Selective Surface Preparation and Templated Atomic Layer Flim Deposition

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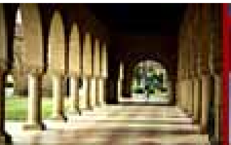
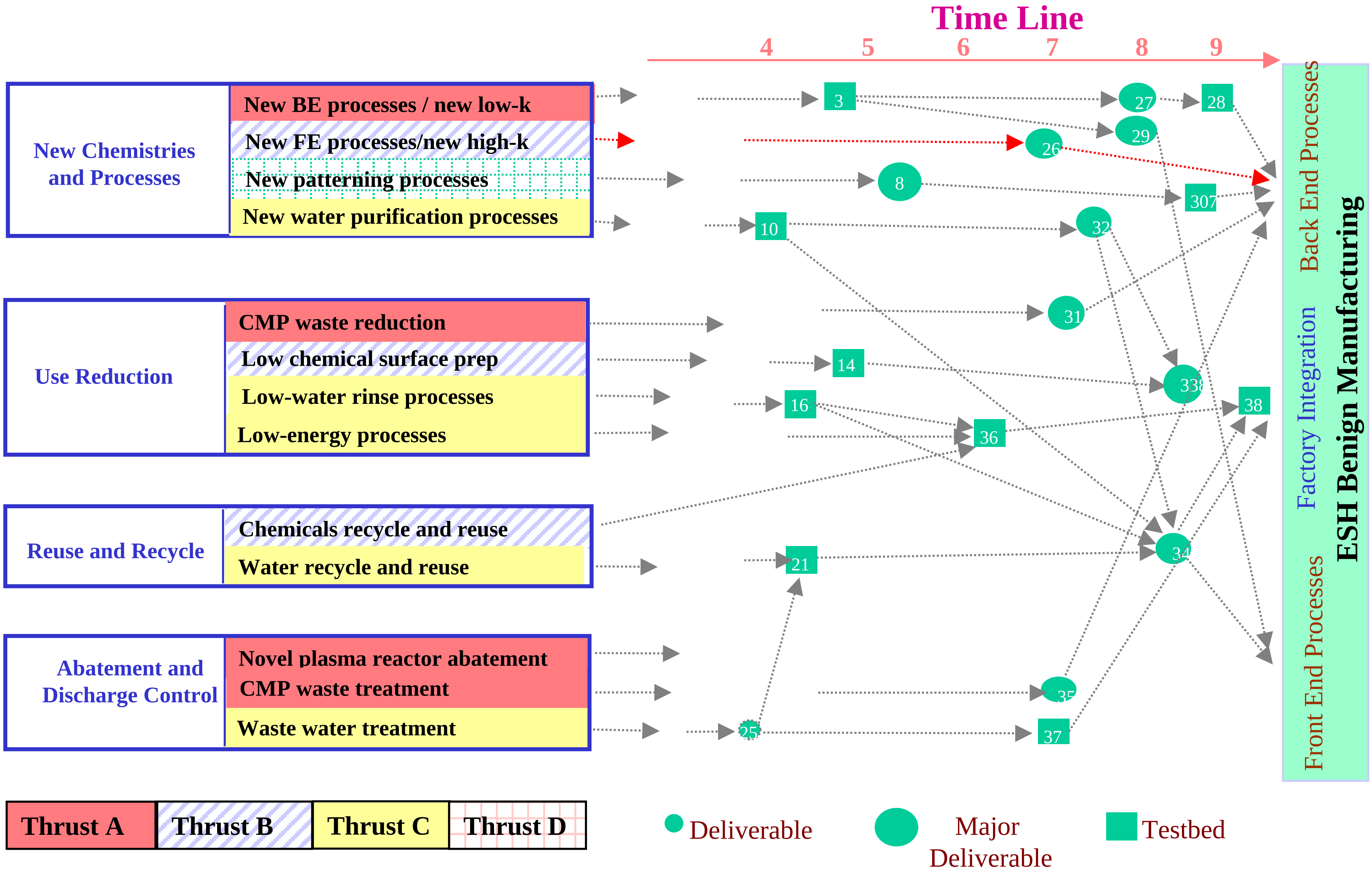
2003-12-11 Tele-seminar



Strategic Plan (Task B-2)



New Chemistries and Processes
- New BE processes / new low-k
- New FE processes/new high-k
- New patterning processes
- New water purification processes

Use Reduction
- CMP waste reduction
- Low chemical surface prep
- Low-water rinse processes
- Low-energy processes

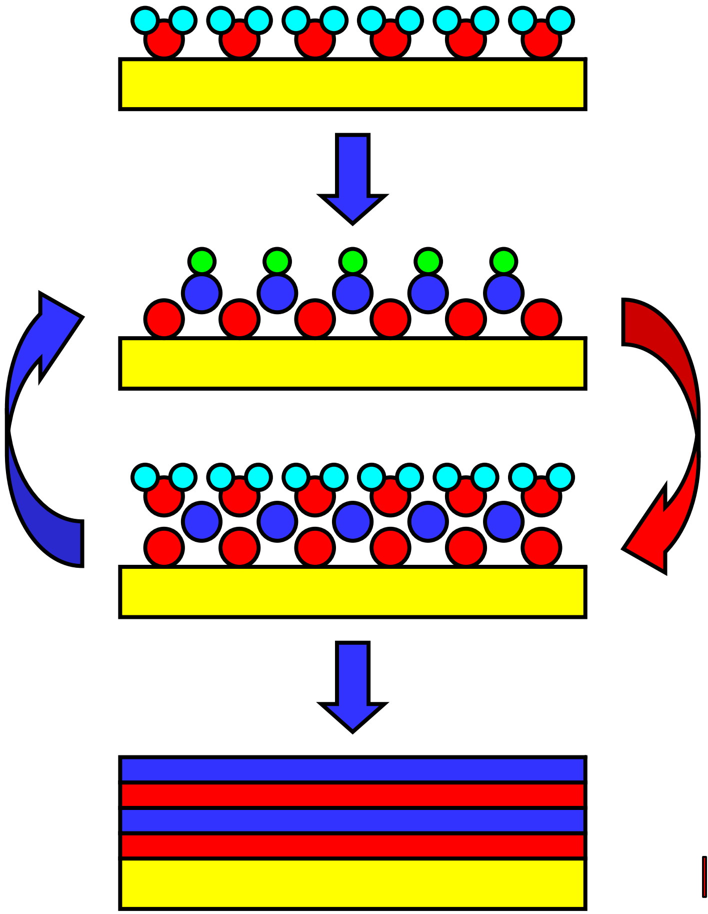
Reuse and Recycle
- Chemicals recycle and reuse
- Water recycle and reuse

Abatement and Discharge Control
- Novel plasma reactor abatement
- CMP waste treatment
- Waste water treatment

Thrust A | **Thrust B** | **Thrust C** | **Thrust D**

● Deliverable ● Major Deliverable 🟩 Testbed

Surface Functional Groups Control ALD

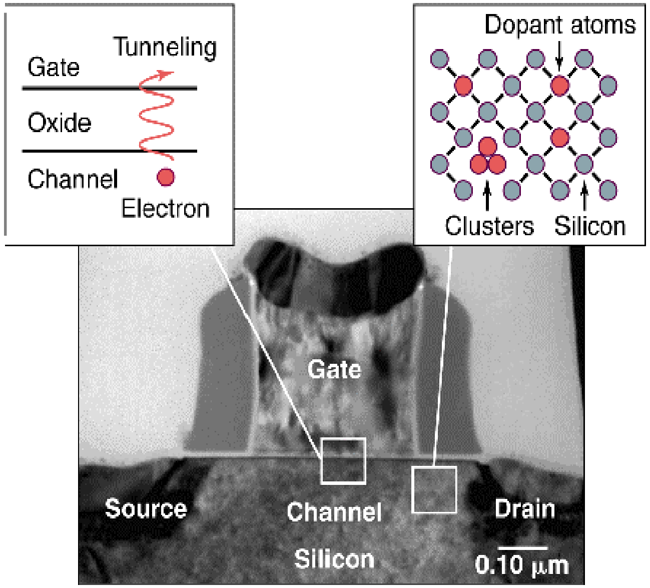


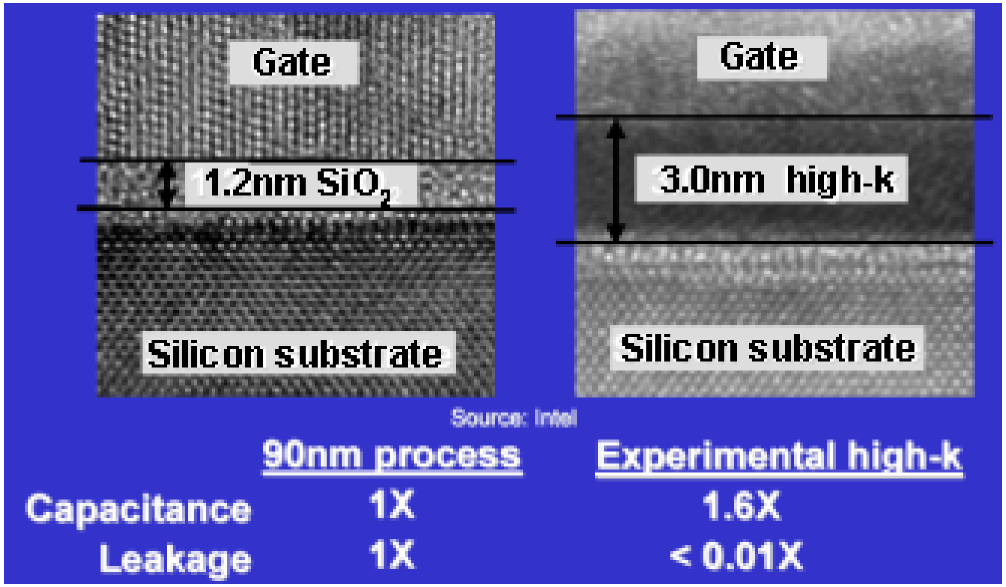
ALD process based upon chemical reaction between the precursors and the film surface.

The reactions depend on the specific reactive functional groups present at the surface.

➡ Manipulate these surface groups to control the ALD process

The Need for High-κ Dielectric Materials





	90nm process	Experimental high-k
Capacitance	1X	1.6X
Leakage	1X	< 0.01X

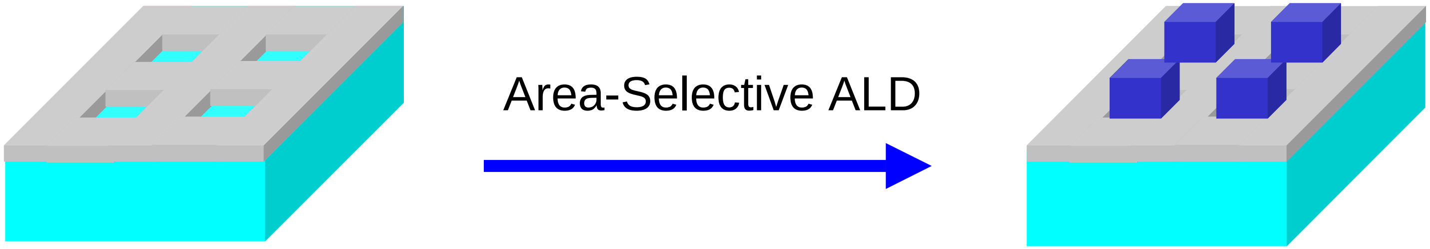
P.A. Packan, Science, 1999

Source: Intel

Capacitance $\propto \frac{\kappa}{t}$

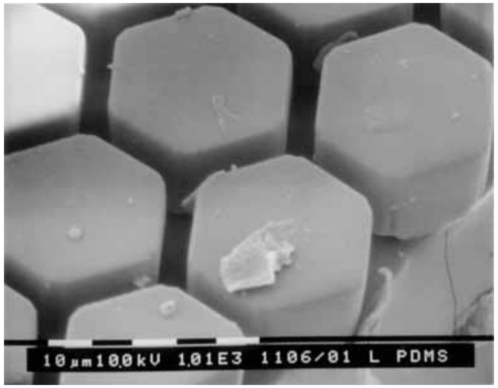
- The scaling of metal-oxide-semiconductor (MOS) devices to sub-nanometer feature sizes requires **thin gate insulators**.
- **Leakage current** caused by **electron tunneling** increases exponentially with decreasing dielectrics thickness.
- Using high-κ materials allows deposition of thick films with an effective thickness equivalent to thin SiO_2 films.
- HfO_2 and ZrO_2 are promising candidates for future gate dielectrics

Generate 3-D Pattern from 2-D Template

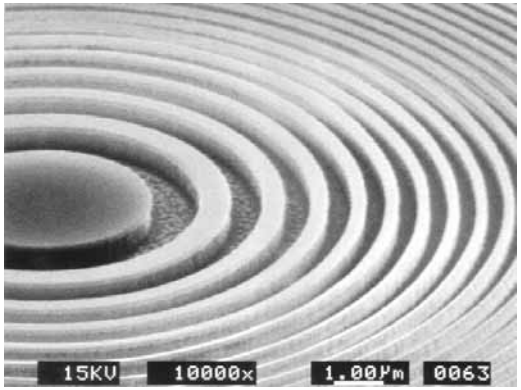


Area-Selective ALD

Microcontact
printing

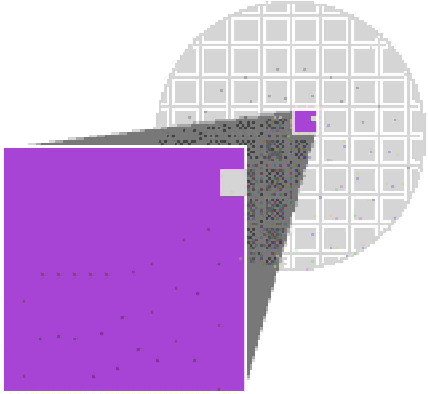


E-beam lithography
(direct writing)



