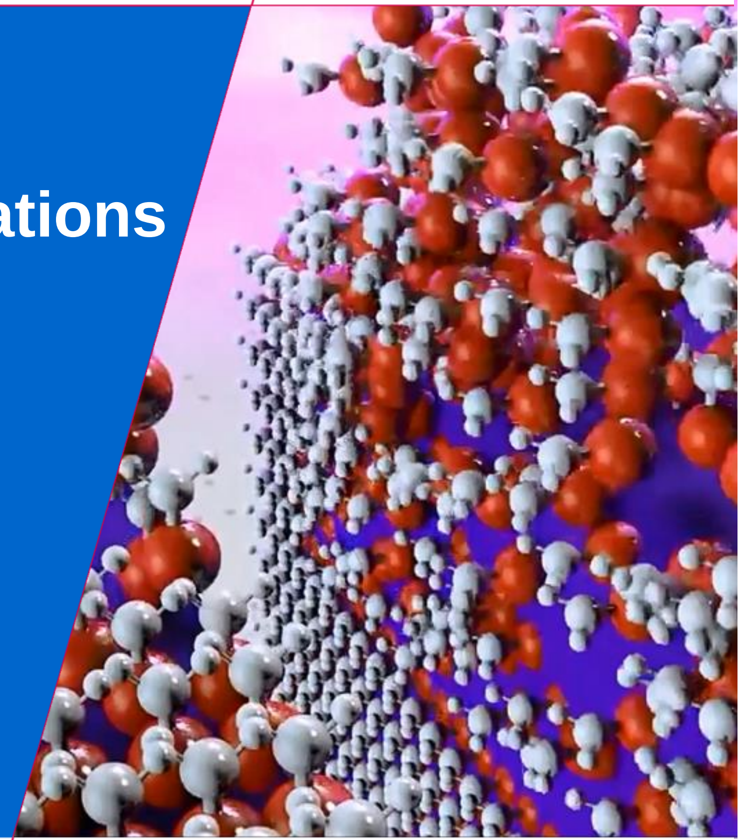
NGC 2017

Atomic Layer Processing:

basics, materials, processes & applications



Fred Roozeboom

TU Eindhoven & TNO - Holst Centre

The Netherlands

f.roozeboom@tue.nl

TNO

Holst Centre
Open Innovation by imec and TNO

TU/e Technische Universiteit **Eindhoven** University of Technology

Where innovation starts

Outline

- Introduction in thin-film technology
  - Basics, history, trends in materials and dimension control
- Atomic Layer Processing (Atomic Layer Deposition, mainly)
  - Key process characteristics and state of the art in ALD / ALE
  - Materials
    - Precursors, films
    - Growth modes (A/B/(C), thermal and radical / plasma enhanced
    - Excursion to patterning / *area-selective* ALD
    - Molecular Layer Deposition
  - Reactors
    - Spatial ALD, some features, Roll-to-Roll, InZnGaO for TFT displays
- Atomic Layer Etching (thermal ALE and selectivity)
- Concluding remarks

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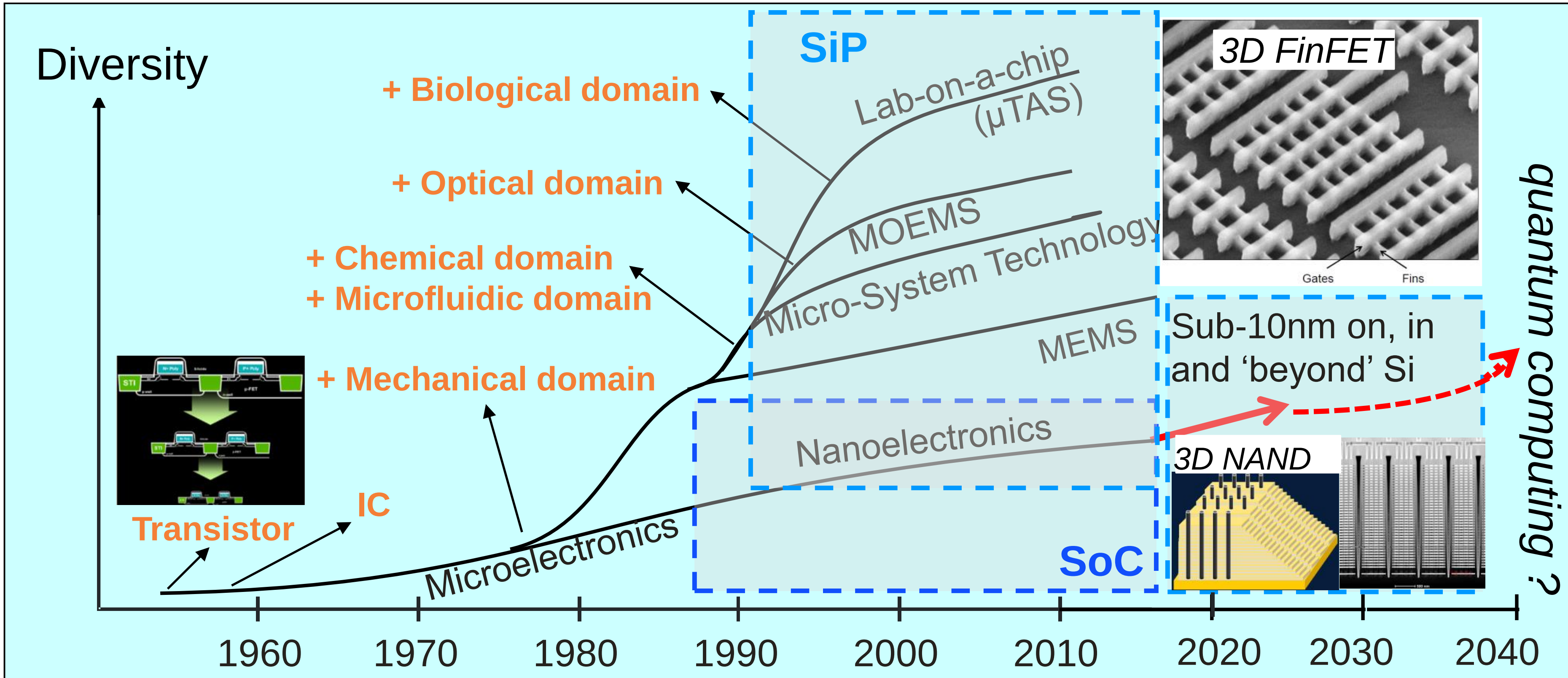
History and future of etching and deposition



wet etch ▲

dry etch ▲ *'ashing'*

dry etch ▲ 'RIE'

enabling *System-on-Chip* **(SoC)**

Deep ▲ RIE

Atomic ▲ Layer Deposition (HfO_2)

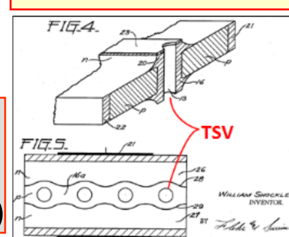
▲ Atomic Layer Etching = "Reverse" ALD

enabling MEMS, **3D** TSV, *System-in-Package* **(SiP)**

enabling
- 3D
- 2D atomic-scale
- ***challenging EUV?***

▲ W. Shockley, 1958
1st patent filed on Through-Si-Via

▲ R. Feynman, 1959
There's plenty of room at the bottom
("…machines of only 100 atoms high…")

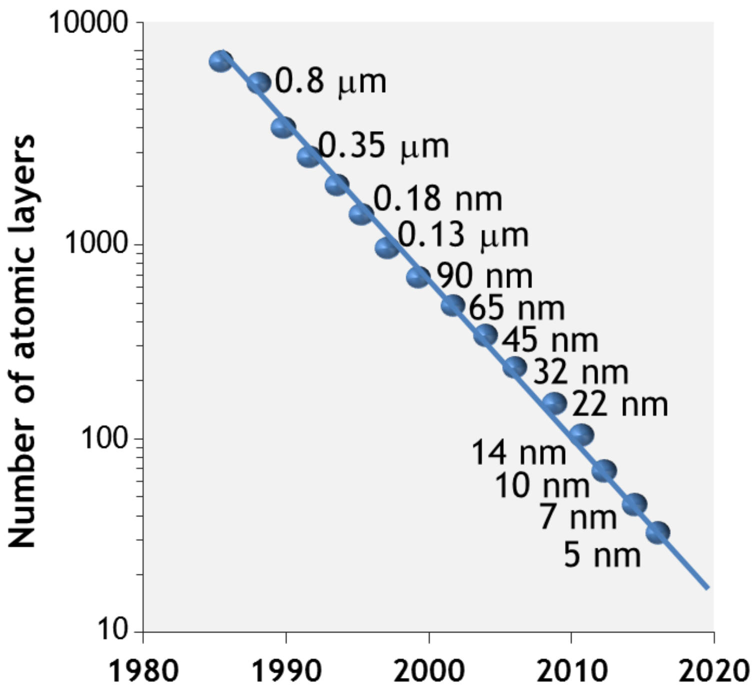


-enabling quantum computing?

Challenges in thin-film technology: *atomic-scale fidelity* (conformality in dep / etch)

"But I am not afraid to consider the final question as to whether, ultimately—in the great future—we can arrange the atoms the way we want; the very atoms, all the way down! What would happen if we could **arrange the atoms one by one** the way we want them (within reason, of course; you can't put them so that they are chemically unstable, for example)."

Richard Feynman, Dec. 29, 1959,
Annual Meeting of American Physical Society



Ever shrinking devices, 2D materials and 3D structures require processing / patterning with Atomic Scale Fidelity and selective area

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Basics of Atomic Layer Deposition

- **ALD**: a method to deposit **ultrathin films** at an **atomic level**

- **Chemical reaction**:

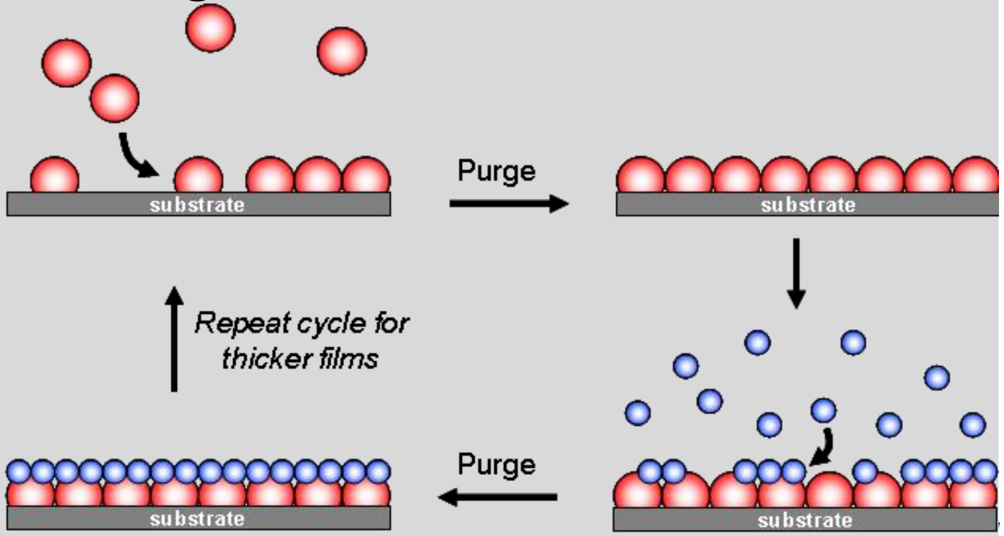
  Vapor-phase chemicals reacting in **layer-by-layer** growth mechanism to form a solid-state thin film:

$$\mathbf{A_{(g)} + B_{(g)} \rightarrow AB_{(s)}}$$

- Separated in **two self-terminating half-reactions**:

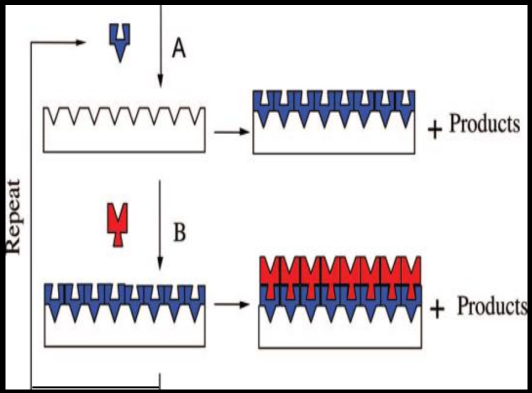
Step 1: $\mathbf{A_{(g)} \rightarrow A_{(s)}}$

Step 2: $\mathbf{A_{(s)} + B_{(g)} \rightarrow AB_{(s)}}$



Thermal ALD of Al_2O_3 from $Al(CH_3)_3$ and H_2O

Atomic Layer Deposition

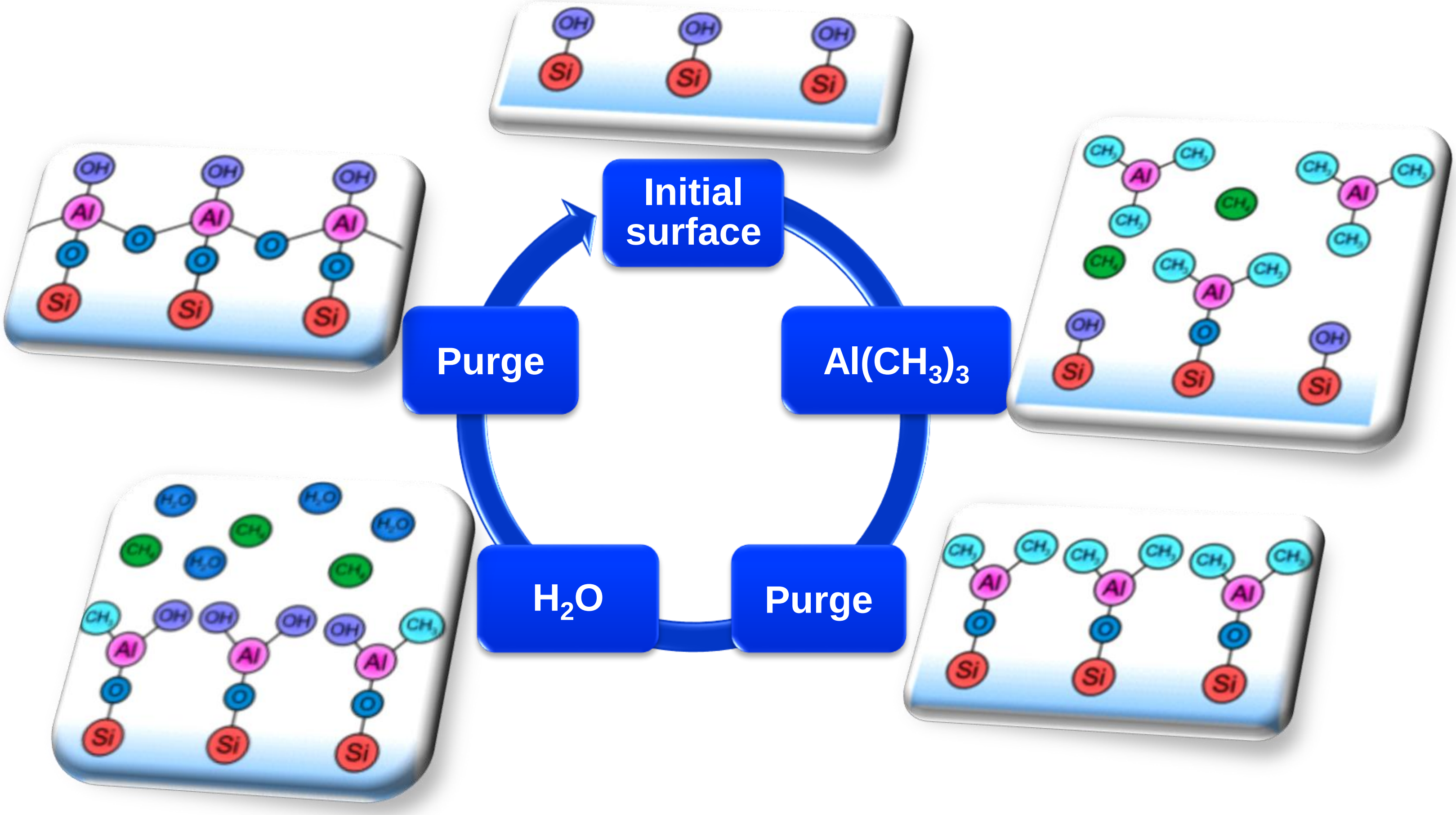


$$AlOH + Al(CH_3)_3\,(g) \rightarrow AlOAl(CH_3)_2 + CH_4\uparrow$$

$$AlCH_3 + H_2O \rightarrow AlOH + CH_4\uparrow$$

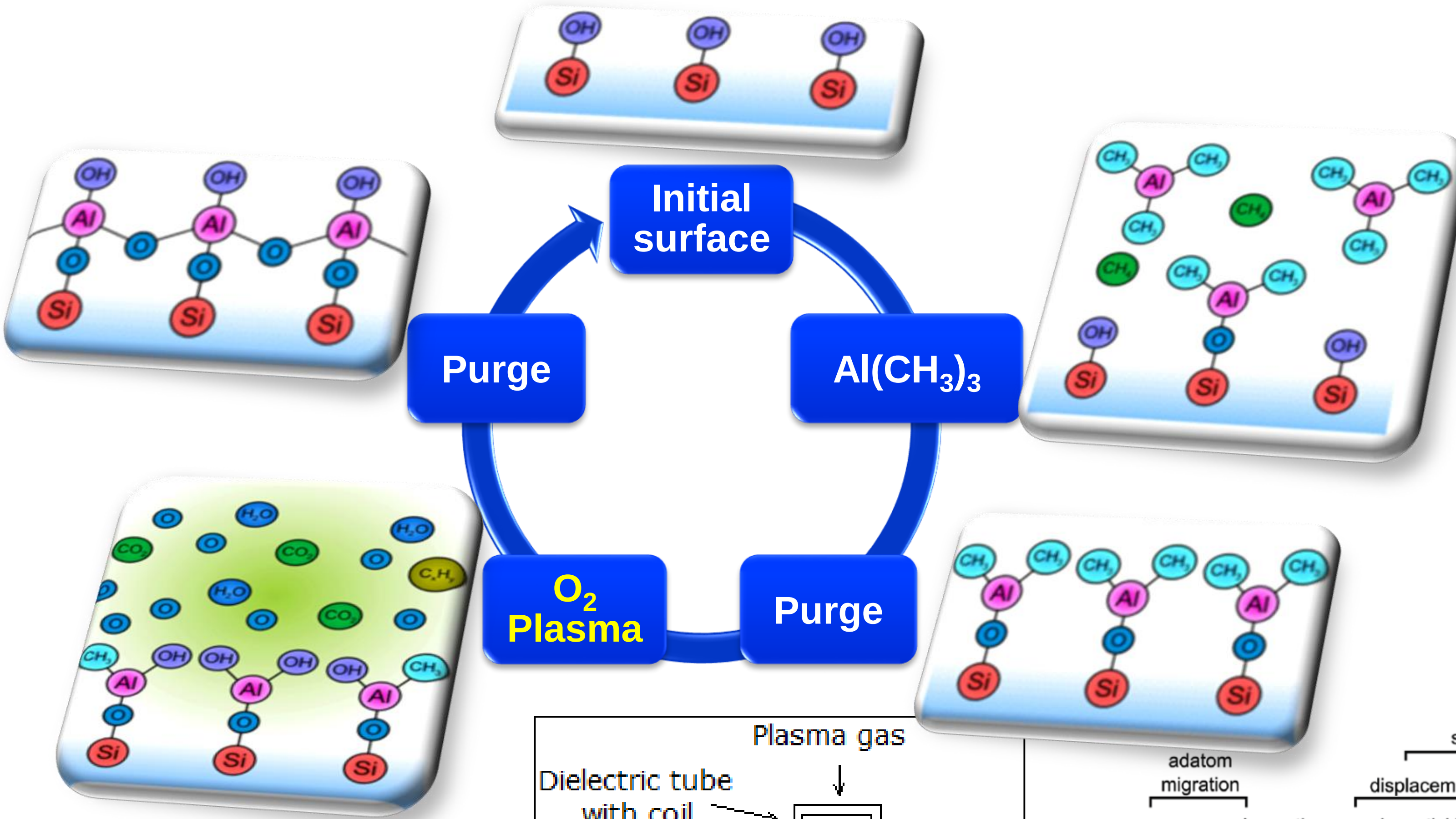
- **Sequential pulsing of precursors**
- **Purge/ vacuum between all pulses**
- **Self-limiting (ligand exchange)**
- **Step conformal, *e.g*. in 3D trenches**

