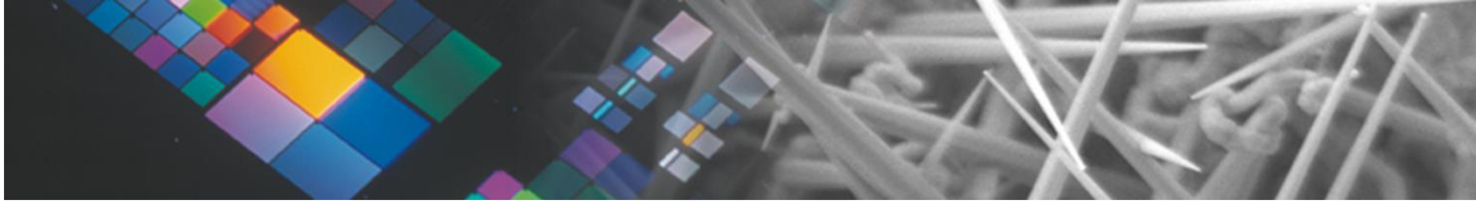

ALD
Atomic Layer Deposition

Christophe Vallée

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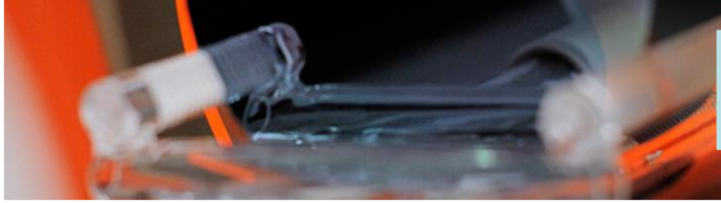
Univ. Grenoble Alpes, Lab. LTM (CEA-LETI/MINATEC) - Grenoble – France

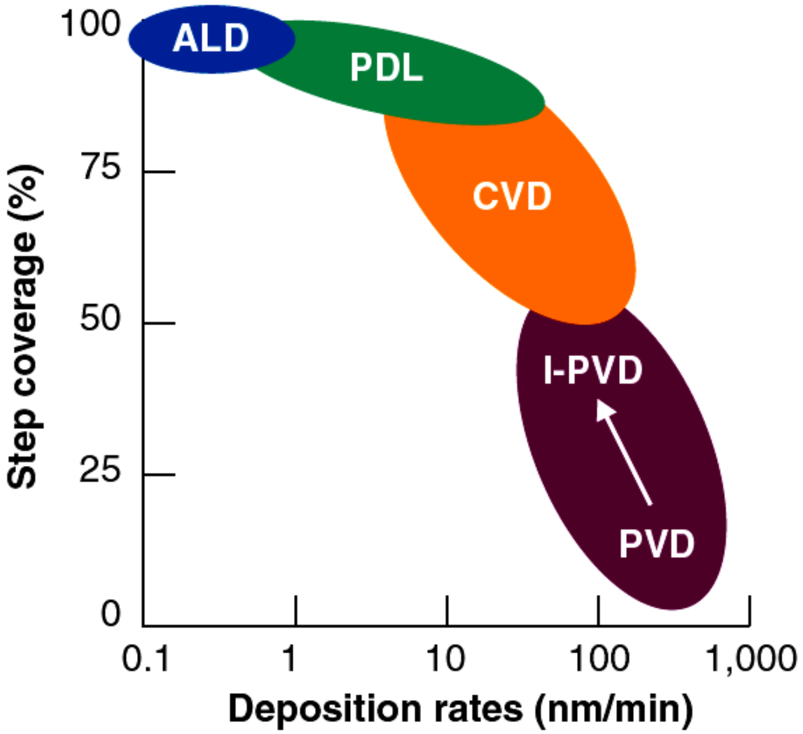
christophe.vallee@cea.fr

1. **Atomic Layer Deposition**
2. ALD set-up: thermal, plasma assisted, batch, temporal vs spatial
3. ALD for SC / Barrier layer / optics
4. Conclusions



Atomic Layer Deposition

Atomic Layer Deposition (ALD) is a sort of CVD process where precursors are admitted separately and alternately into the reactor



Advantages:

Self-limiting surface reactions relatively insensitive to gas pressure and temperature:

→ Conformal in nm-scale features to aspect ratios of *e.g.* 100:1

→ Pinhole-free films

→ Uniform across m-scale objects

→ Low impurity levels, high quality

→ Å-level control of thickness

→ i.e. slow

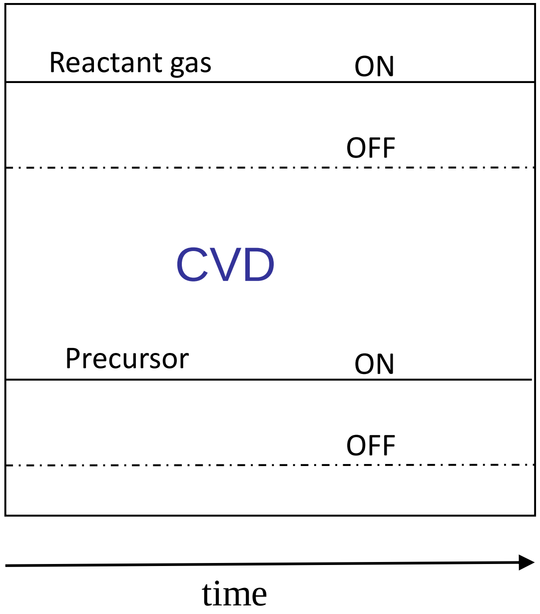
Disadvantages:

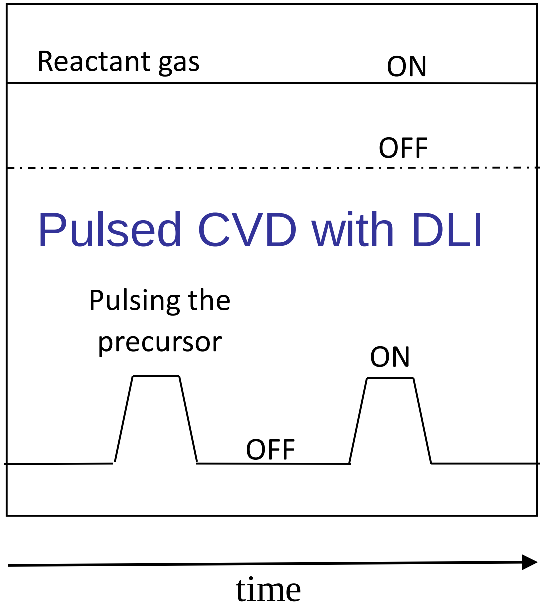
Very low growth rate (1Å/cycle)

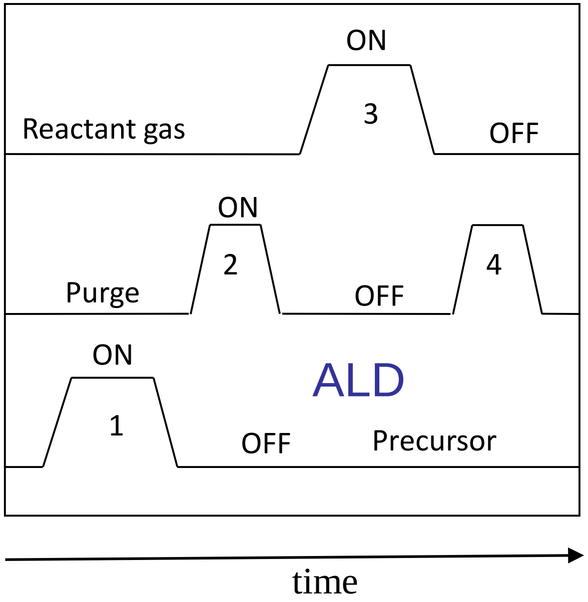
time for cycle ~ few seconds to tens of seconds

Ref: "Technology Backgrounder: Atomic Layer Deposition," IC Knowledge LLC, 24 April 06. <www.icknowledge.com/misc_technology/Atomic%20Layer%20Deposition%20Briefing.pdf>.