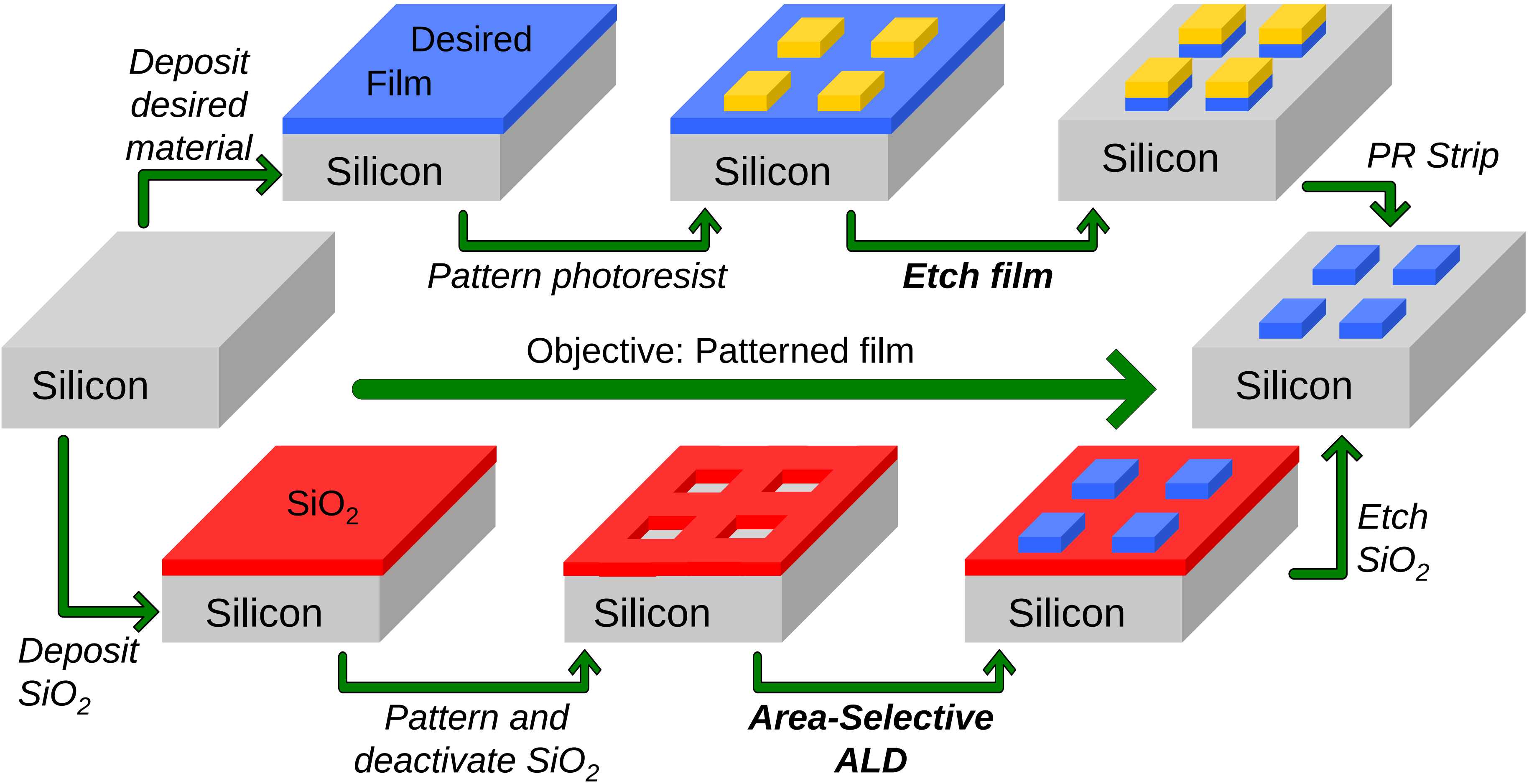
Source: Paul Scherrer Institut

Photolithography
patterned SiO_2/Si



Source: Intel

Additive vs. Subtractive Patterning

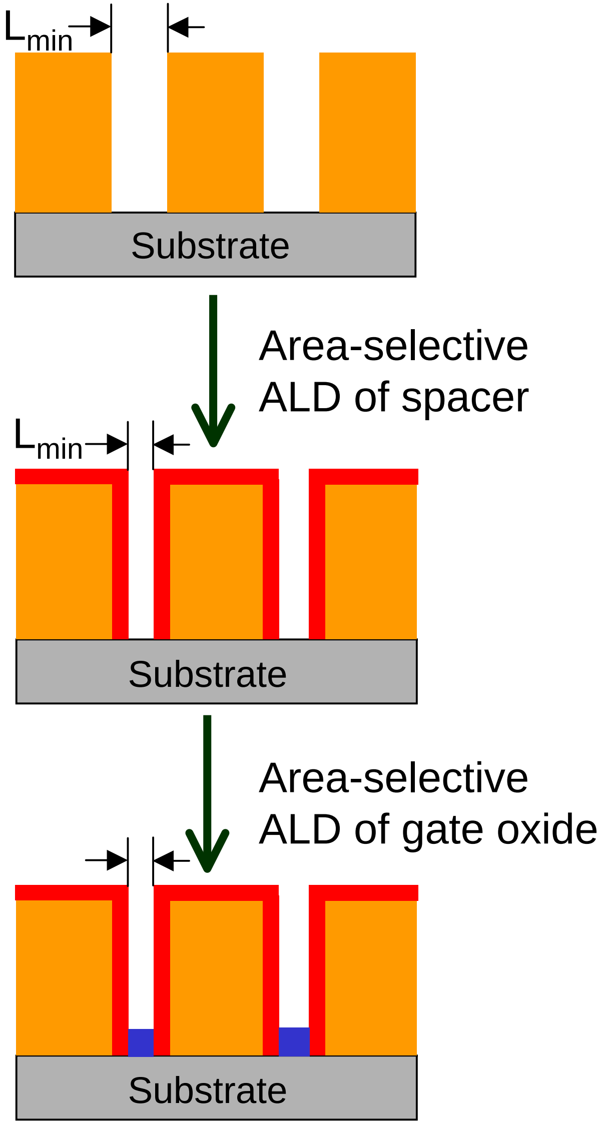


Advantages of additive patterning:

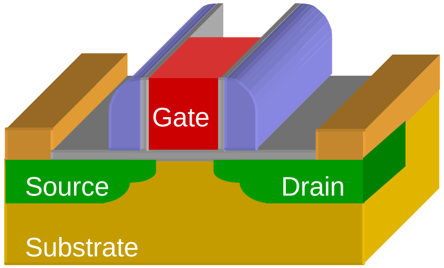
- Avoid difficult etch step
- Deposit material only where desired → cheaper, no residual contamination

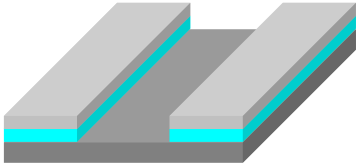
Possible Applications of Area-Selective ALD

- **Self-aligned gate stack**
  - Deposit high-κ dielectric and metal gate by ALD.
  - Avoid high-κ etch
  - Avoid possible contamination
  - Proposed process sequence is self-aligned with respect to gate dielectric and metal.
- **Feature size reduction**
  - Selective deposition over mask
  - Precise dimensional control
- **Deposition of expensive materials**
- **Patterning of materials difficult to etch**

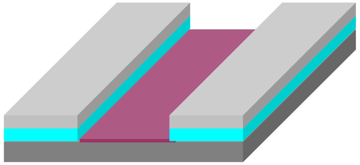


Process Flow for Area-Selective ALD

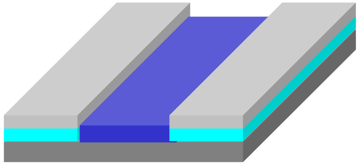




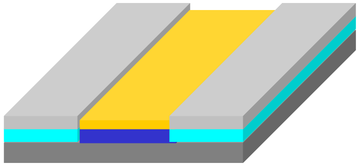
patterned and protected surface



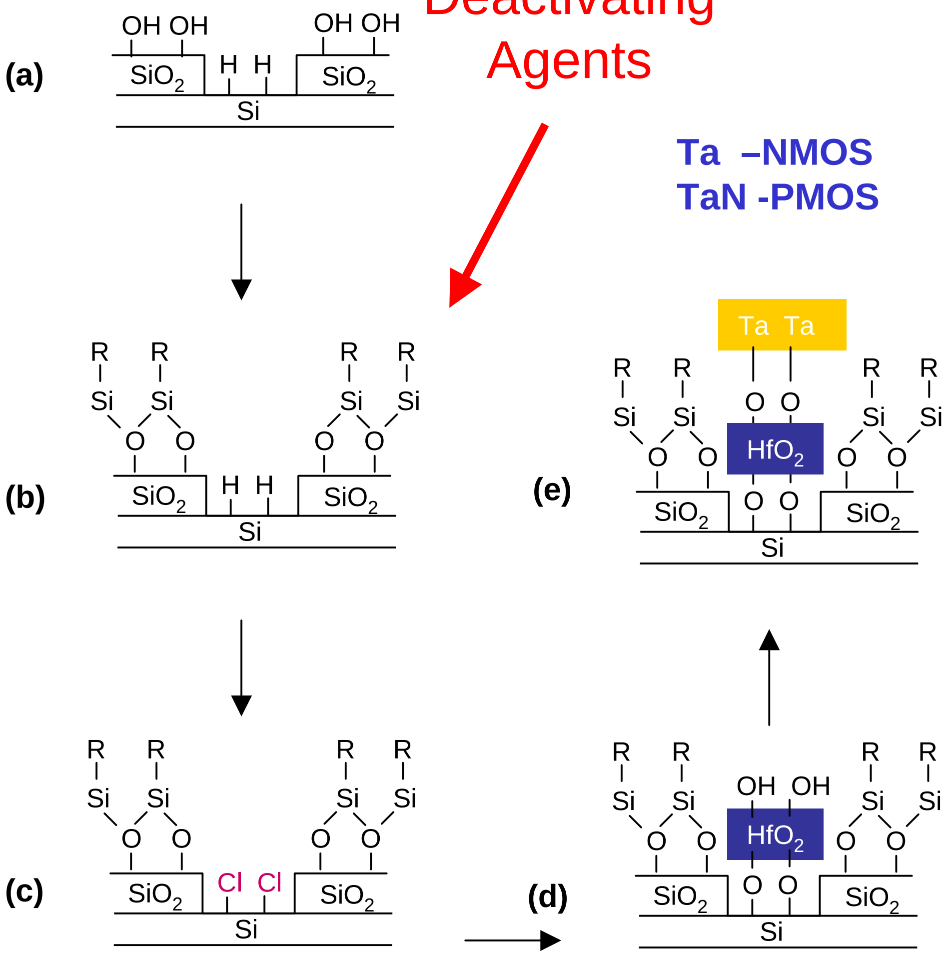
surface activation



high-κ material ALD deposition



metal gate ALD deposition



Deactivating Agents

Ta –NMOS
TaN -PMOS

Requirements for Area Selective ALD

- **Fundamental**
  - *Deactivate* surfaces to prevent growth
  - *Activate* surfaces where growth is desired
- **Process Integration**
  - *Selective deposition* **or** *patterning* of activating/deactivating agents
    - Compatible with front-end processes
  - *Etching* of deactivating agents
    - No residual contamination
    - No damage to substrate/deposited films
  - Activation agents must provide excellent interface
    - No contamination, trapped charge, etc.
  - Prevent incorporation of deactivating agents into growing film along interfaces (esp. sidewalls)

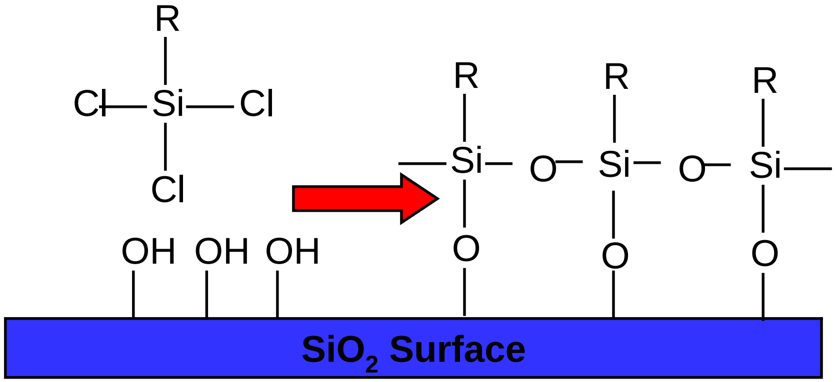
Deactivation of SiO_2

Good deactivating agents should have:

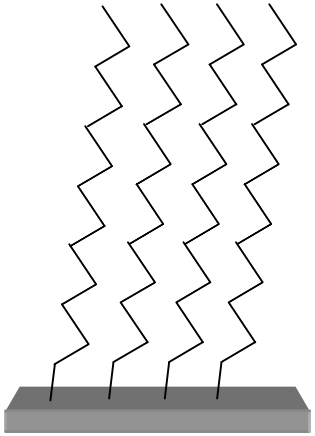
- High reactivity with surface Si-OH group
- Selectivity toward Si-OH over Si-H
- Stability at ALD temperature
- No reaction or competition with ALD precursors
- Ease of integration into process

- Self-assembled monolayers (SAMs) have been investigated for a few decades.

- We are exploring the use of a series of different length silylating organic molecules as the deactivating agents through both solution and gas phase delivery.



silylating reactions



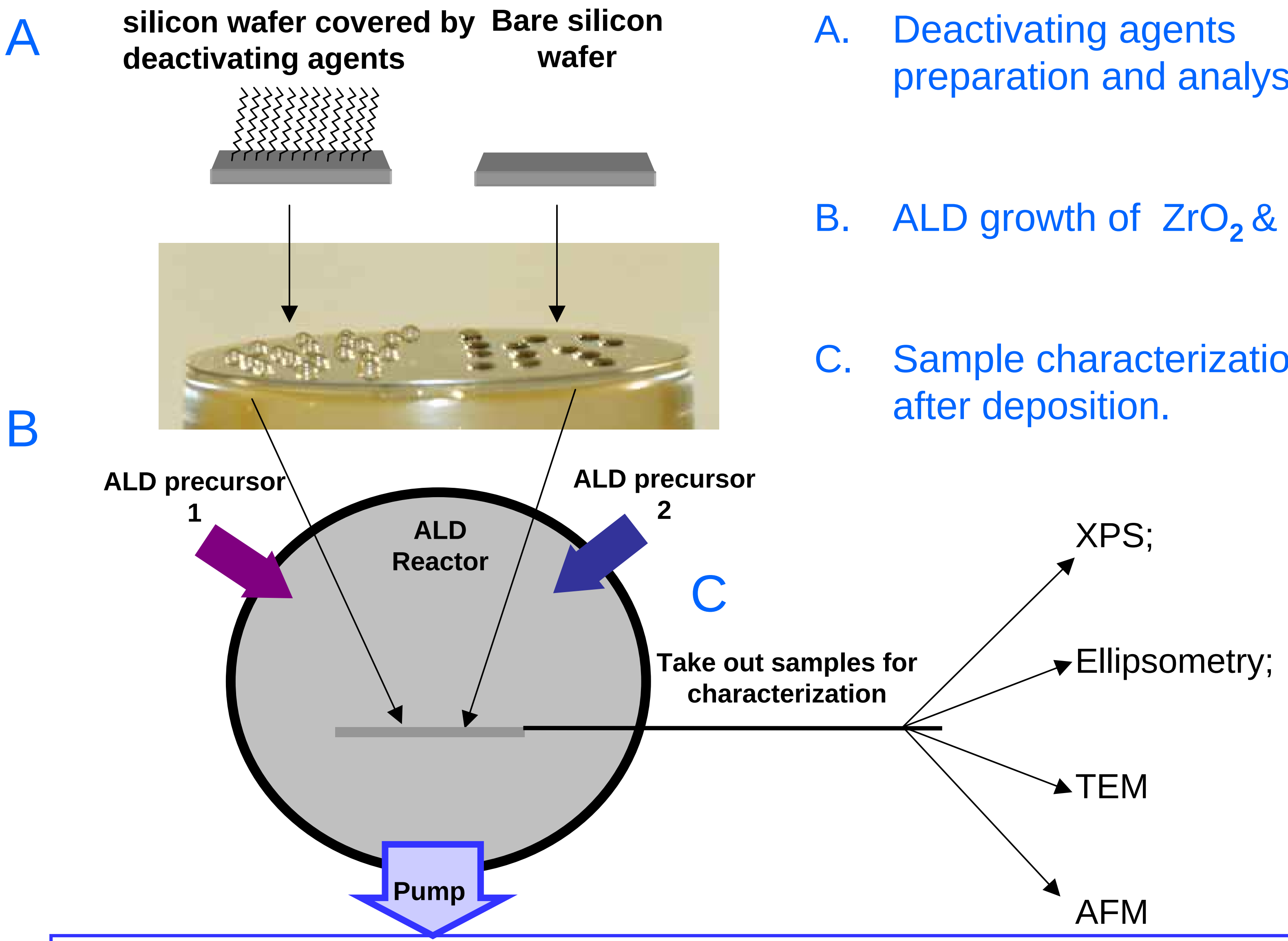
self-assembled monolayer (SAMs)

