



# Thin film deposition for next generation DRAM structures



ISPR 2017

13.09.2017

J. Torgersen, F. Berto, F. Prinz, W. Cai  
NTNU Trondheim/ Stanford University



**40000 students**  
**50 faculties**  
**Nobel prize winner 2014**



# NTNU Team

## Our group:

3 Faculty

10 PhD students

15 Master Students/ year

Addlab, Fatigue and Nanolab

~ Supported by workshop and admin staff



## Research Directions:

Material Design

Material Property Prediction

Surface and Interface Science

Biocompatible Implants

Light weight components

Protective Coatings

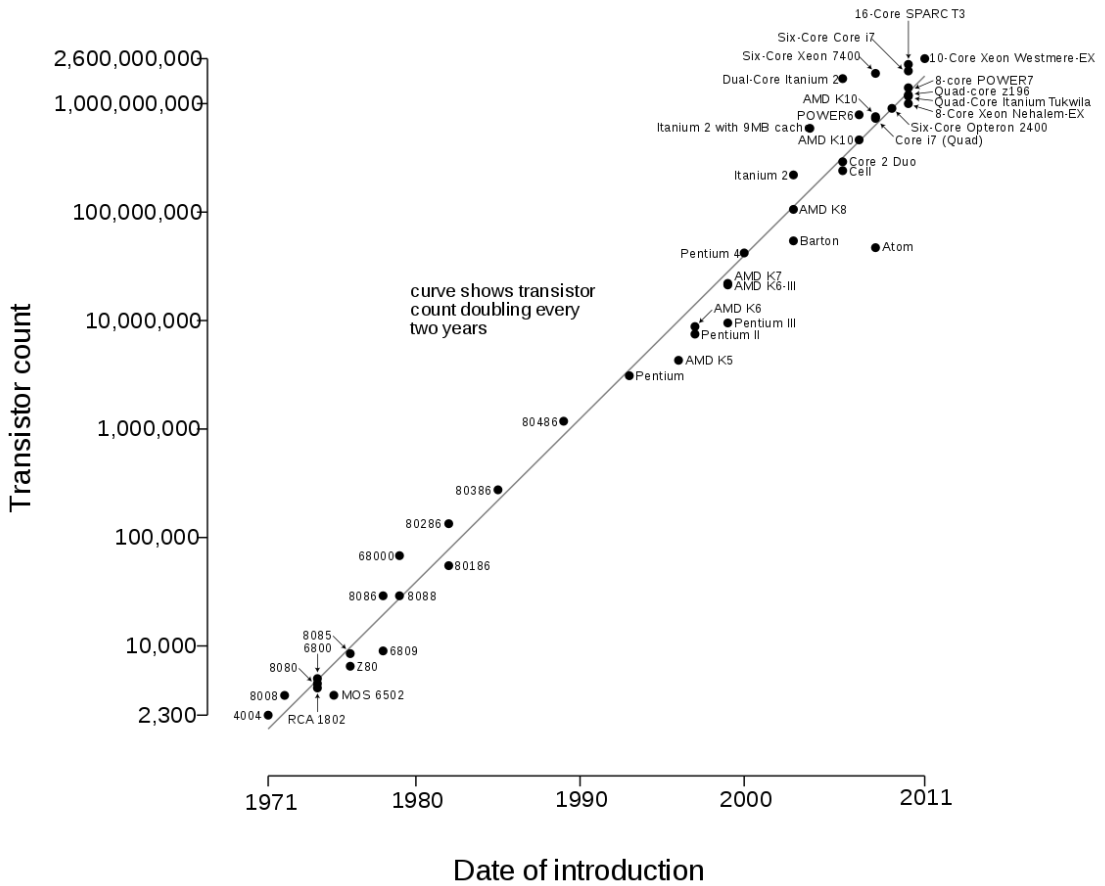


# Atomic Layer Deposition- Motivation

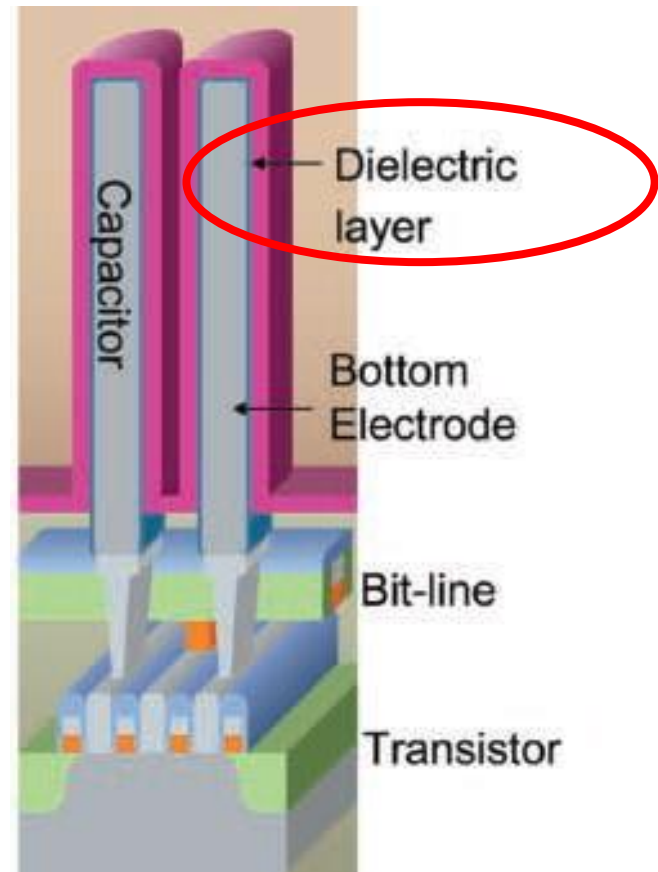
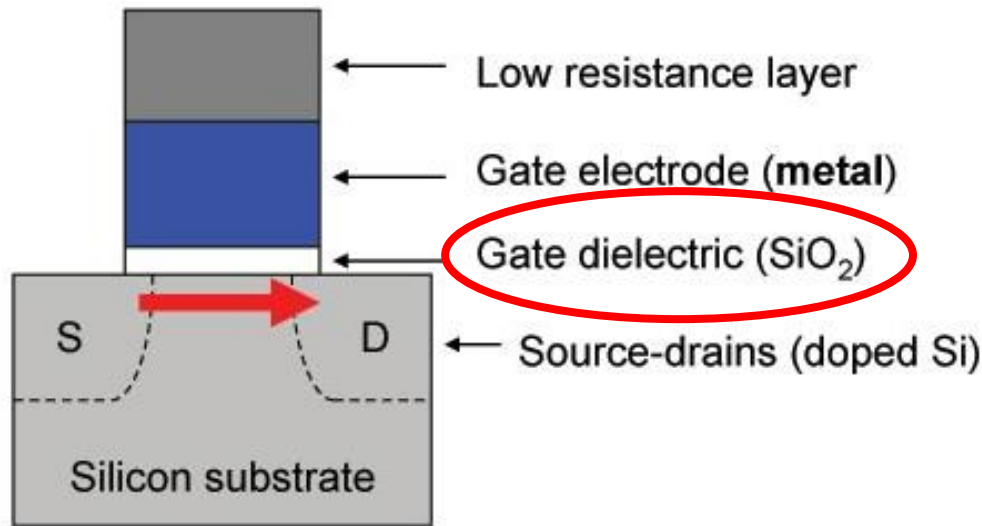
## Moore's law

- One of humanity's greatest achievements
- Over 40 years of exponential improvement
- What is the limit?

Microprocessor Transistor Counts 1971-2011 & Moore's Law



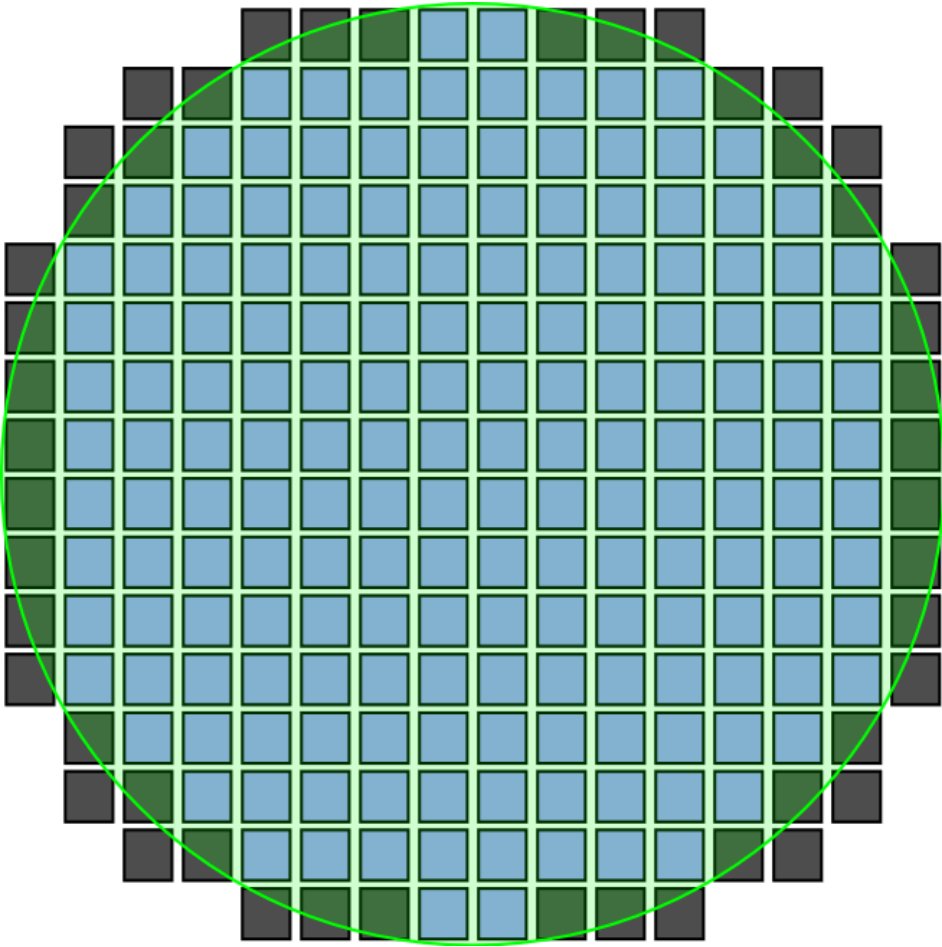
# Atomic Layer Deposition- Motivation



How to Increase the Capacitance?

$$U = \frac{1}{2} CV^2 \quad C = \epsilon_0 \epsilon_r \left( \frac{A}{d} \right)$$

