Atomic Layer Deposition process Basics, Applications

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Context

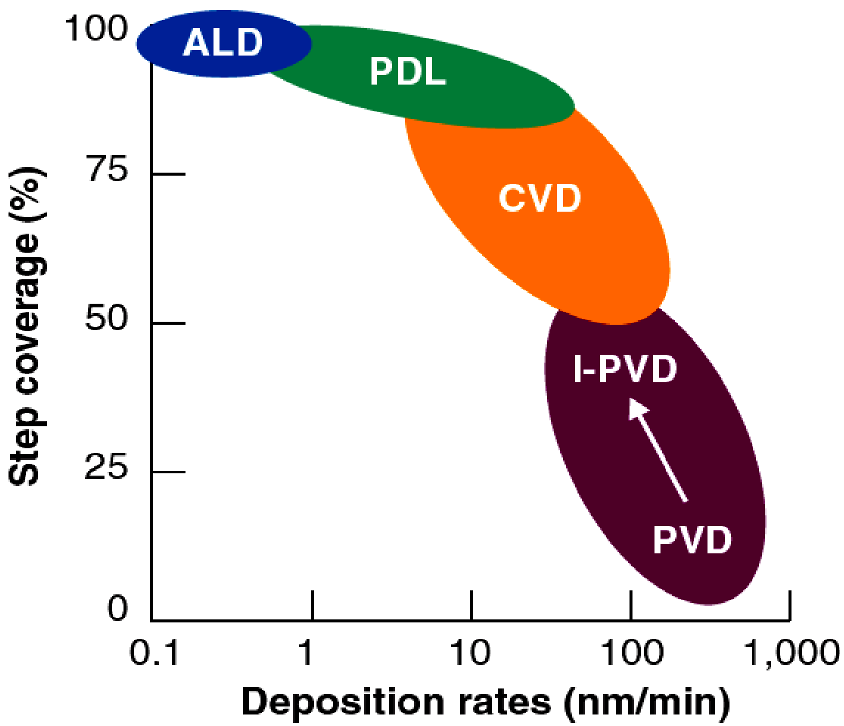
- Main goal : Tailor materials functions in a controlled way to provide solutions in high-value applications :

nanoelectronics, photonics, sensors, catalysis, communications, medicine, nanobiotechnology, energy, environmental …..

- provide new physical, chemical, and/or biological properties to a given substrate to be capable of surpassing standard materials

Through the modification of surface properties or through the building of complex thin film, or the fabrication of multimaterial structures