Combined Deactivating Agents & ALD

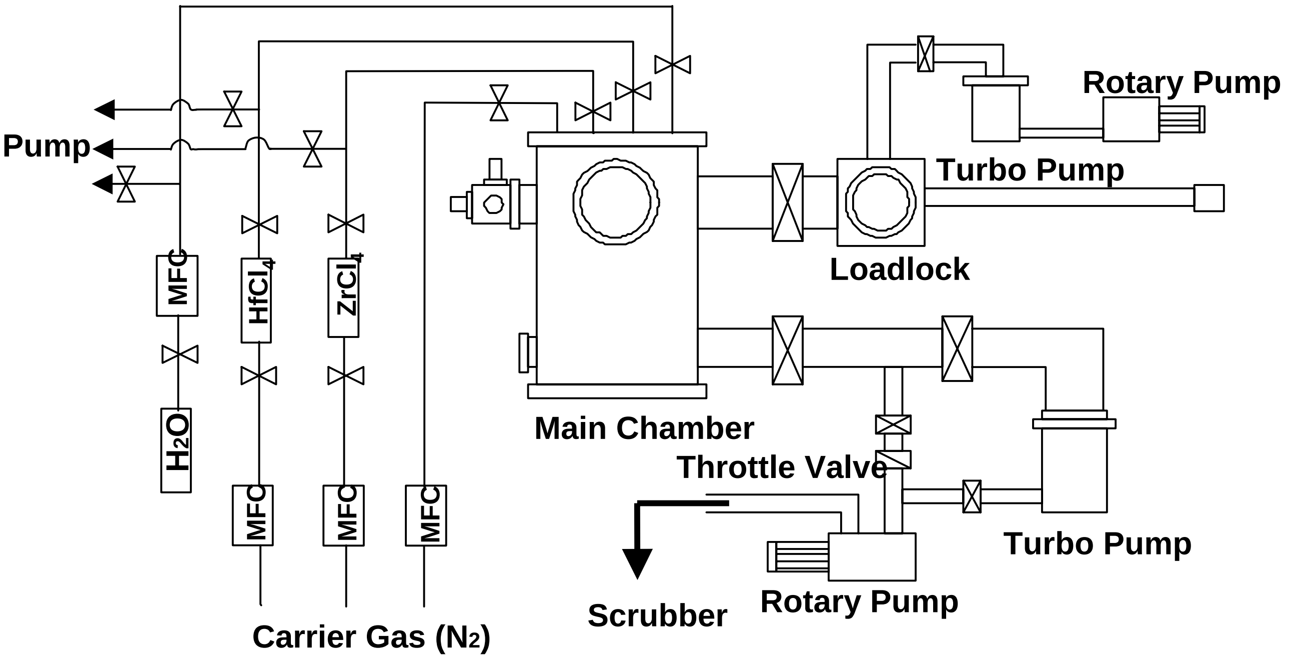
A. Deactivating agents preparation and analysis;

B. ALD growth of ZrO_2 & HfO_2 ;

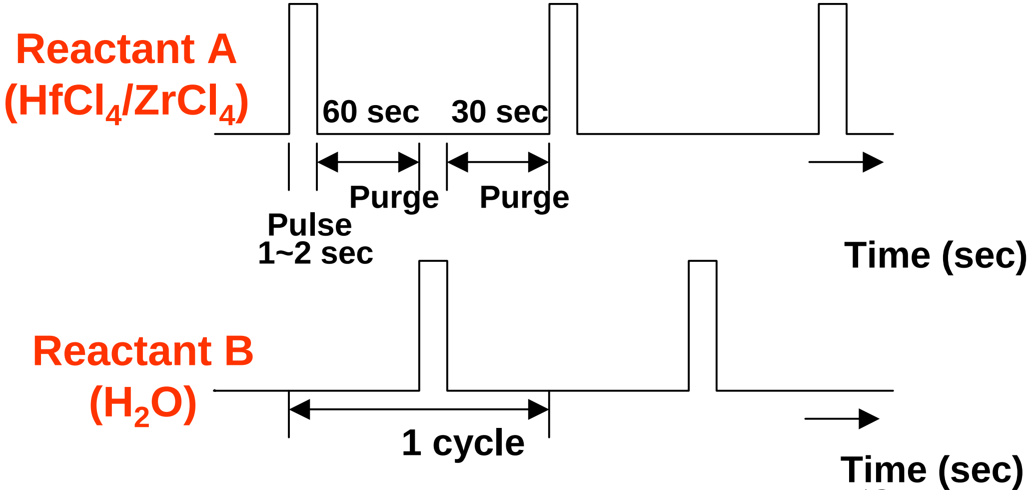
C. Sample characterization after deposition.



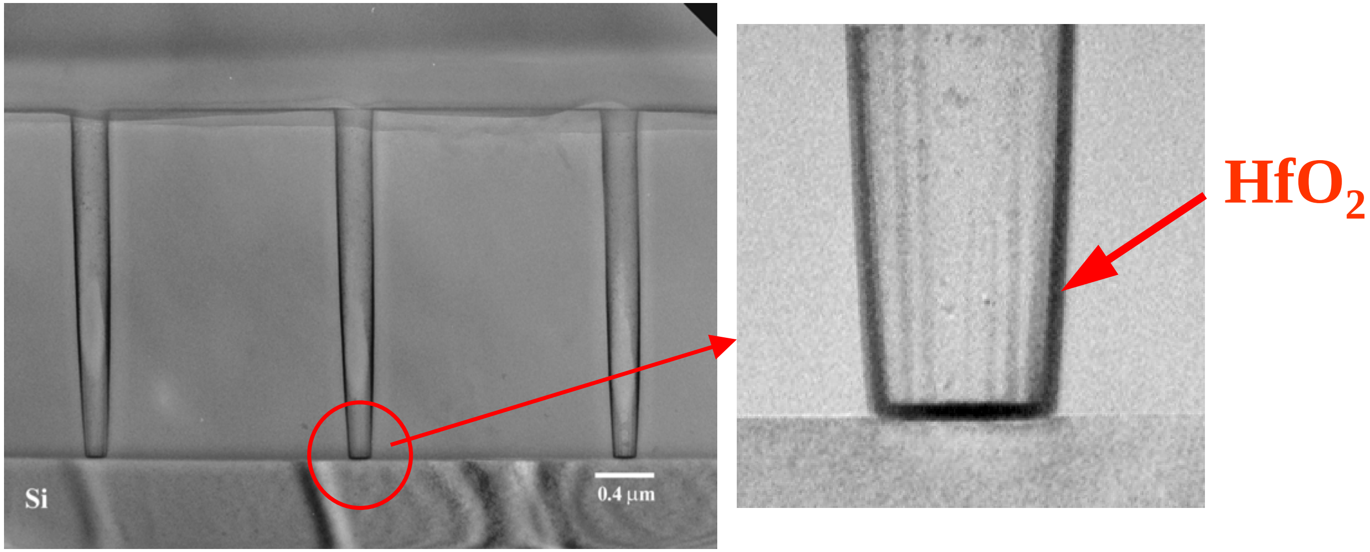
Schematic Diagram of ALD System

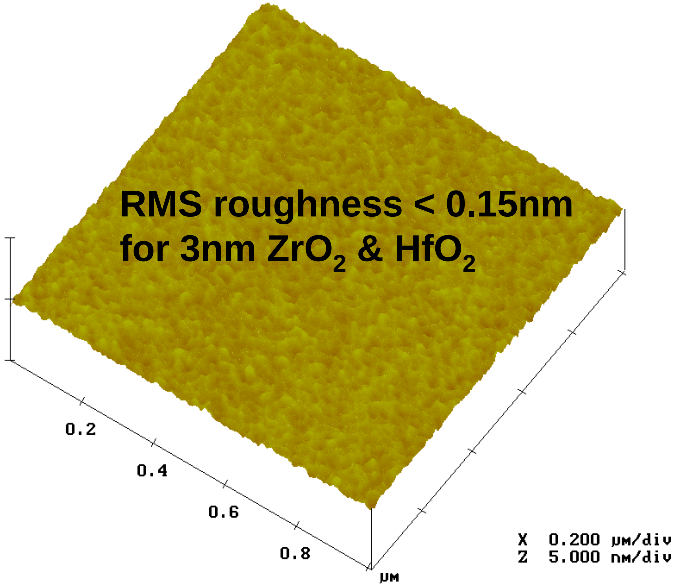


- **Base pressure = $5*10^{-8}$ Torr**
- **Process temperature : 300°C**
- **Process pressure : 0.5 Torr**
- **Source temperature :**
  H_2O (liquid) = 20°C
  $HfCl_4$ /$ZrCl_4$(solid) = 150°C



Conformality and Surface Roughness of ALD Films



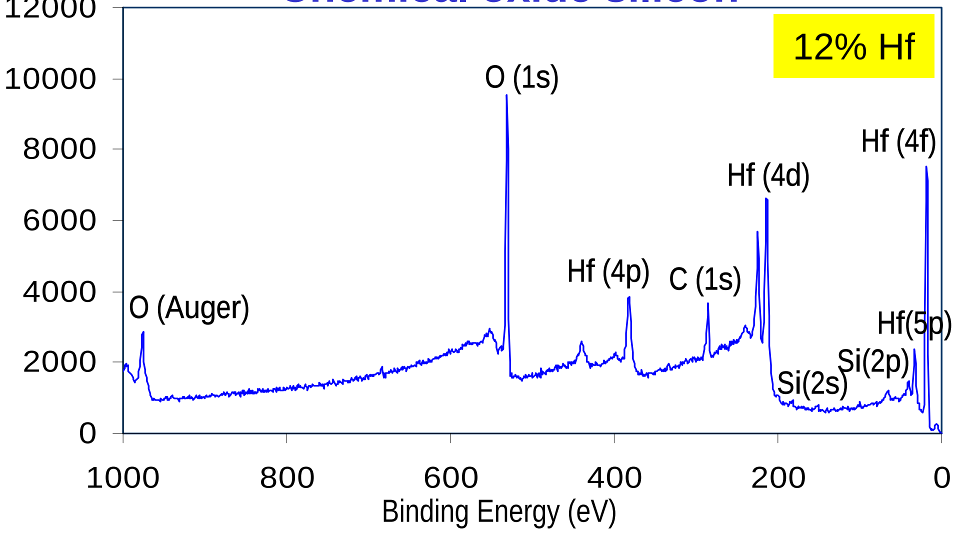

RMS roughness < 0.15nm for 3nm ZrO_2 & HfO_2

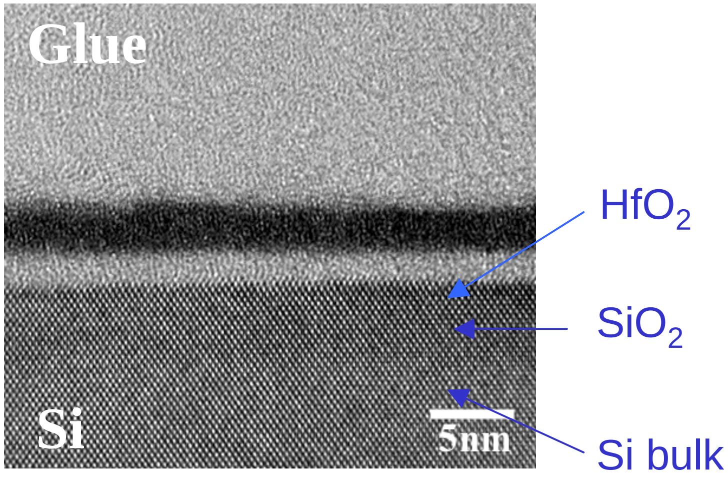
ALD deposition of metal-oxide films

- Excellent step coverage (~100%) on complicated geometric structures
- Smooth and uniform deposition

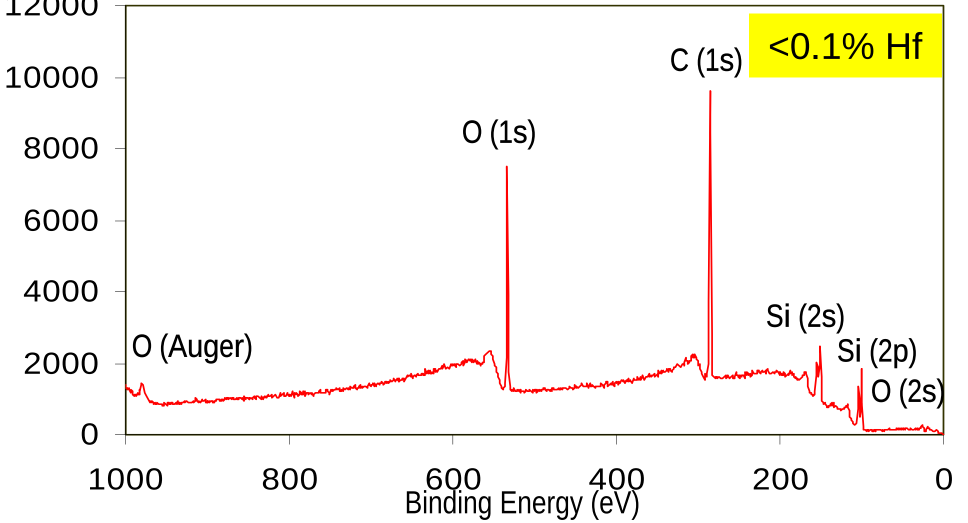
ALD Inhibition by Octadecyltrichlorosilane (ODTS) SAM

