Surface Modification for Area-selective Atomic Layer Deposition

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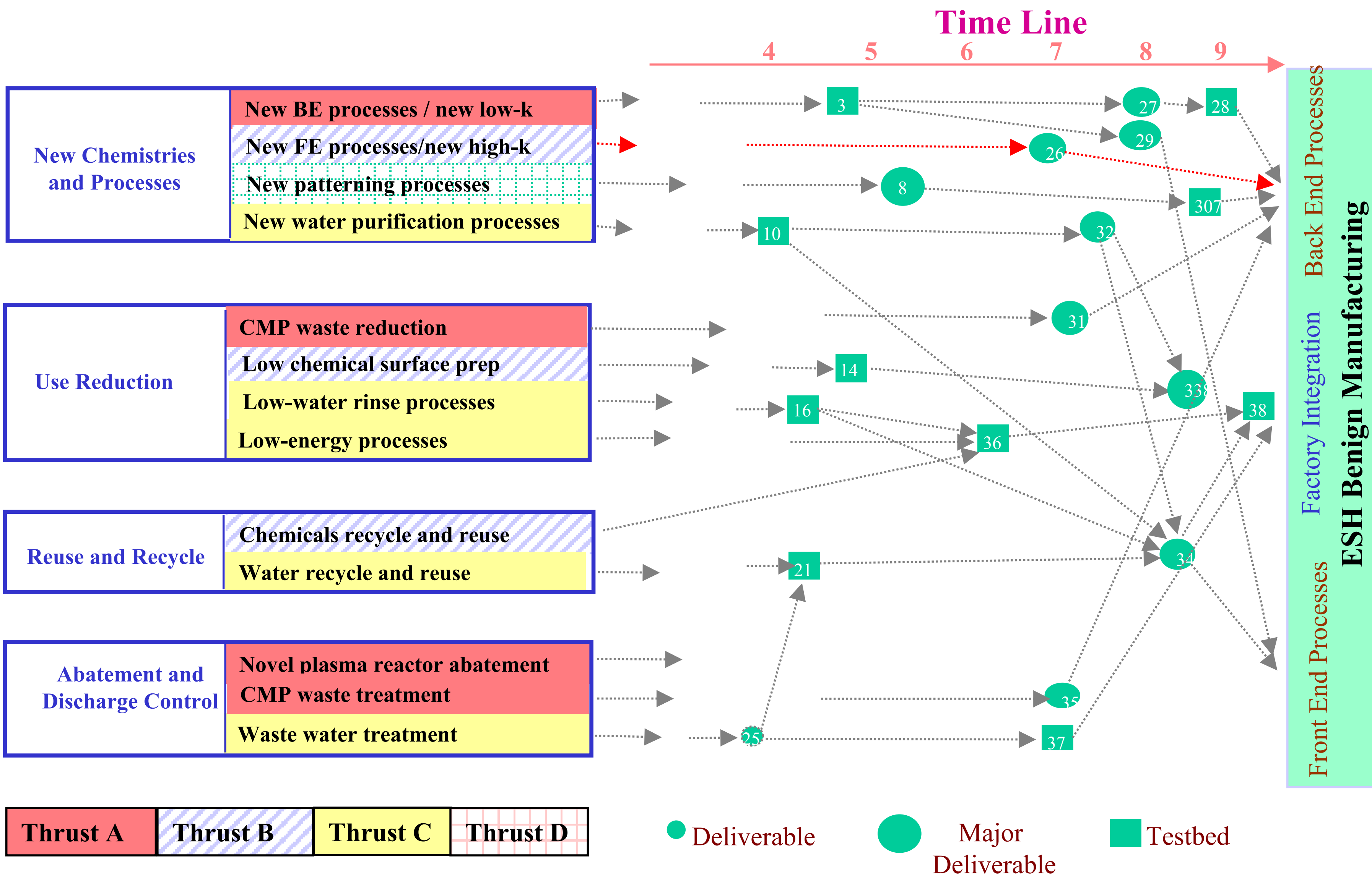
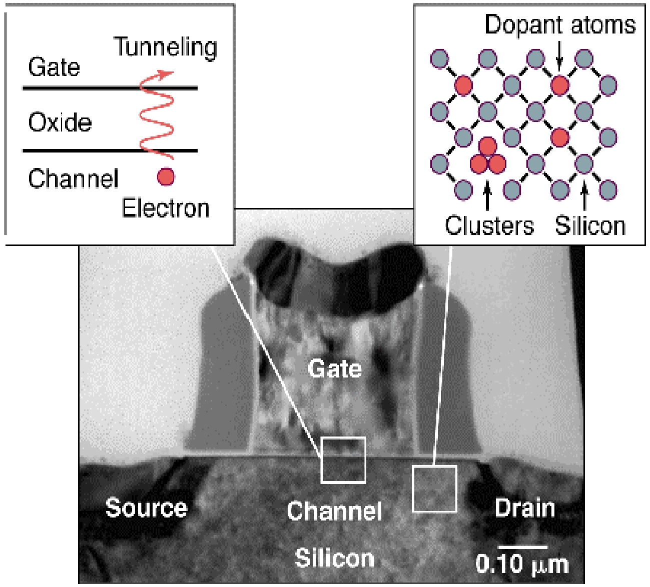
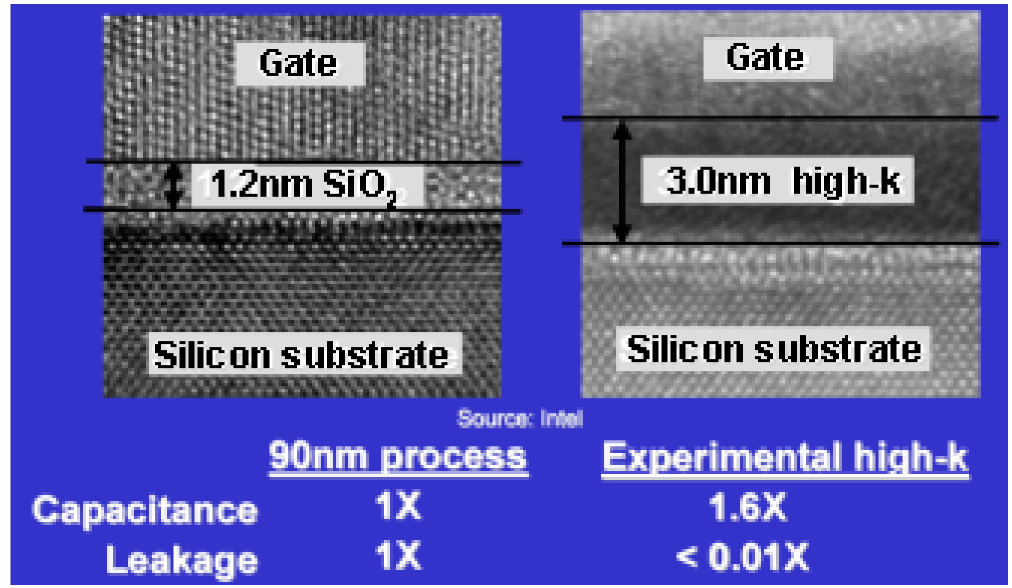
Strategic Plan (Task B-2)



The Need for High-κ Dielectric Materials





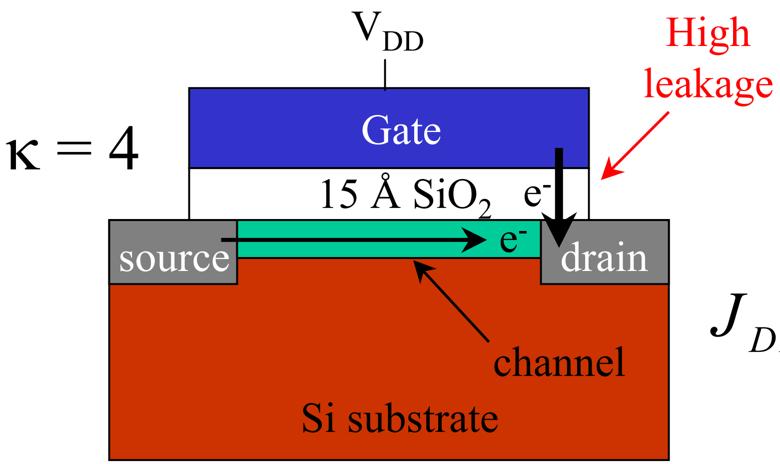
P.A. Packan, Science, 1999

Source: Intel

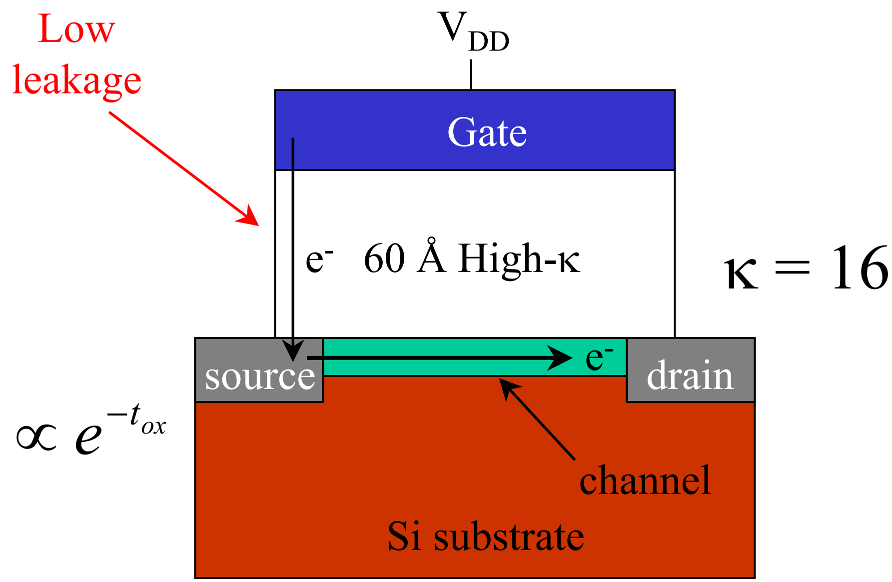
$$\text{Capacitance} \propto \frac{\kappa}{t}$$

- 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.

Benefits of High-κ Gate Dielectrics



$$J_{DT} \propto e^{-t_{ox}}$$



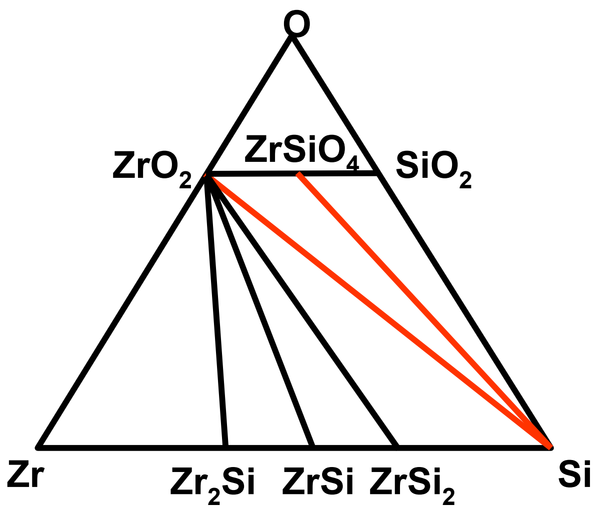
Higher-κ film ⇒ thicker gate dielectric ⇒ lower leakage and power dissipation with the same capacitance

$$C_{ox} = \frac{\kappa \varepsilon_0 A}{t_{ox}} \Rightarrow t_{high-\kappa} = \left(\frac{\kappa_{high-\kappa}}{\kappa_{SiO_2}} \right) \cdot t_{SiO_2}$$

What factors need to be included in choosing a high-κ replacement?