ALD vs CVD vs PVD

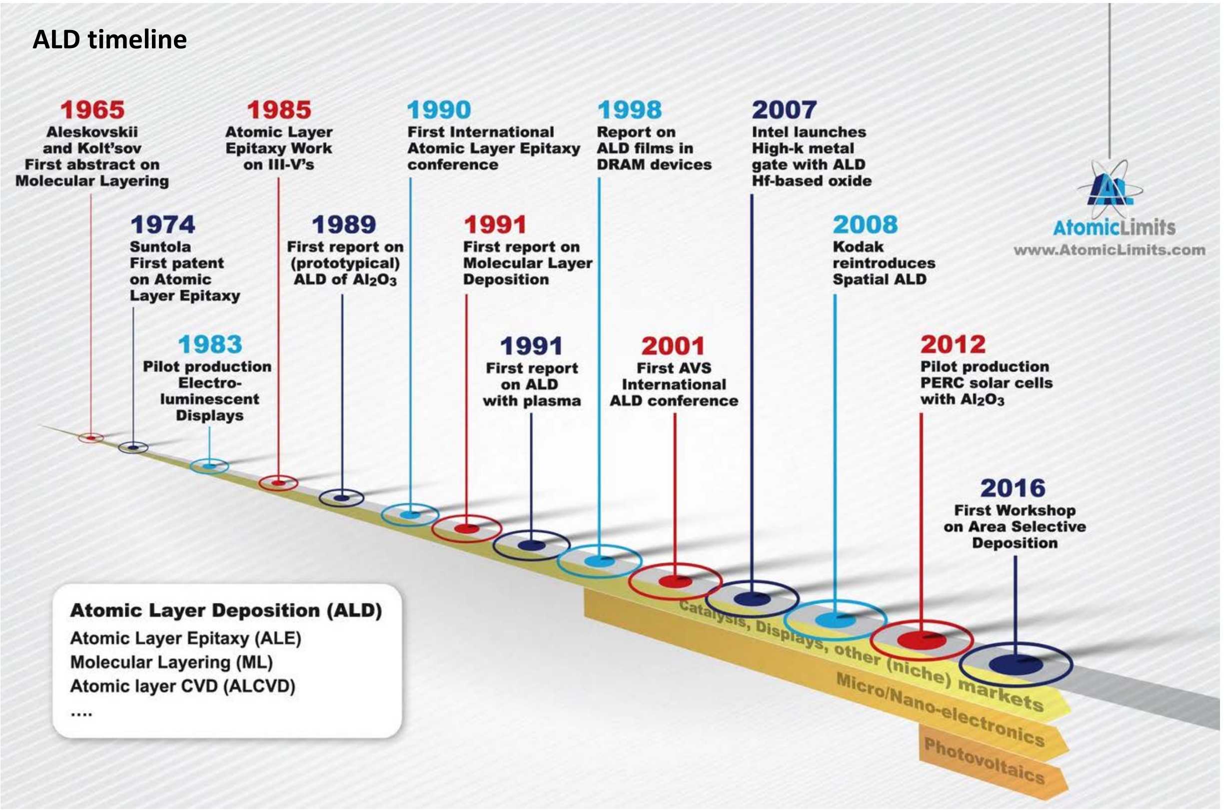


Technology Backgrounder: Atomic Layer Deposition," IC Knowledge LLC, 24 April 06.
<www.icknowledge.com/misc_technology/Atomic%20Layer%20Deposition%20Briefing.pdf"

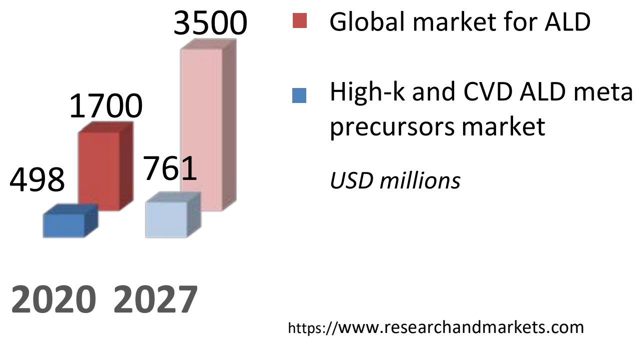
CVD vs ALD

	Criteria	ALD	CVD
Principle	Deposition reaction	Surface reaction	Surface reaction + gas phase reaction
Synthesis conditions	Deposition temperature	**RT – 400°C**	**300 – 800°C**
	Vacuum requirement	Medium	
	Precursor	Highly reactive precursors Precursors must not decompose at process T	Less active precursors Precursors can decompose at process T
Process features	Deposition rate	**Slow** (0,01-0,1 nm/s)	**Fast** (0,5-10 nm/s)
	Process window	**<1% dependency** on 10% process parameter change	**Strong dependency** on process parameter changes
Film features	Uniformity control	**Å range** Controlled by counting the number of reaction cycles Ensured by the saturation mechanism	**10 Å range** Controlled by process control and monitoring, time Requires uniform flux of reactant and uniform T
	Film quality	Excellent stoichiometry Low pinhole count Stress control possible	
	Conformality	100% step coverage in **60:1** aspect ratio	100% step coverage in **10:1** aspect ratio
	Cleanliness	No particles due to separated half reactions	Particles due to gas phase reactions