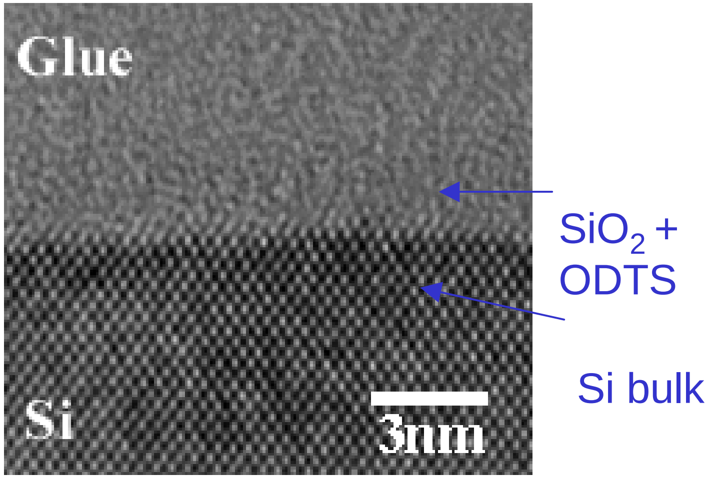
Chemical oxide silicon





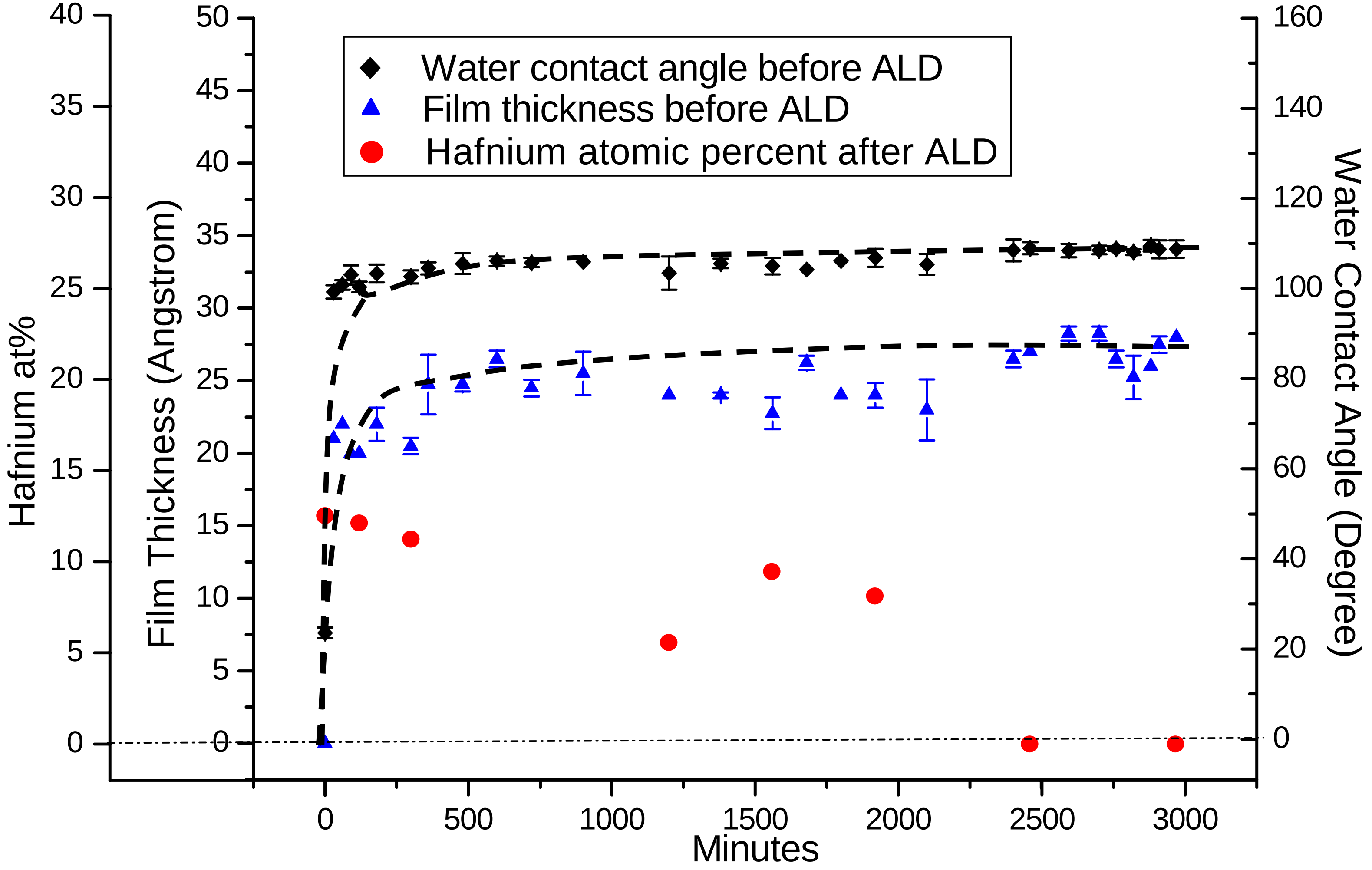
ODTS SAM on silicon





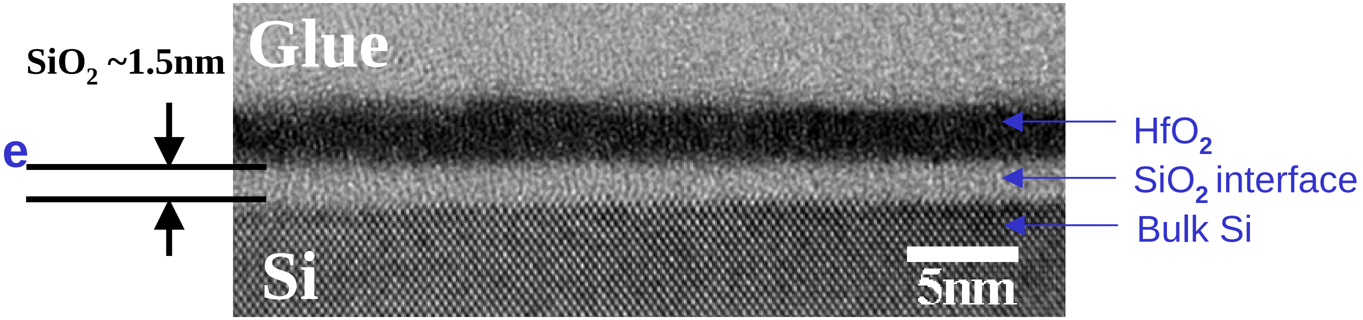
Silylation Time Dependence for ODTS

$CH_3(CH_2)_{17}SiCl_3$

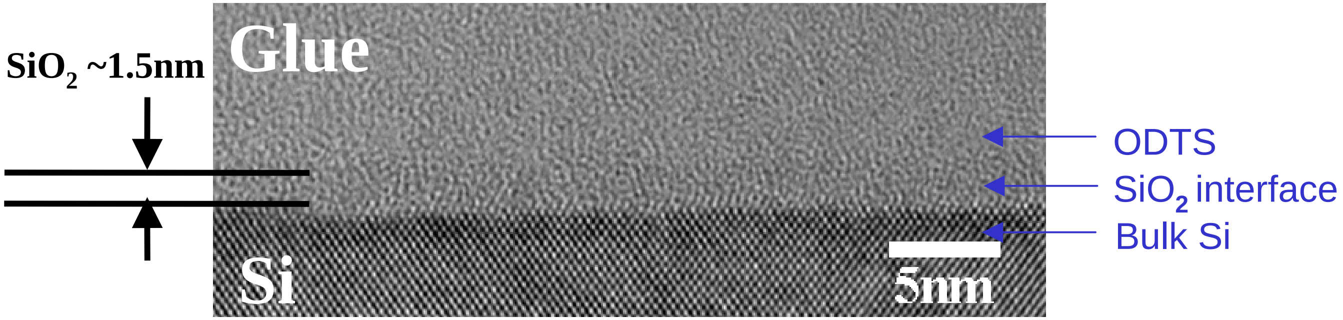


Interface Analysis by Cross-sectional TEM

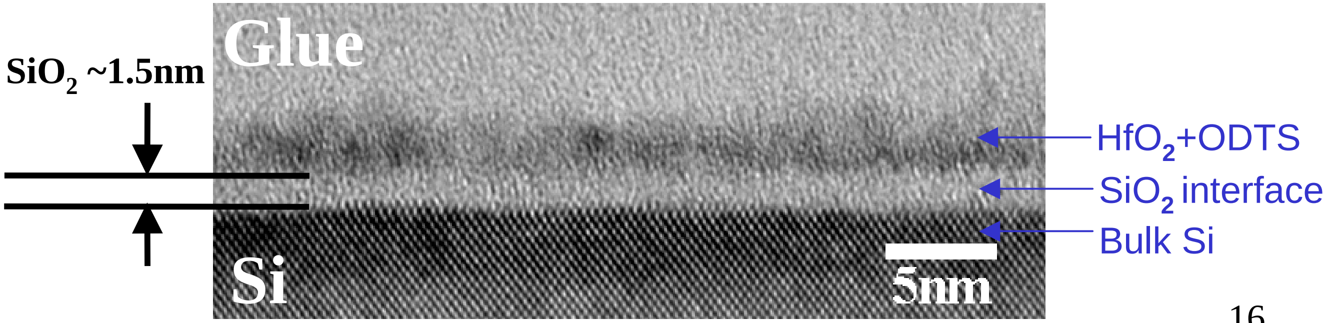
Chemical oxide silicon wafer



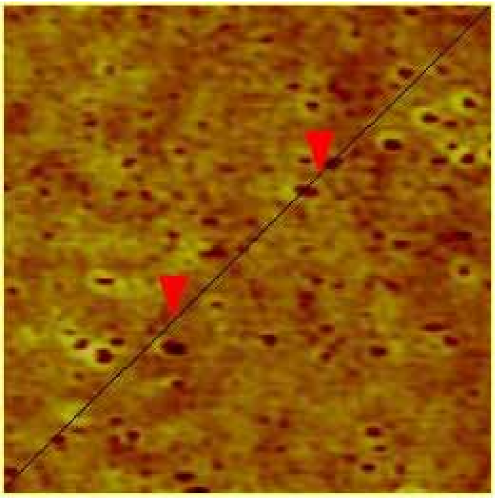
Densely ODTS coated silicon wafer



Loosely ODTS coated silicon wafer

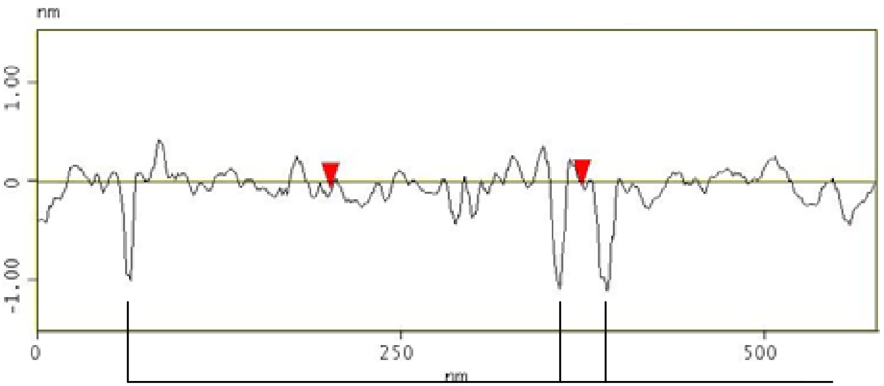


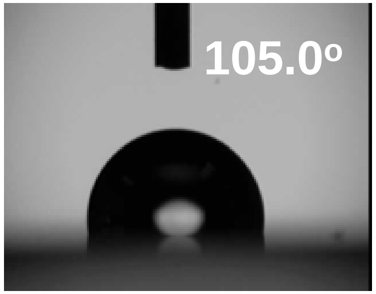
ODTS Films Analysis before ALD Process



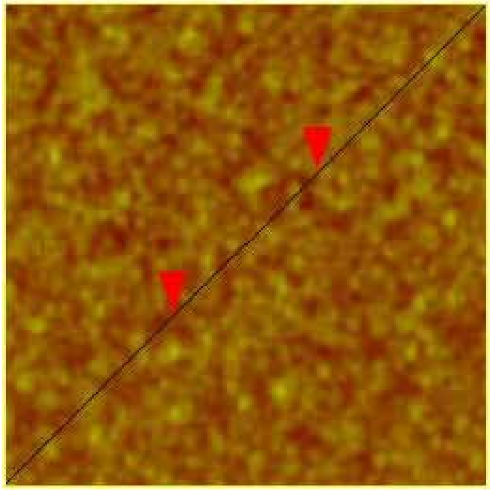
Loosely packed ODTS film

WCA: 105.0°
RMS: 0.20nm



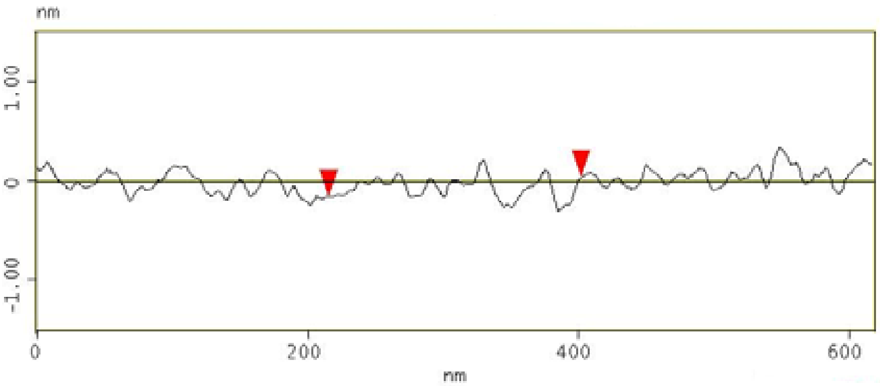


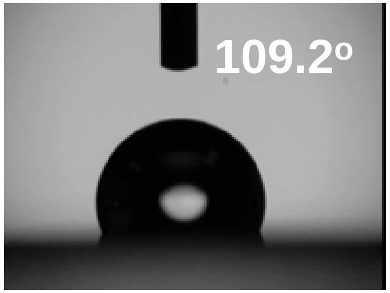
Some pinholes on SAMs



Densely packed ODTS film

WCA: 109.2°
RMS: 0.10nm

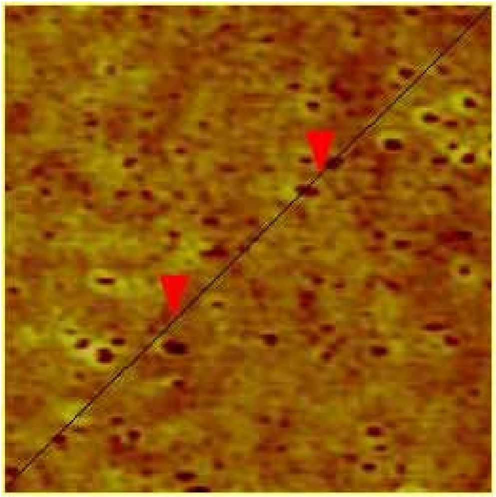


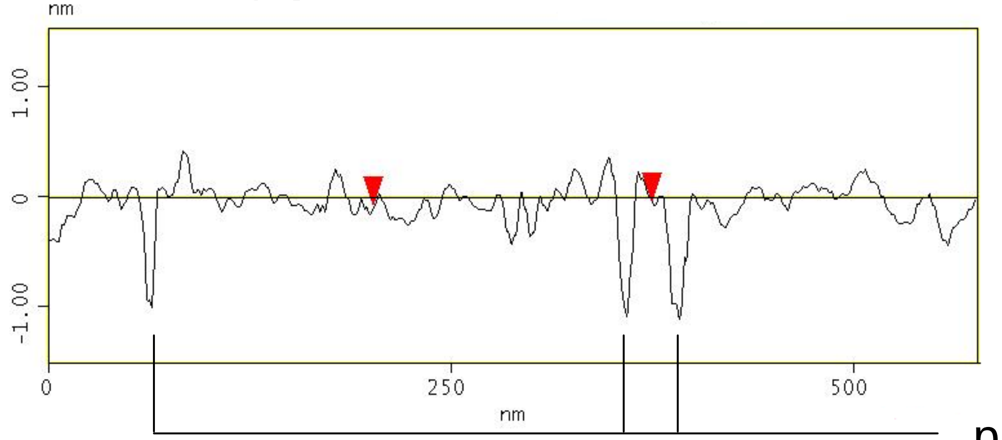


Smooth and Uniform SAMs

AFM Analysis of ODTS before & after ALD

Loosely packed ODTS film before ALD

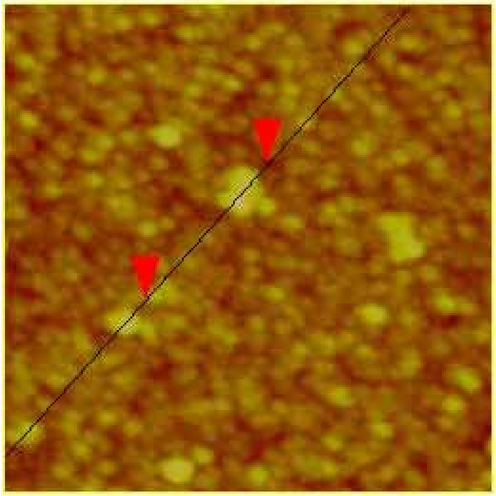


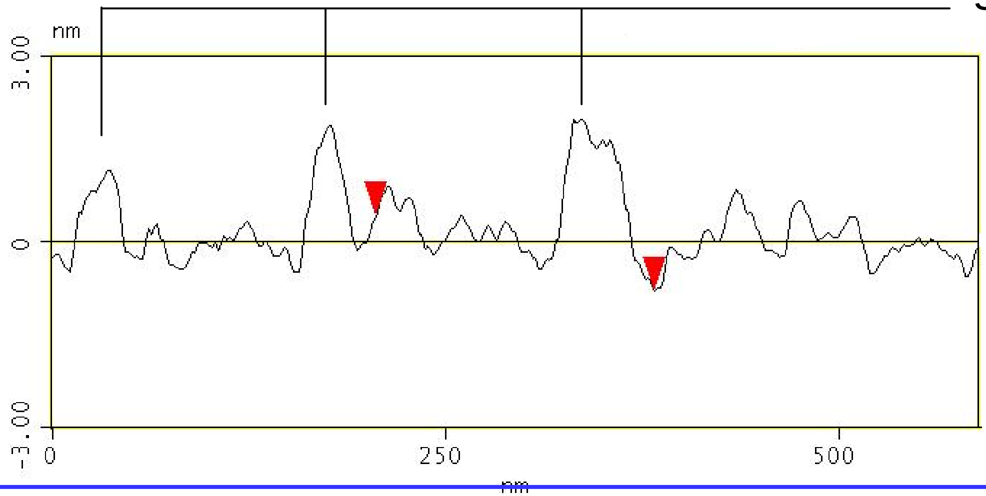


pinholes