Desirable High-κ Gate Dielectric Properties

Material Properties	Electrical Properties
k > 15; uniform	Equivalent Tox < 1 nm
Thermally stable on Si (no **need** for barrier layer)	Low leakage current at the same equivalent Tox
No reaction with electrode (stop B penetration if poly-Si)	No mobility degradation (low interface trap density)

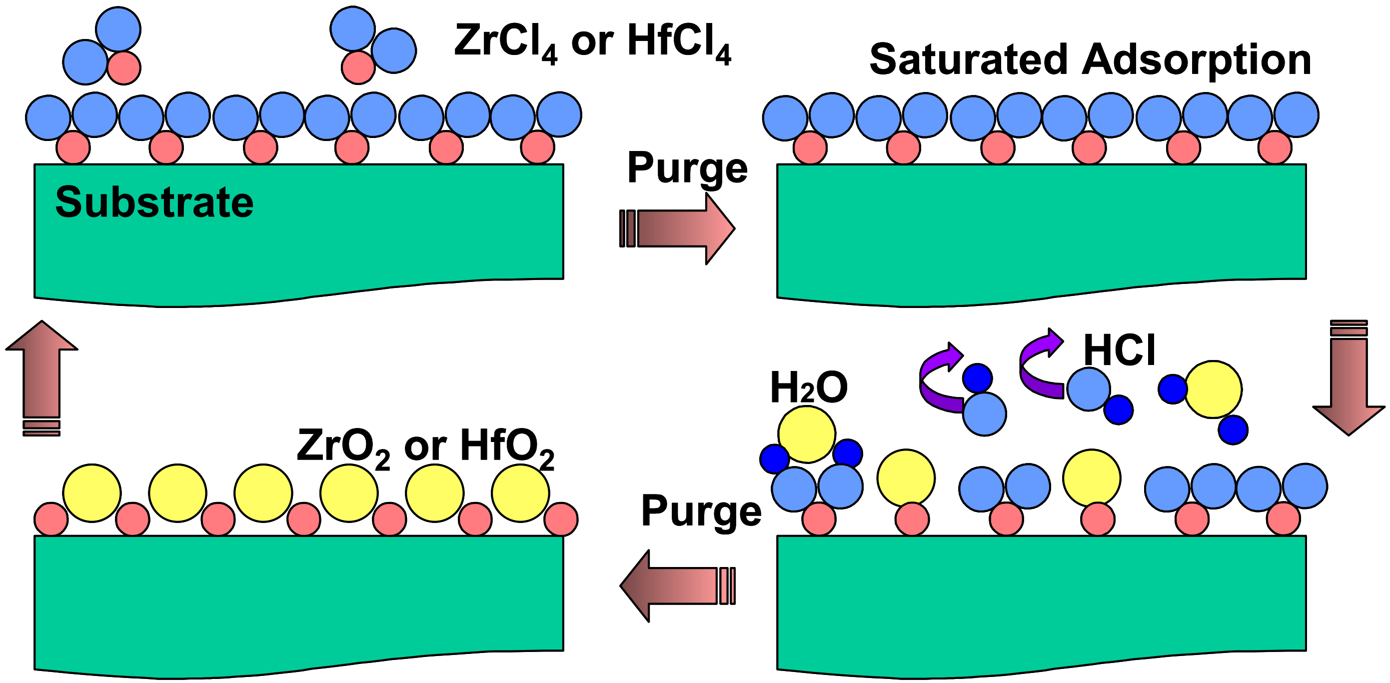


700 ~ 900°C

Ref.) Beyers et.al, J.Appl.Phys., 56, 147(1984)

Material	SiO_2	ZrO_2/HfO_2	Silicate (Zr,Hf)
Dielectric Constant	3.9	**~25**	15 ~ 25
Band Gap (eV)	8.9	**~5.7**	~6

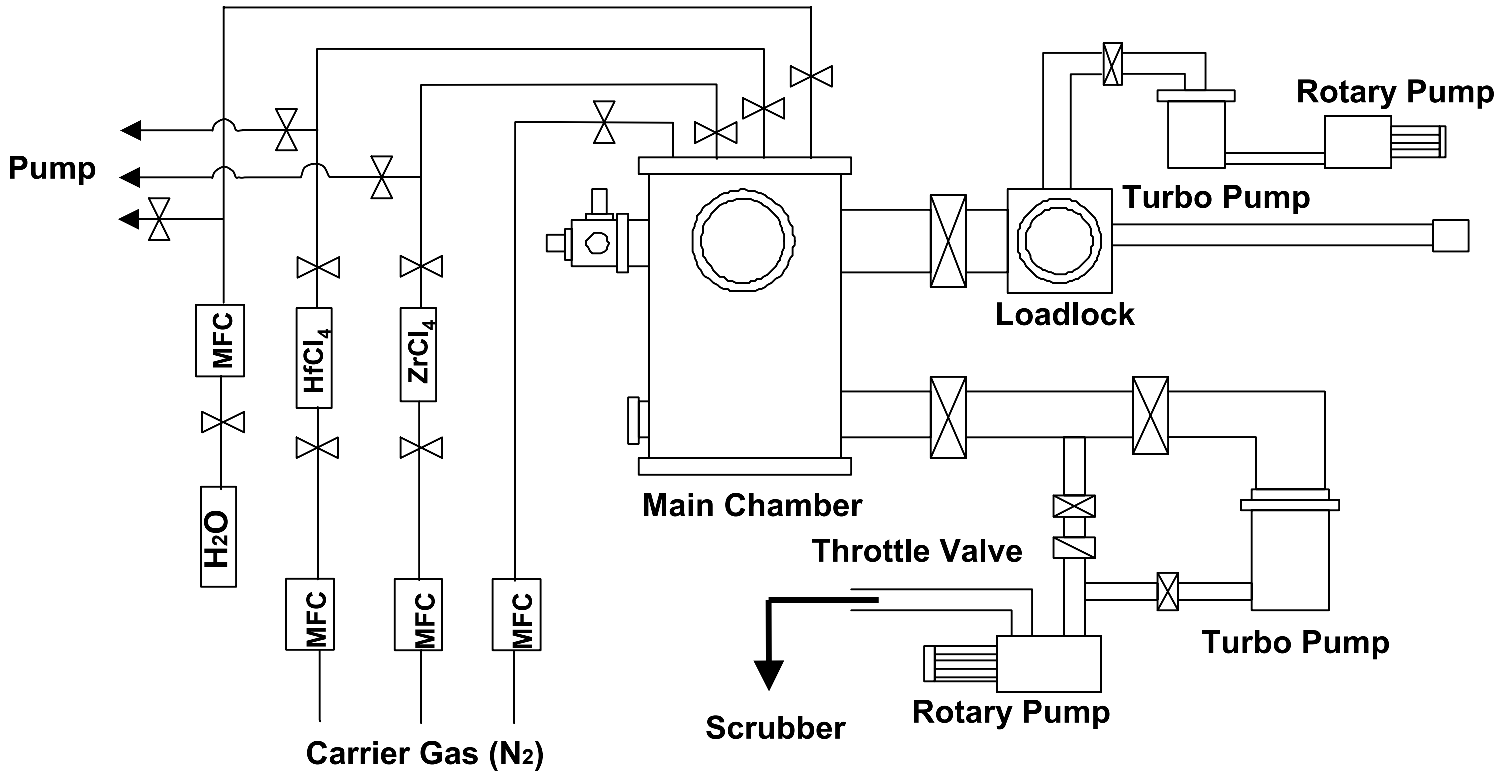
Atomic Layer Deposition of Metal Oxide



$ZrCl_4$(ad.) + $2H_2O$(g) -> ZrO_2(s) + 4HCl(g)
$HfCl_4$(ad.) + $2H_2O$(g) -> HfO_2(s) + 4HCl(g)

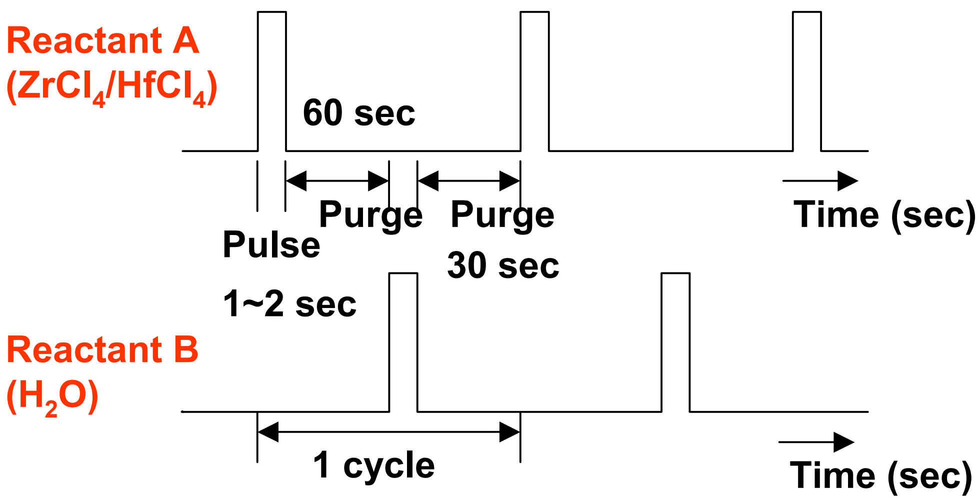
- Surface saturation controlled deposition
- Surface condition prior to deposition is critical
- Layer-by layer deposition
- Excellent film quality and step coverage

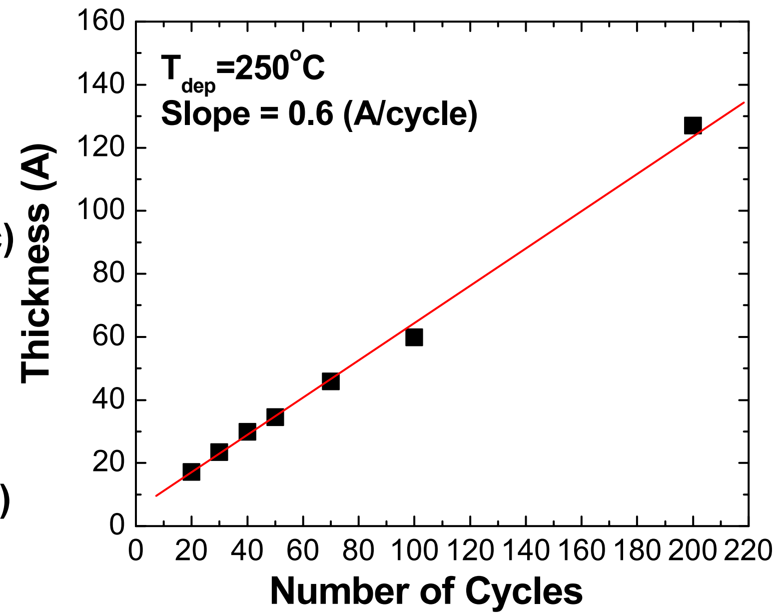
Schematic Diagram of Stanford ALD System

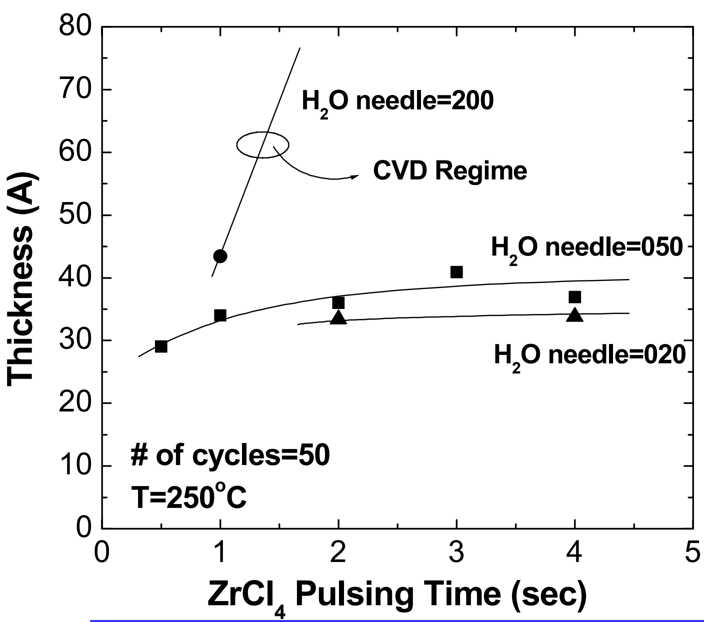


- **Base pressure = ~10^{-8} Torr**
- **Process temperature : 300°C**
- **Process pressure : 0.5 Torr**
- **Source temperature : H_2O (liquid) = 20°C, $HfCl_4$ (solid) = 150°C**

ALD : Surface Saturation Controlled Process







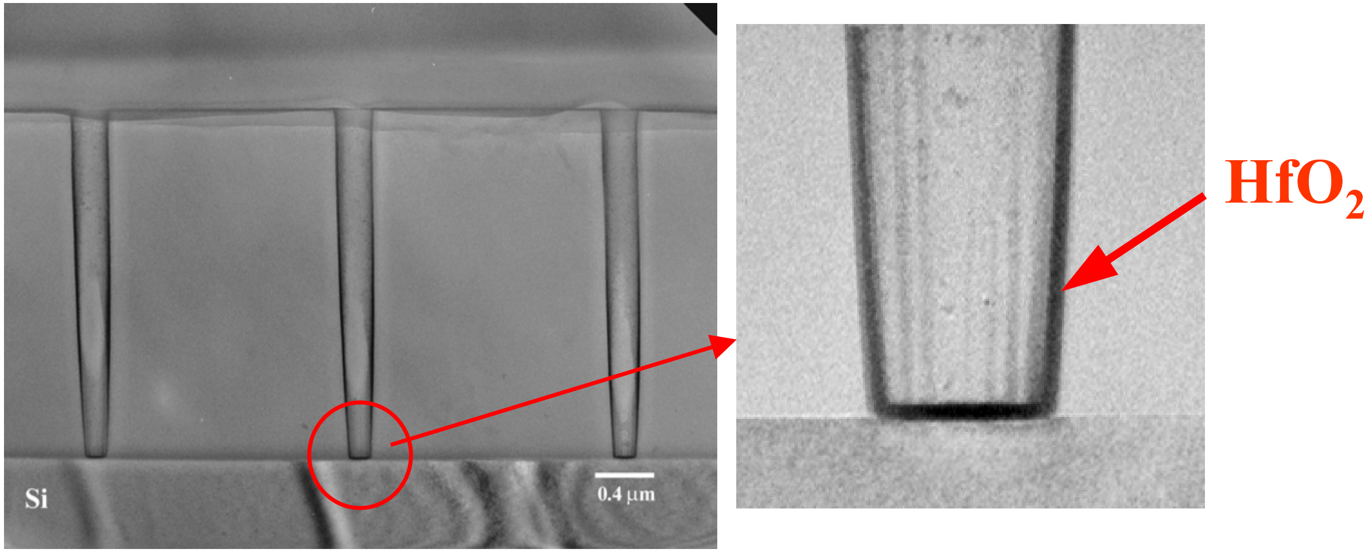
Layer-by layer deposition process

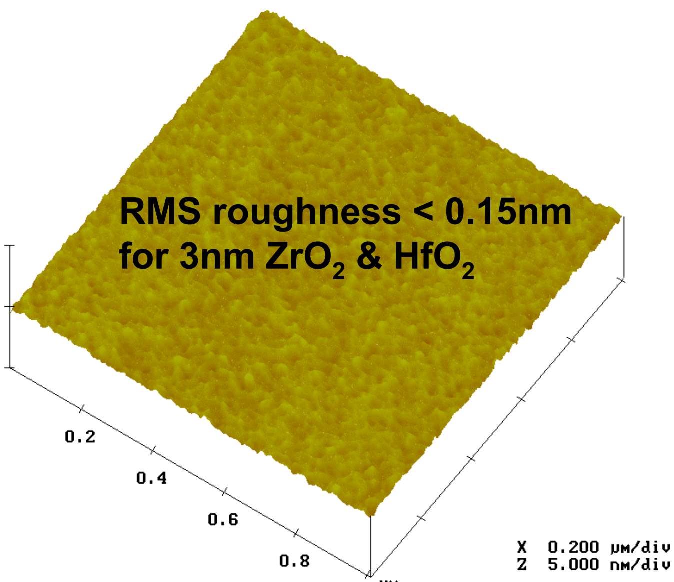
- Linear sub-monolayer growth rate
- Independence of precursor pulsing time