ALD of Al_2O_3 from $Al(CH_3)_3$ and H_2O / thermal

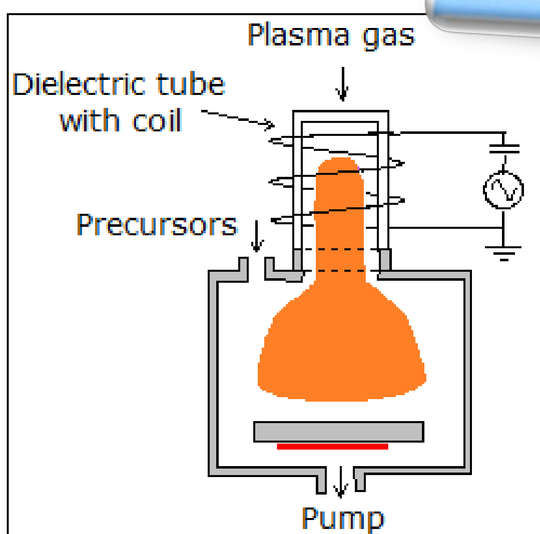


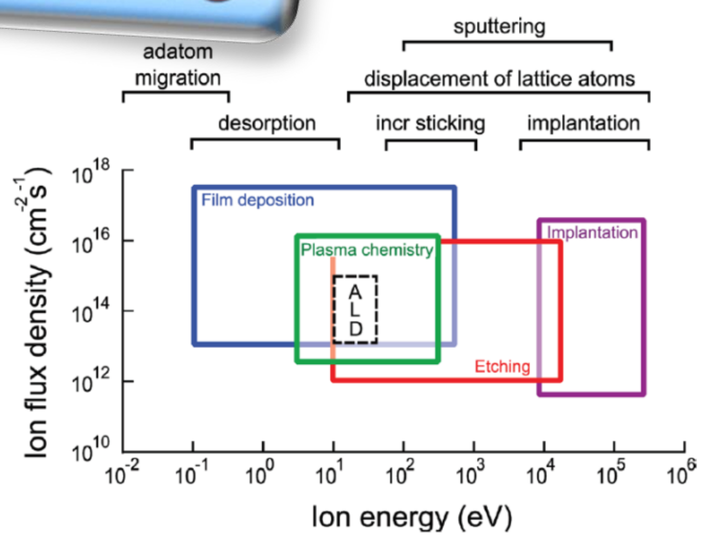
- Sequential pulsing of precursors
- Purge/ vacuum between all pulses
- Self-limiting (ligand exchange)
- Step conformal, *e.g*. in 3D trenches

ALD of Al_2O_3 from $Al(CH_3)_3$ and H_2O / plasma

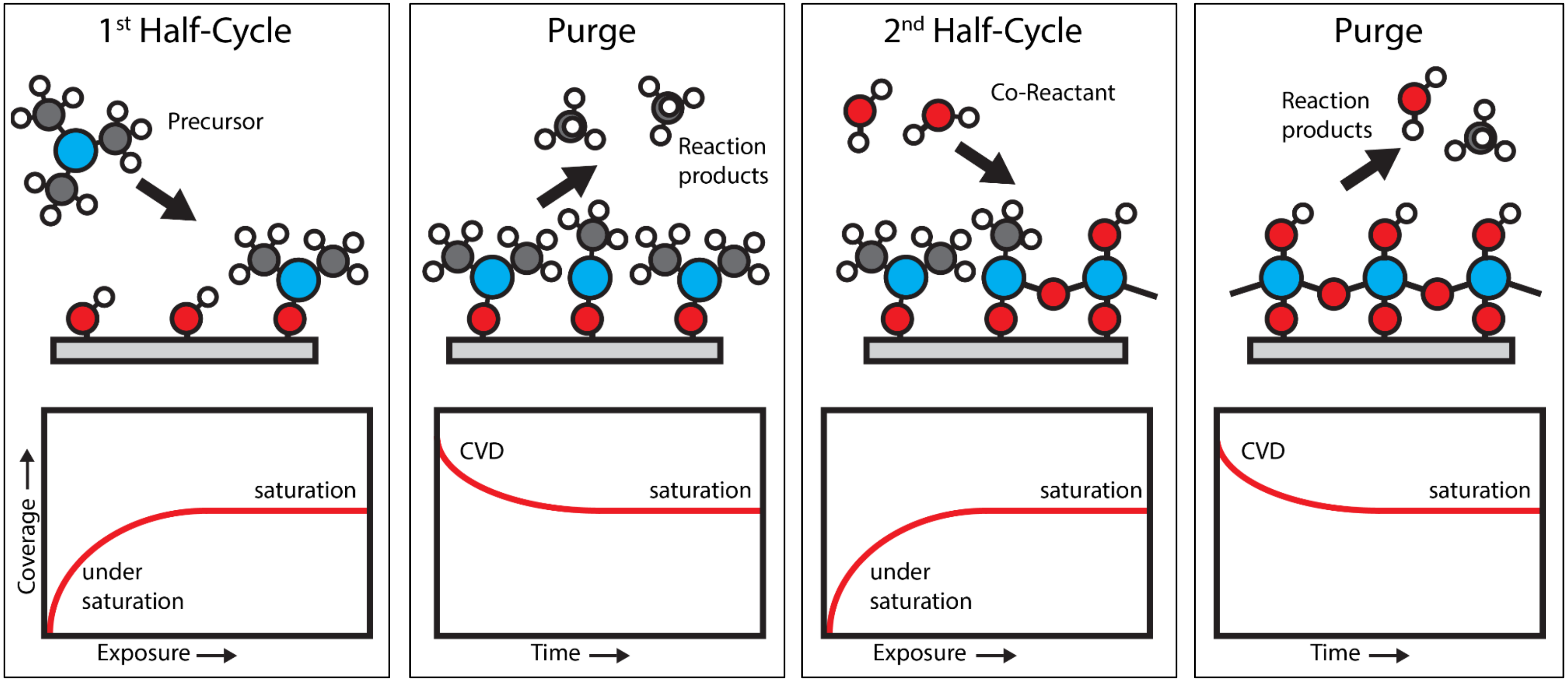


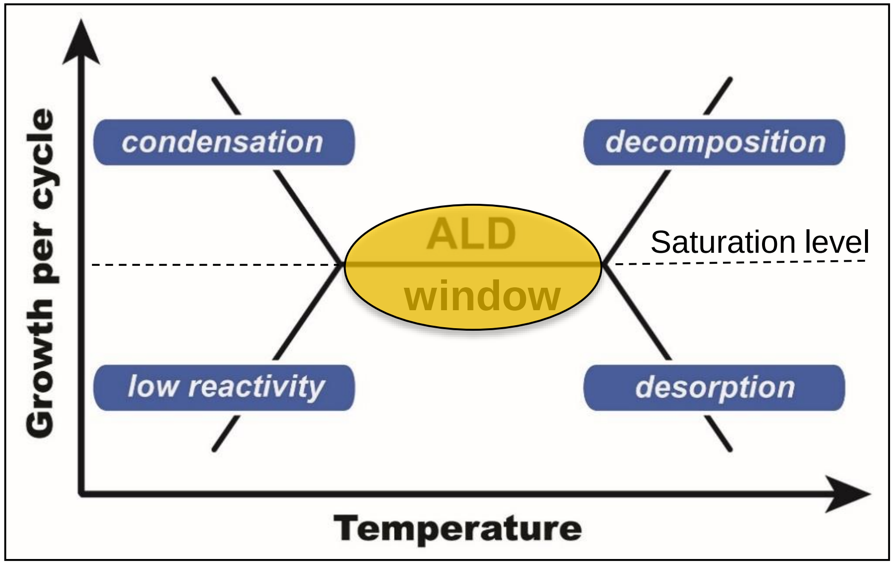
- Mild ion bombardment (ion energy < 20 eV)
- More materials possible
- Lower temperatures

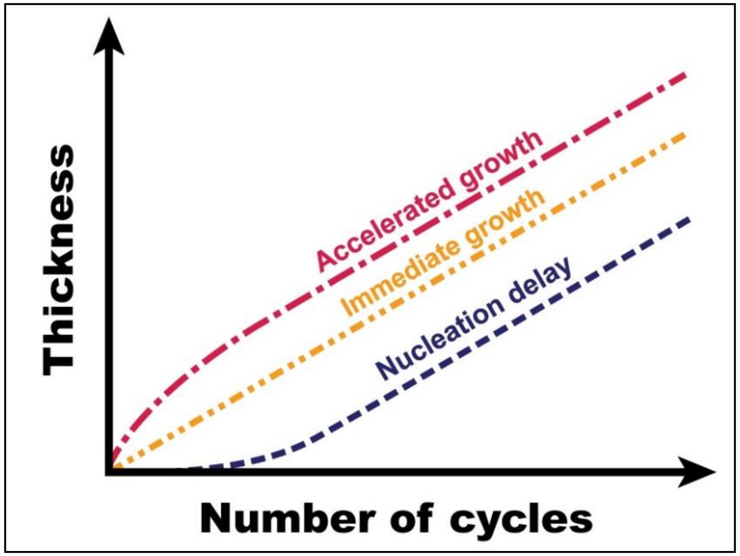




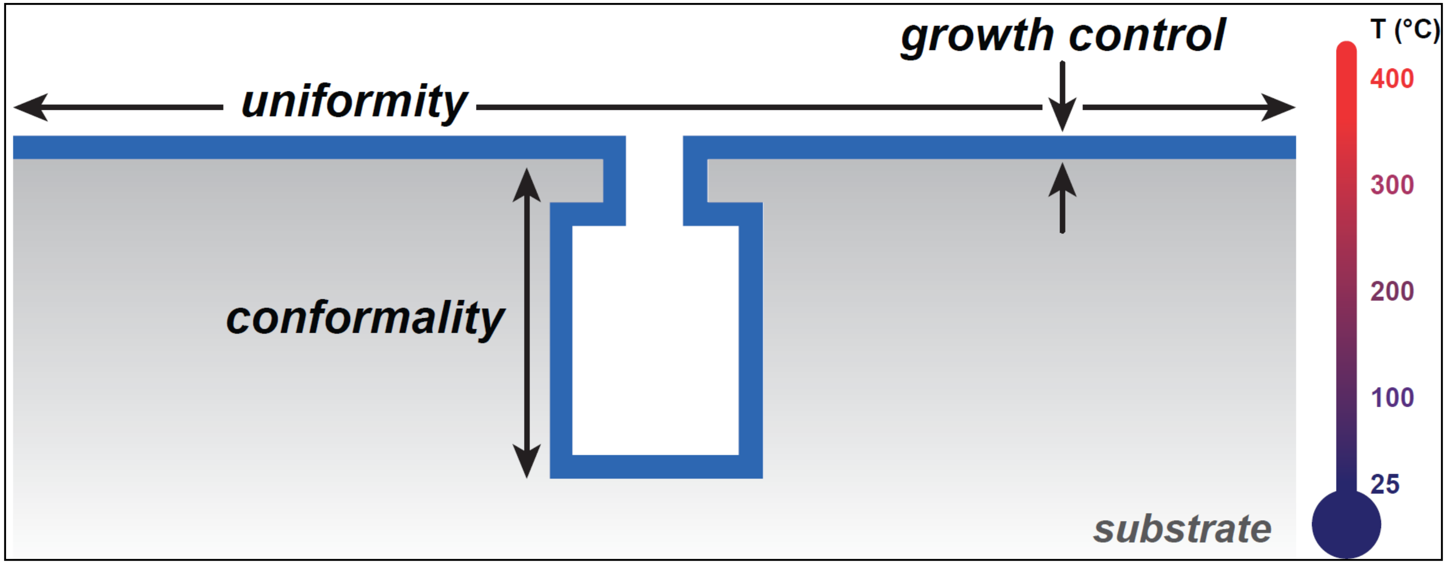
Characteristics and imperfections of ALD







Intrinsic benefits of Atomic Layer Deposition



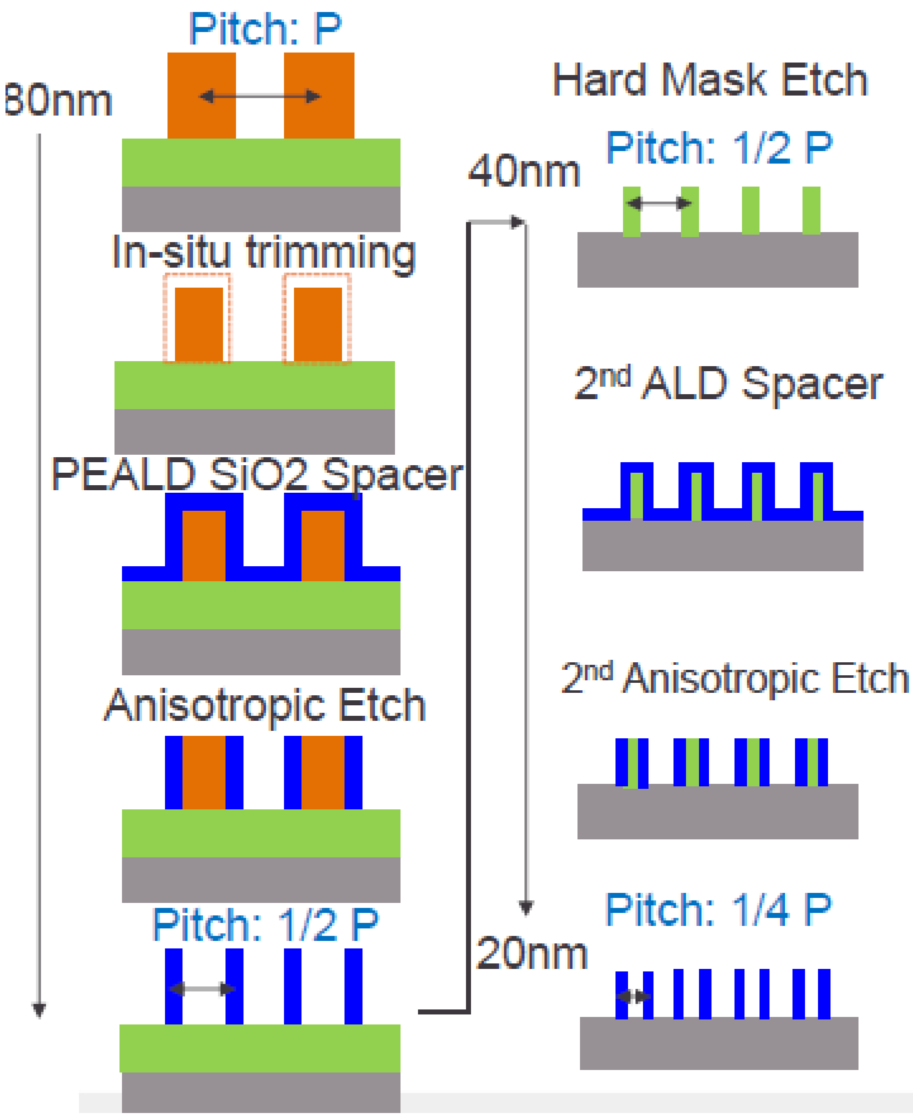
- Growth control at sub-nm level
- Uniform film thickness over large substrate areas
- Conformality for complex 3D substrate topologies
- Low substrate temperatures possible
- Superior quality: low pinhole levels, dense films
- Wide variety of materials

Knoops et al., *Handbook of Crystal Growth, Vol. 3, 2nd edition*, p. 1101 (2015)

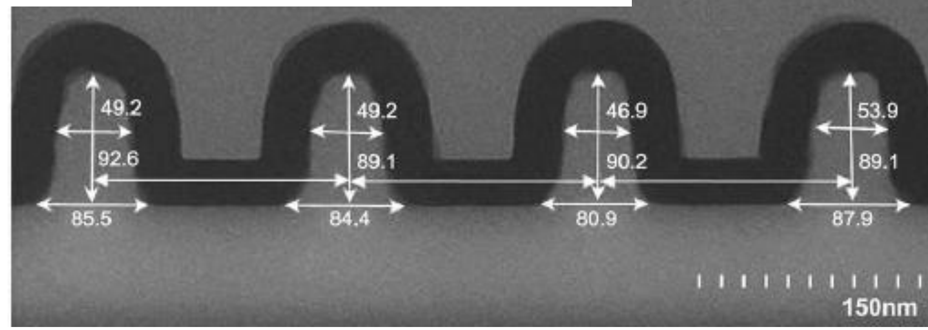
State-of-the-art: ALD enabling < 20 nm patterning

ALD ENABLING LITHOGRAPHY:
SPACER DEFINED DOUBLE/QUADRUPLE PATTERNING

ASM



Plasma ALD SiO_2 on resist

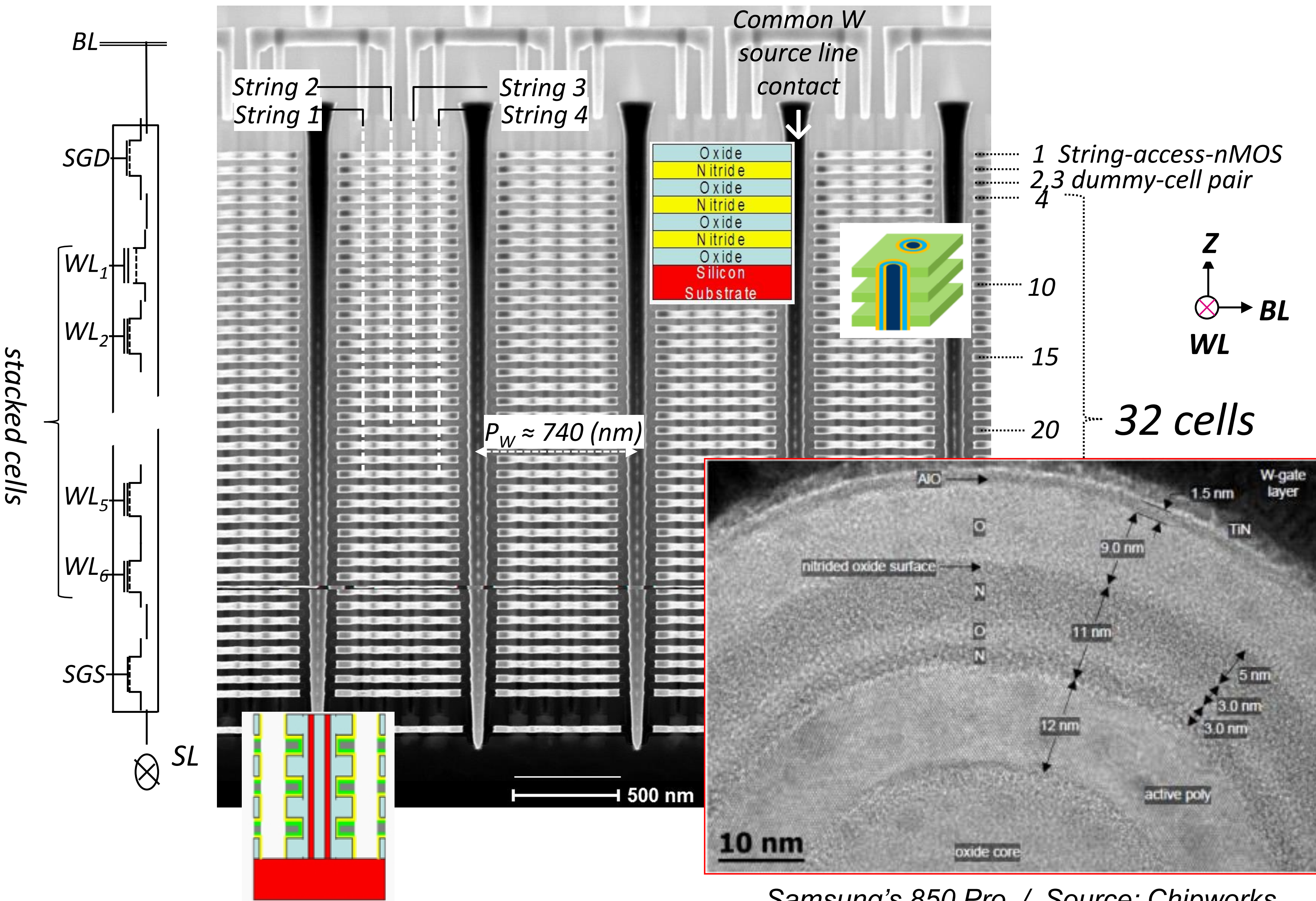


- ✓ Spacer Defined Double Patterning (SDDP) with ALD in production since 3x nm DRAM and Flash
- ✓ Spacer Defined Quadruple Pattering (SDQP) in production for 1x nm Flash
- ✓ SDDP/SDQP qualified with 10nm Logic customers