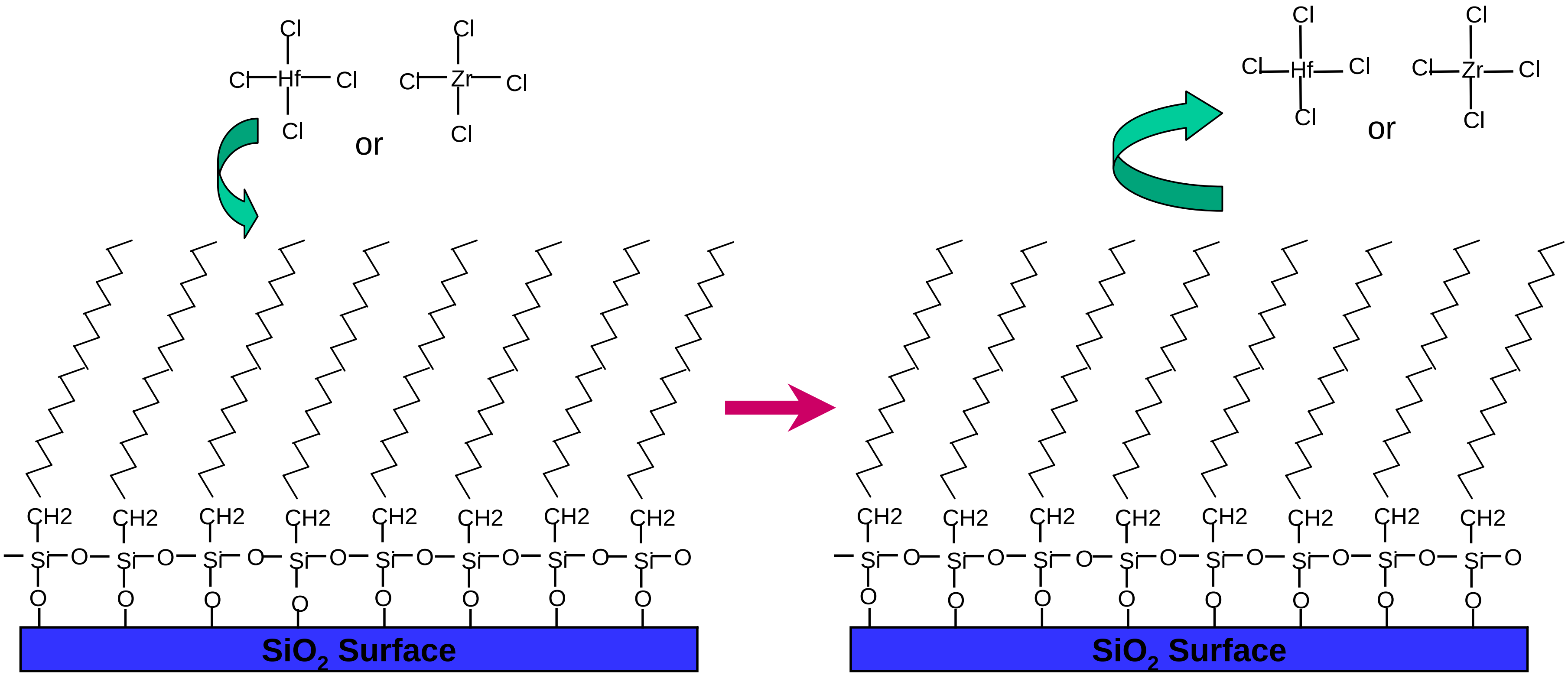
Loosely packed ODTS film after ALD

spikes





Mechanism of ALD inhibition on densely-packed ODTS

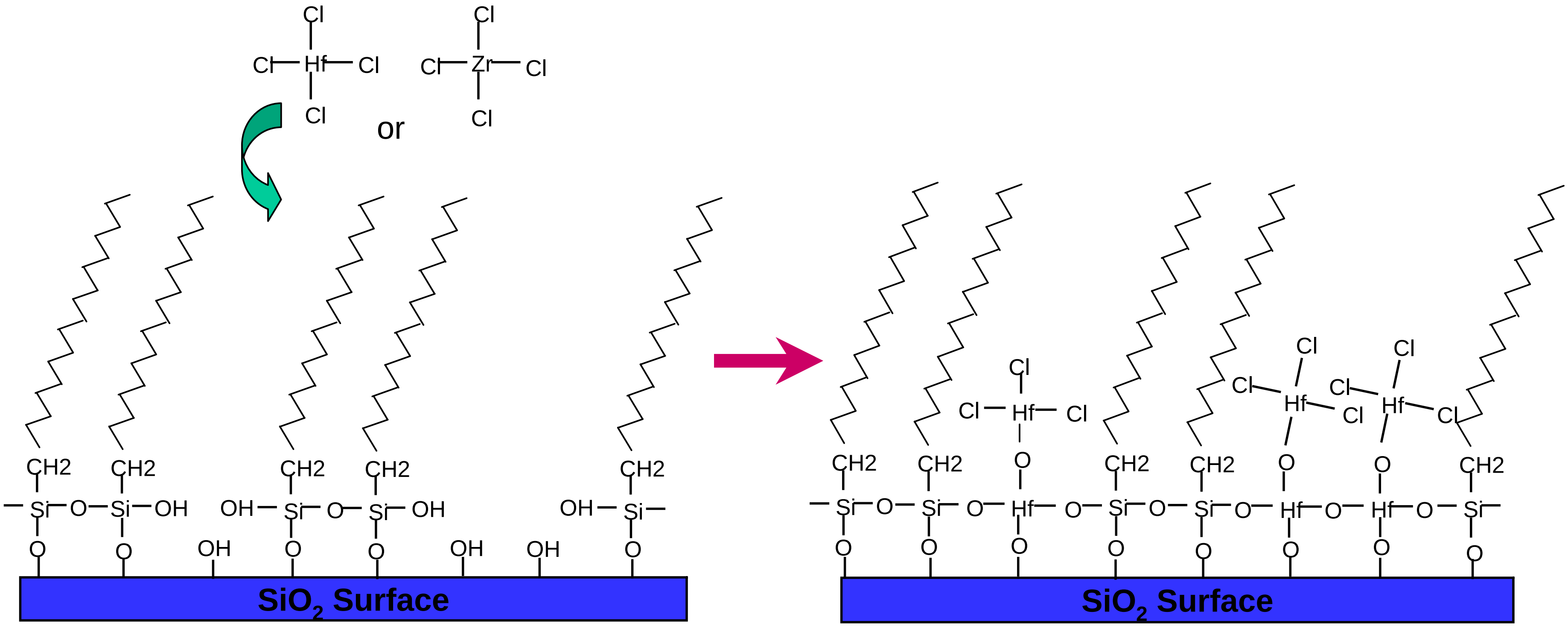


Densely packed ODTS

The organic SAM blocks the underlying oxide from the ALD precursors

Octadecyltrichlorosilane (ODTS), $CH_3 (CH_2)_{17} SiCl_3$

Mechanism of ALD growth on loosely-packed ODTS



Loosely packed ODTS

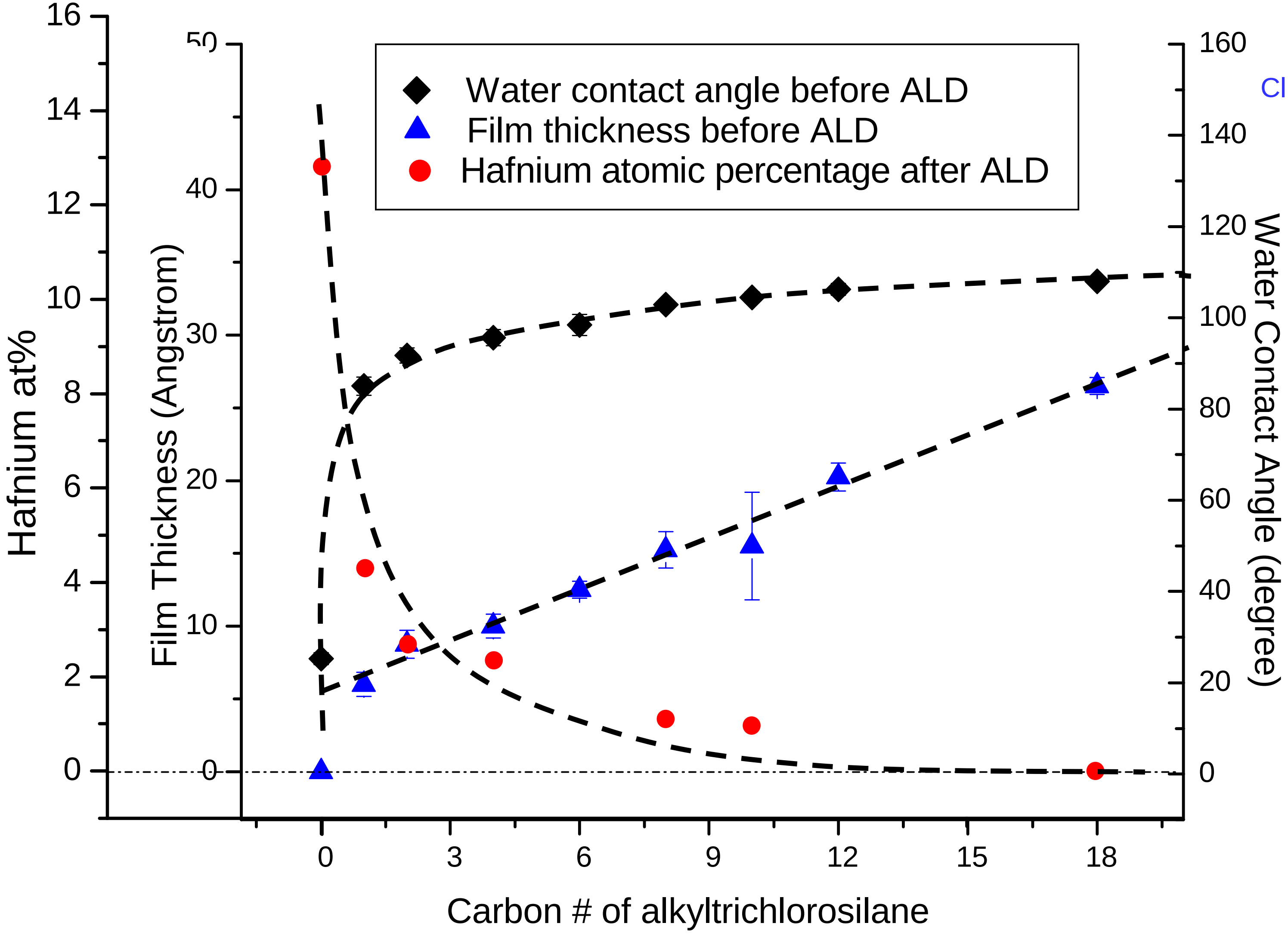
Pinholes in the SAM leave native oxide hydroxyl groups accessible to ALD precursors

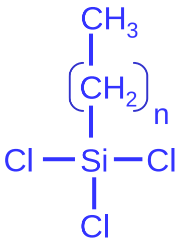
ALD precursors react at these surface sites and growth nucleates from those sites

Octadecyltrichlorosilane (ODTS), CH_3 $(CH_2)_{17}$ $SiCl_3$

Let’s examine other deactivating agents, such as shorter chain alkylhalosilanes.

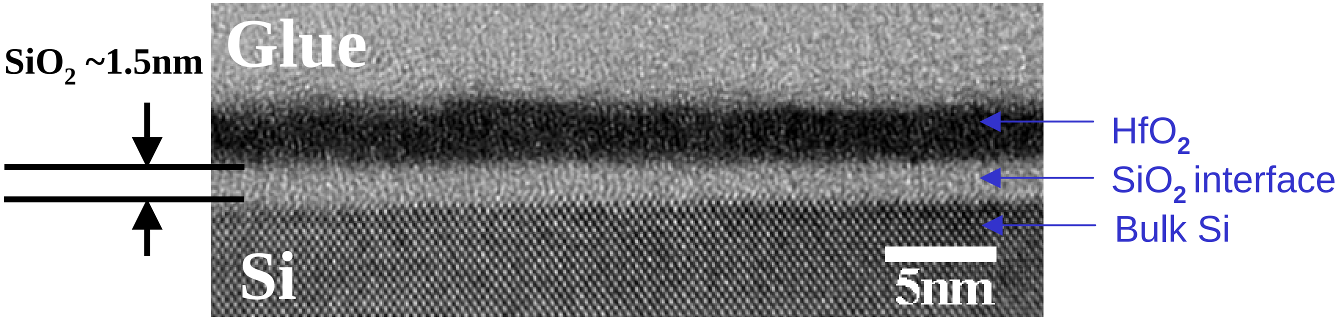
Alkyltrichlorosilane Chain Length Dependence

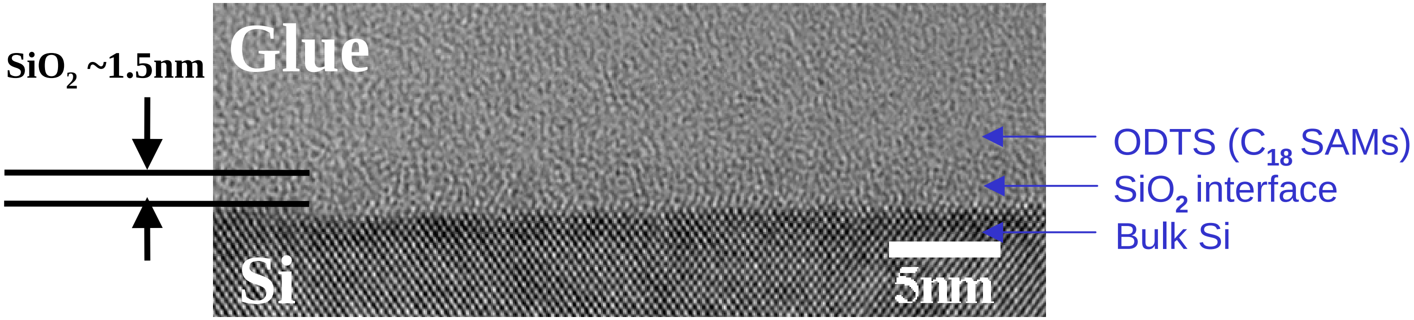


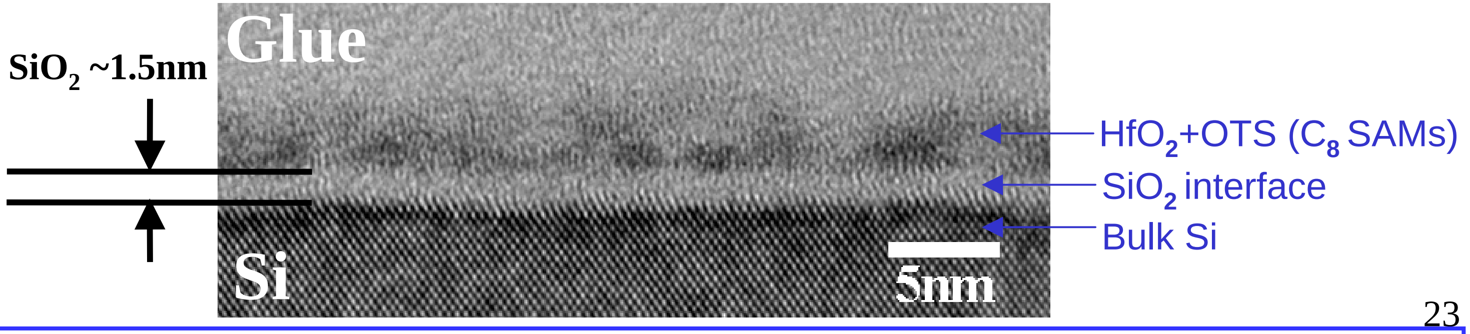


$CH_3(CH_2)_nSiCl_3$

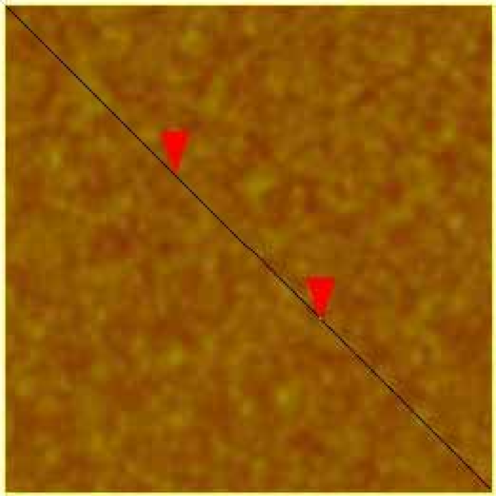
Cross-sectional TEM



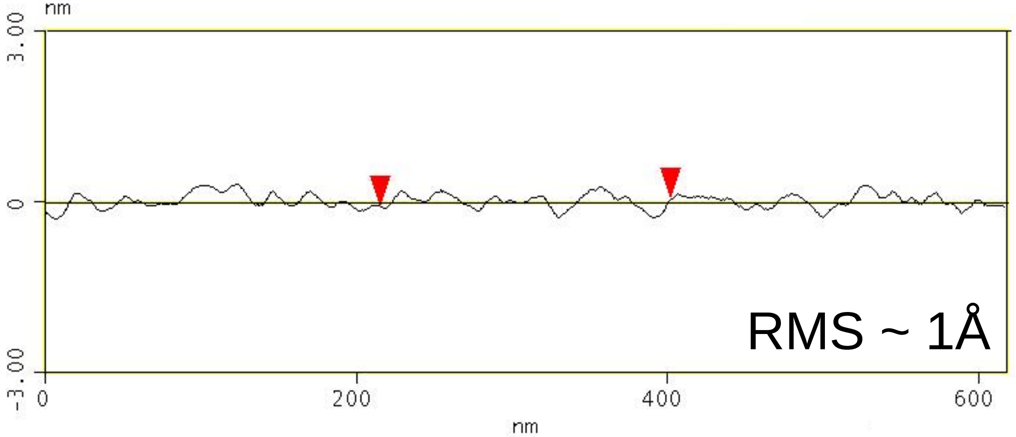




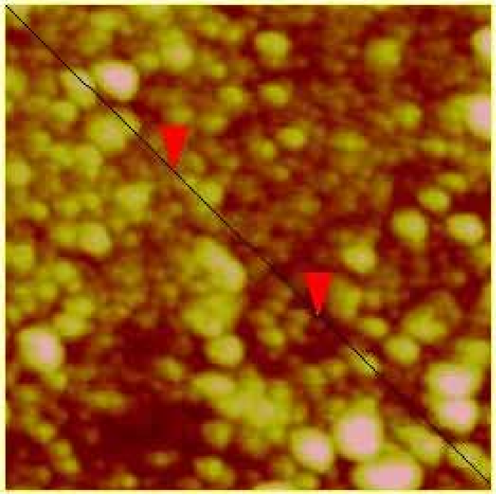
AFM Analysis of Octyltrichlorosilane before & after ALD