Surface sensitive deposition process

- uniform deposition only on hydrophilic surface

Conformality and Surface Roughness of ALD Films

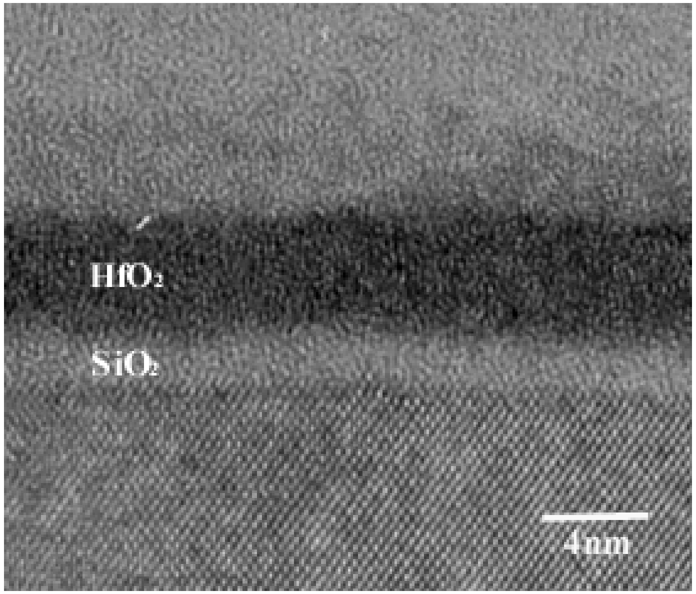


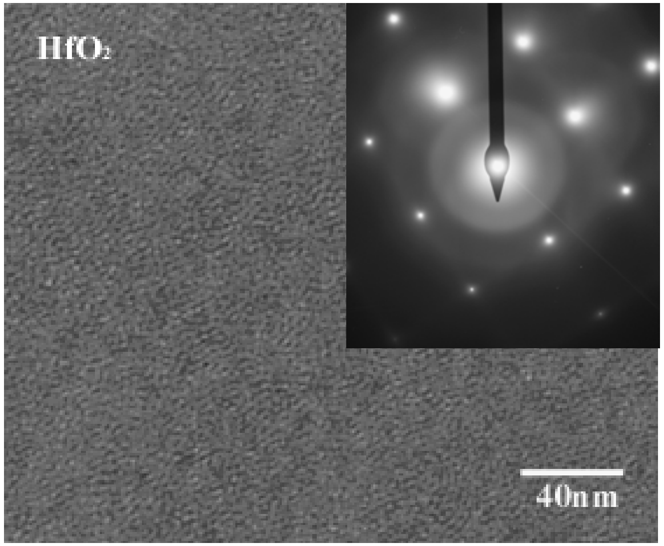


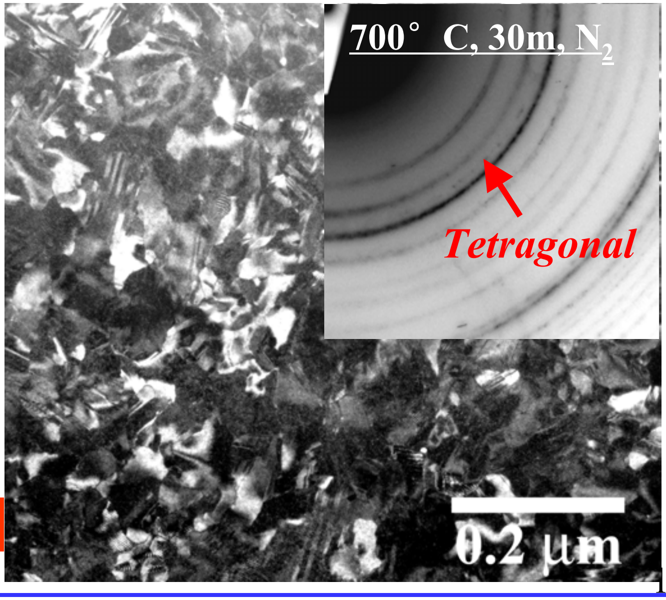
ALD deposition of metal-oxide films

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

Microstructural Properties of ALD-HfO_2





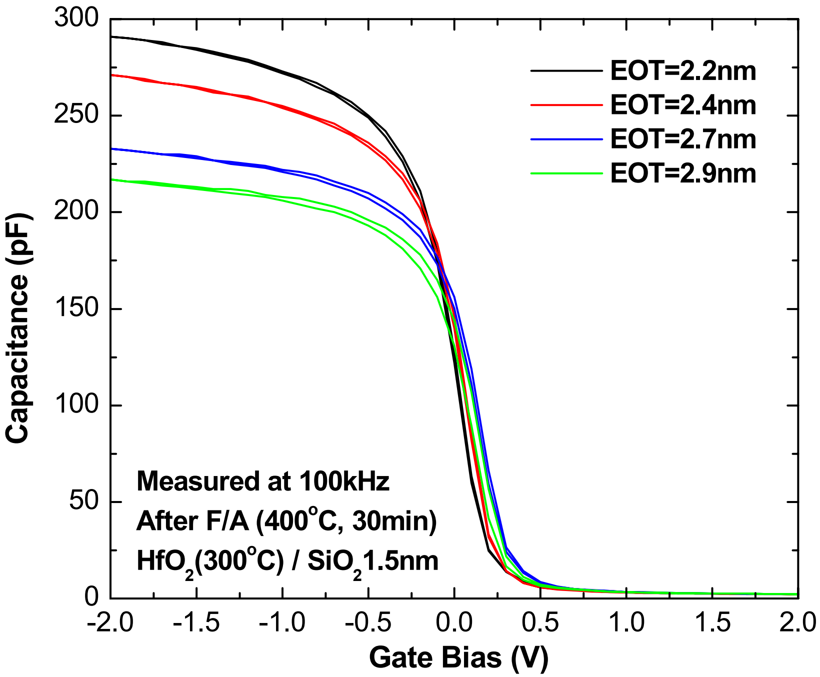


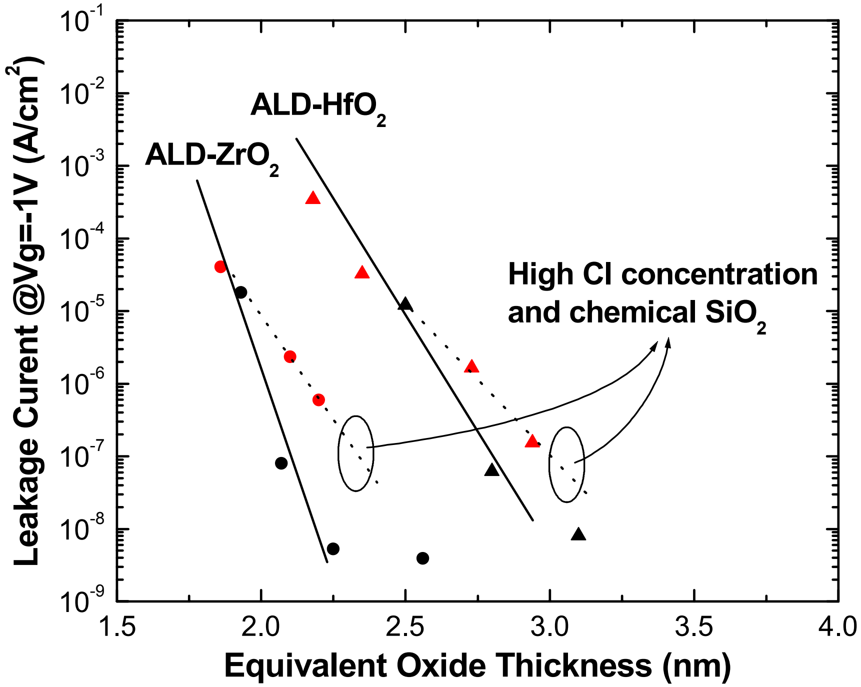
Micrstructure of ALD-HfO_2

- As-deposited HfO_2 : Amorphous
- Crystallization : starts over 500°C and majorly monoclinic phase having some tetragonal

After complete crystallization

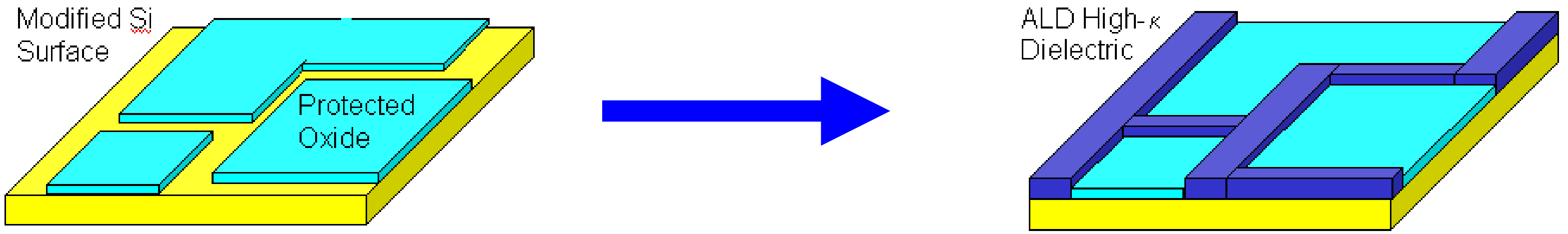
Electrical Properties of ALD-HfO_2



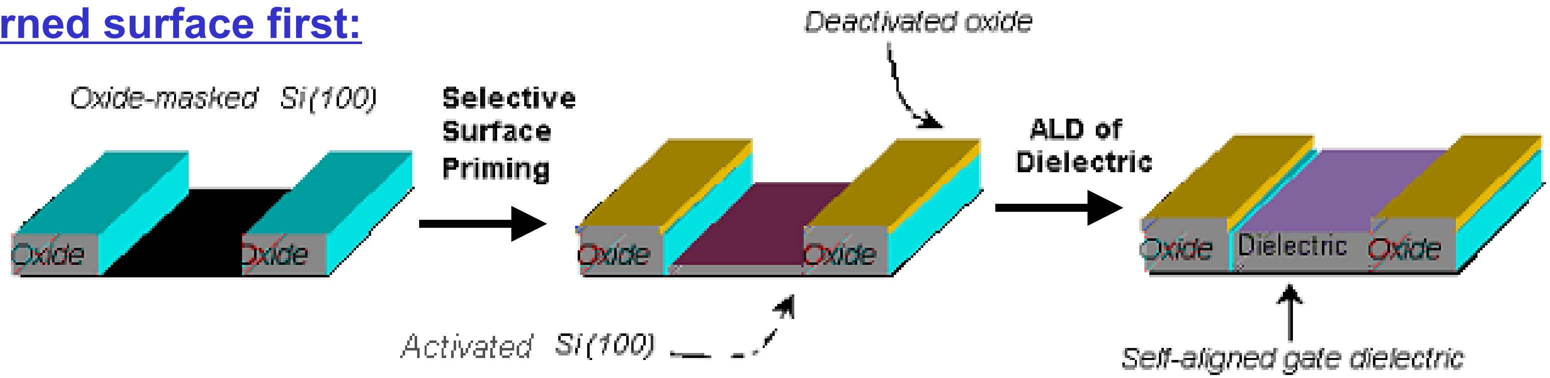


- Series Pt electrode/HfO_2/p-Si/Backside Al contact structure
- Significant hysteresis not observed for thick dielectric layers: reduce bulk trap density by reducing Cl impurity content at T_{dep} = 300°C.
- Optimized electrical properties by reducing Cl concentration in HfO_2 film.
- Calculated dielectric constant of ALD-HfO_2 is around 17.