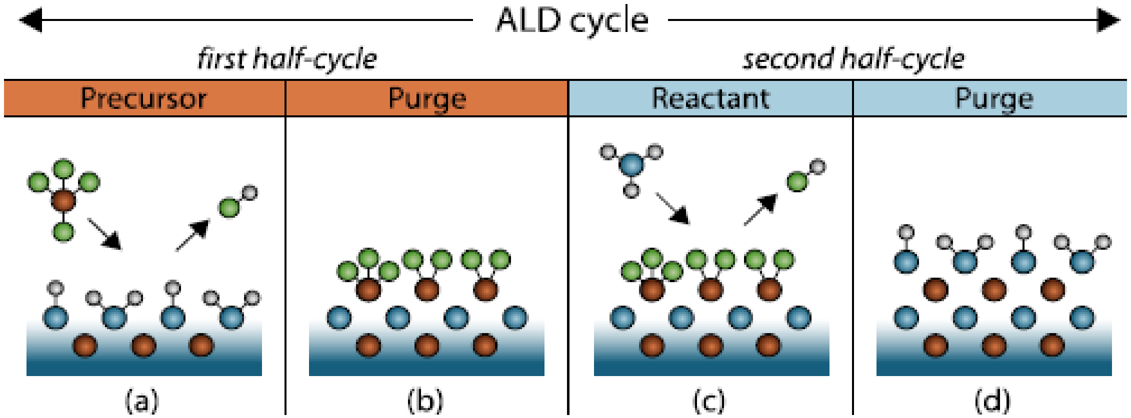
Atomic Layer Deposition







1 ALD cycle = 4 steps : precursor / purge / reactant / purge

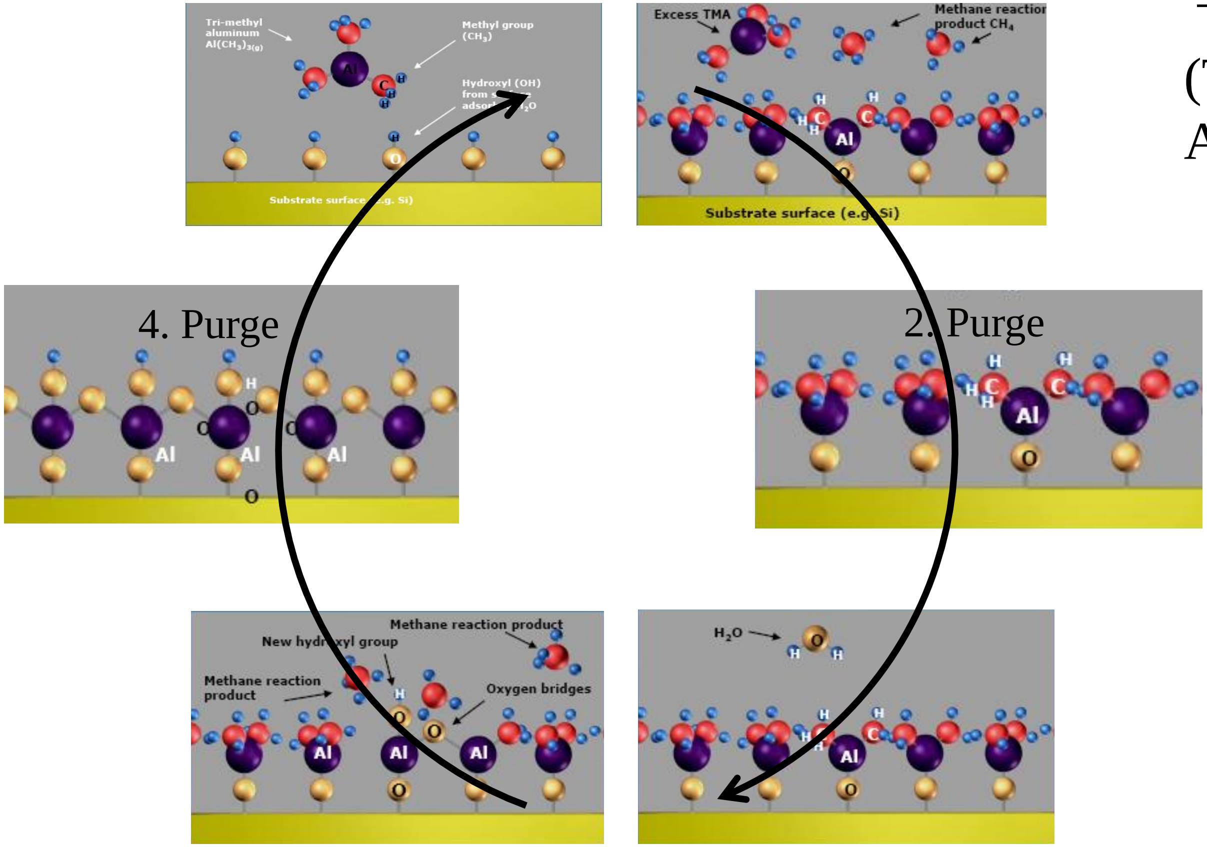


E Langereis *et al*, 2009 J. Phys. D: Appl. Phys. 42 073001

Example:

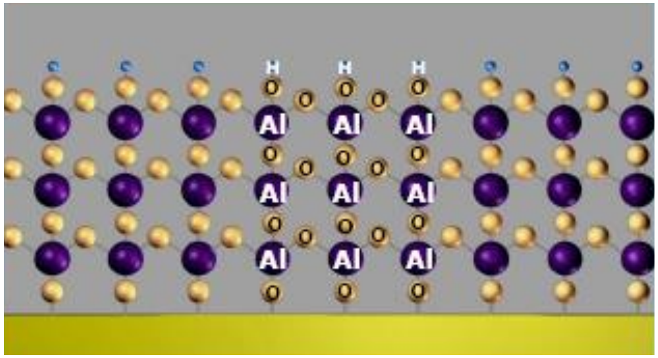
(Thermal) ALD of Al_2O_3 from $Al(CH_3)_3$ and H_2O

1. Precursor pulse



3. Reactant pulse

After X ALD cycles



Figures adapted from Cambridge Nanotech Inc.

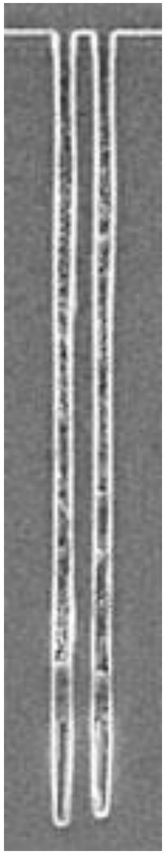
YouTube

**Video from
S. Elliott (Tyndall)**

ALD of hafnium oxide from $HfCl_4$ and water

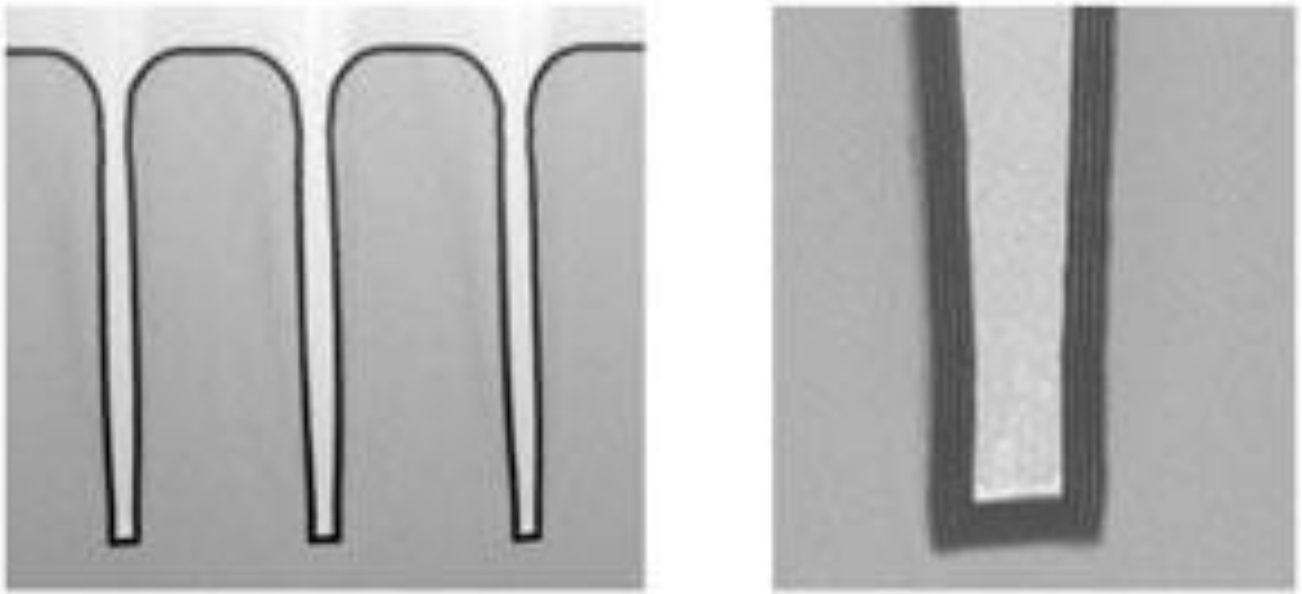
Growth rate is no more proportional to free radicals incident flux

→ It is possible to coat all surfaces, features and object shapes conformally down to the nanoscale, and uniformly across meter-scale