Key enablers brought by ALD

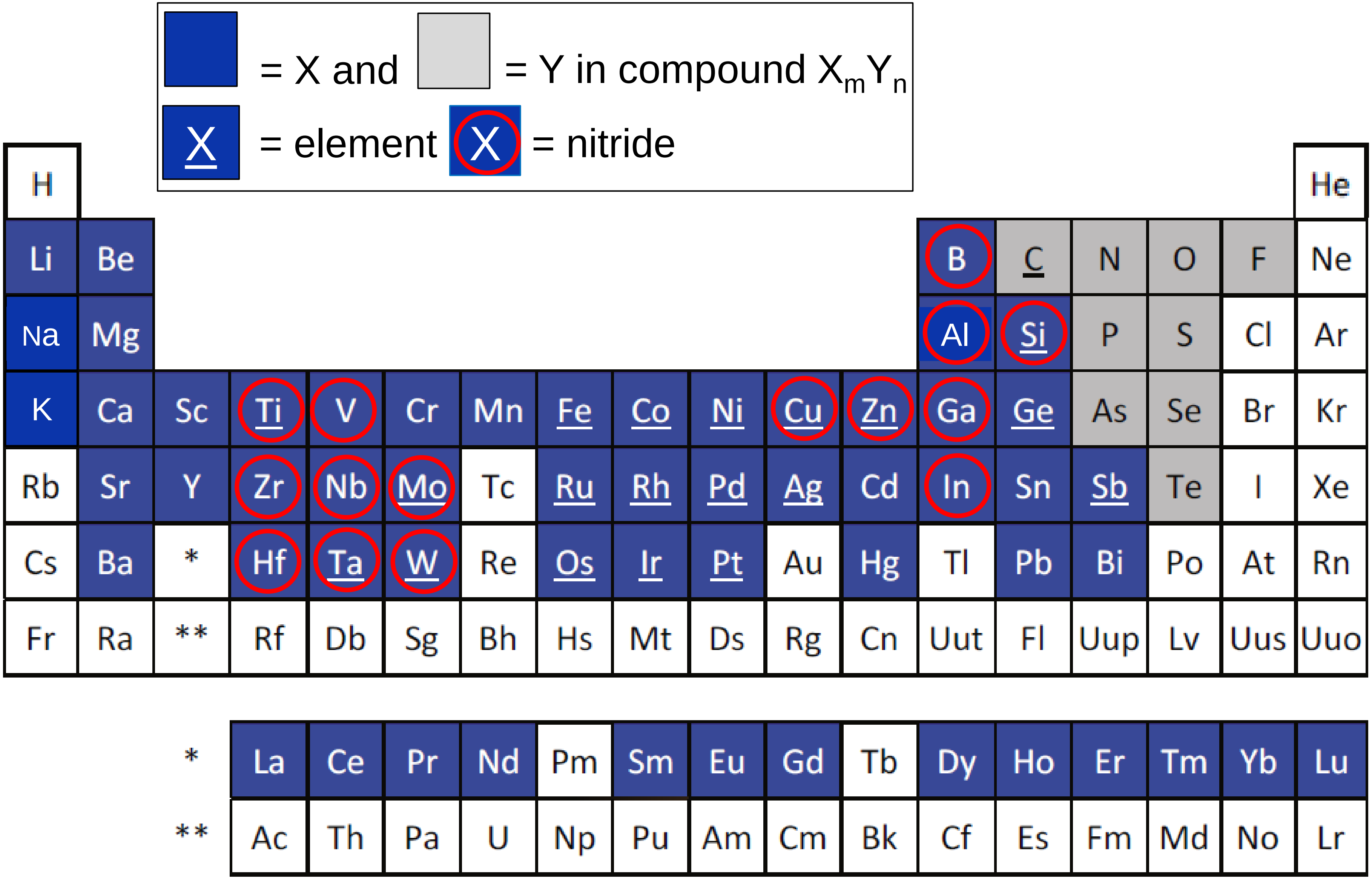
- Uniformity: CD control
- Low temperatures (<100C)
- Good step coverage
- Dense film
- In-situ trimming capability
- Extendible to other materials with etch selectivity

State-of-the-art: ALD (and ALE !) in 3D NAND



Samsung's 850 Pro / Source: Chipworks

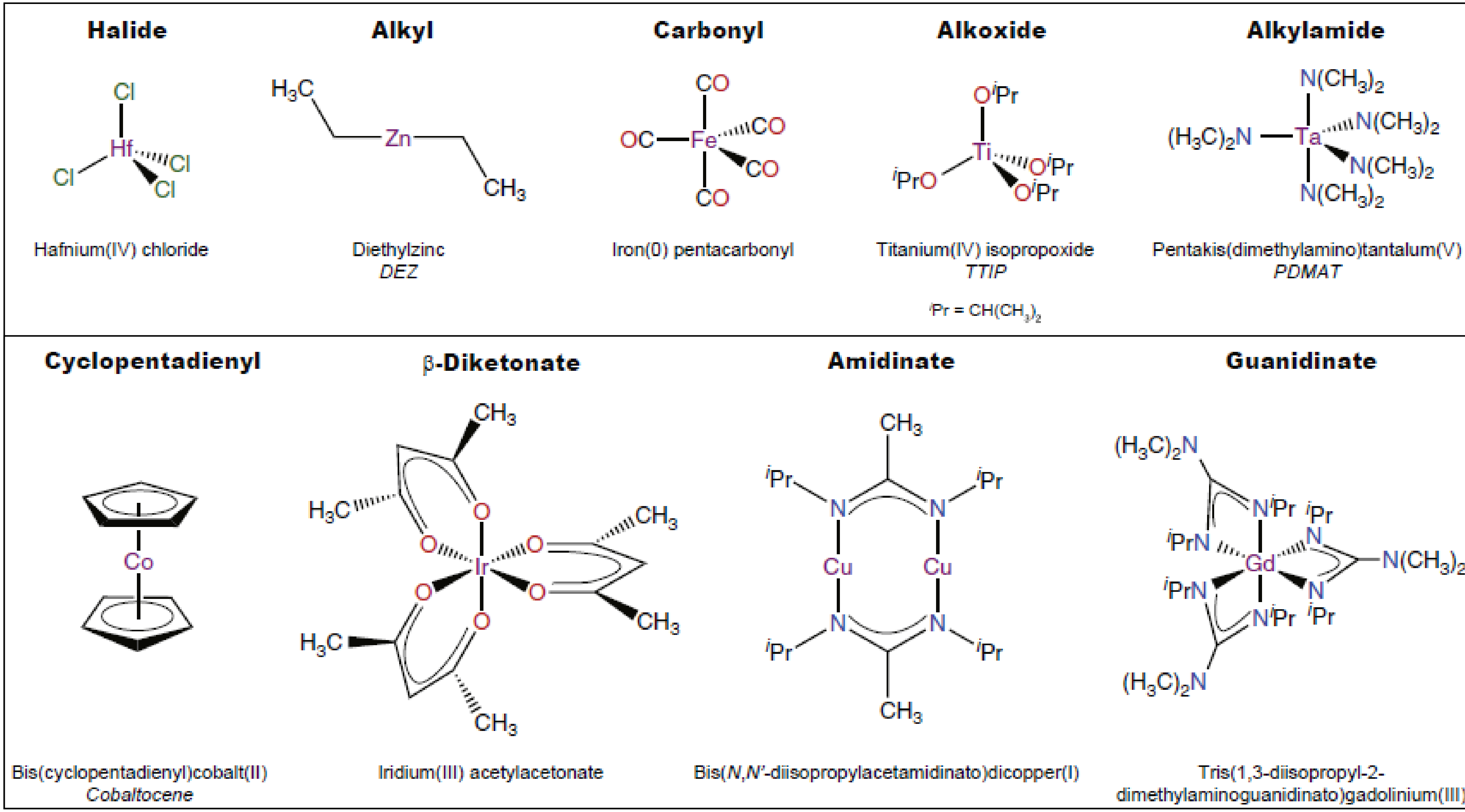
Materials deposited by ALD



Adapted from: - Puurunen, J. Appl. Phys. **97**, 121301 (2005)

- Miikkulainen *et al.*, J. Appl. Phys. **113**, 021301 (2013)

Metal precursors (*homoleptic*, i.e. identical ligands)



Criteria for ALD: • volatility • **reactivity** • thermal stability • volatile, non-etching products • non-toxic • preferably liquid • low-cost • easy in scale-up

Knoops et al., *Handbook of Crystal Growth, Vol. 3, 2nd edition*, p. 1101 (2015)

Co-reactant precursors for metal compounds ALD

Material	Common Co-reactants
Metal oxides	H_2O, H_2O_2, ROH, R(CO)H, R(CO)OH, R_2CO, O_2, O_3, O_2 plasma, O radicals, $M(OR)_x$, CO_2, N_xO_y, air
Metal nitrides	NH_3, NR_3, R_2NNR_2, NH_3 plasma, H_2 plasma, N_2 plasma, H_2-N_2 plasma, NH_x radicals
Metal carbides	C_xH_y, BR_3
Metal phosphides	PR_3, $POCl_3$, $P(OR)_3$, $PO(OR)_3$, $P(NR_2)_3$
Metal arsenides	AsH_3, AsR_3, $As(NR_2)_3$
Metal sulfides	H_2S, S_2R_2
Metal selenides	H_2Se, R_2Se, $Se(SiR_3)_2$
Metal tellurides	H_2Te, $Te(SiR_3)_2$
Metal fluorides	HF, MF_x
Pure element (metal)	H_2, H_2 plasma, NH_3, NH_3 plasma, H_2 plasma, N_2 plasma, H_2-N_2 plasma, NH_x radicals, O_2, O_2 plasma, O radicals, Si_xH_y, formalin

R = H or C_xH_y (any alkyl or aryl group) [1].

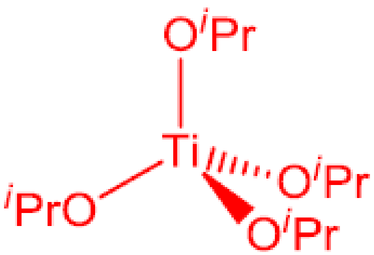
Workhorses for oxides: • H_2O, O_2 plasma, $O^\bullet$ radicals, O_3

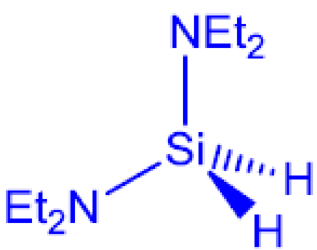
for nitrides: • NH_3, N_2 plasma, N_2-H_2 plasma, $NH_x^\bullet$ radicals

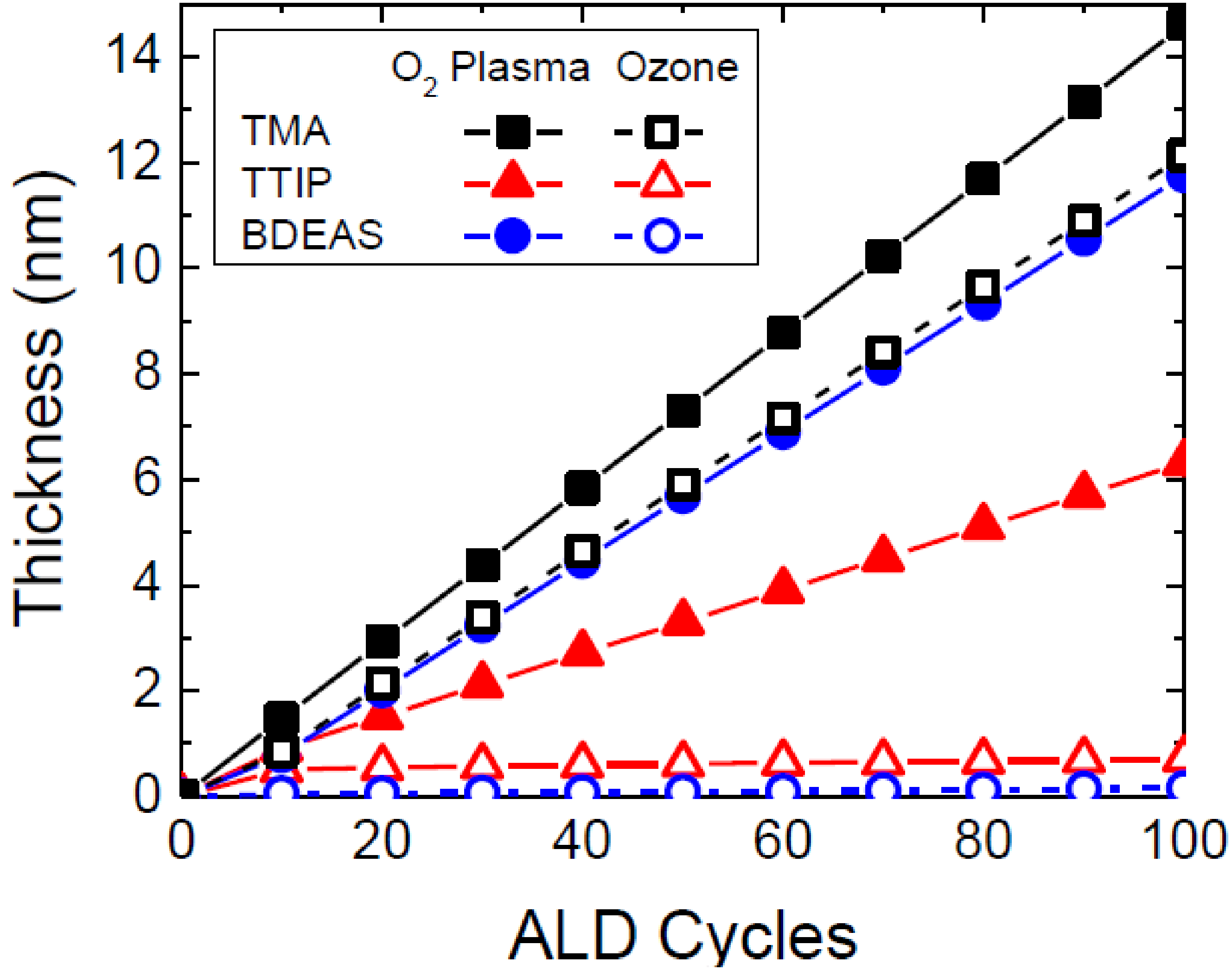
for metals: • mix of the above A/B/C (often redox chemistry)

H. Knoops et al., *Handbook of Crystal Growth, Vol. 3, 2nd edition*, p. 1101 (2015)

Room-temperature ALD growth of oxides



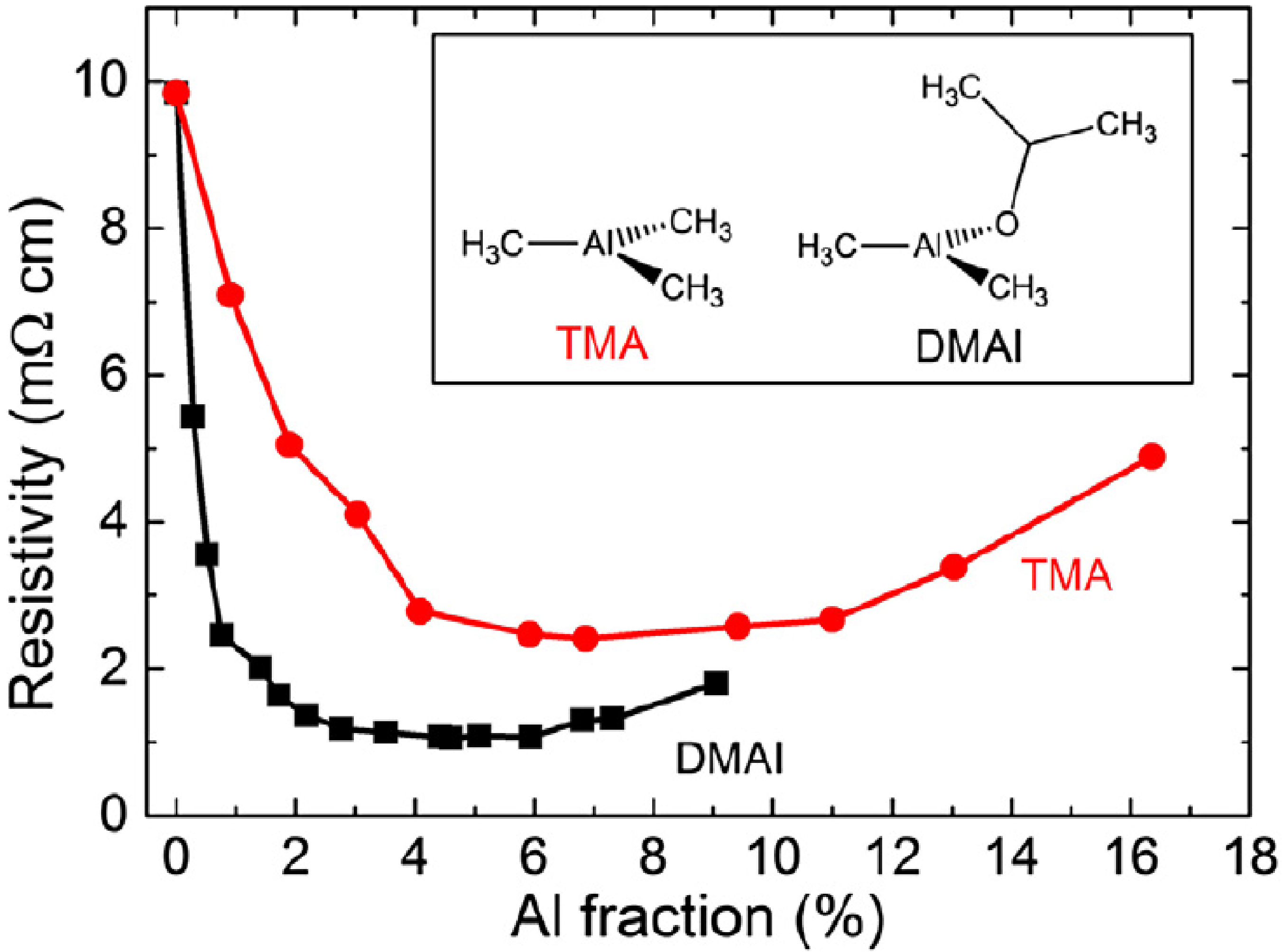




O_3 not reactive enough to fully oxidize surface groups at 300 K

Knoops et al., *Handbook of Crystal Growth, Vol. 3, 2nd edition*, p. 1101 (2015)

Other factors affecting ALD growth of oxides



heteroleptic, i.e. non-identical ligands

Using **steric hindrance** of DMAI precursor to disperse Al-dopant in ZnO more effectively and optimize δ-doping in Al-doped ZnO in superlattice ALD

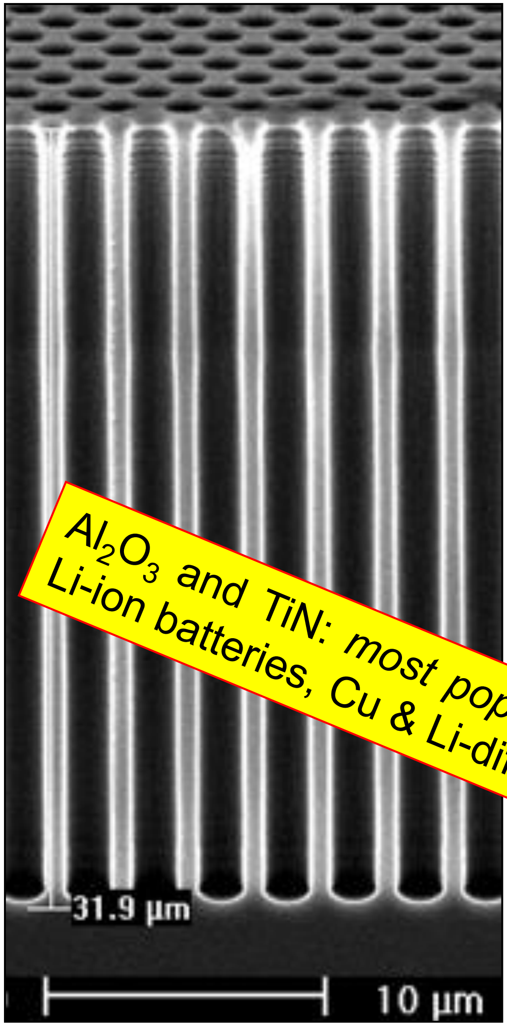
Y. Wu et al., Chem. Mater. **25**, 4619 (2013)

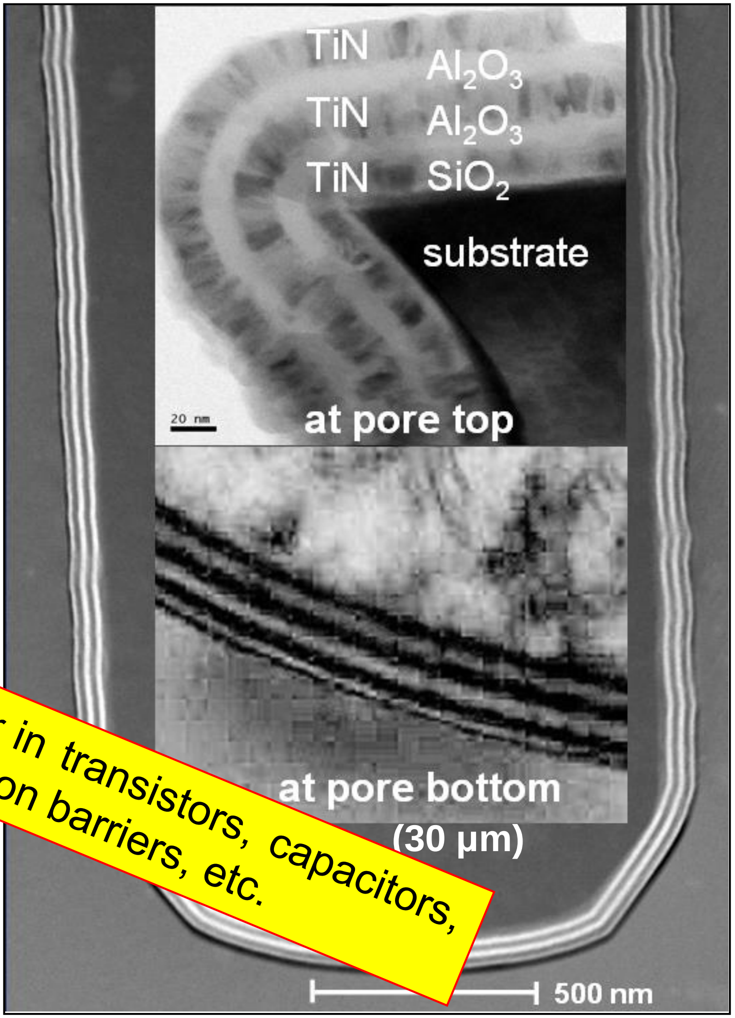
Al_2O_3/TiN in 30x1 µm^2 trenches: uniform, reproducible

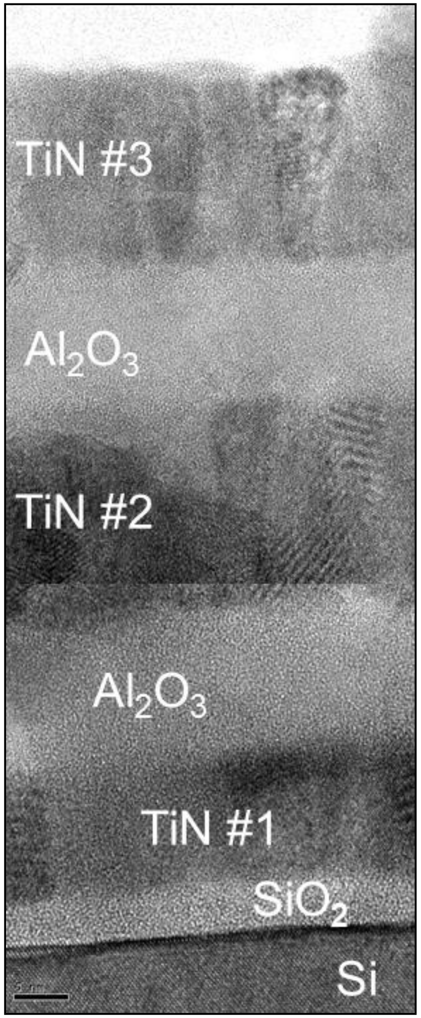
PHILIPS

- Al_2O_3 ALD at 380 °C using TMA and O_3 -cycle time: 3.5 s
- TiN ALD at 400 °C using $TiCl_4$ and NH_3 -cycle time: 1.8 s

NXP founded by Philips







Al_2O_3 and TiN: *most popular* in transistors, capacitors, Li-ion batteries, Cu & Li-diffusion barriers, etc.