# Atomic Layer Deposition- Motivation



## **Smallest die size:**

0.683 mm × 0.683 mm at the 90 nm  
151.527 dies

## **Average die size**

2.130 mm × 2.130 mm at the 65 nm  
1434 dies

## **Biggest die size:**

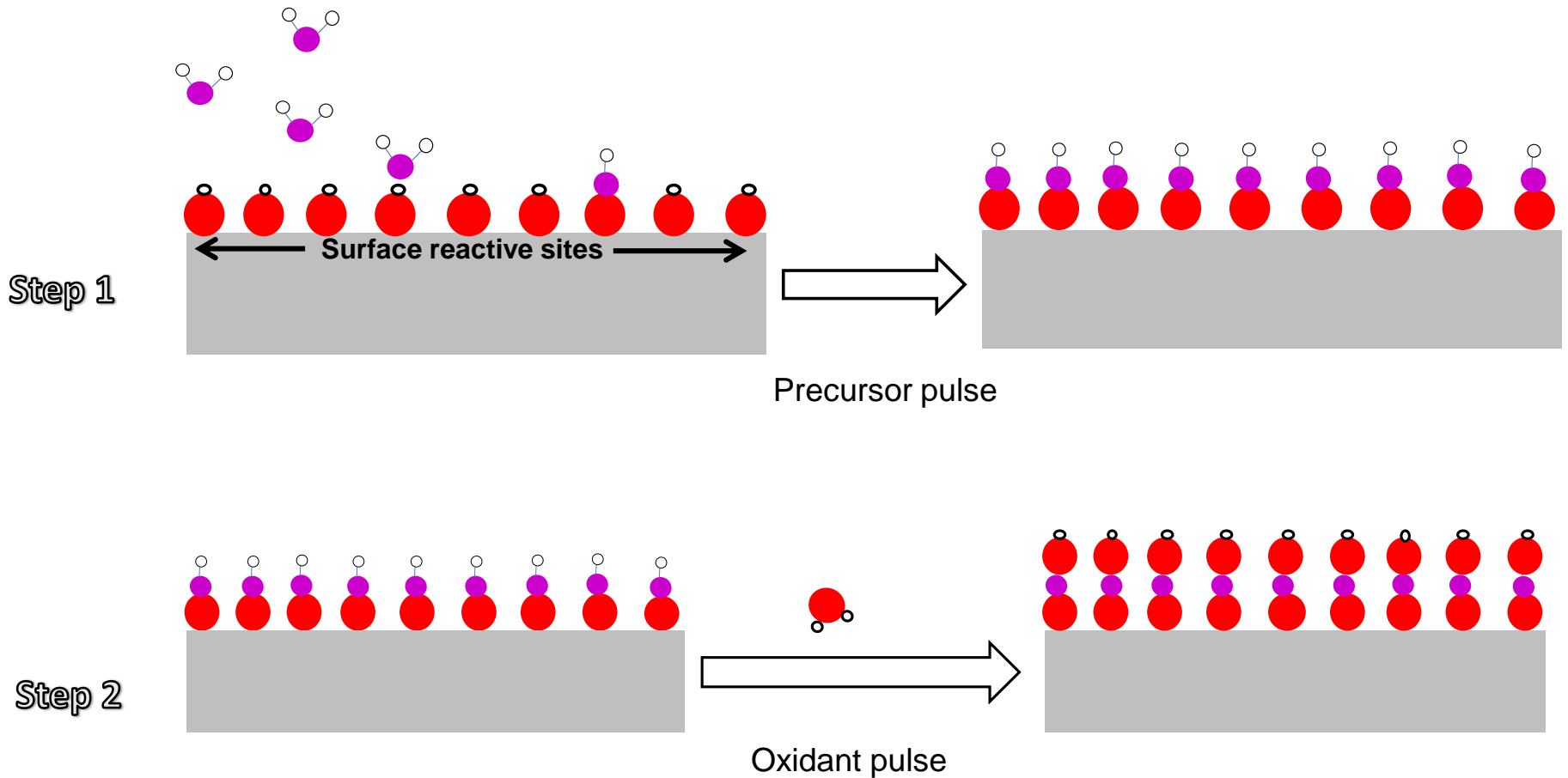
20.253 mm × 20.253 mm at the 65 nm  
127 dies

Core i3-2310E

Transistors: 624 million

Die size: Average (149 mm<sup>2</sup>)

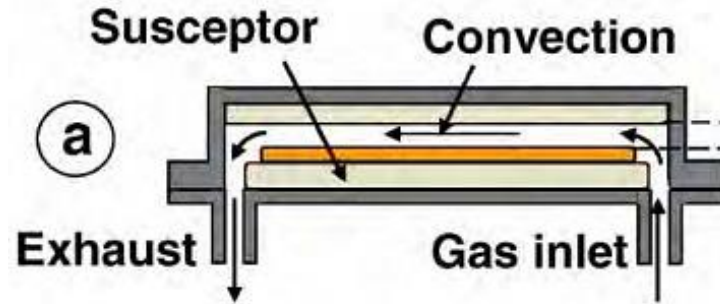
# Atomic Layer Deposition- The principle



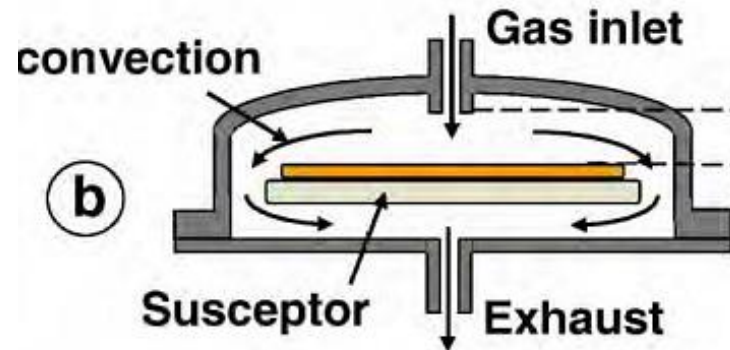


# Atomic Layer Deposition- Scale Up

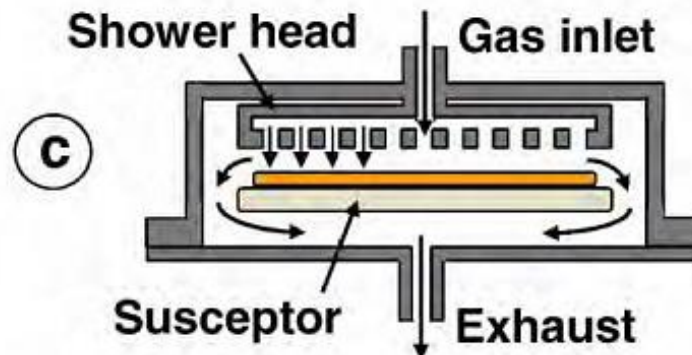
Crossflow



Single Injector

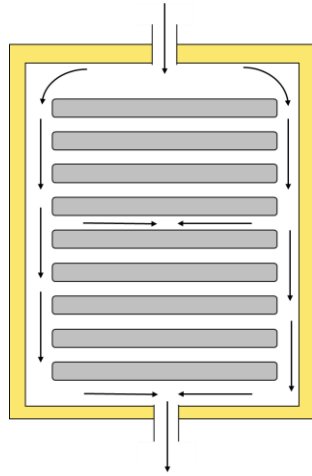


Showerhead



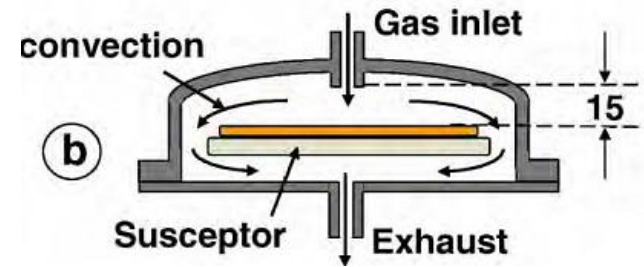
**Self-limiting  
nature enables  
easy scale up**

# Atomic Layer Deposition- Scale Up

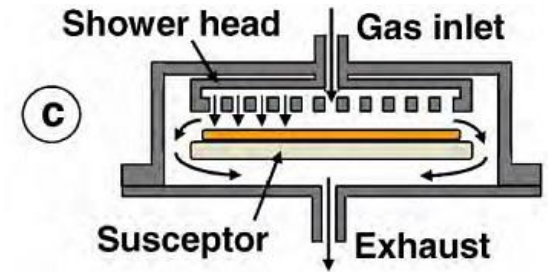
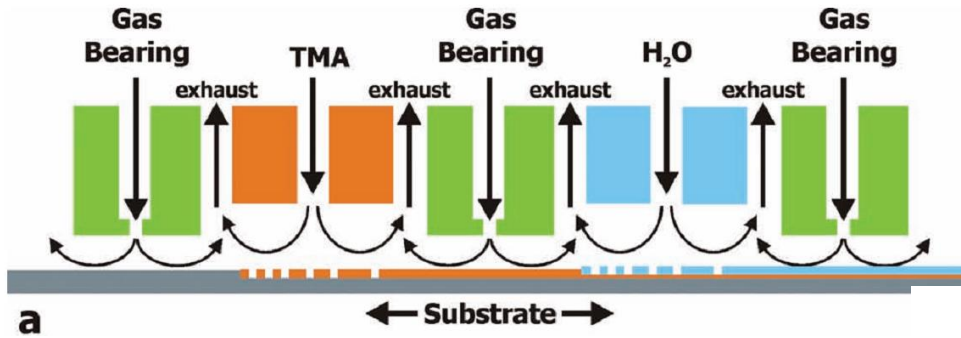


## ASM A400C

- Batch size of 125 8-inch wafers
- Dual tube for material stacks
- Process line integration
- Different wafer sizes processable
- Major applications for silicon nitride, amorphous silicon, doped polysilicon
- Wide range of metals and dielectrics processable