Trench filling (aspect ratio 35:1) by HfO_2

« ALD break materials, conformality barriers », A.E. Braun, Semiconductor Int. October 2001



MEB picture of multilayer Al_2O_3 (5 couche de 14 Å) and Ta_2O_5 (5 couches de 27 Å

1. Atomic Layer Deposition

2. **ALD set-up: thermal, plasma assisted, batch, temporal vs spatial**

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4. Conclusions

Cross flow / Traveling Wave Reactor

Typical pressure 1-10 Torr

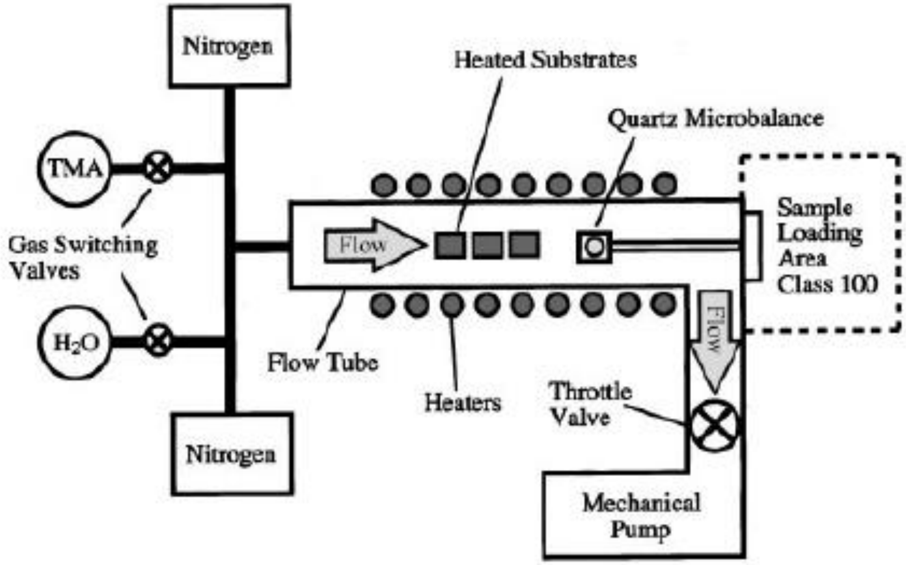


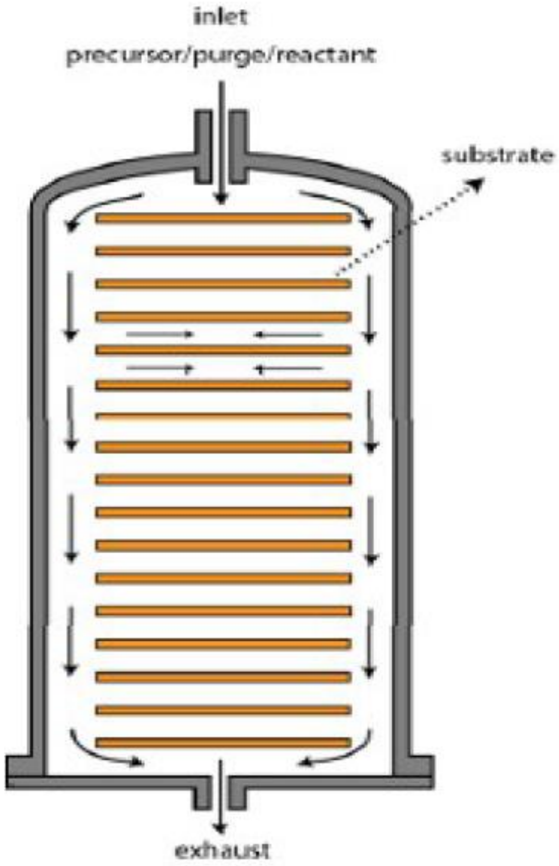
FIG. 1. Schematic view of viscous flow reactor for ALD.

Sources: Univ. Colorado

Batch ALD

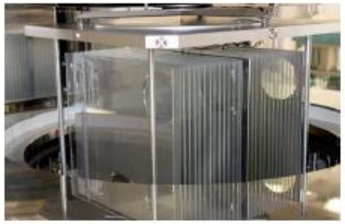
Large reactor volume

Typically long deposition runs with 50-100 planes substrates in parallel



Examples of the use of ALD in various industrial products.

Product	ALD film function
Medical implants (dental, joint), surgical fixators	Bioactive layer to enhance osseointegration, biocompatible encapsulant
Implantable medical devives (e.g. pacemakers, Cochlear implants)	Biocompatible encapsulant
Collector coins	Anti-tarnish coating
Watch parts	Anti-tarnish and/or decorative coating
Jewelry	Anti-tarnish and/or decorative coating
PCBs	Protection against tin whiskering and corrosion



PICOSUN™ P-1000 Pro ALD System

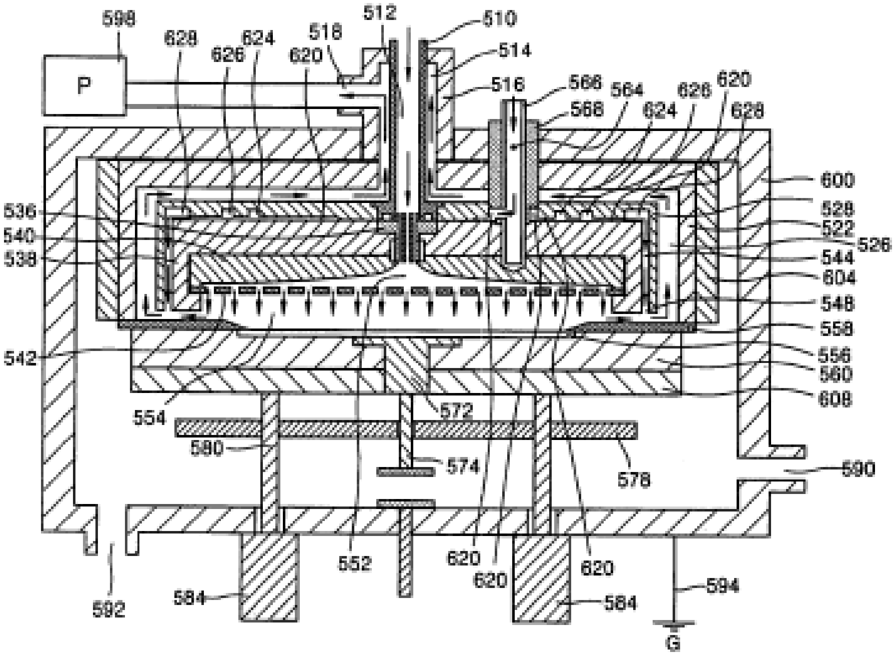
Picosun's batch ALD technology allows cost-efficient processing of e.g. surgical implants, coins, printed circuit boards, jewelry items, and watch parts.

Picosun

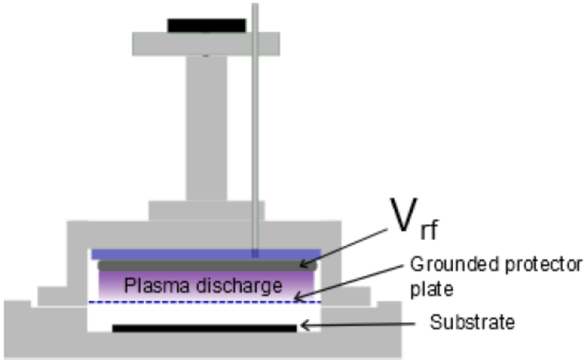
Showerhead Reactor

Well adapted for wafers

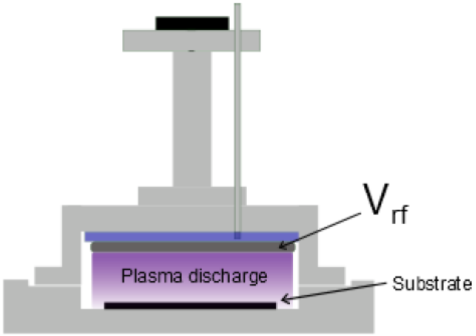
Can be integrated with plasma by tuning showerhead into electrode