JUSUNG ENGINEERING

After • F. Roozeboom et al., ALD 2008, Bruges, Belgium
• IEEE Electron Device Letters **29** 740 (2008)

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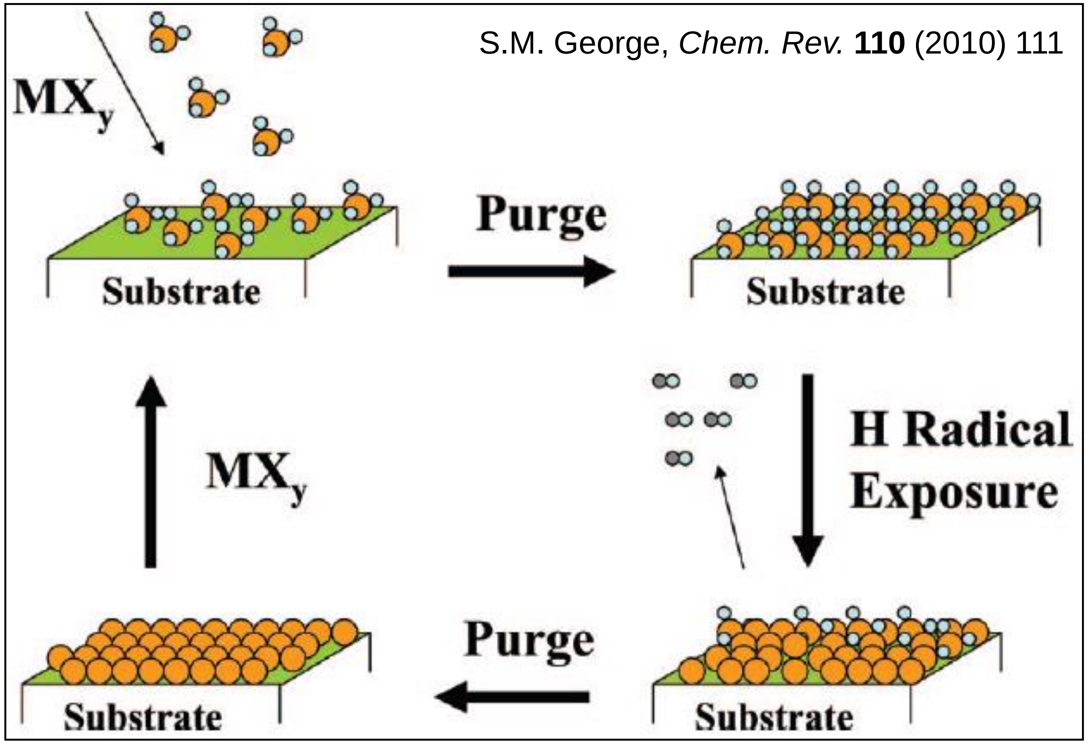
Radical-enhanced ALD by A/B chemistry: H•



Step A: █- + $TaCl_5 \rightarrow$ █-$TaCl_5$

Step B: █-$TaCl_5$ + 5H•$\rightarrow$ █-Ta + HCl$\uparrow$

Application of Ta:

e.g., in Cu-diffusion barrier into Si

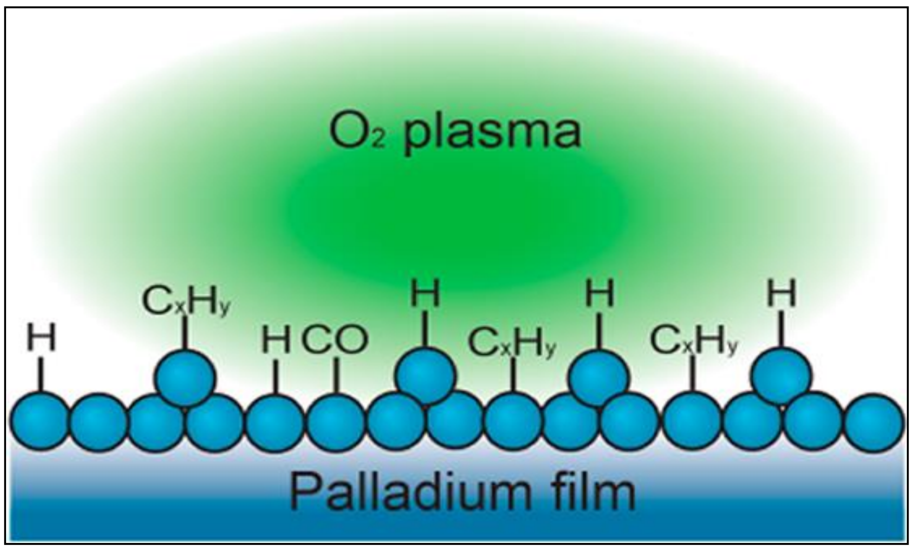
Noble metals with A/B/C chemistry: redox plasmas

Hydrogen reduction chemistry:

***For Pd*:** **A**. ■-PdH + $Pd(hfac)_2$ → ■-Pd-Pd(hfac) + H(hfac) ↑

B. ■-Pd-Pd(hfac) + H_2* → PdH* + H(hfac) ↑

C. **O_2 plasma** pulse required to remove C-contaminants from Pd-surface that remain after the H_2 plasma reduction step:



Insights from gas-phase infrared spectroscopy:

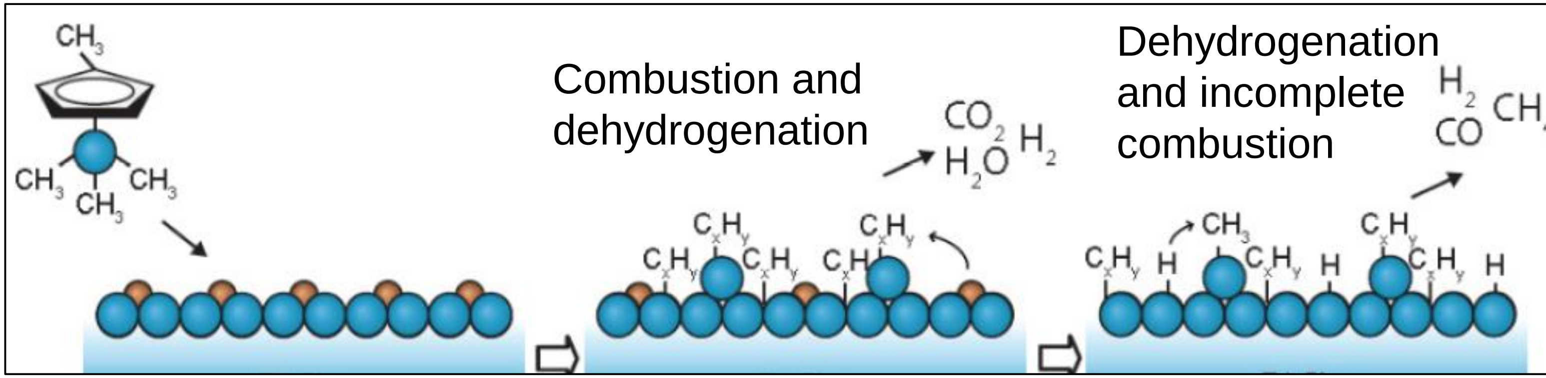
* M.J. Weber, et al., J. Phys. Chem. C, **118**, 8702 (2014)

Applications *e.g.*, heterogeneous catalysis, conductors, ...

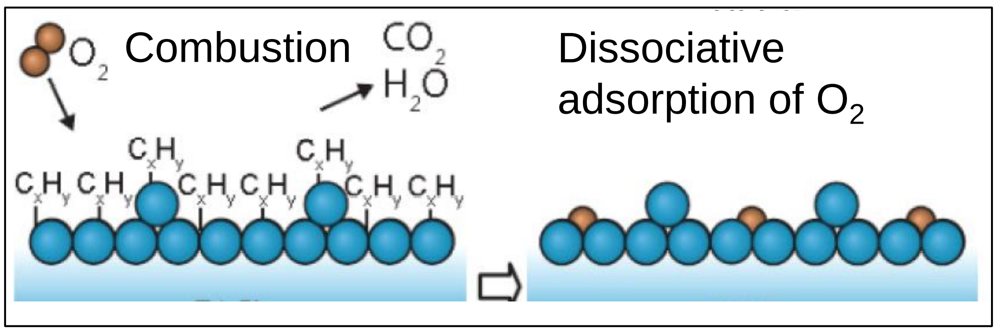
Combustion chemistry:

***For Pt*:**

A.



B.



O_2 plasma pulse required to remove C-contaminants from Pt surface

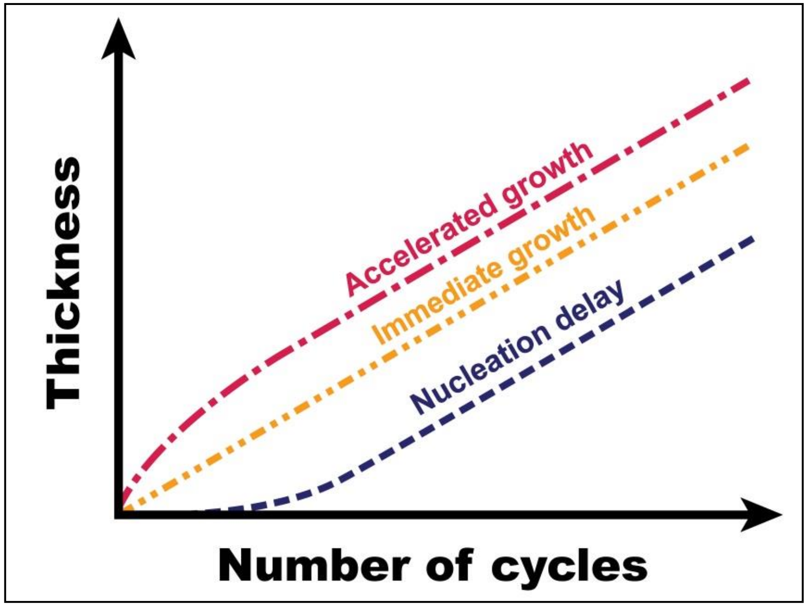
* From: I.J.M. Erkens, AVS 2011 and PhD thesis, Eindhoven, 2014

***Similar for Ru*:**

A. ■-RuO_x + $Ru(Cp)_2 \rightarrow$ ■-RuRu(Cp) + 5 CO_2 + 5/2 H_2O

B. ■-RuRu(Cp) + $y\ O_2 \rightarrow$ ■-RuO_x + 5 CO_2 + 5/2 H_2O

Nucleation and seeding in ALD (e.g., Pt at ~200 ºC)



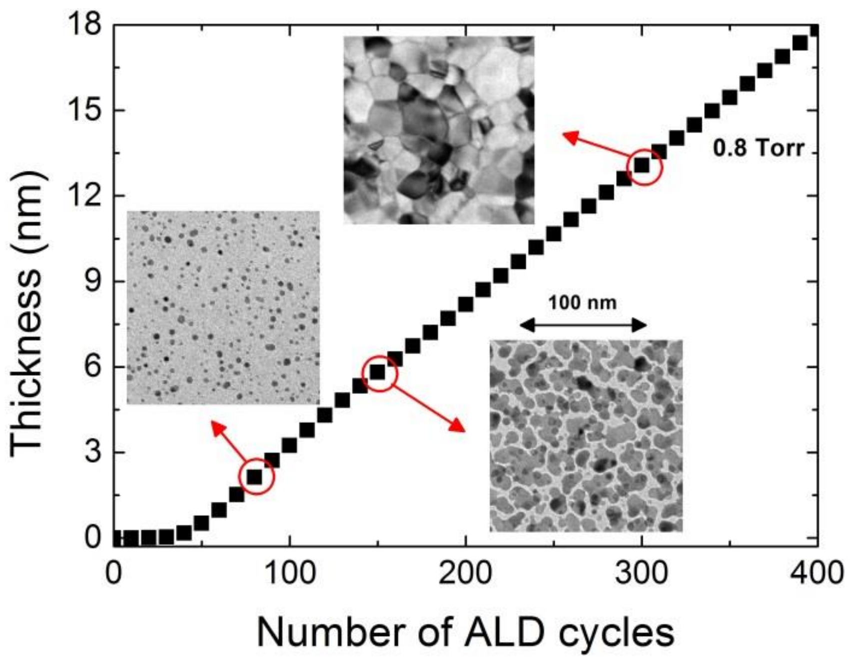
Early growth on SiO_2 substrate: delayed

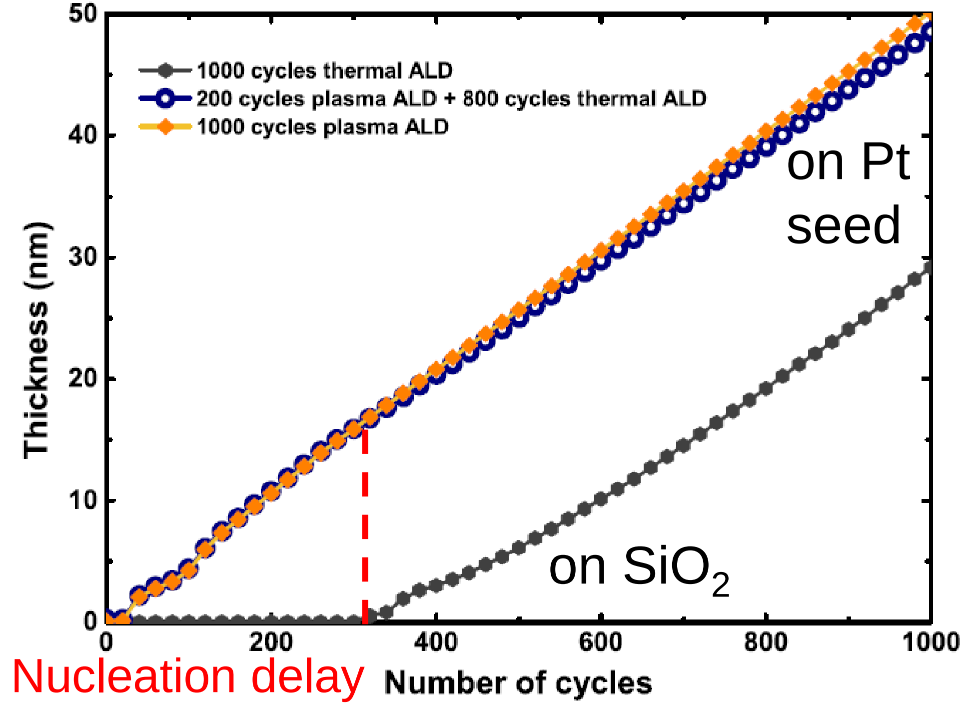
►Nucleating islands (Volmer-Weber growth)

Once seeded (coalescence):

► *Layer-by-layer*: Frank-Van der Merwe

► Delay used for **area-selective growth**

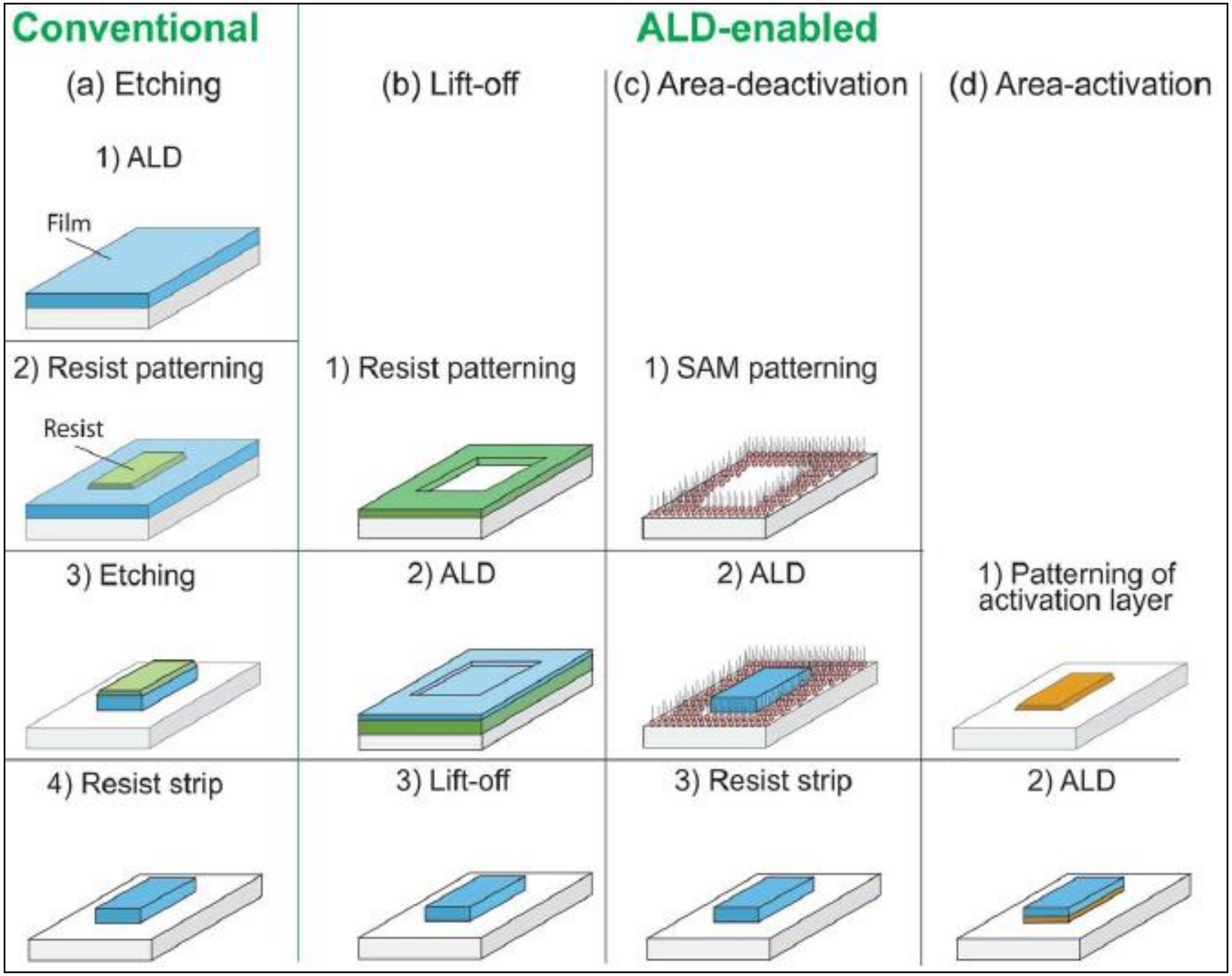




I.J.M. Erkens, et al., J. Chem. Phys., **146**, 052818 (2017)