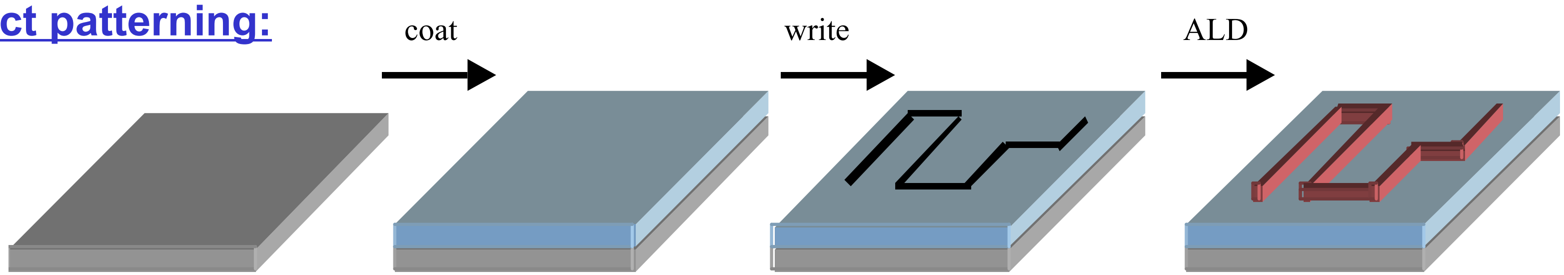
Approaches for Area-Selective ALD



Patterned surface first:



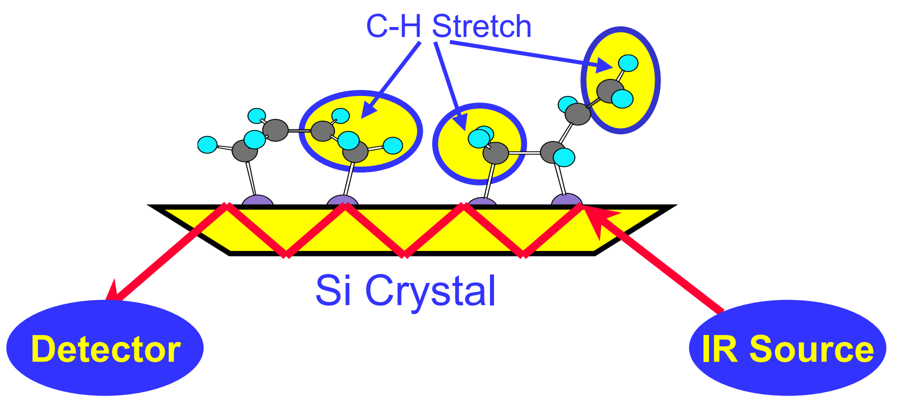
Direct patterning:



- It eliminates several photolithography, wet etching and plasma etching steps during IC fabrication (environmentally benign).
- It is an innovational method for making nano-scale transistors and other devices.

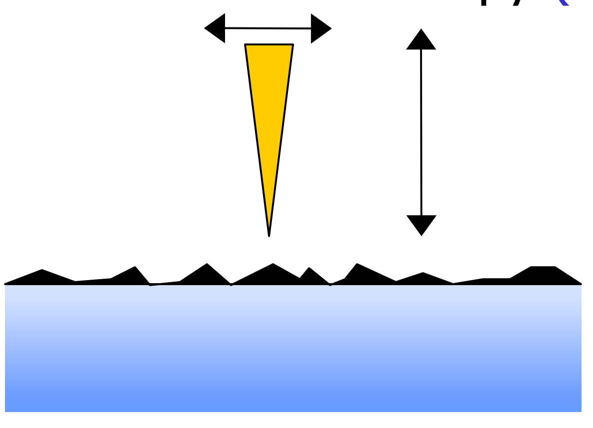
Experimental Investigating Methods

1. **A**ttenuated **T**otal **R**eflection **F**ourier **T**ransform **I**nfra**R**ed Spectroscopy (ATR-FTIR)



Investigation of surface reactivity both *in-situ* and *ex-situ*

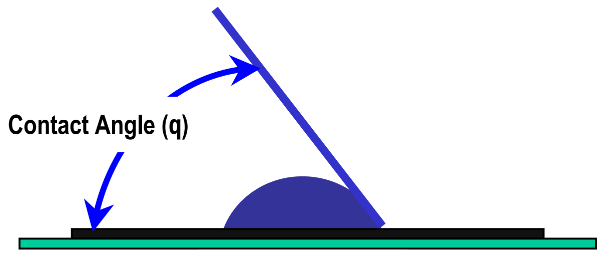
2. Atomic Force Microscopy (AFM)



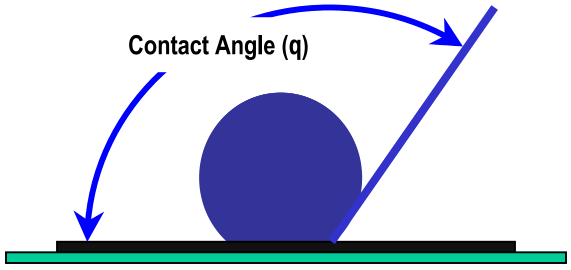
Film quality investigation by exploring surface roughness

Contact Angle Measurement

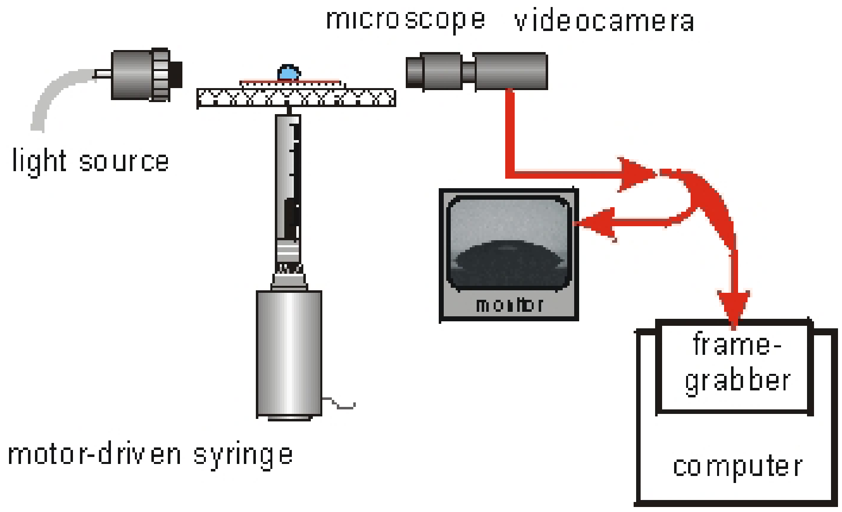
3. The hydrophobicity/hydrophilicity of a solid surface is usually expressed in terms of wettability which can be quantified by contact angle measurements.



q < 90° Hydrophilic



q >90° Hydrophobic

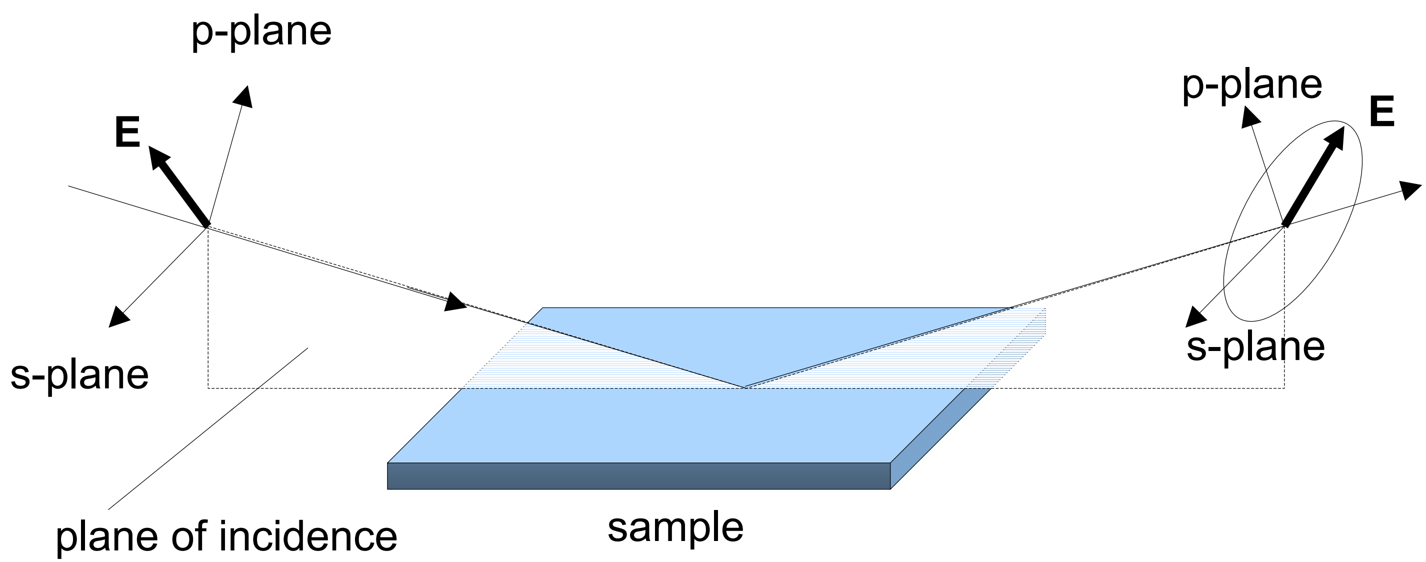


Film quality investigation by exploring hydrophobic properties

http://www.ipfdd.de

Ellipsometry Measurement

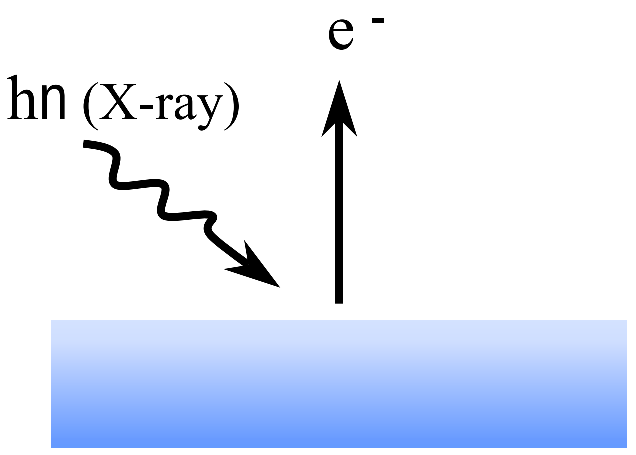
4. An ellipsometer enables to measure the refractive index and the thickness of semi-transparent thin films.



Quick way for film thickness and conformality measurement

Experimental Investigating Methods (Con't)

5. X-ray Photoelectron Spectroscopy (XPS)



Elemental quantity analysis

6. Scanning Electron Microscopy (SEM)

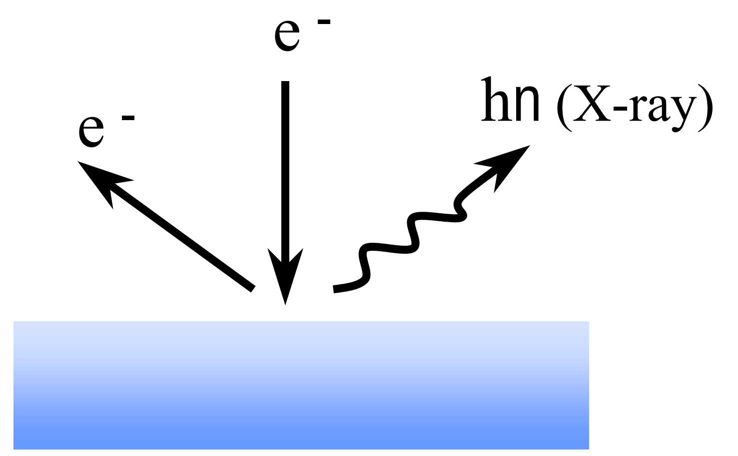
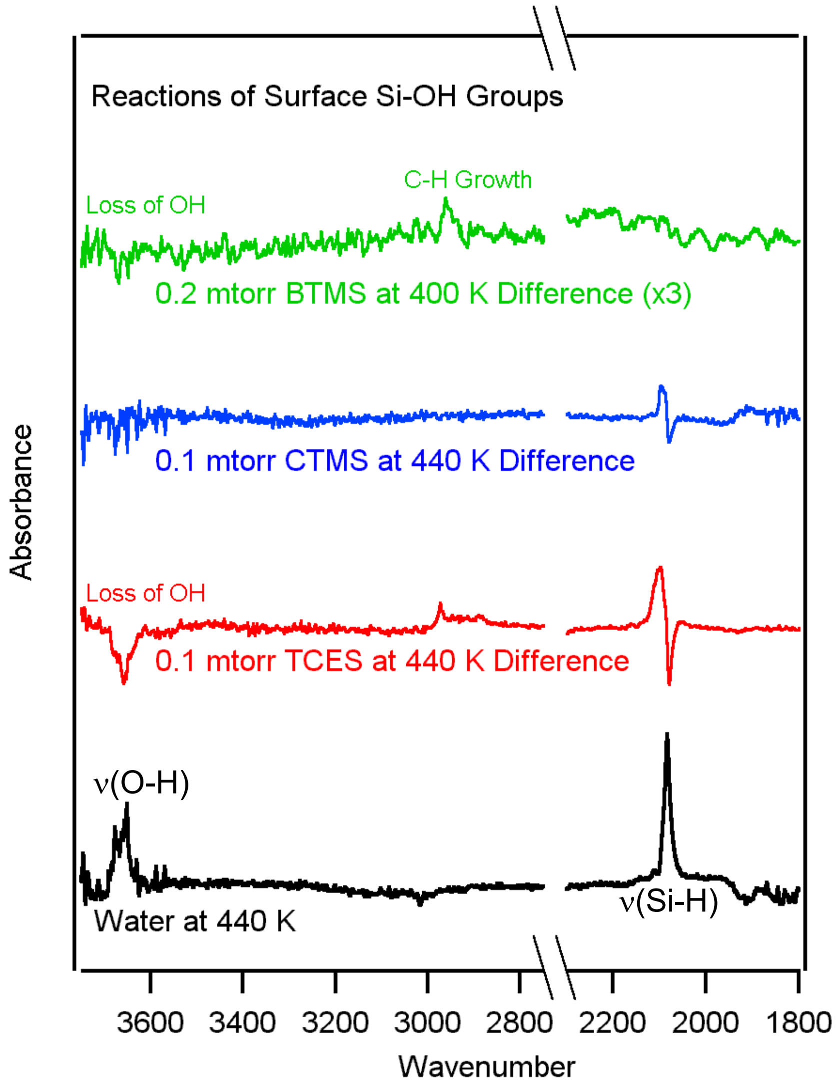


