

# Procédés de dépôt plasma avec injection pulsée de précurseurs (PECVD et PEALD) :

## Impact du réacteur et de la pression et développement de dépôts sélectifs

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A. Chaker<sup>1</sup>, O. Salicio<sup>1</sup>, N. Posseme<sup>2</sup>, P. Gonon<sup>1</sup>, M. Bonvalot<sup>1</sup>,  
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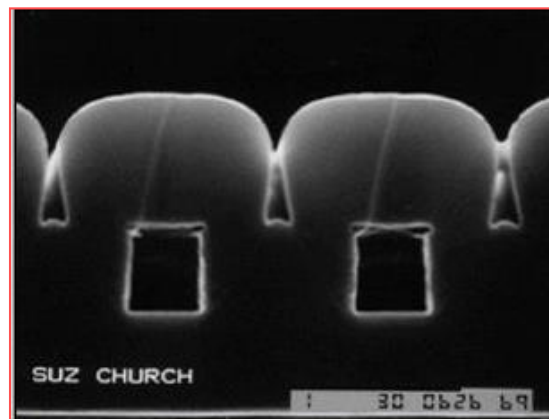
<sup>2</sup>CEA-LETI / MINATEC – Grenoble – France

<sup>3</sup>University of Tsukuba, Faculty of Pure and Applied Physics – Tsukuba – Japan

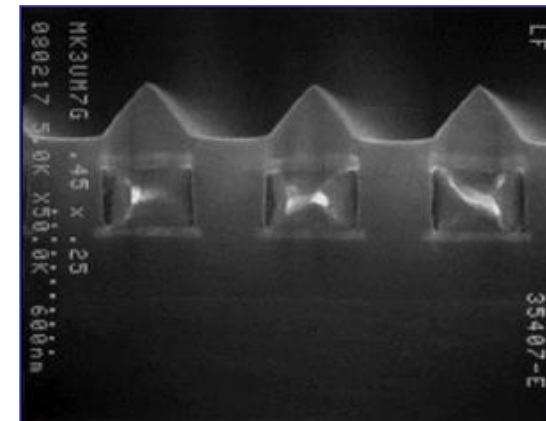
## PECVD in microelectronics

- Mainly capacitive discharges working at high pressure ( $> 1$  Torr)
  - Plasma damage, no need for ions
  - High throughput manufacturing
  - Uniformity (2% from center to edge)
- 
- HDP-CVD process for gap filling is using a low pressure plasma discharge with inductive source

PECVD TEOS



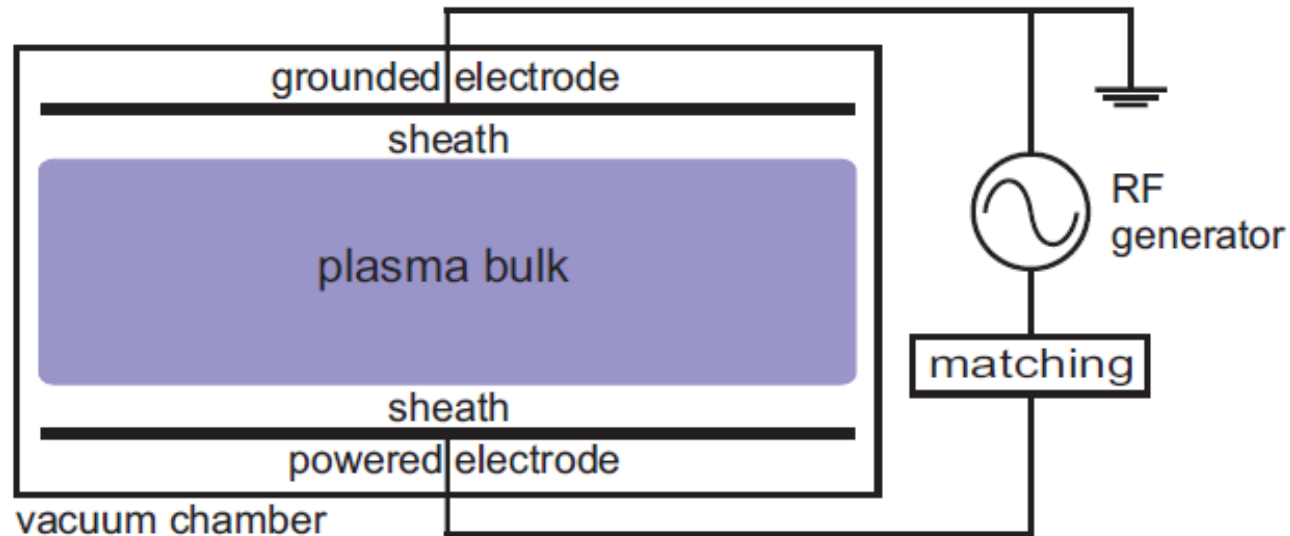
HDP CVD silane



*D.R. Cote et al, IBM  
Journal of Research  
and Development,  
Plasma processing, 43  
(1/2), 1999*



## PECVC process with CCP RF reactor



### Parameters to turn for the process:

- **Plasma Power:** plasma density, flux, energy
- **Pressure:** reactions in the plasma,  $T_e$ , **sheath collisionless or not**
- **residence time:** plasma/surface interactions



## Can we find more parameters to turn?

RF generator frequency

Pulsing the plasma or the precursors

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### What can be pulsed?

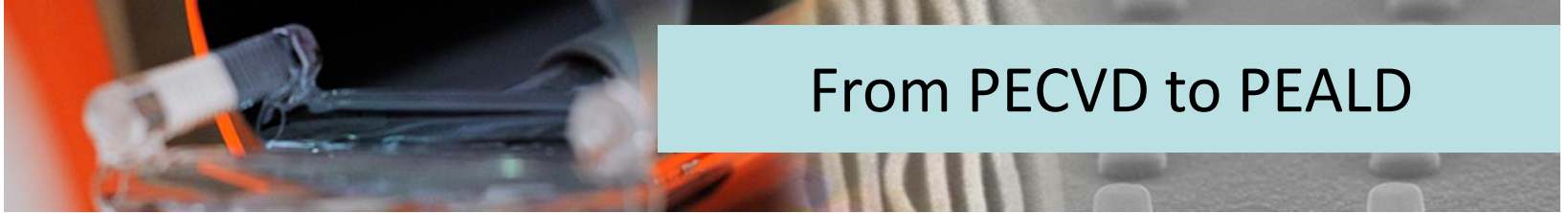
All parameters can be pulsed:

Plasma modulation: modification of discharge chemistry, decrease the ion to neutral flux ratio on the substrate, presence of long life time active species which act as precursors to the film growth, decrease substrate temperature...

Precursors: control of thickness, plasma chemistry, conformality...

→ composition, stress and properties of thin film





## PECVD

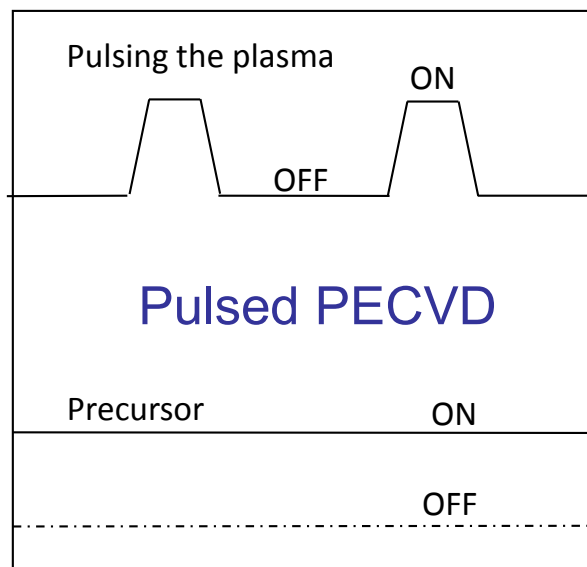
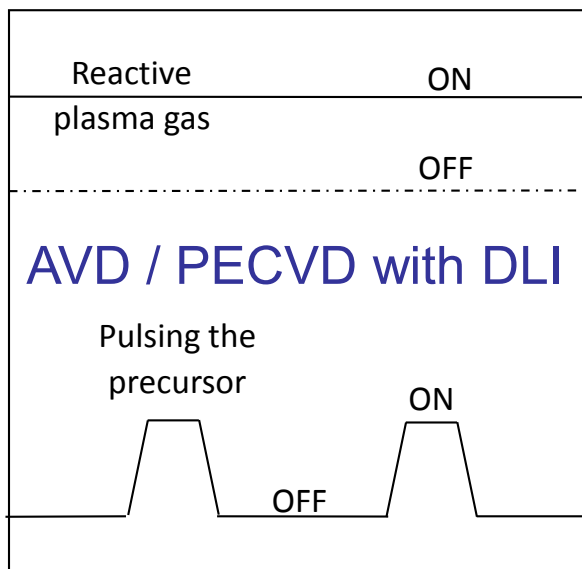
|            |     |
|------------|-----|
| Reactive   | ON  |
| plasma gas | OFF |
| <hr/>      |     |
| Precursor  | ON  |
|            | OFF |
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# From PECVD to PEALD

## PECVD

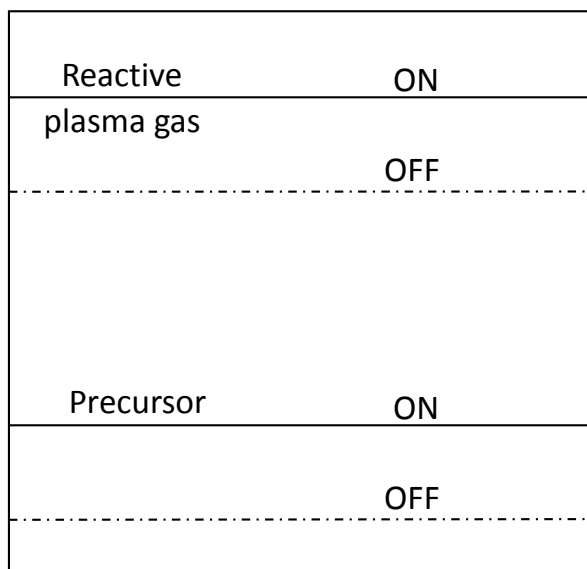
|            |     |
|------------|-----|
| Reactive   | ON  |
| plasma gas | OFF |
| <hr/>      |     |
| Precursor  | ON  |
|            | OFF |
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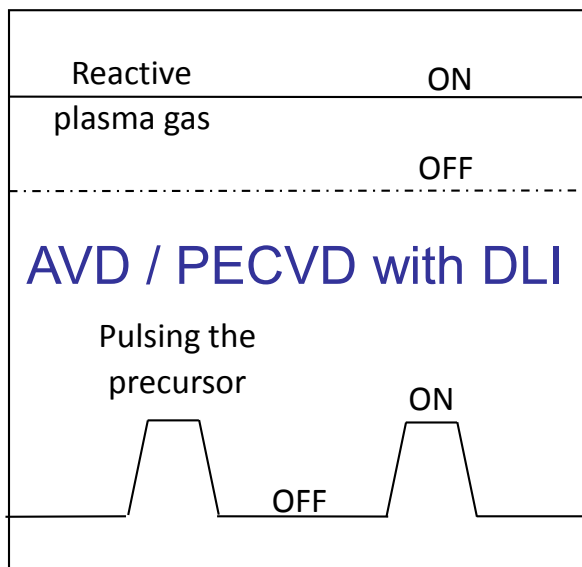


# From PECVD to PEALD

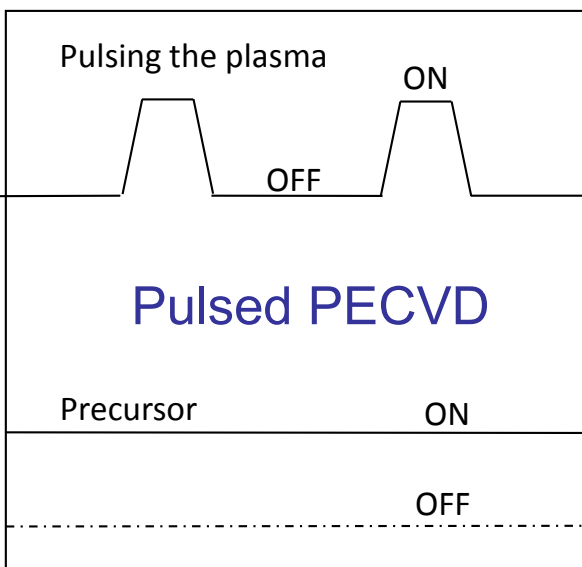
## PECVD



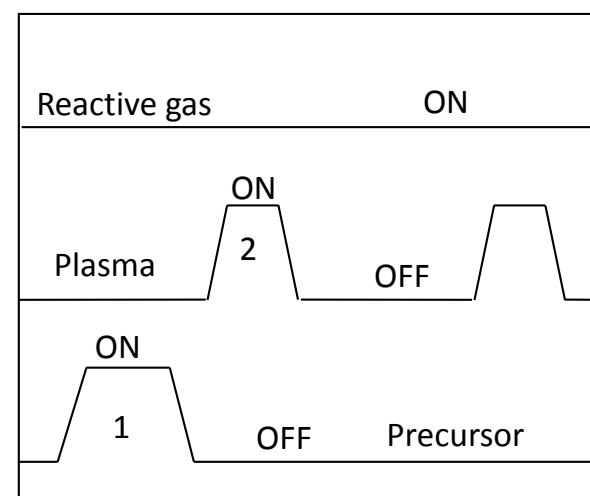
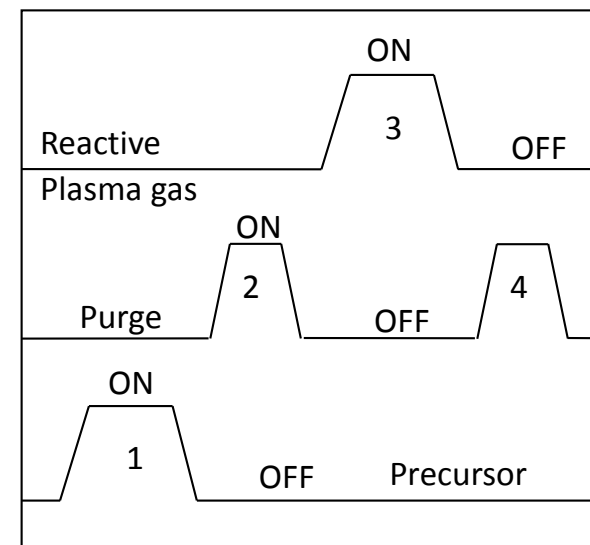
## AVD / PECVD with DLI



## Pulsed PECVD



## PEALD





Atomic layer deposition (ALD) is a CVD technique that can achieve unparalleled control at the atomic scale.

ALD achieves 'bottom-up' control through chemical reactions with special characteristics:

reactions take place at the surface only

→ gas-phase reactions are inhibited;

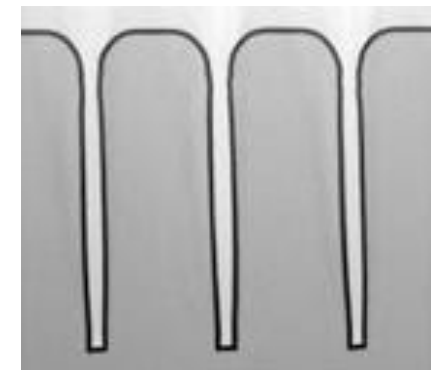
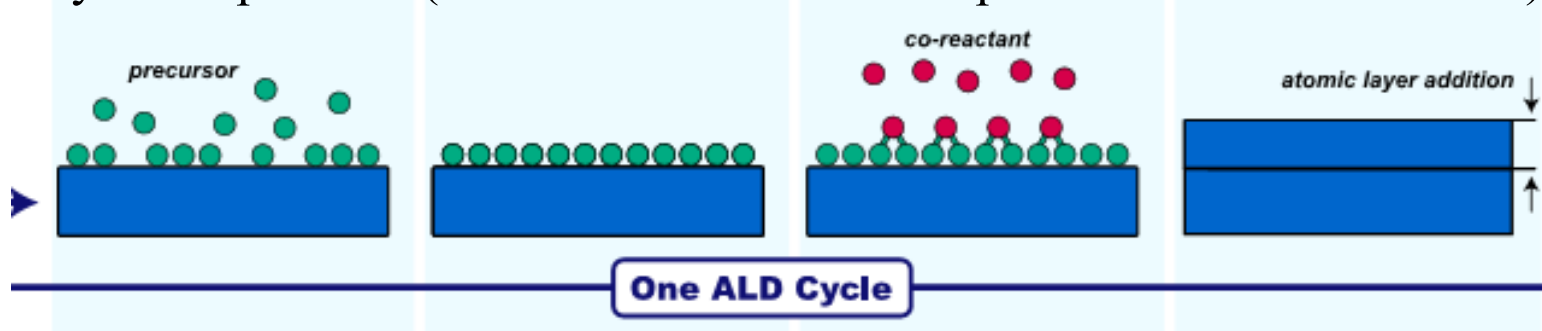
reactions are self-limiting

→ but can be re-activated;

reactions take place independent of fluctuations in external conditions

→ the same chemistry thus applies at all scales

Cyclic deposition (no reactions between the precursor and the reactant)

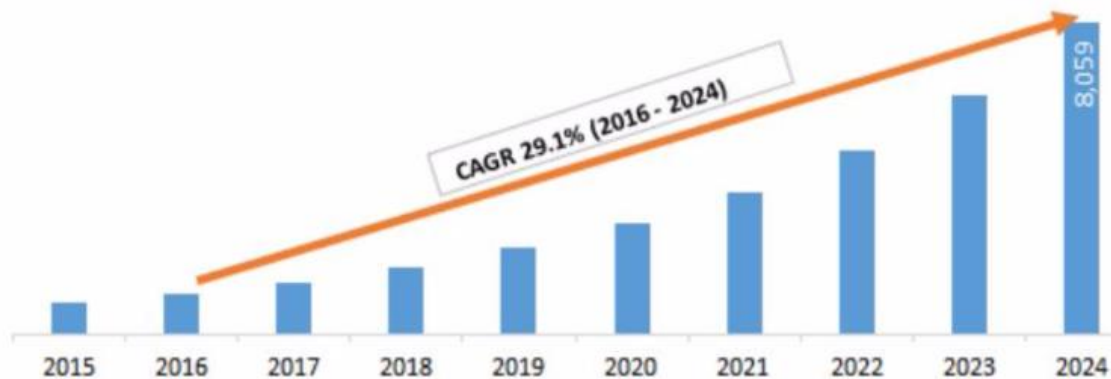




Solid State Technology and Global Industry Analysts (GIA): *the global deposition equipment market will hit \$13.6 billion by 2020. Atomic layer deposition (ALD) is forecasted to be the fastest growing segment, with a compound annual growth rate of 19.9 percent, the market research firm estimates.*

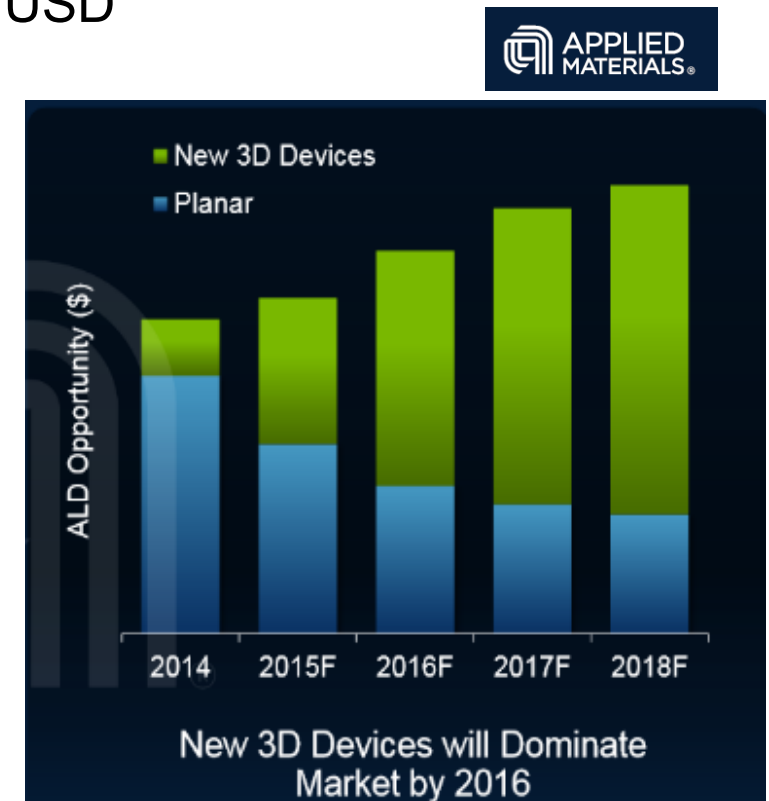
**Global Atomic Layer Deposition Equipment Market Size and Forecast, 2015 - 2024 (US\$ Million)**

8 billions USD



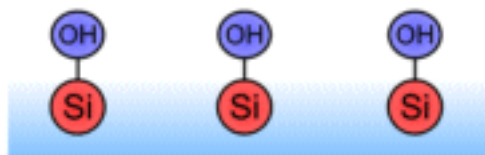
Source: Variant Market Research

The 3D device inflection is driving growth in ALD with demands for new patterning films, new conformal materials and lower thermal budgets





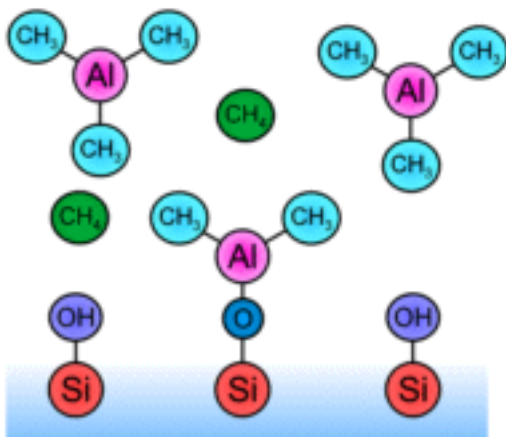
1)



Surface Initiale



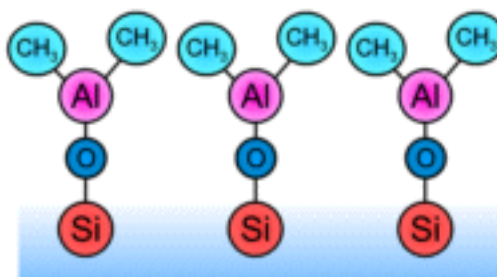
2)



$\text{Al}(\text{CH}_3)_3$  exposure



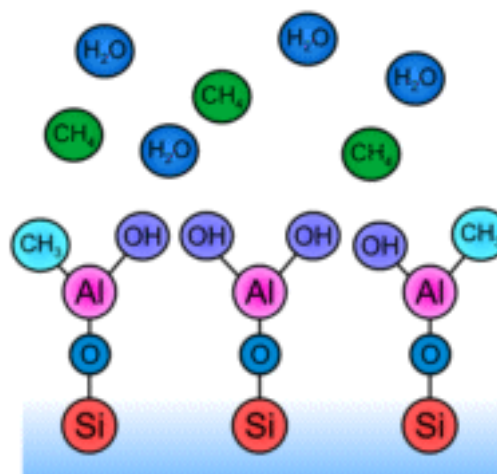
3)



Purge



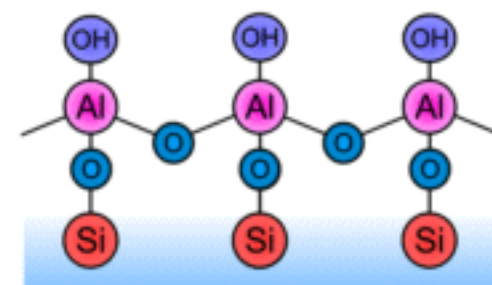
4)



$\text{H}_2\text{O}$  exposure



5)



Purge

From Oxford instrument

Profijt *et al.*, J. Vac. Sci. Technol. A 29 (5) 050801 (2011)

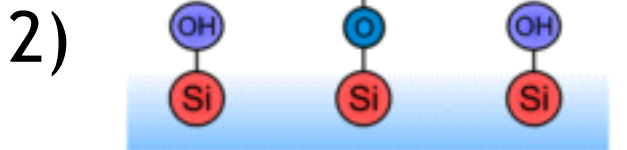
Comparison between  
thermal ALD and PE-ALD

$\text{Al}_2\text{O}_3$  -  $\text{Al}(\text{CH}_3)_3$  and  $\text{H}_2\text{O}$





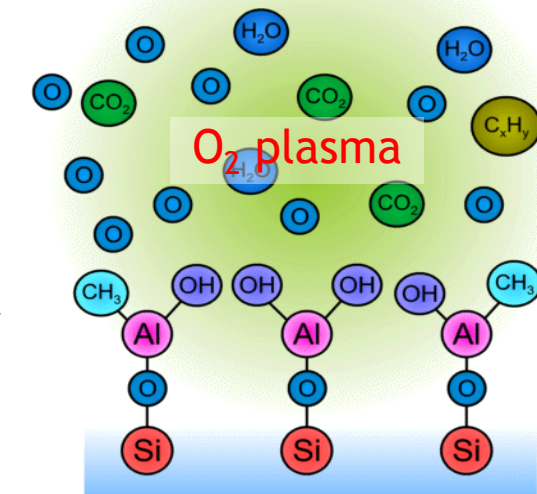
Surface Initiale



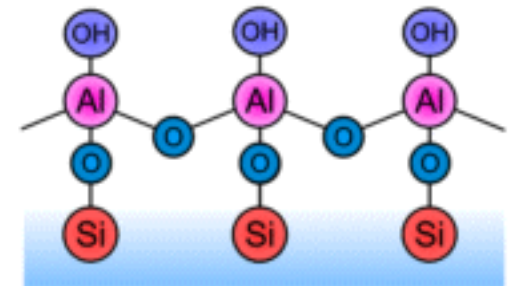
$\text{Al}(\text{CH}_3)_3$  exposure



Purge



$\text{O}_2$  plasma exposure



Purge

From Oxford instrument

Profijt *et al.*, J. Vac. Sci. Technol. A 29 (5) 050801 (2011)

## Comparison between thermal ALD and PE-ALD

$\text{Al}_2\text{O}_3$  -  $\text{Al}(\text{CH}_3)_3$  and  $\text{O}_2$  plasma



Only used for the activation step. If used during the injection of precursor: PECVD process without self-limited reaction

**Cold plasmas reservoir of radicals** for oxidation (**O** from  $O_2$  plasma), or reduction (**H** from  $H_2$  or  $NH_3$  plasma) steps

General idea: ions flowing to the surface are too energetic particles for ALD with creation of defects, roughness and not self-limiting step

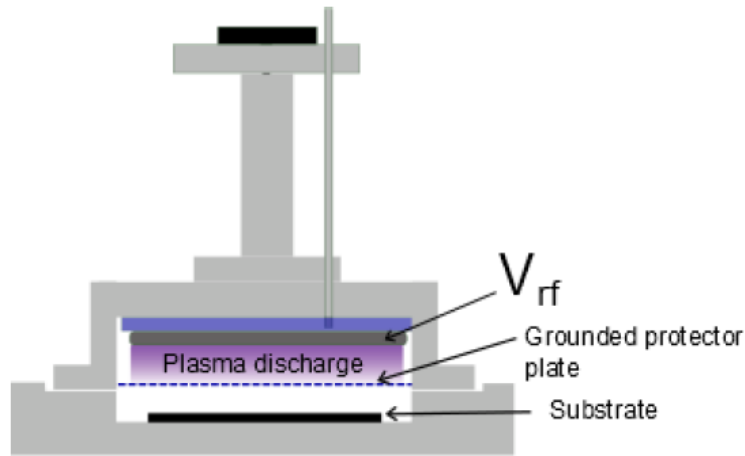
→ they must be removed → specific design of plasma reactors for PEALD

→ capacitive discharge with grids to remove ions

→ high density plasma sources (inductive, microwave) used as a remote discharge: distance between plasma source and substrate is higher than the mean free path of ions ; all ions are loosed when travelling from their creation to the substrate

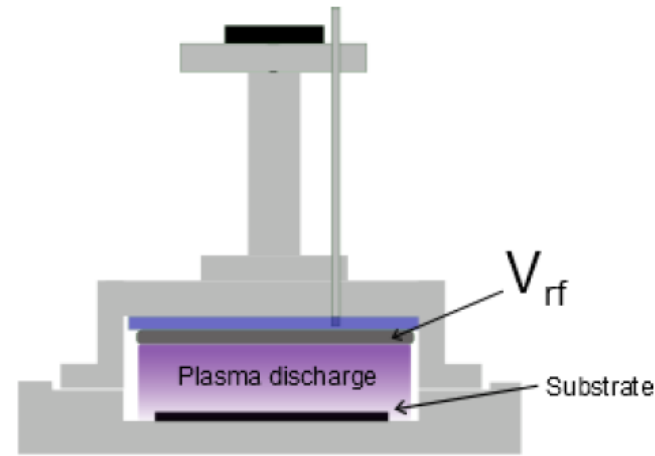


All reactor have **advantages** and **defaults**  
ASM / BENEQ / TEL ...