Sources: ASM ; Aviza



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

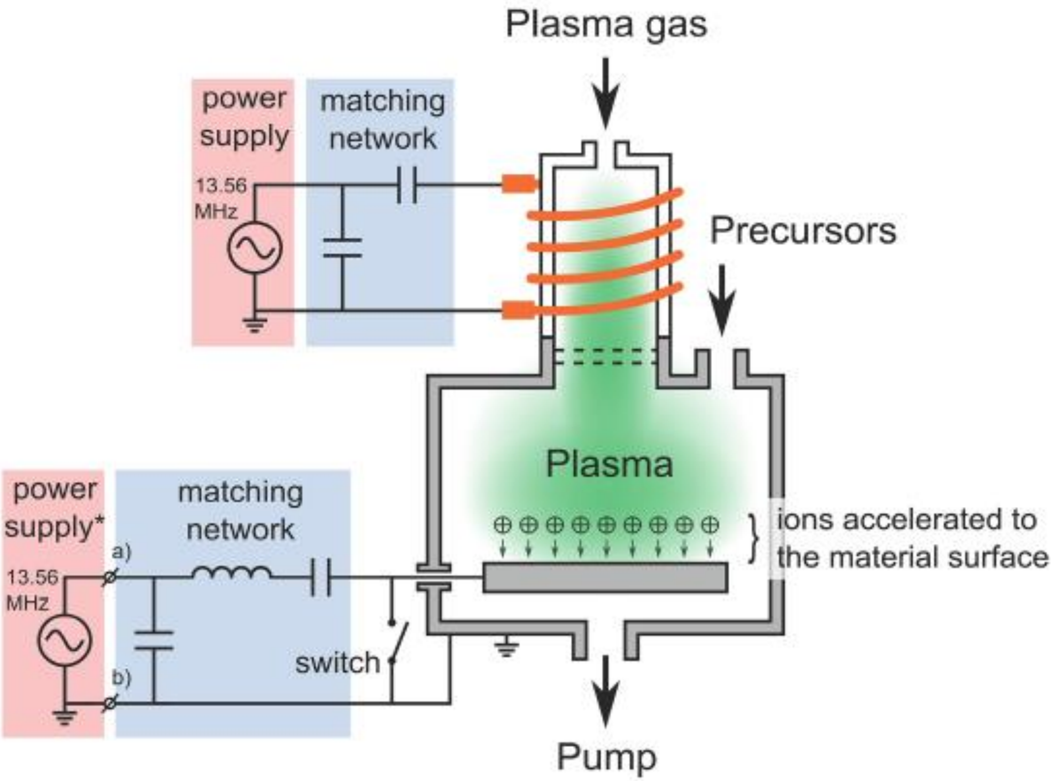


- Direct plasma
  - Possible to tune film properties *e.g.* film stress
  - Adhesion pre-treatments etc... possibilities

PEALD with CCP system

PEALD with remote plasma

Picosun



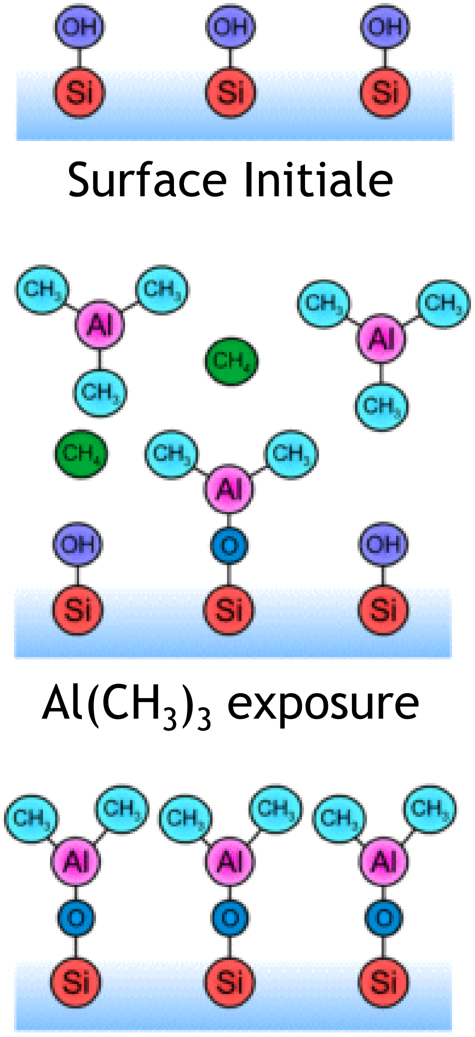
Source: TU Eindhoven

From Oxford instrument

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

Comparison between thermal ALD and PE-ALD

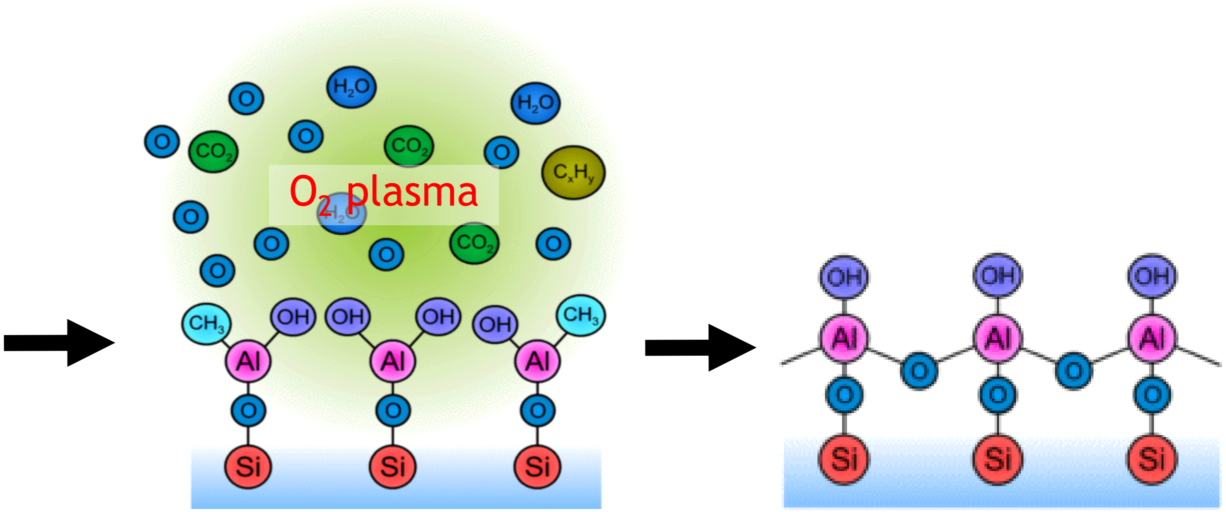
Al_2O_3 - $Al(CH_3)_3$ and O_2 plasma



1) Surface Initiale

2) $Al(CH_3)_3$ exposure

3) Purge



4) O_2 plasma exposure

5) Purge

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

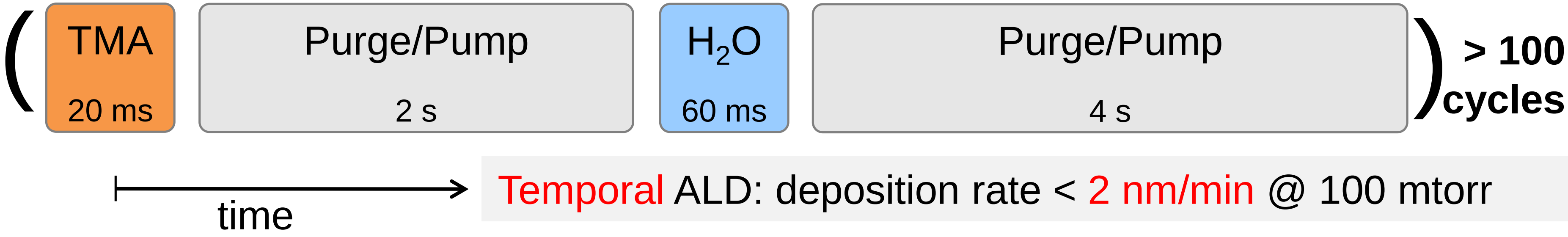
Material	**ALD precursor**	**Plasma gas**
Oxide	H_2O ou O_3	O_2
Nitride	NH_3	N_2/H_2
Metal	O_2, N_2/H_2, …	H_2

from Oxford Instrument

TEMPORAL ALD:

Precursor pulses alternate in time, separated by purges.

Substrate is stationary and is exposed to each precursor for a limited period of time.



(TMA 20 ms | Purge/Pump 2 s | H_2O 60 ms | Purge/Pump 4 s) **> 100 cycles**

time

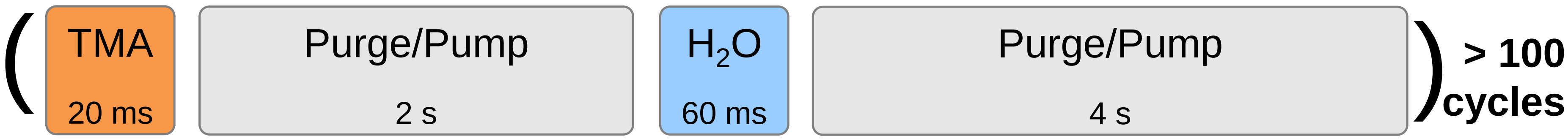
Temporal ALD: deposition rate < 2 nm/min @ 100 mtorr

SPATIAL ALD:

Continuous flow of precursors limited to certain zones in space, separated by inert gas curtains.