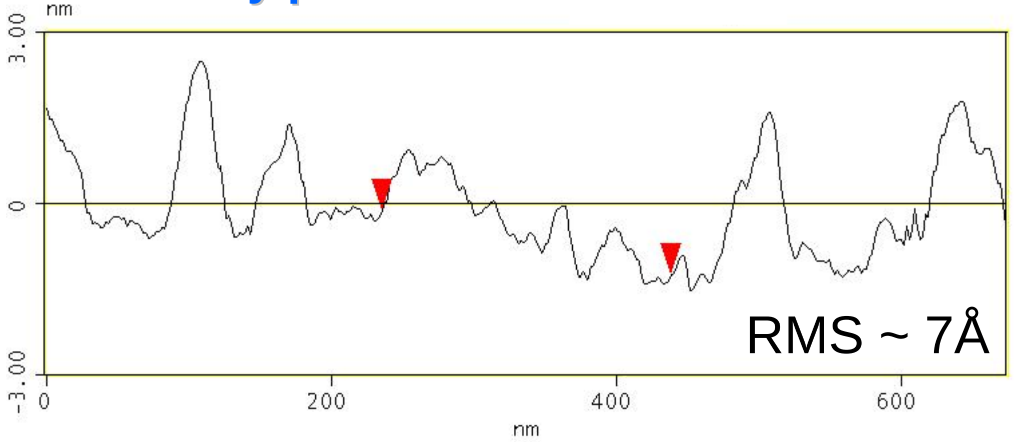
Densely packed OTS film before ALD



RMS ~ 1Å

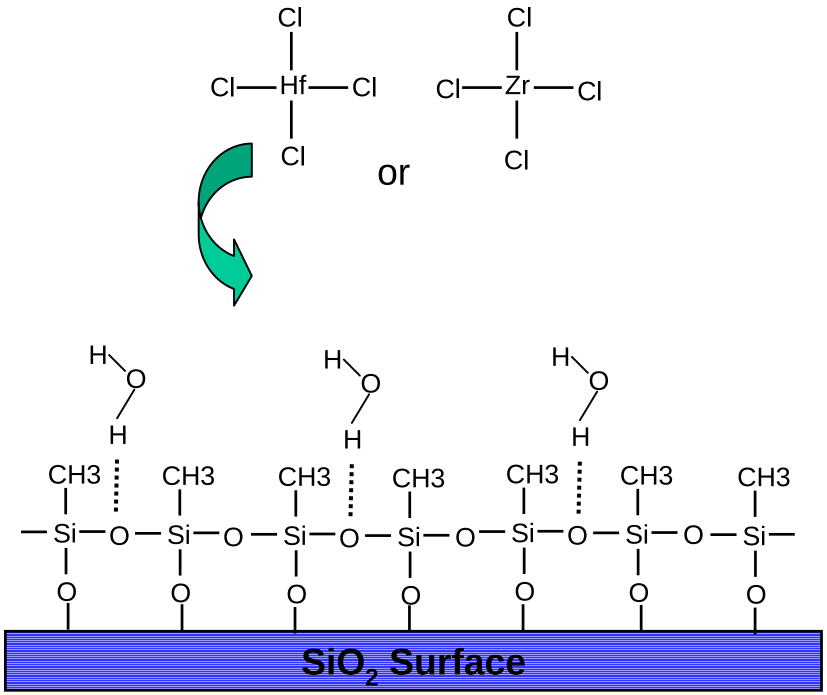


Densely packed OTS film after ALD



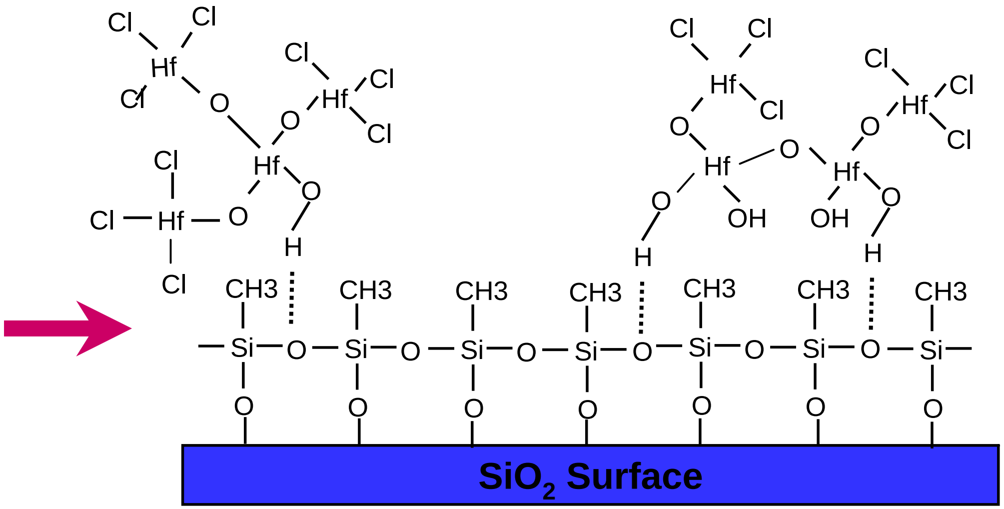
RMS ~ 7Å

Mechanism of ALD growth on shorter chain SAM



CH_3SiCl_3

Methyltrichlorosilane (MTCS)



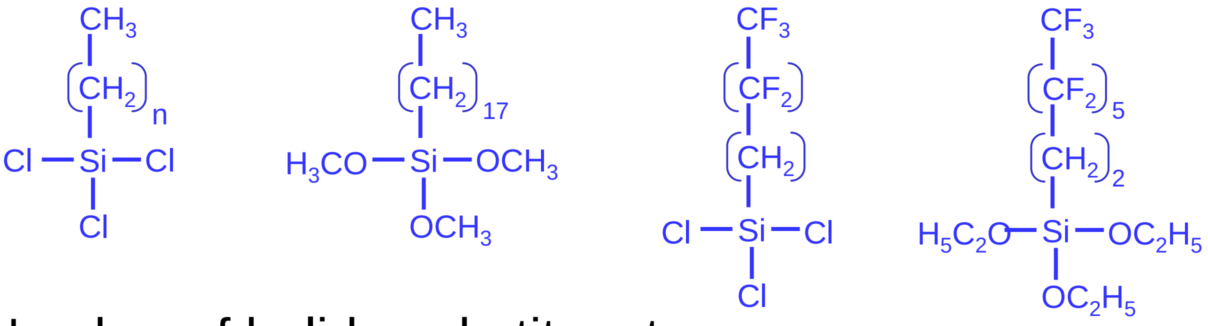
Densely packed MTCS

oxygen atoms provide hydrophilic regions for ALD growth

ALD growth nucleates at exposed oxygen atoms, but some precursor attachment may be unstable

Deactivating Agents Studied

1. Chain lengths, reacting groups, and chain monomers



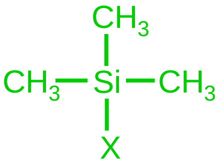
Alkyltrichlorosilane

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

2. Number of halide substituents

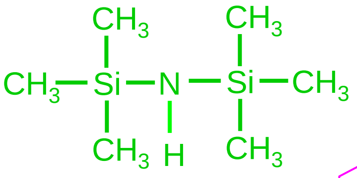
$Si(CH_3)_nCl_{4-n}$ n=1,2,3

3. Reactive groups



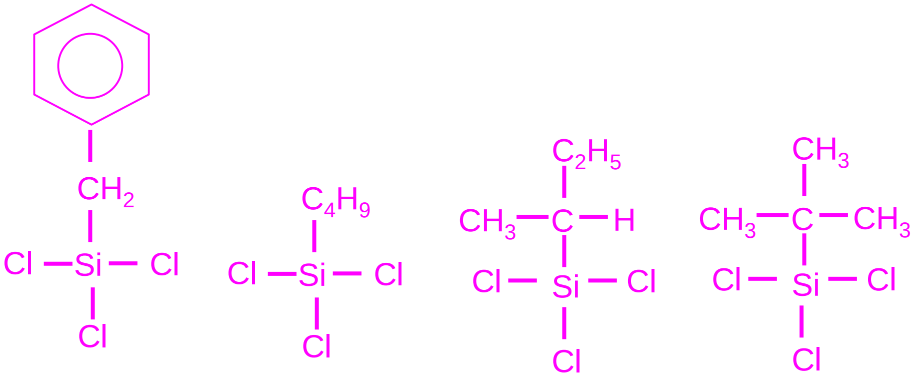
X=Cl, Br, I

Trimethylhalosilane



HMDS

4. Type of carbon chain

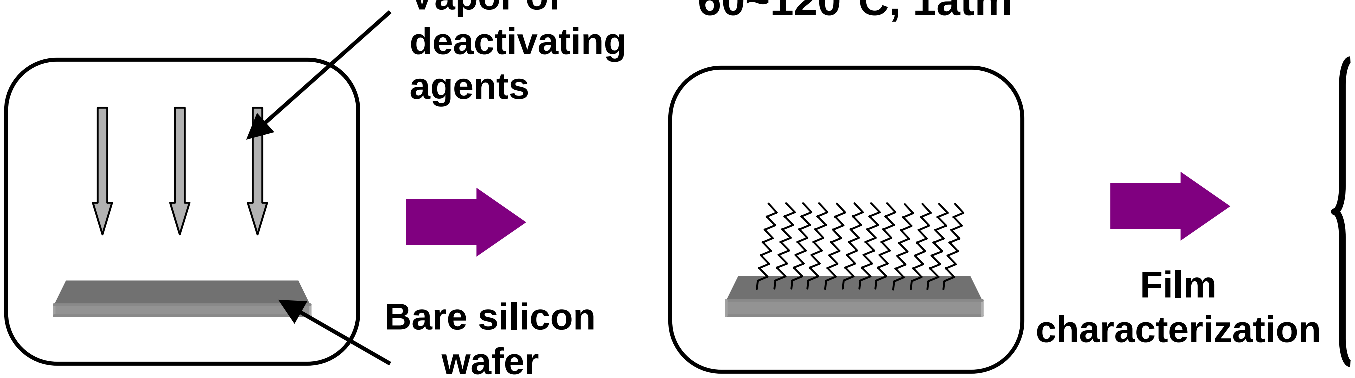


Solution based delivery

Vs.

Gas phase delivery

Gas Phase Delivery of Deactivating Agents



Vapor of deactivating agents

60~120°C, 1atm

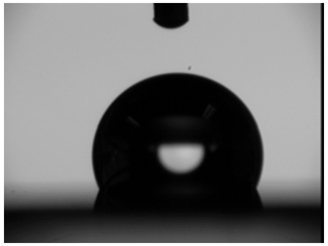
Bare silicon wafer

sealed container

Film characterization

- Contact Angle analysis;
- Ellipsometry;
- AFM;
- XPS.

Water Contact Angle



organosilane film
θ =110.5º
Hydrophobic

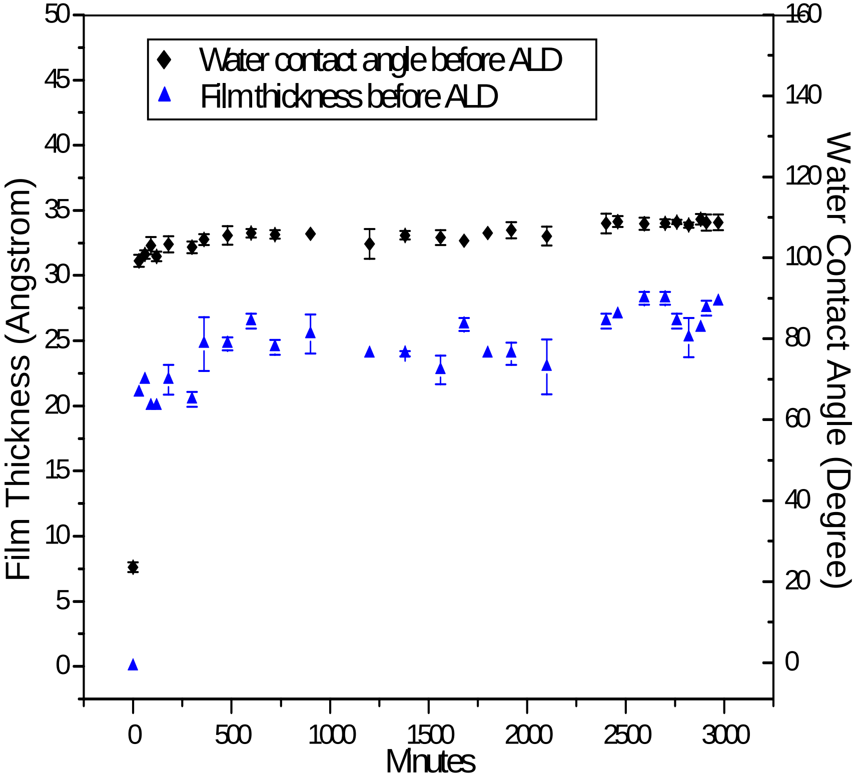
Ellipsometry monolayer thickness of organosilane

AFM analysis shows deactivating agents films formed by gas phase delivery are uniform and smooth.