- ❑ Remote plasma
  - Most common PEALD type
  - No ion bombardment on substrate

Plasma uniformity / substrate  
High flux of radicals (/ions)  
Double frequency  
High Pressure (collisional sheath)  
No ion bombardment (grid)



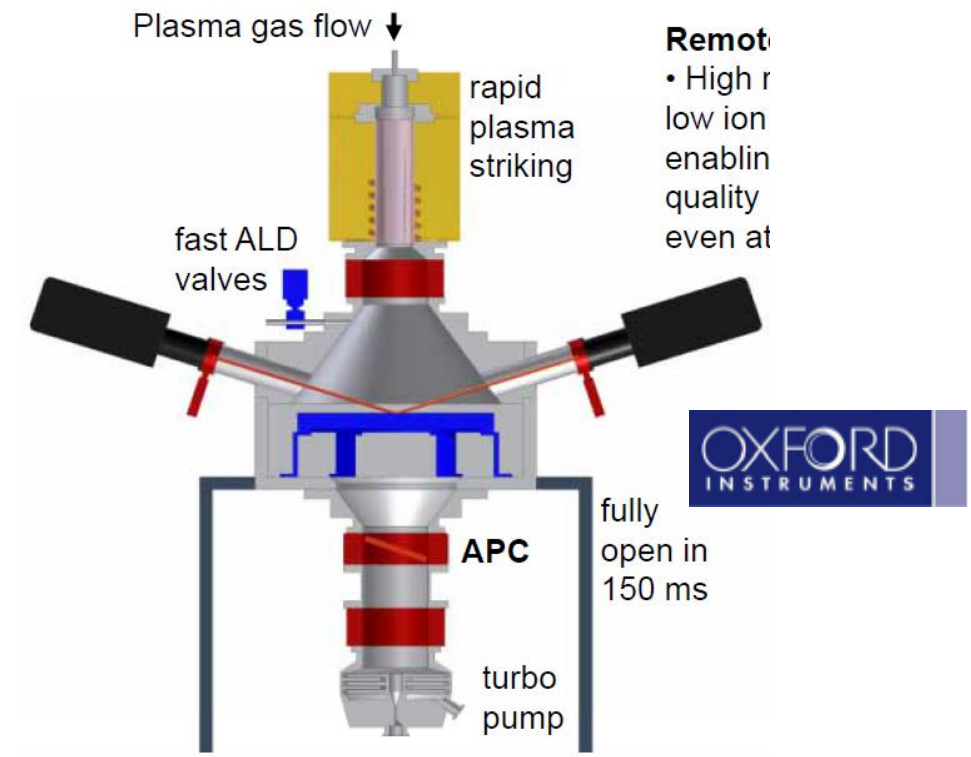
- ❑ Direct plasma
  - Possible to tune film properties *e.g.* film stress
  - Adhesion pre-treatments etc... possibilities

Substrate where the plasma is ignited  
Ion bombardment (direct plasma)  
Plasma damage  
Substrate heating  
No control of ion energy





All reactor have **advantages** and **defaults**  
PICOSUN / OXFORD ...



**Remote plasma**  
**Substrate not in the plasma ignition zone**  
**Control of ion energy may be possible**

**Plasma uniformity**  
**Plasma damage**  
**Limited to low/moderate pressure**

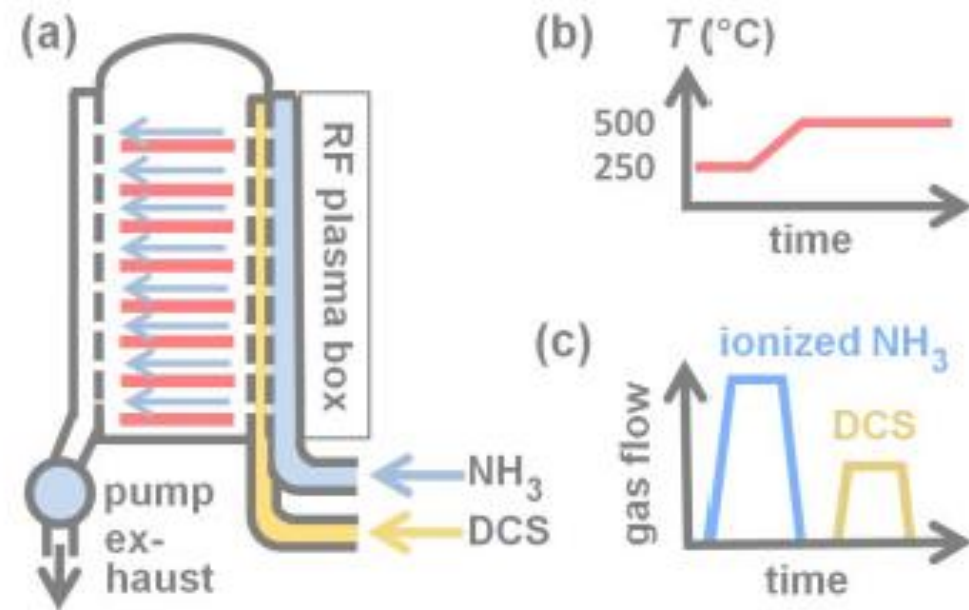


## TELINDY PLUS



A batch furnace can process up to 100 wafers at the same time, which makes the process more cost effective compared to single wafer process. (5nm ~1 hour)

$\text{Si}_3\text{N}_4$  ALD process with dichlorosilane (DCS) and ionized (plasma) ammonia ( $\text{NH}_3$ ) at 500°C in a furnace



**Figure 2** Cross-flow reactor, the red lines symbolize the wafers (a), temperature profile of the reaction chamber (b) and gas flows (c) of one ALD cycle.

Fabian Koehler<sup>\*</sup>, Dina H. Triyoso, Itasham Hussain<sup>™</sup>, Bianca Antonioli, and Klaus Hempel  
Phys. Status Solidi C 11, No. 1, 73–76 (2014) / DOI 10.1002/pssc.201300157

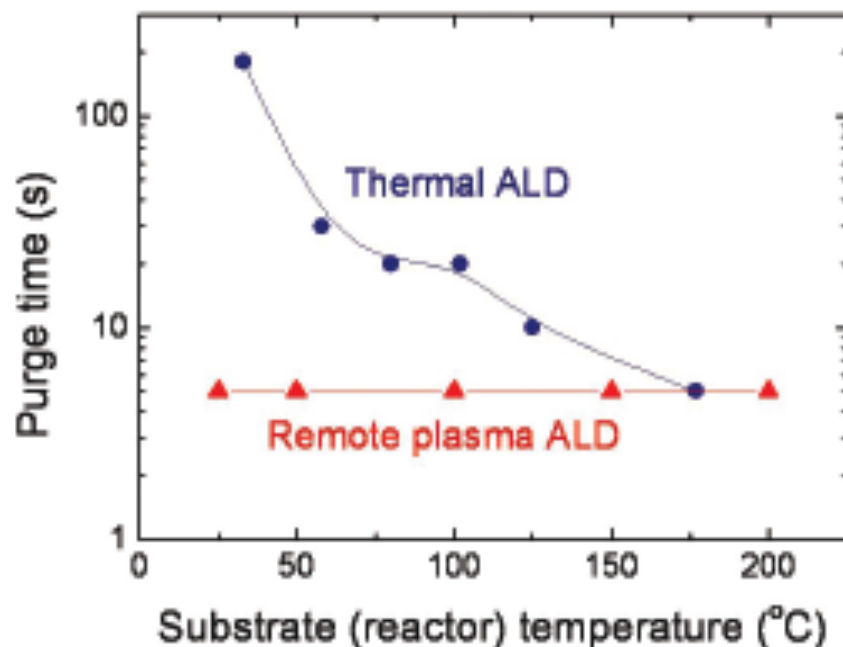


Plasma ALD is (may) using same precursors than thermal ALD  
Only the gas nature of the activation step is modified

| Material | ALD precursor                                         | Plasma gas                     |
|----------|-------------------------------------------------------|--------------------------------|
| Oxide    | H <sub>2</sub> O ou O <sub>3</sub>                    | O <sub>2</sub>                 |
| Nitride  | NH <sub>3</sub>                                       | N <sub>2</sub> /H <sub>2</sub> |
| Metal    | O <sub>2</sub> , N <sub>2</sub> /H <sub>2</sub> , ... | H <sub>2</sub>                 |

from Oxford Instrument

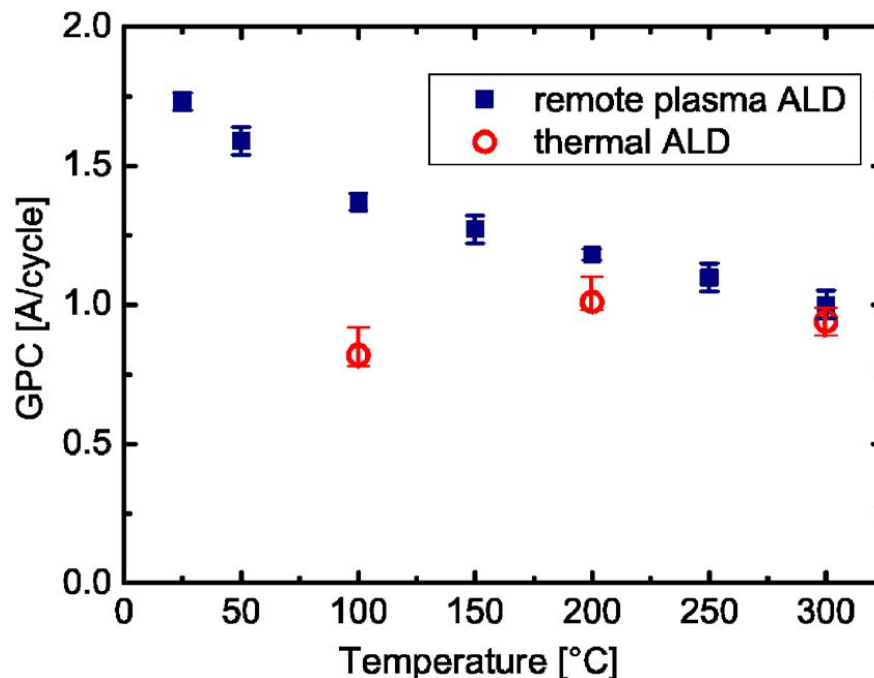




Purge time for thermal ALD of  $\text{Al}_2\text{O}_3$  ( $\text{H}_2\text{O}$ ) and remote plasma ALD of  $\text{Al}_2\text{O}_3$  ( $\text{O}_2$ ). Data courtesy of Eindhoven University of Technology

Long purge times with  $\text{H}_2\text{O}$   
at low temperature

Source: Oxford instruments



Decrease is attributed to thermally activated recombination reactions of surface hydroxyl groups – OH (dehydroxylation)

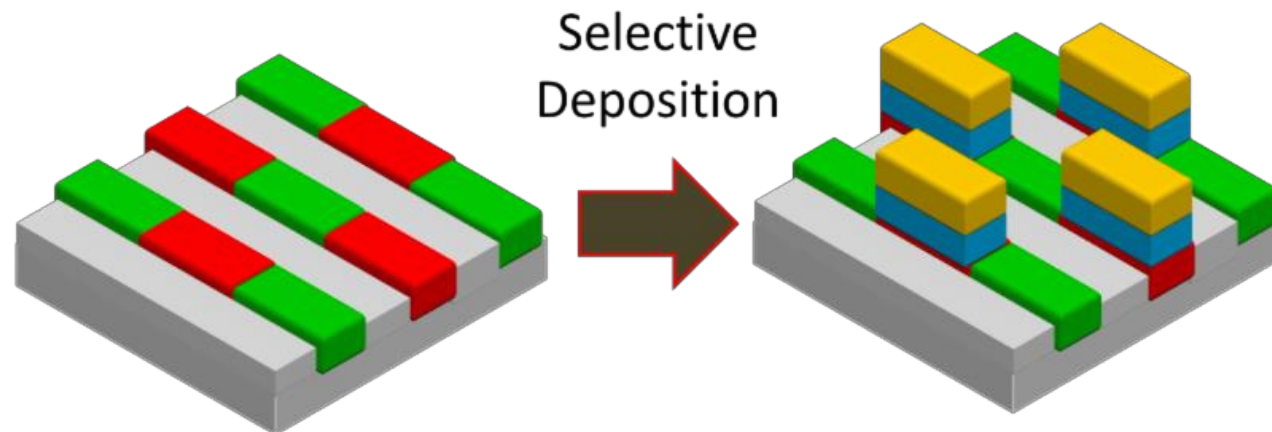
J. L. van Hemmen,<sup>a</sup> S. B. S. Heil,<sup>a,\*</sup> J. H. Klotwijk,<sup>b</sup> F. Roozeboom,<sup>c,\*\*</sup>  
C. J. Hodson,<sup>d</sup> M. C. M. van de Sanden,<sup>a</sup> and W. M. M. Kessels<sup>a,\*,z</sup>

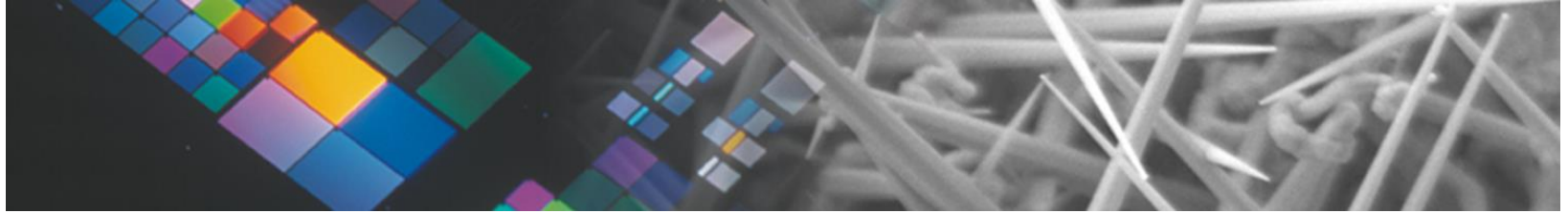
*Journal of The Electrochemical Society*, **154** (7) G165-G169 (2007)



# PEALD For Area Selective Deposition

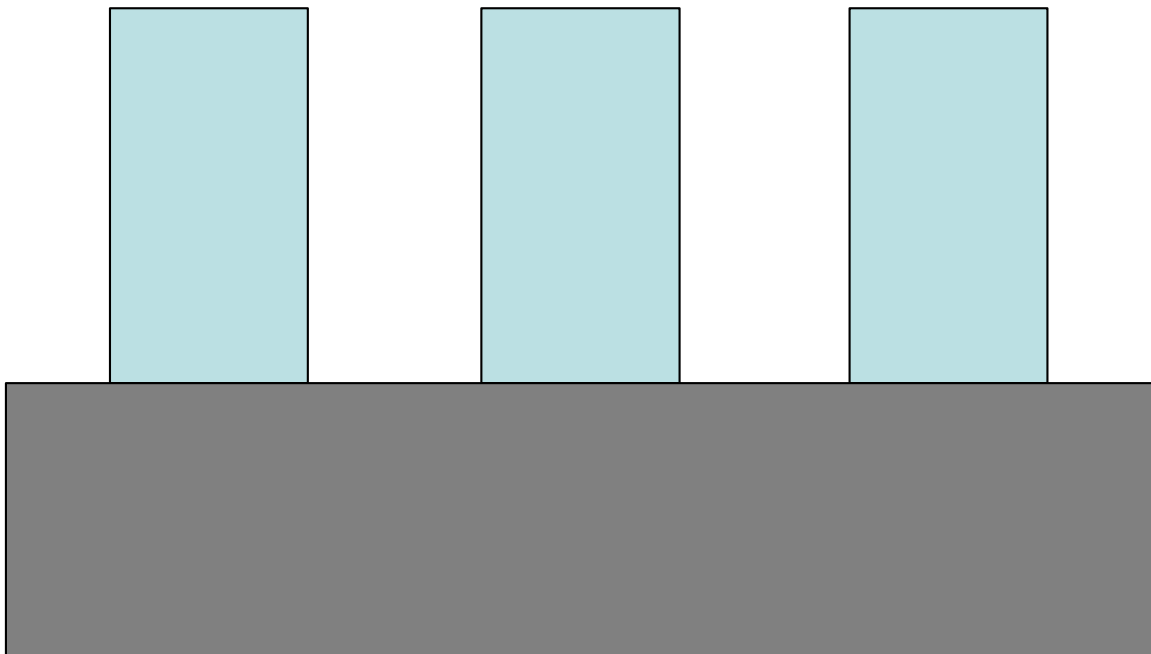
- What is ASD?
- ASD for microelectronics?
- A way to do it: add a plasma etching step in PEALD step

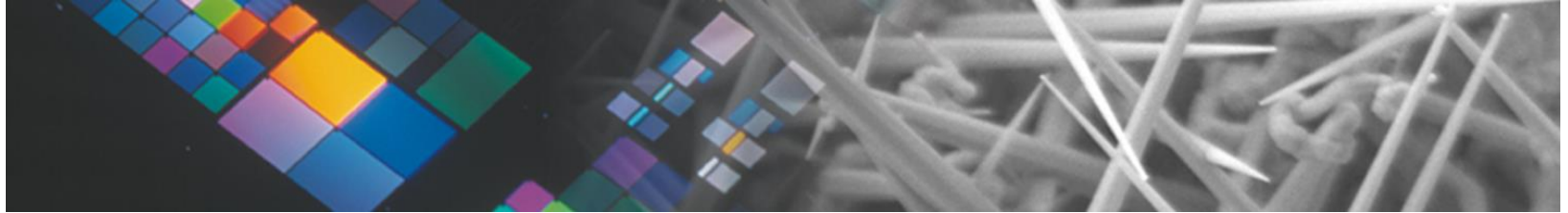




## What is Area Selective Deposition?

Hey guys I need a thin oxide deposition on my two wafers

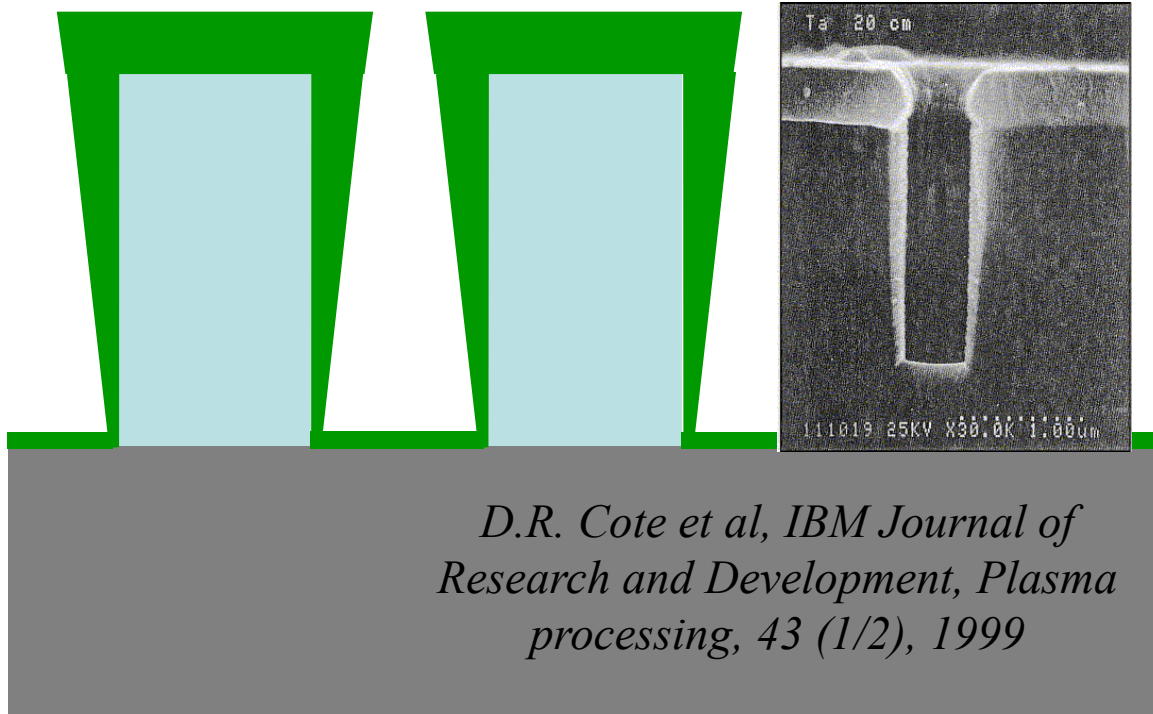


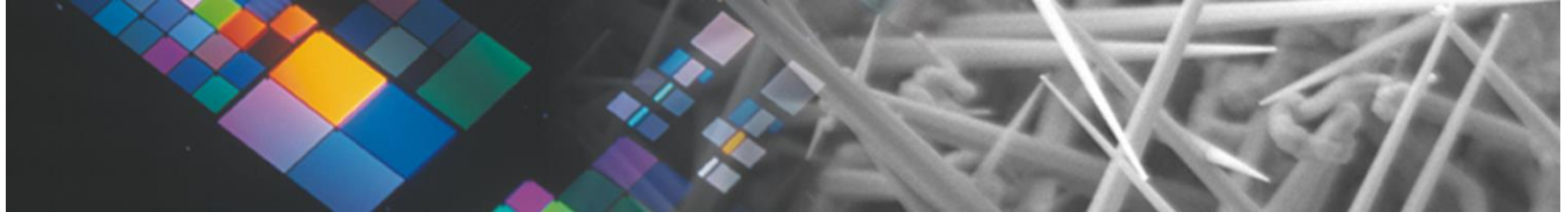


## What is Area Selective Deposition?

Hey guys I need a thin oxide deposition on my two wafers

PVD man (70/80's): let's go!

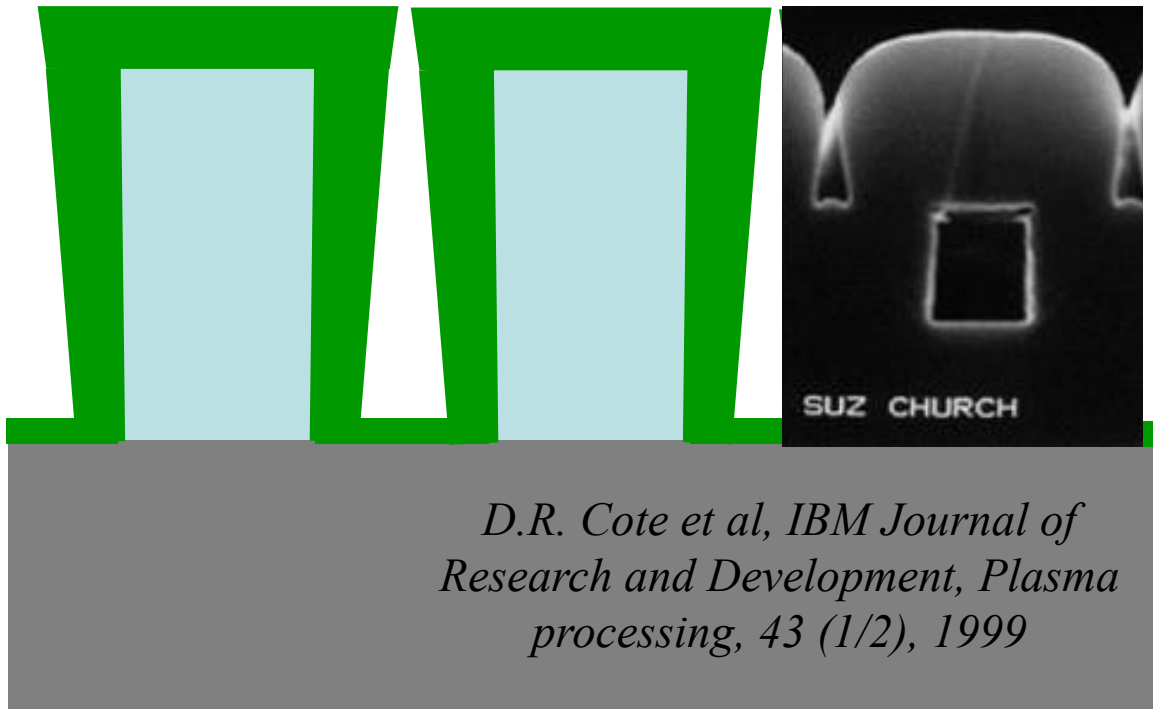




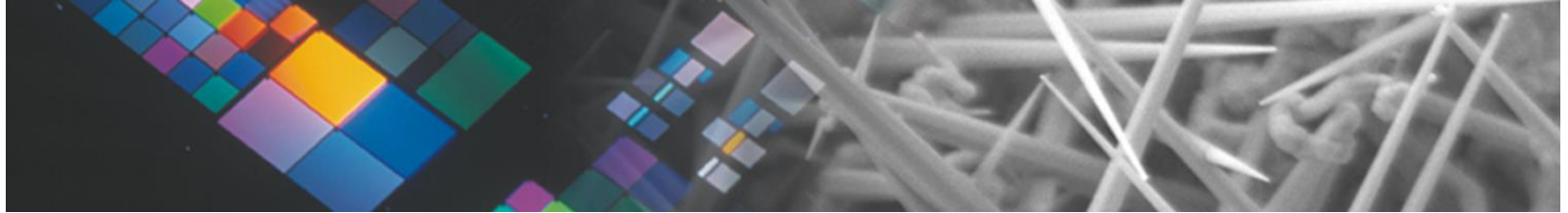
## What is Area Selective Deposition?

Hey guys I need a thin oxide deposition on my two wafers

(PE)CVD man (80/90's): In can do better for the 3D substrate!



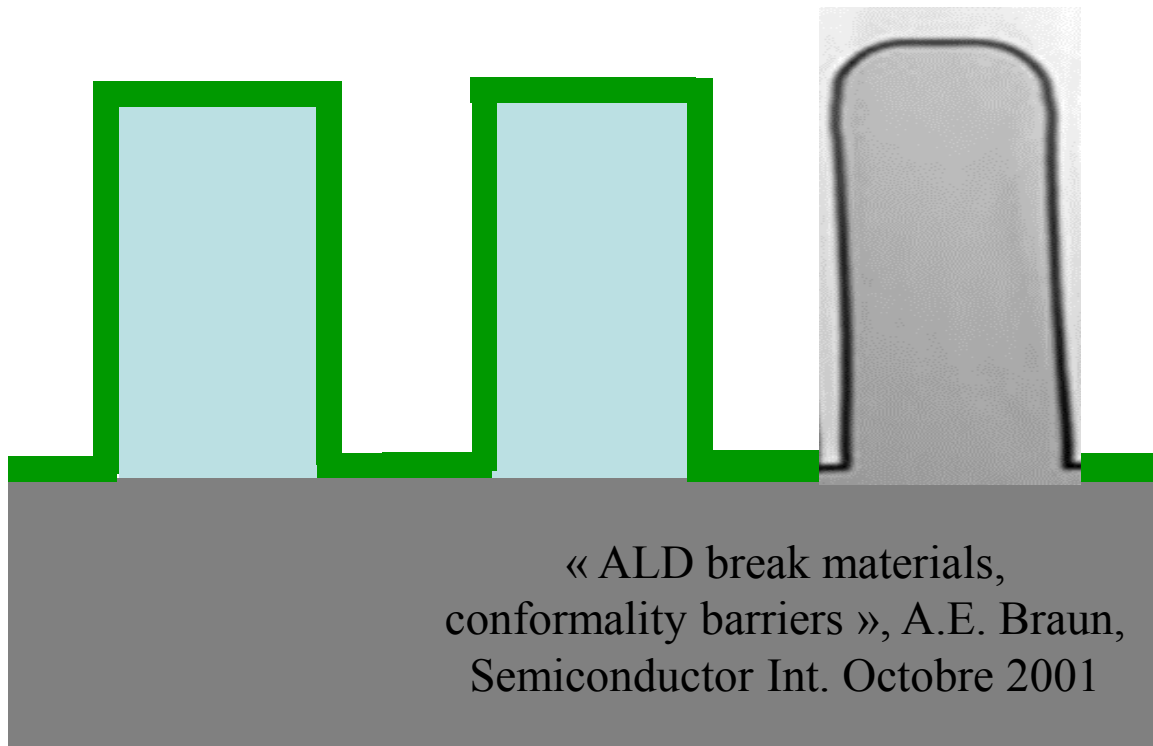


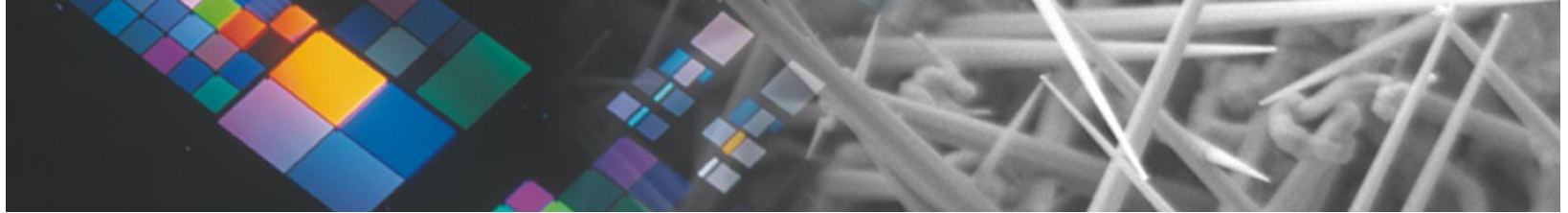


## What is Area Selective Deposition?

Hey guys I need a thin oxide deposition on my two wafers

(PE)ALD man (2000's): No ways, I am the best!