Substrate moves so as to alternate periodically between precursor zones.

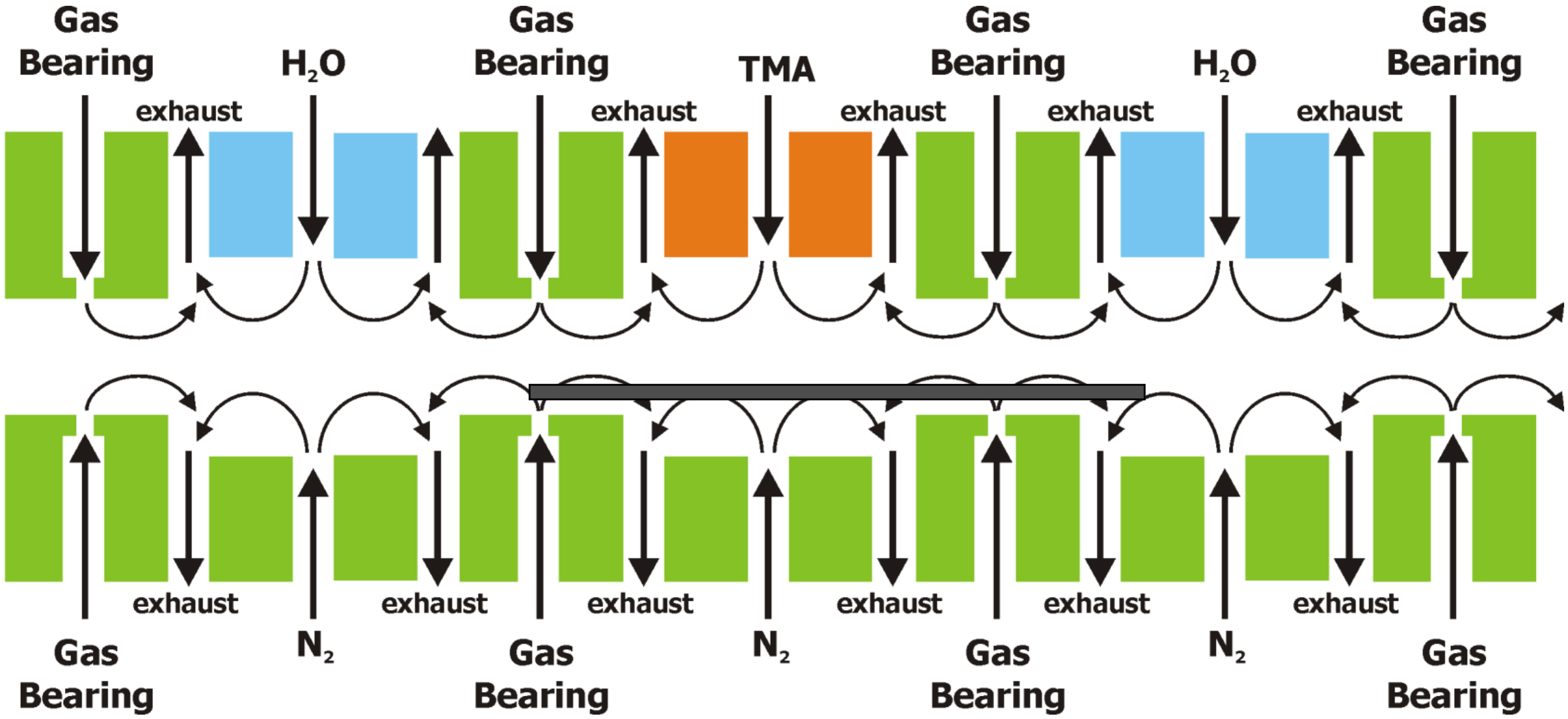
Temporal vs. spatial processing: *the thermal ALD case (Al_2O_3)*



(TMA 20 ms | Purge/Pump 2 s | H_2O 60 ms | Purge/Pump 4 s) **> 100 cycles**

time

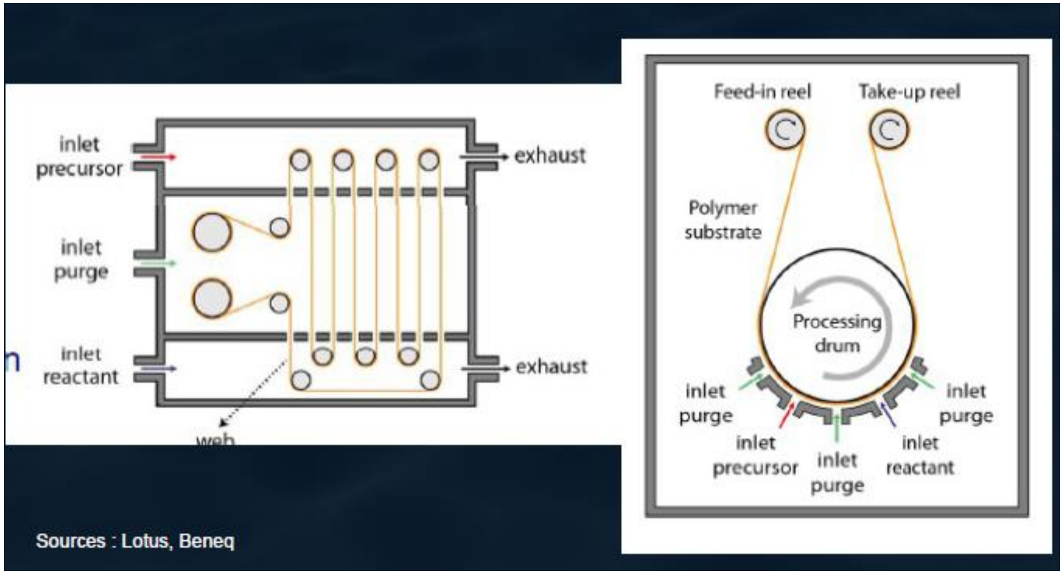
Temporal ALD: deposition rate < 2 nm/min @ 100 mtorr



Spatial ALD: deposition rate up to 70 nm/min @ 1 atm.

P. Poodt, *et al.*, Adv. Mater., **22**, 3564 (2010), *and* ALD 2010 Conf., June 2010

Spatial ALD with Roll to Roll system



Sources : Lotus, Beneq

From Lotus Technology, Beneq

1. Atomic Layer Deposition
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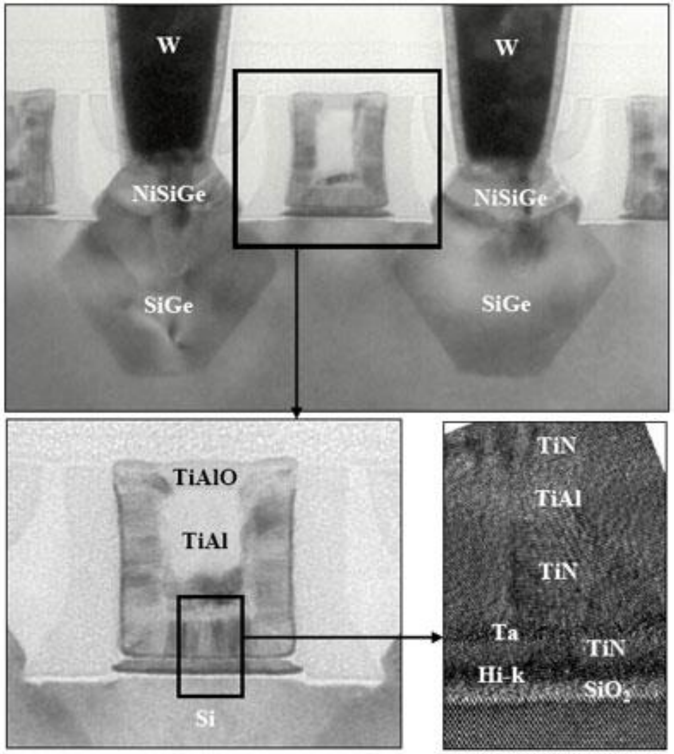
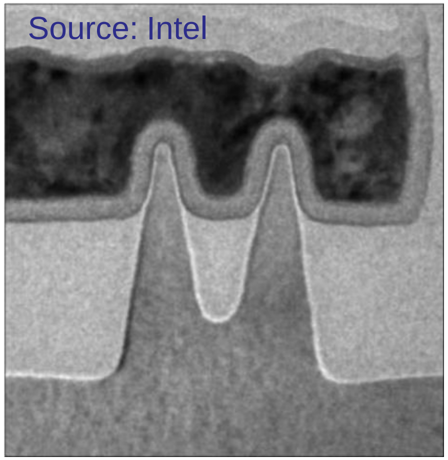
HfO_2 for CMOS: mass production by Intel since 2007 (45 nm node)