# Atomic Layer Deposition- Scale Up



## Solaytec

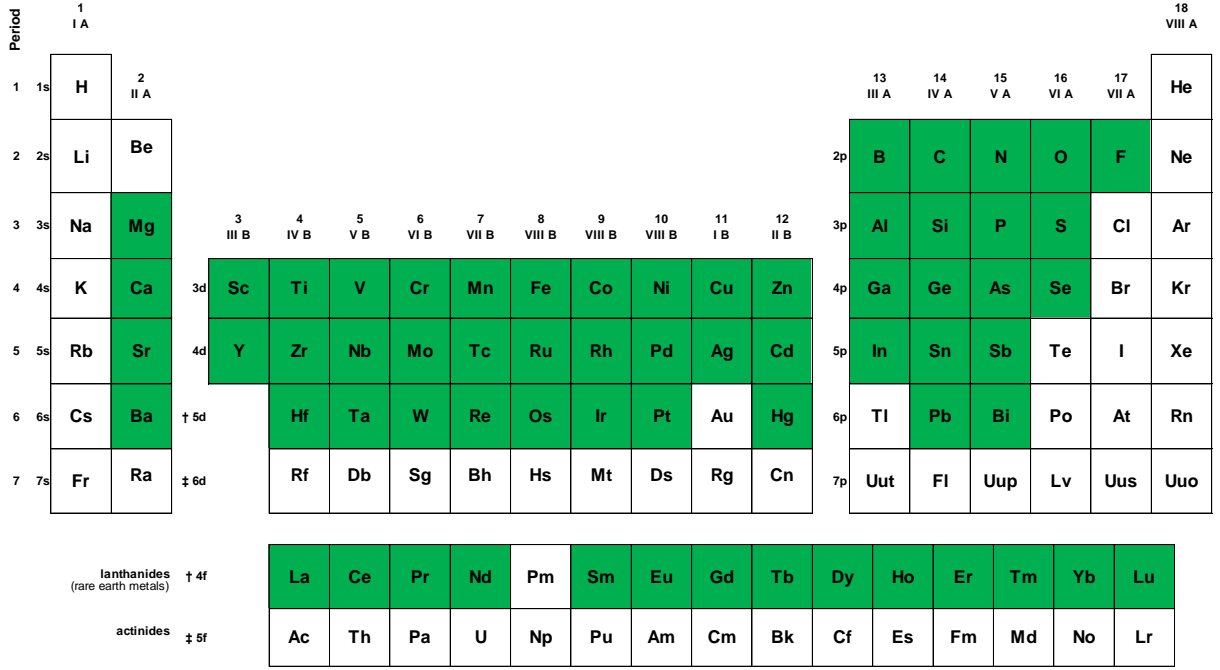
- Wafer moves back and forth performing 4 cycles at a time
- 8 depositions/s with one head
- 5000 wafers/h
- Atmospheric pressure, no pump required
- Deposition rate 1nm/s per module
- Only TMA and H<sub>2</sub>O so far



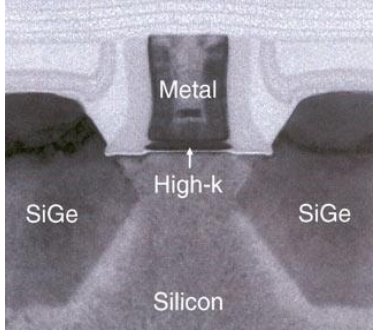
[http://www.solaytec.com/images/stories/flexicontent/l\\_solaytec-2919-v1.jpg](http://www.solaytec.com/images/stories/flexicontent/l_solaytec-2919-v1.jpg)

# Atomic Layer Deposition- The materials

## Depositing elements all across the periodic table

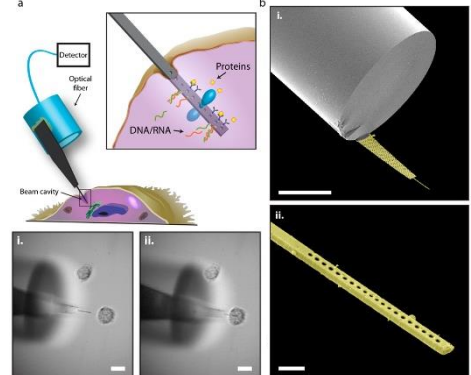


Intel's 45-nm high-k transistor



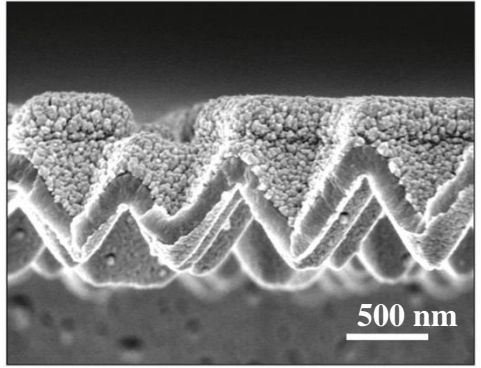
Mistry, K. et al, *Electron Devices Meeting, 2007. IEDM 2007. IEEE International*, pp.247-250 (2007)

Nanoprobe for protein detection in cells



Shambat et al.; *Nano Lett.* 2013, 13, 4999-5005.

Thin film solid oxide fuel cell

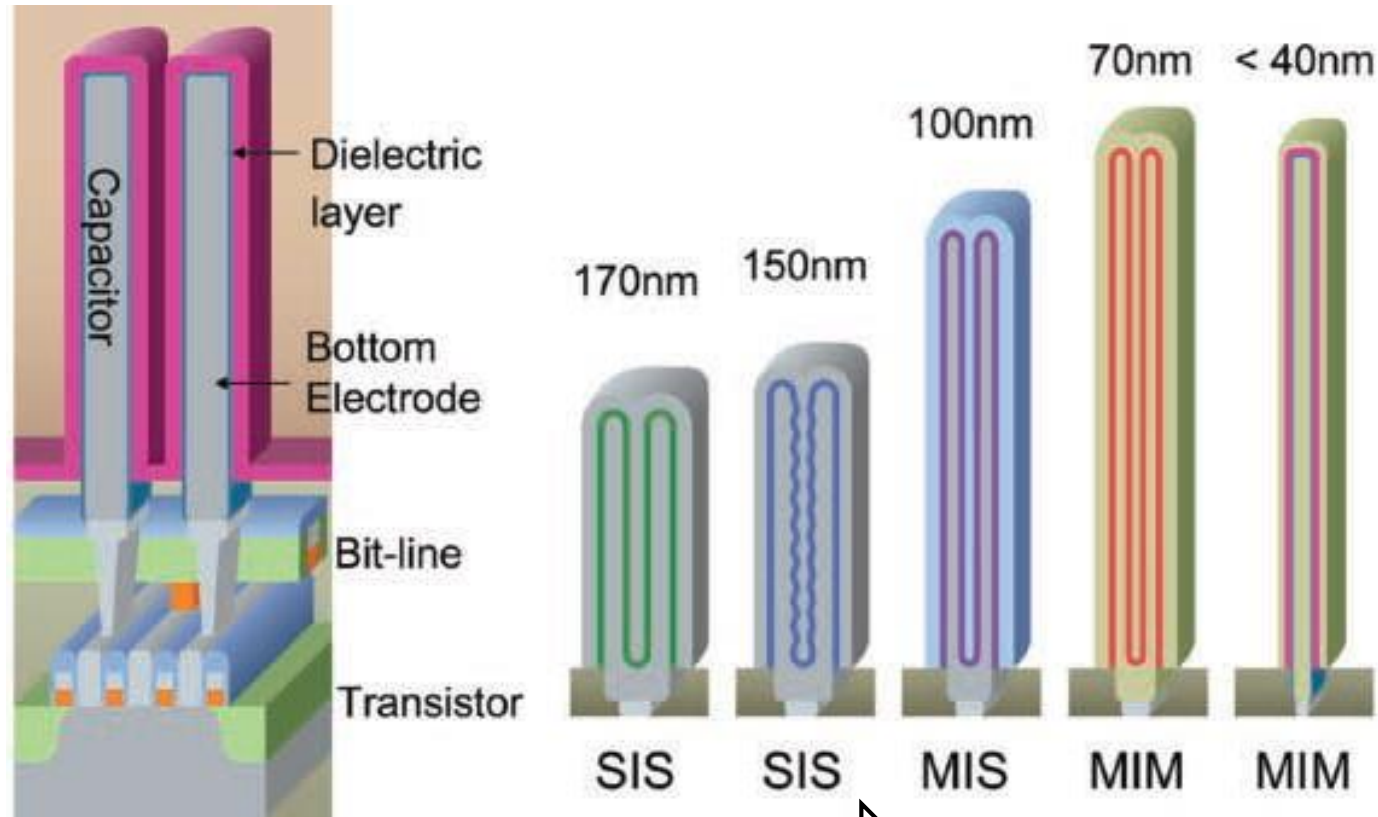


Chao, C. C., Hsu, C. M., Cui, Y., Prinz, F. P. , *ACS Nano*, 5, 5692-5696 (2011).

# High-k thin films for DRAMs

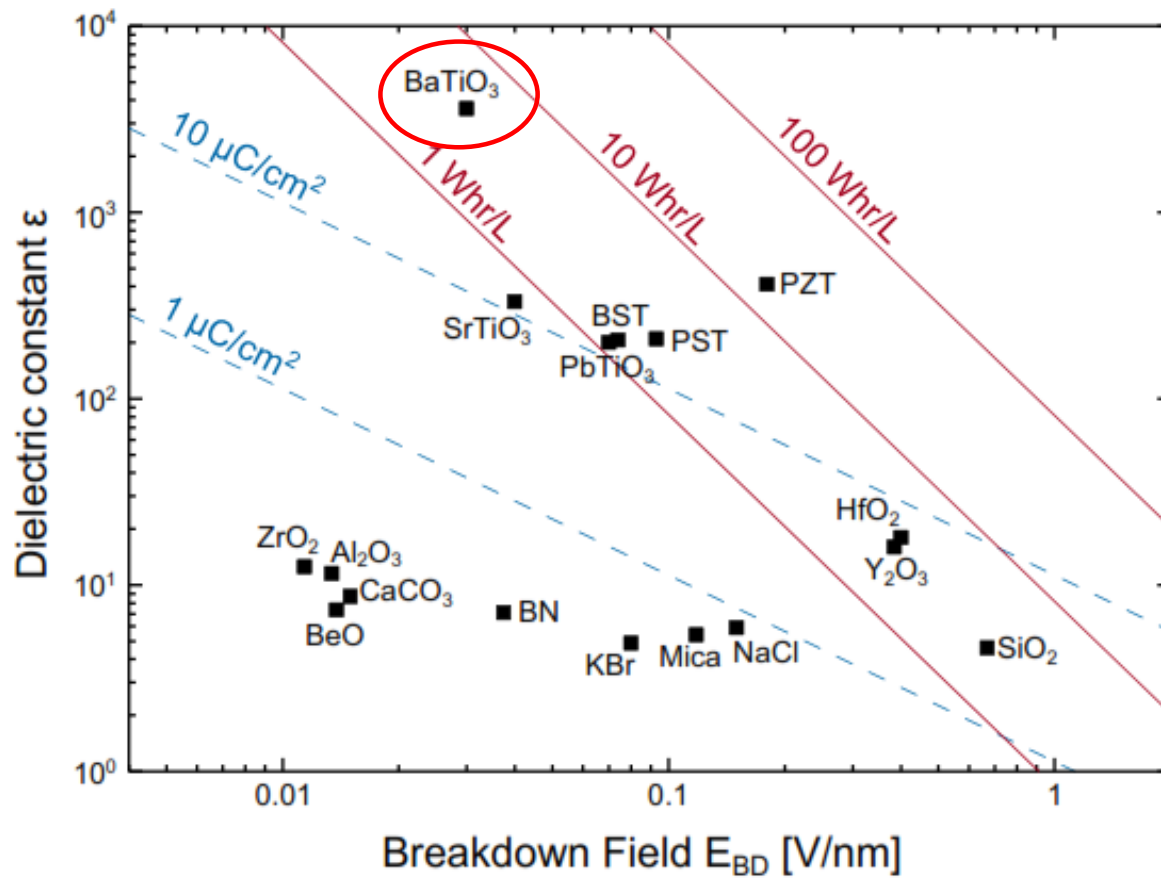
How to Increase the Capacitance?