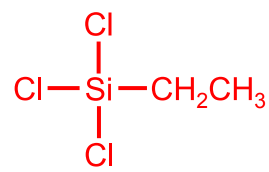
Image of patterned surface

FTIR Investigation of Reactivity and Selectivity

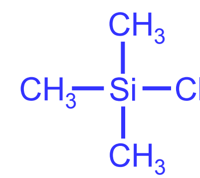


By Courtesy: Collin Mui

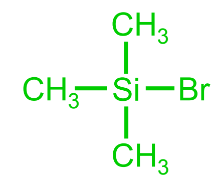
Precursors Investigated:



Tri-Cl-ES



Chloro-TMS



Bromo-TMS

Experimental Results:

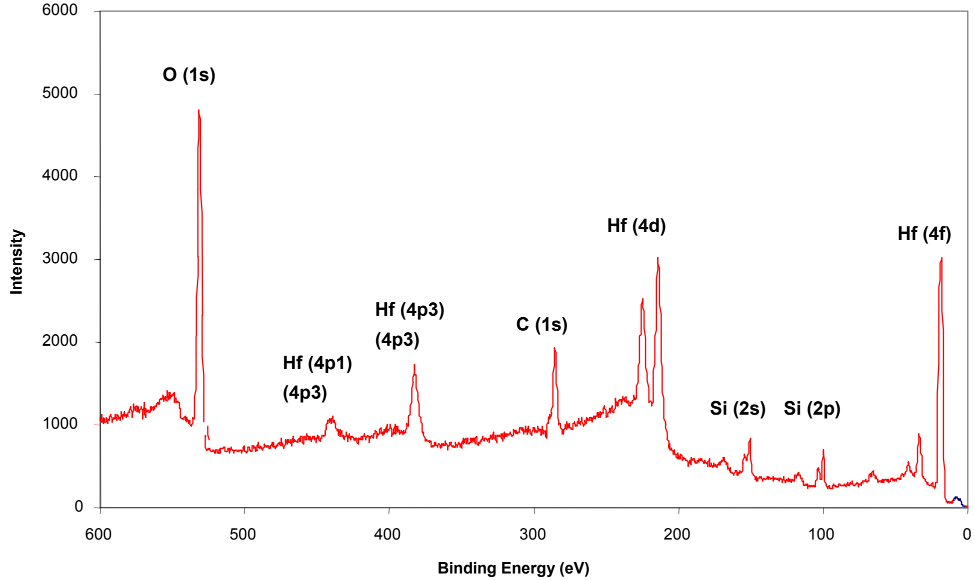
- Chemical attachment of the compounds is evidenced by loss of Si-OH stretch and growth of C-H stretch
- Whereas the trichloro-compound (Tri-Cl-ES) reacts with Si-OH groups, the monochloro-compound (Chloro-TMS) did not.
- However, the monobromo-compound (Bromo-TMS) does appear to react with Si-OH

Conclusion:

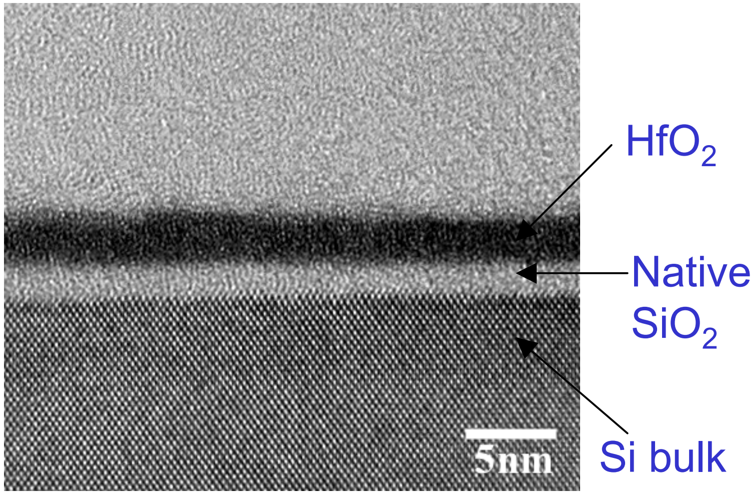
- Reactivity increases with more Cl substitution and moderately with Br substitution.

Gas Phase Delivery of Deactivating Agent for HfO_2 ALD

XPS after HfO_2 deposition



Cross-Sectional TEM Image



- Deactivating agent : TCES
- HfO_2 (50cycles) at 300°C

Results:

Some precursors (e.g. TCES) react well at the surface, yet fail to deactivate the surface toward HfO_2 deposition, according to XPS, ellipsometry, and TEM

Discussion of Gas Phase Delivery of Deactivating Agent

Discussion:

• Those small organic molecules might not completely cover the whole surface under current reaction condition, or

• Those small organic molecules might not survive at current ALD temperature (300˚C), or

• ALD precursors compete with organic molecules and react or cause desorption at current ALD temperature (300˚C) .

Solution:

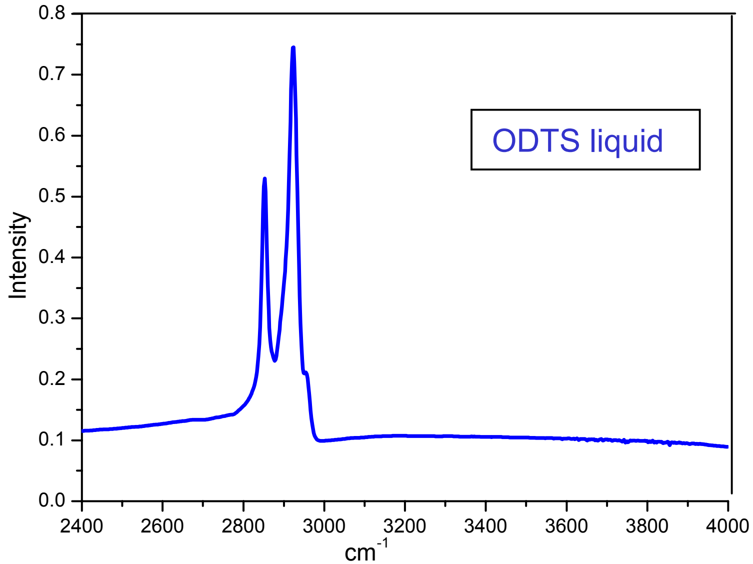
• Find longer chain deactivating agents which can provide a better barrier to block ALD growth;

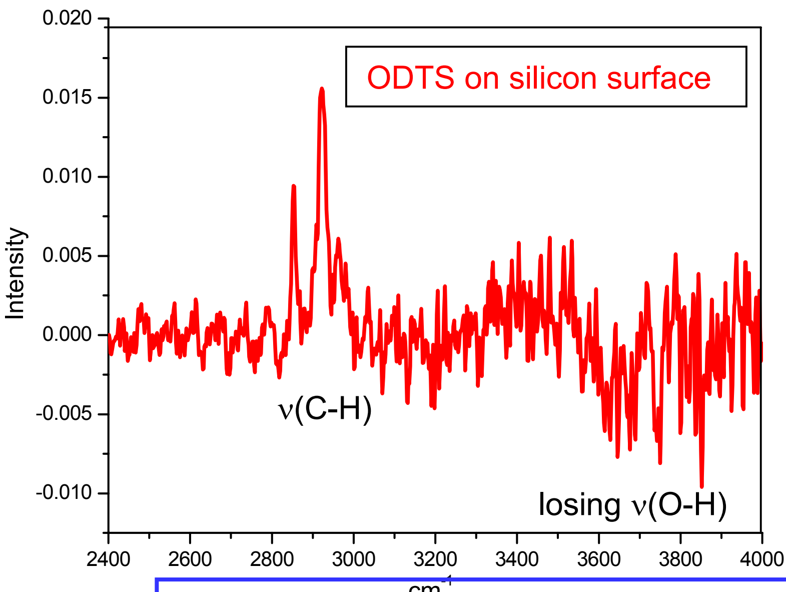
• Modify the ALD process (e.g. new ALD precursors, conditions) for lower reaction temperature

Current Work:

Solution based attachment of alkyltrichlorosilanes

Longer Chain Alkylhalosilane Reaction on Surface



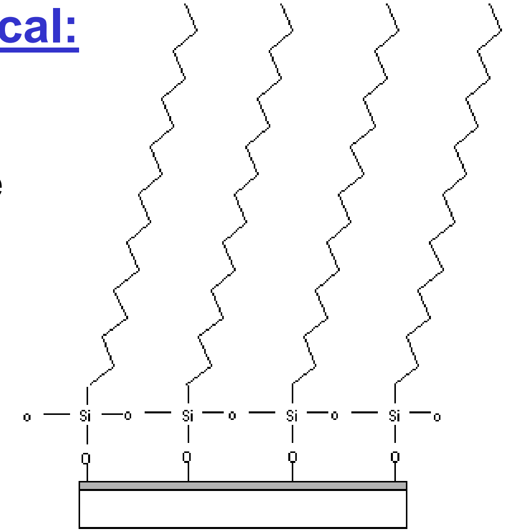


Deactivation Chemical:

ODTS

Octadecyltrichlorosilane

CH_3-$(CH_2)_{17}$-$SiCl_3$



Reason:

One of the most popular silylating agents on native oxide silicon surface, it has high reactivity and relative stability at high temperature.

FTIR results:

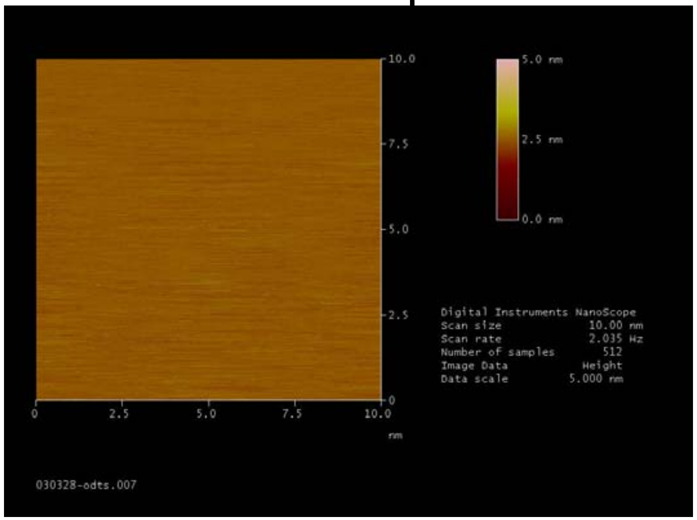
Show high reactivity at room temperature and long-term stability in air.

Conclusion:

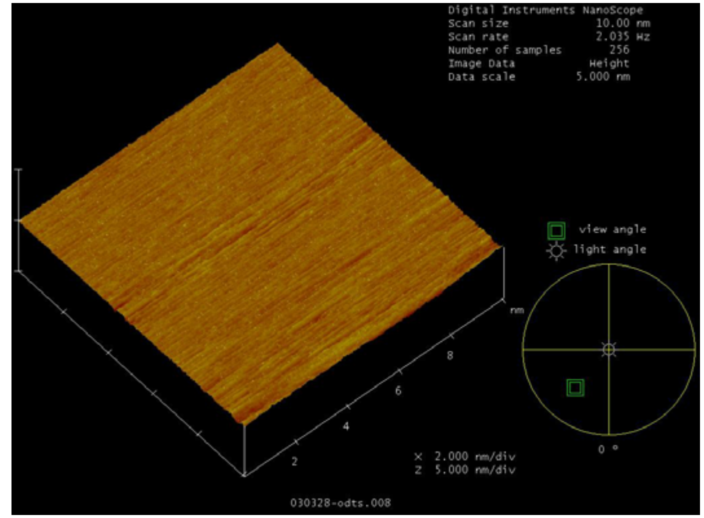
ODTS may be effective for deactivating HfO_2 deposition.

