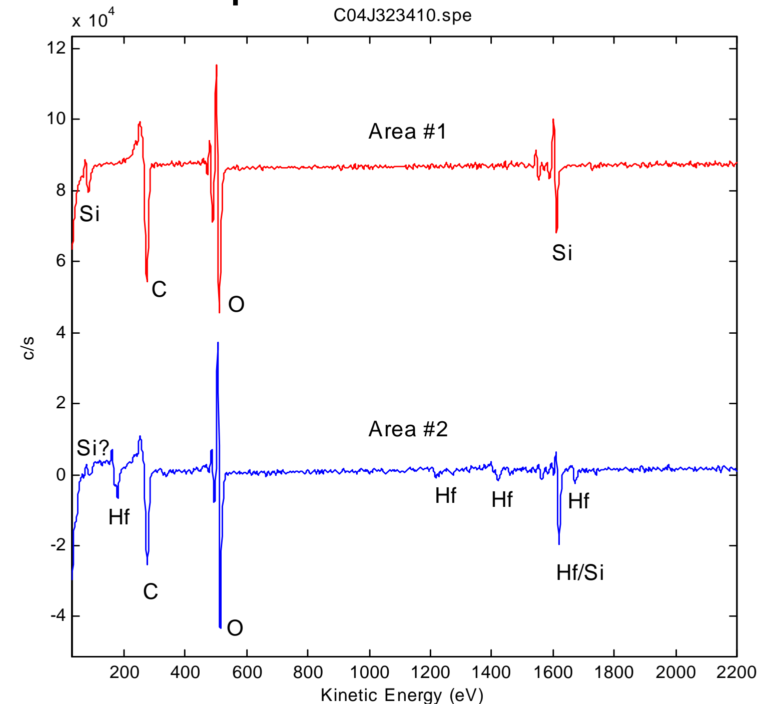


SEM Image on Patterned Oxide & AES Survey Spectra

SEM image on patterned area

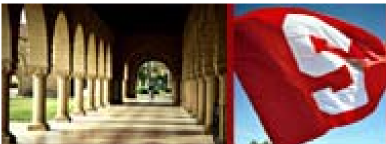


Auger survey spectra on patterned area



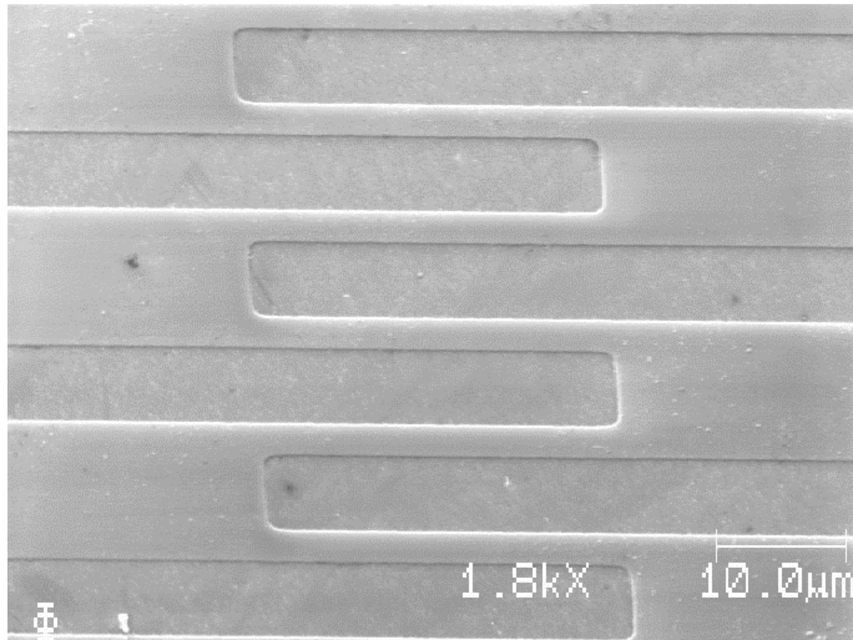
1. Thermal oxide coated with ODTS
2. Activated region for HfO_2 ALD process