Patterned ALD: conventional and area-selective

Many patterning and blocking chemistry options



A. Mackus, et al. Nanoscale, **6**, 10941 (2014)

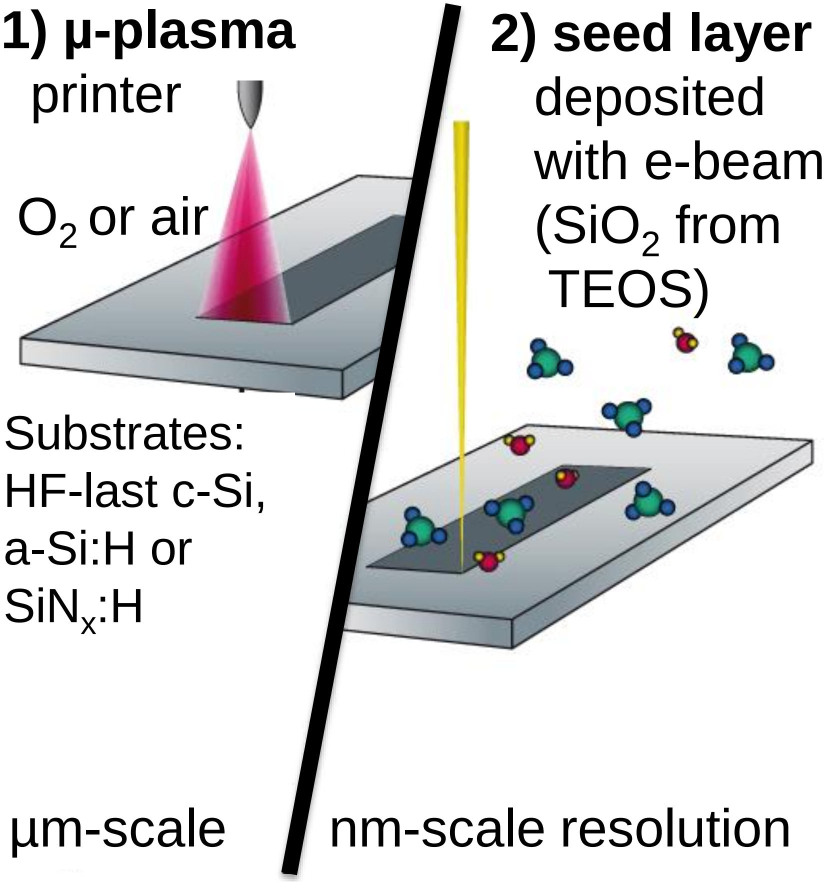
Patterned ALD: conventional and area-selective

Patterning step:

Surface modification by

1) µ-plasma printer

2) seed layer deposited with e-beam (SiO_2 from TEOS)



Substrates: HF-last c-Si, a-Si:H or SiN_x:H

µm-scale

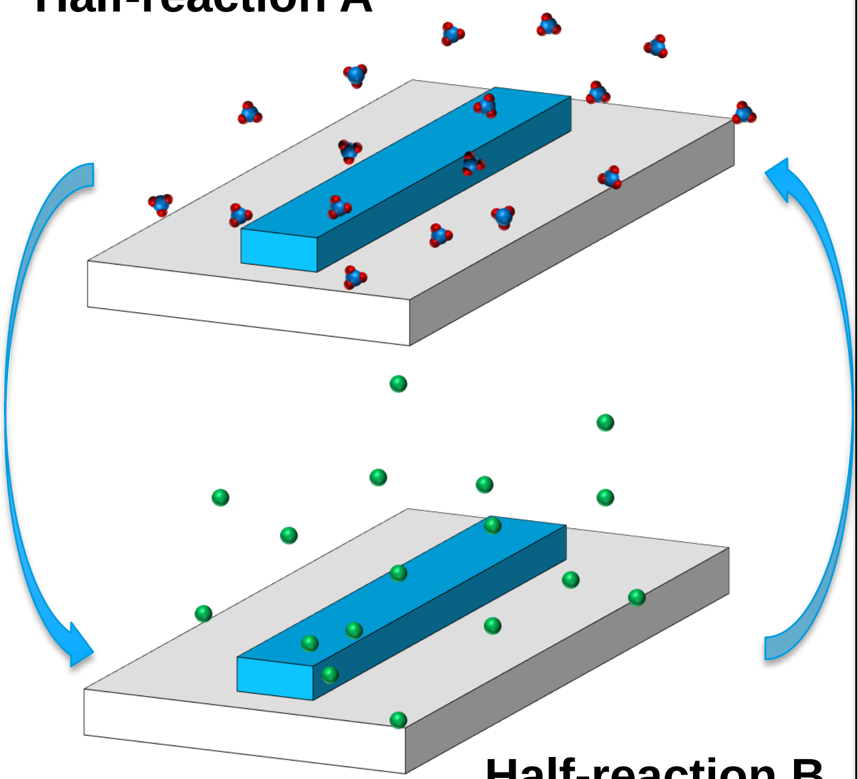
nm-scale resolution

1) A. Mameli, et al., Chem. Mater., **29**, 921 (2017)

2) A. Mameli, et al., ACS Nano; doi 10.1021/acsnano.7b04701

Building step:

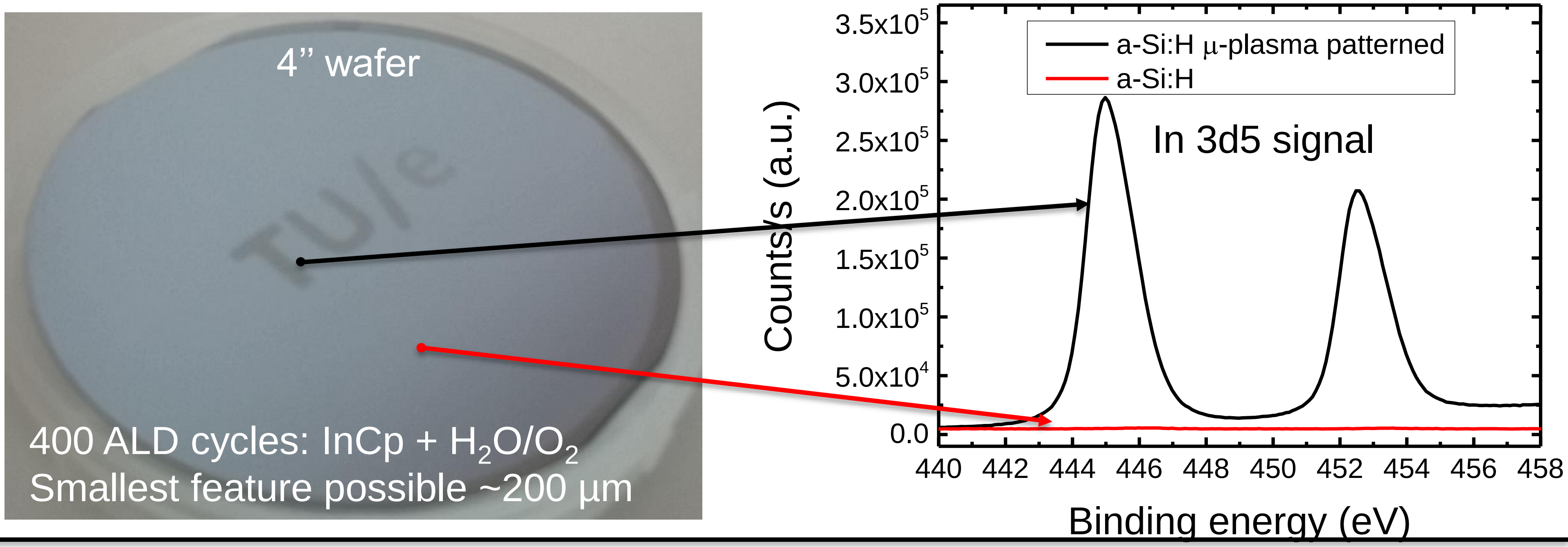
Area-selective ALD

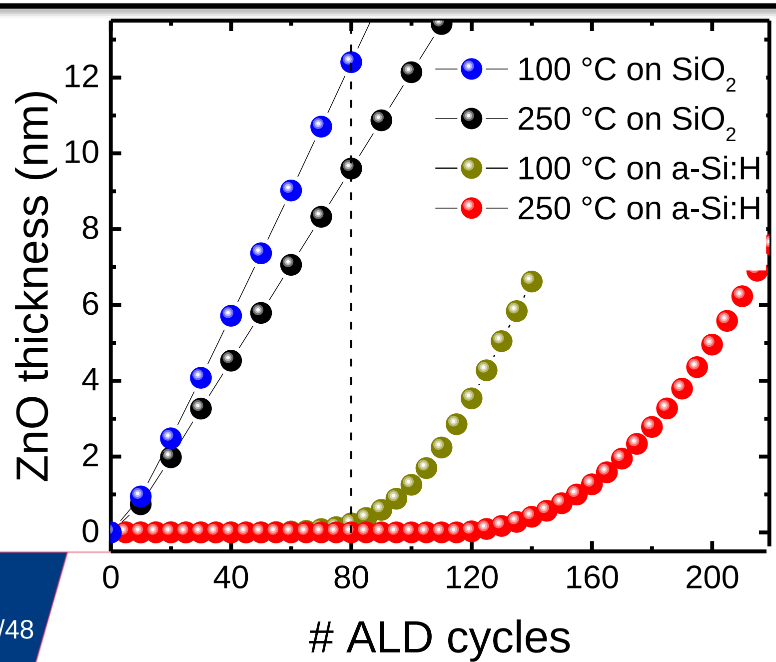


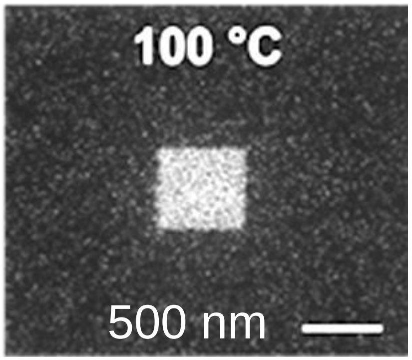
High-quality ALD materials

▶ *Direct-write* ALD of metal oxide at both micro and nanoscale

Direct-write ALD of In_2O_3:H and ZnO





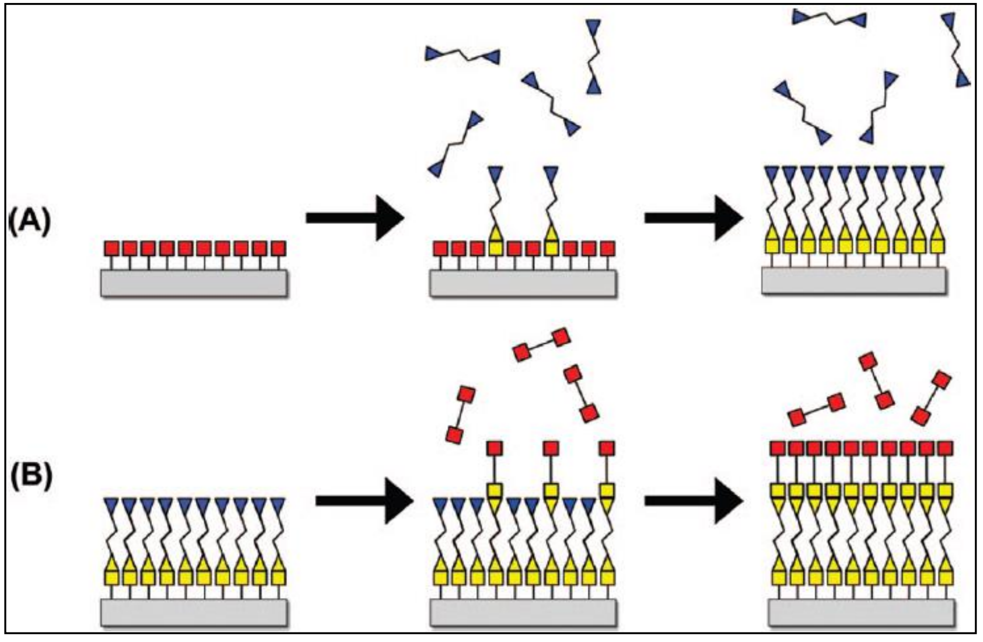


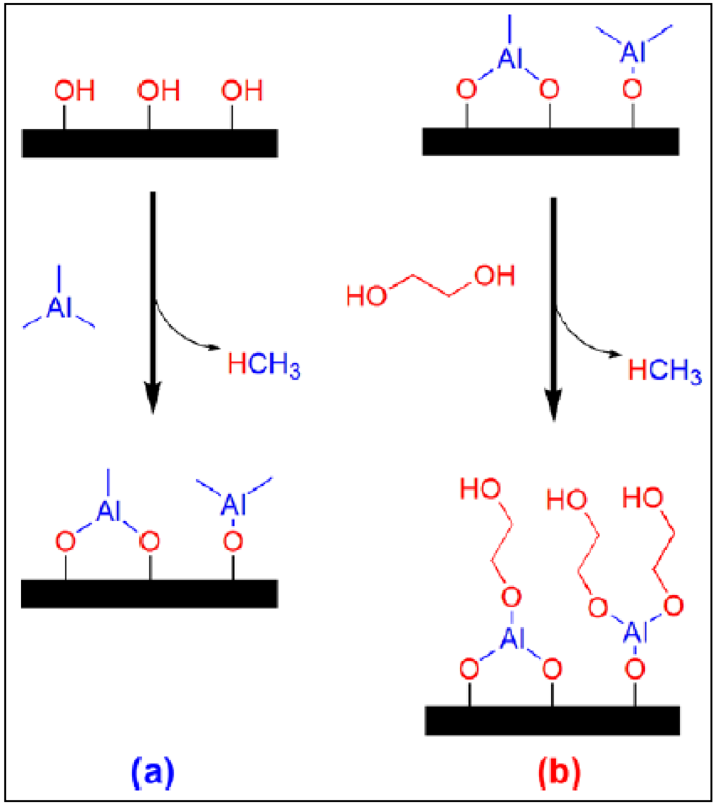
80 ALD cycles: DEZ + H_2O
Smallest feature possible ~20 nm

A. Mameli, et al., Chem. Mater., **29**, 921 (2017)
A. Mameli, et al., ACS Nano; doi 10.1021/acsnano.7b04701

Molecular Layer Deposition, principle and examples

- Same self-limiting surface chemistry as in conventional ALD, but new hybrid chemistry (organic/inorganic laminates)
- Multifunctional applications: thermo/mechanical, optical (e.g. fluorescent), diffusion barriers, …



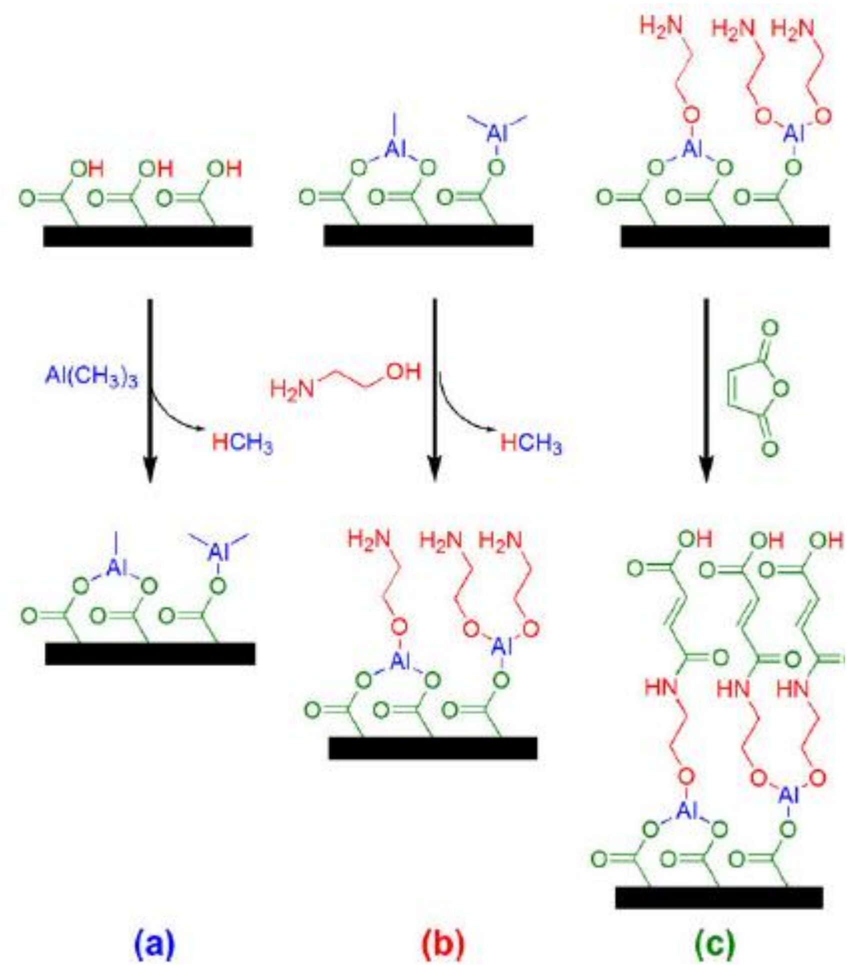


Aluminum alkoxide (alucone) from TMA and ethylene glycol

 Y. Du, S.M. George, *J. Phys. Chem. C.*, **111**, 8509 (2007)

D.C. Miller et al., Acta Materialia **57** 5083 (2009)

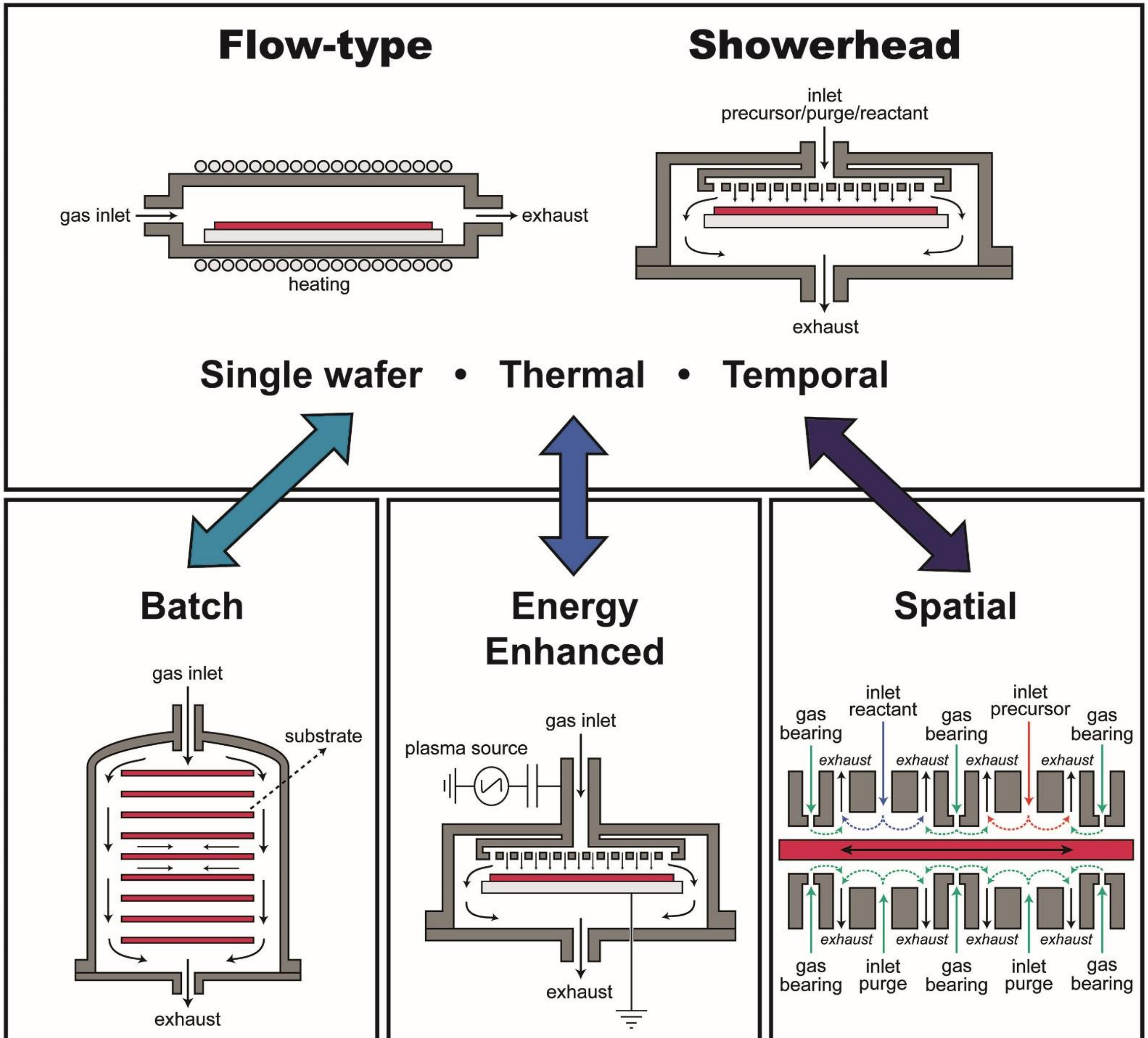
Molecular Layer Deposition, principle and examples



‘ABC’ type ALD of ‘alucone’ from (a) TMA,
(b) ethanolamine and (c) maleic anhydride

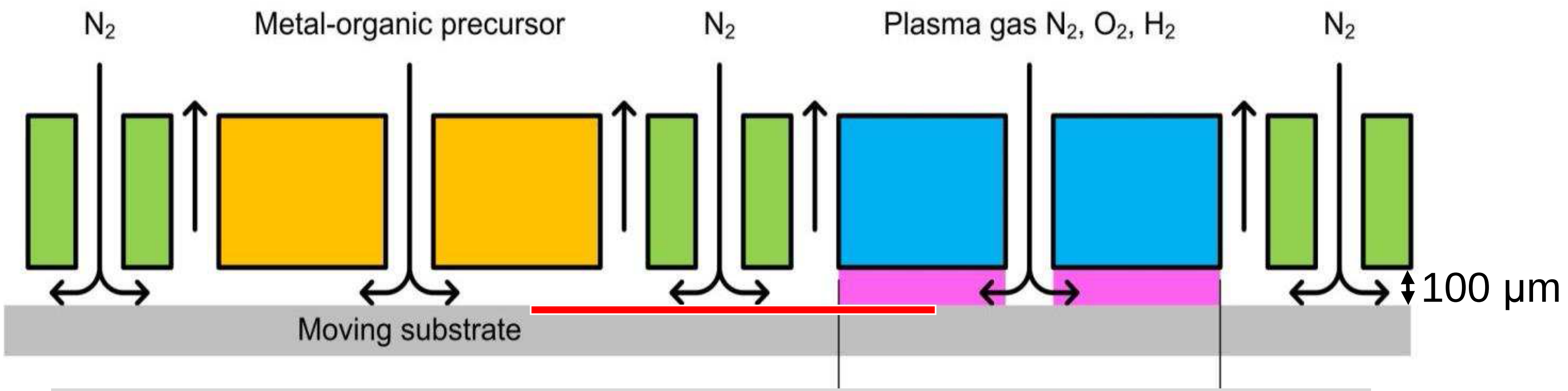
Y. Du, S.M. George, *J. Phys. Chem. C.*, **111**, 8509 (2007)