History and market relevance

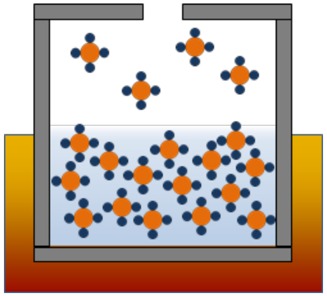


ALD market revenue (2020, 2027)

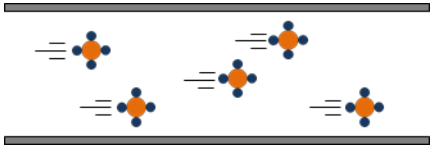


https://www.researchandmarkets.com

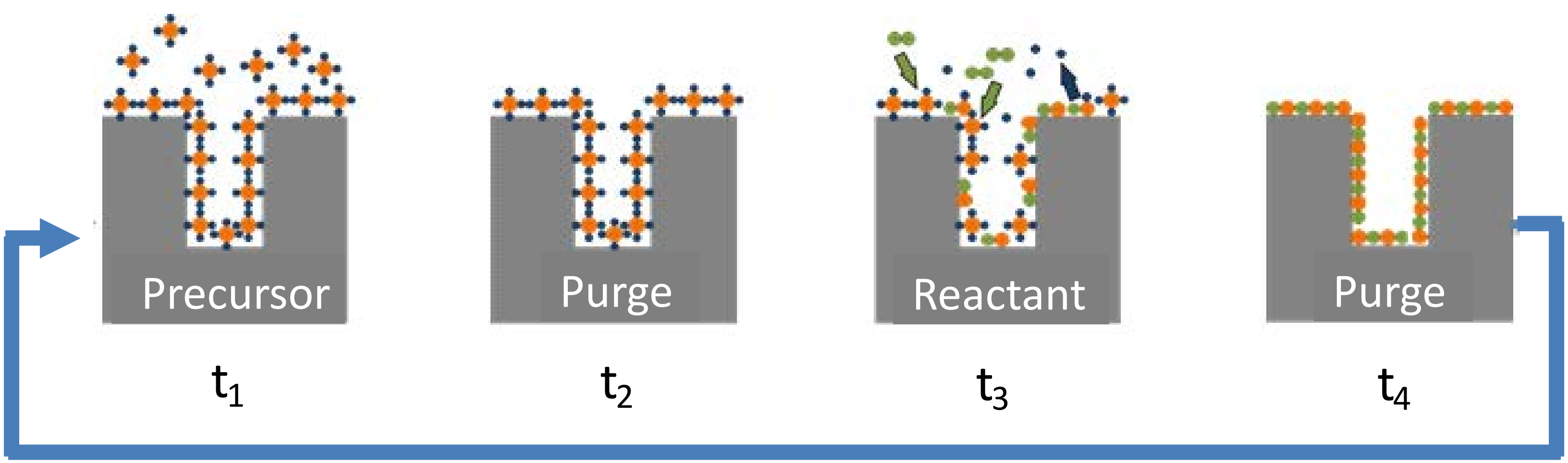
Basics



Precursor vaporization

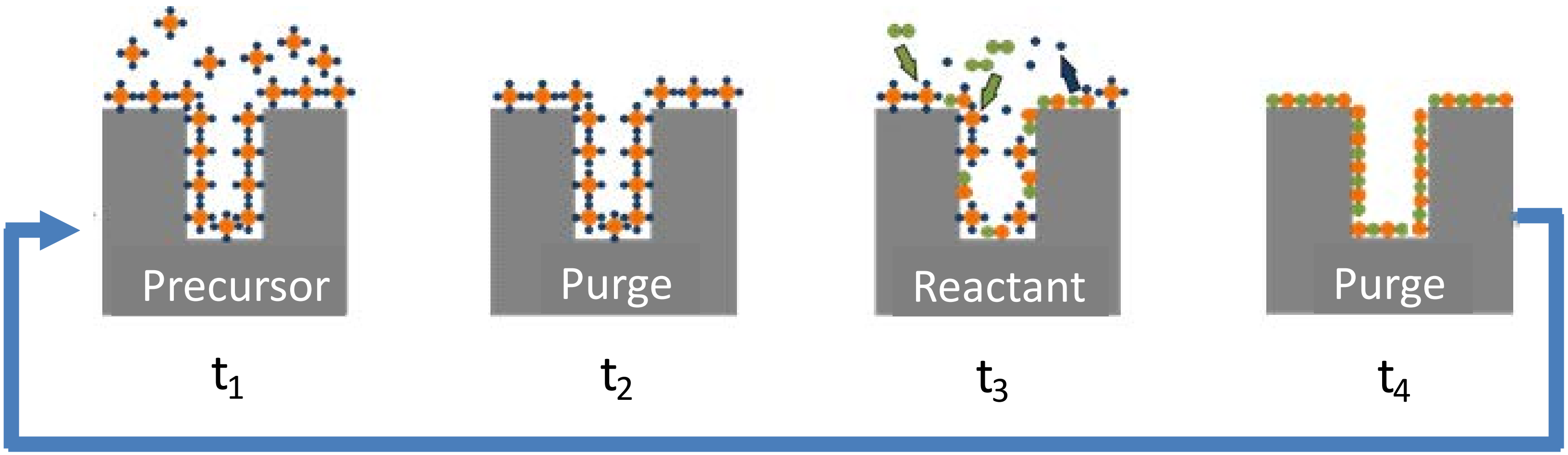


Precursor Transport



1 ALD cycle

Basics



1 ALD cycle repeated n times → targeted thickness (from nm)

Two main mechanisms:

- ❑ Chemisorption till saturation
- ❑ Reactivity between the surface sites and the precursor molecule

- ❑ Surface saturation
- ❑ Conformal deposition
- ❑ Growth Rates : 1 to 10 nm/h