$$U = \frac{1}{2} CV^2 \quad C = \epsilon_0 \epsilon_r \frac{A}{d}$$

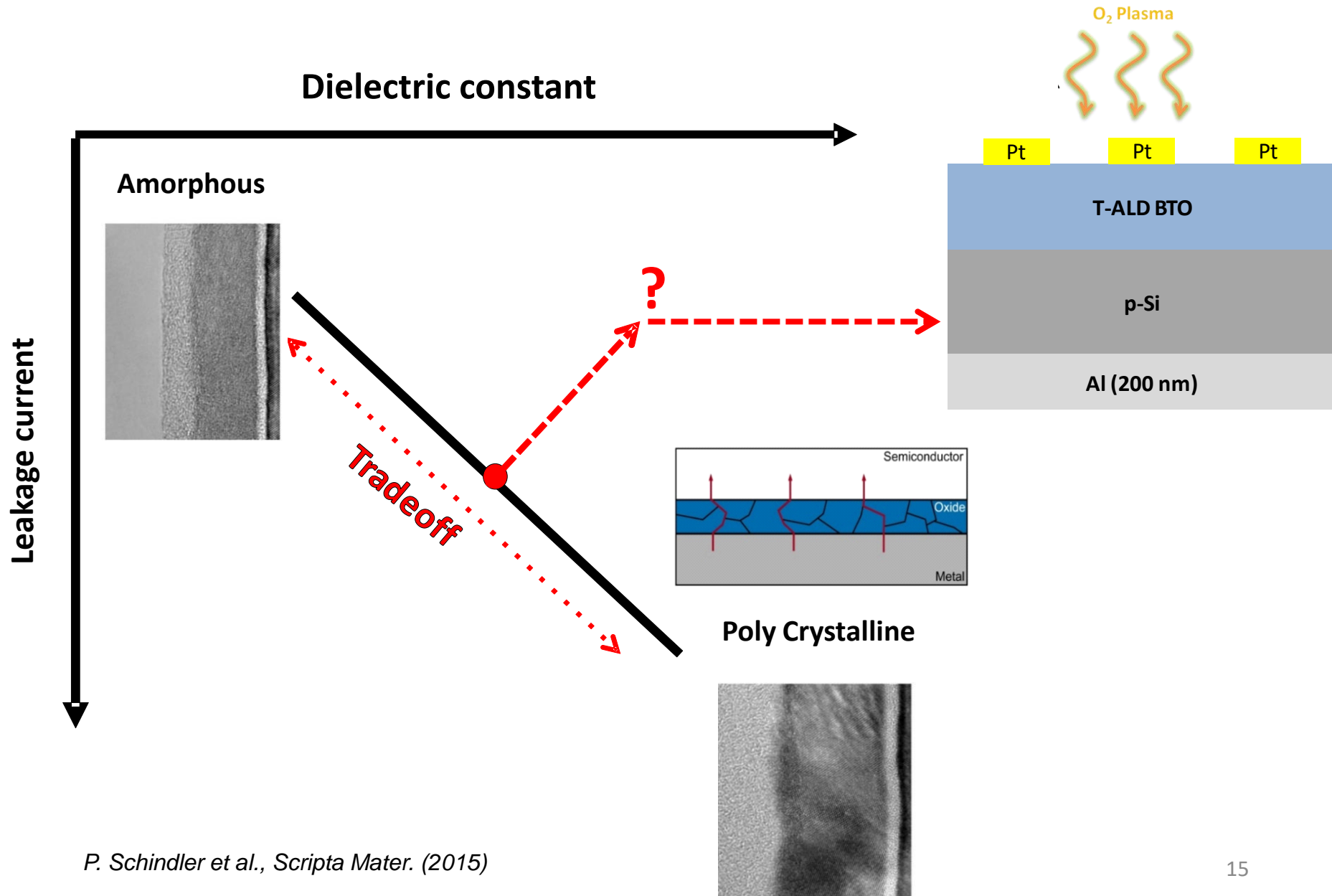


# High-k materials

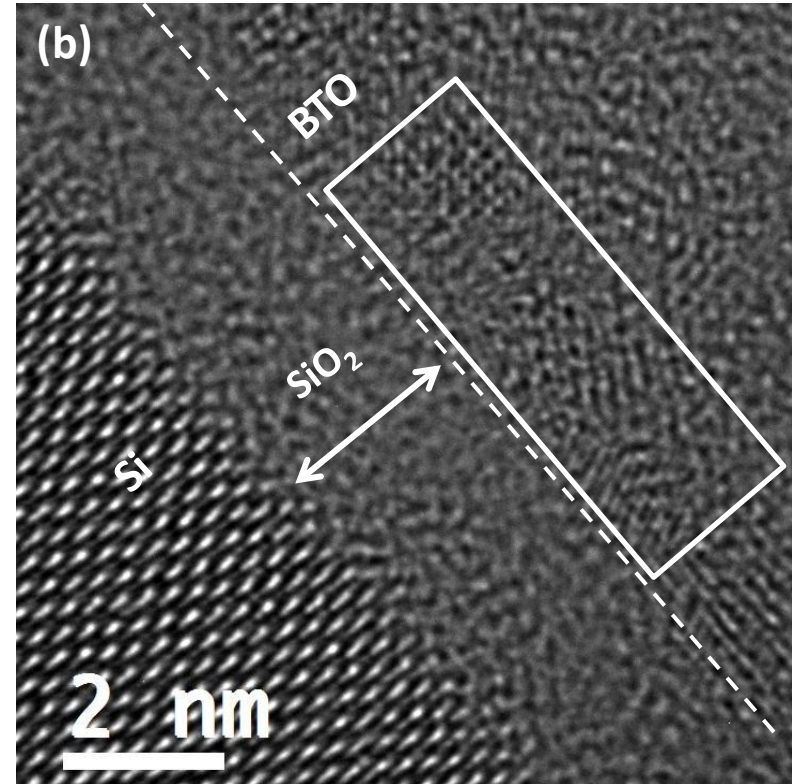
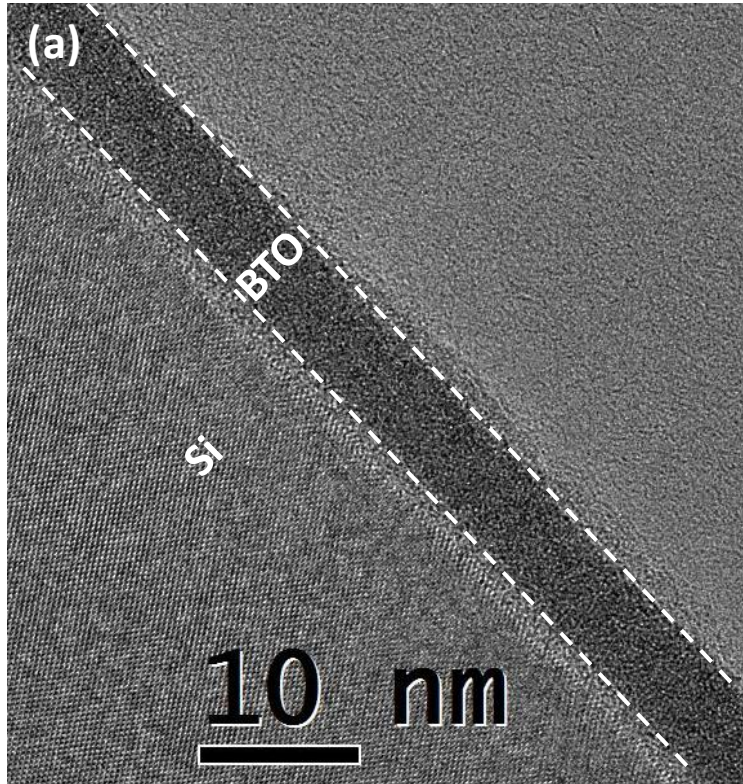
$$C = e_0 e_r \frac{A}{d}$$



# High-k thin films for DRAMs



# High-k thin films for DRAMs

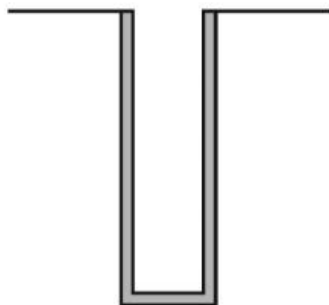


Crystallites buried in amorphous matrix of 7 nm thick BaTiO<sub>3</sub>

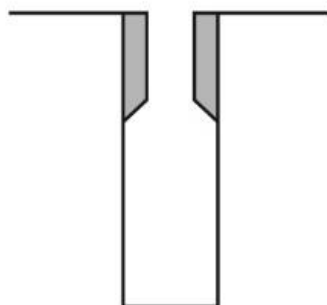


# High-k thin films for DRAMs

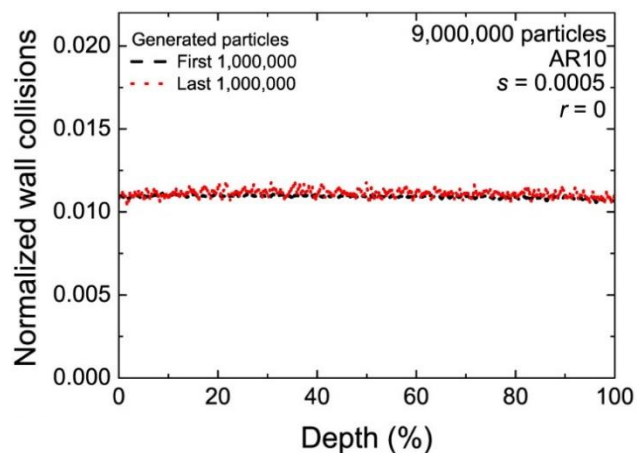
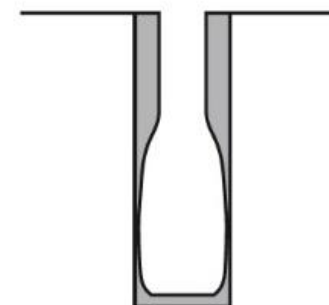
Reaction limited