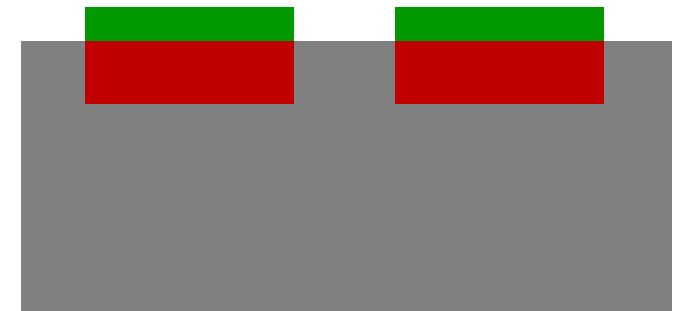
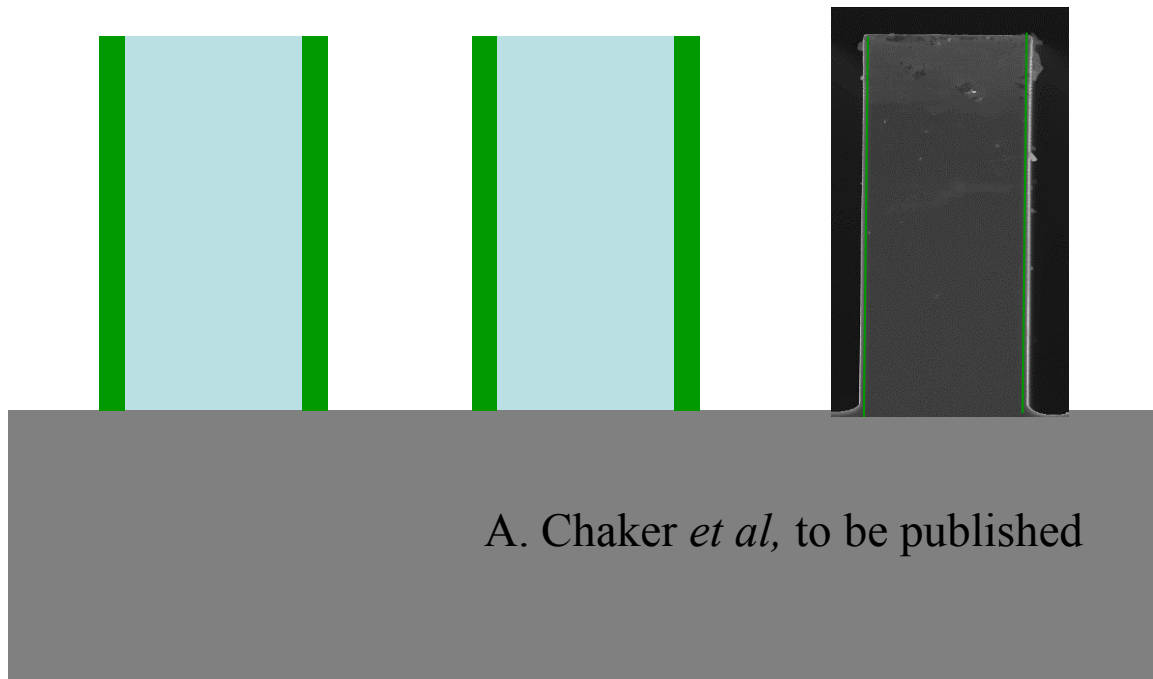




## What is Area Selective Deposition?

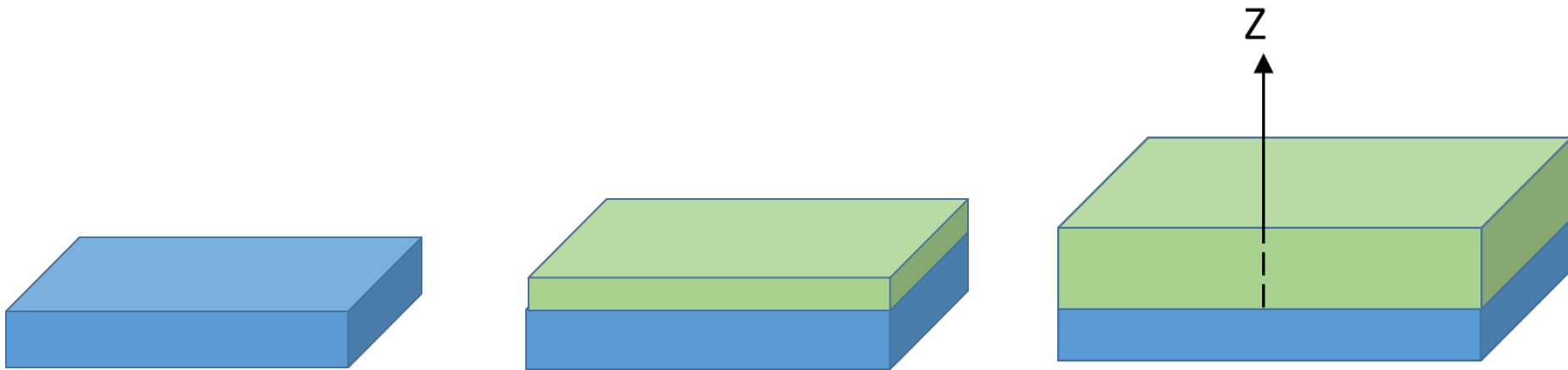
Hey guys I need a thin oxide deposition on my two wafers

ASD man (now to.....): I can select the area!





PVD, (PE)CVD, ALD:  
Deposition of thin films is made in the  $z$  direction  
(control of the thickness)

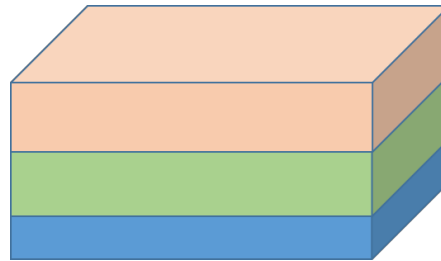


How can we obtain the control of the two other directions ( $x,y$ )?

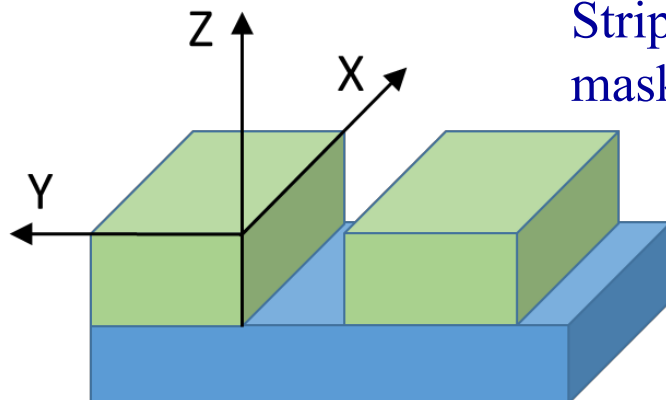
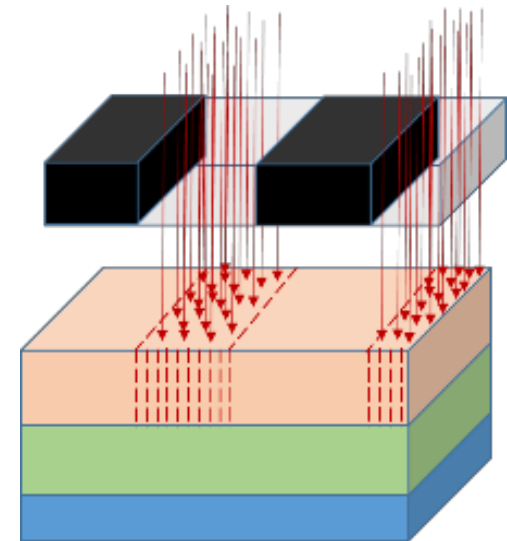
Patterning – top down approach



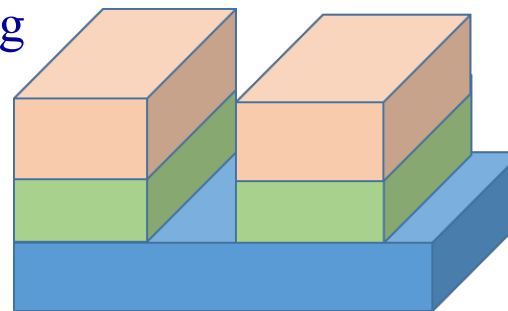
## Patterning steps – TOP DOWN approach



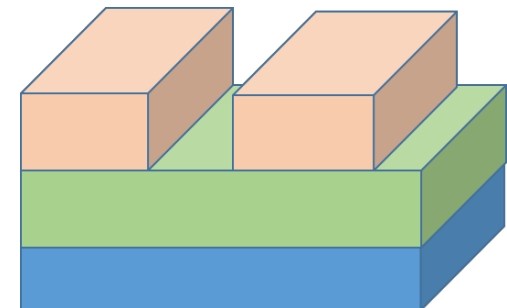
Lithography step: resist deposition  
+ mask definition



Stripping:  
mask etching

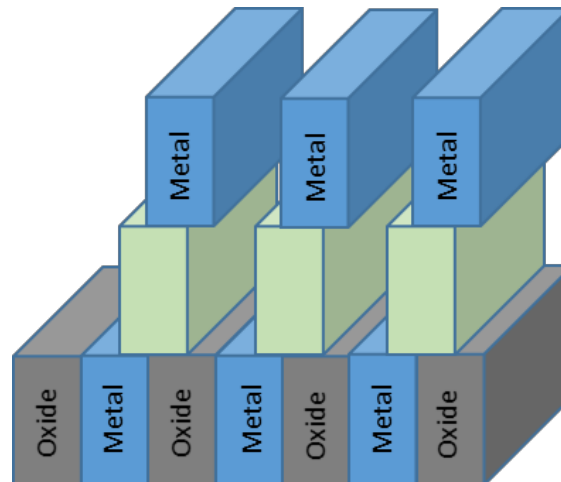
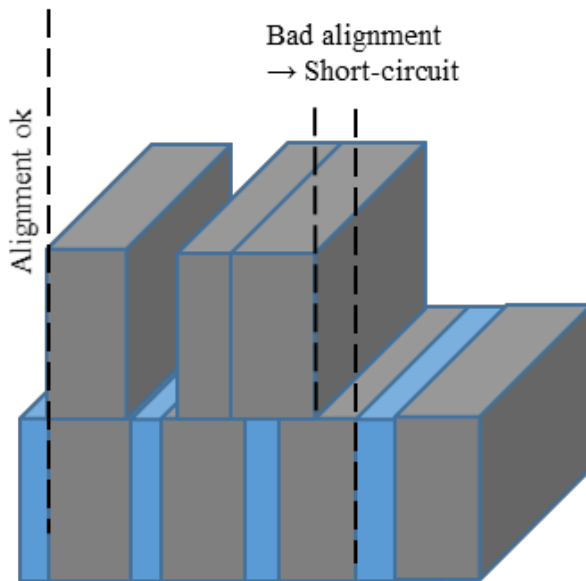
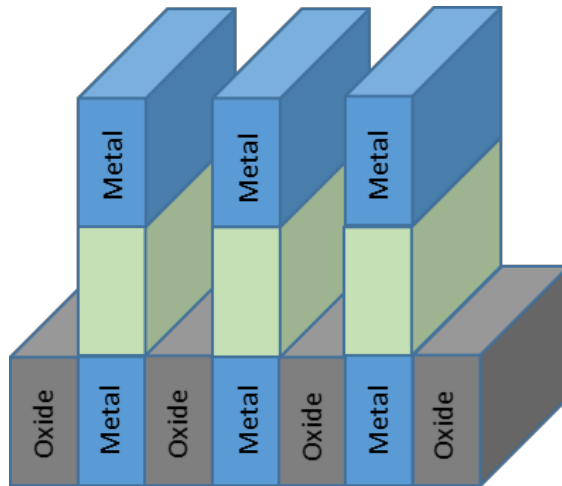


Plasma etching step:  
mask transfer

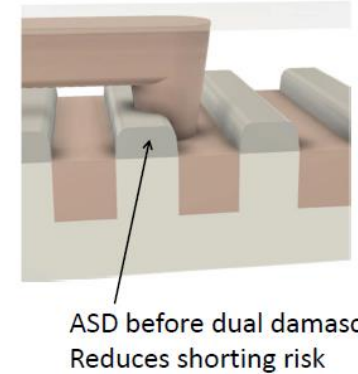
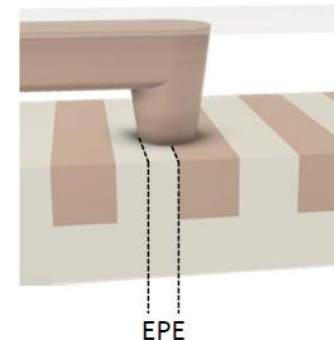




More and more complex patterning using two of several steps of patterning (masks and exposure) – alignment for is crucial



ASD in Semiconductor Manufacturing  
Fully Aligned Via (FAV) for Edge Placement Error (EPE)



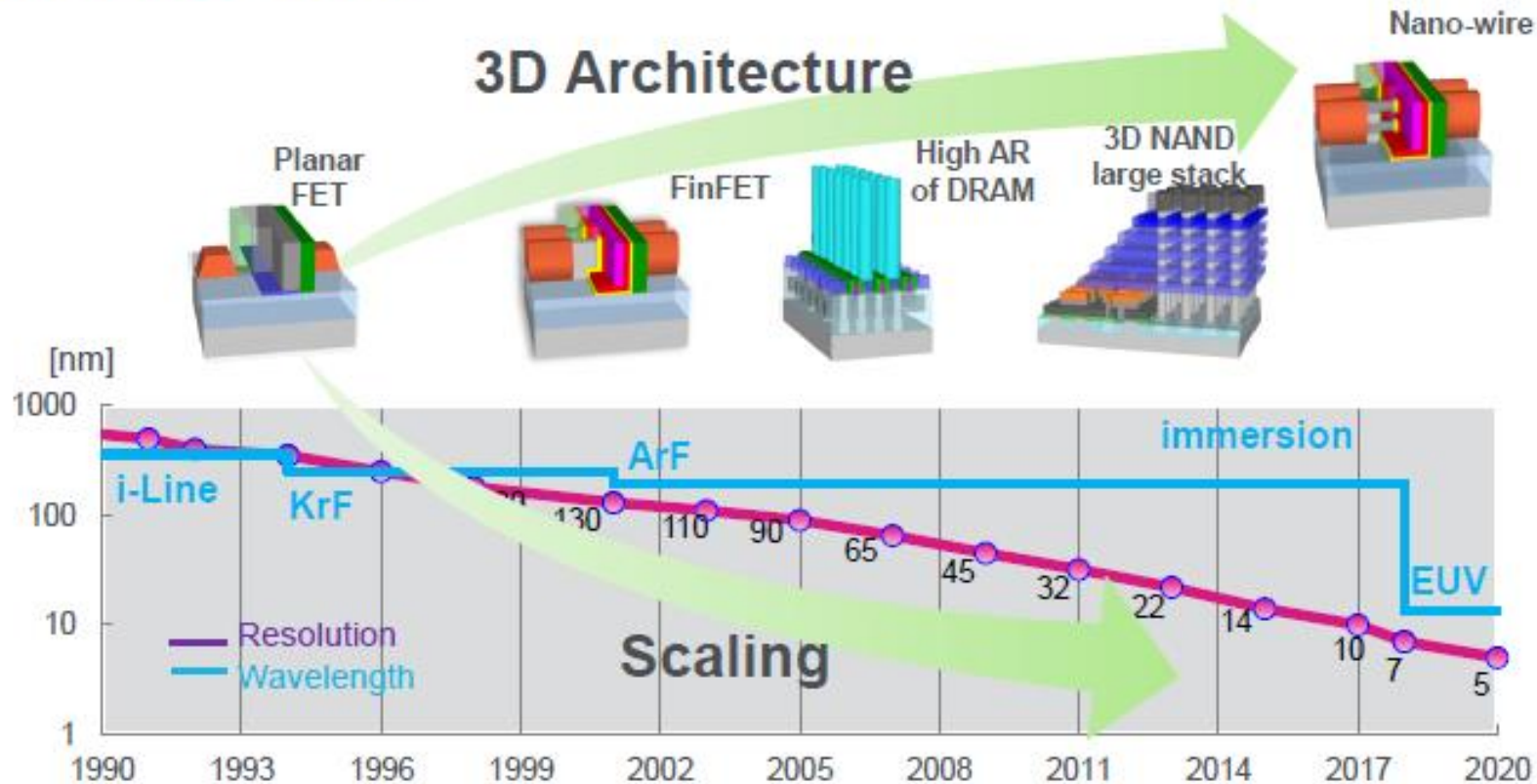
G.N. Parsons  
ALD2018 tutorial





Gert Leusink  
Director, Thin Films Process Technology & Integration  
Sr. Member Technical Staff  
TEL Technology Center, America, LLC

## Technology trend



Vertical utilization is the key approach towards sub-10nm generation

ASD-2017 Workshop

TEL

Resolution needed for the scaling of the pitch is no more following the wavelength of the stepper  
→ introduction of complex **multiple patterning processes**



# Self-Aligned Quadruple Patterning: the pitch is reduced by a factor of 4

ALD ENABLING SUB-RAYLEIGH LIMIT LITHOGRAPHY WITH  
SPACER DEFINED DOUBLE/QUADRUPLE PATTERNING



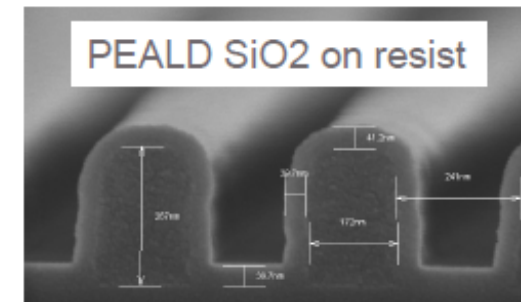
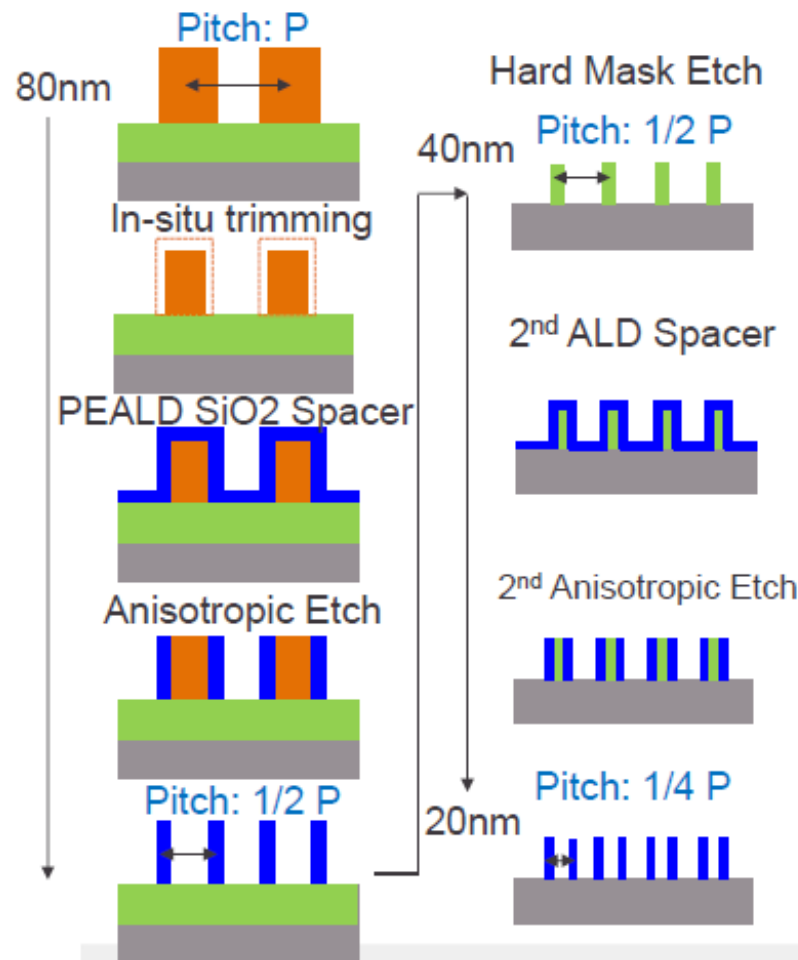
Material used for  
spacer »

$\text{SiO}_2$  and  $\text{Si}_3\text{N}_4$  by  
PEALD

Low  $T^\circ$   
(300 – 500  $^\circ\text{C}$ )

Conformal  
deposition

High quality



- ✓ **Spacer Defined Double Patterning with PEALD in production since 3x nm DRAM and Flash**
- ✓ **Spacer Defined Quadruple Patterning in production for 1x nm Flash**

## Key enablers brought by PEALD

- Uniformity: CD control
- Low temperatures (<100C)
- Good step coverage
- Dense film
- In-situ trimming capability
- Extendible to other materials with high etch selective



Multipatterning processes is needed for actual and future transistors

- Increase of wafer cost
- Misalignment errors

| Patterning method                         | Normalized cost per wafer |
|-------------------------------------------|---------------------------|
| Single Exposure (SE)                      | 1                         |
| Litho Etch Litho Etch (LELE)              | 2.5                       |
| Litho Etch Litho Etch Litho Etch (LELELE) | 3.5                       |
| Self-Aligned Double Patterning (SADP)     | 2                         |
| Self-Aligned Quadruple Patterning (SAQP)  | 3                         |
| Extreme UV (EUV) Single Exposure (SE)     | 4                         |
| EUV + SADP                                | 6                         |

*A. Raley et al., Proc. SPIE 9782, 97820F (2016)*

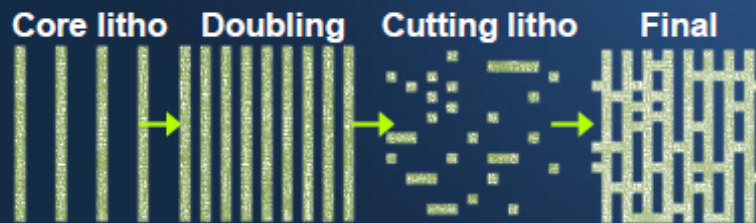


## Self-Aligned Multiple Patterning

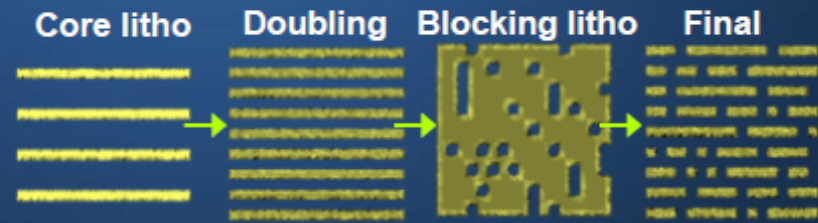
|         | 32nm              |           | 10nm              |           | 7nm               |           |
|---------|-------------------|-----------|-------------------|-----------|-------------------|-----------|
| Active  | 193i              | 1         | SADP + Cut        | 1+1       | SAQP + LE2 Cut    | 1+2       |
| Gate    | 193i + Cut        | 1+1       | SADP + Cut        | 1+1       | SADP + Cut        | 1+1       |
| Contact | 193i + 193i       | 2         | LE2+LE2           | 4         | LE2 + LE3         | 5         |
| Via 0   | 193i              | 1         | LE2               | 2         | LE3               | 3         |
| Metal 1 | 193i + Cut        | 1+1       | LE3               | 3         | SADP + LE3 Block  | 1+3       |
| Via 1   | 193i              | 1         | LE2               | 2         | LE4               | 4         |
| Metal 2 | 193i + Cut        | 1+1       | SADP + Block      | 1+1       | SAQP + LE3 Block  | 1+3       |
|         | <b>Mask Count</b> | <b>12</b> | <b>Mask Count</b> | <b>17</b> | <b>Mask Count</b> | <b>25</b> |

Source: Julien R, IMEC

### Metal 1



### Gate



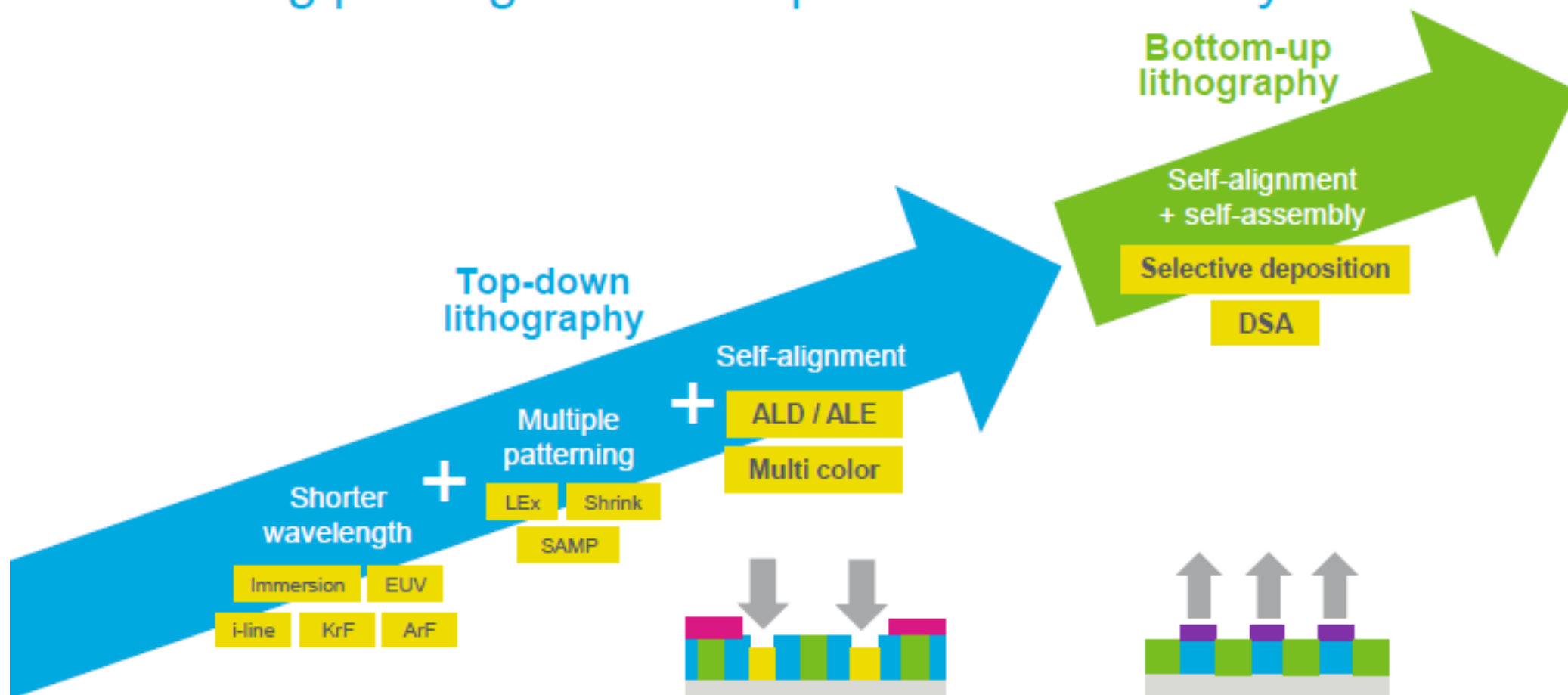
**SaMP also increase process complexity**