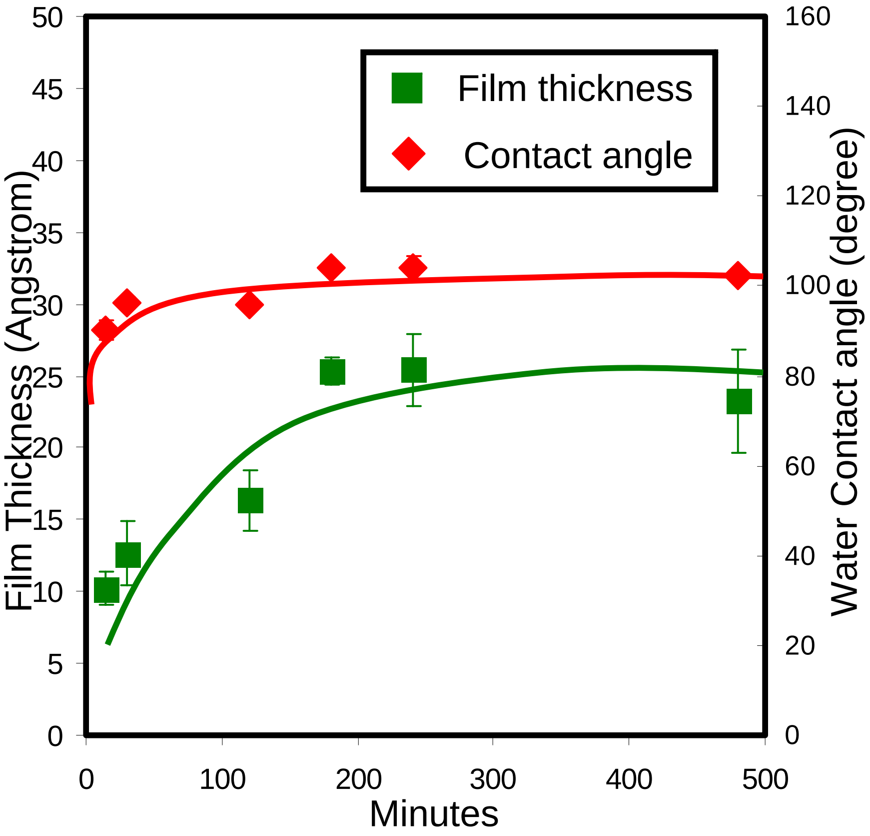
Conclusion: Both solution phase and gas phase delivery of deactivating agents can achieve uniform, high quality films, which can be used for direct patterning

Solution based Reaction vs. Gas Delivery Reaction

Solution Delivery Reaction



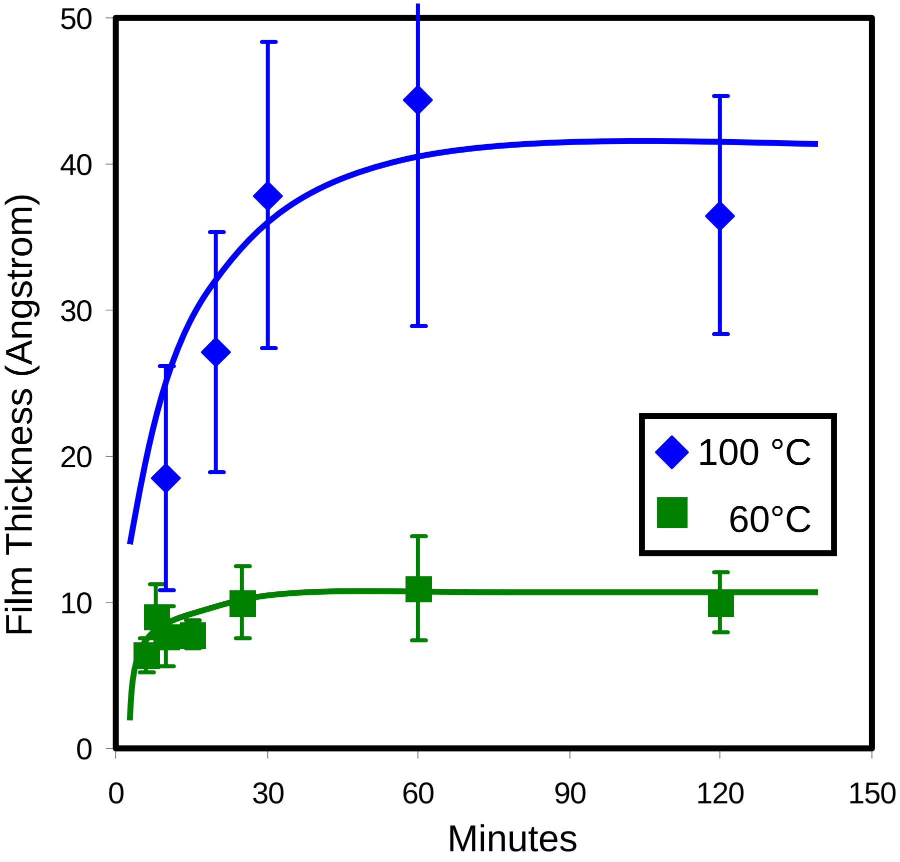
Gas Delivery Reaction



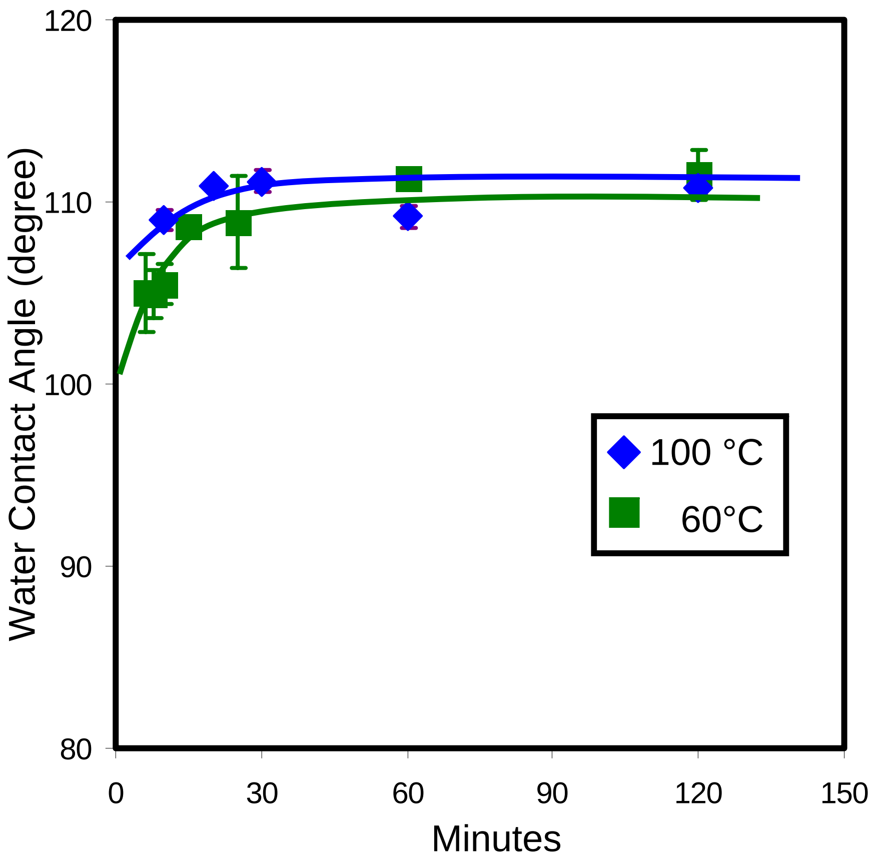
- Gas delivery reaction is much faster than solution based reaction

Surface Passivation as a function of CVD Temperature

- Tridecafluoro-1,1,2,2-tetrahydrooctyl trichlorosilane (FOTS)

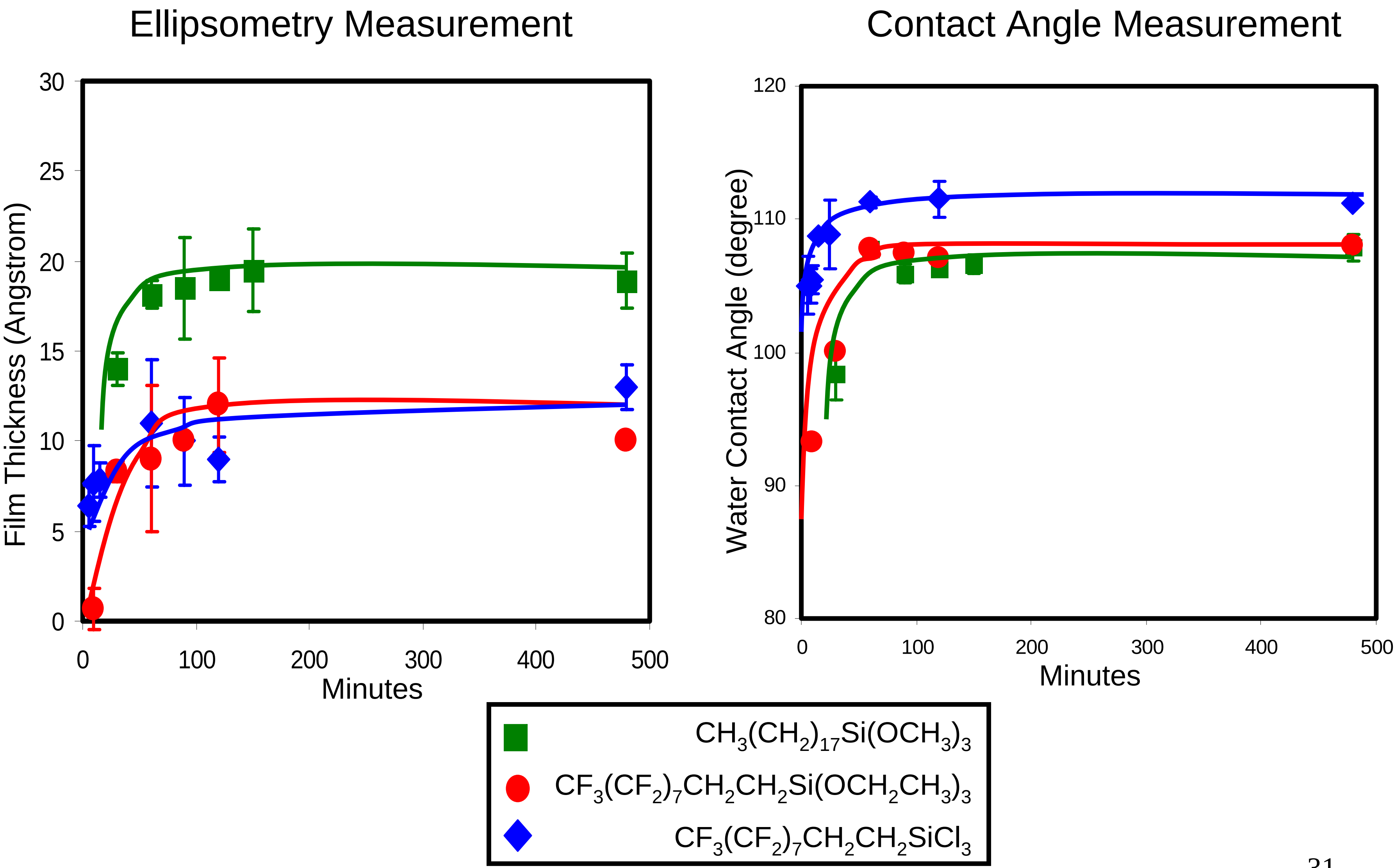


Ellipsometry Measurement



Contact Angle Measurement

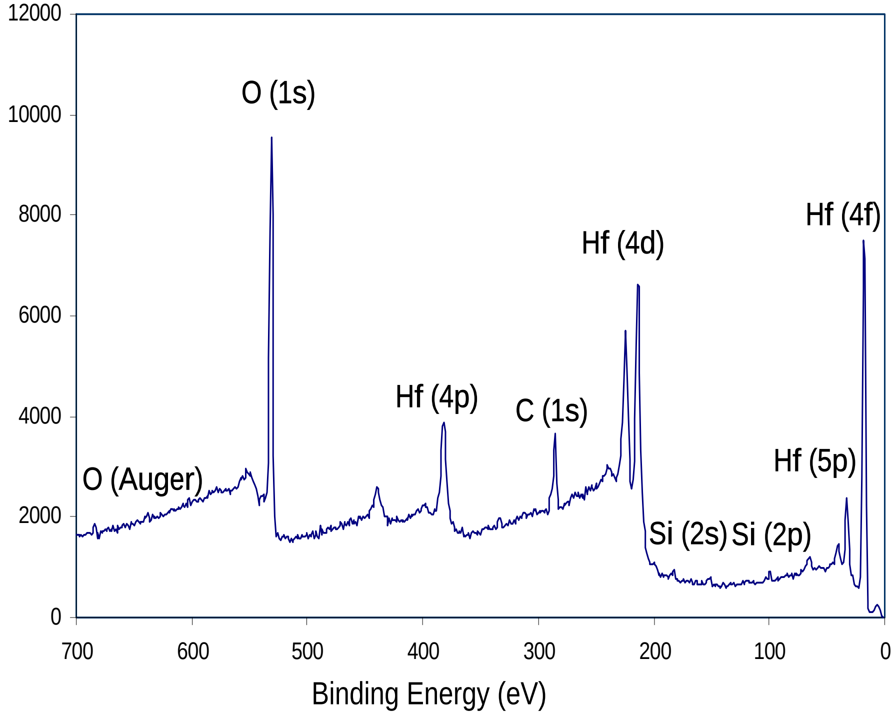
Surface Passivation of different molecules



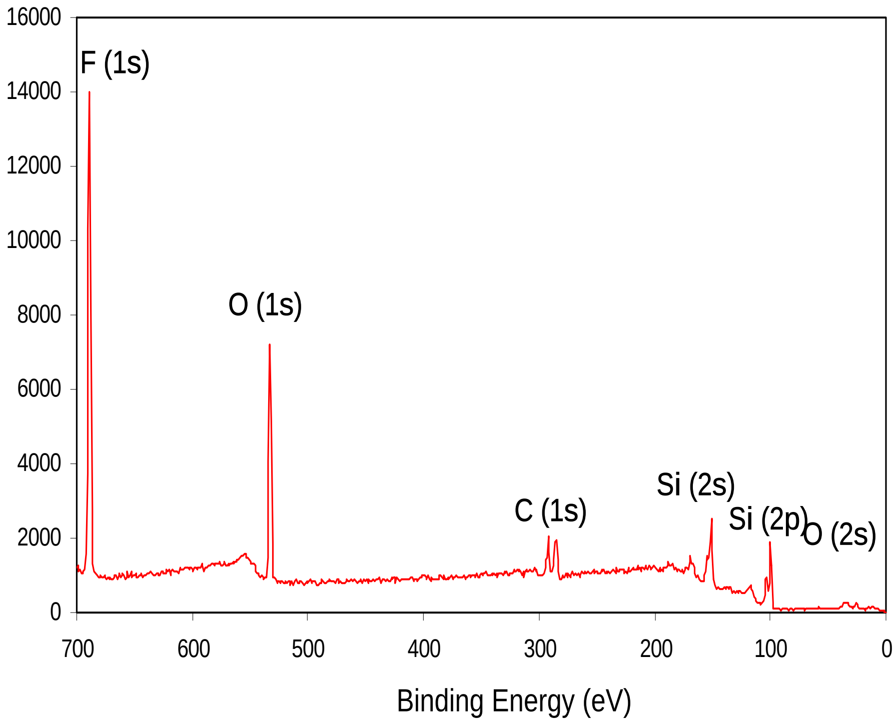
ALD Results of Gas delivered SAMs

- Tridecafluoro-1,1,2,2-tetrahydrooctyl trichlorosilane (FOTS)