Data: Charles Evans & Associates

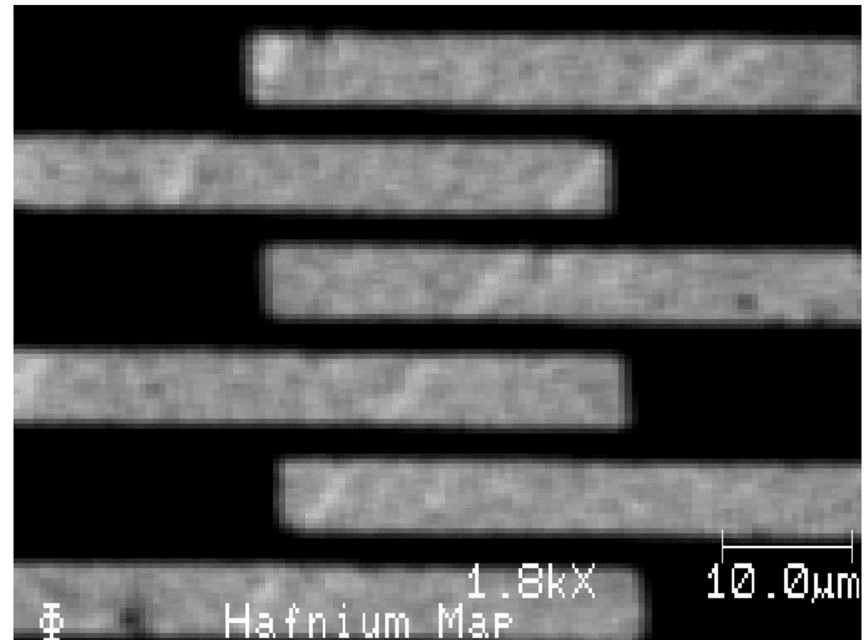


SEM Image vs. Hafnium Elemental Mapping

SEM image on patterned area



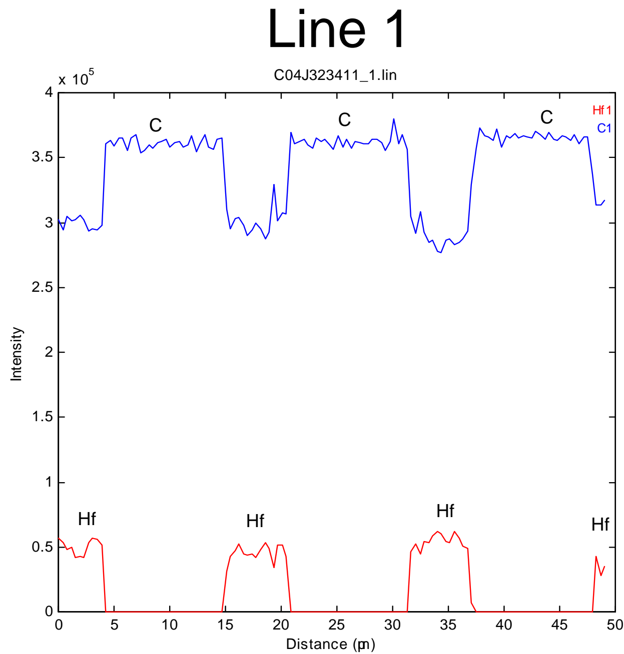
Hafnium elemental mapping on patterned area