Reactor designs



H. Knoops, et al., *Handbook of Crystal Growth, Vol. 3, 2nd edition*, p. 1101 (2015)

Atomic Layer Deposition from time- to space-divided



- Spatial separation of half-reactions, instead of time-separated
- Gas bearing gap: ~ 20 µm, providing excellent diffusion barrier
- No deposition on reactor walls
- Small reactor volume → high precursor yield
- Atmospheric pressure
- No purge + 10-100 ms reaction timescales → high deposition rate
- Control of composition and thickness at atomic scale
- Large area uniformity and excellent conformality
- Deposition rates up to nm/s: **hours becoming minutes**

P. Poodt et al. J. Vac. Sc. and Technol. **30,** 010802 (2012)

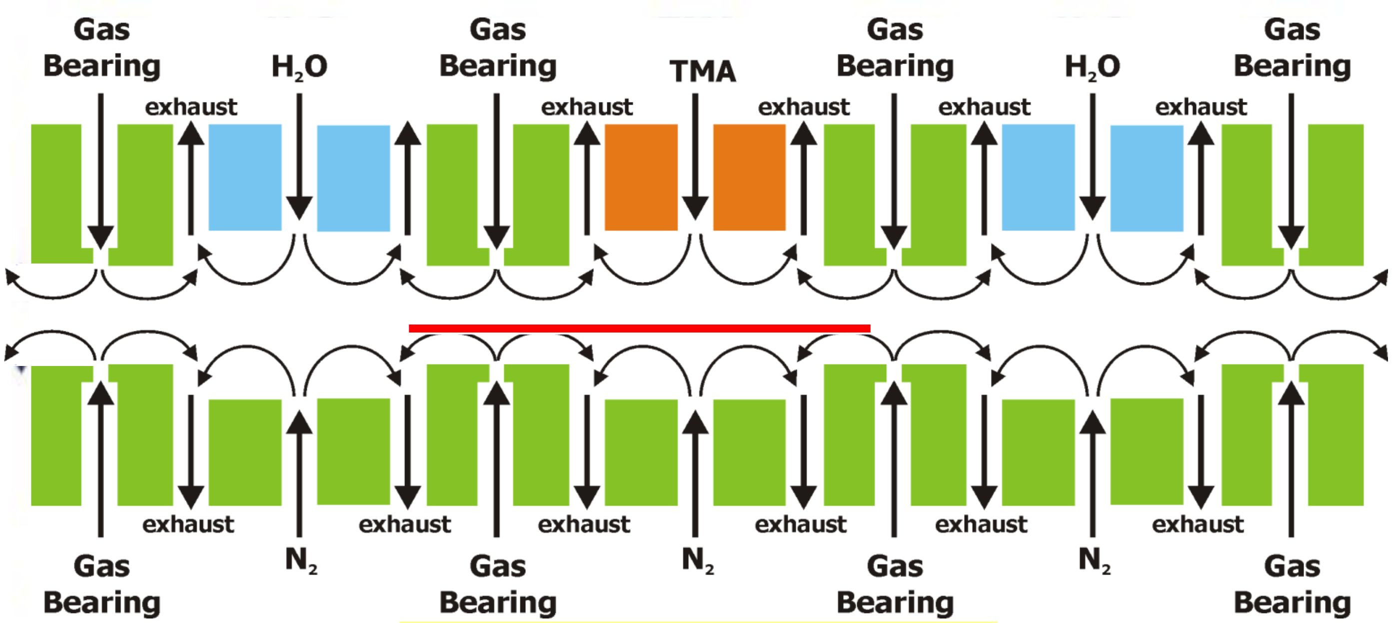
WO2010024671, 27 Aug 2008

Atomic Layer Deposition from time- to space-divided

Spatial ALD commercialized by TNO (and others) for solar

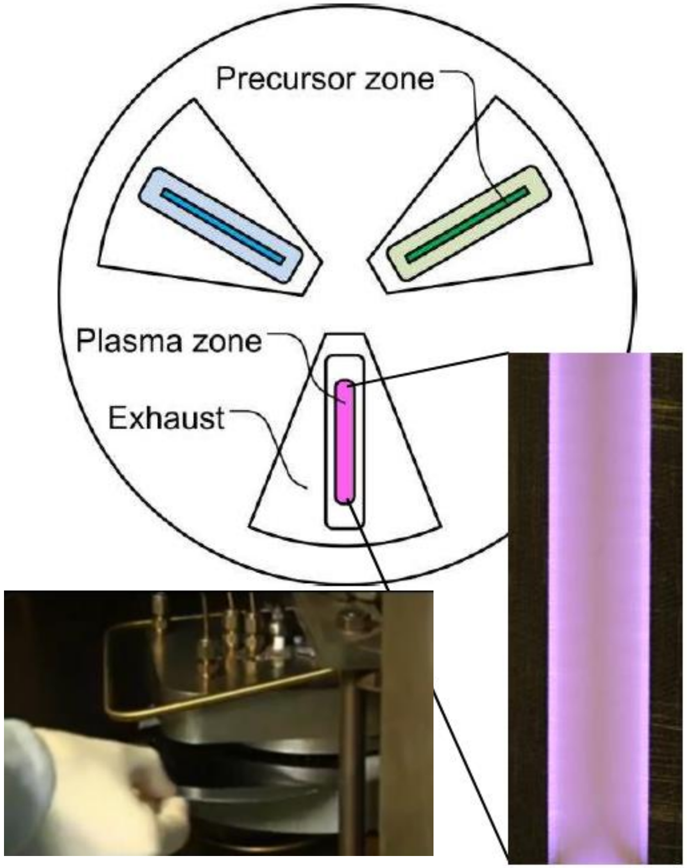
Development tool for 100 wafers/ h

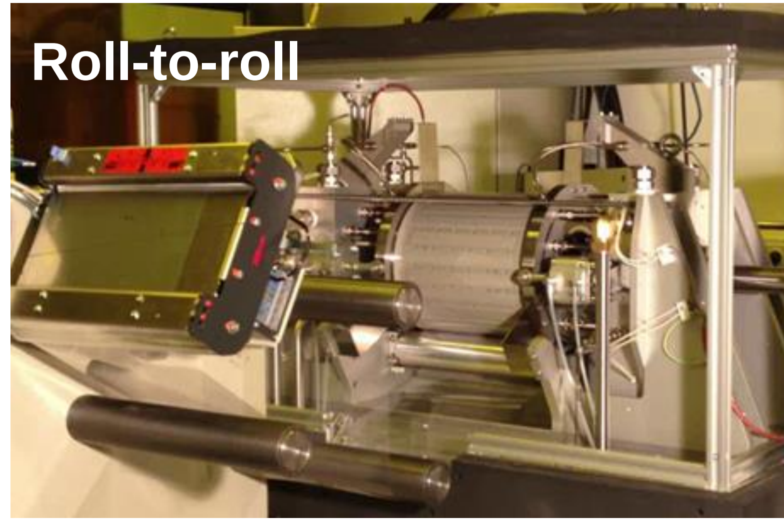
Production tool for 10 nm Al_2O_3
~ 3600 wafers/hr

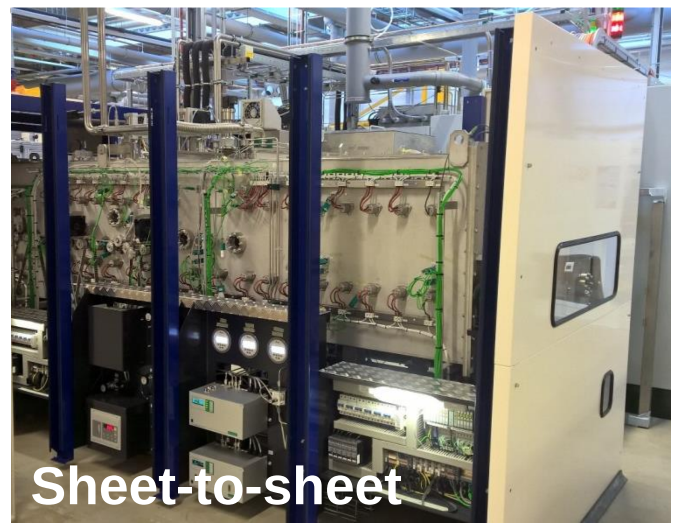


http://www.solaytec.com/

Spatial ALD from lab-scale to large-area



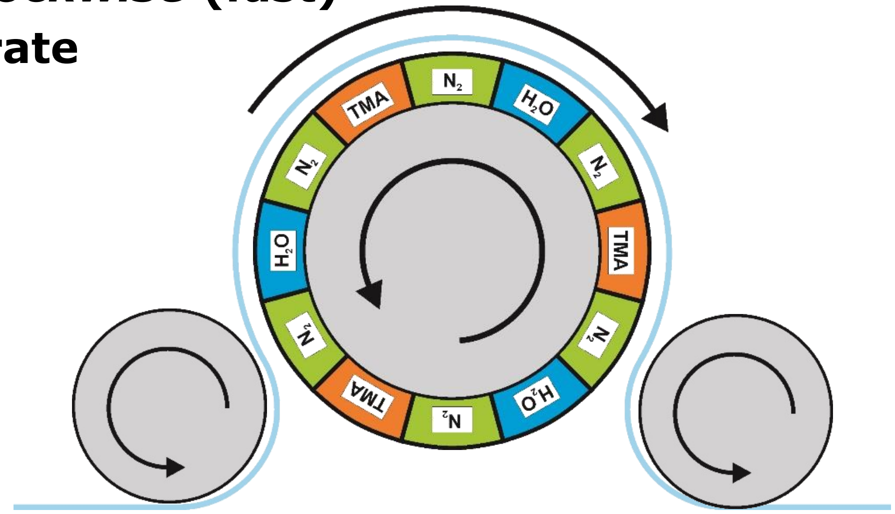




Materials: TiO_2, ZrO_2, HfO_2, SiO_2, ZnO, Al_2O_3, Zn(O,S), Al:ZnO, InGaZnO, ZnSnO, In_2O_3, $H{:}In_2O_3$, Ag, MLD (organics)

Roll-to-roll spatial ALD: TNO approach

- **Center part: foil surrounding a drum with several reaction zones and gas-bearings**
- **Foil moves *clockwise* (slowly)**
- **Fast ALD injector rotates *counter-clockwise* (fast)**
- **Combination gives high deposition rate**



US 9,297,077, March 2016
US 9,567,671, Feb. 2017

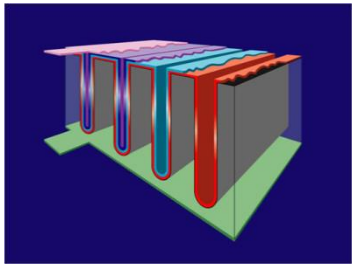
- **No mechanical contact between drum and foil**
- **Flexibility in foil and layer thickness**
- **Compact**

Further potential of Spatial ALD industrialization

1. **High quality and uniformity over large areas**
2. **Atmospheric pressure, high throughput, high performance → low cost!**
3. **Freedom in substrate: rigid and flexible**

Application areas include:

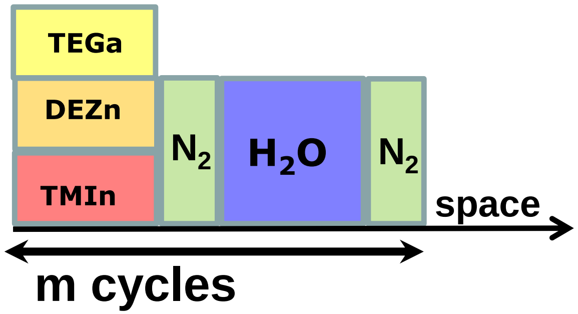
- **OLEDs**
  - Encapsulation
- **Display**
  - Semiconductor and dielectric in TFTs
- **Photovoltaics**
  - Transparent conductors, active layers, encapsulation, passivation
- **Thin-film batteries**
  - 3D integration, solid state electrolyte, electrodes, passivation
- **Microelectronics**
  - ALD for 300 - 450 mm

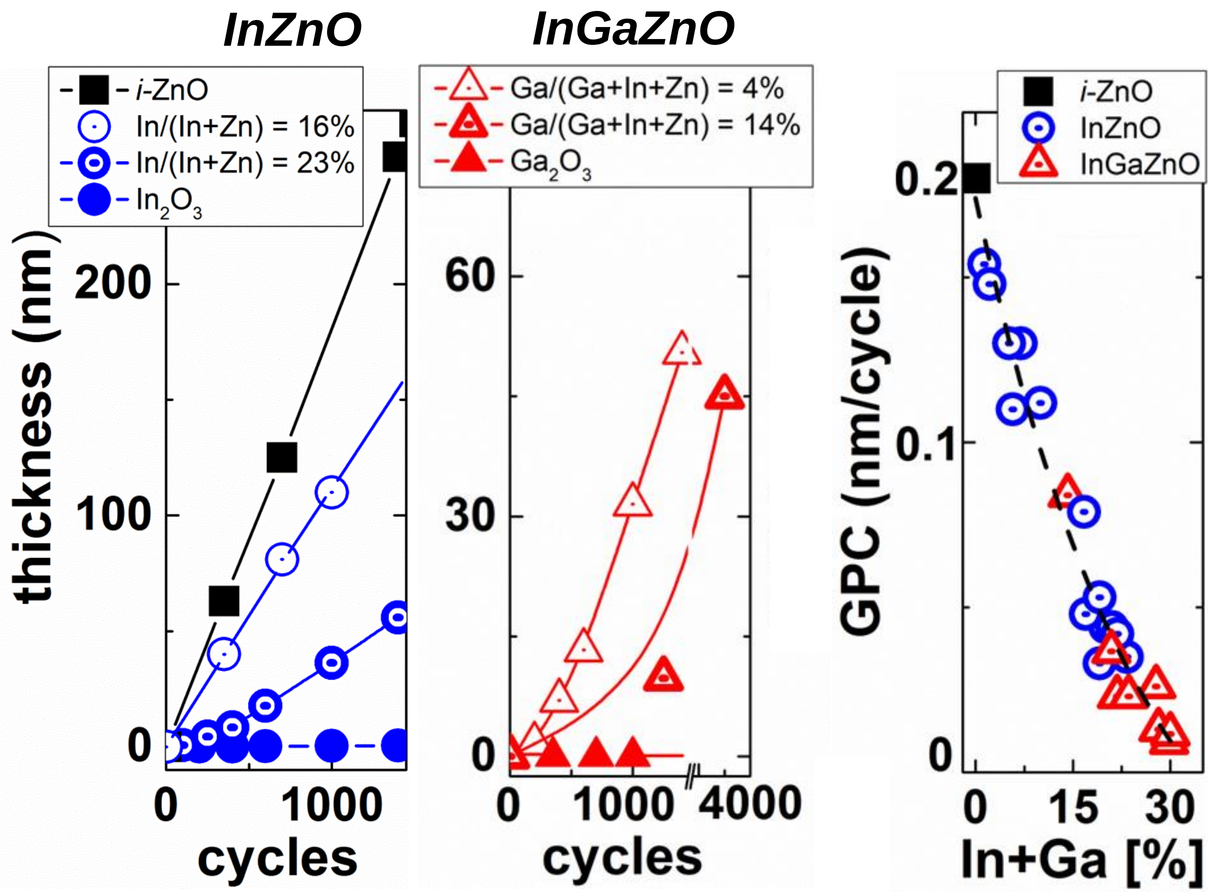


Amorphous oxide semiconductors

Spatial ALD of InGaZnO for TFT

Nucleation and growth

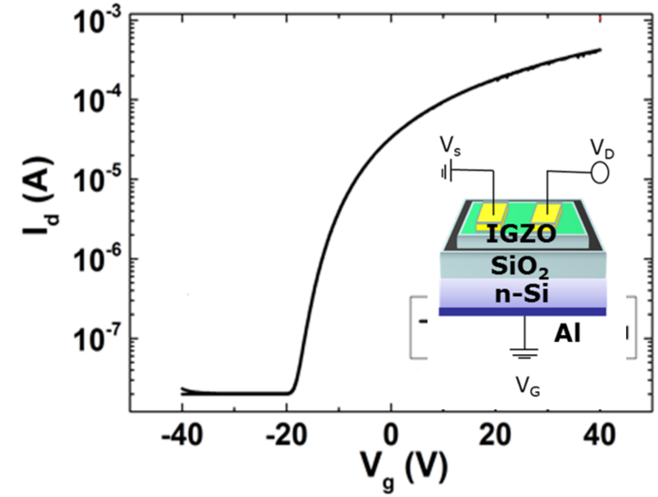


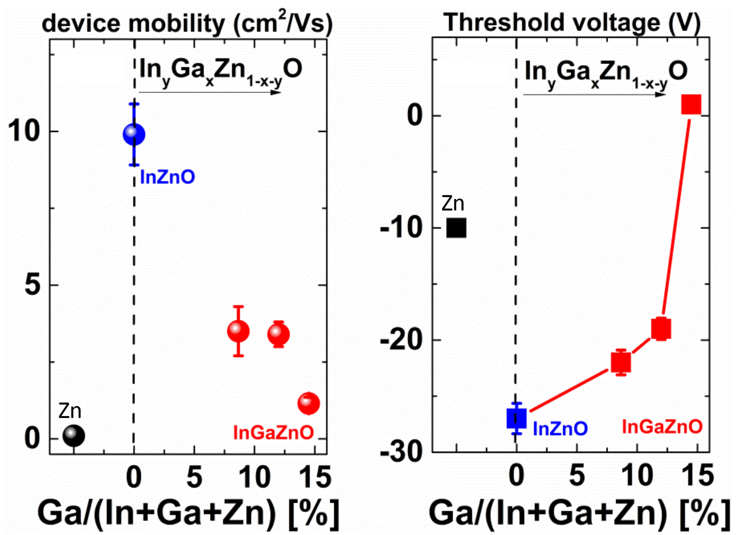


Amorphous oxide semiconductors
Spatial ALD of InGaZnO for TFT

- **Method developed for making multicomponent oxides with spatial ALD**
  - No delta-doping/nanolaminates: uniform composition
  - Accurate control of composition and thickness

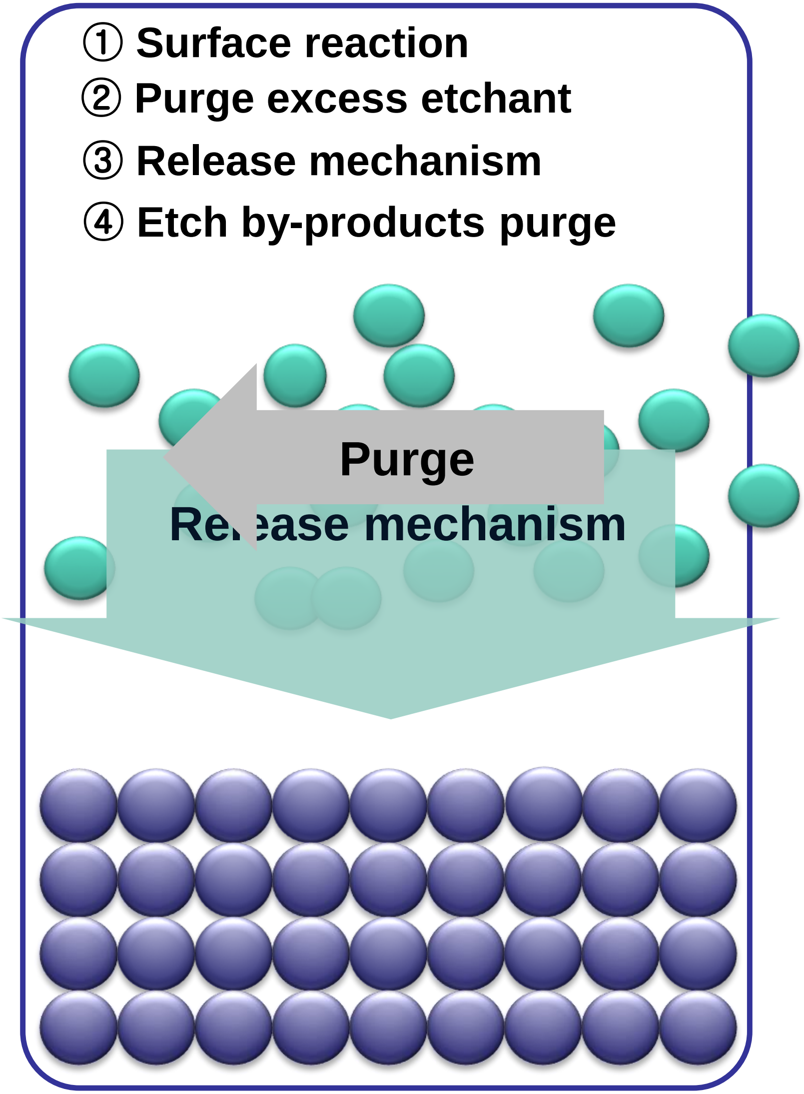
- **Example: amorphous InZnO (IZO) and InGaZnO (IGZO)**
  - Amorphous semiconductors, used in OLED display backplanes TFT circuits
  - First TFTs made with S-ALD IZO and IGZO (Device mobility up to **30 cm²/Vs**)