Takashi Hayakawa / Tokyo Electron Limited / March 18<sup>th</sup>, 2015



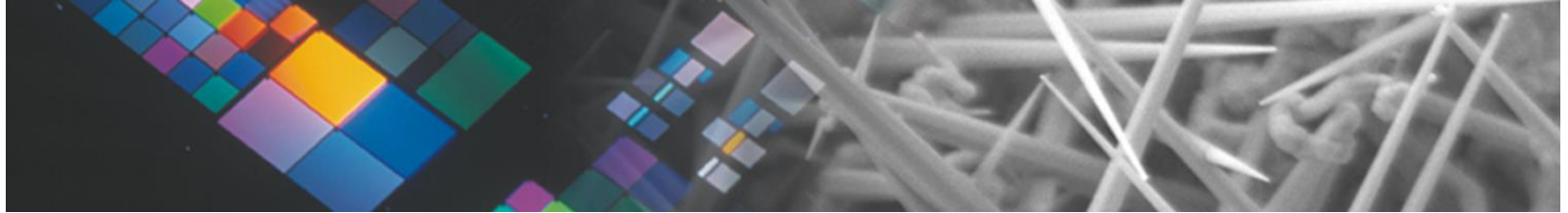


## Patterning paradigm towards placement accuracy

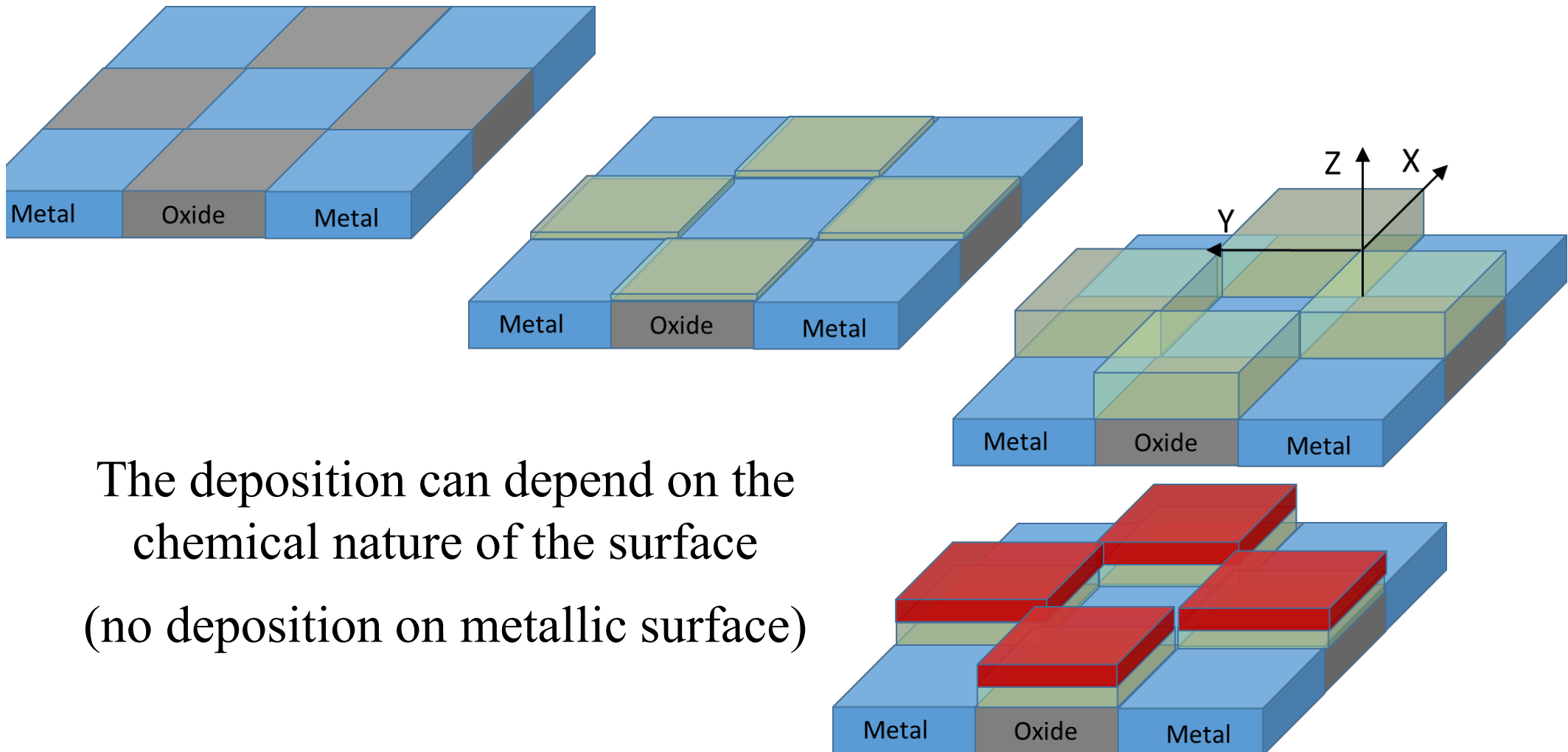


The paradigm is expanding to self-alignment and bottom up approach

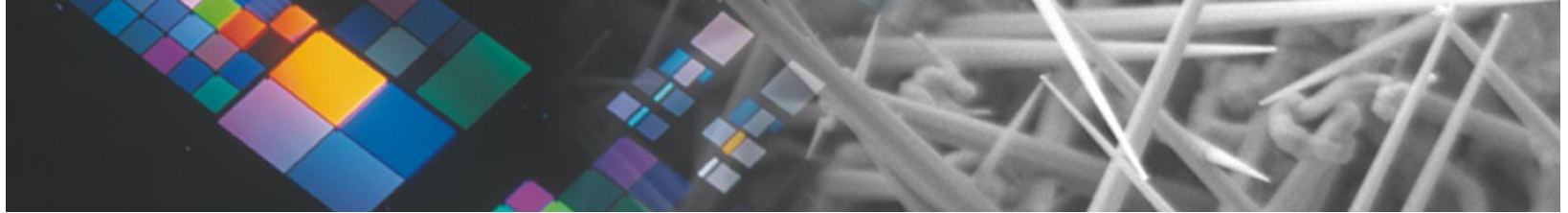




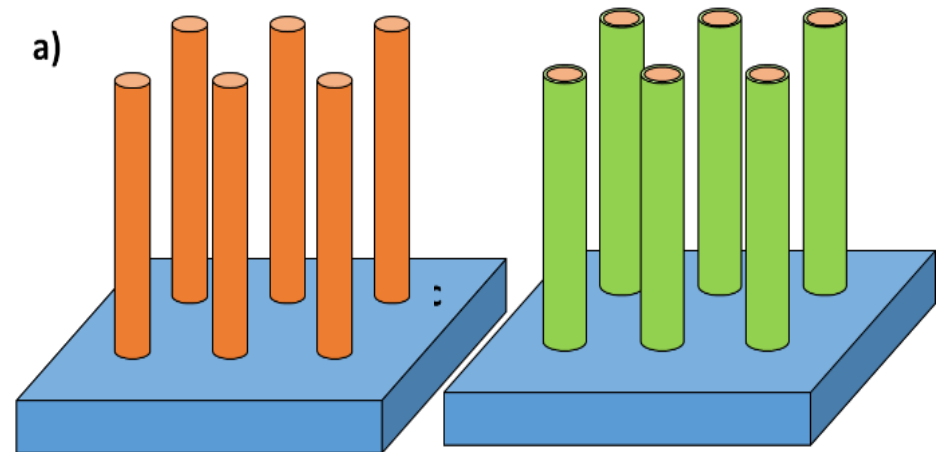
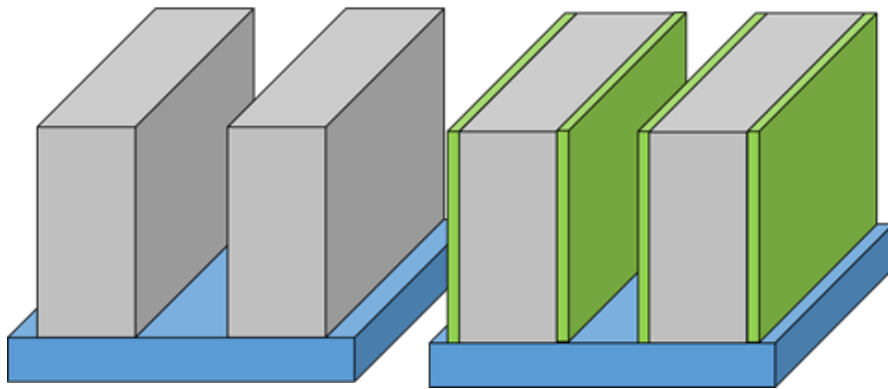
## Area Selective Deposition: new bottom-up approach growth is controlled in the 3 directions



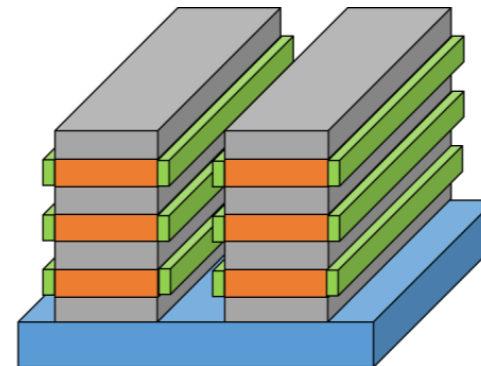
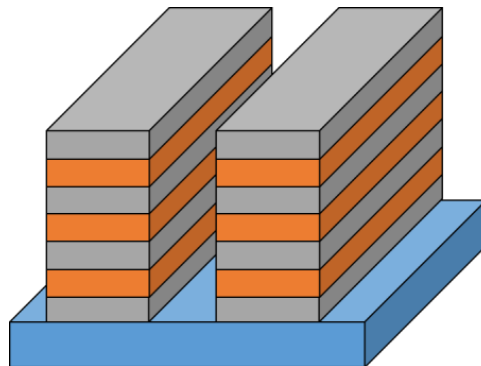
The deposition can depend on the  
chemical nature of the surface  
(no deposition on metallic surface)



The deposition can also be selective in one direction versus the others



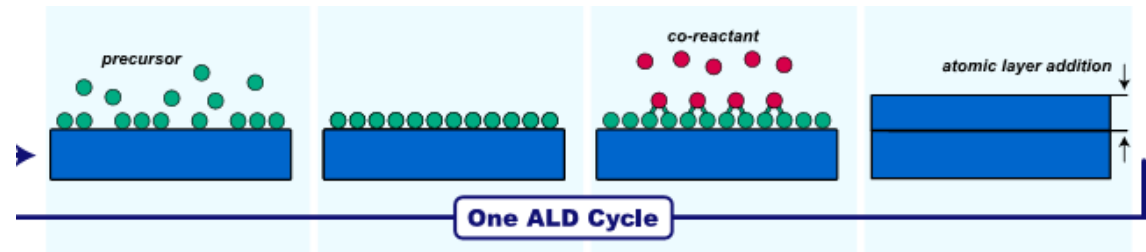
More complex: surface selectivity + directional growth



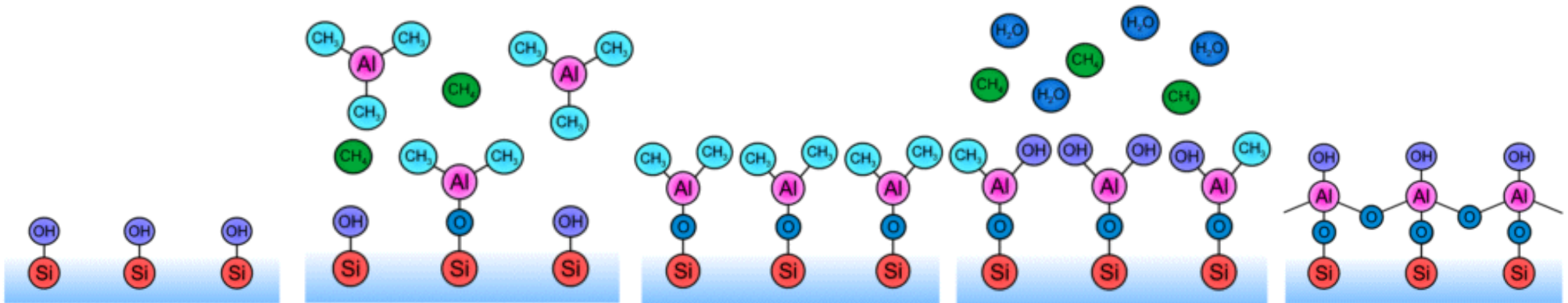


## Why using ALD for ASD?

**ALD** Cyclic deposition  
Self-limiting reactions  
Very conformal



**Very sensitive to the surface**



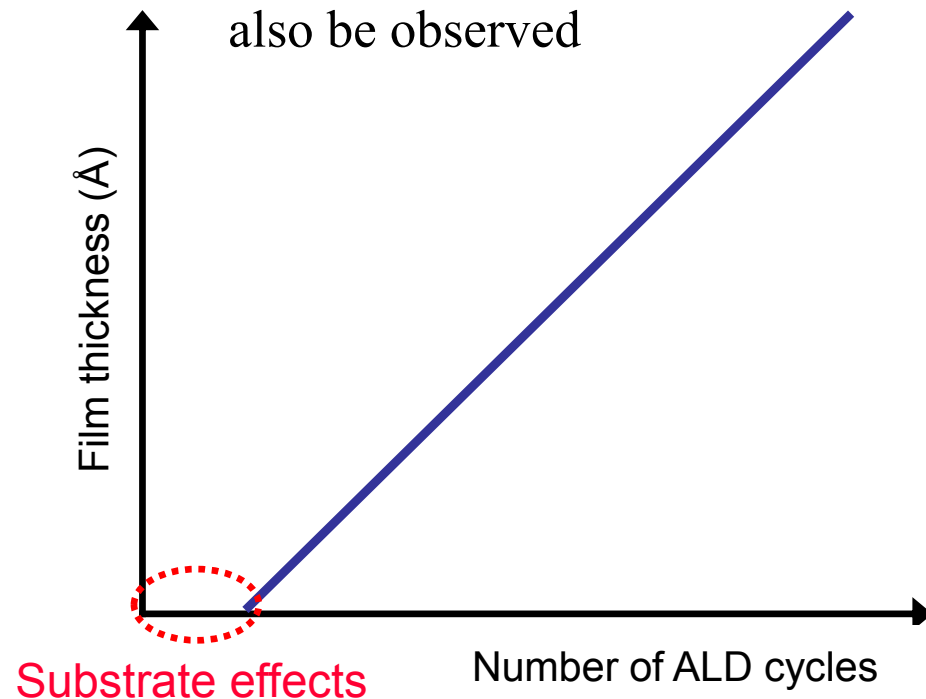
In this ALD example, deposition starts from a  $\text{-OH}$  terminated surface



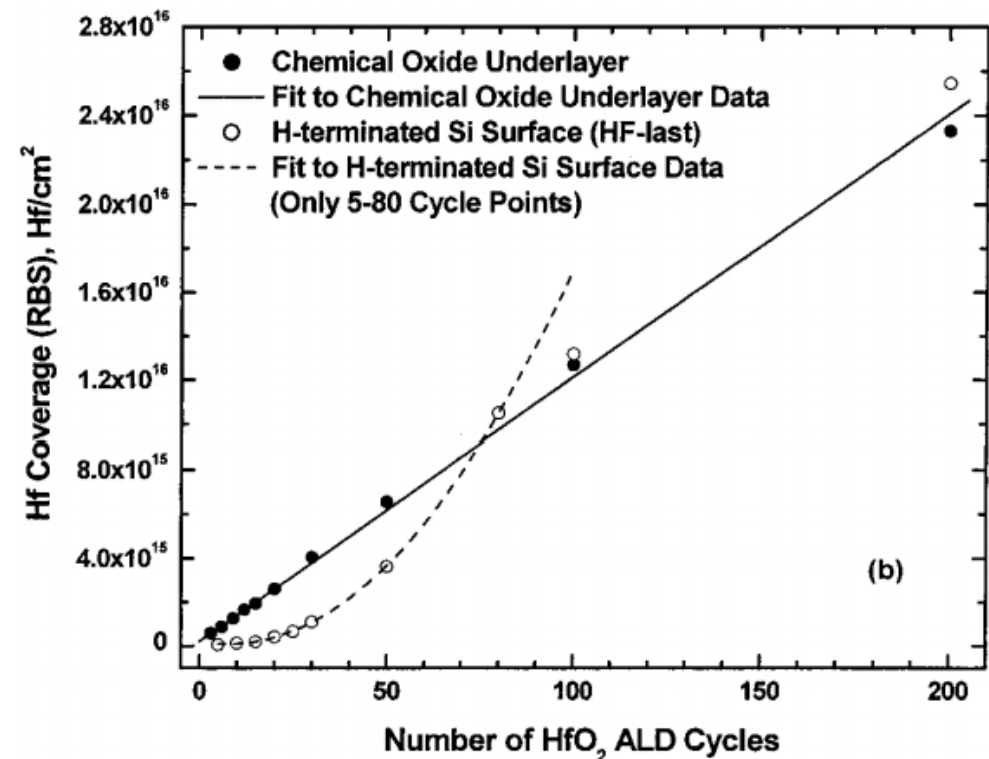
## Precursors may react with one substrate, but not with another

A precursor may etch away a substrate or react with subsurface layers. Or a precursor may not react at all on a substrate - such nucleation delays are common, *e.g.* for oxides on H-terminated silicon or for metals on oxides

The ADL growth can start from the first cycle but delays may also be observed



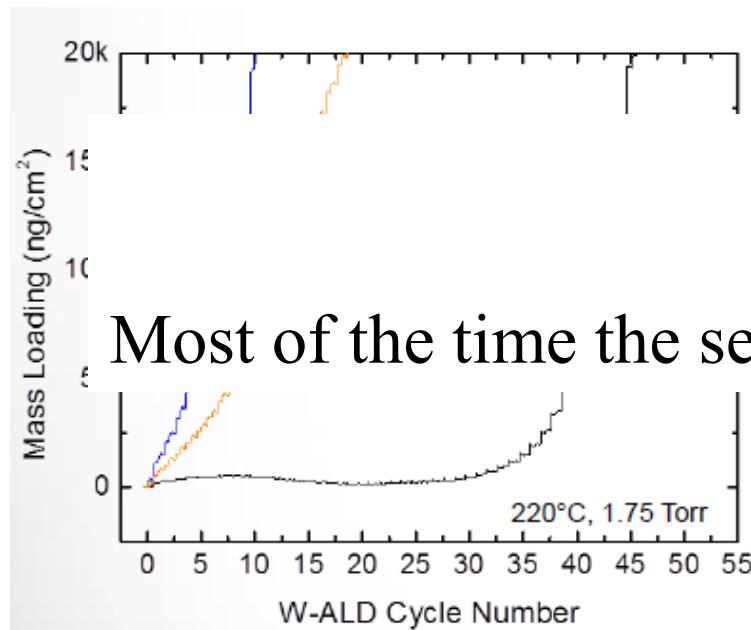
M. A. Alam, and M. L. Green  
*Journal of Applied Physics*, (2003)





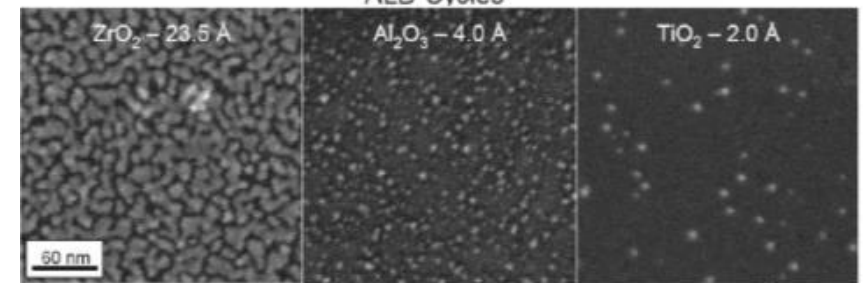
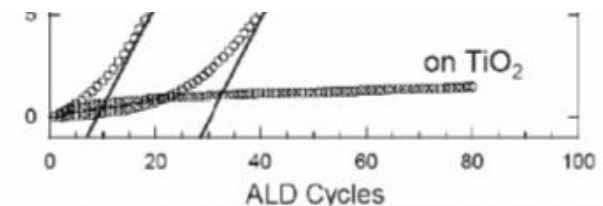
This can be used for ASD, it is ASD by inherent selectivity

- It can be inherent or induced by a post deposition treatment
- Need better understanding between surface and precursors interactions



BUT:

Most of the time the selective thickness is limited to few nm



- Tungsten nucleation delay is substrate dependent
- Surface bound water inhibits W-ALD nucleation
  - $\text{SiH}_4$  pre-exposure promote nucleation

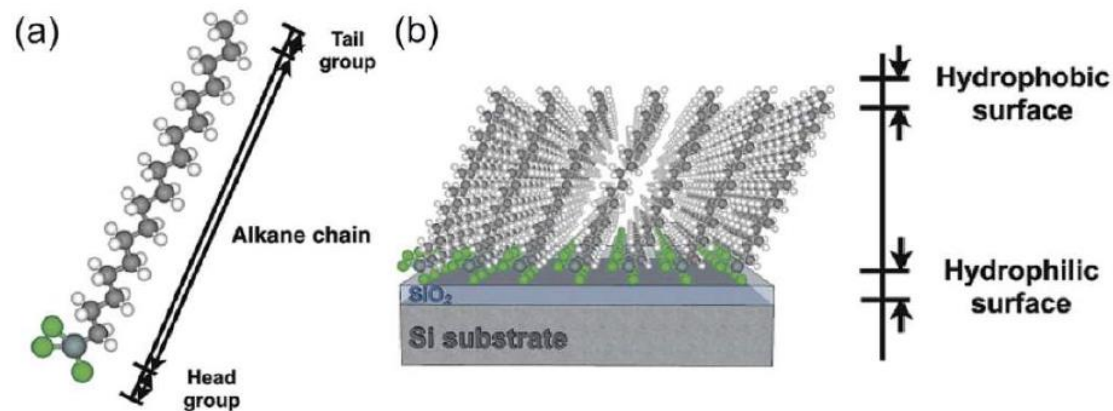




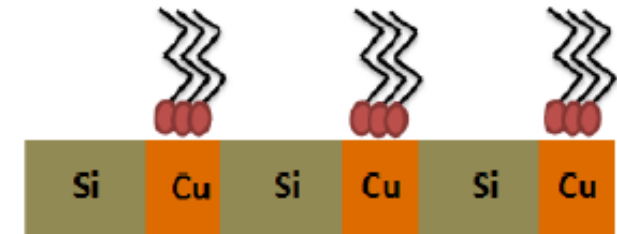
Two strategies to improve the selectivity:

- using an area activation,
- using an area deactivation

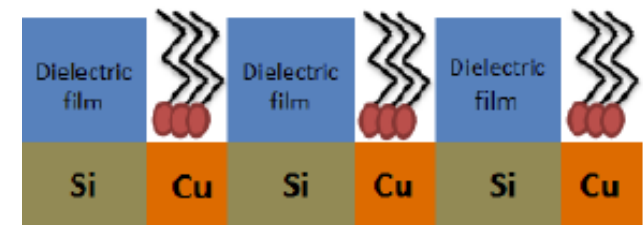
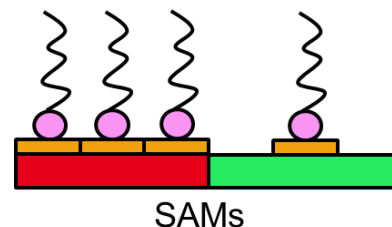
Review paper: *The use of ALD in advanced nanopatterning*  
Mackus et al., *Nanoscale* 6, 10941 (2014)



**Selective ALD deposition** of  
dielectrics (or metals)  
using self-assembled monolayers



| Types of SAMs    |                                  |
|------------------|----------------------------------|
| Thiols           | R-SH                             |
| Silanes          | R-SiCl <sub>3</sub>              |
| Alkenes          | R-C=C                            |
| Alkanoic acids   | R-COOH                           |
| Phosphonic acids | R-PO <sub>3</sub> H <sub>3</sub> |



(Bent, et al, Stanford, 2014)

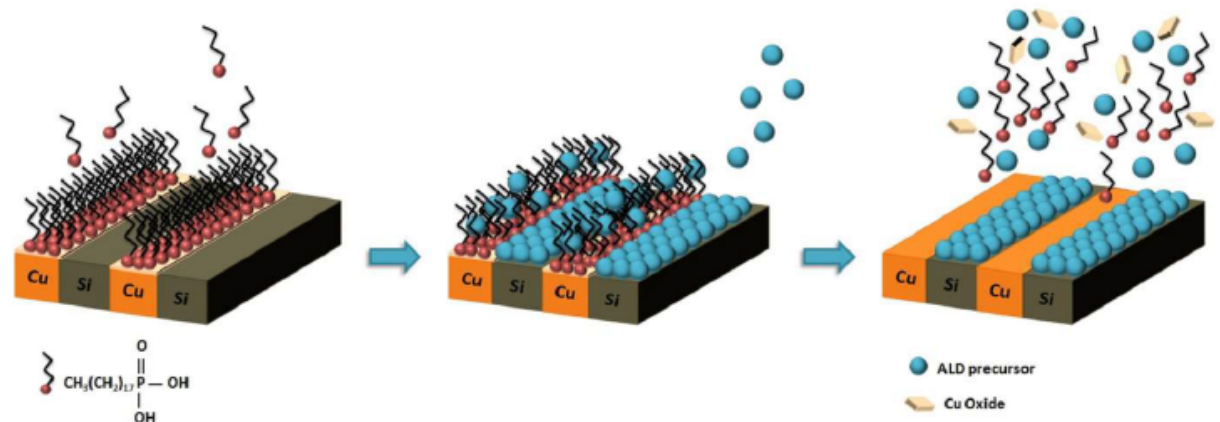


BUT: whatever the choice, a deposition may occur where it is not wanted after a given number of cycles (SAM not dense enough, SAM are reduces/modifies by a plasma,....)

Need to introduce  
corrective action:

etching of undesired  
material

### Improve selectivity by chemical etching



- Use an etchant to attack the underlying  $\text{CuO}_x$  and consequently remove the dielectric layer deposited on top of that
  - $\text{CuO}_x$  etchants: acetic acid, hydrochloric acid, nitric acid

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



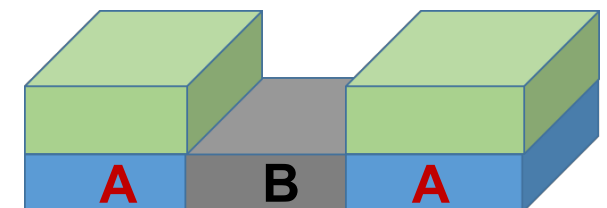
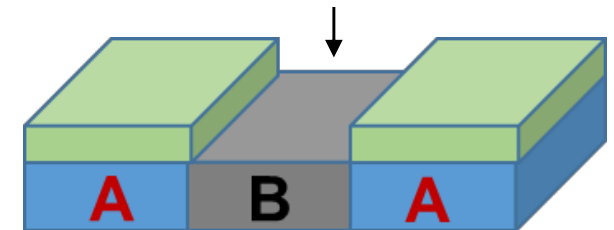
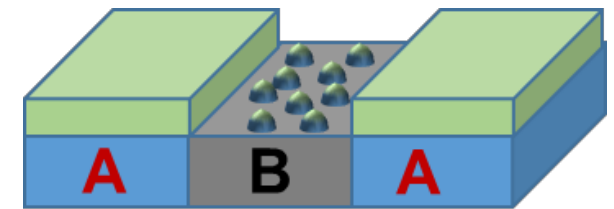
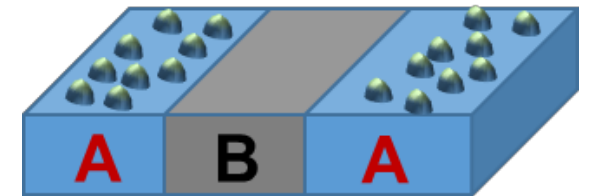


## Etching will enable a “perfect” ASD?

1. Different nucleation time between two surfaces A and B is needed (inherent selectivity, surface treatment...)

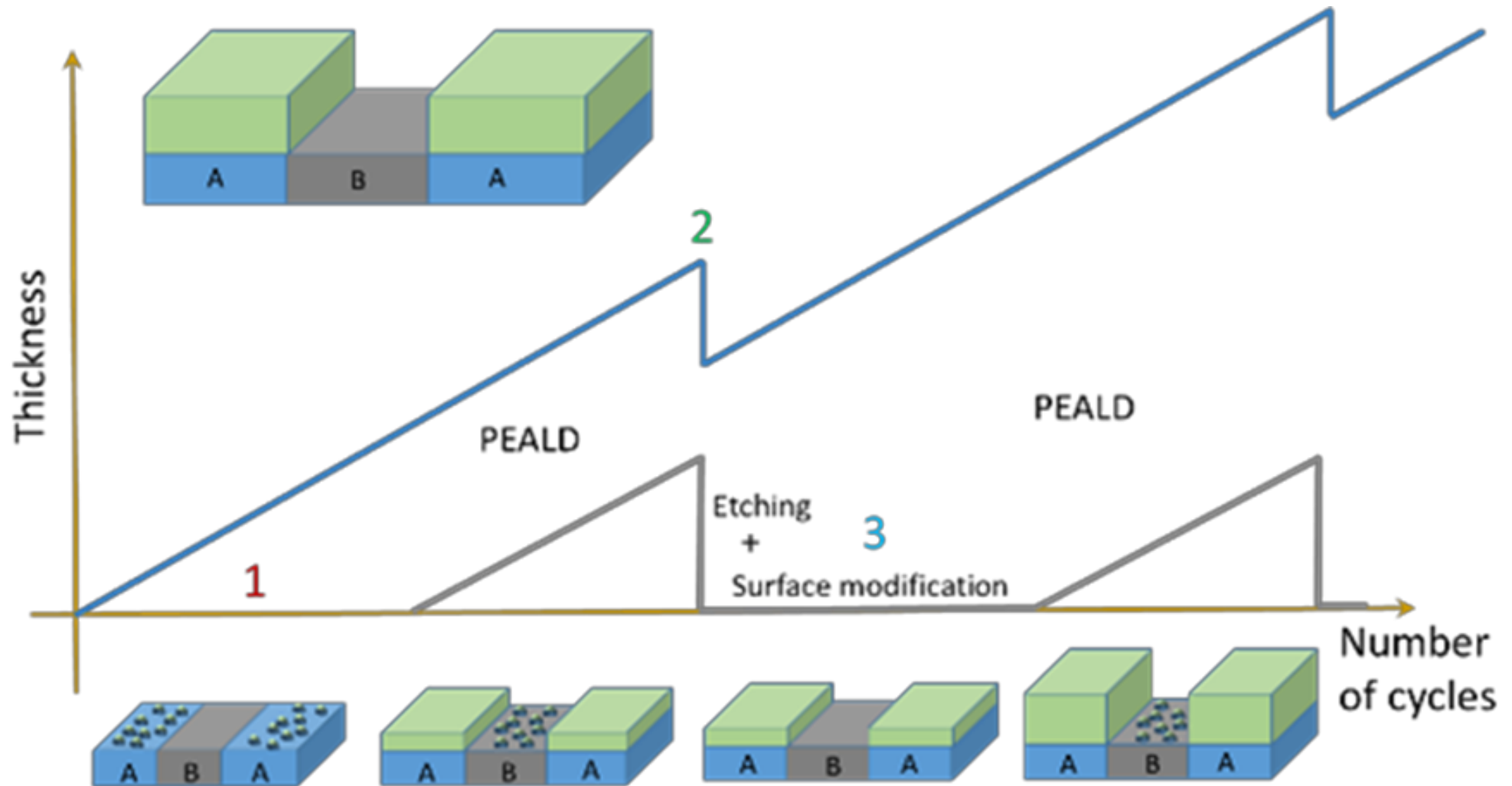
2. Precise etching at the nanometer scale to remove the deposited material from surface B