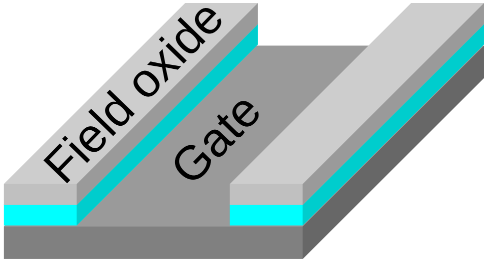
Chemical oxide silicon wafer



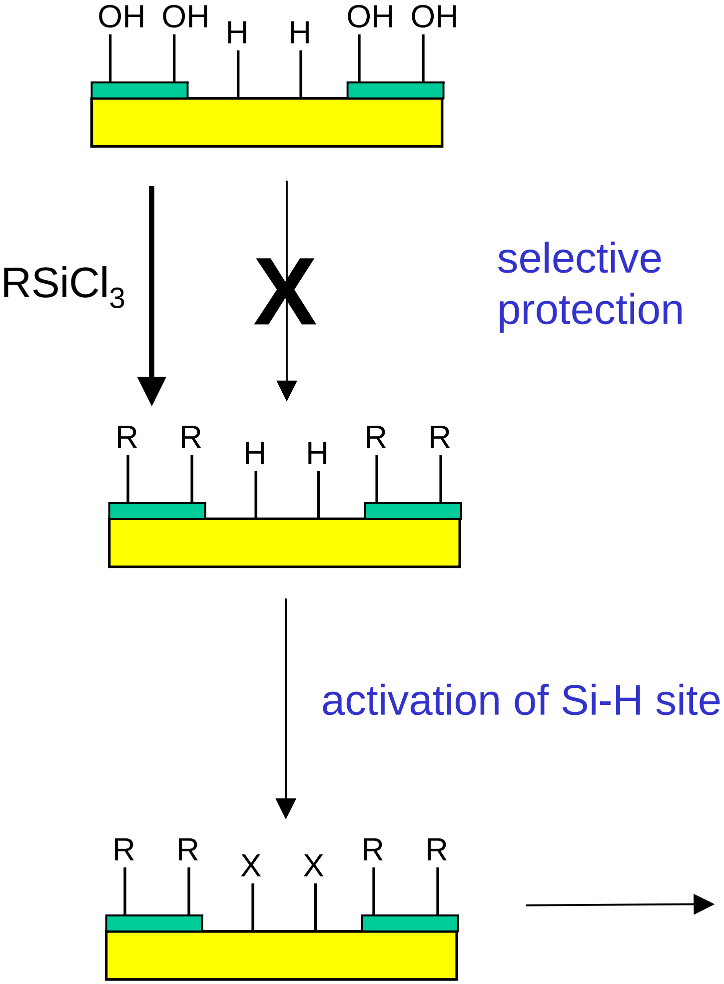
Silicon wafer coated with FOTS



Can We Achieve the Necessary Selectivity?



patterned oxide



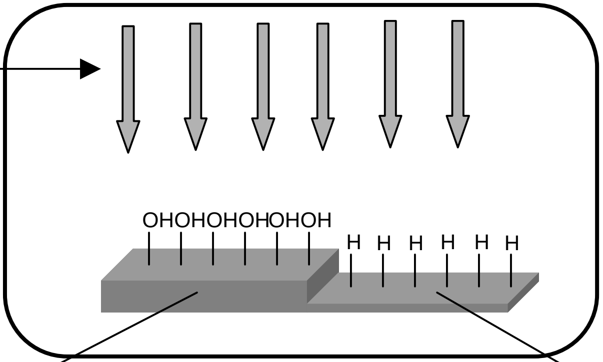
selective protection

activation of Si-H site

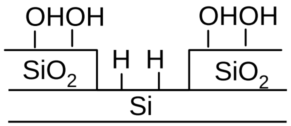
ALD

Selectivity for Si-OH vs Si-H under Gas Phase Delivery

Vapor of deactivating agents

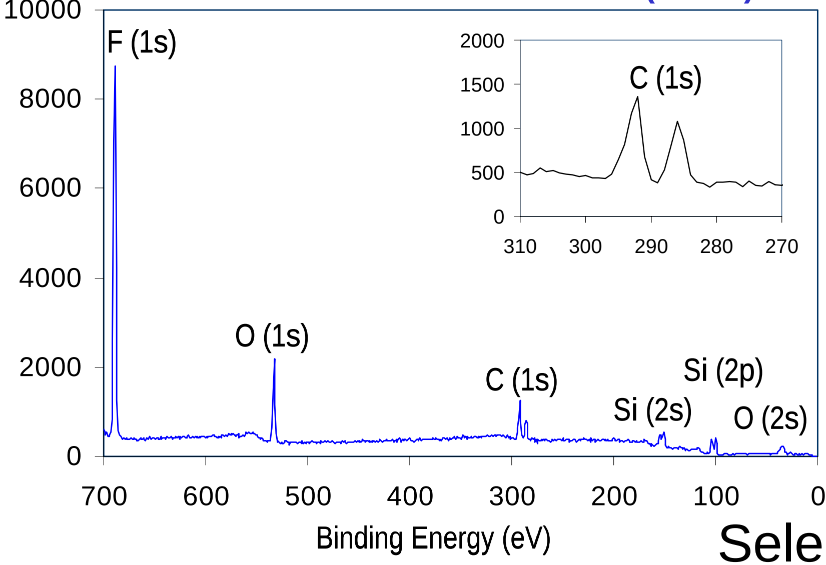


Tridecafluoro-(1,1,2,2 tetrahydrooctyl)-trichlorosilane (FOTS)

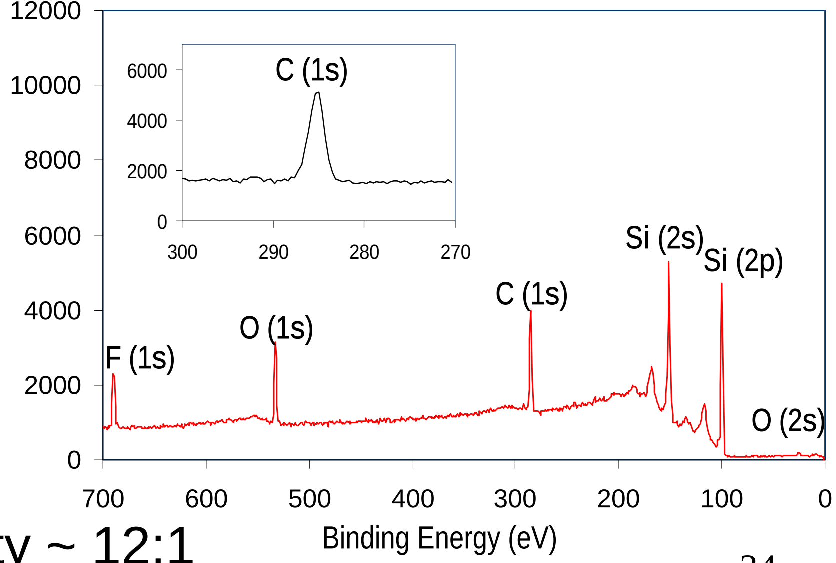


XPS Analysis

Bare silicon wafer after Piranha (Si-OH)



Bare silicon wafer after HF etching (Si-H)

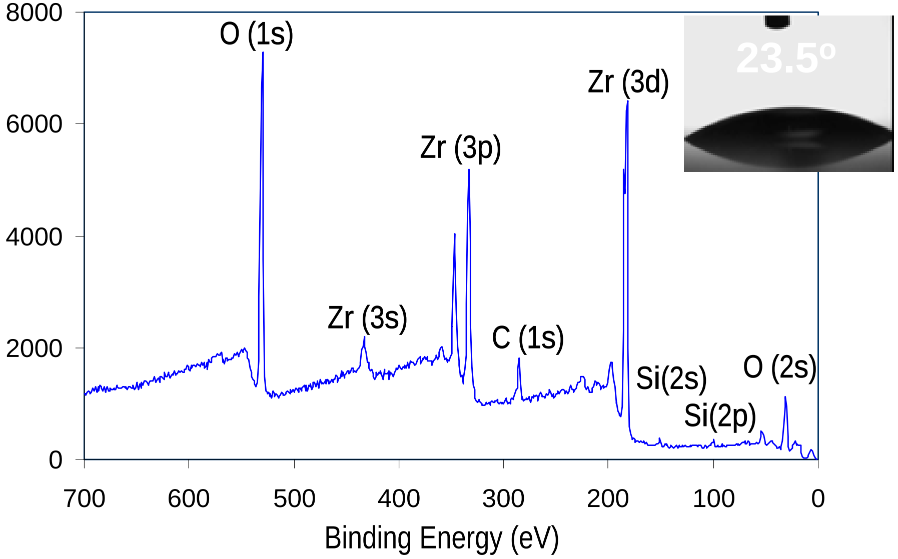


Selectivity ~ 12:1

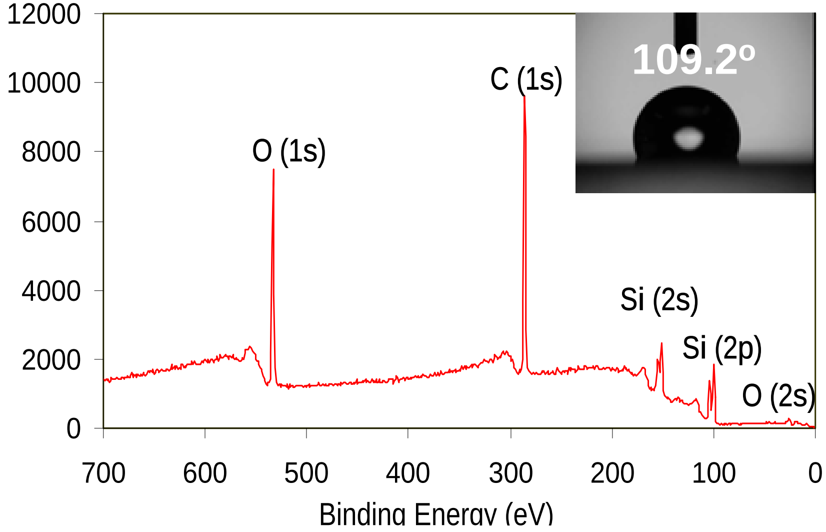
Area Selective ALD for ZrO_2

XPS Spectra after ZrO_2 ALD on various surfaces:

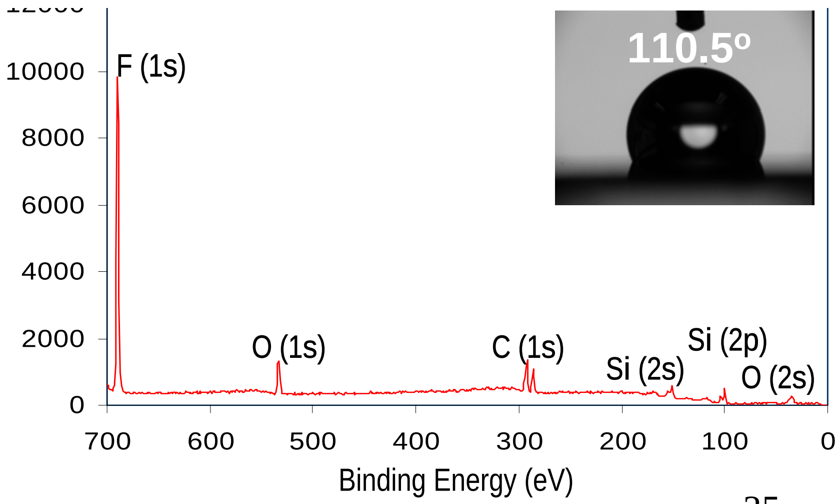
Bare silicon wafer



Si wafer coated with alkylsilane

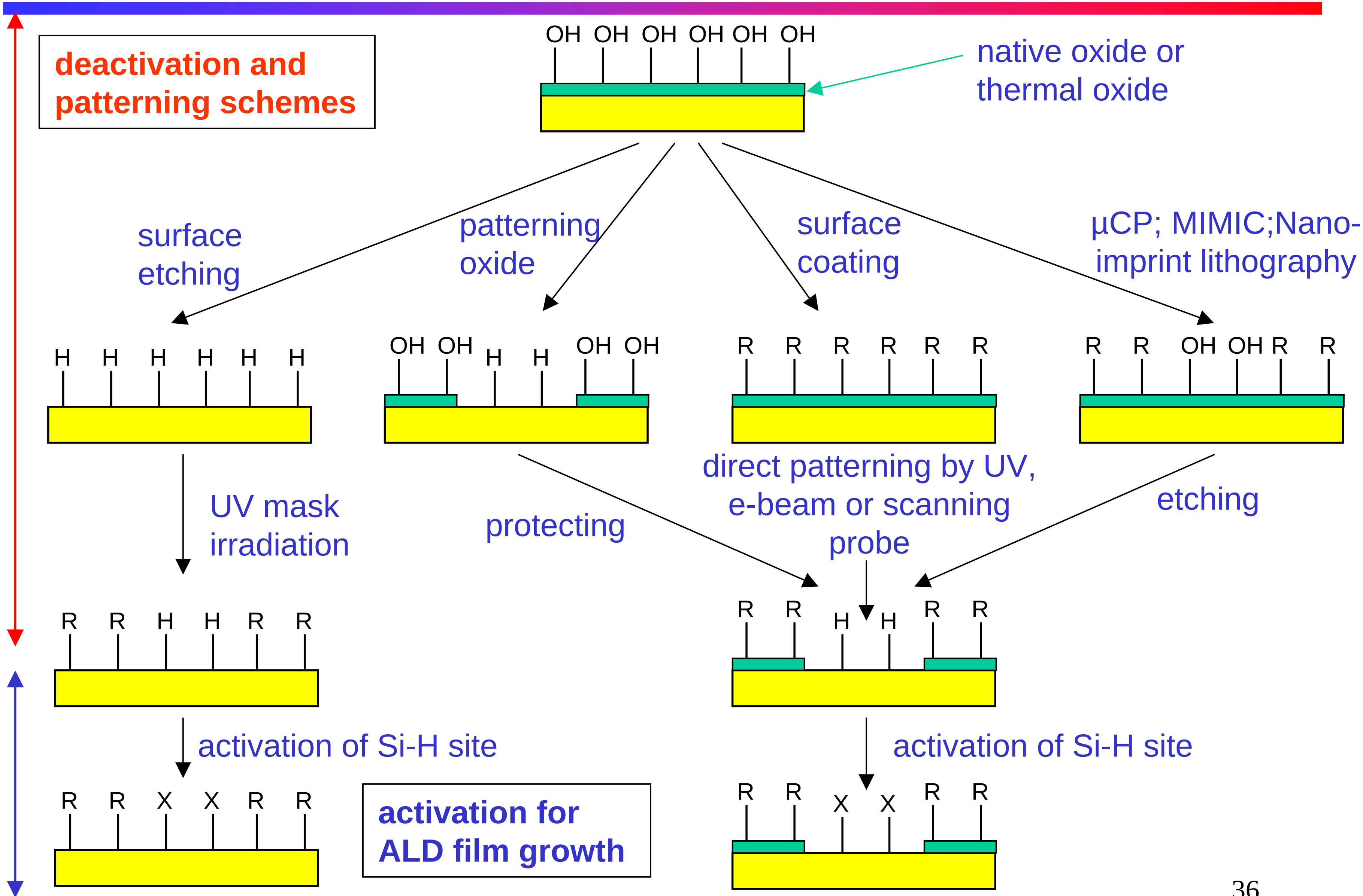


Si wafer coated with fluoro-alkylsilane



→ ZrO_2 ALD can also be effectively blocked by the deactivating agents for HfO_2 ALD .

Surface Modification for Selective ALD



deactivation and patterning schemes

native oxide or thermal oxide

surface etching

patterning oxide

surface coating

µCP; MIMIC;Nano-imprint lithography

UV mask irradiation

protecting

direct patterning by UV, e-beam or scanning probe

etching

activation of Si-H site

activation of Si-H site

activation for ALD film growth

Conclusions

- A variety of deactivating agents have been investigated
- Organosilanes are effective deactivating agents toward HfO_2 and ZrO_2 ALD
- Longer chain alkylhalosilanes which form more hydrophobic films can provide better deactivation toward ALD
- The blocking mechanisms have been investigated as a guidance for future experiment
- Both solution and gas phase delivery are promising methods for achieving high quality, dense SAMs, which can be used as a monolayer resist for area selective ALD
- Selectivity of Si-OH over Si-H is satisfactory for achieving area-selectivity

Future Work

- Deactivating strategies on Germanium substrate
- Activation strategies
- Patterning and etch methods for deactivating agents
- Extension of area-selective ALD to other chemistries
- Integration of area-selective ALD into CMOS process flow

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Laboratory of Advanced Materials
Stanford University

Stanford Nano-Fabrication

Center on Polymer Interfaces and Macromolecular Assemblies