ALD : principles

Assets:

→ Already upscalable [1]

→ **Soft deposition conditions**

(P ~ mbar, T = RT-500°C)

→ Good control over the **thickness** and **composition** [2]

→ Dense, homogeneous films, High **conformity**

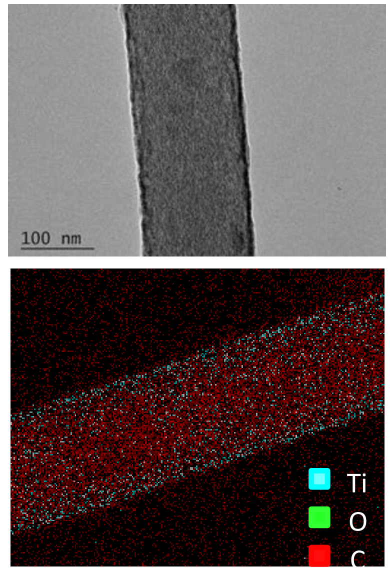
Weaknesses:

→ Slow process (low growth per cycle)

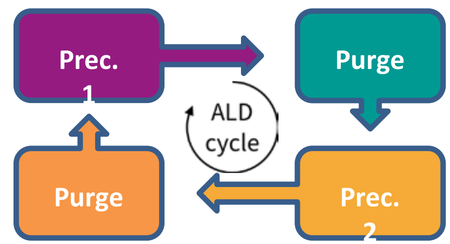
→ Control of the transport and stability of the precursors

→ Film contamination

10 nm ALD-TiO_2 on carbon NW



- **Chemical** deposition process in vapor phase
- **Self-limiting surface reactions**
- Sequential introduction of the precursors
- Growth during a cycle