3. Add a new nucleation delay time for the surface B after or during the etching step



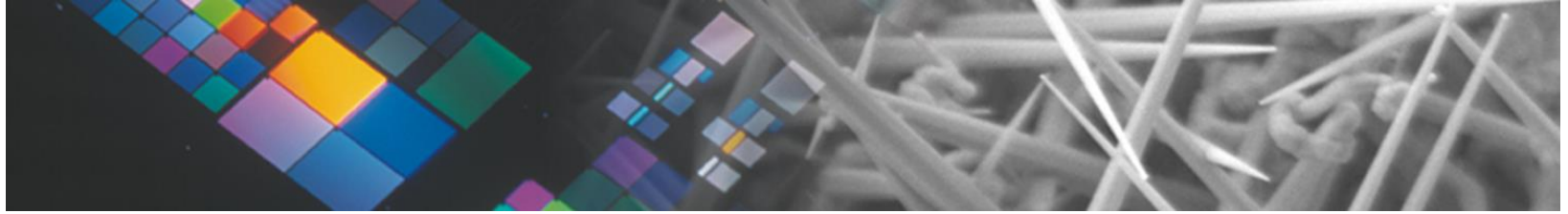


R. Vallat, R. Gassilloud, B. Eychenne, and C. Vallée, J. Vac. Sci Technol. A 35(1) 01B104 (2017)

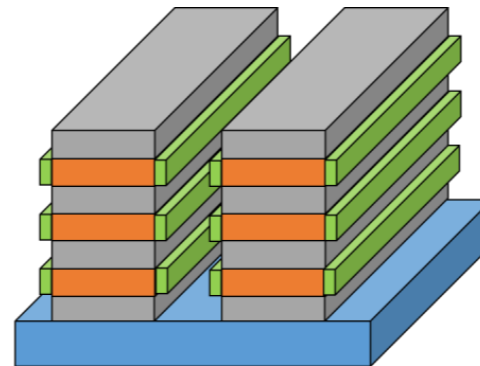
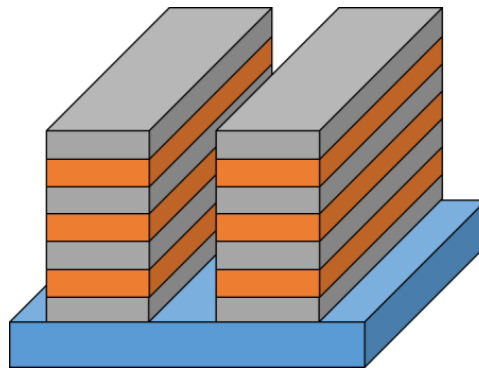
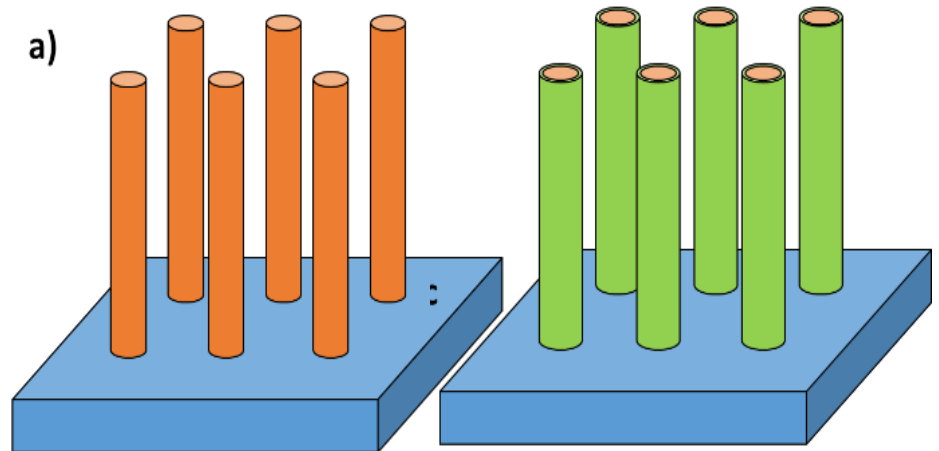
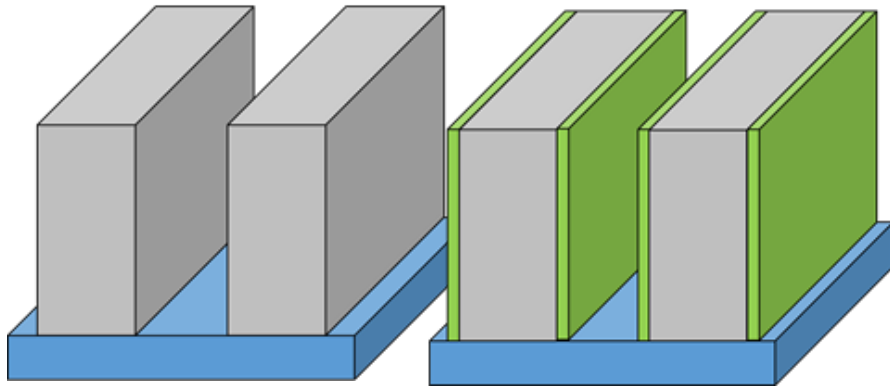


Need to do **both** Deposition (**PEALD**) and Etching (**ALE...**) in the **same tool**

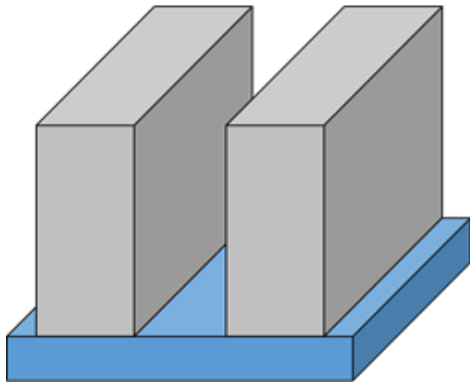
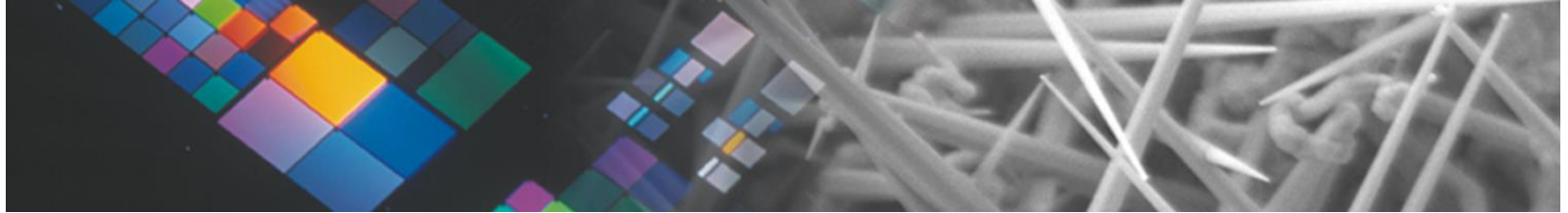




GO BACK TO SLIDE 13: HOW CAN WE DO THAT WITH THIS APPROACH?



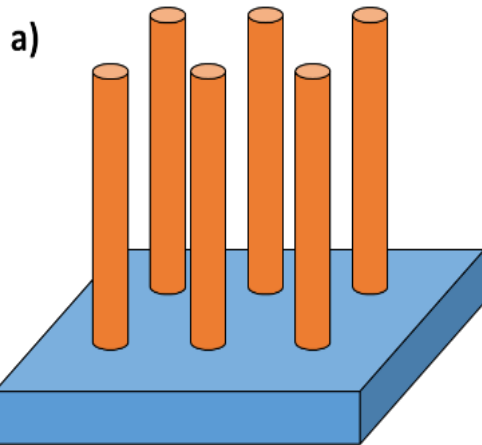
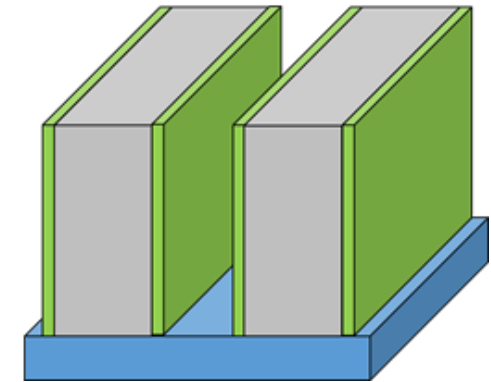




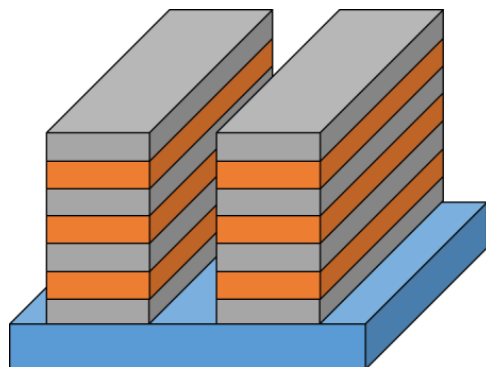
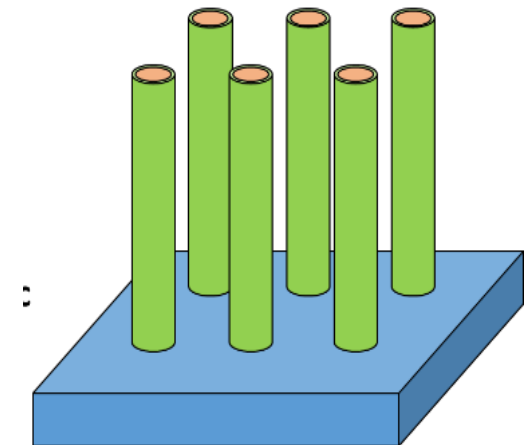
## Selective Deposition



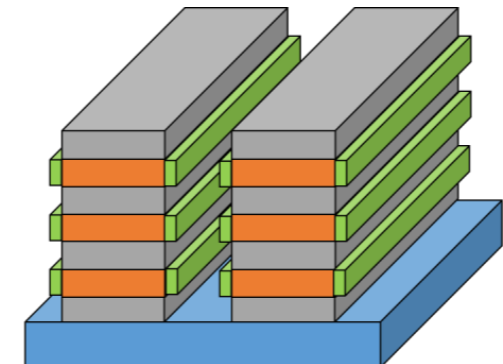
anisotropic etching  
ion sputt., RIE, anisotropic ALE

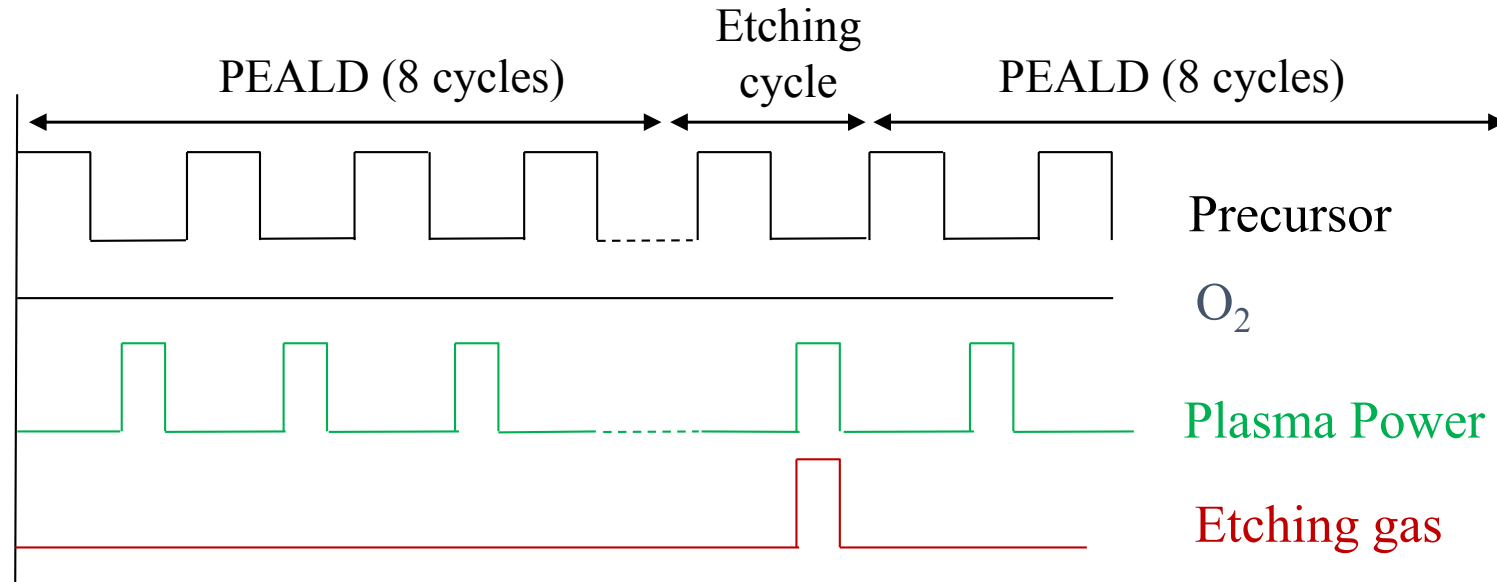


anisotropic etching  
ion sputt., RIE, anisotropic ALE



isotropic etching  
chem. etching, isotropic ALE





When? Every cycle, every 5 cycles, ... → throughput of the process

How long? 1s? 3s?... → throughput of the process, not perfect ASD  
(undesired material not removed / all the desired material is removed)

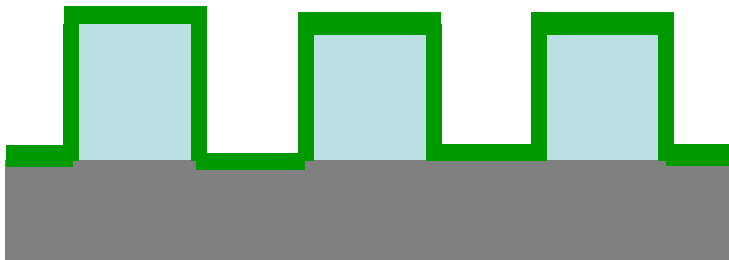
Why does it work and how improve it? → Plasma and precursor /surface reactions, contamination...



## Ta<sub>2</sub>O<sub>5</sub> ASD: PEALD Ta<sub>2</sub>O<sub>5</sub> + Ar plasma

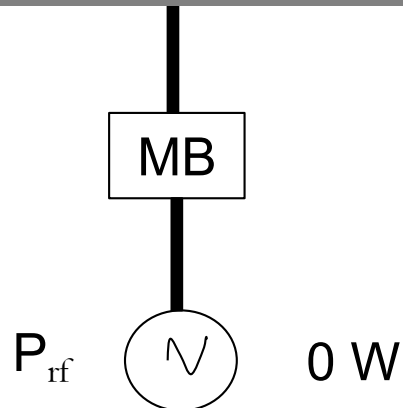
PEALD – deposition step

Plasma  
potential  
 $V_p$



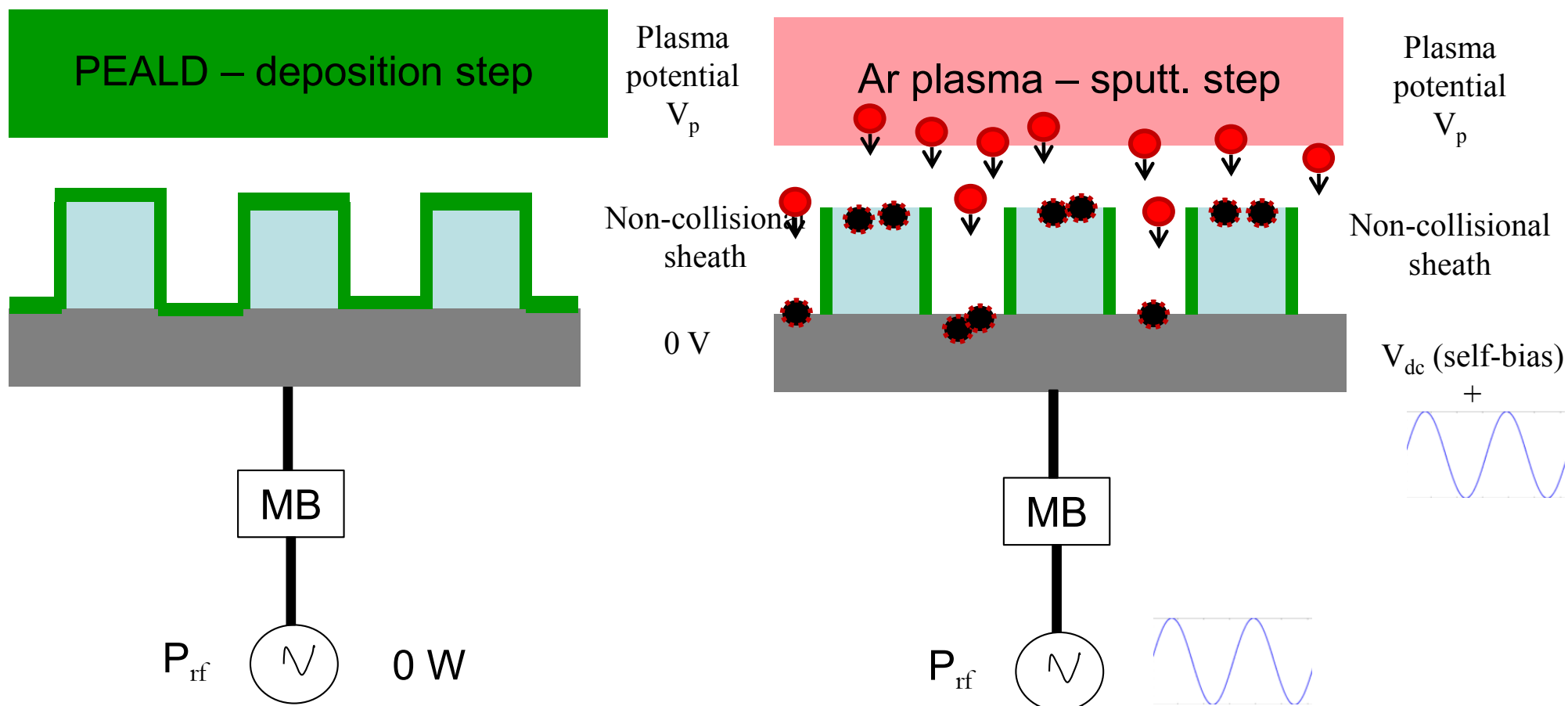
Non-collisional  
sheath

0 V





## Ta<sub>2</sub>O<sub>5</sub> ASD: PEALD Ta<sub>2</sub>O<sub>5</sub> + Ar plasma





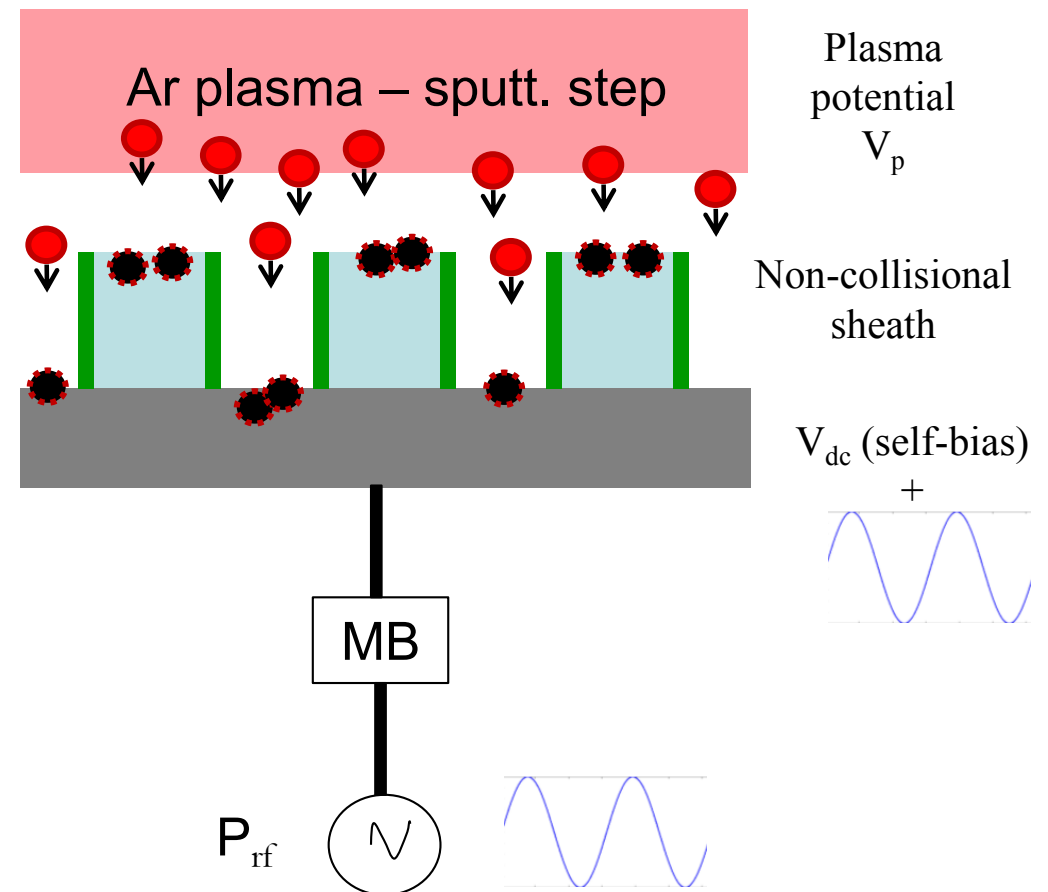
## Ta<sub>2</sub>O<sub>5</sub> ASD: PEALD Ta<sub>2</sub>O<sub>5</sub> + Ar plasma

Need a good control of  
ion energy

Low pressure plasma  
(non-collisional sheath)

HDP source  
(inductive...)

$$\text{Ion energy} = e(V_p - V_{dc})$$

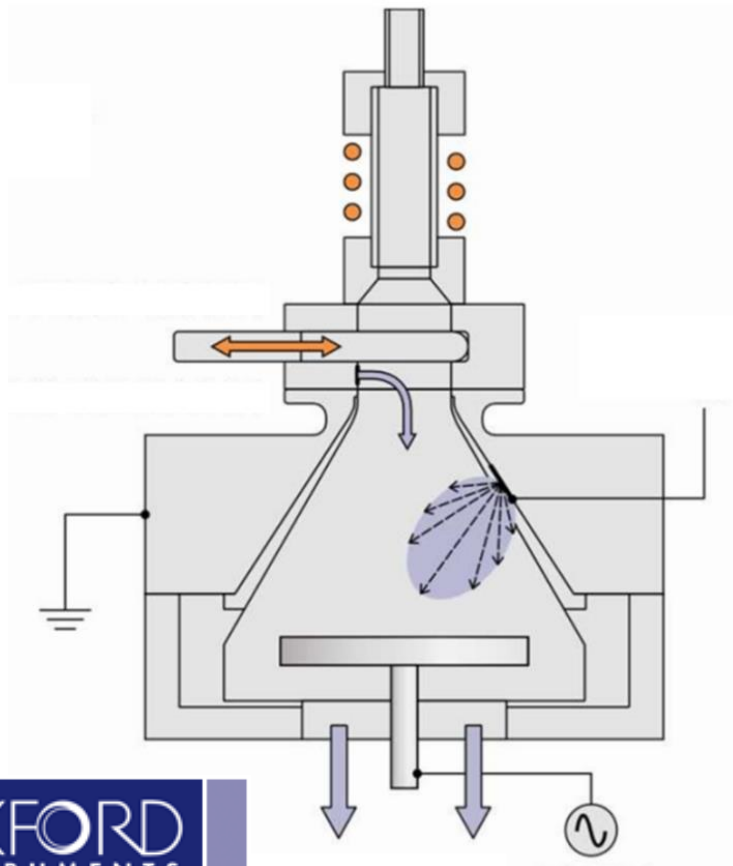




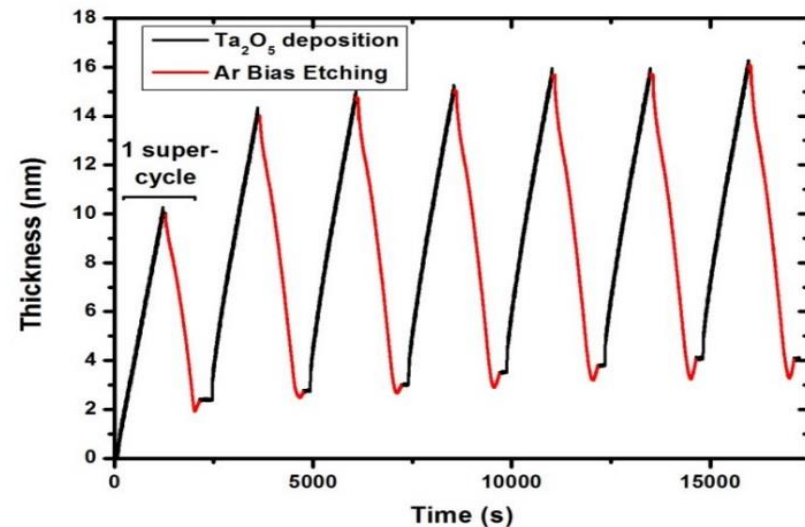
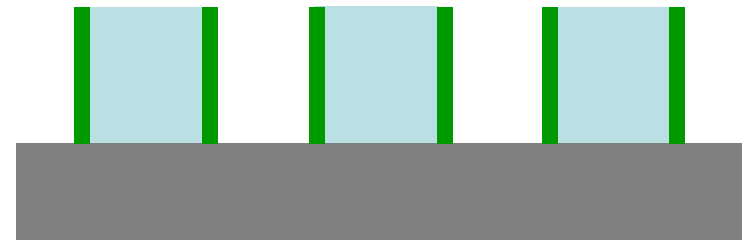


Ta<sub>2</sub>O<sub>5</sub> ASD: PEALD Ta<sub>2</sub>O<sub>5</sub> + Ar plasma

PEALD tool from Oxford (FLEXAL) with substrate biasing platform and *in situ* ellipsometry (film sense)

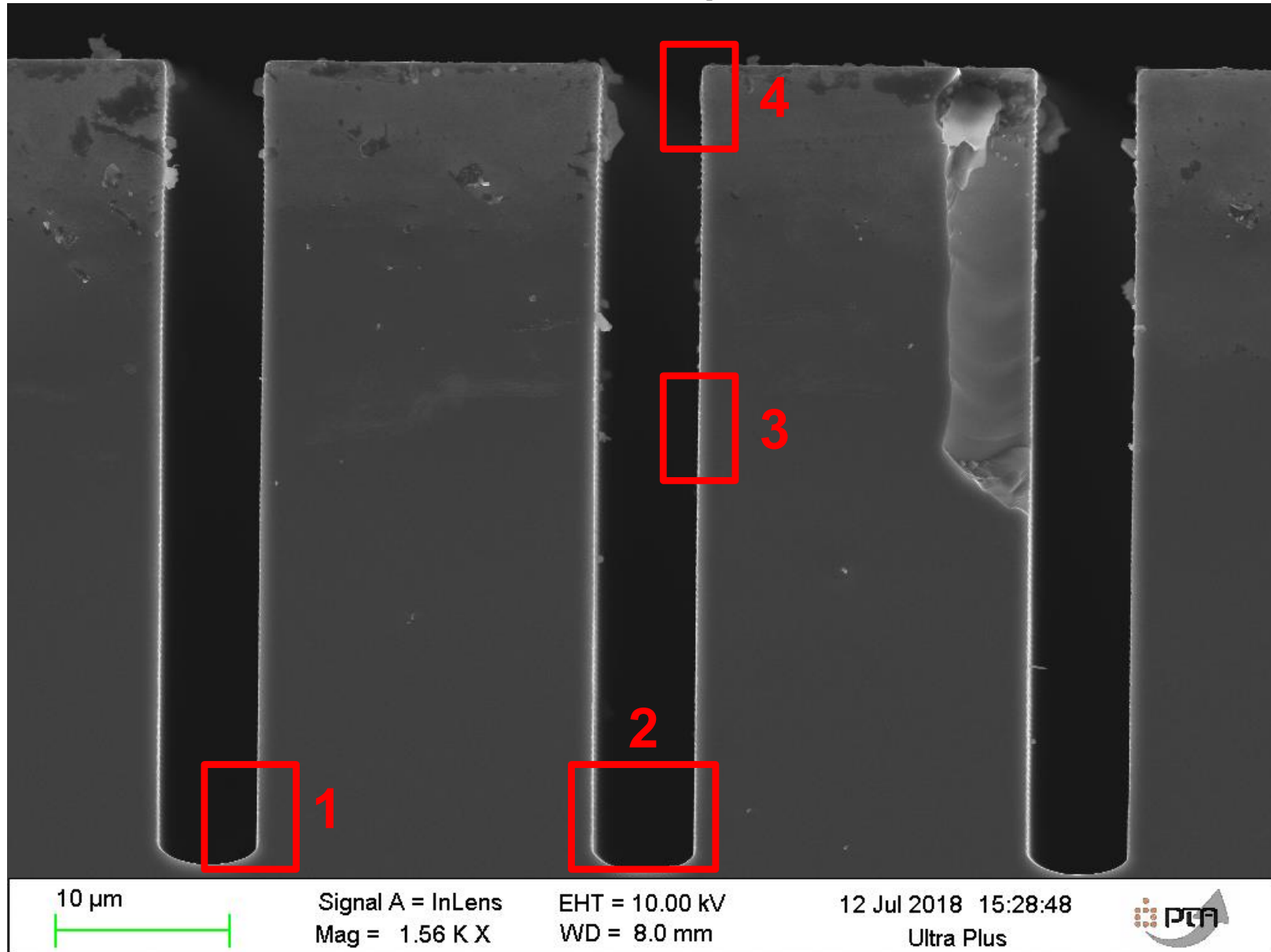


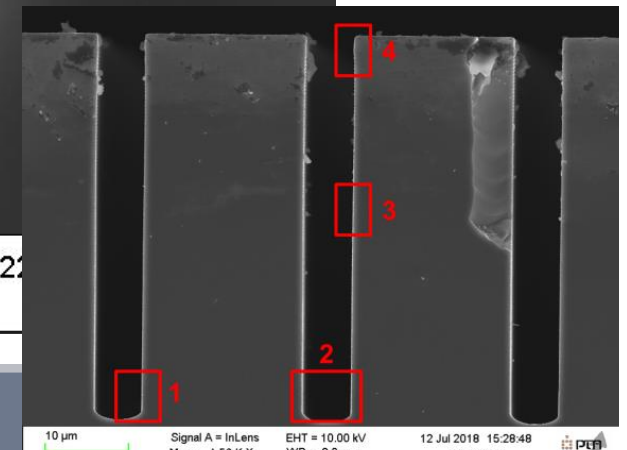
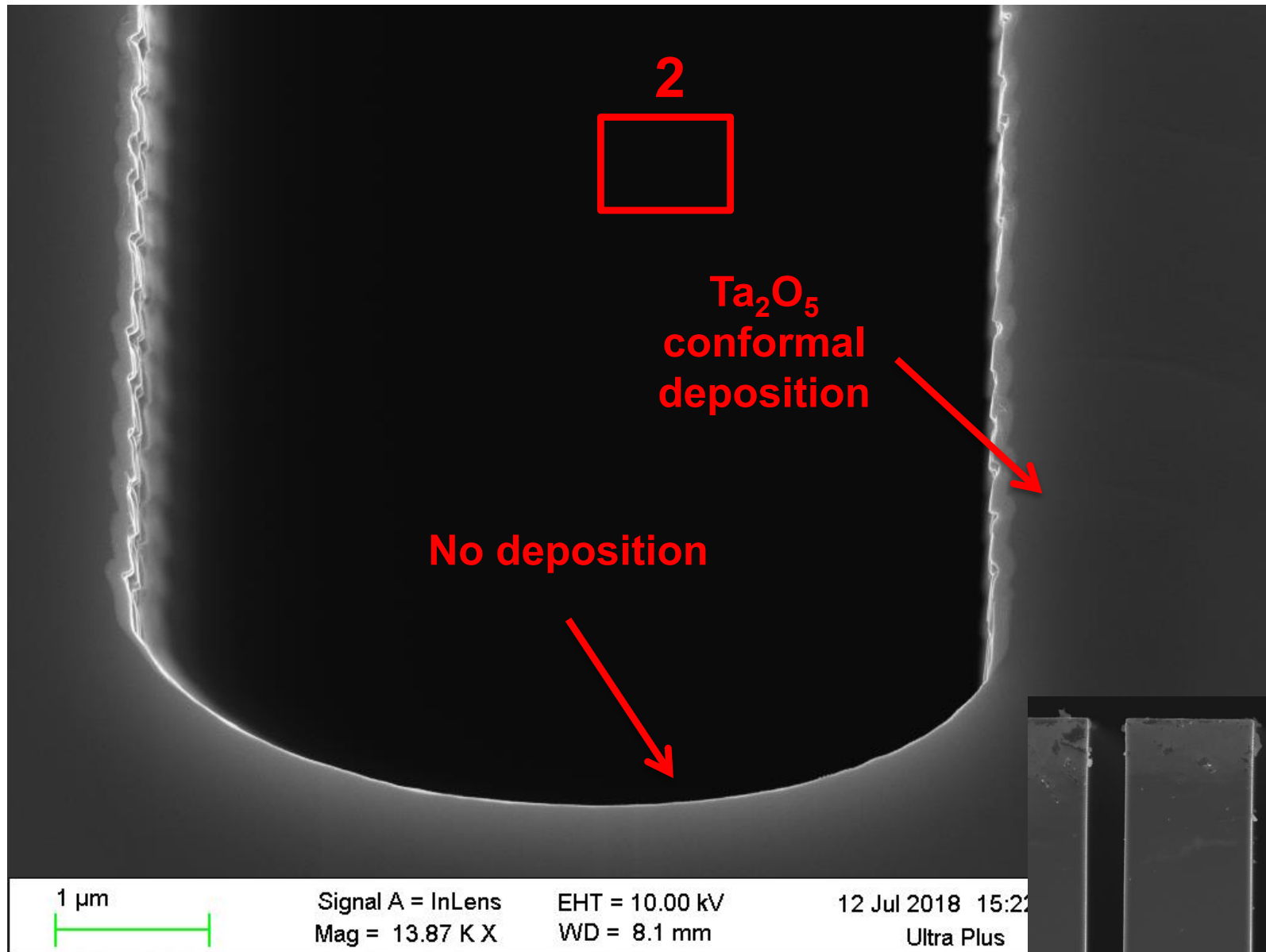
The Business of Science®