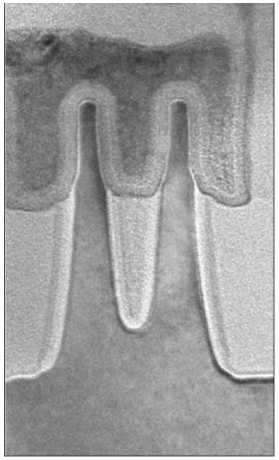
Semiconductor International, 5/6/2008

Intel Xeon PMOS transistor features embedded SiGe (25-30% Ge) and a replacement high-k/metal gate



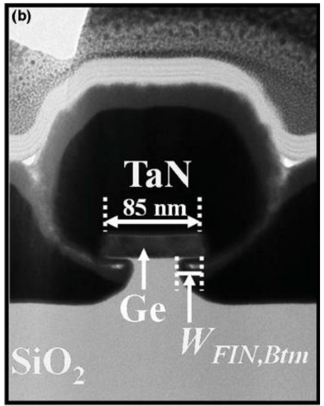
Source: Intel

22 nm 1st generation Tri-gate Transistor

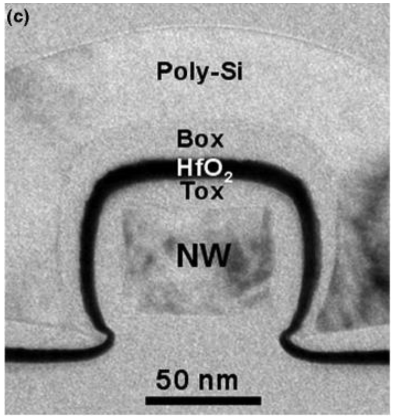


14 nm 2nd generation Tri-gate Transistor

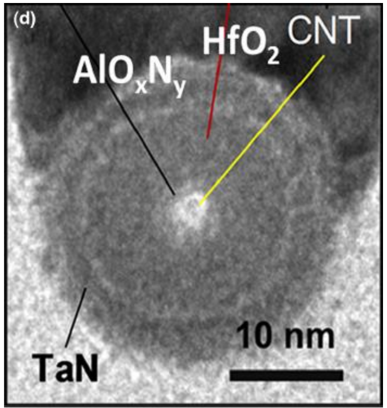
b: Ω-gate structure



c: pi-gate strusture



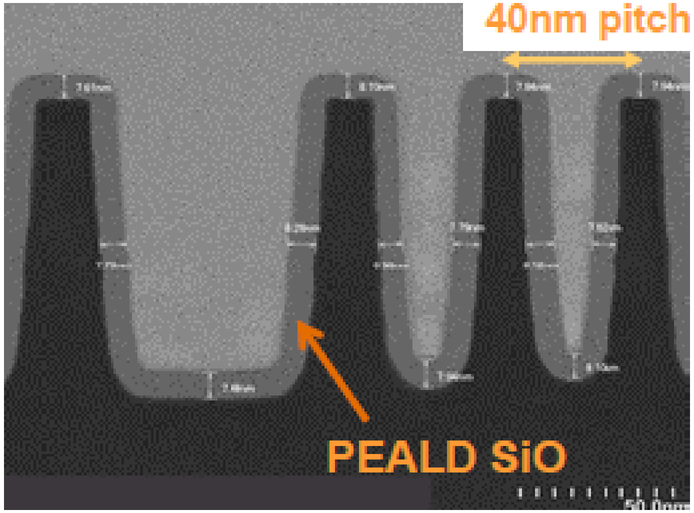
d: Carbon nanotube with gate all around



Johnson *et al.*, Mater. Today 17 (5), 236-246 (2014)

SiO_2 spacer

ASM

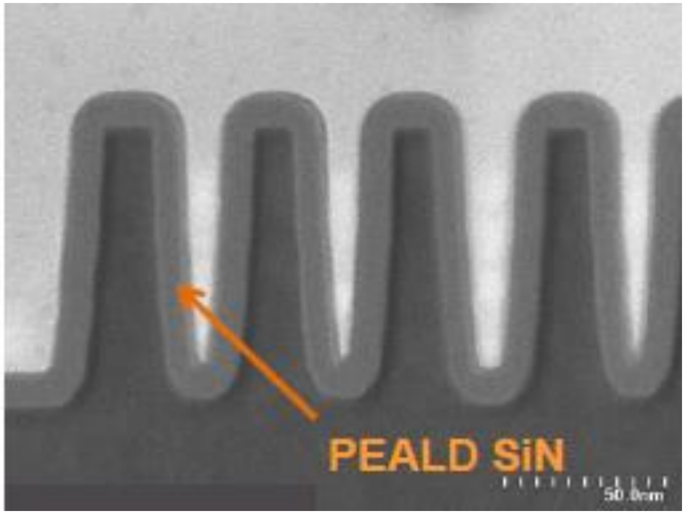


<u>ALD deposition at 25°C</u>

Low T° SiO_2 is mature process for SC

Manufacturing: cost reduction throughput improvement, defect, reduction

Si_3N_4 spacer



<u>ALD from 250°C</u>

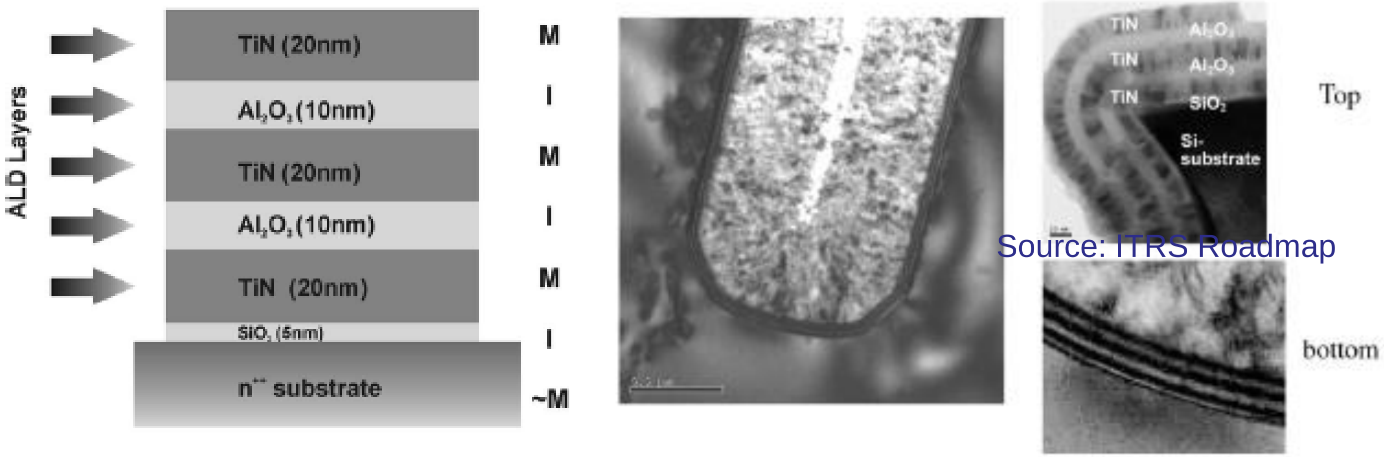
Si_3N_4 low T° deposition not yet in HVM

Only films deposited at high T° (>550°C) are used in mass production

Engineering: process tuning for WER and plasma improvement for conformality

From a presentation of D. Haussmann, Lam Research, at the AVS2015 conference

ALD allows multilayers structures
⇨whole MIM stack could be made by ALD



Source: ITRS Roadmap

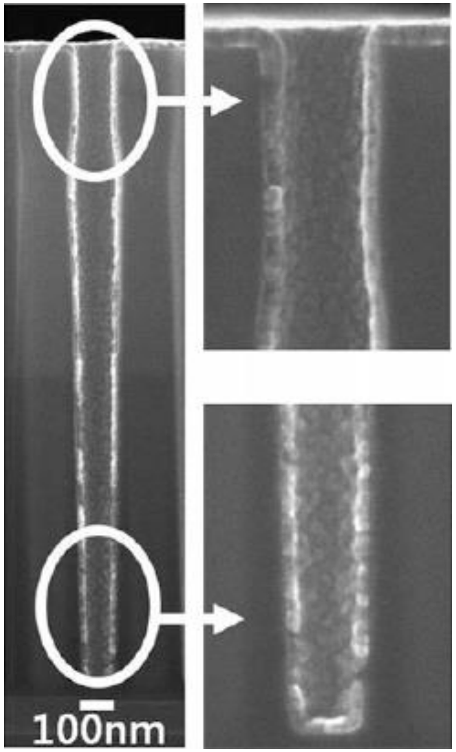
KLOOTWIJK *et al.*: ULTRAHIGH CAPACITANCE DENSITY FOR MULTIPLE ALD-GROWN MIM CAPACITOR STACKS