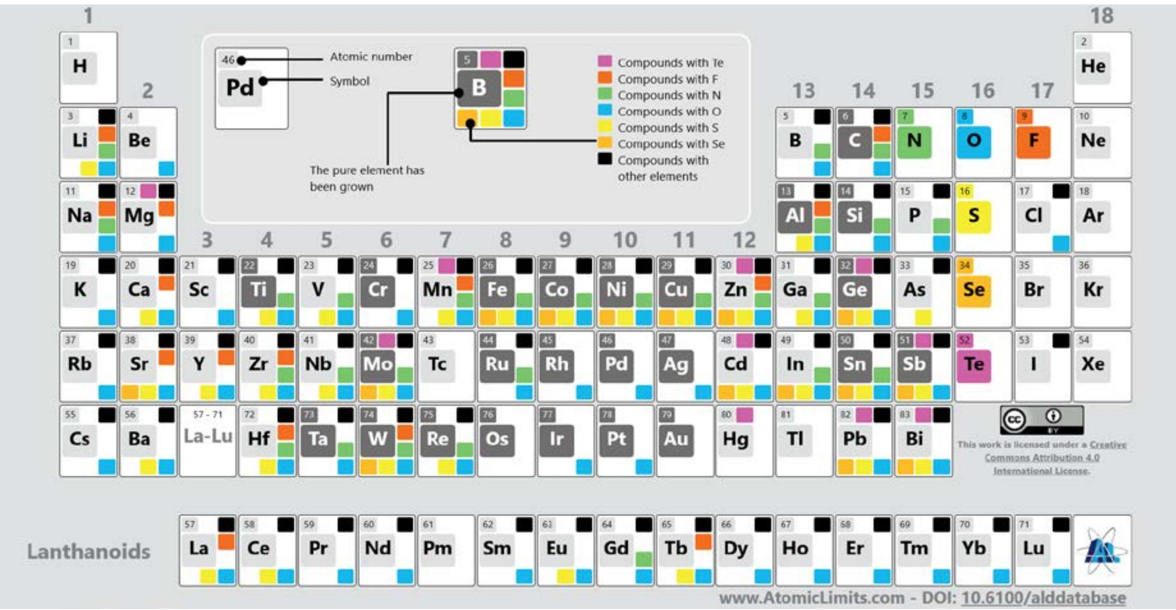


Access to **inorganic** (oxydes, nitrides, metal films, sulfides, multi-elements) and **hybrid organic-inorganic materials**
Very thin layer < 50 nm,
nanomaterial functionalization, Interface engineering, ….

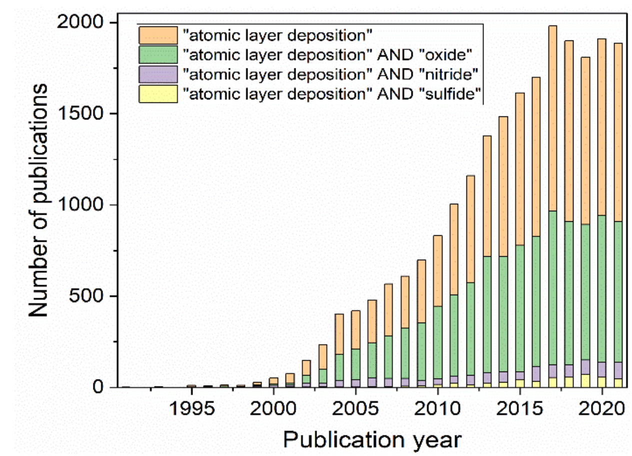
[1] Ritala et al., *ACS Transac., 25, 8, 2009*
[2] Meyer et al., *App. Phys. Lett., 94, 23, 2009*