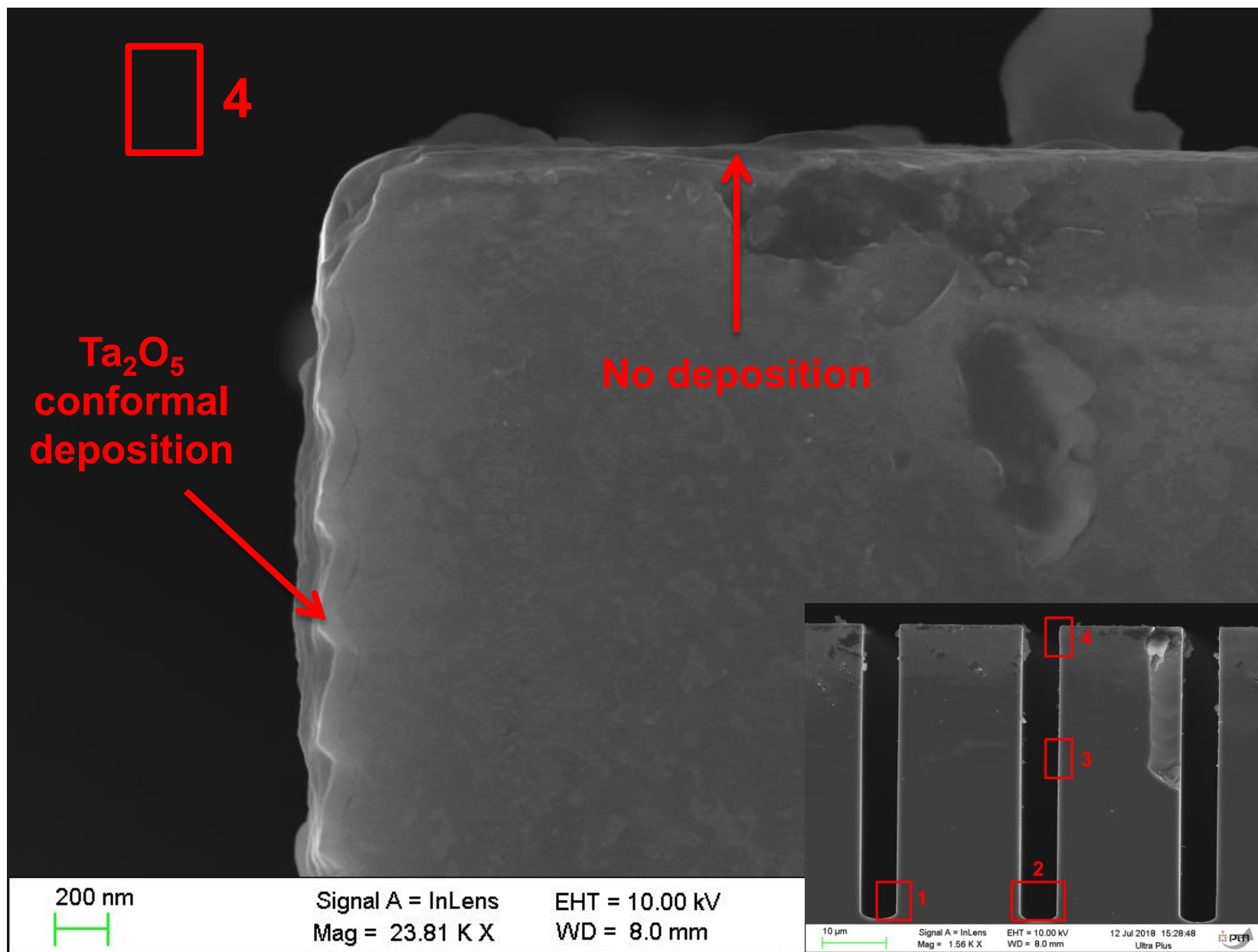




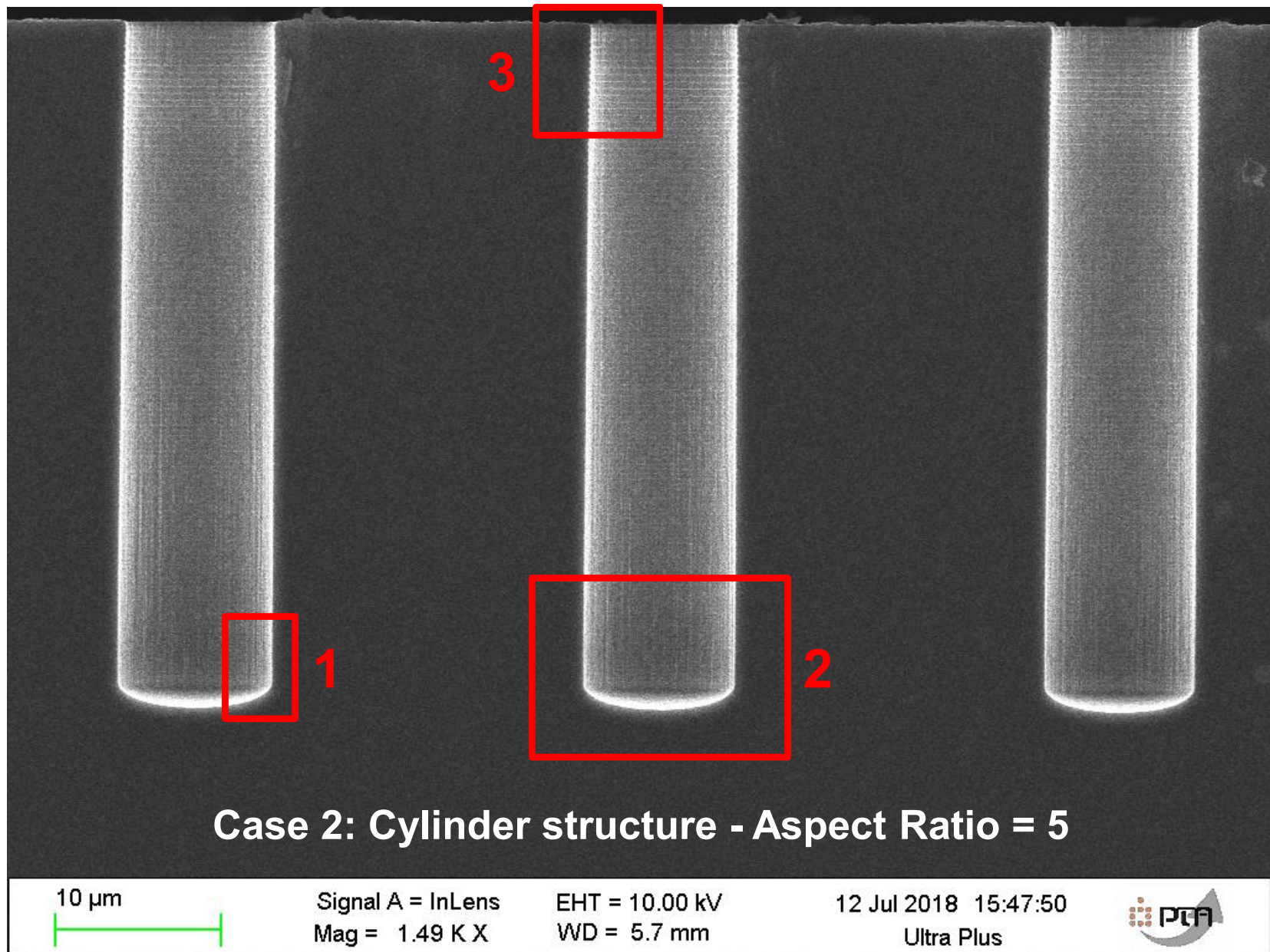
## Case 1: Trenches - Aspect Ratio = 8



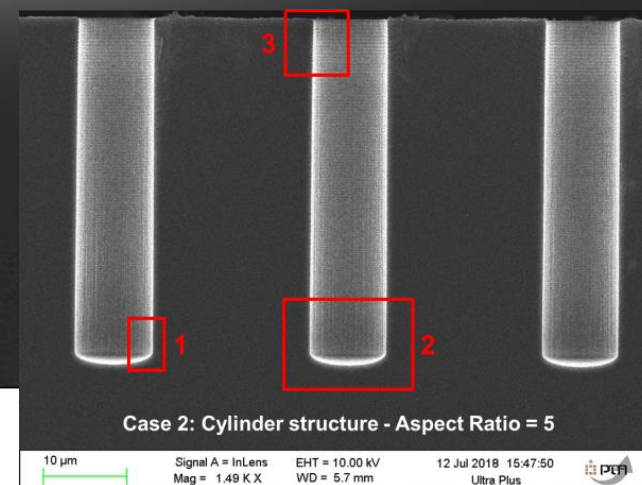
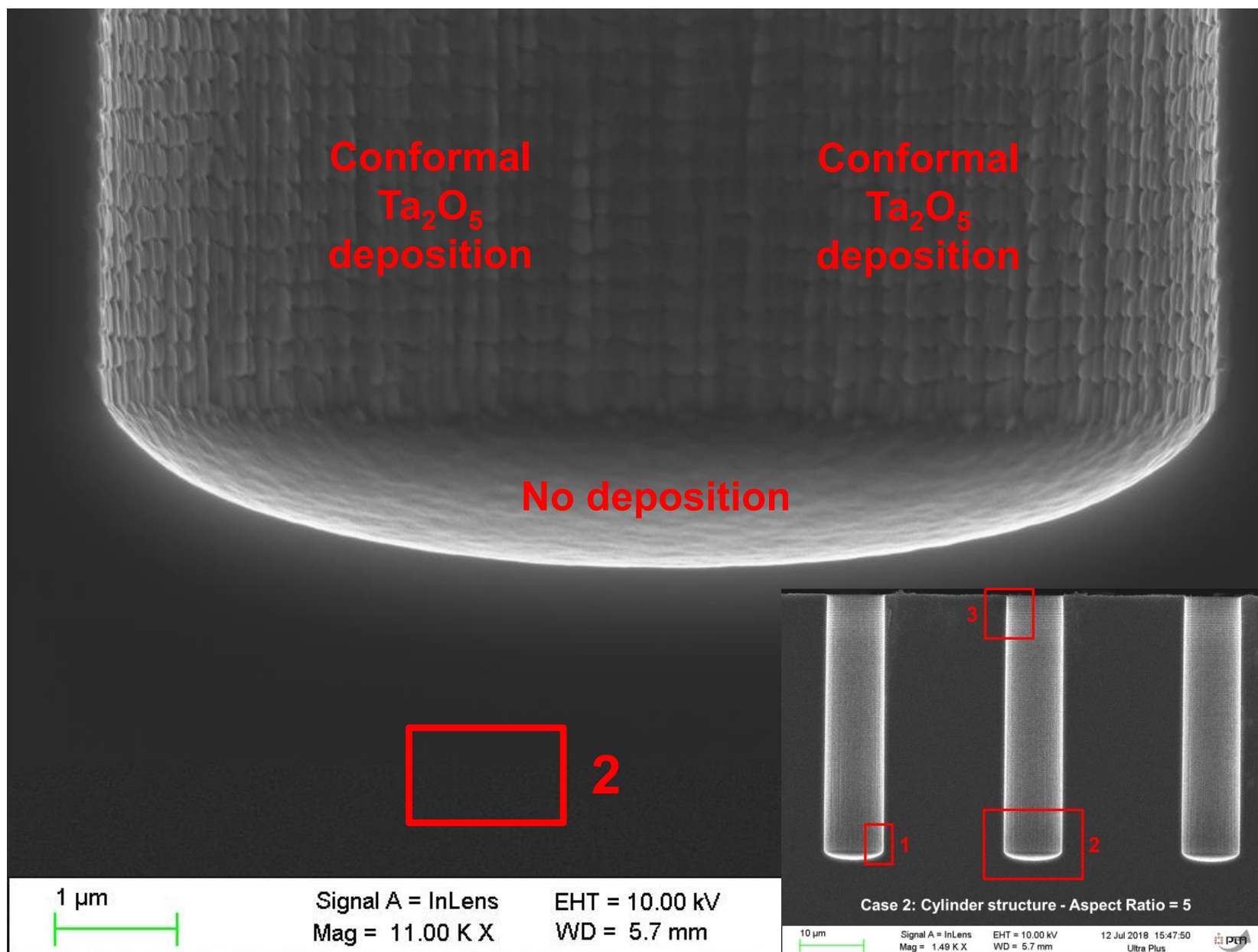


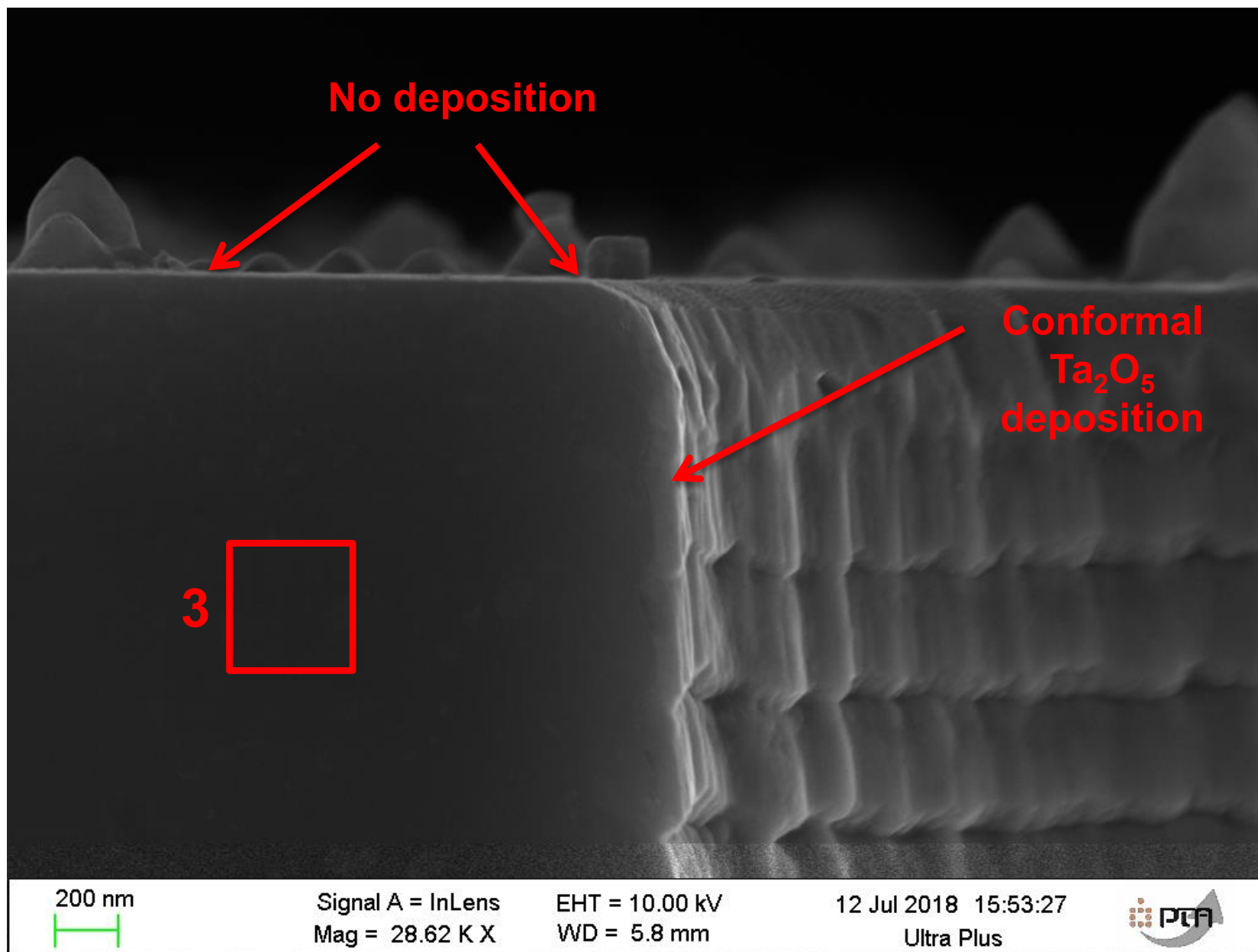




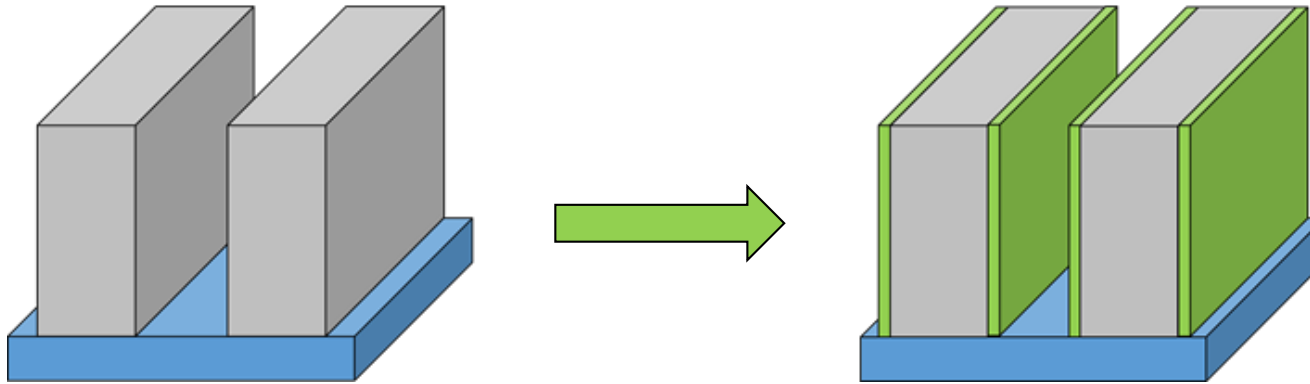




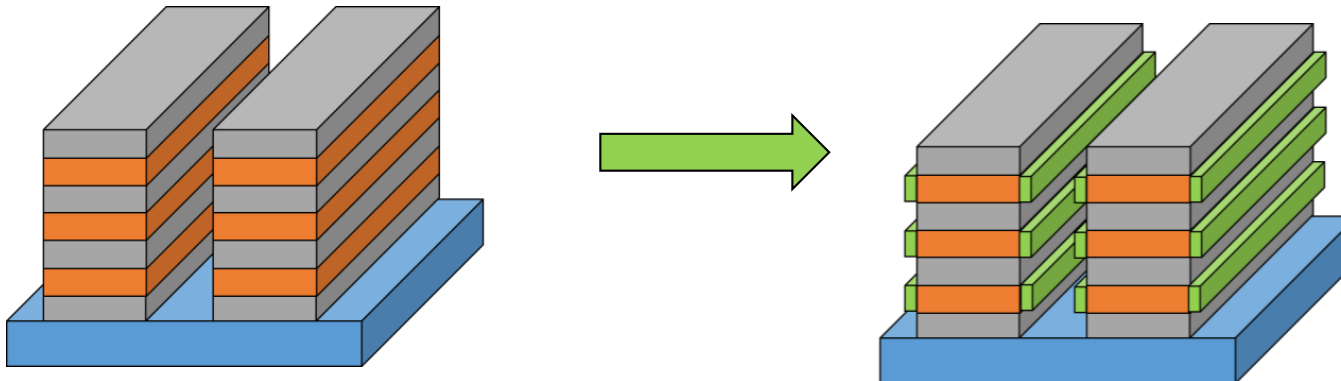




## Example 2 of ASD using etching



OK this is done but can we do something more complicated



directional selective deposition + surface selective deposition  
using ion sputtering is no more a good solution

## Example 2 of ASD using etching

Need of a chemical ISOTROPIC etching  
Etching must be done by radicals only

Can be done in CCP discharge at high pressure (collisional sheath)



Process developed in 300 mm tool  
from KOBUS (capacitive discharge)  
with in situ XPS

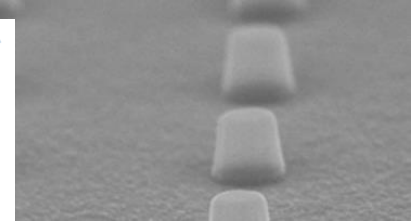
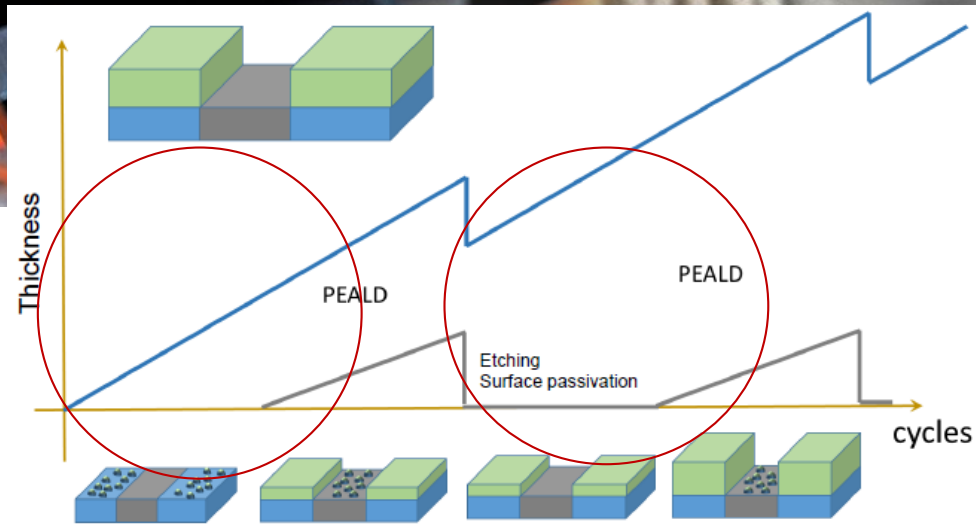
300 mm CCP PEALD tool

**KEMSTREAM**  
ADVANCED VAPORIZERS ● ● ●

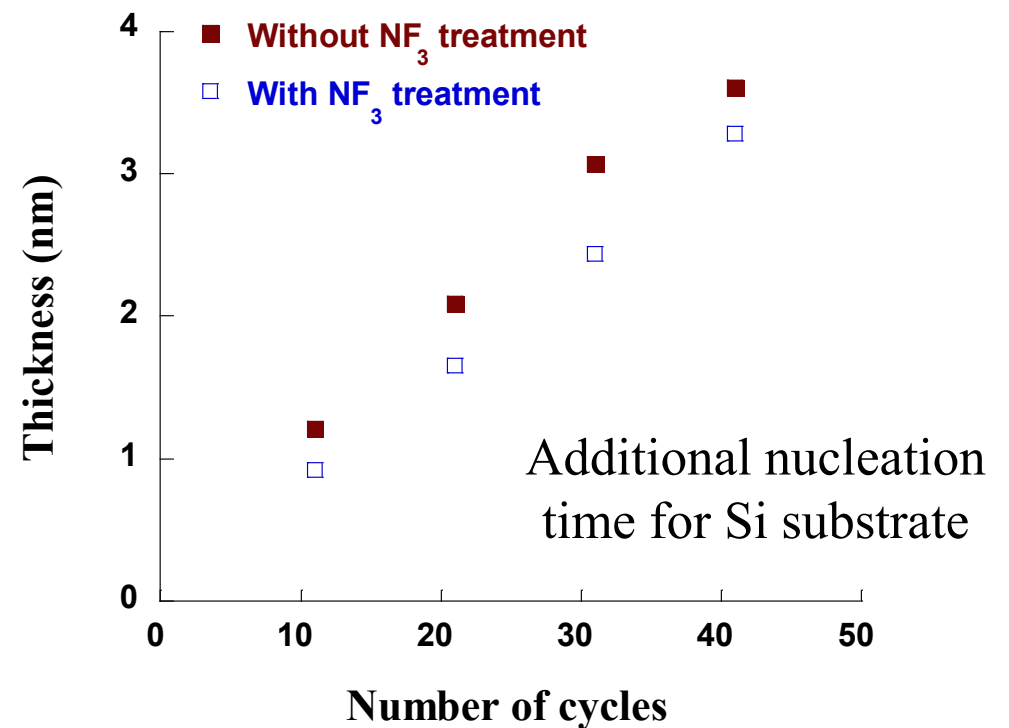
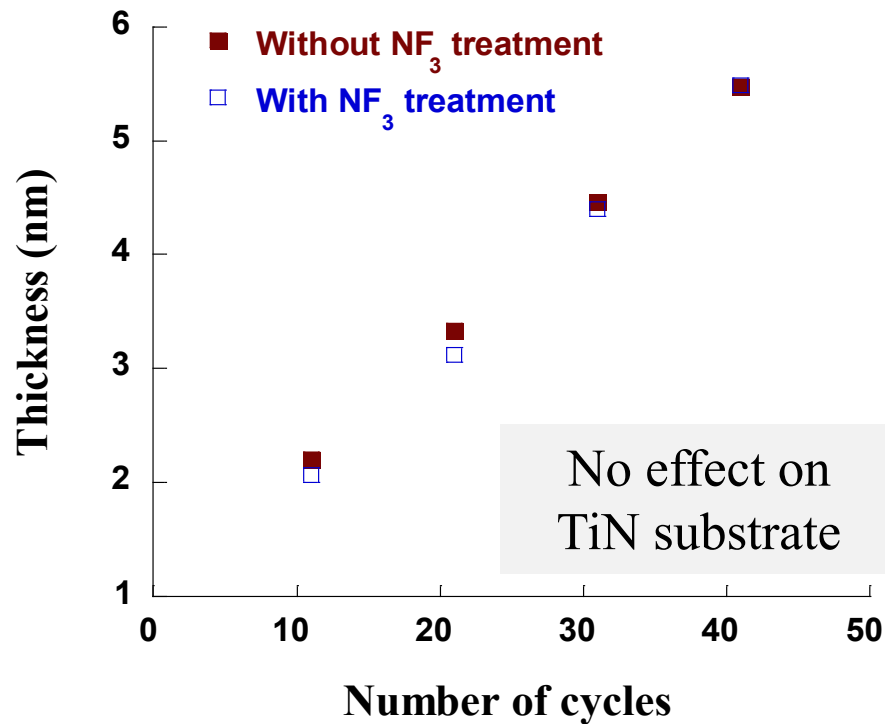
**KOBUS**  
Process  
like no one