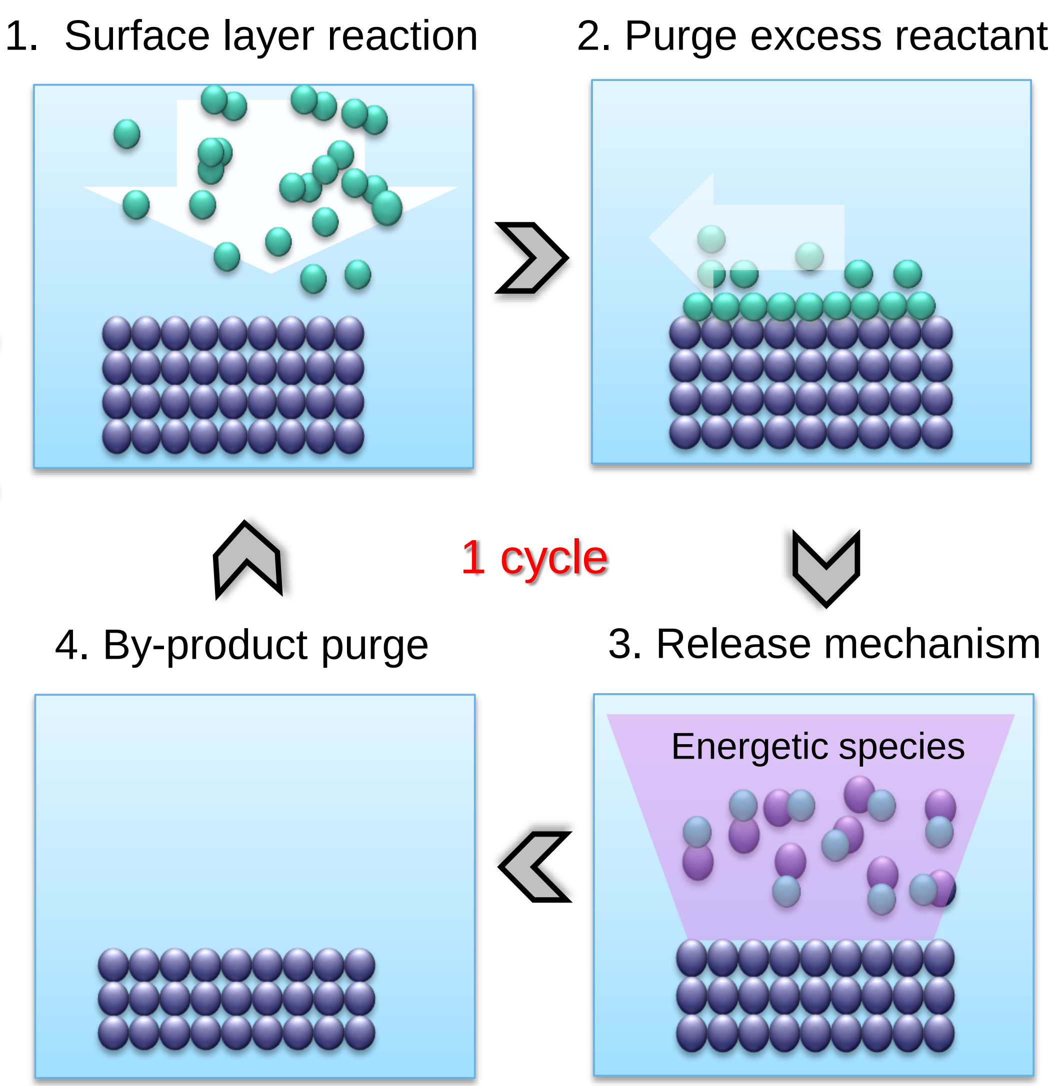




Atomic Layer Etching concept

'Reverse ALD", "digital etching" needed for *high-fidelity* etching

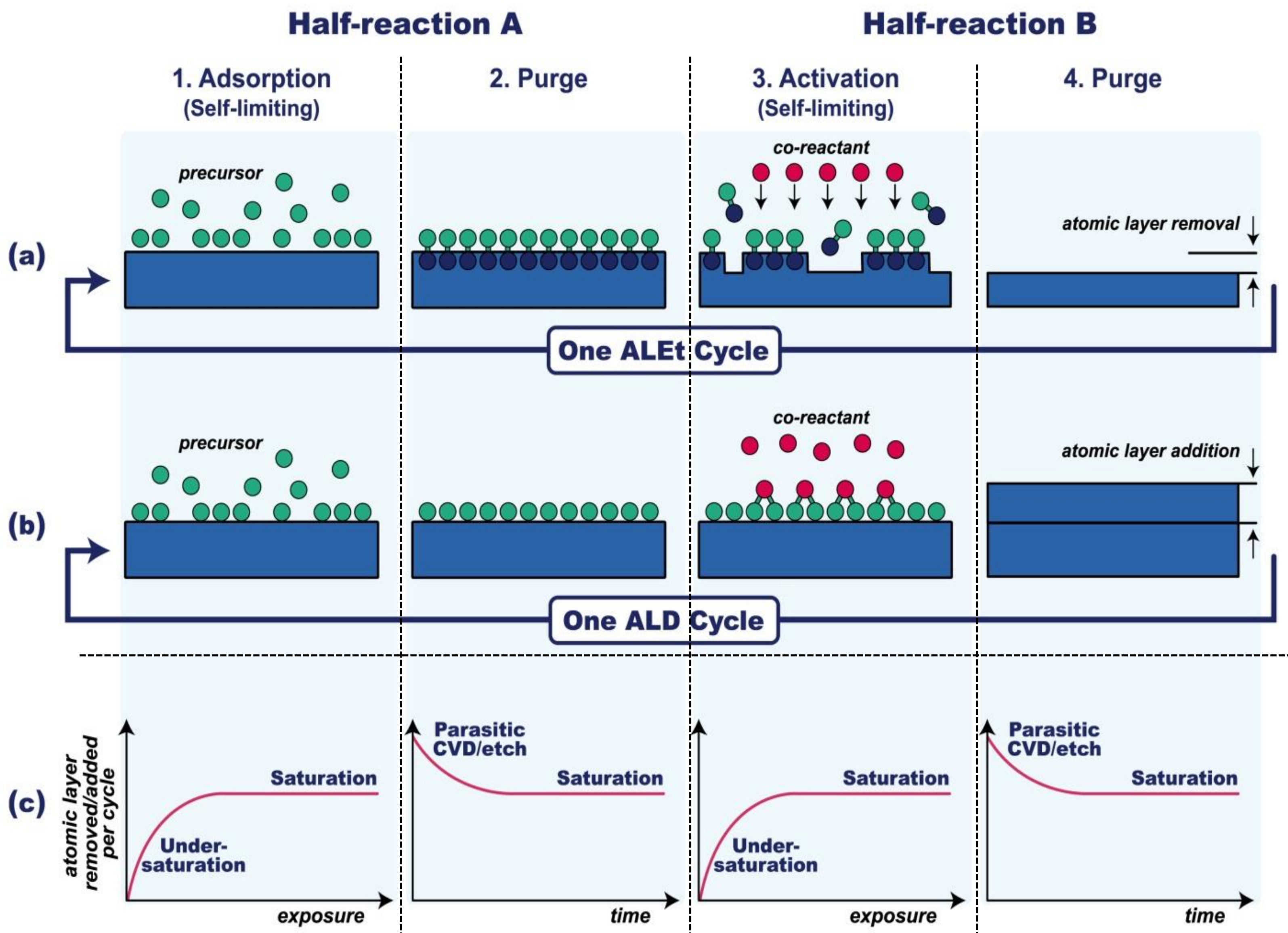




Source: *E. Joseph et al.(IBM)*

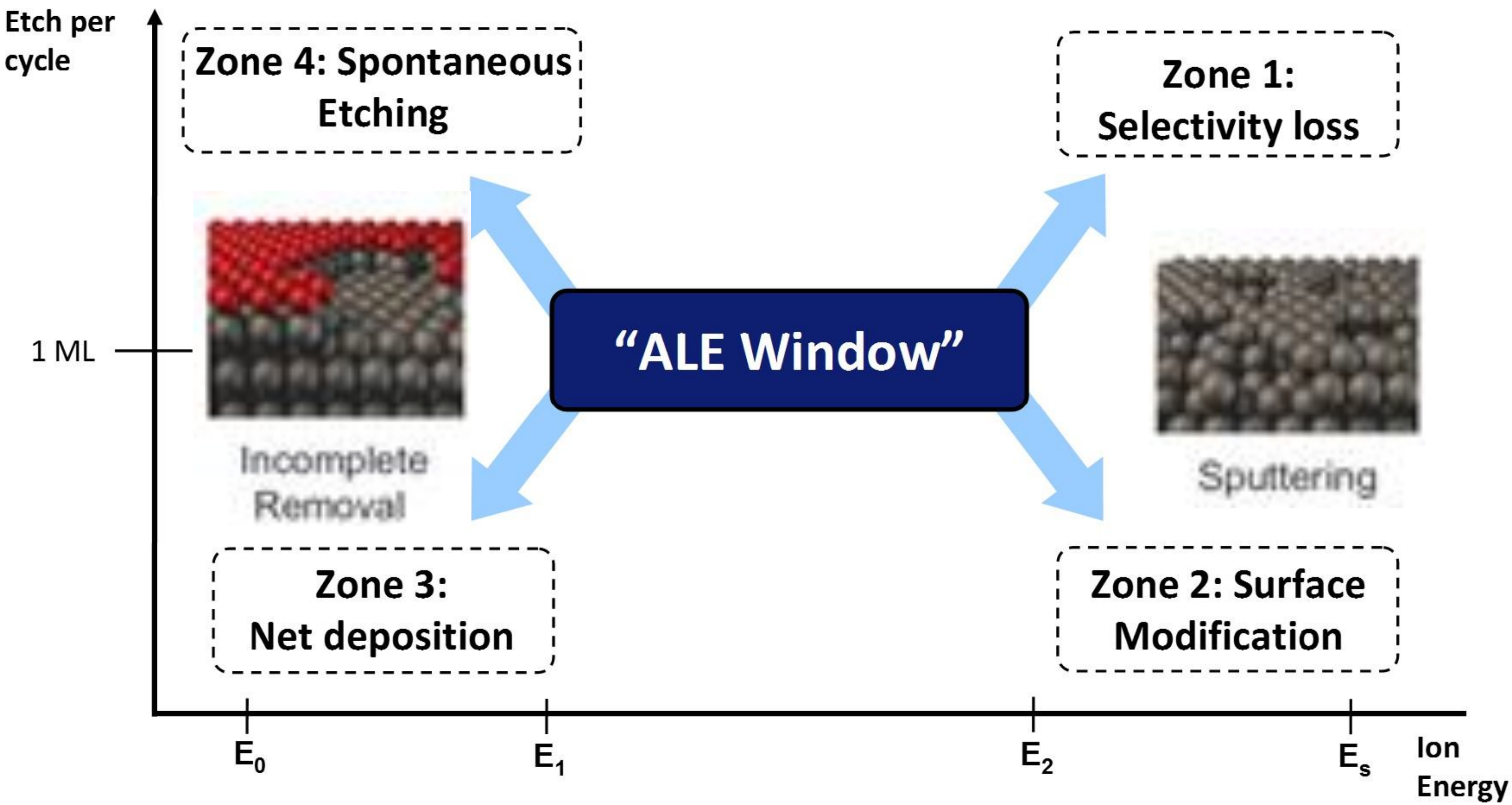
Atomic Layer Etching (ALE)

'Reverse ALD", "digital etching" needed for *high-fidelity* etching



From: T. Faraz et al., J. Solid State Sci. Technol. **4**, N5023 (2015)

PE-ALE Process space

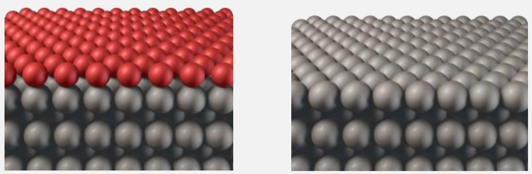
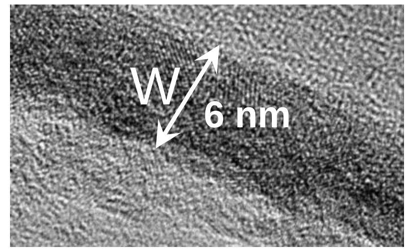
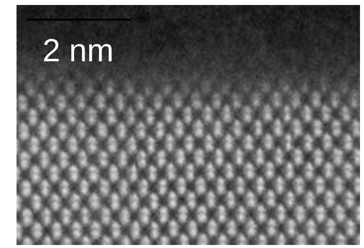
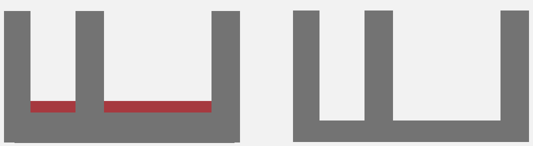
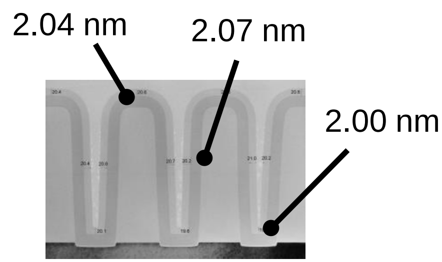
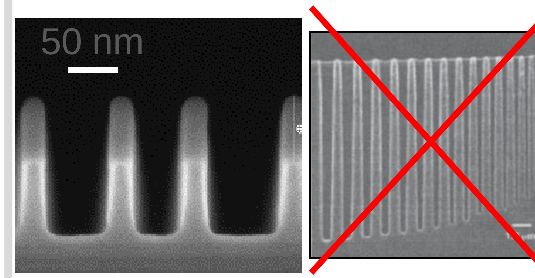
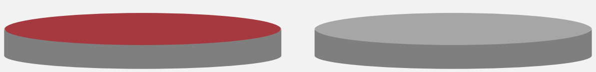
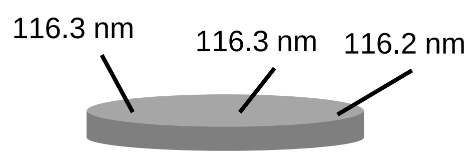
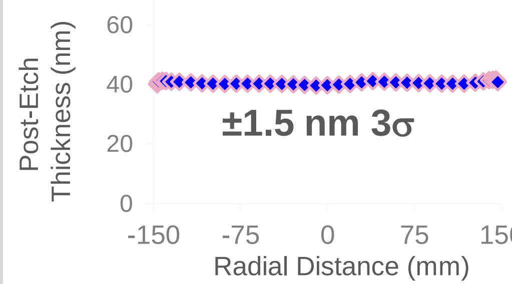


ALE "window" driven by:

- Energy of desorption process
- Plasma chemistry and radical physi-/chemisorption

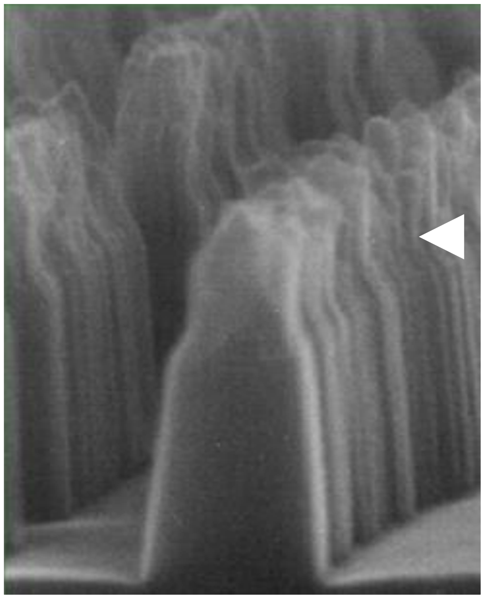
Source:
- E. Joseph et al., IBM
- K. Kenerik, Lam Research

Distinct benefits for ALD and ALE, today

	Mechanism	Example Benefits - ALD	Example Benefits - ALE
Surface	**Smooth** 		
Feature	**Aspect ratio independence** 		
Wafer	**Uniform** 	 **± 0.15 % range**	

Source T. Lill et al. (Lam Research)

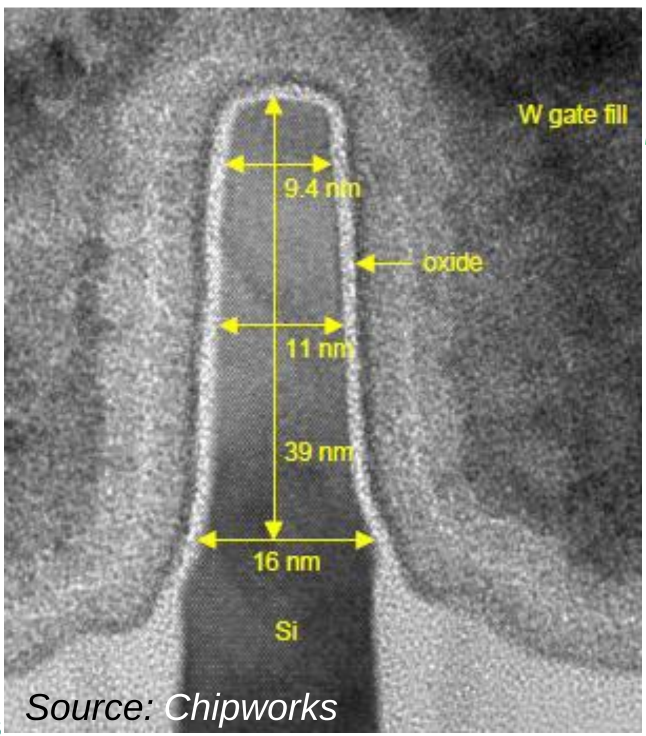
Challenge in FinFETs



line edge roughness

non-ideal: redeposition in fin etch

ALE + ALD
for better shape control
steps,
like these



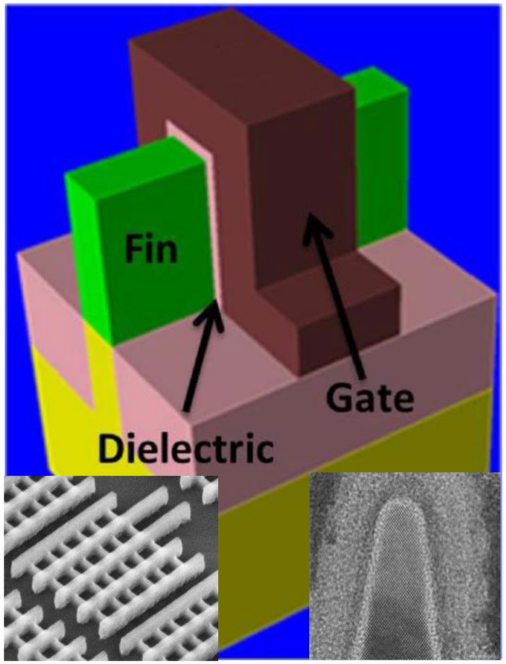
Source: Chipworks

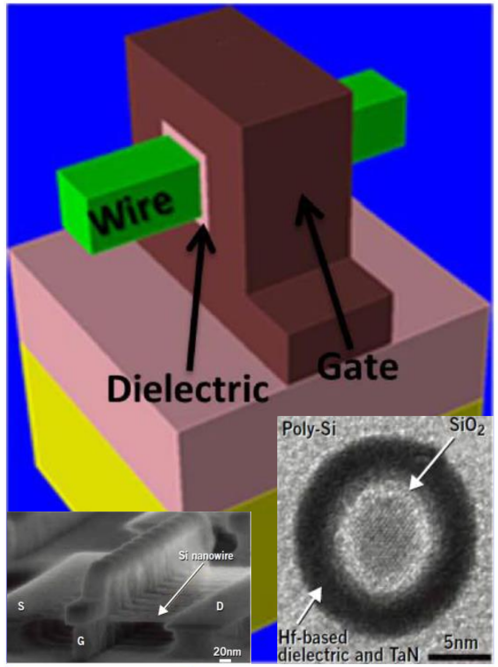
Intel’s 14 nm Broadwell FinFET

- Improved Fin width shape control (V_{th} less sensitive to width variation)
- With ALE best preservation of crystallinity
- Ideal surface structure to deposit gate oxide (minimal interface defects)

State-of-the-art ALD fill /coating in logic and memory

3D transistor topographies

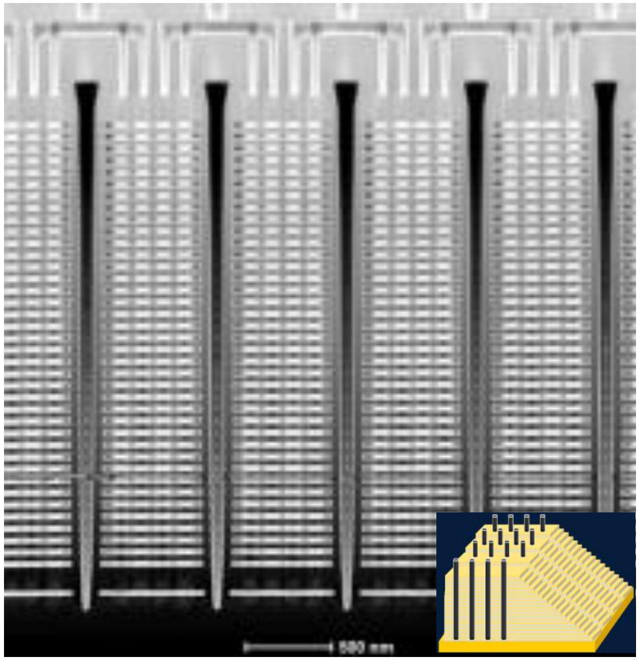




3D FinFET | Gate-All-Around transistor

Intel: ECS J. Sol. State Sci. and Technol., ***4*** *N5005 (2015)*

High Aspect Ratio 3D memories



3D NAND Flash memory

Source: Chipworks

Current technology requirements for 3D-IC:

Deposition:

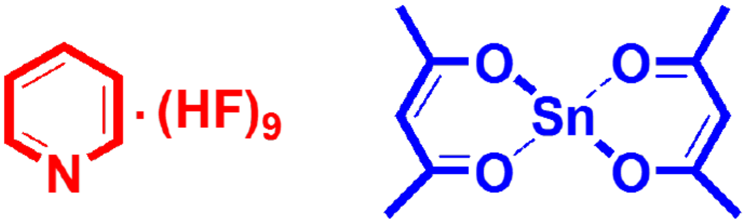
- Precise process control
- Layer thickness uniformity
- Step conformality
- Low temperature
- No damage (by plasma, ...)