ALD/ materials

Binary materials **2 precursors**



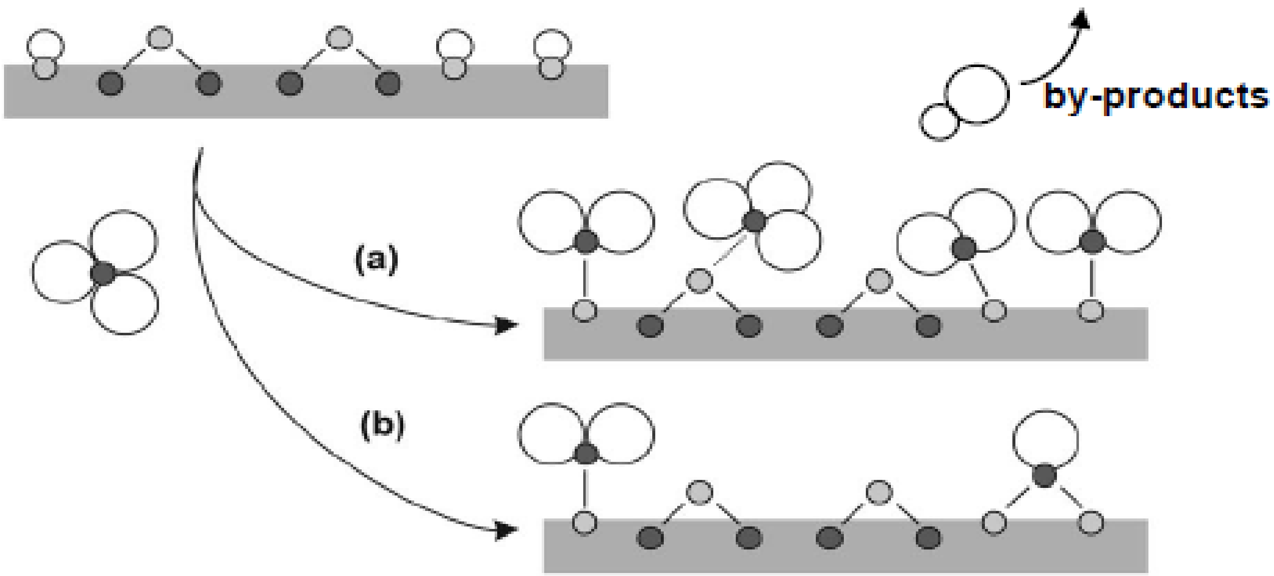
- **Wide variety (oxide,** nitride, metal, sulfide, ..) of deposited materials



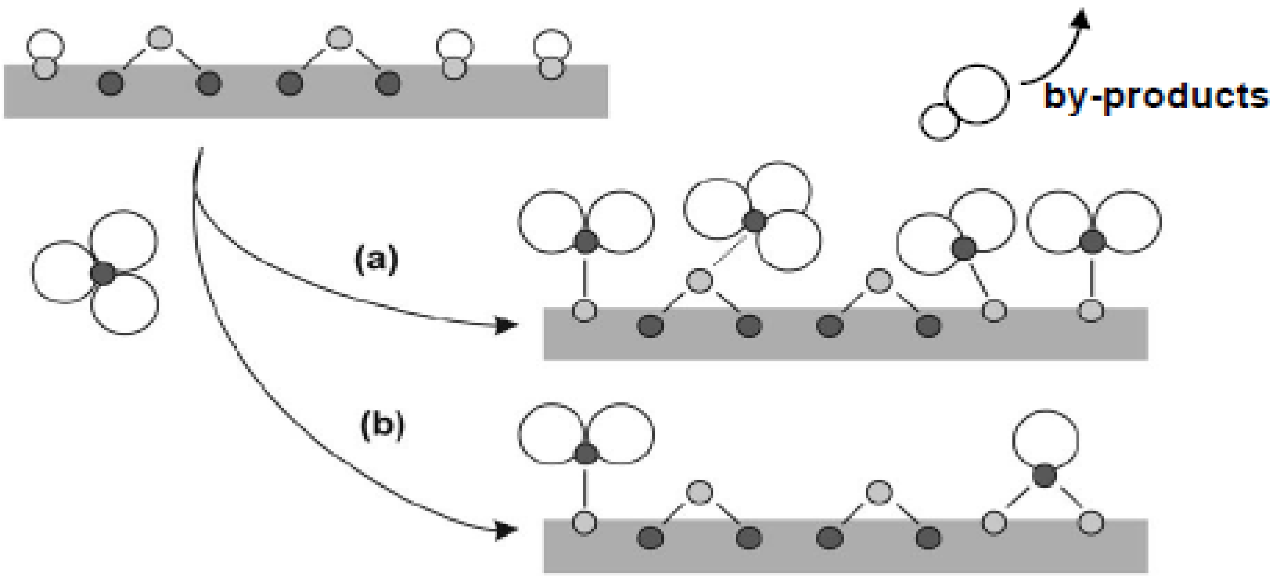
Web of Science (accessed on 2022/03/29)