IEEE ELECTRON DEVICE LETTERS, VOL. 29, NO. 7, JULY 2008

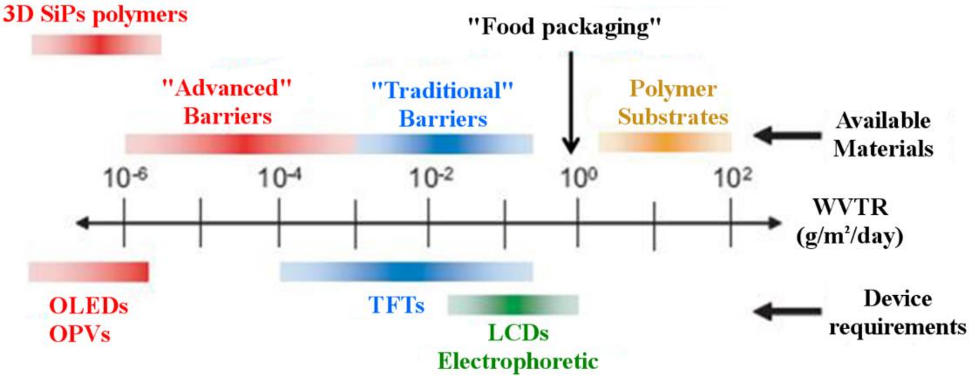
Years	2009 – 2016	2017 – 2024
Top electr.	TiN	Ru, RuO_2, Ir, IrO_2
High-k	ZrO_2, HfO_2, Ta_2O_5	TiO_2, ATO, STO, BST
Bottom electr.	TiN	Ru, RuO_2, Ir, IrO_2, $SrRuO_2$

Kim *et al.*, JES 154 (2), D95:D101 (2007)

Ru on SiO_2 (AR 17)



☐ ALD barrier for OLEDs, OPVs, 3D SiPs polymers…



Material	WVTR ($g.m^{-2}.day^{-1}$)	OTR ($cm^3.m^{-2}.day^{-1}$)
Polyethylene (PE)	1.2 [2]	5.9 [2]
PETerephtalate (PET)	3.9 – 17 [3]	1.8 – 7.7 [3]
15 nm Al/PET	0.18 [3]	0.2 – 2.29 [3]
100 nm PECVD SiN	0.02 [4]	/
25 nm ALD Al_2O_3	**$1.7\ 10^{-5}$** [4]	**$< 5\ 10^{-3}$** [4]

Barrier performances for different materials

Device	WVTR ($g.m^{-2}.day^{-1}$)	OTR ($cm^3.m^{-2}.day^{-1}$)
Snack food	0.2 – 5 [1]	/
LCDs	0.1 [2]	0.1 [2]
CIGS solar cells	10^{-4} [3]	0.1 [3]
Organic solar cells	10^{-5} [3]	10^{-5} [3]
OLEDs	10^{-6} [2]	$10^{-3} – 10^{-5}$ [2]

Barrier performance requirements

[1] «Packaging of snack food»
http://www.iip-in.com/foodservice/22_snackfood.pdf

[2] J. S. Lewis *et al.*, *IEEE Journal of Selected Topics in Quantum Electronics,* Vol. 10, p. 45 (2004).

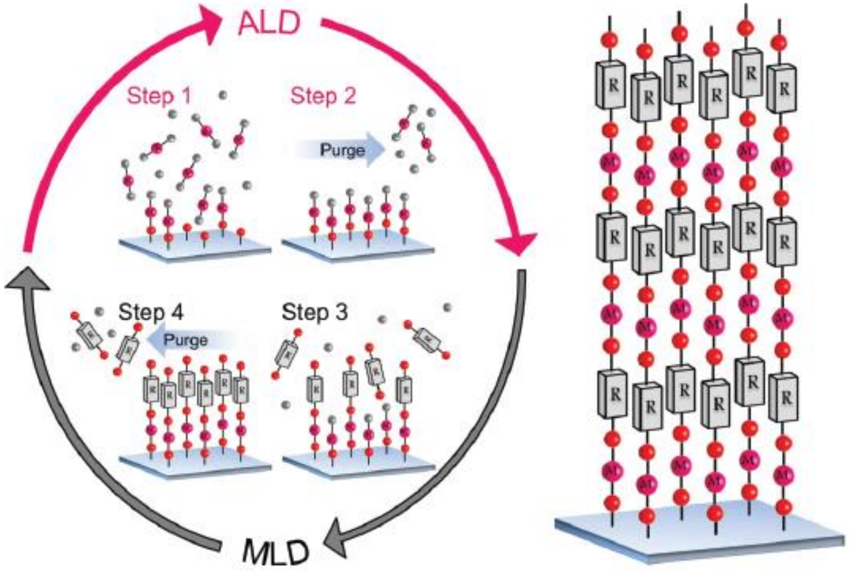
[3] Fraunhofer ISC Annual Report 2004.

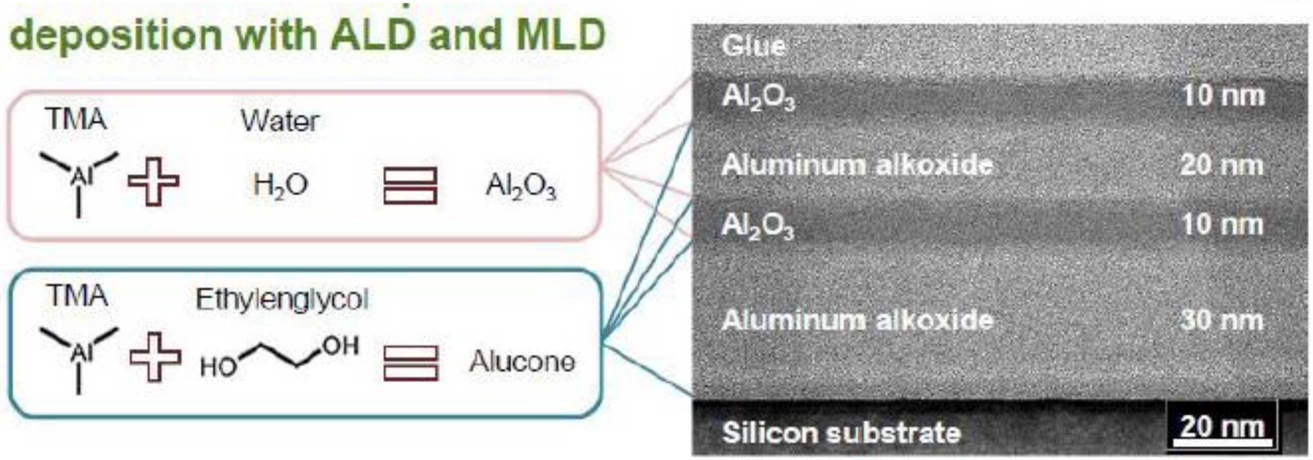
[4] P.F. Carcia *et al.*, *Applied Physics Letters*, Vol. 89, pp. 031915 (2006).

❑ Laminates Inorganic/Organic (ALD/MLD)

Pia Sundberg

Atomic/molecular layer deposition of hybrid inorganic-organic thin films





U. Schröder

ALD and MLD passivation layers for flexible OLED and OPV

http://mldtech.com/technology/atomic-layer-deposition/

ALD process delivers pinhole-free, very large optics

MLD Technologies has scaled up its atomic-layer-deposition (ALD) process to provide uniform (less than ±1% variation), low-loss (typically less than 50 ppm total loss) precision optical coatings on substrates up to 800 mm in diameter.

Coatings are pinhole-free and can be deposited from a number of metal-oxide film materials.