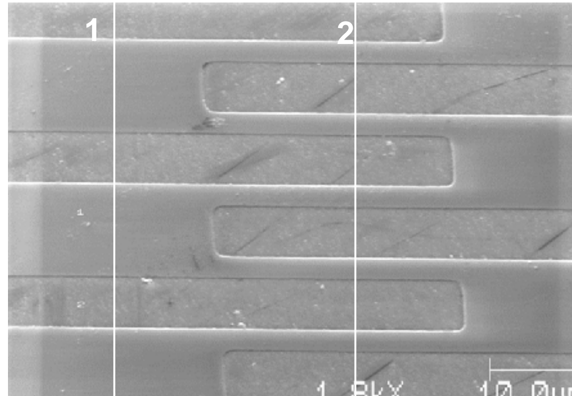


Data: Charles Evans & Associates

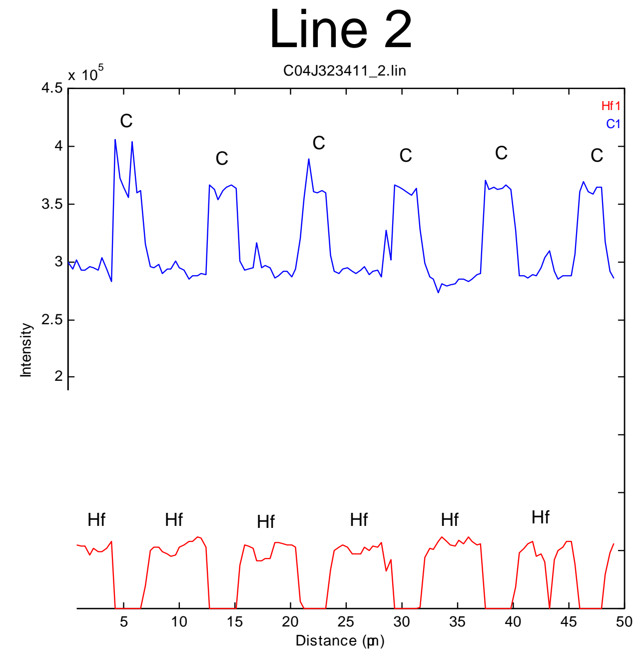
SEM Image: Defined Lines for Line-Scan

Line 1

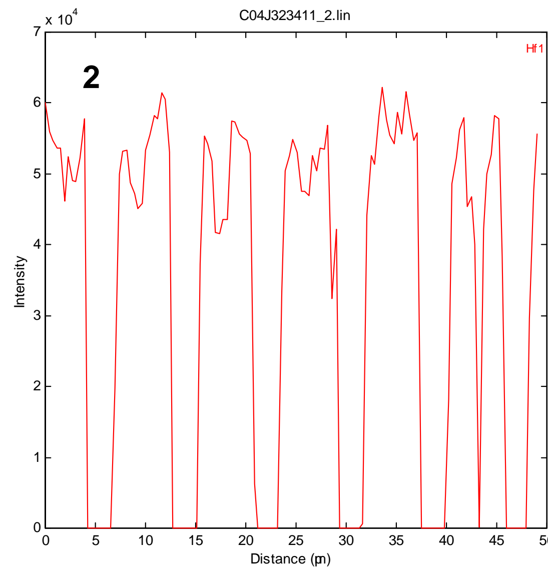




Line 2



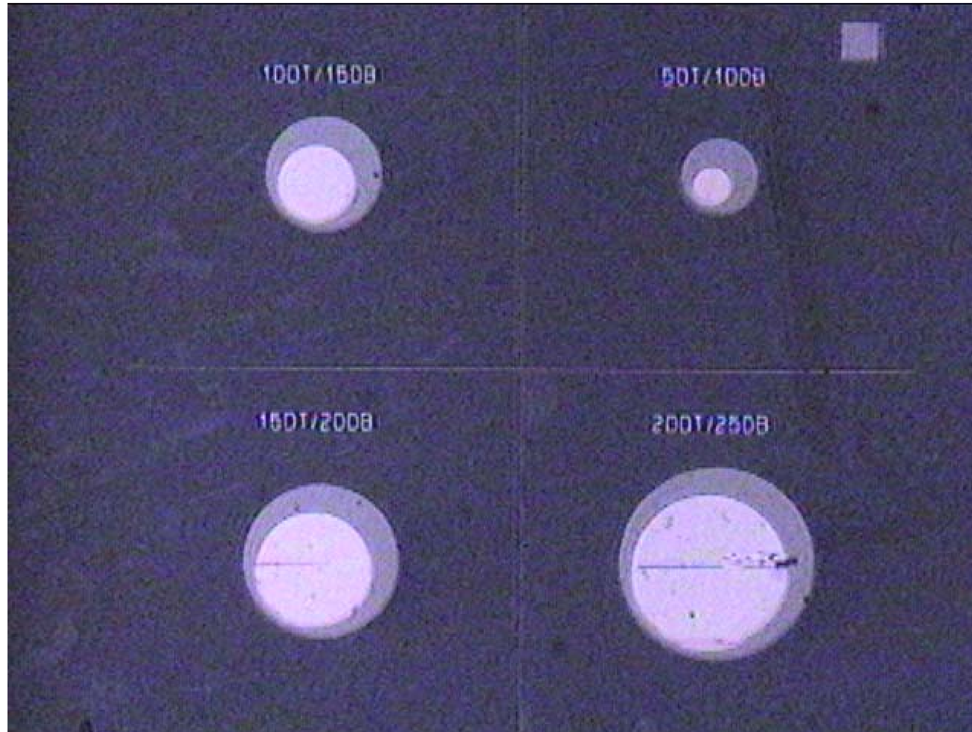
Line scan, Area 2: Intensity vs. Distance, Hf only