Factors causing self limiting reactions

steric hindrance of the precursor ligands
number of reactive surface sites



Selection of precursor and reactant; surface chemistry



- NOT atomic layer by atomic layer
- Saturated layer of adsorbate after each cycle
- GPC – Growth Per cycle

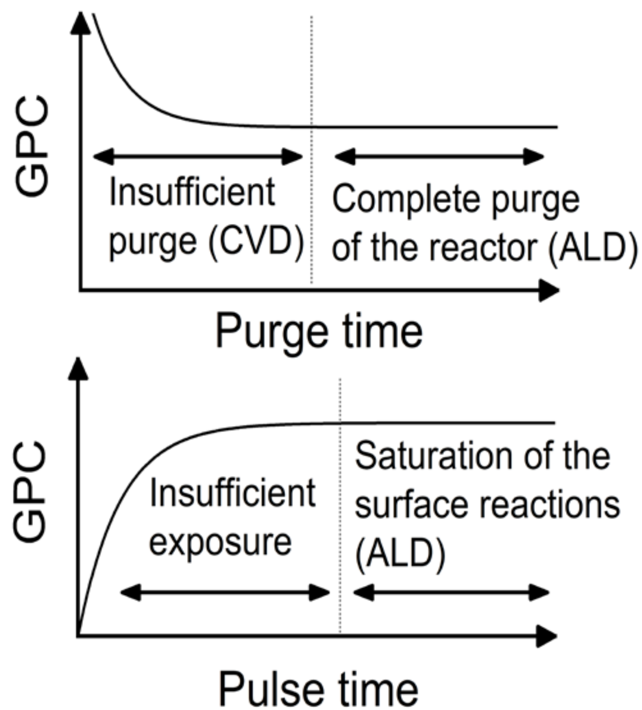
GPC (Å/cycle)
directly impacted by the nature of the precursors
less than 1 atomic layer/cycle
(steric hindrance due to ligand)

Process characteristics – self limiting reactions

Saturation curves

to be determined to ensure self-limiting reactions, to ensure that all the subsrate is covered

Purge/pulse times depend on vapour pressure of precursors, 0,02 – 30 s



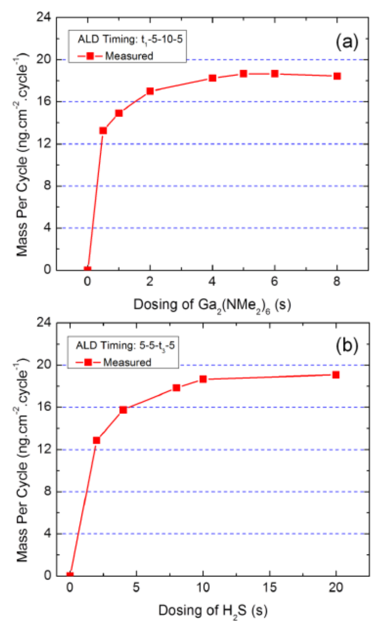


Figure SI-1. Effects of precursor dosing on ALD Ga_xS growth: (a) The effect with the extended $Ga_2(NMe_2)_6$ dosing; (b) The effect with the extended H_2S dosing.