AFM Study of Dense ODTS Coated Surface (10nm*10nm)

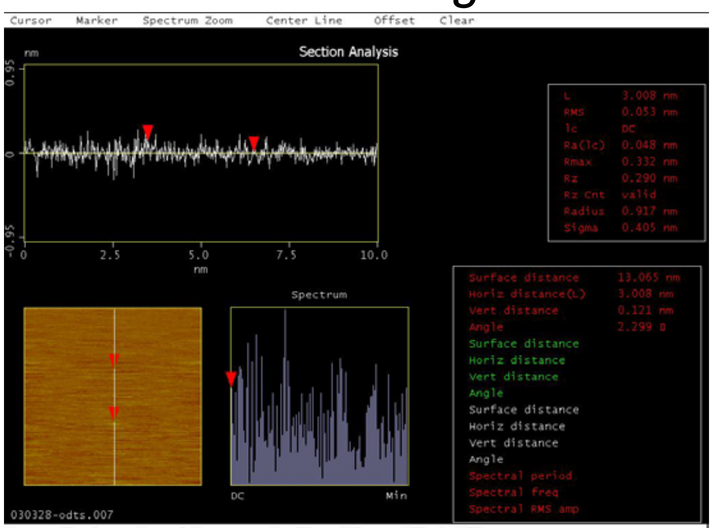
*10nm*10nm | 5 nm*



3D Image



Sectional Image

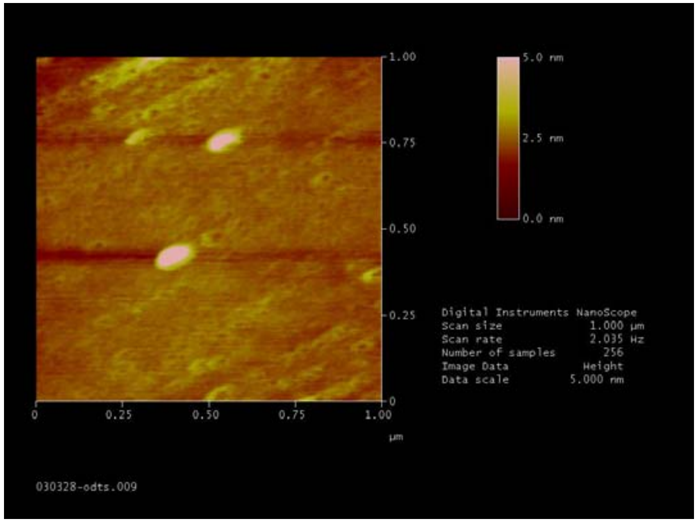


Surface roughness is 0.053nm over the whole region

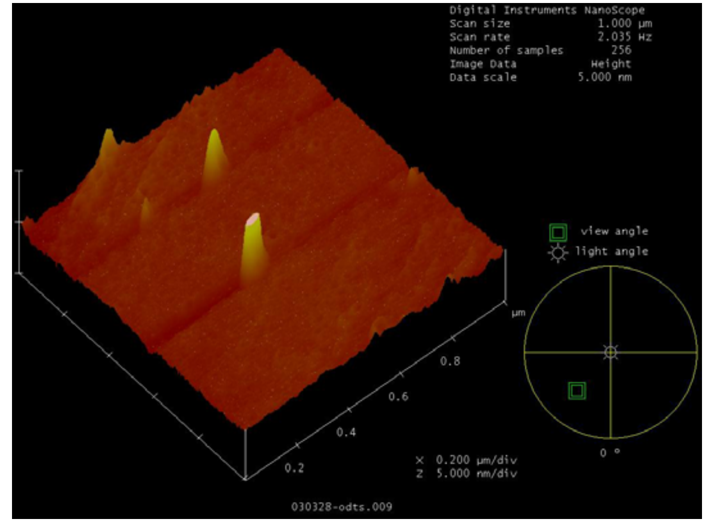
*Surface is atomic level flat over 10nm*10nm region*

AFM Study of Dense ODTS Coated Surface (1µm* 1µm)

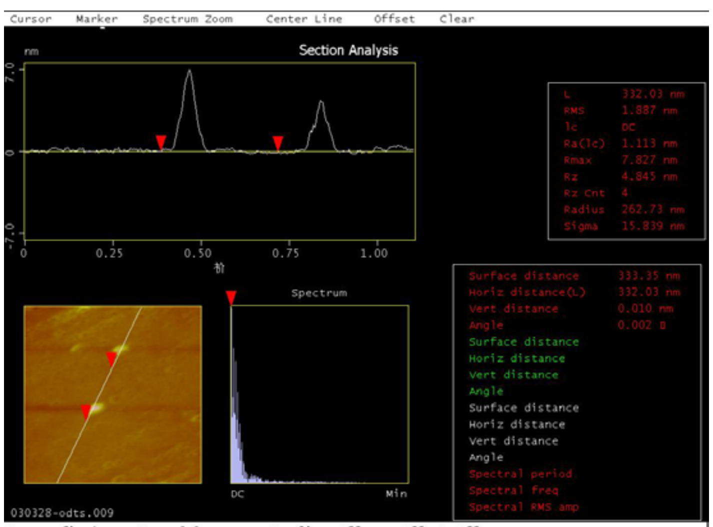
*1µm*1 µm | 5 nm*



3D Image



Sectional Image

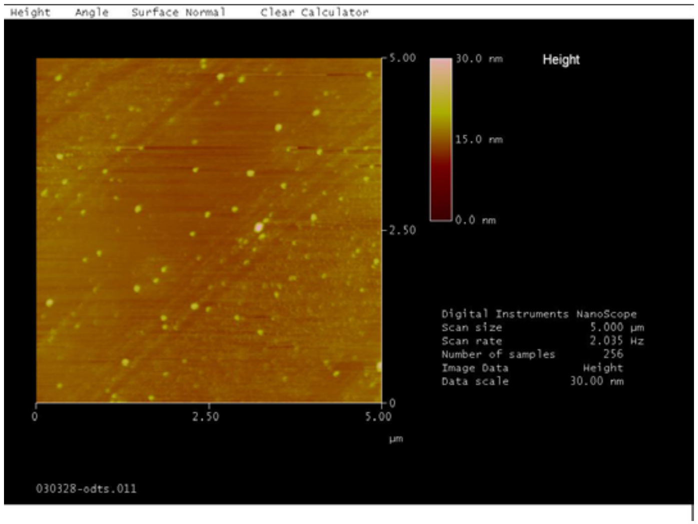


Surface roughness is 0.49 nm over the whole scanning region

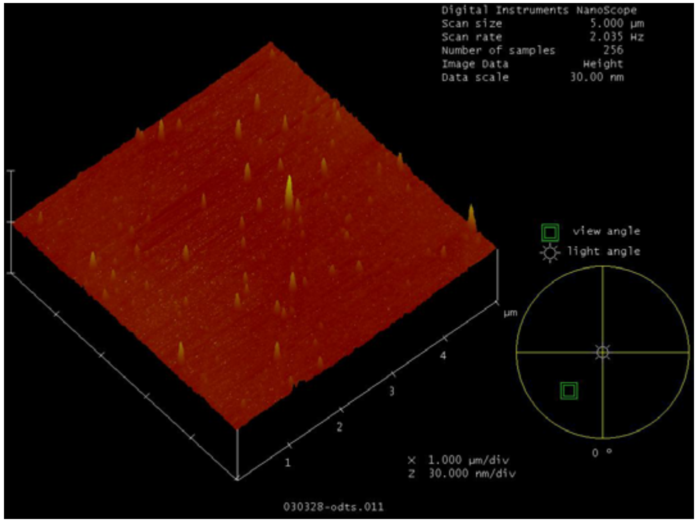
The height of bumps are around 5~7nm

AFM Study of Dense ODTS Coated Surface (5μm* 5μm)

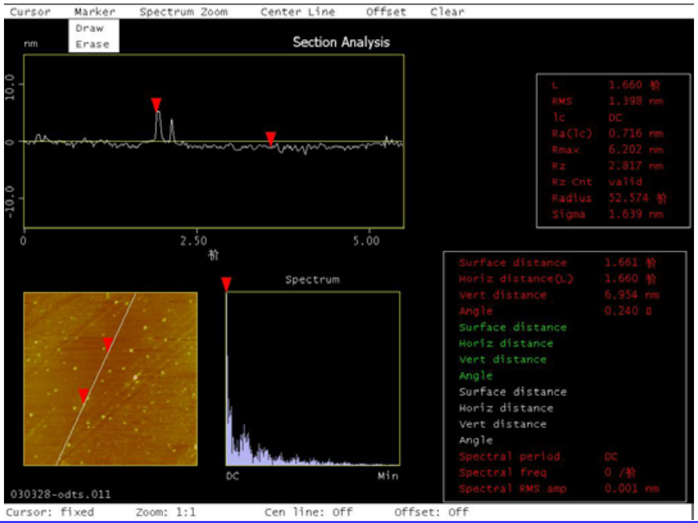
*5μm*5 μm | 30 nm*



3D Image



Sectional Image

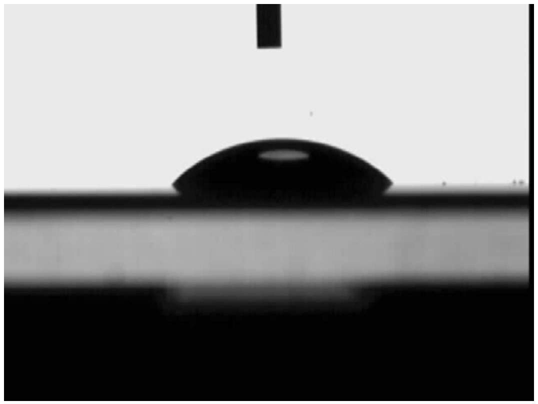


Surface roughness is 1.009 nm over the whole scanning region

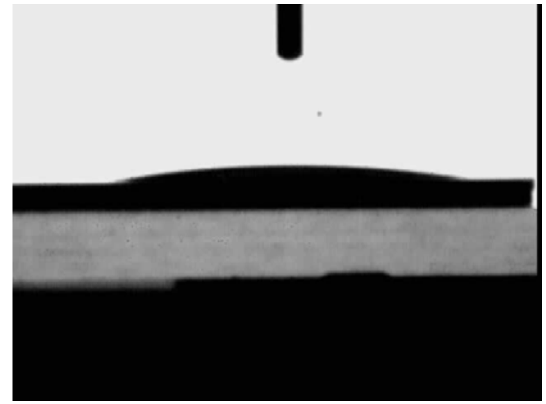
The height of bumps are around 5~7nm, which is consistent with literature suggestion that these bumps originate from polymerization during SAMs formation

Contact Angle Study

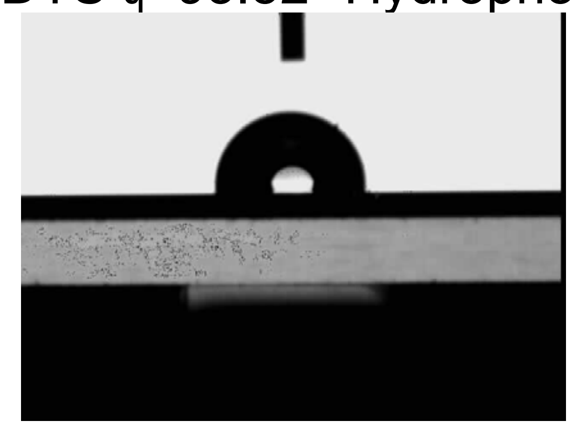
Native oxide silicon wafer
q=23.51° Hydrophilic



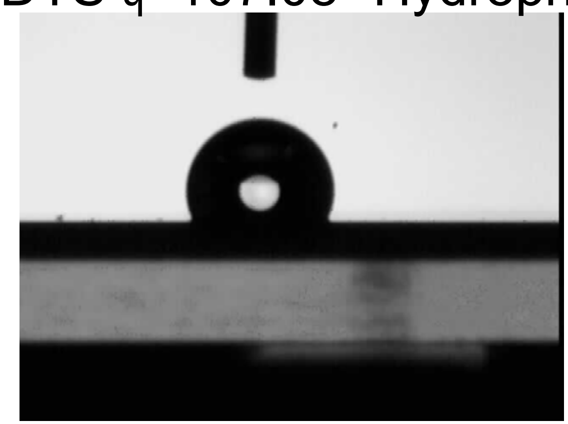
Wafer treated by plasma Ozone
q=3.47° Extremely Hydrophilic