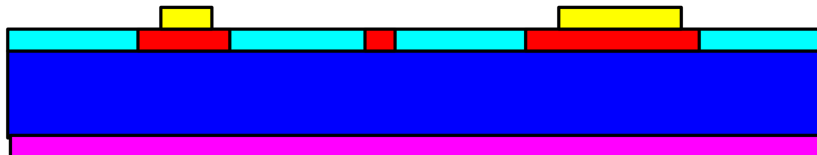


ta: Charles Evans & Associates

Initiation of Electrical Measurements

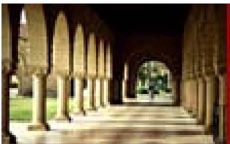
Optical micrograph of capacitor structures:



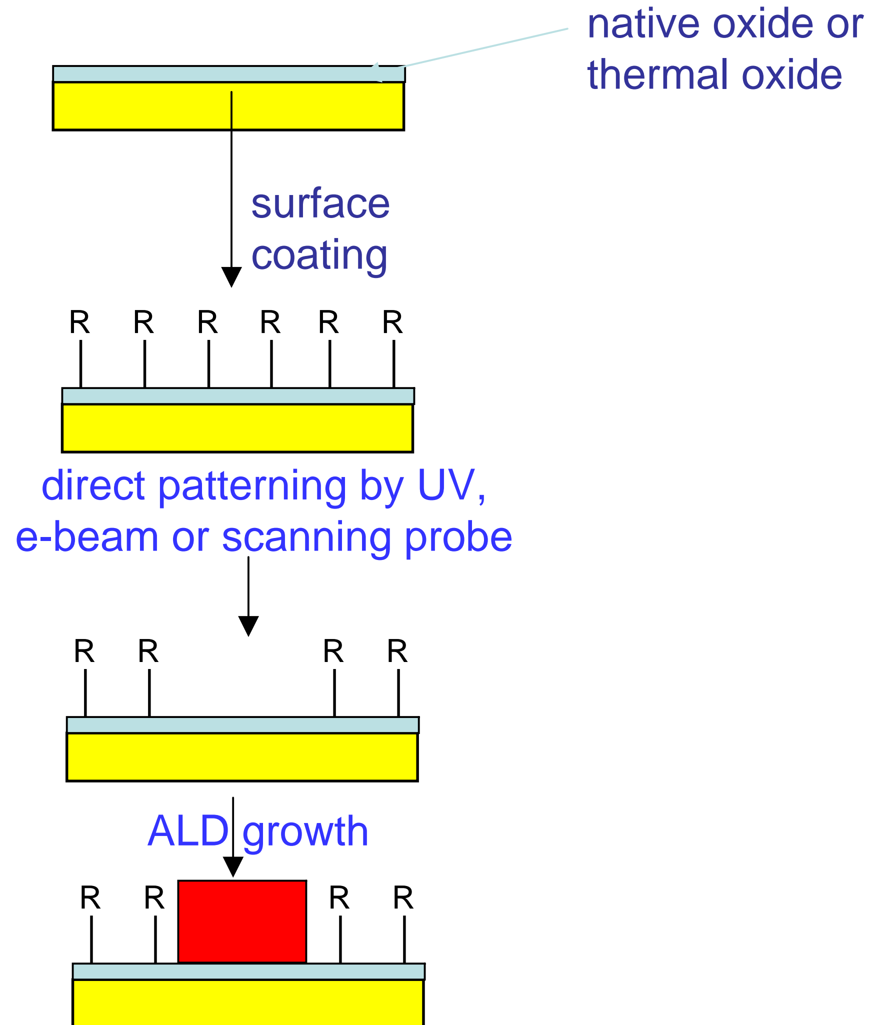


Capacitor structures fabricated

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



Direct e-Beam or UV Patterning

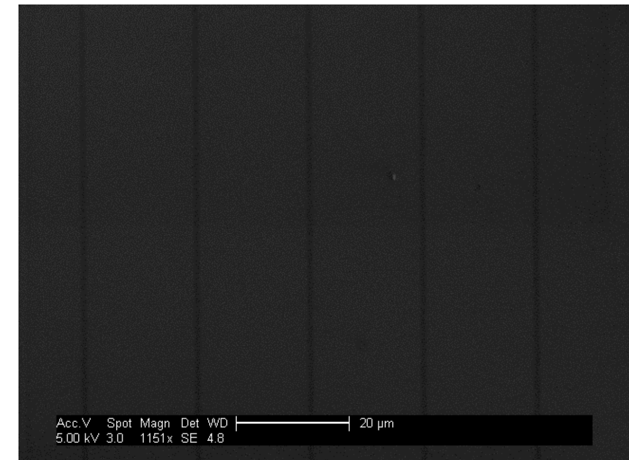