Plasma is used to  
create delays in  
nucleation



## PEALD of $\text{TiO}_2$ before and after $\text{NF}_3$ plasma (Kobus tool)

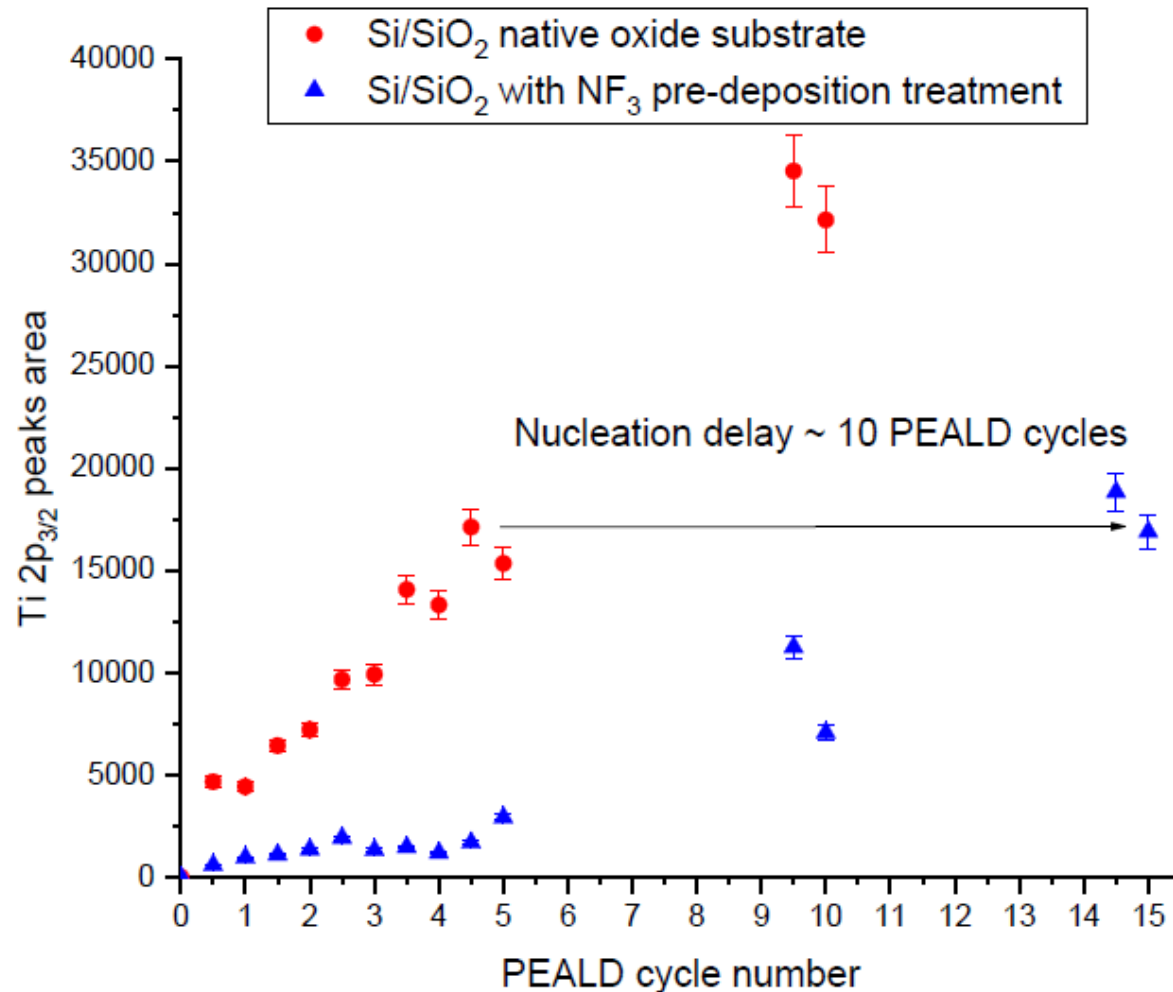






## Impact of Fluorine-based plasma? (Example with ASD of $\text{TiO}_2$ )

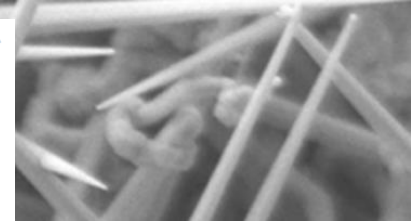
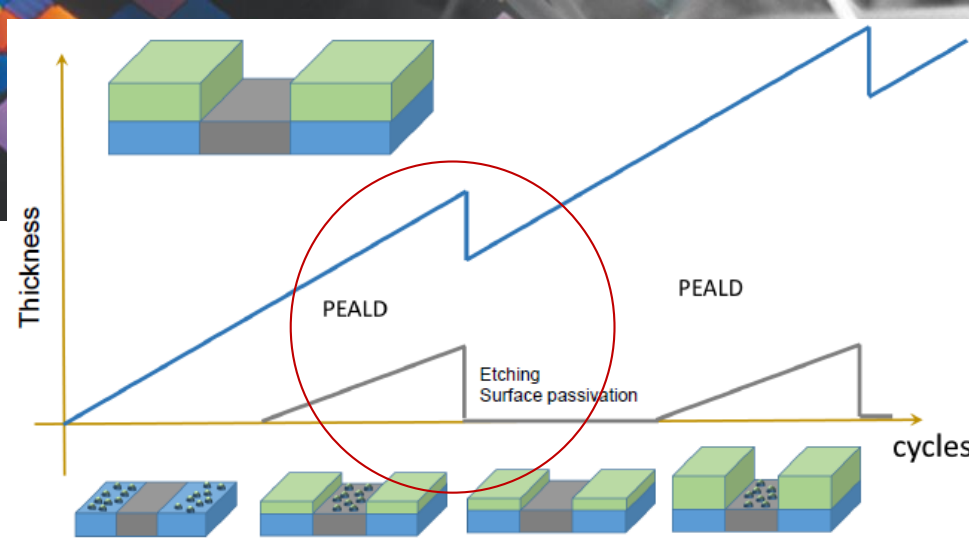
*Quasi in situ XPS* to understand and optimize the passivation step



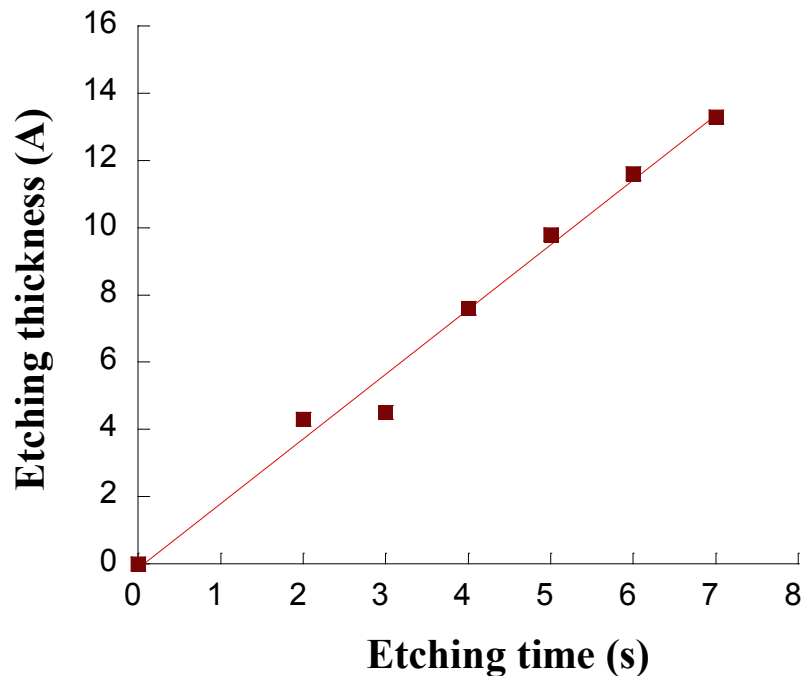
From *quasi in situ* XPS we can estimate the nucleation delay induced by Fluorine-based plasma to be 5-10 PEALD cycles

O. Salicio *et al*, to be published

Plasma is also used  
to etch material



Etching of  $\text{TiO}_2$  in  $\text{NF}_3/\text{O}_2/\text{Ar}$  plasma

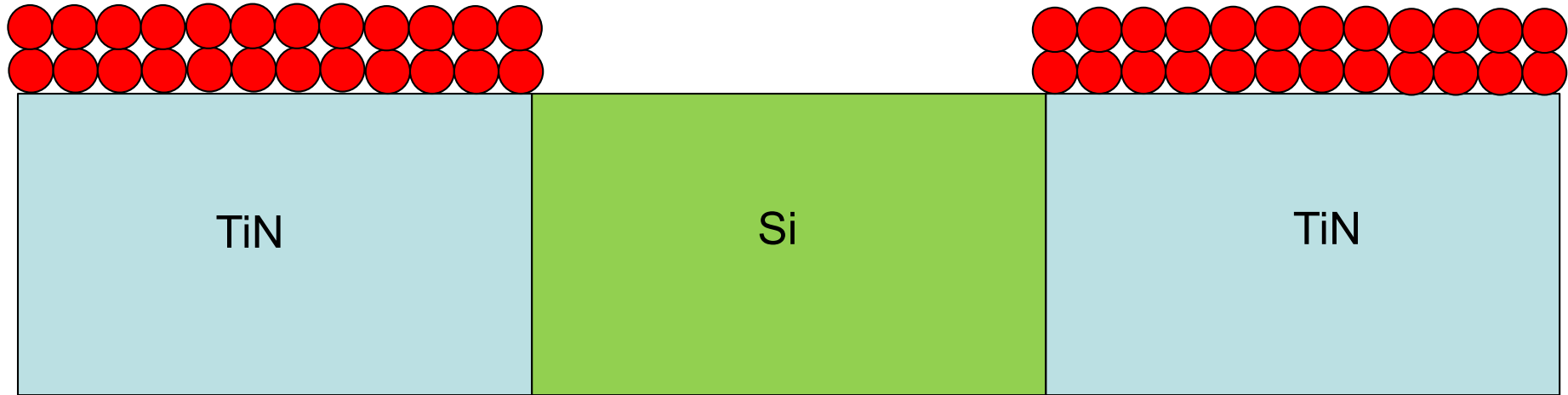


The etching step must be made at  
the same temperature than the  
deposition temperature

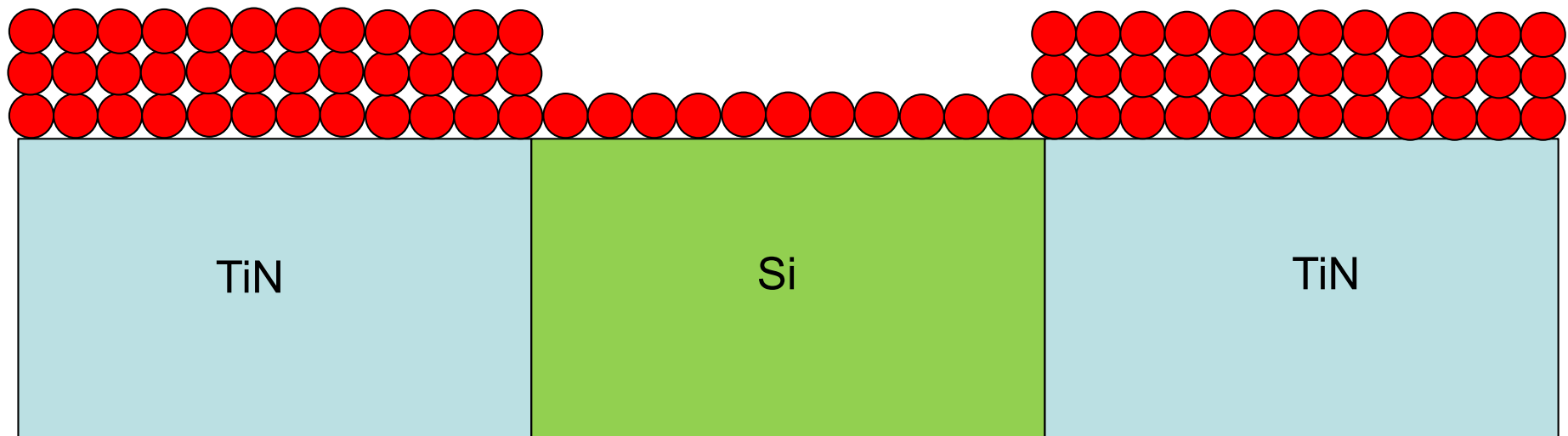
→ F-based plasma good candidate:  
 $\text{TiF}_4$  volatile at  $250^\circ\text{C}$



Growth starts faster on TiN substrate (inherent or plasma treatment)

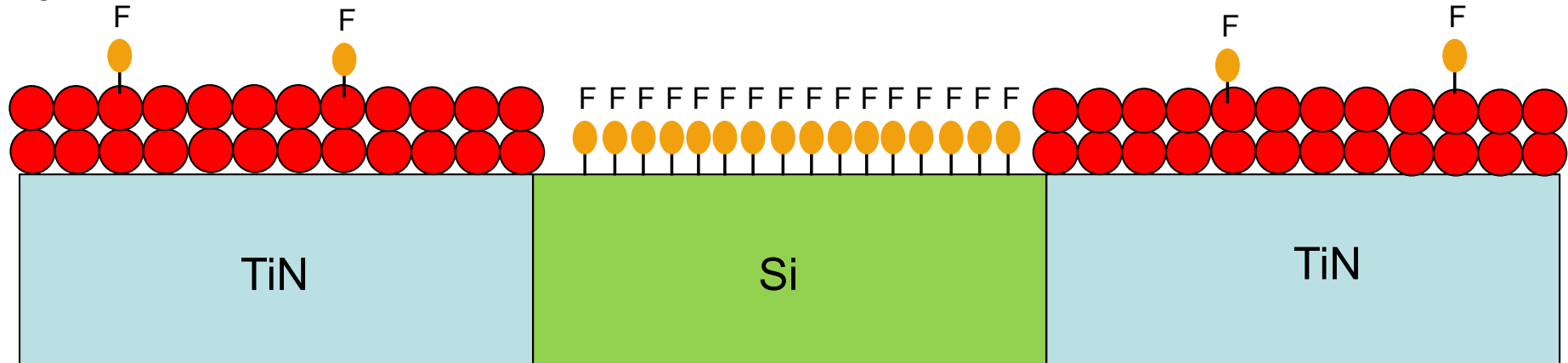


After X cycles  $\text{TiO}_2$  starts to growth on both substrates

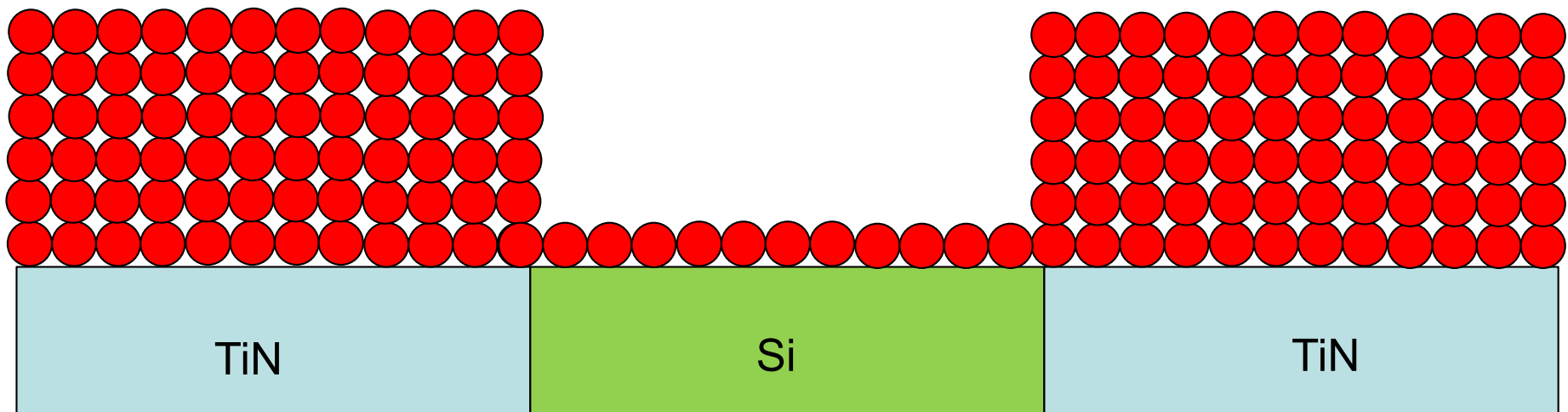




$\text{NF}_3$  is added to  $\text{O}_2$  plasma to etch  $\text{TiO}_2$  and create Si-F bonds (few Ti-F bonds)

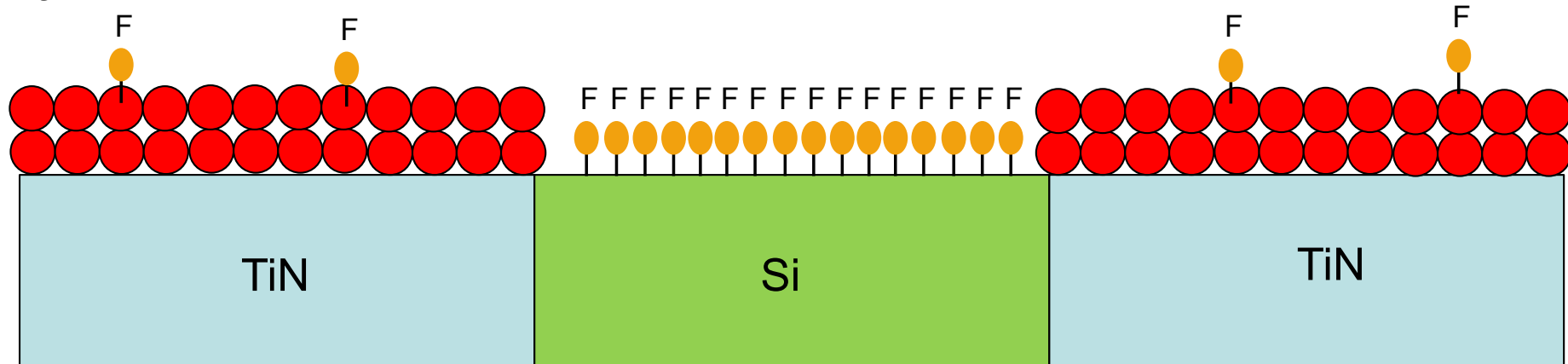


After a number of PEALD cycles  $\text{TiO}_2$  starts to grow on both substrates due to F removal on Si substrate by  $\text{O}_2$  plasma:  $\text{NF}_3$  again to etch and create new Si-F bonds

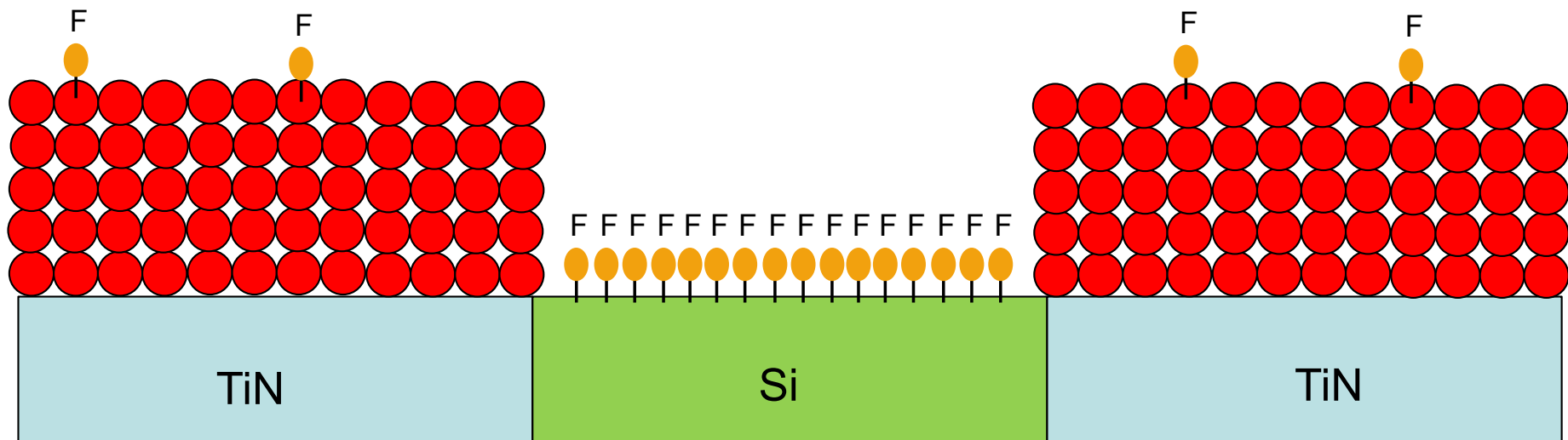




$\text{NF}_3$  is added to  $\text{O}_2$  plasma to etch  $\text{TiO}_2$  and create Si-F bonds (few Ti-F bonds)



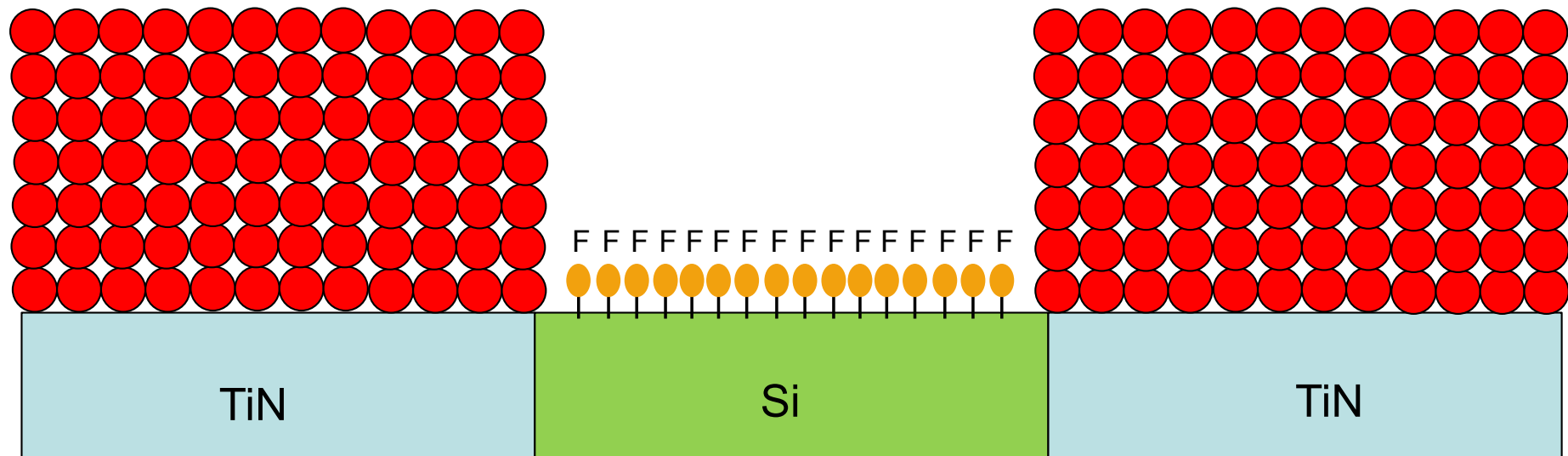
After a number of PEALD cycles  $\text{TiO}_2$  starts to grow on both substrates due to F removal on Si substrate by  $\text{O}_2$  plasma:  $\text{NF}_3$  again to etch and create new Si-F bonds







Need to optimize the PEALD / etching cycles ratio !





## Selective deposition of $\text{TiO}_2$ and $\text{Ta}_2\text{O}_5$ on TiN versus Si substrate

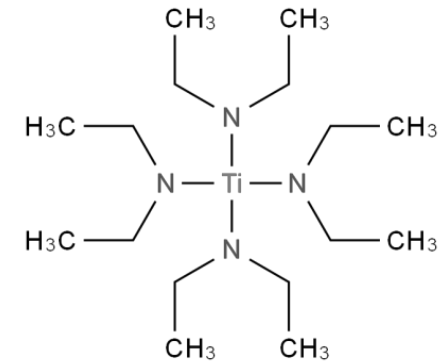
PEALD (x cycles) + plasma etching (1 cycle) = 1 super cycle

Selective deposition = x super cycles

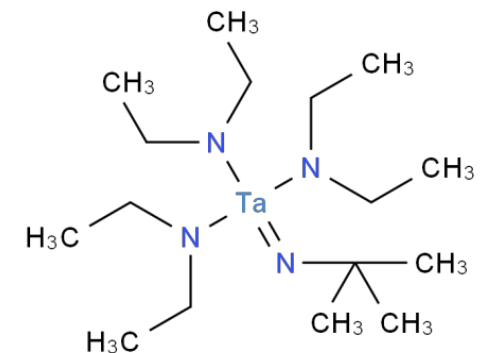
Presentation today: selective deposition of  $\text{Ta}_2\text{O}_5$  and  $\text{TiO}_2$

PEALD of  $\text{Ta}_2\text{O}_5$  ( $\text{TiO}_2$ ) with TBTDET (TDEAT) and  $\text{O}_2$  plasma

Etching cycle by adding fluorine-based plasma



Tetrakis(diethylamido)titanium (TDEATi)

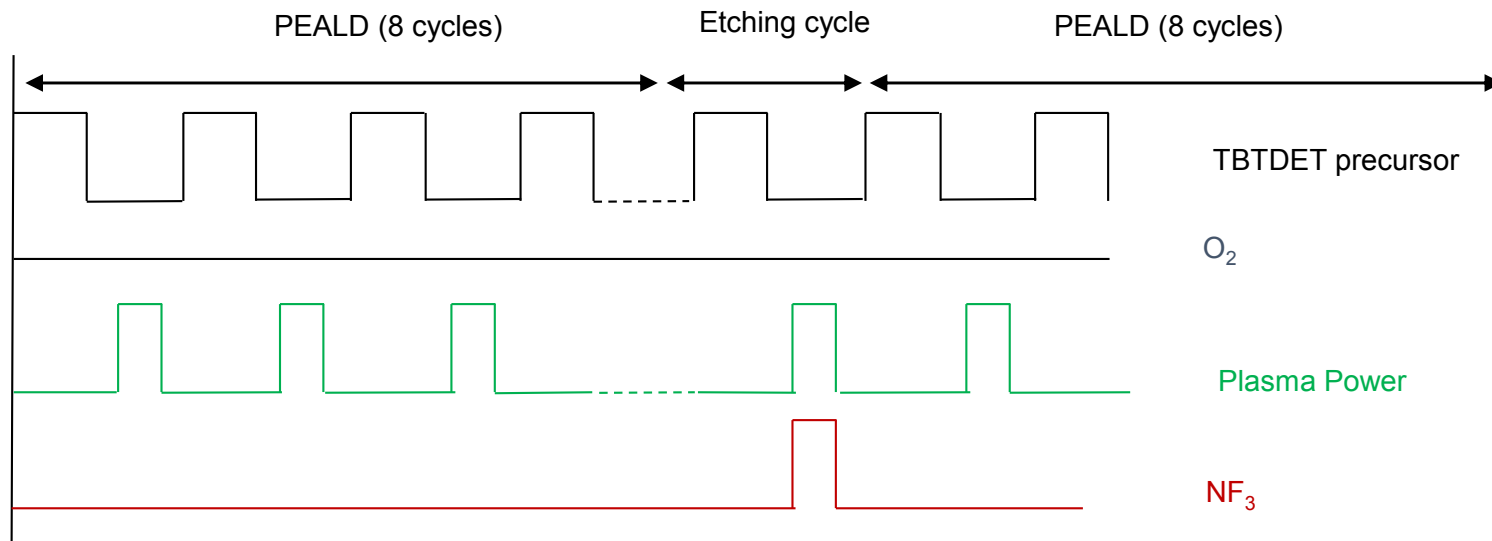


*tert*-Butylimido)tris(diethylamido)tantalum (TBTDET)



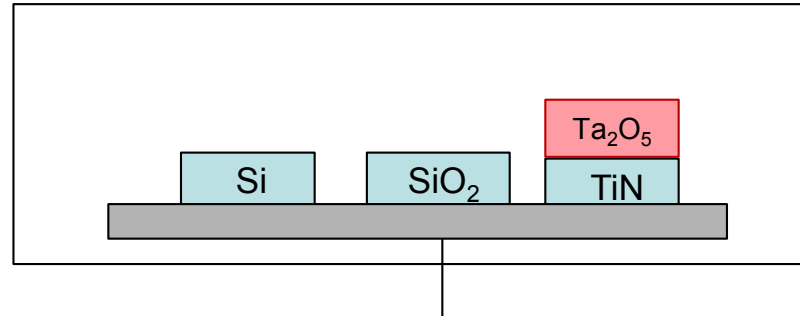
**All requirements are ok! Let's go for selective deposition**

- In the selective deposition process for  $\text{Ta}_2\text{O}_5$  we only slightly modified the PEALD process by adding a  $\text{NF}_3$  pulse in  $\text{O}_2$  pulse every 8 cycles\* ( $\text{O}_2/\text{Ar}$  (250 / 2500 scm - 75W plasma – 2 Torr)



- For  $\text{TiO}_2$  the number of PEALD cycles before plasma etching exposure has been fixed to 20

\*More details in: R. Vallat, R. Gassilloud, B. Eychenne, and C. Vallée  
J. Vac. Sci Technol. A 35(1) 01B104 (2017)



| Number of<br>super cycles | Ta <sub>2</sub> O <sub>5</sub> thickness<br>on Si / SiO <sub>2</sub> (nm) | Ta <sub>2</sub> O <sub>5</sub> thickness<br>on TiN (nm) | Ta <sub>2</sub> O <sub>5</sub> density<br>(g.cm <sup>-3</sup> ) |
|---------------------------|---------------------------------------------------------------------------|---------------------------------------------------------|-----------------------------------------------------------------|
| 11                        | 0 / 0                                                                     | 3.6                                                     | 6.4                                                             |
| 22                        | 0 / 0                                                                     | 7.1                                                     | 6.1                                                             |