Diffusion limited



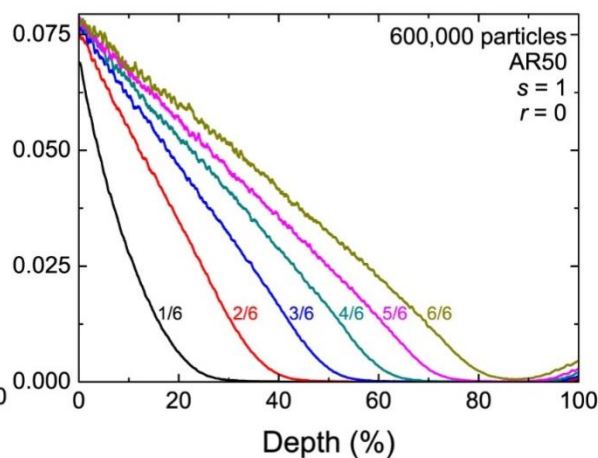
Recombination limited



$$s \ll 1$$

$$r = 0$$

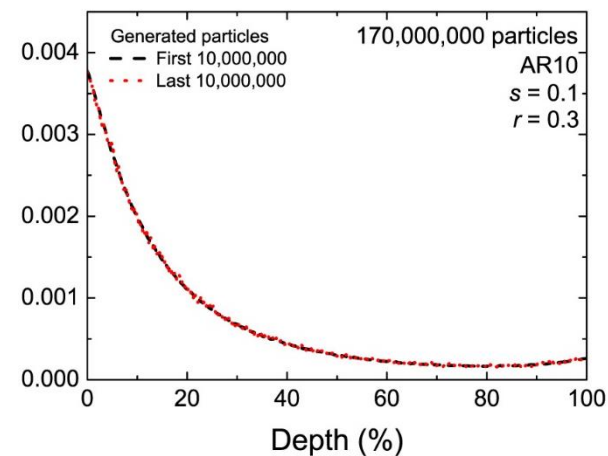
AR independent



$$s = 1$$

$$r = 0$$

AR dependent

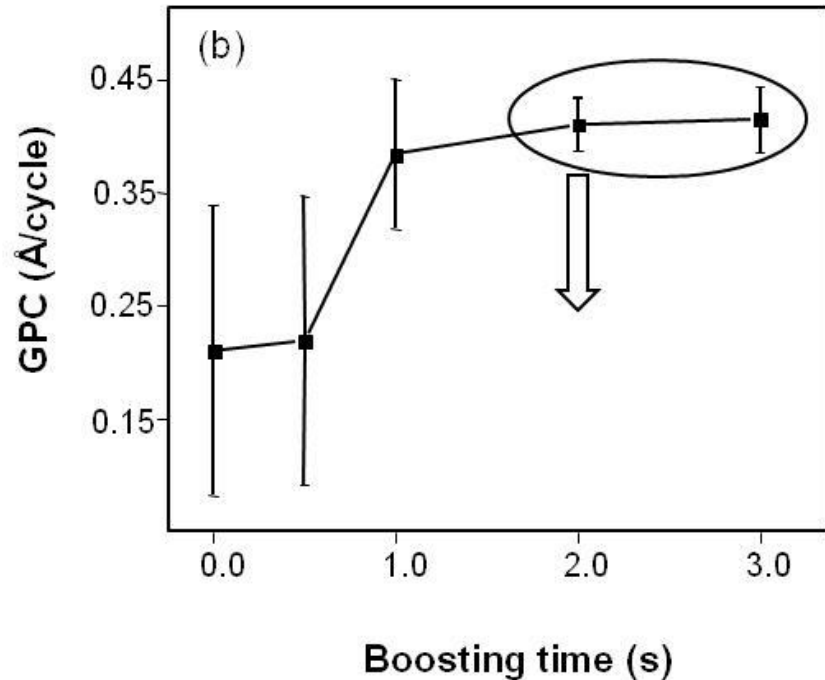
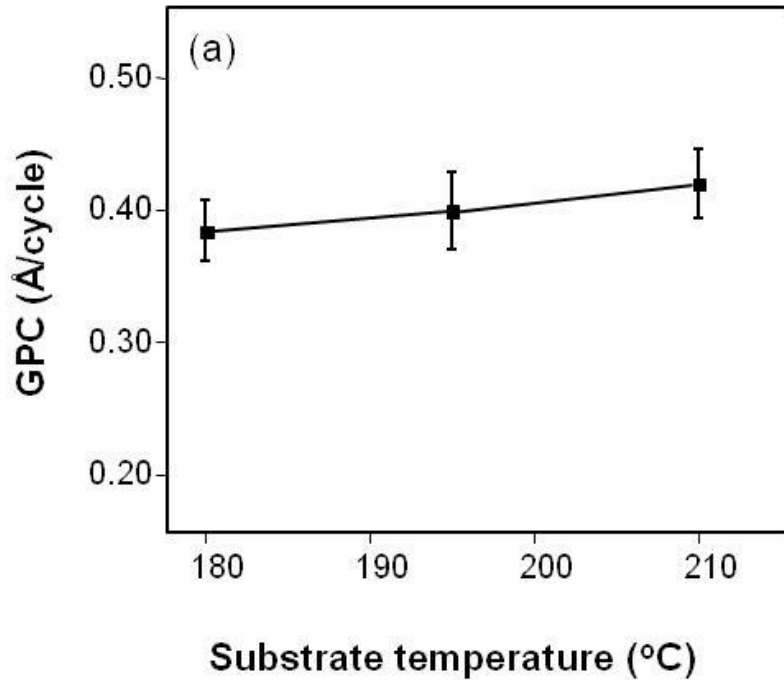


$s$  independent

$$r > 0$$

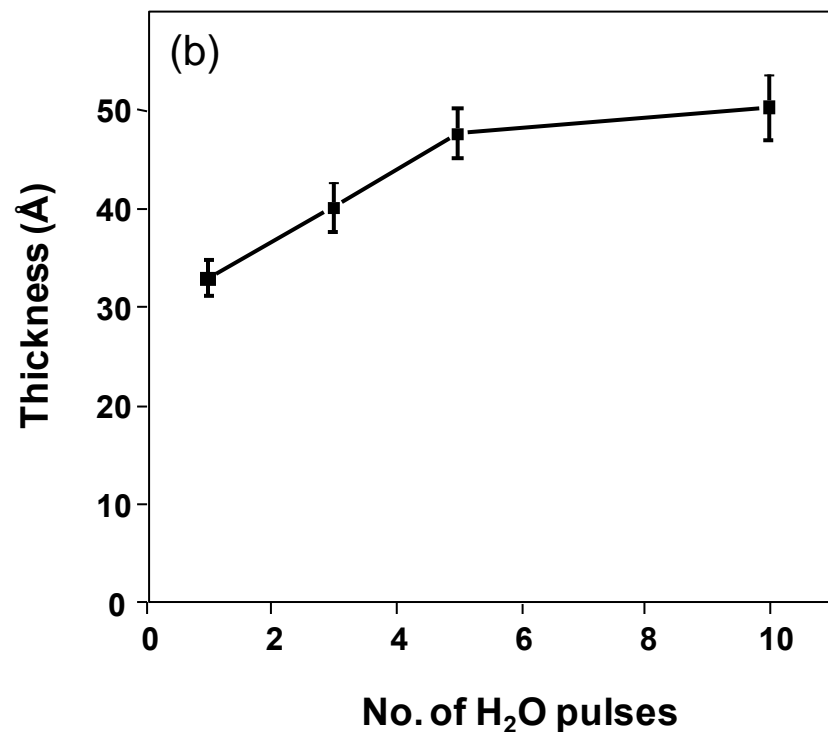
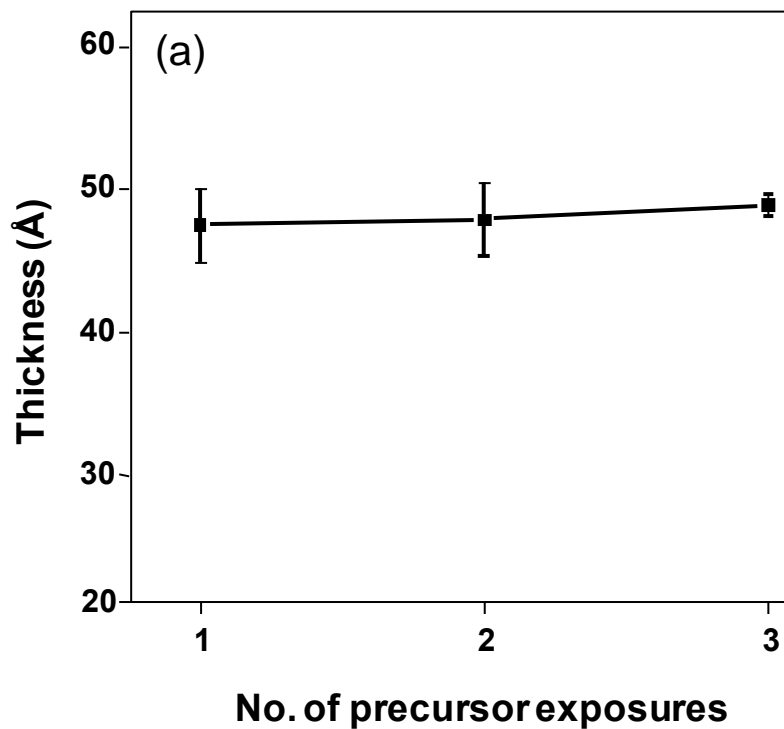
AR dependent

# High-k thin films for DRAMs



GPC ~ 0.45 Å/cycle

# High-k thin films for DRAMs



Self-limiting mode of growth in both half cycles of reaction

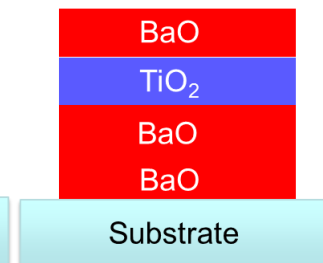
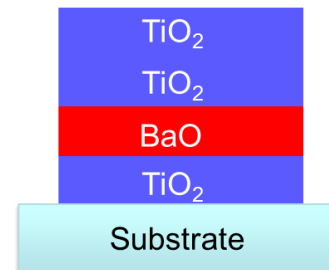
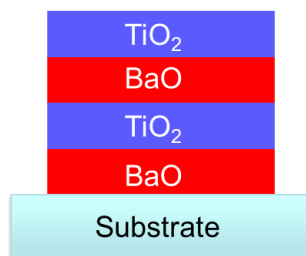
# High-k thin films for DRAMs