E-Beam Patterning of ODTS/SiO_2

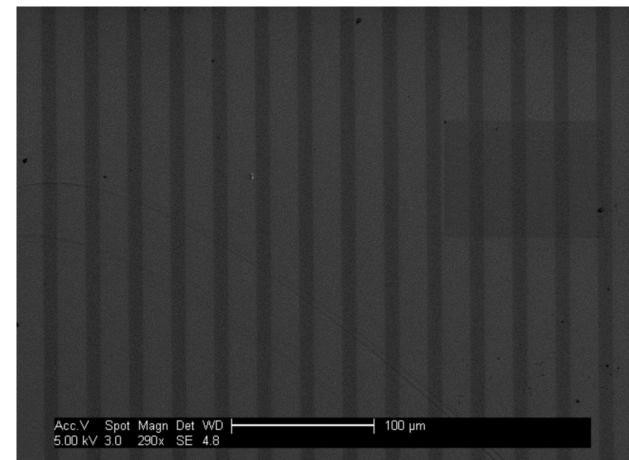
SiO_2 + ODTS

- **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***

Hemanth Jagannathan

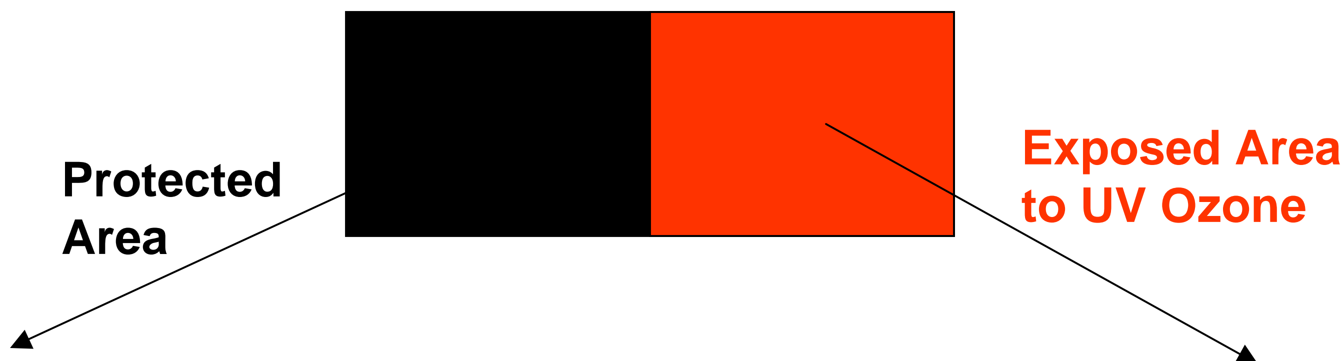


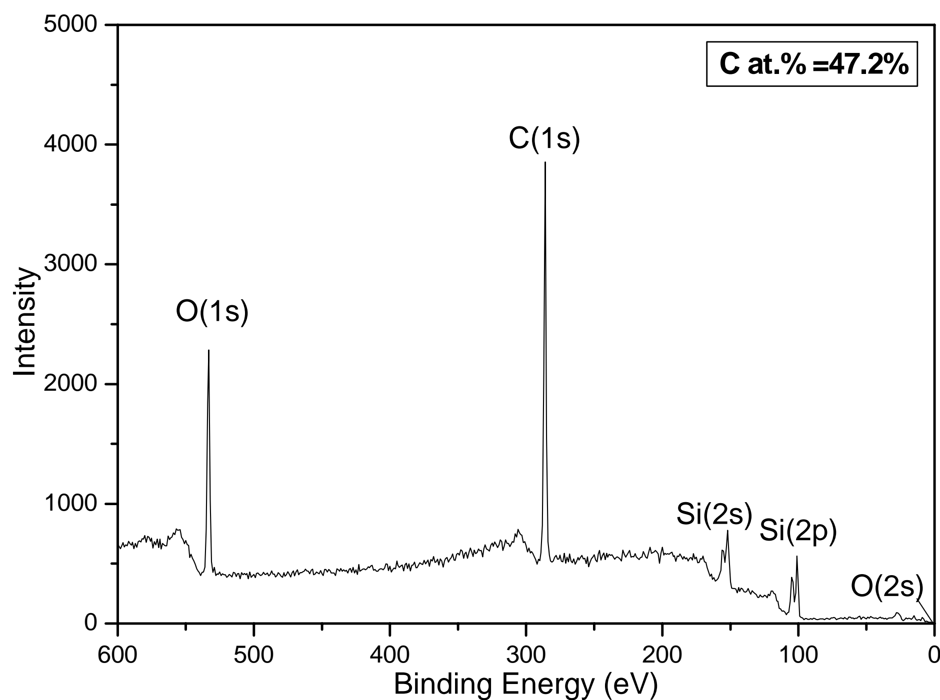
1 *μ*m lines

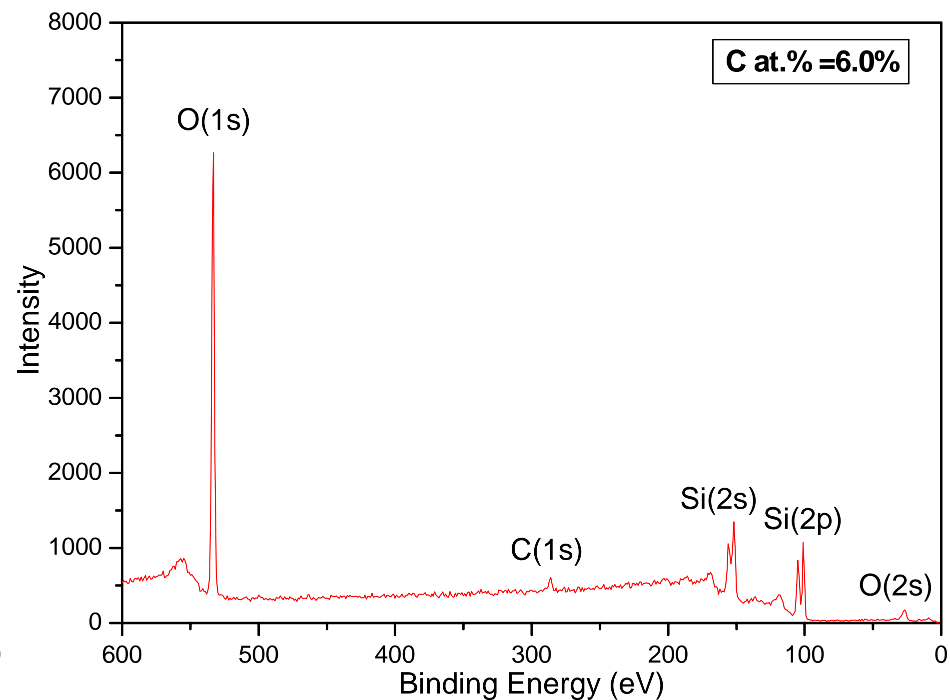


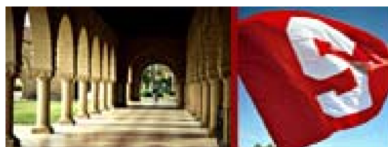
10 *μ*m lines

UV Ozone Direct Exposure on ODTS for Area-selective ALD





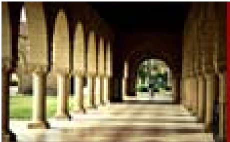




Summary and Acknowledgments

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-κ growth
- Exploration of other substrates (e.g. nitride)
- Investigation of high-κ / substrate interfacial properties
- Study of ALD mechanisms

Acknowledgments

Funding

Center for Environmentally Benign Semiconductor Manufacturing

Facilities