R. Vallat, R. Gassilloud, B. Eychenne, and C. Vallée  
 J. Vac. Sci Technol. A 35(1) 01B104 (2017)



| Number of<br>super cycles | Ta <sub>2</sub> O <sub>5</sub> thickness<br>on Si / SiO <sub>2</sub> (nm) | Ta <sub>2</sub> O <sub>5</sub> thickness<br>on TiN (nm) | Ta <sub>2</sub> O <sub>5</sub> density<br>(g.cm <sup>-3</sup> ) |
|---------------------------|---------------------------------------------------------------------------|---------------------------------------------------------|-----------------------------------------------------------------|
| 11                        | 0 / 0                                                                     | 3.6                                                     | 6.4                                                             |
| 22                        | 0 / 0                                                                     | 7.1                                                     | 6.1                                                             |

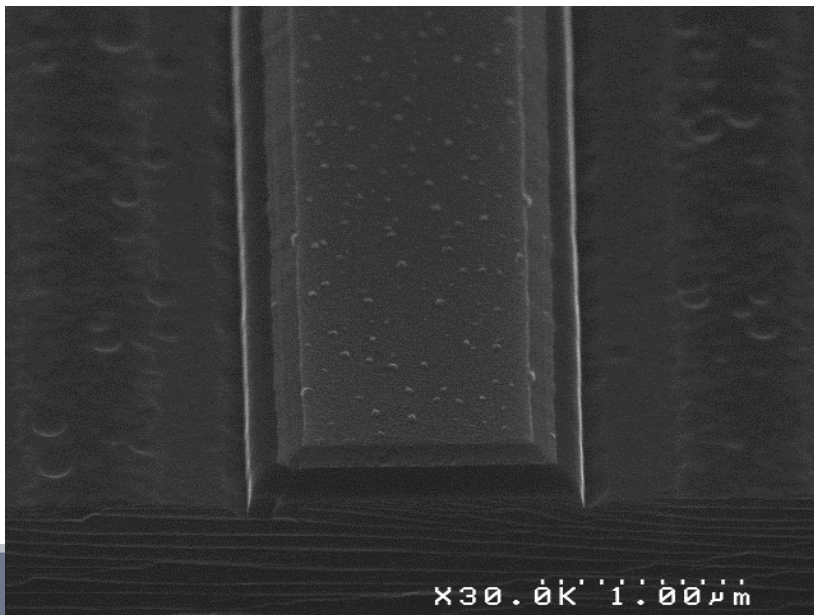
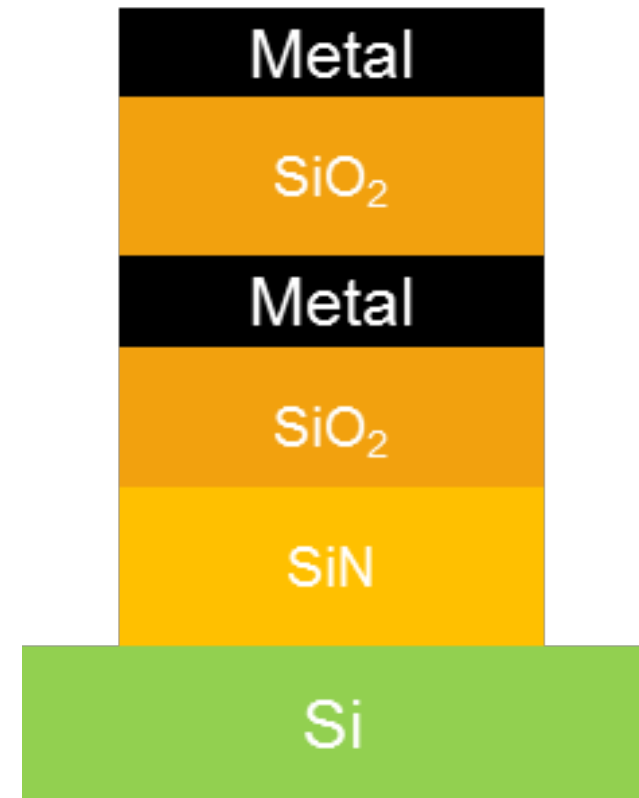
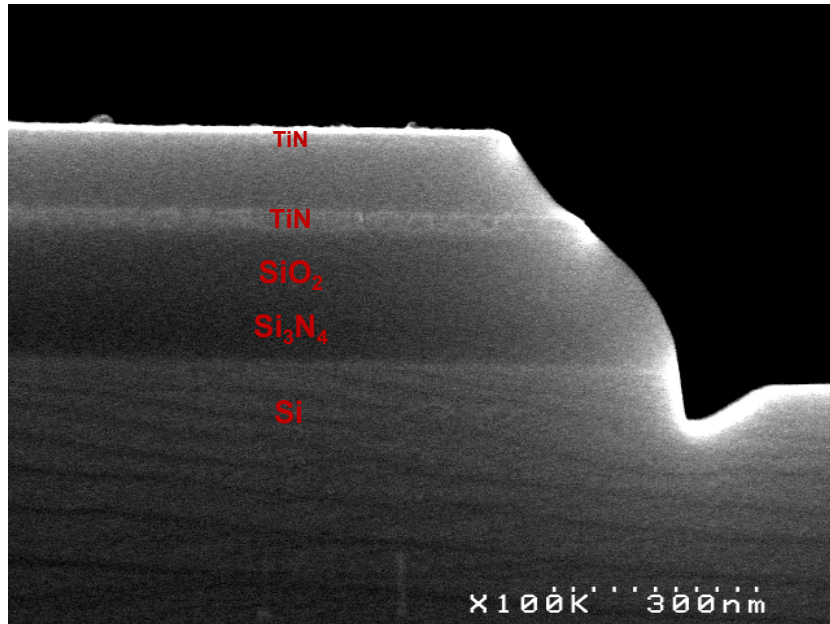
| Number of<br>super cycles | TiO <sub>2</sub> thickness<br>on Si (nm) | TiO <sub>2</sub> thickness<br>on TiN (nm) | TiO <sub>2</sub> density<br>(g.cm <sup>-3</sup> ) |
|---------------------------|------------------------------------------|-------------------------------------------|---------------------------------------------------|
| 6                         | 0                                        | 4.3                                       | 4.1                                               |
| 12                        | 0                                        | 6.4                                       | 3.9                                               |

Density is slightly reduced when increasing the number of super cycles:  
Origin? Voids? Contamination by F atoms? Impact on electrical properties?





ASD on 3D patterned substrate (SEM image by M. Fraccaroli)

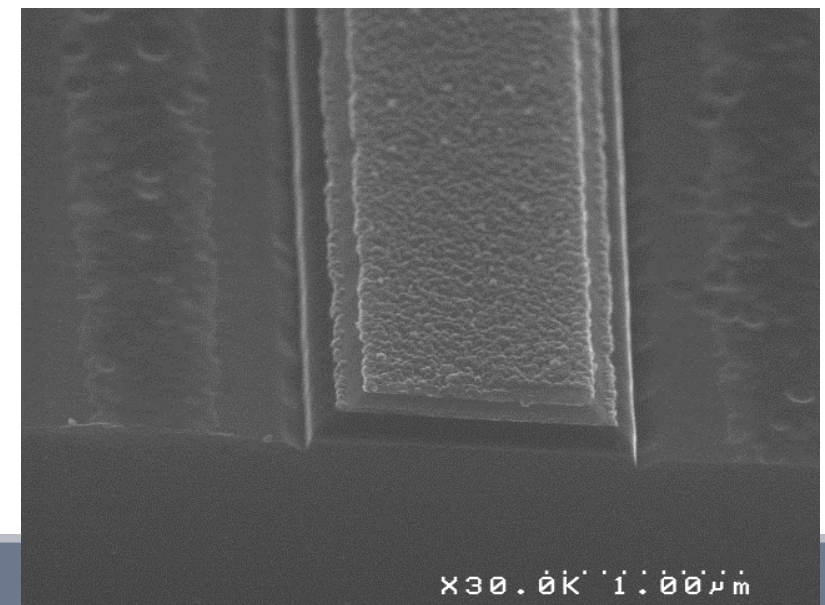
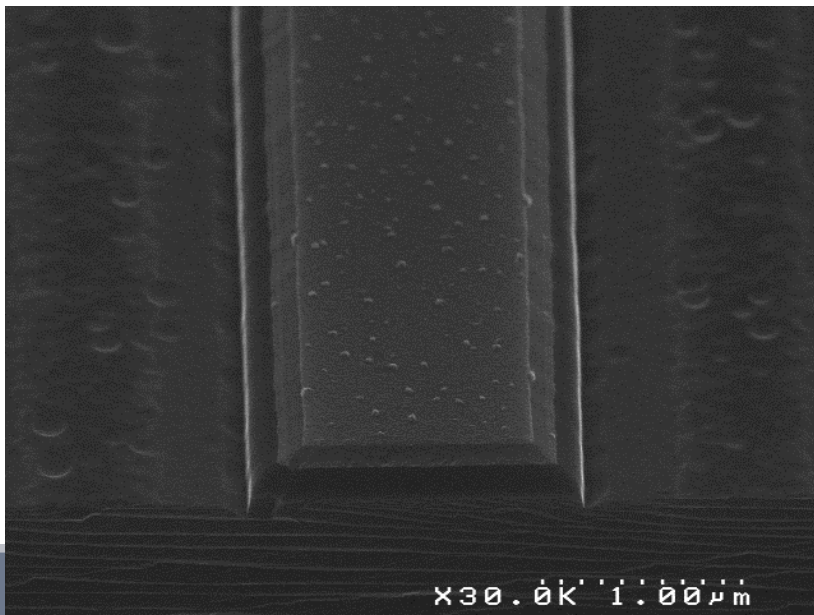
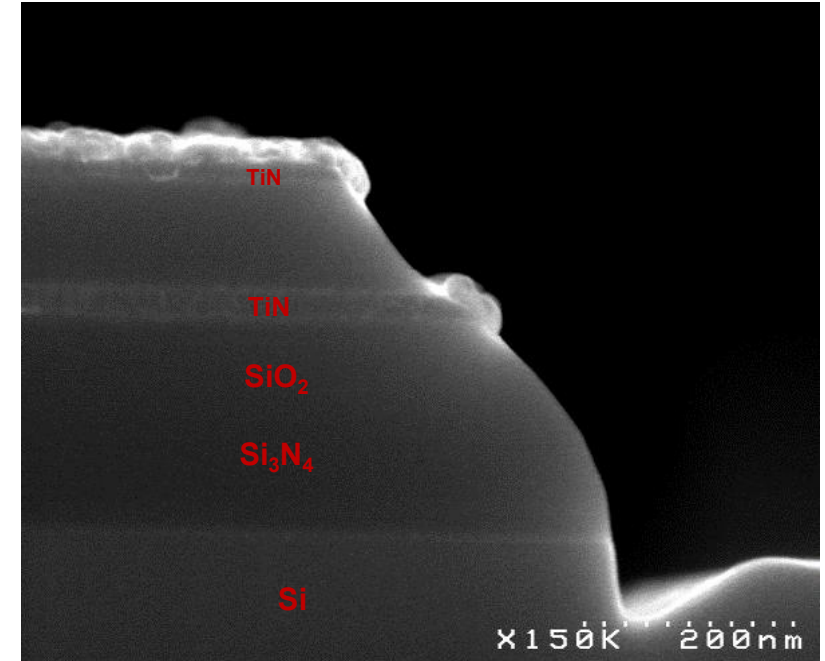
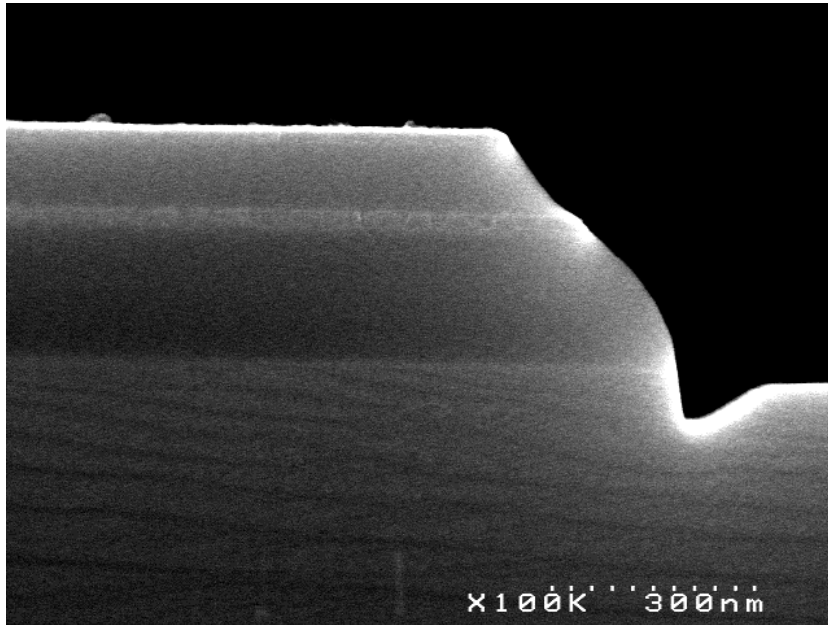


R. Vallat *et al.* submitted to JVSTA

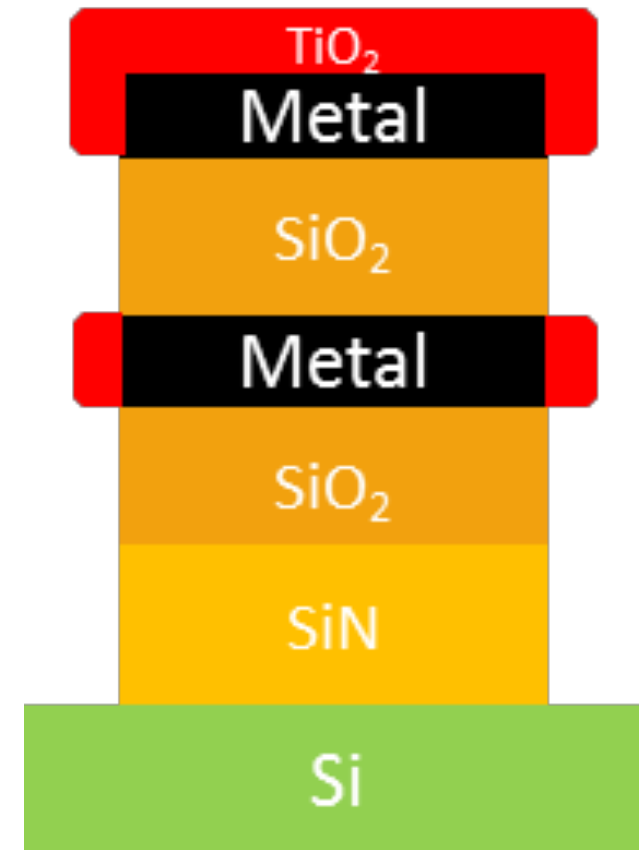
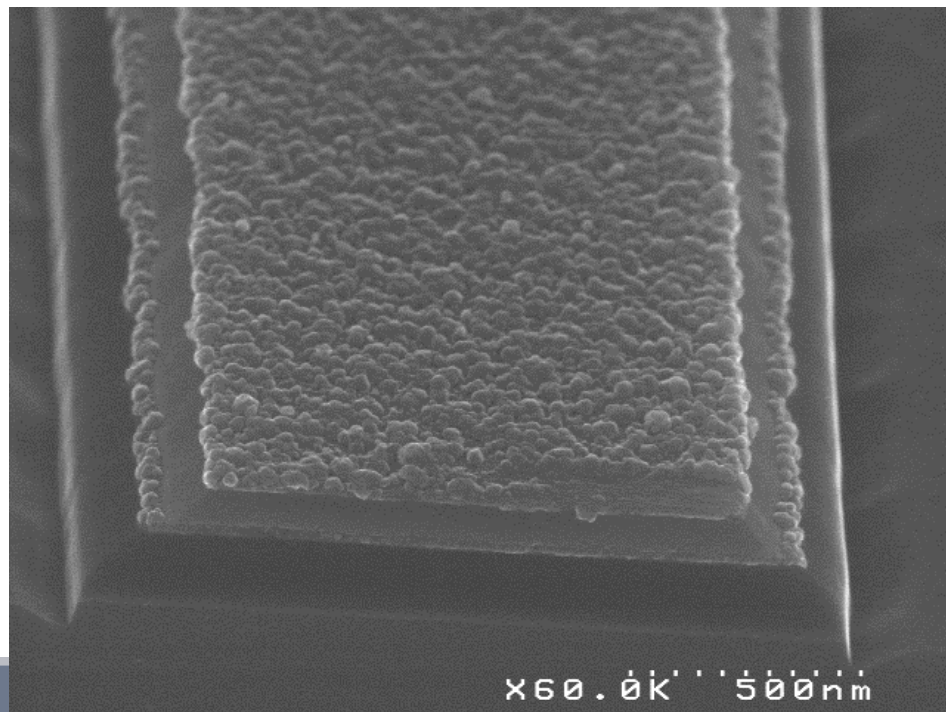
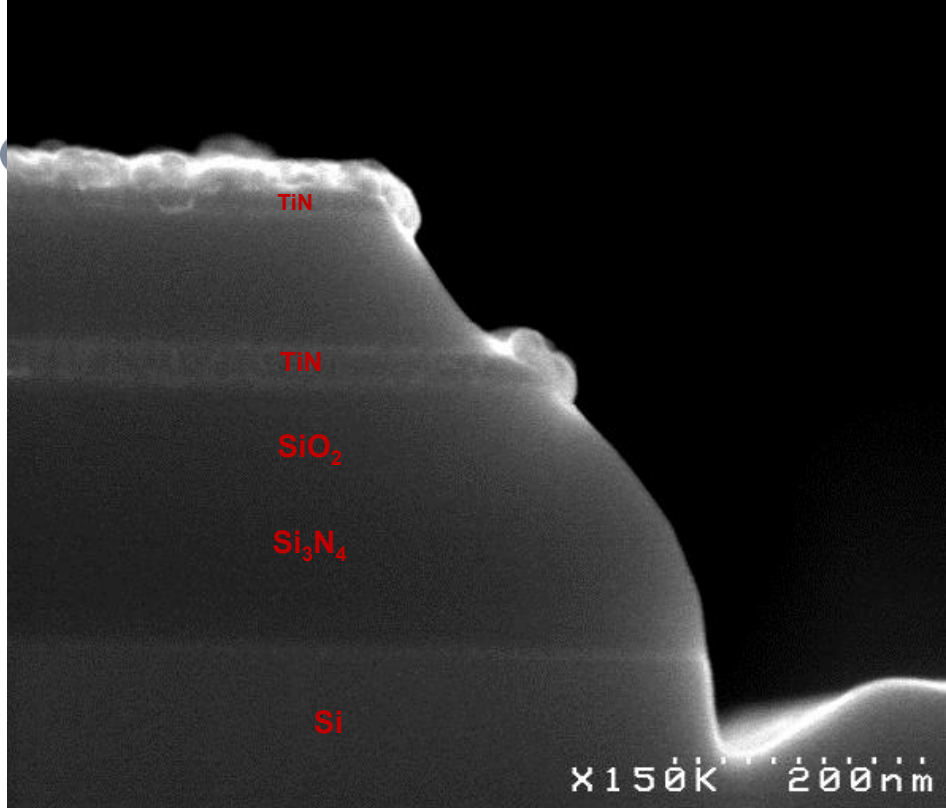


ASD on 3D patterned substrate (SEM image by M. Fraccaroli)

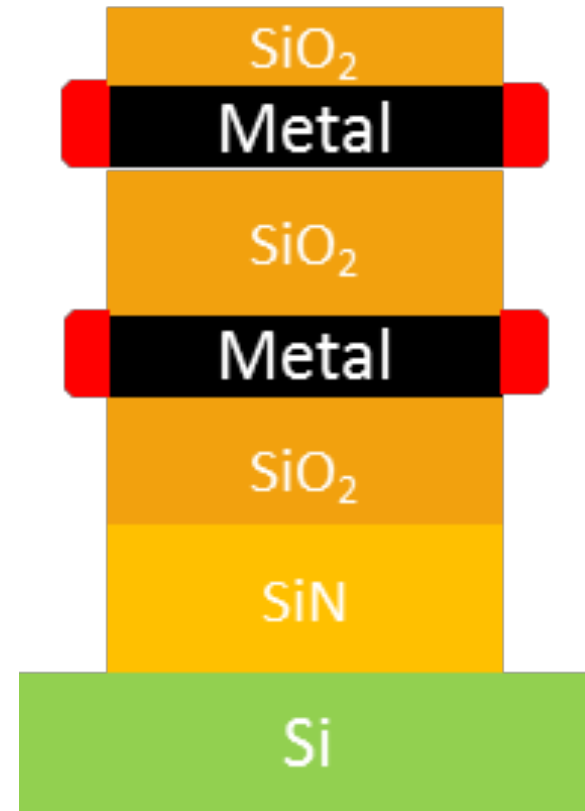
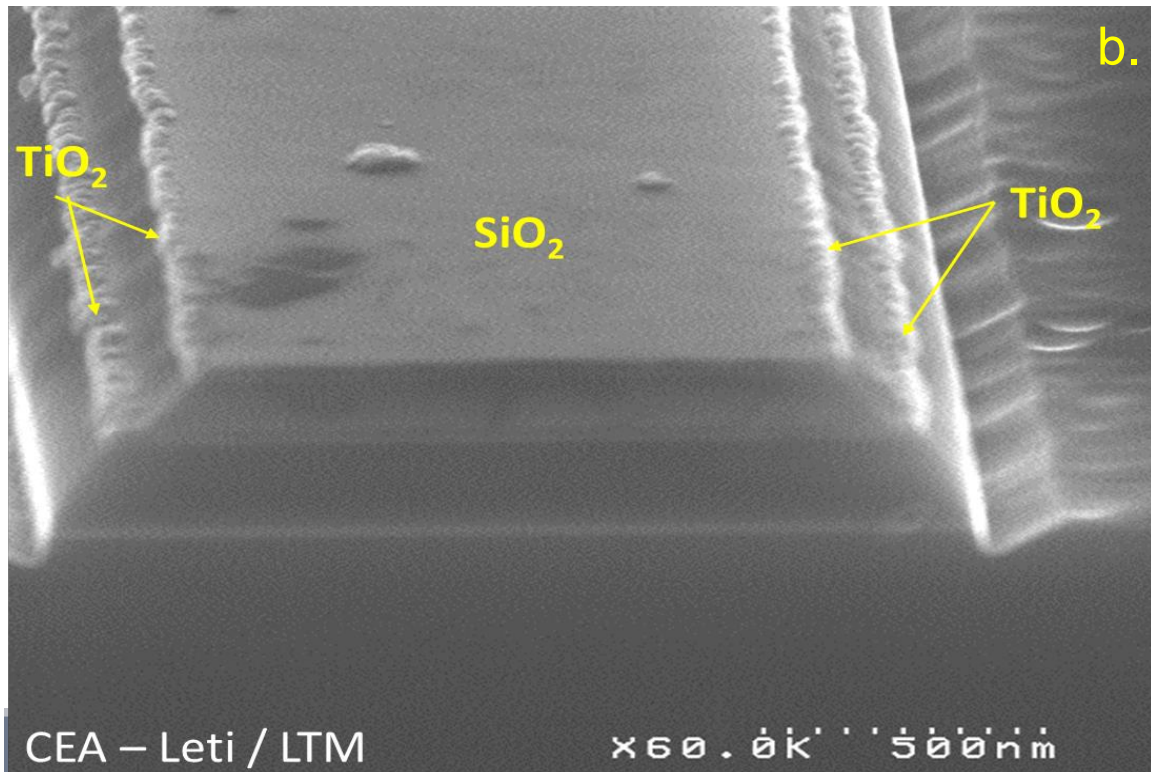
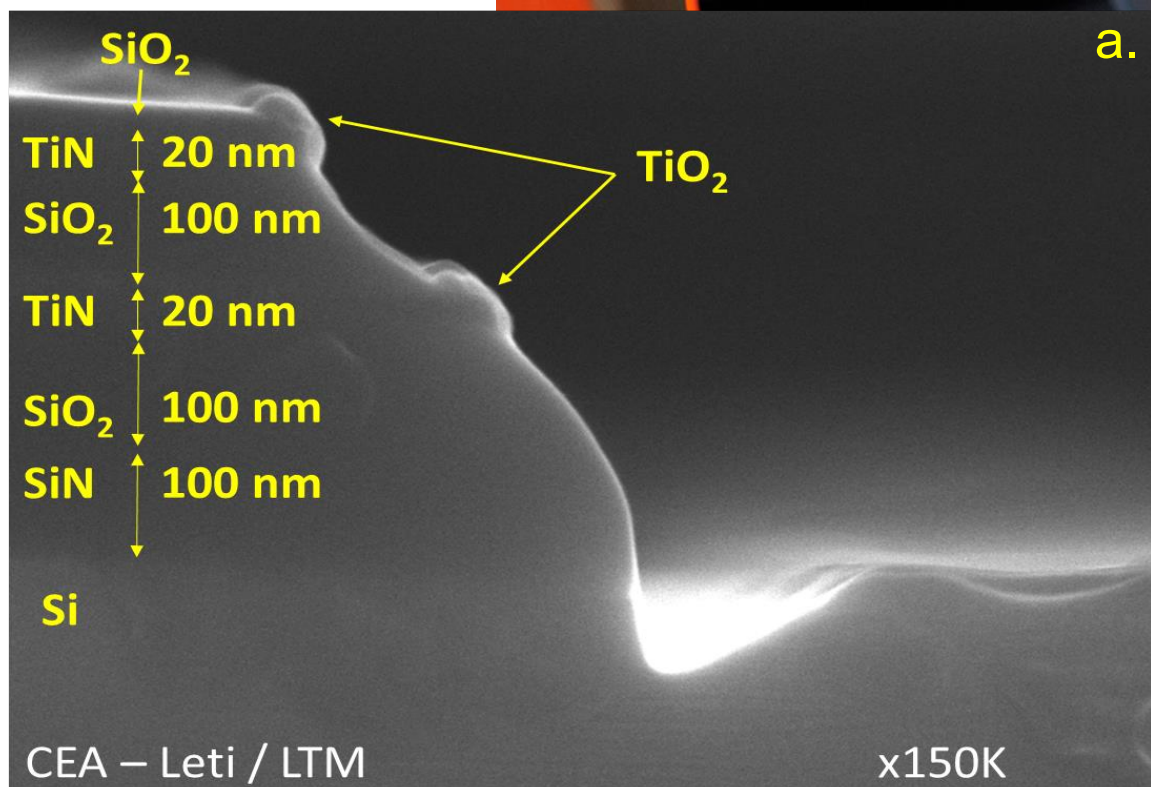
R. Vallat *et al.* submitted to JVSTA







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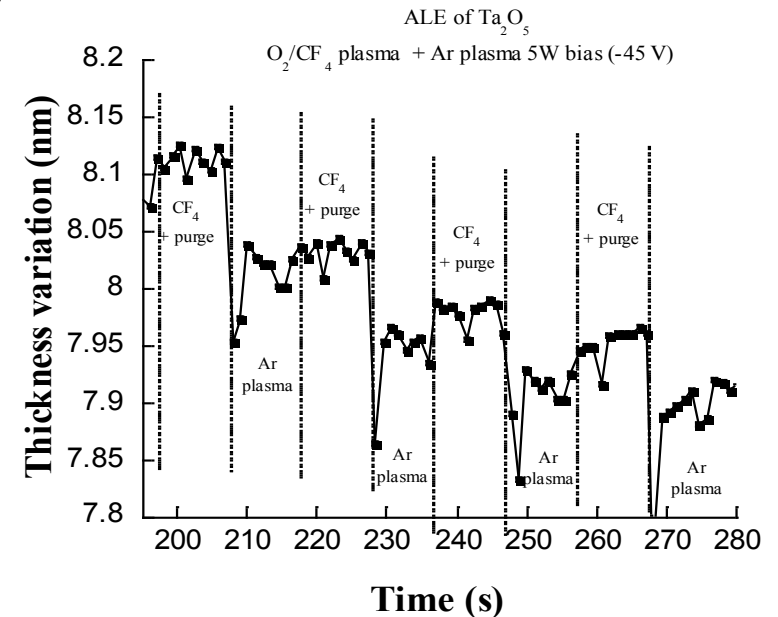
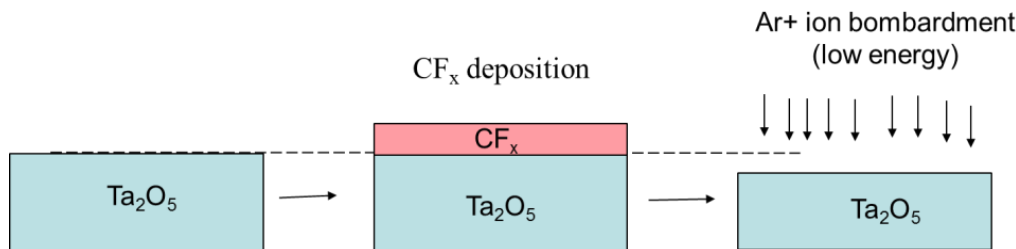


R. Vallat et al. submitted to JVSTA

# Conclusion

- Not radicals only can be useful for PEALD processes
- Depending on the materials, ions can increase/decrease the GPC, modify the density, roughness, crystalline phase. Ions can also be used for area selective deposition on 3D patterned substrates
- What about the others? UV photons,  $O_3$ ....
- Whatever the ASD process (SAM,...), etching is needed to improve selectivity
- Optimum goal: ALD + ALE

ALE in the PEALD FLEXAL  
tool is now optimized







## Futur trends: All is Atomic Layer Processing

- Atomic layer deposition
- Atomic layer etch
- Atomic level planarization
- Atomic level contamination control
- Atomically pure materials
- Atomic level characterization
- Atomic level measurement



<http://rafald.org>