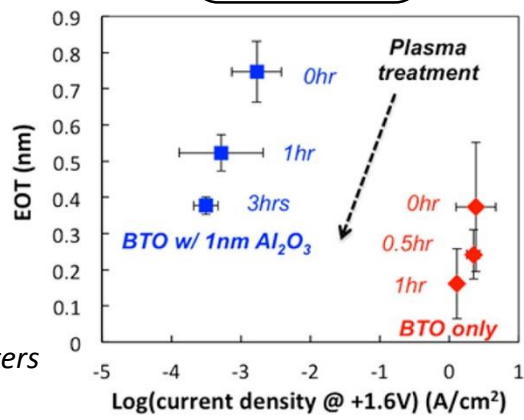
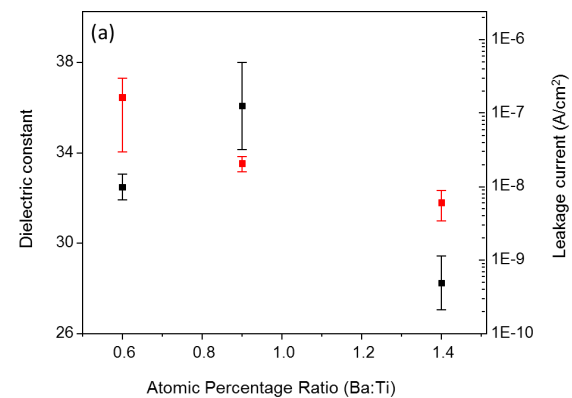
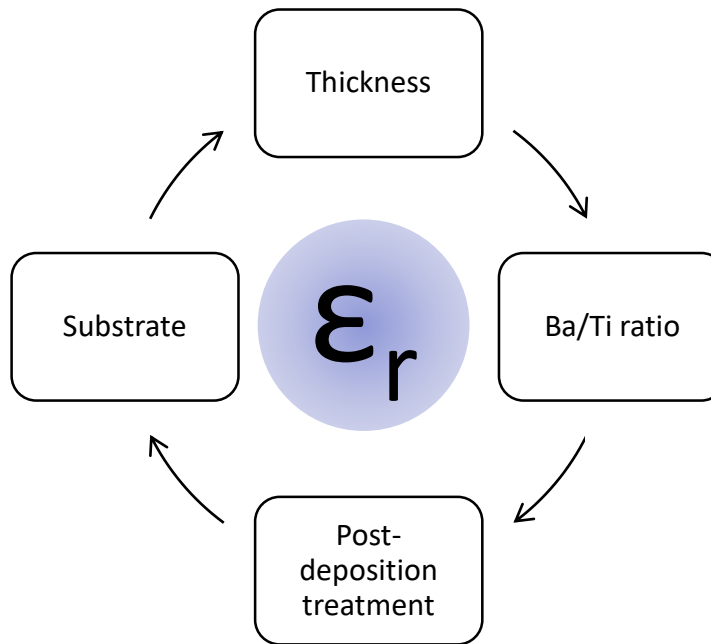
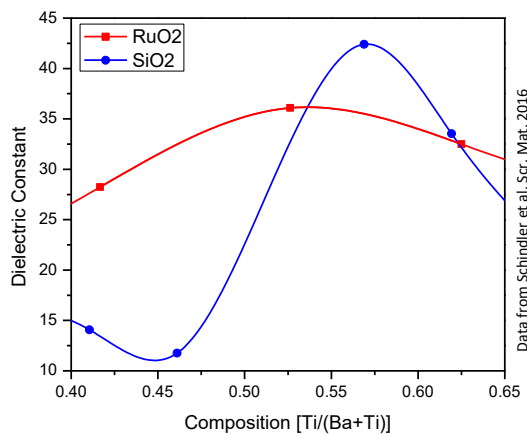
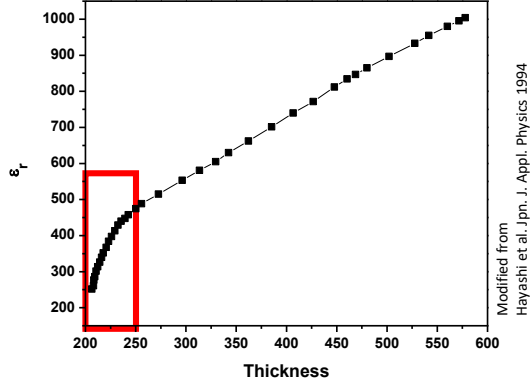
Period	1 1 A																18 VIII A	
1	1s H	2 II A He																
2	2s Li	Be																
3	3s Na	Mg	3 III B	4 IV B	5 V B	6 VI B	7 VII B	8 VIII B	9 VIII B	10 VIII B	11 I B	12 II B	3p Al	14 IV A Si	15 V A P	16 VI A S	17 VII A Cl	Ar
4	4s K	Ca	3d Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	4p Ga	Ge	As	Se	Br	Kr
5	5s Rb	Sr	4d Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	5p In	Sn	Sb	Te	I	Xe
6	6s Cs	Ba	† 5d	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	6p Tl	Pb	Bi	Po	At	Rn
7	7s Fr	Ra	‡ 6d	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	7p Uut	Fl	Uup	Lv	Uus	Uuo

lanthanides  
(rare earth metals) † 4f

actinides ‡ 5f

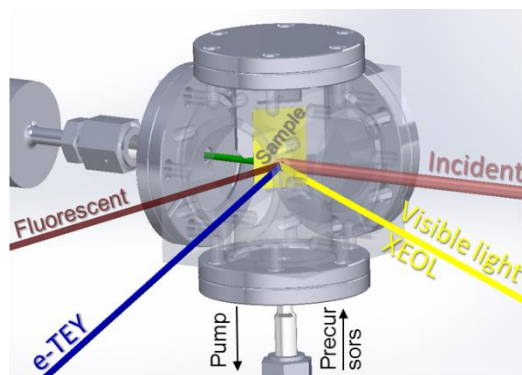
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr



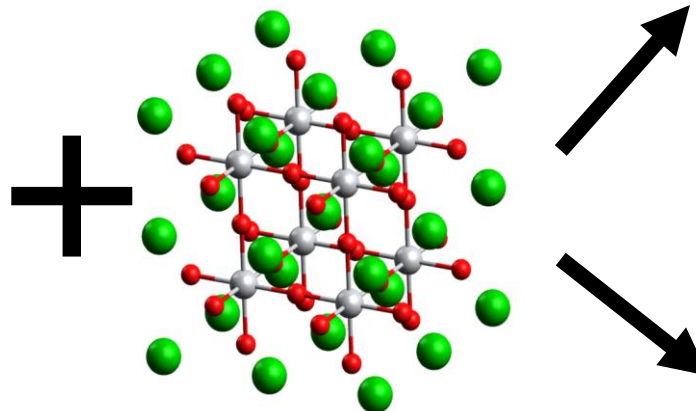


# ALD characterization in the SSRL

What is the chemical and structural nature for thin film performance modifications?



XANES



Quantum Simulations

## Provides

Chemical Identity  
Oxidation State  
Coordination  
Local geometric  
Structure  
Local Density of  
unoccupied States

## Allows studying

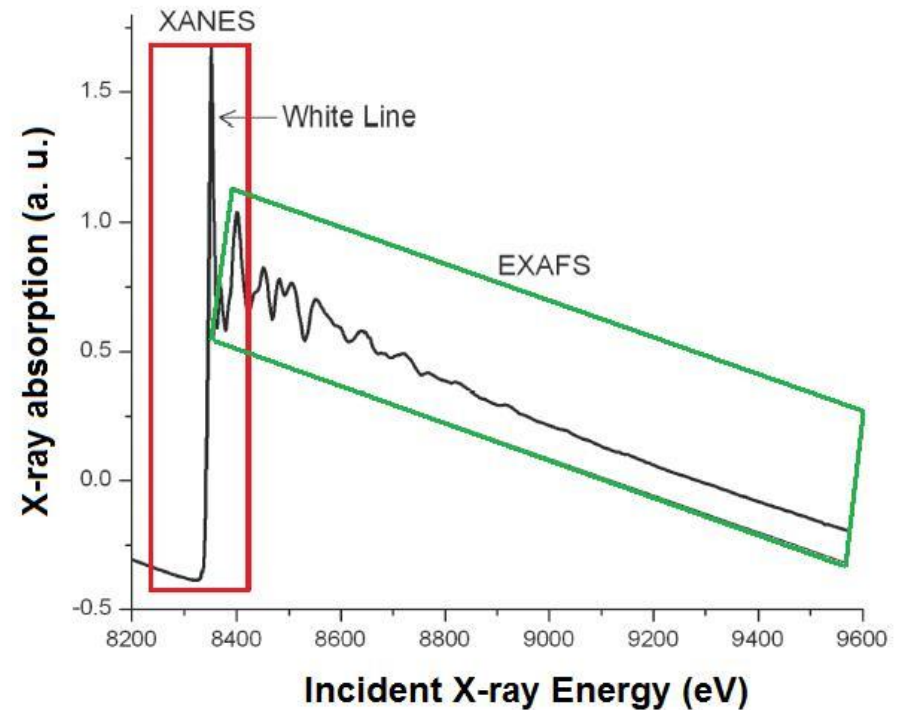
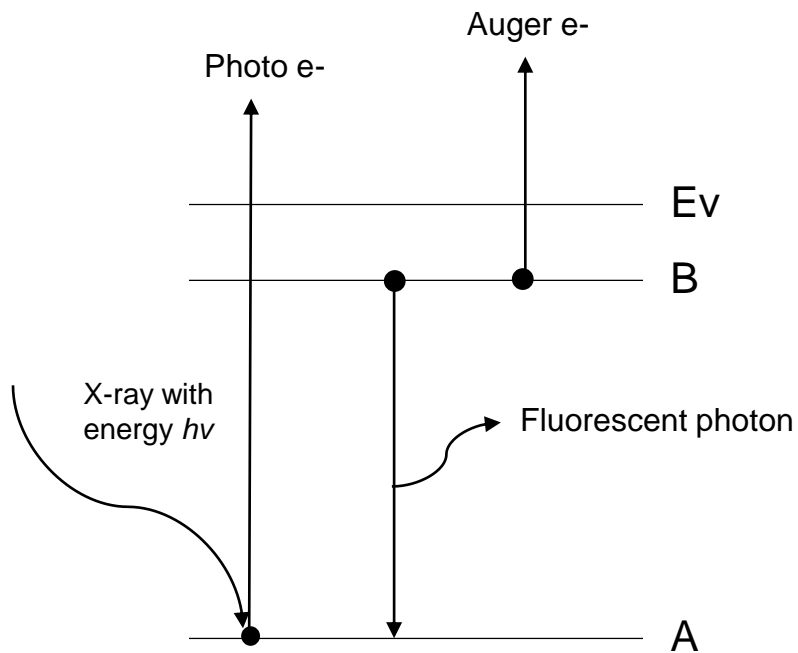
Interfaces  
Structural distortions  
Dopant atoms  
Nucleation process