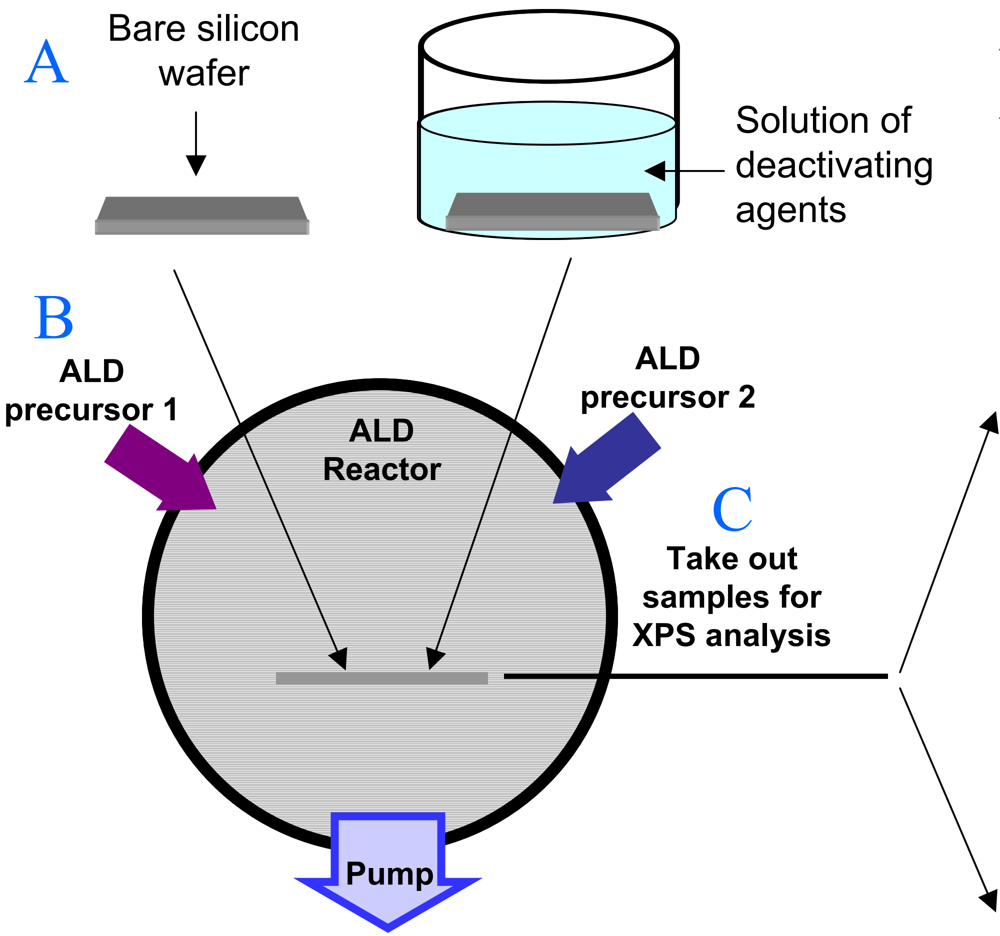
Silicon wafer coated with loose
ODTS q=93.52° Hydrophobic

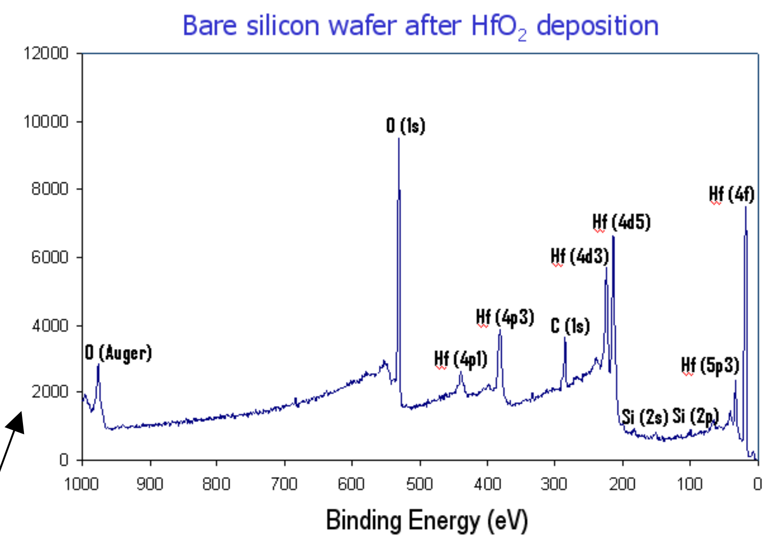


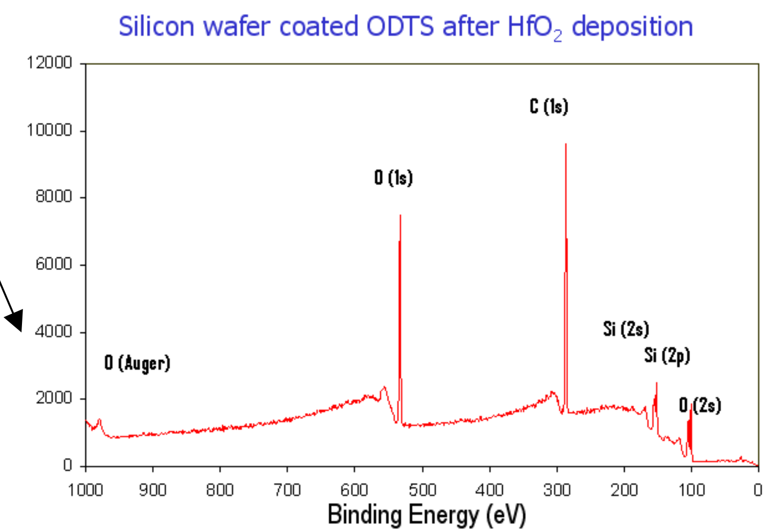
Silicon wafer coated with dense
ODTS q=107.08° Hydrophobic



Combined Deactivating Agents & ALD







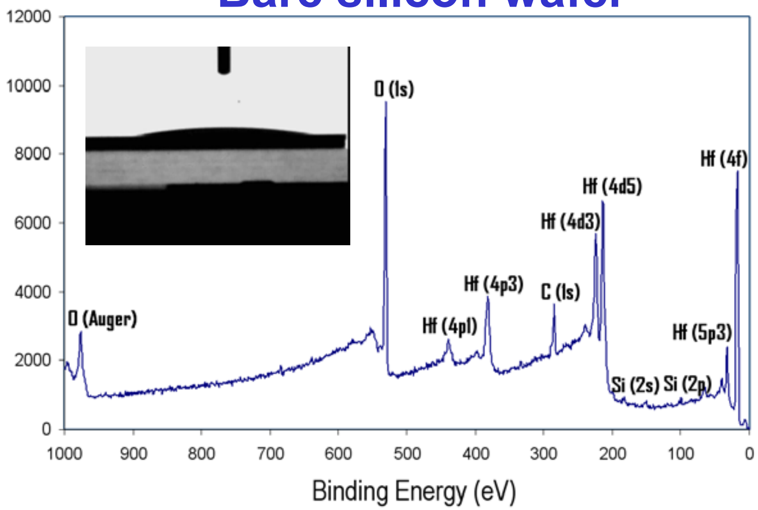
A. Deactivating agents preparation and analysis;

B. ALD growth of HfO_2 ;

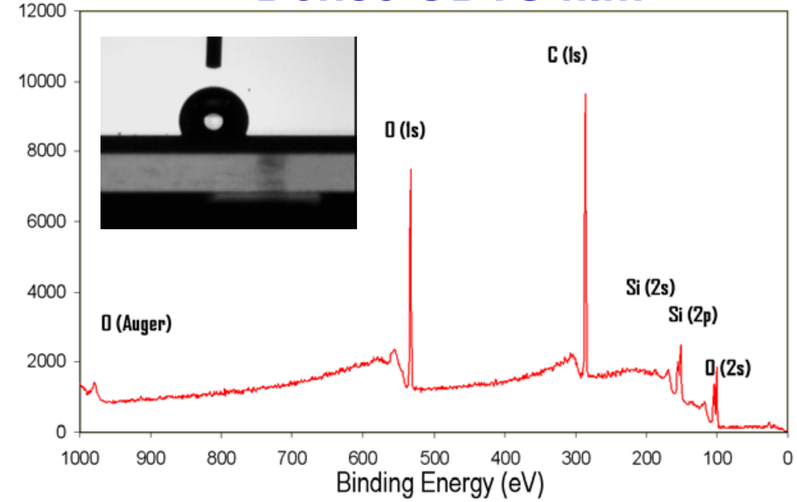
C. Sample characterization after deposition.

XPS Study of Different Starting Surface for HfO_2 ALD

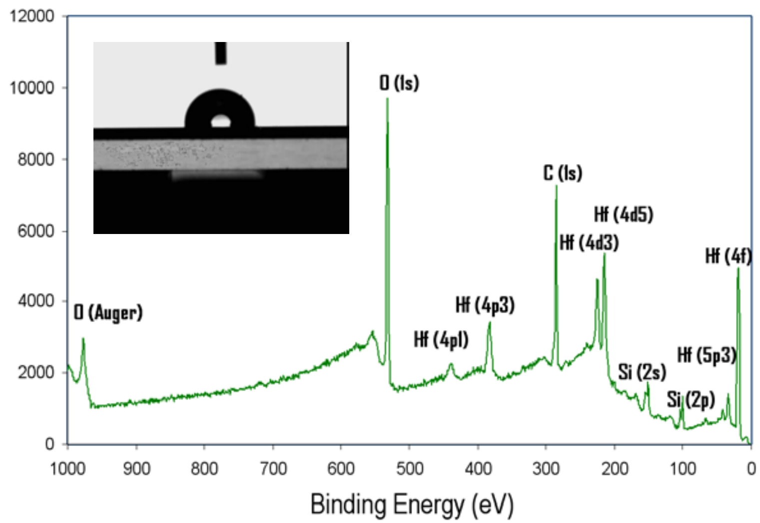
Bare silicon wafer



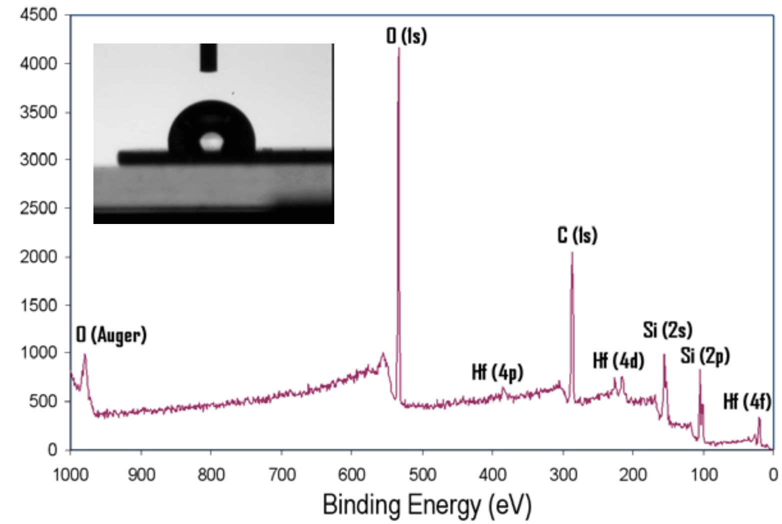
Dense ODTS film



Loose ODTS film



Dense Tri-Cl-Et film



Ellipsometry Study

Chemical	Thickness of native SiO_2 (Å)	Thickness of deactivating agents (Å)	Thickness of HfO_2 (Å)	Hf amount by XPS (%)	HfO_2 amount by XPS (%)
Bare Silicon wafer	15~16	/	34~36	11.99%	35.97%
Dense ODTS film	15~16	28~30	/	<0.19%	<0.57%
Loose ODTS film	15~16	12~14	9~11	4.72%	14.16%
Dense Tri-Cl-Et film	15~16	4~6	1~2	1.09%	3.27%