Extra for Etching:

- Materials selectivity
- No Aspect Ratio Dependent Etching
- Control over etch directionality (isotropic and anisotropic etch)
- No ellipticity in holes

Atomic Layer Etching: Selectivity of Thermal Al_2O_3

Isotropic ALE
("reverse ALD")

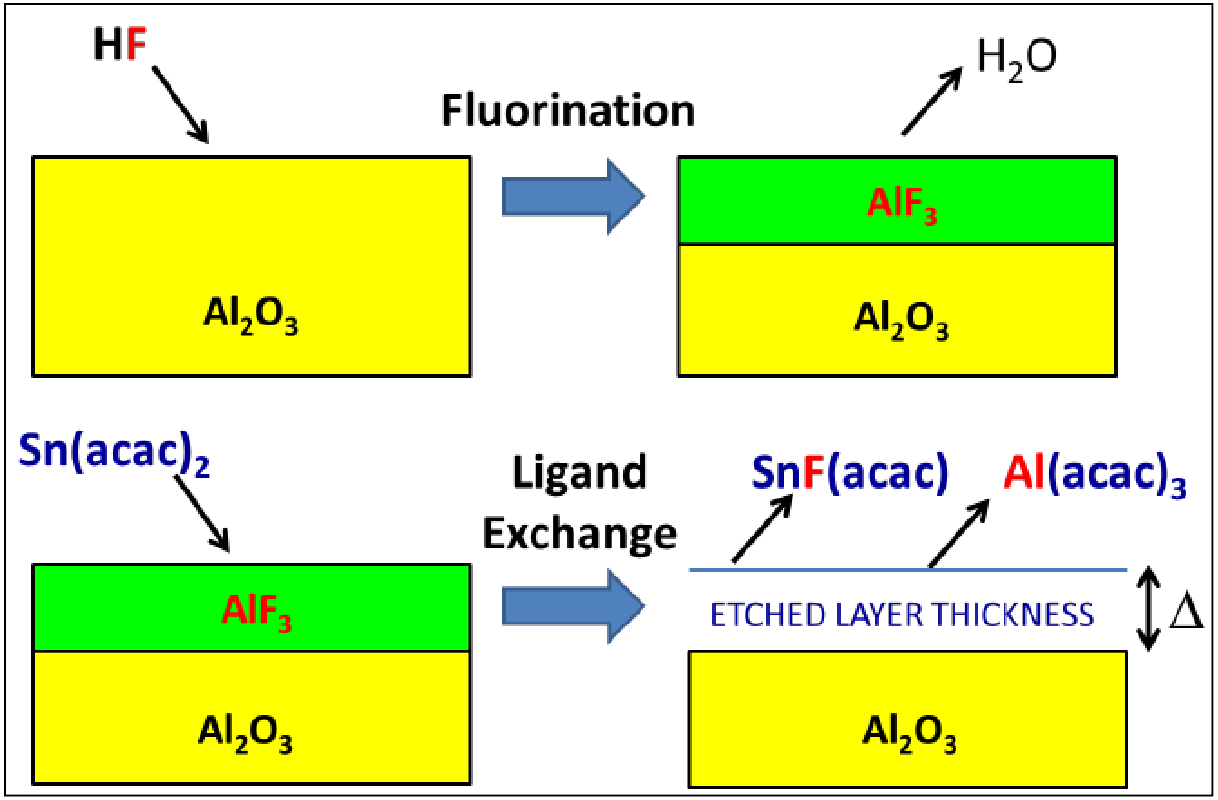


HF-Pyridine

Sn(acac)2

Fluorination Reaction

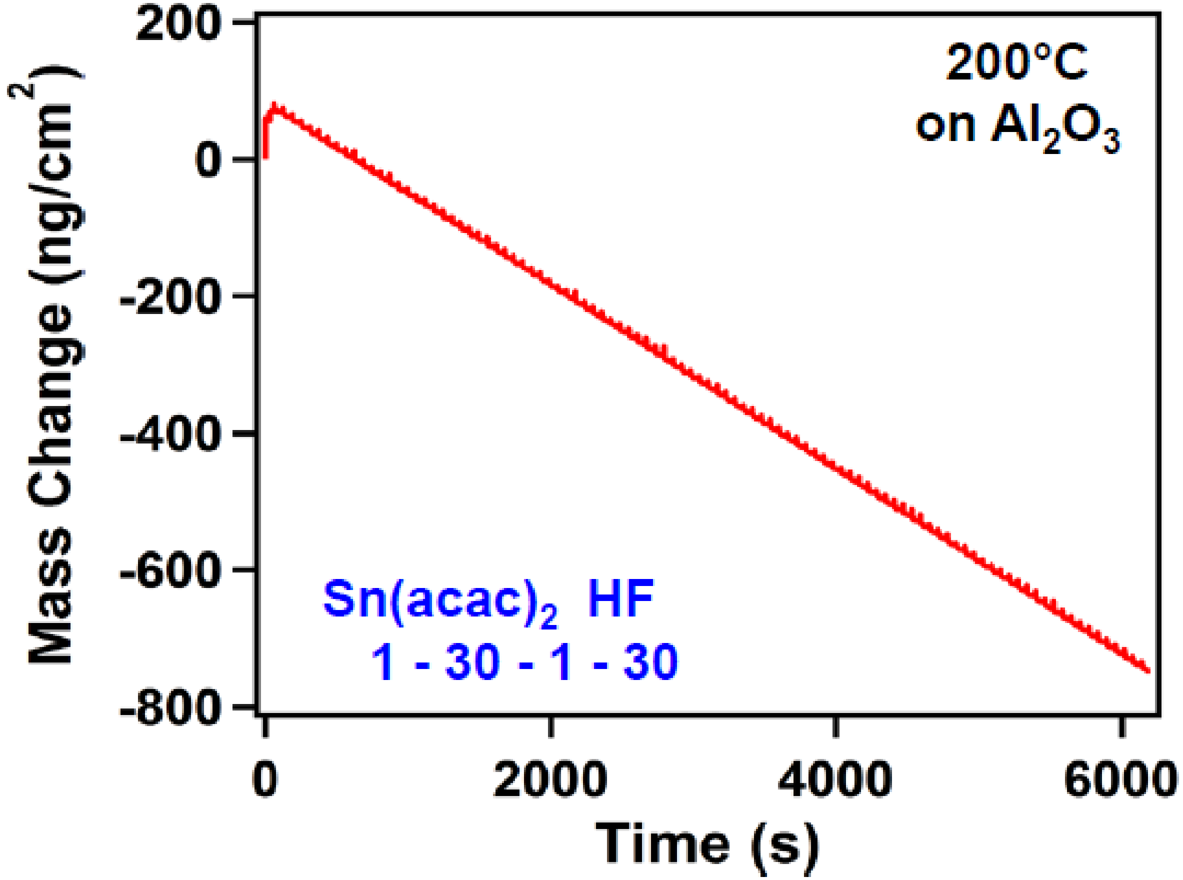
Ligand-Exchange Reaction



Source: S. George group

Lee *et al.*, ACS Nano **9**, 2061 (2015)

Thermal Al_2O_3 ALE: linear mass loss upon cycling $Sn(acac)_2$ and HF



Source: S. George group

Lee *et al*., ACS Nano **9**, 2061 (2015); J. Solid State Sci. Technol. **4**, N5013 (2015)

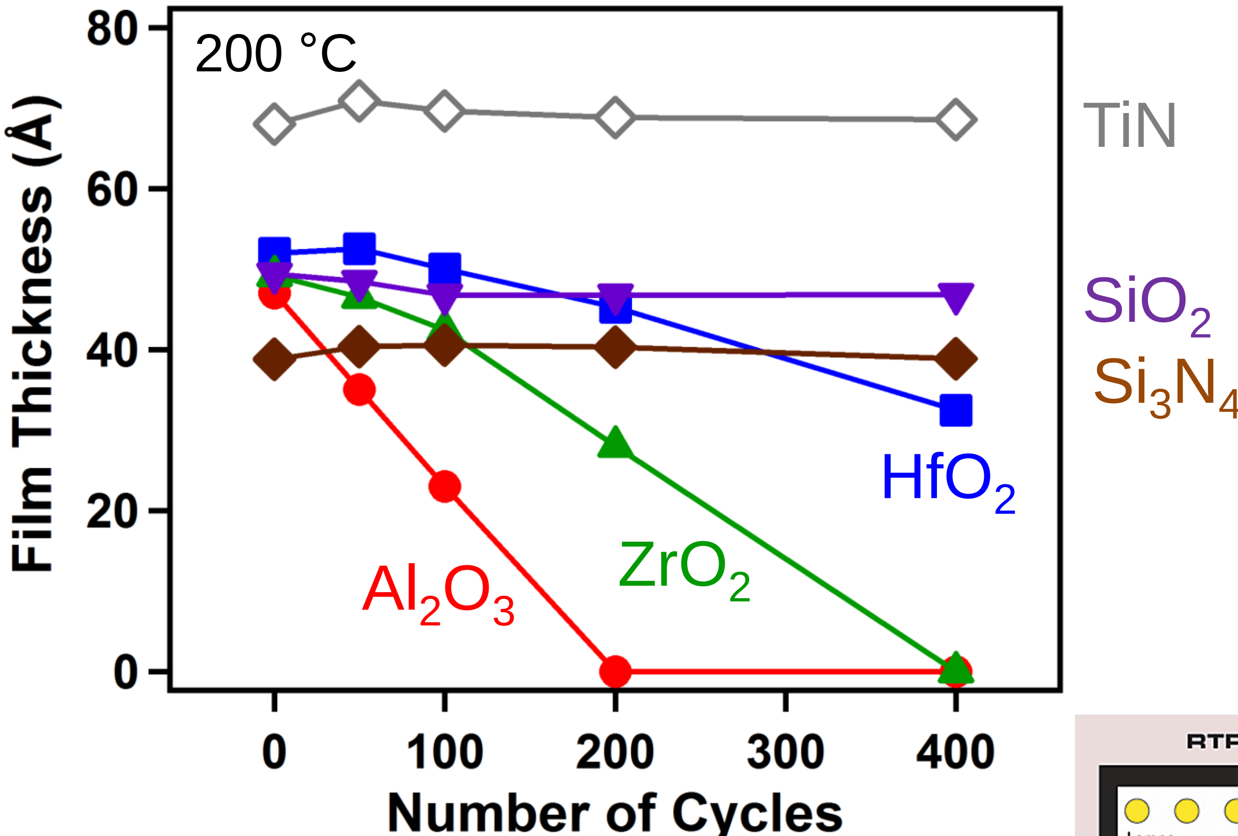
Selective ALE for different materials

- Different materials represent various colors*
- Goal to etch just one material in a background of other materials
- Selectivity determined by stability & volatility of reaction products

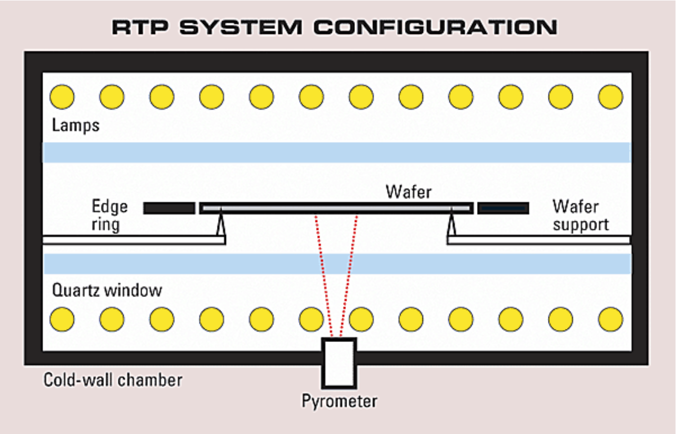
After:* - C.T. Carver et al., *ECS J. Solid State Sci. Technol.* **4, N5005 (2015)
- and S. George, 228^{th} ECS Meeting, Oct. 2015

Selective ALE for different materials

ALE survey using HF and Sn(acac)$_2$



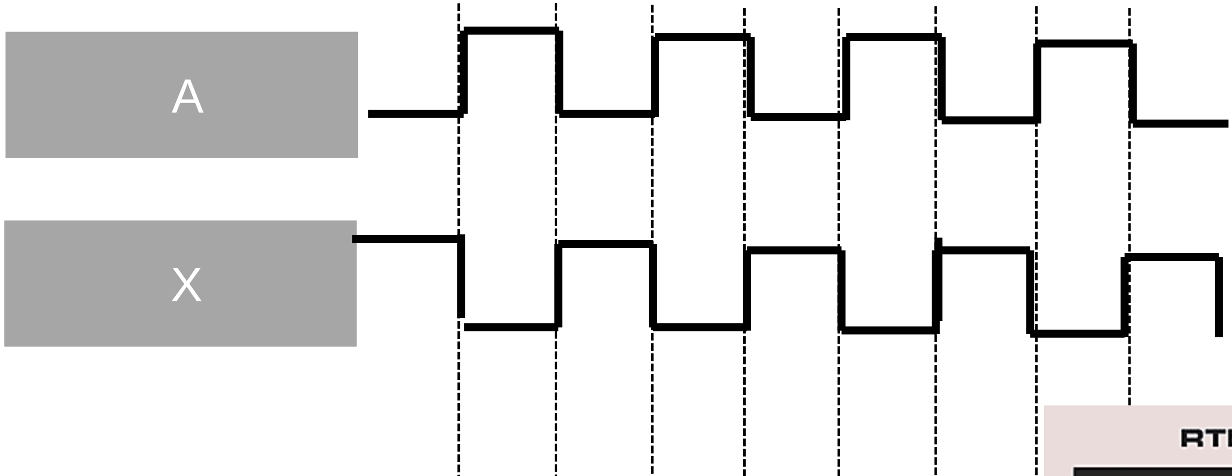
Source: S. George,
228th ECS Meeting, Oct. 2015



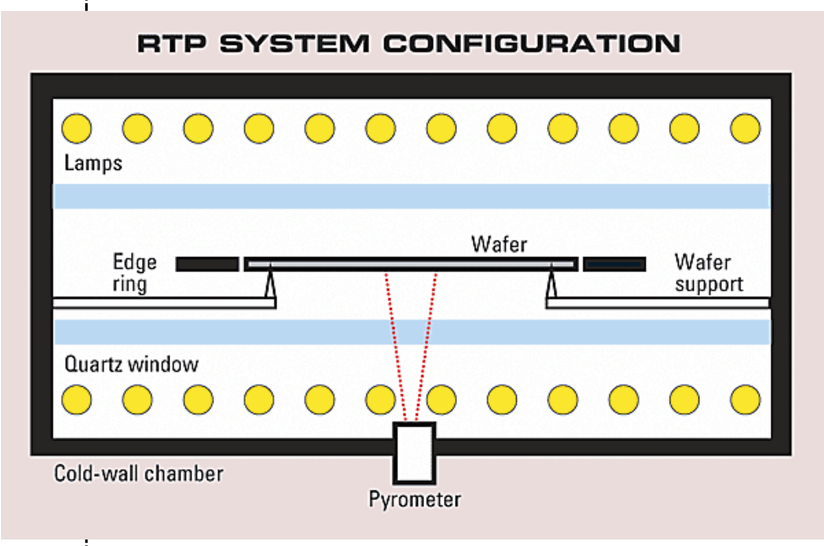
► Promote selectivity with **-plasma?**

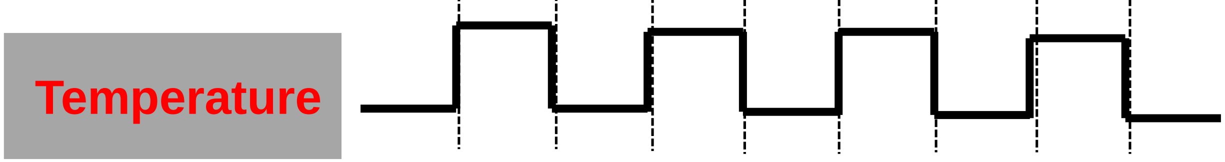
or **–flash RTA-ALP (no damage)**

Selective ALP for different materials



Promoting etch (+ dep/clean) reactions with higher E_a and suppress undesired half-reactions with lower E_a





Ramp-up 100 ^{o}C/s

„ „-down ~ 50 ^{o}C/s

Suggested reading

1. S.M. George, *Atomic Layer Deposition: An Overview*, *Chem. Rev.* **110** 111 (2010) .
2. H.C.M. Knoops, *et al.*, *Atomic Layer Deposition ,* in Handbook of Crystal Growth, Vol. 3, 2nd edition, p. 1101 (2015)
3. P. Poodt, A. Lankhorst, F. Roozeboom, C. Spee, D. Maas, A. Vermeer, *High-speed atomic layer deposition of aluminum oxide layers for solar cell passivation*, Adv. Mater., **22**, 3564 (2010).
4. P. Poodt, D.C. Cameron, E. Dickey, S.M. George, V. Kuznetsov, G.N. Parsons, F. Roozeboom, G. Sundaram, A. Vermeer, *Spatial Atomic Layer deposition: a route towards further industrialization of ALD*, J. Vac. Sc. Technol. A, **30** (2012) 010802-1/11
5. A.J. M. Mackus, et al., *The use of atomic layer deposition in advanced nanopatterning*, Nanoscale, **6**, 10941 (2014)
6. H. Van Bui, F. Grillo and J. R. van Ommen, *Atomic and molecular layer deposition: off the beaten track*, Chem. Commun., **53**, 45 (2017)
7. T. Faraz, H.C.M. Knoops, F. Roozeboom, W.M.M. Kessels, *Atomic Layer Etching: What can we learn from Atomic Layer Deposition?*, ECS J. of Solid State Science and Technology, **4** (6), (2015) N5023. http://jss.ecsdl.org/content/4/6/N5023.full.pdf+html
8. T. Lill, *et al.*, *Directional Atomic Layer Etching*, Encyclopedia of Plasma Technology, 1st edition, Taylor & Francis, 2016. DOI: 10.1081/E-EPLT-120053939
9. F. Roozeboom, '*Atomic Layer Processing for future 3D-IC Technologies*', Tutorial at 3rd International Workshop on Atomic Layer Etching (ALE 2016), July 24 - 25, 2016 Dublin, Ireland https://www.youtube.com/watch?v=XZ0Qgd3hHfk
10. A. Mameli, *et al.*, *Area-selective Atomic Layer Deposition of In_2O_3:H using a µ-plasma printer for local activation,* Chem. Mater., **29**, 921 (2017)
11. A. Mameli, *et al.*, *Area-Selective Atomic Layer Deposition of SiO_2 using acetylacetone as a chemoselective inhibitor in an ABC-type cycle*ACS Nano; doi 10.1021/acsnano.7b04701

TNO Holst Centre Open Innovation by imec and TNO TU/e Technische Universiteit Eindhoven University of Technology

Concluding remarks

- The next era of scaling (to sub-10 nm) has just begun, not just for electronics, also for many other application fields (displays, solar, microsystems, …)
- ALD and MLD enable new materials and new applications, esp. in 3D
- Lithography and Atomic Layer **Deposition / Etching / Cleaning** will (have to) grow together to meet atomic-scale fidelity needs in future electronics and many other applications
- ALE (etching) strongly coming up, alone and in combination with

  → ***Area-Selective* Atomic Layer Processing**
- Many problems still to be identified and tackled including those for advanced device manufacturing: e.g. need for chemical precursors, (an)isotropy & selectivity,…

Thank you, f.roozeboom@tue.nl or
Спасибо , fred.roozeboom@tno.nl

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