# ALD characterization in the SSRL

## Photoelectron

$E = h\nu - \text{binding energy}$

Ejected to unoccupied state



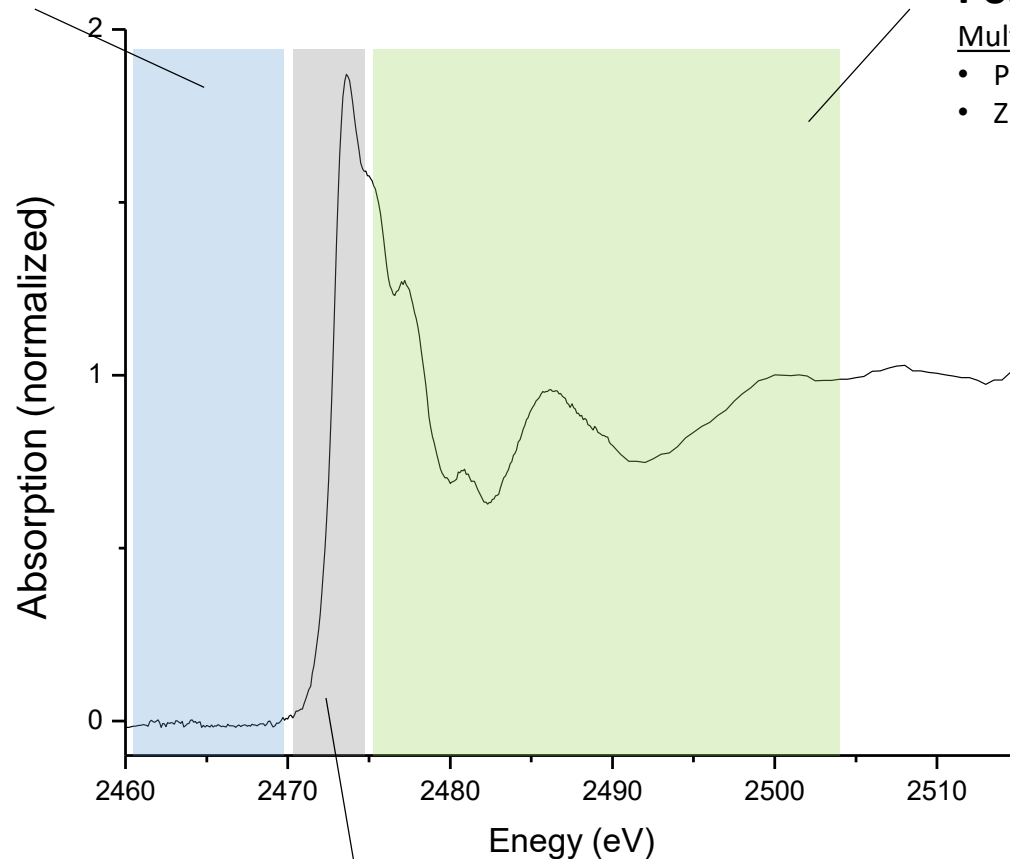
Beer's law: Absorbance =  $\log(I_0/I_t)$  or  $\log(I_0/I_f)$

# X-ray absorption near edge structure (XANES)

## Pre-edge:

### Molecular symmetry

- Forbidden transitions
- Weak intensity
- Featureless



## Post-edge:

### Multiple scattering paths

- Photo e- longer than Zn-S bond
- Zn-S-Zn

## Edge-jump:

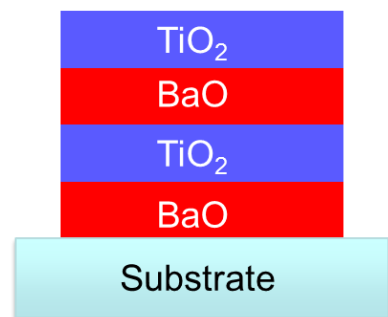
### Oxidation state

- Unoccupied state in valence orbitals
- Empty S 3p and Zn 4 sp orbitals

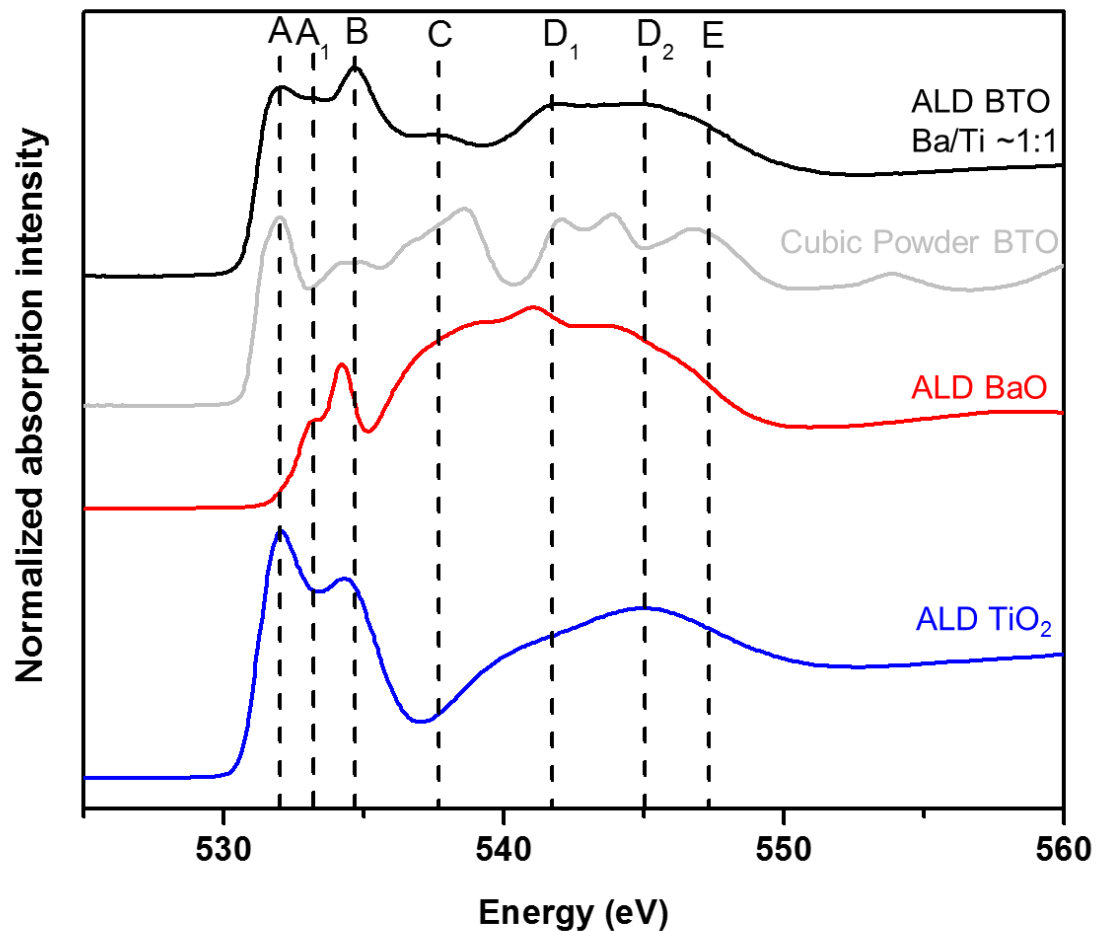
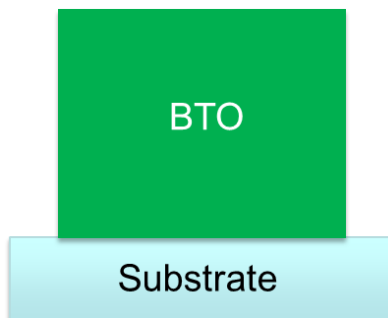


# XANES of ALD BTO

## Mixing of BaO and TiO<sub>2</sub> to form BaTiO<sub>3</sub>



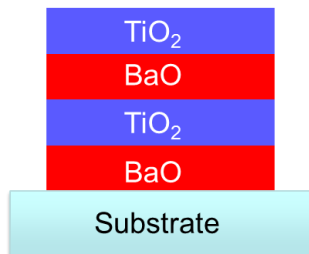
VS.



# XANES of ALD BTO

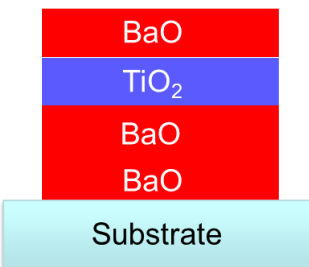
## Changing Ba/Ti composition

Stoichiometric



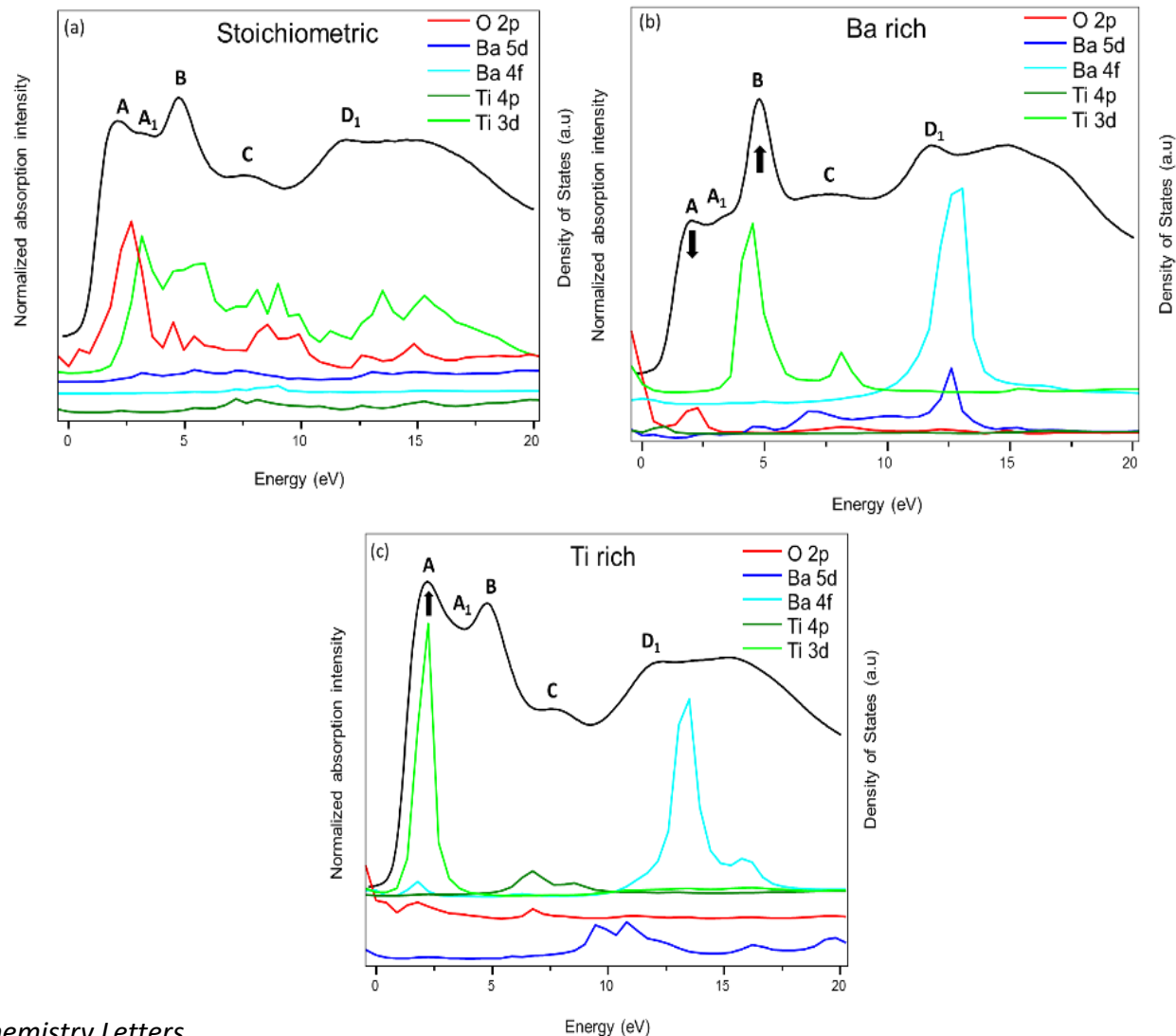
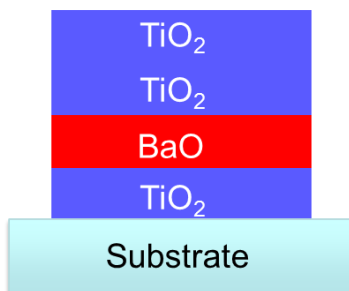
VS.