The production-scale ALD chamber designed and built by MLD is capable of coating planar, 3D, and large curved optical elements..

http://www.laserfocusworld.com/articles/print/volume-49/issue-07/newsbreaks/ald-process-delivers-pinhole-free-very-large-optics.html

Metal-like coatings for watch parts

Challenge: decorative coating on fine mechanics and watch parts is challenging due to the conformal nature of the parts

Beneq solution: a thin ALD-based optical coating stack providing the desired color while providing environmental protection on corrosive parts

Optical coatings for lenses in high power lasers

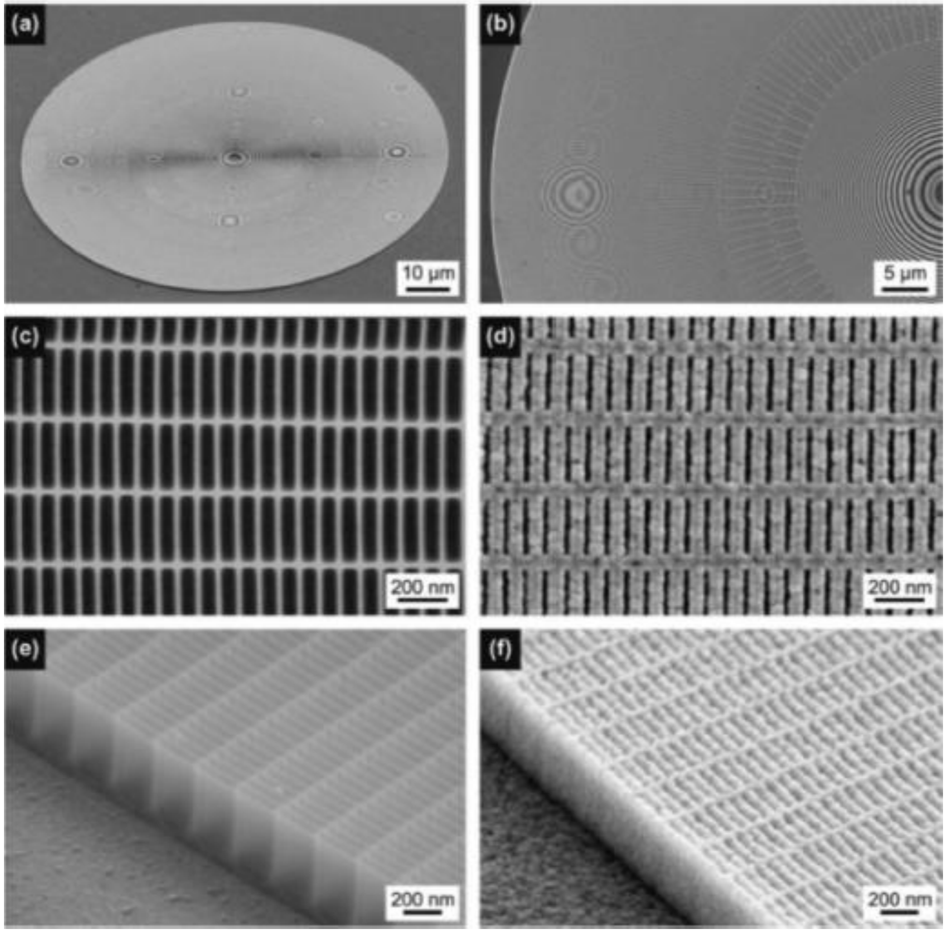
Challenge: High-power lasers require high-performance optical coatings on conformal optics lenses. Due to the complex 3D shapes, the components are difficult to coat and beyond the reach of conventional coating technologies such as PVD

Beneq solution: a conformal high- and low-index multilayer optical coating on customer optics, deposited by TFS 500 batch ALD system

From Beneq website: https://beneq.com/en/thin-films/applications/optical-coatings

Optique / photonique

(a, b) Scanning electron micrographs of a diffractive Fresnel zone plate X-ray lens where ALD Ir has been deposited on a hydrogen silsesquioxane resist template to double the frequency of the diffractive rings.
(c−f) High-magnification top and tilted images
(c, e) before and (d, f) after ALD Ir coating.



(17) Vila-Comamala, J.; Gorelick, S.; Färm, E.; Kewish, C. M.; Diaz, A.; Barrett, R.; Guzenko, V. A.; Ritala, M.; David, C. *Opt. Express* **2011**, *19*, 175.

1. Atomic Layer Deposition

2. ALD set-up: thermal, plasma assisted, batch, temporal vs spatial

3. ALD for SC / passivation / optics

4. **Conclusions**

ALD is a unique self-limiting process for growing ultra-thin pinhole-free films that is enabling new developments in high-tech manufacturing sectors such as electronics, energy and coatings

ALD gives highly conformal and dense films (1 – 100 nm)

Just a few review articles:

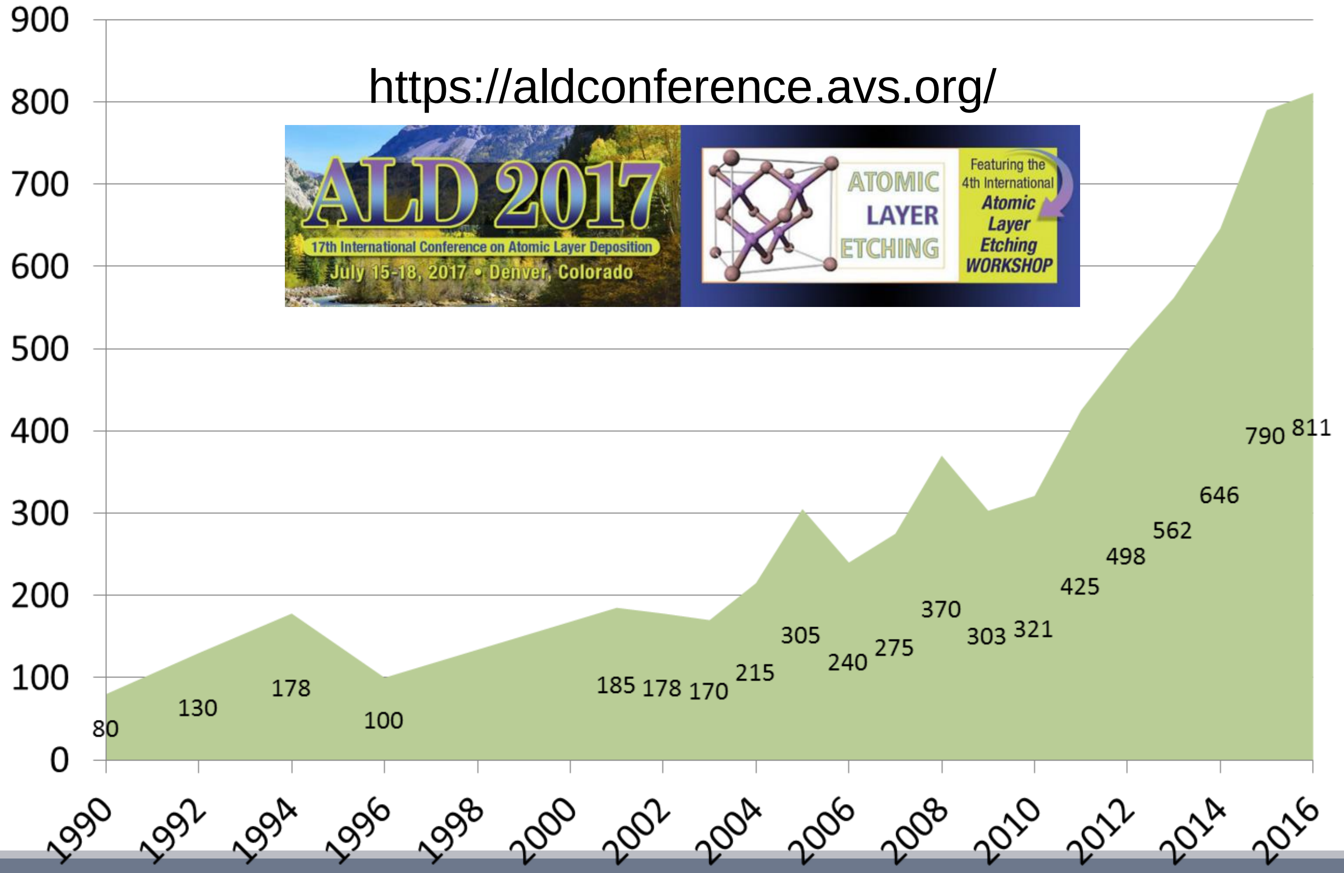
S. M. George, *Chem. Rev.* **110**, 111 (2010)

R. L. Puurunen, *J. Appl. Phys.* **97**, 121301 (2005)

V. Miikkulainen, M. Leskelä, M. Ritala, R. L. Puurunen, *J. Appl. Phys.* **113**, 021301 (2013)

H.B. Profijt et al, J. Vac. Sci. Technol. A 29, 050801 (2011)

Number of delegates at annual *International Conference on Atomic Layer Deposition* has grown by factor of 4 in the last decade. At the 2016 conference, 150 companies attended, comprising 50% of the delegates, of which 50 were exhibitors and 26 were sponsors.



European action for ALD: COST HERALD

Hooking together European research in Atomic Layer Deposition

COST action MP1402

HERALD

Hooking together European Research
in Atomic Layer Deposition

http://www.european-ald.net/

French research group: GDR RAFALD + workshop RAFALD

Réseau des Acteurs Français de l'ALD

7-9 Nov. Montpellier (France)

https://sites.google.com/site/rafaldepot/home

Thank you for your attention