Results & Conclusion of Deactivating Agents Study

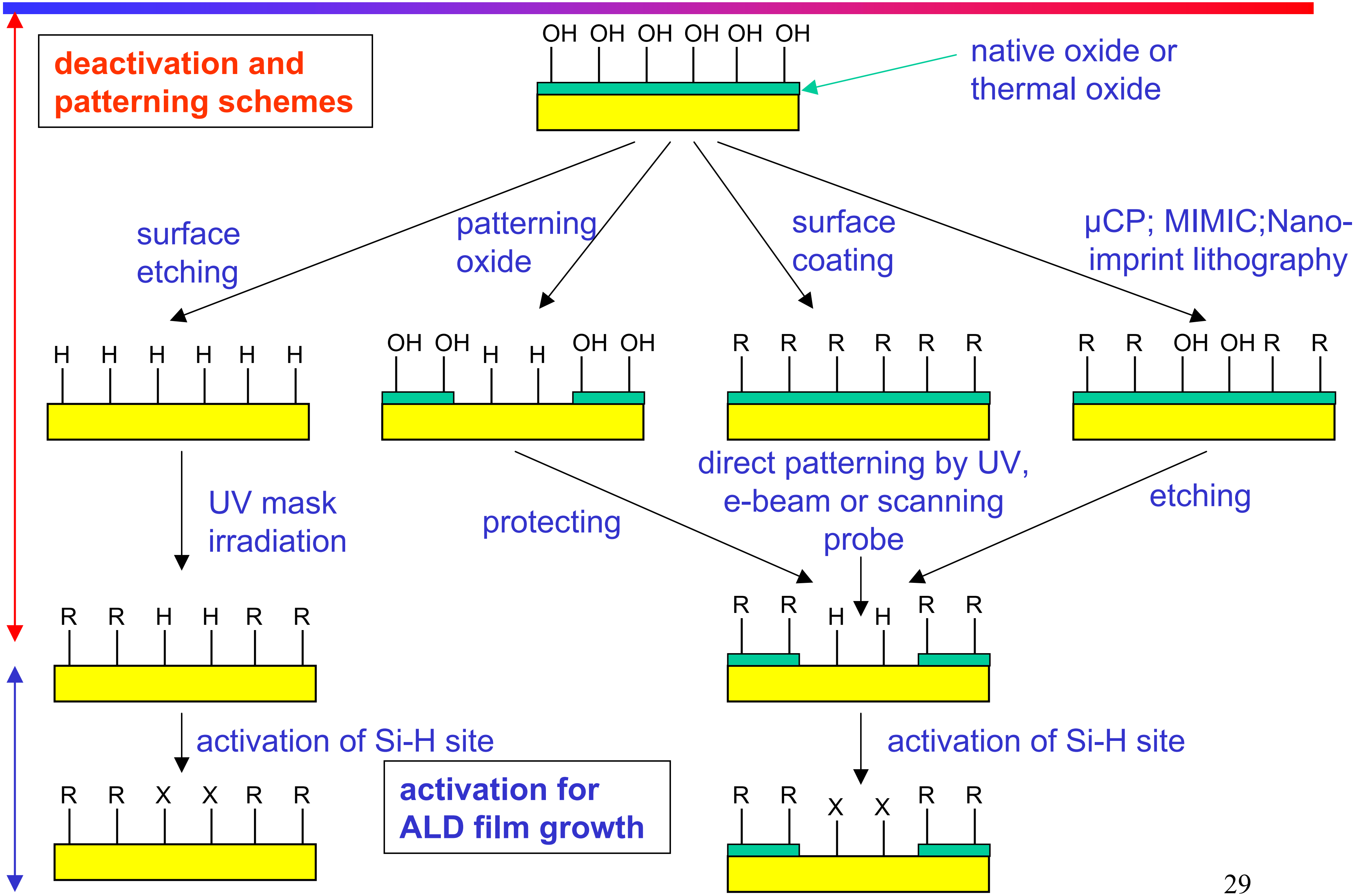
Results:

- AFM experiments show we have formed a pretty smooth SAMs on silicon surface;
- Contact angle, Ellipsometry and XPS show consistent results;
- Dense chemical films show good blockage effect for HfO_2 ALD growth;
- The chain length might not be the only key factor for good deactivating agent.

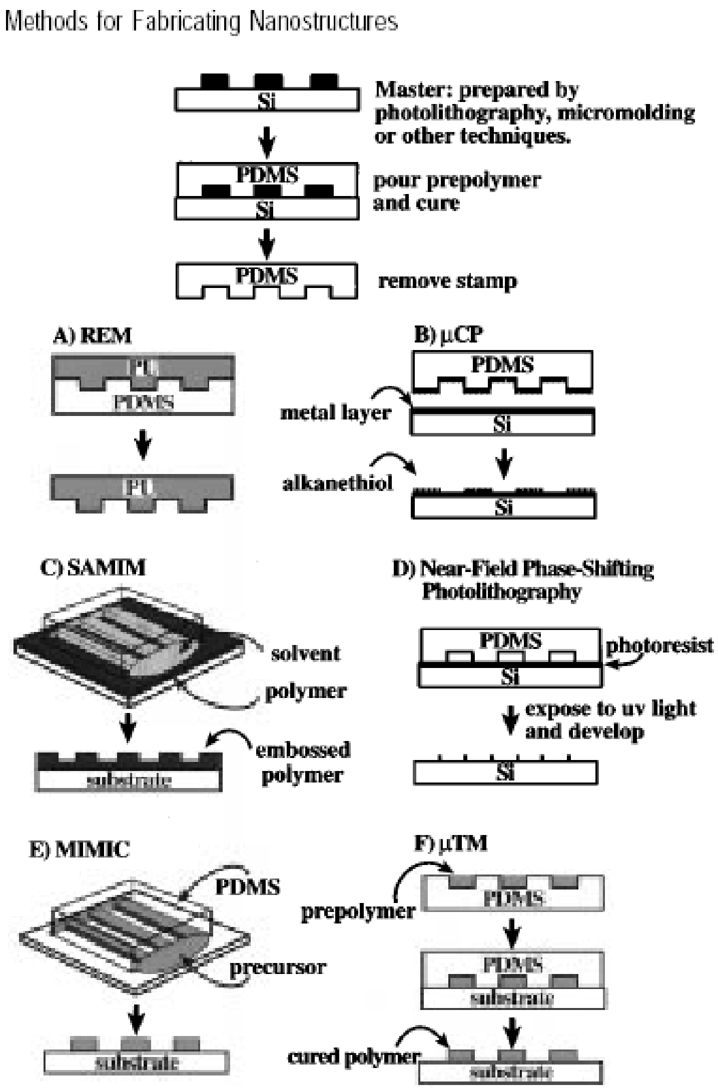
Conclusion:

- Densely formed ODTS film effectively deactivates for HfO_2 ALD growth;
- Formation of dense films by deactivating agents is one of the most important factors for achieving selective ALD;
- Need to modify gas phase delivery to achieve densely packing deactivating agents.

Surface Modification for Selective ALD

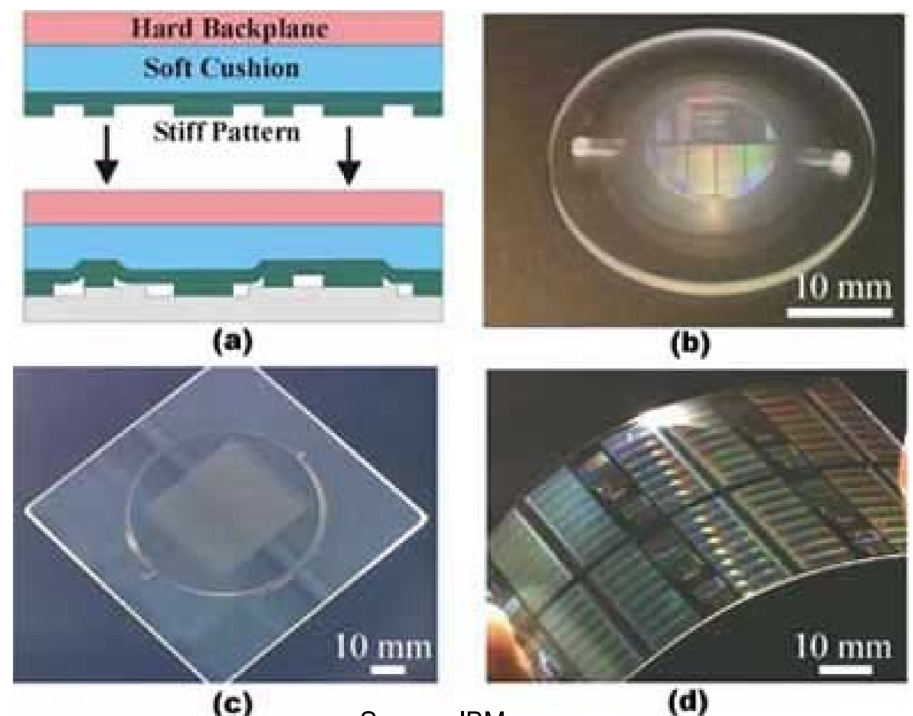


New Surface patterning strategy — Soft Lithography



Xia, Rogers,Paul, Whitesides, Chem. Rev. 1999, I99.1823

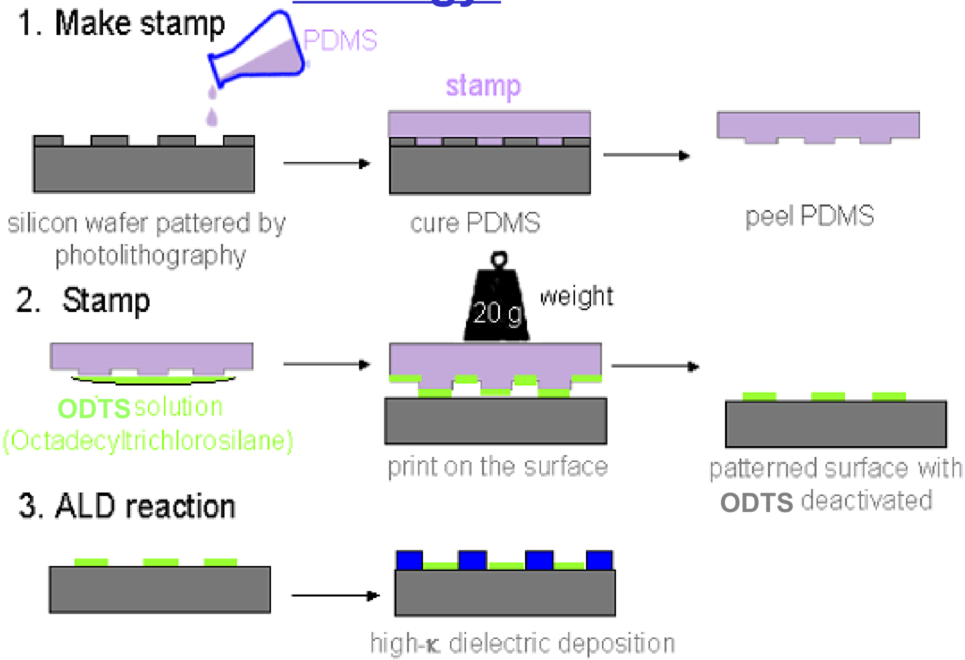
- Longer chain alkyltrichlorosilanes are difficult to introduce into vacuum chamber through leak valve.
- Several new methods for fabricating nano-structures are suitable to pattern the surface.
- High resolution soft lithography techniques are used for test structure.



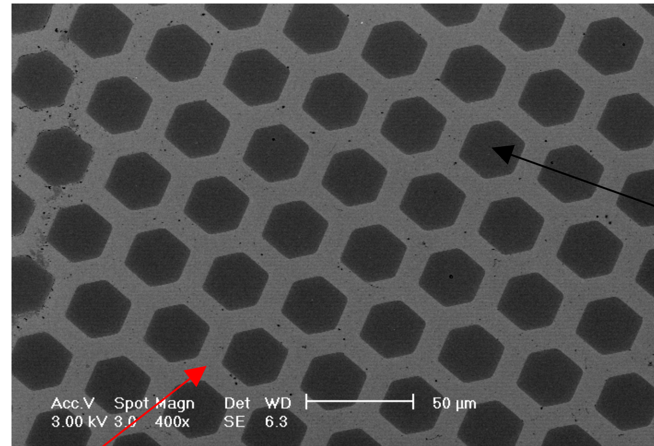
Source: IBM

Micro-contact Printing

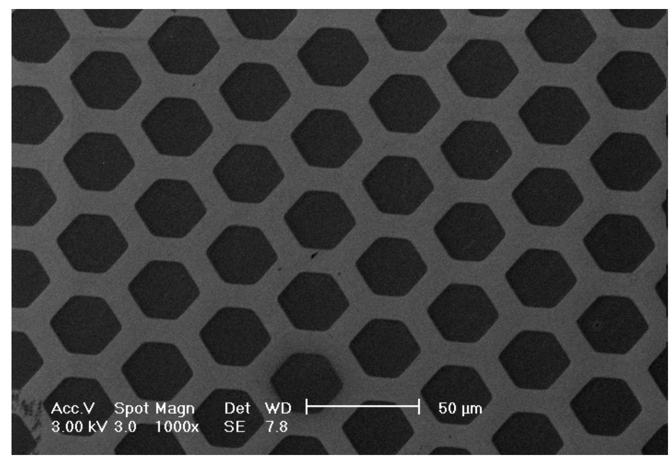
Strategy:



SEM image:



ODTS patterned surface before HfO_2 deposition



ODTS patterned surface after HfO_2 deposition

Results & Discussion:

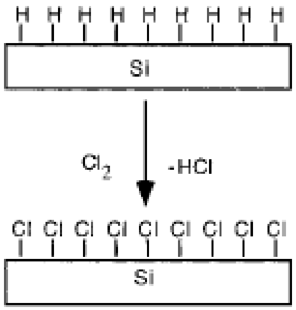
- SEM shows PDMS pattern can be well transferred to Si substrate
- ODTS can survive current ALD temperature
- Both OTS and HfO_2 films are quite thin (around 20-40Å). So it is quite difficult use SEM to investigate the topographic change
- Needs new analytical technology such as Scanning Auger Microscopy (SAM), etc.

Conclusions

- HfO_2 gate dielectric ALD on blanket thin thermal and chemical (peroxide-last) oxide surfaces has been optimized.
- Microstructural and electrical properties of blanket ALD-HfO_2 have been investigated.
- Longer chain alkylhalosilanes appear to provide better deactivation toward ALD.
- Wet chemistry is a good way for achieving dense SAMs compared with vacuum gas phase delivery.
- Soft lithography provides a good experimental platform for testing performance of deactivating precursors and the area-selective ALD process.

Future Work

- Develop process which utilizes gas phase delivery to achieve dense films of deactivating agents;
- Modify and investigate other deactivating agents;
- Use different methods for patterning and analyze patterned sample;
- Set-up and optimize new HfO_2 precursors ($Hf(NMe_2)_4$) to lower ALD temperature (< 150°C);
- Explore surface activation process for optimal dielectric/silicon interface.



→ HfO_2 ALD growth