Ba Rich



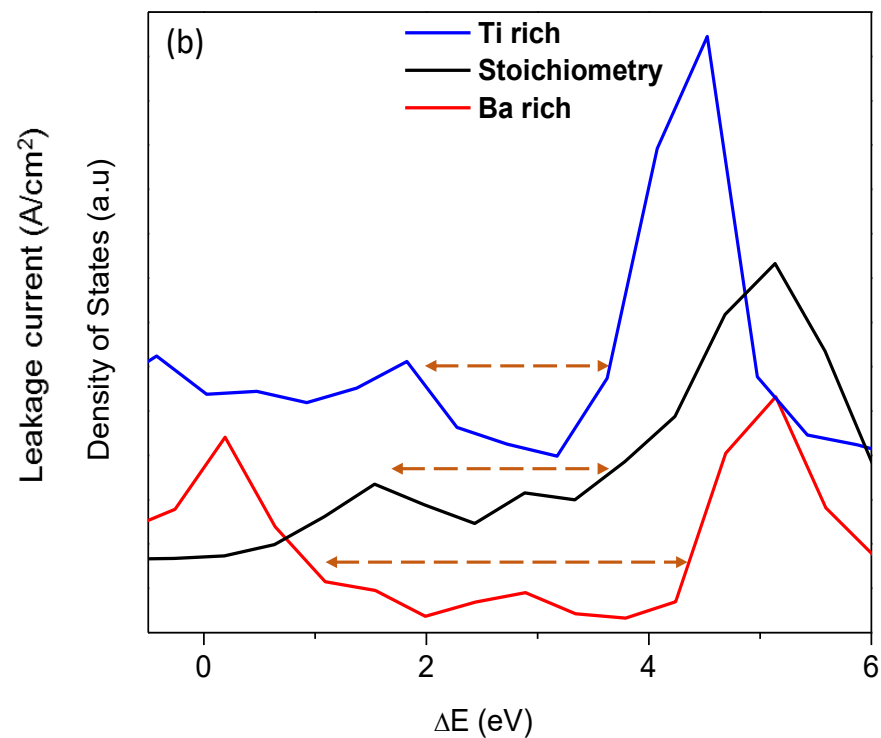
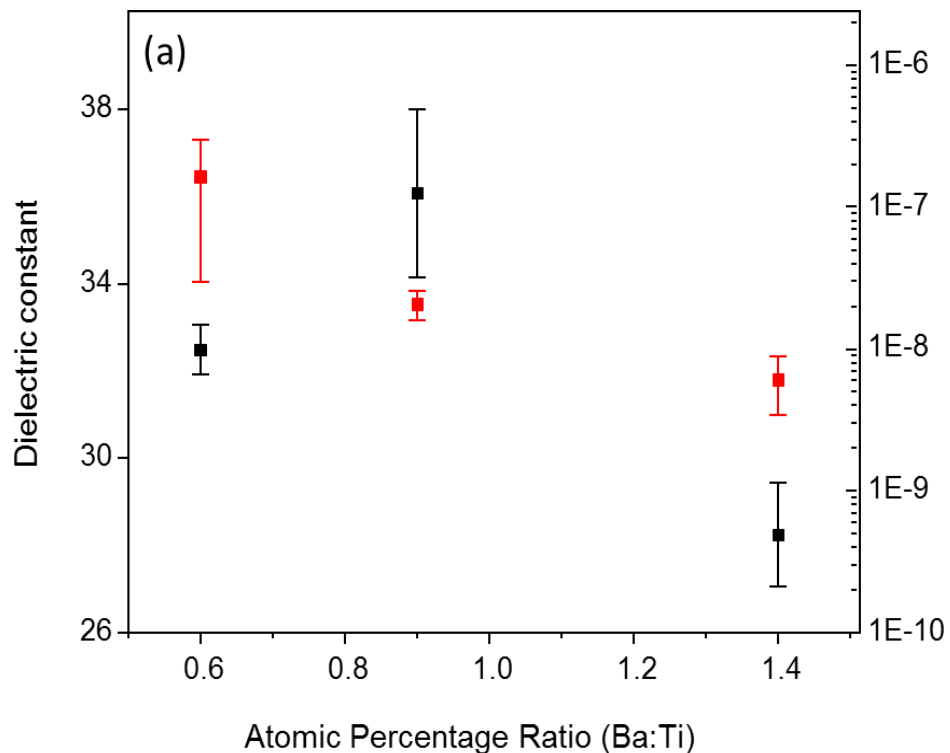
VS.

Ti Rich

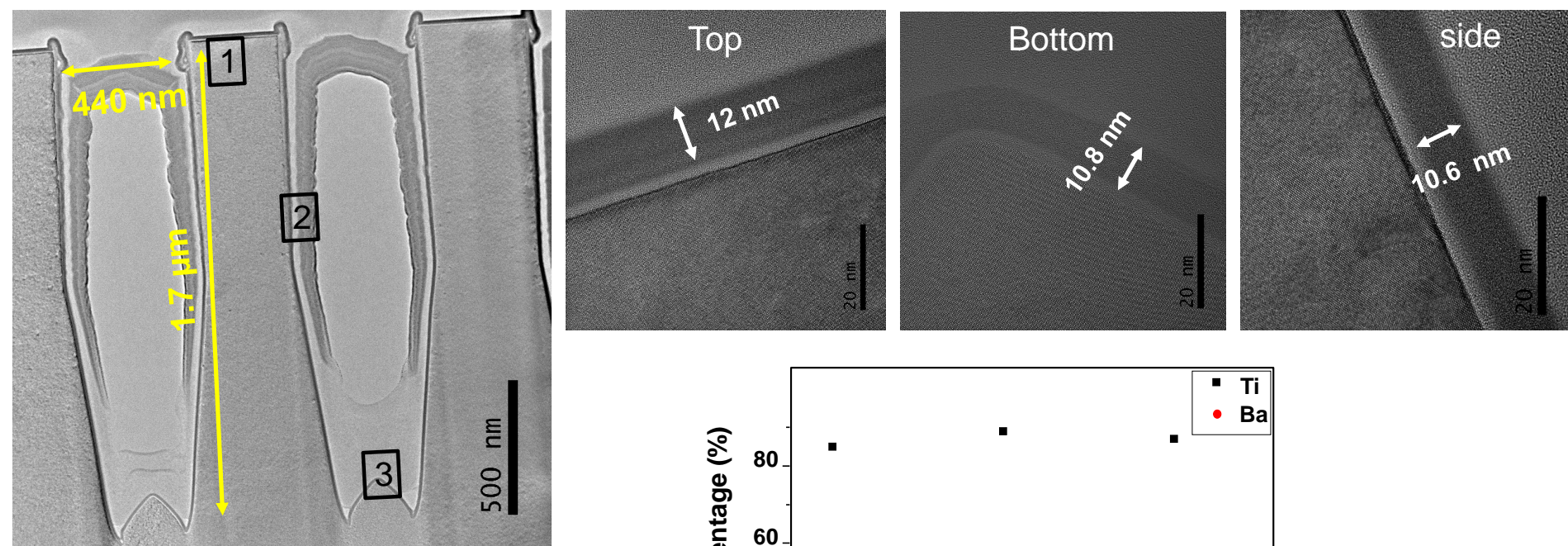


# XANES of ALD BTO

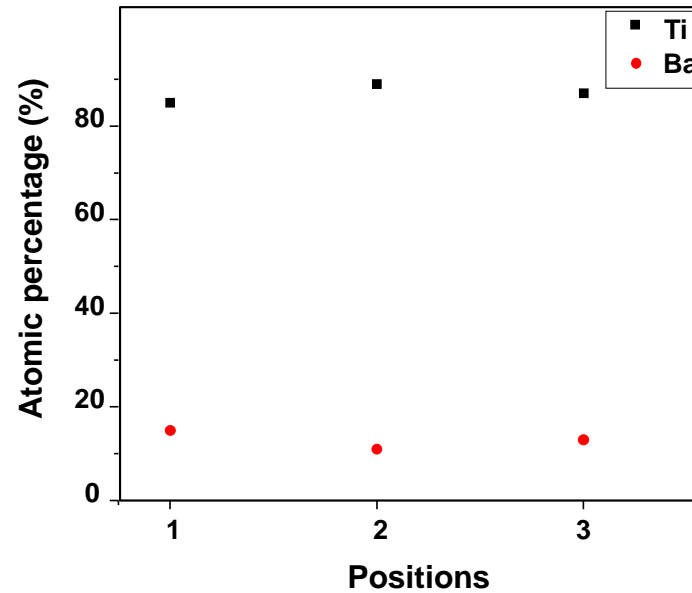
## Leakage current and band gap



# High-k thin films for DRAMs

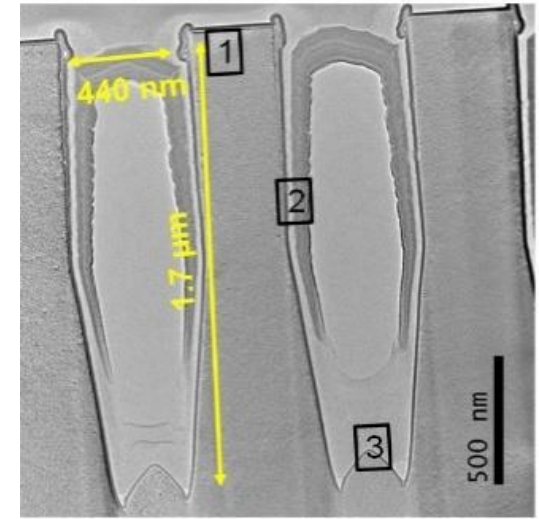


- Aspect ratio of the trench  $\sim 1:3.9$
- Step coverage ( $d_{\text{bottom}}/d_{\text{top}}$ )  $\sim 90\%$
- Uniform composition distribution.



# Summary

- **ALD for reaching the ultimate limit in downscaling**
- **ALD high-k Barium Titanate for next generation DRAM structures**
- **Novel chemistry for self limiting growth of BTO**
- **Explanation of dielectric properties with electronic structure revealed by synchrotron based X-ray absorption**



Shinjita



Yongmin



Ioannis



Anup



# Ongoing activity with TU Wien

## Additive Manufacturing Technical Committee



**ESIS Technical committee 15 (Chief)**

**ESFRI HORIZON 2020 PROPOSAL (180 ME, 13 PARTNERS)**