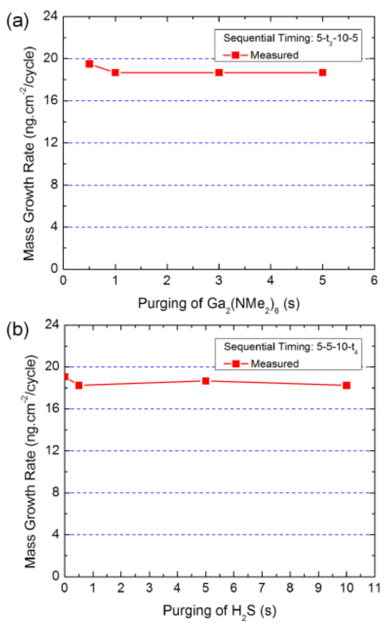
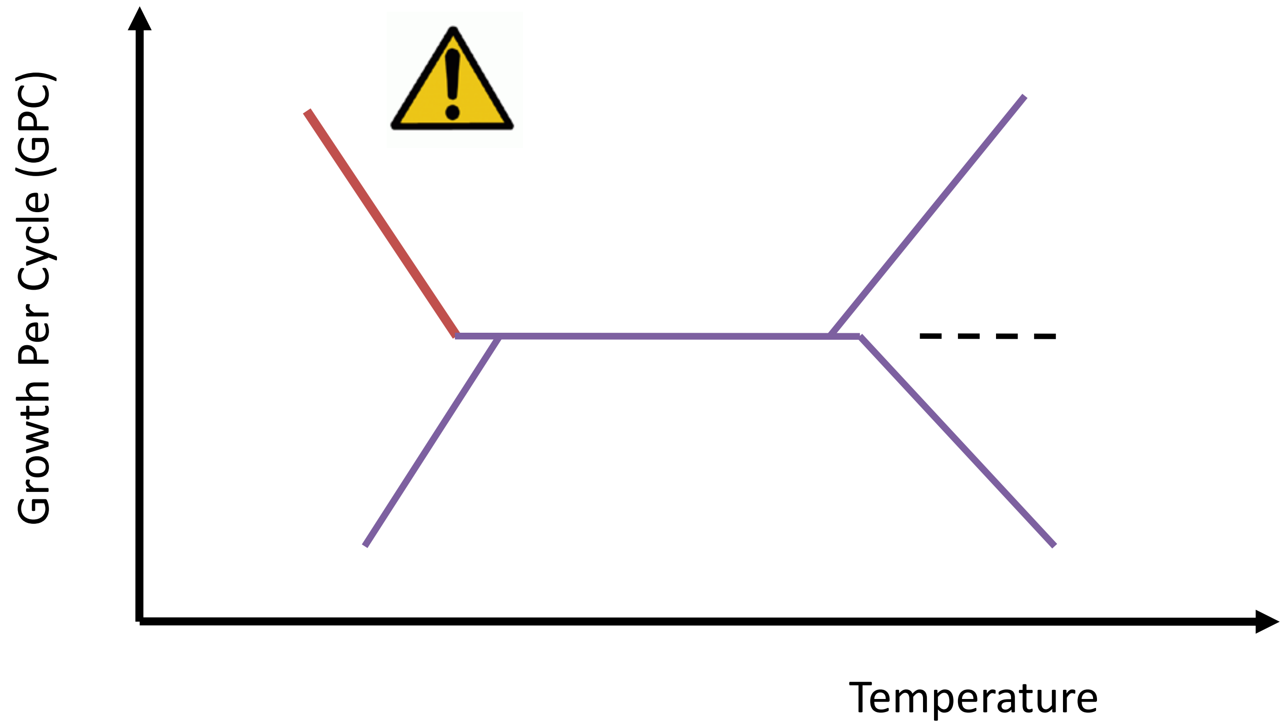


Figure SI-2. Effects of precursor purging on ALD Ga_xS growth: (a) The effect with the extended purging after $Ga_2(NMe_2)_6$ dosing; (b) The effect with the extended purging after H_2S dosing.

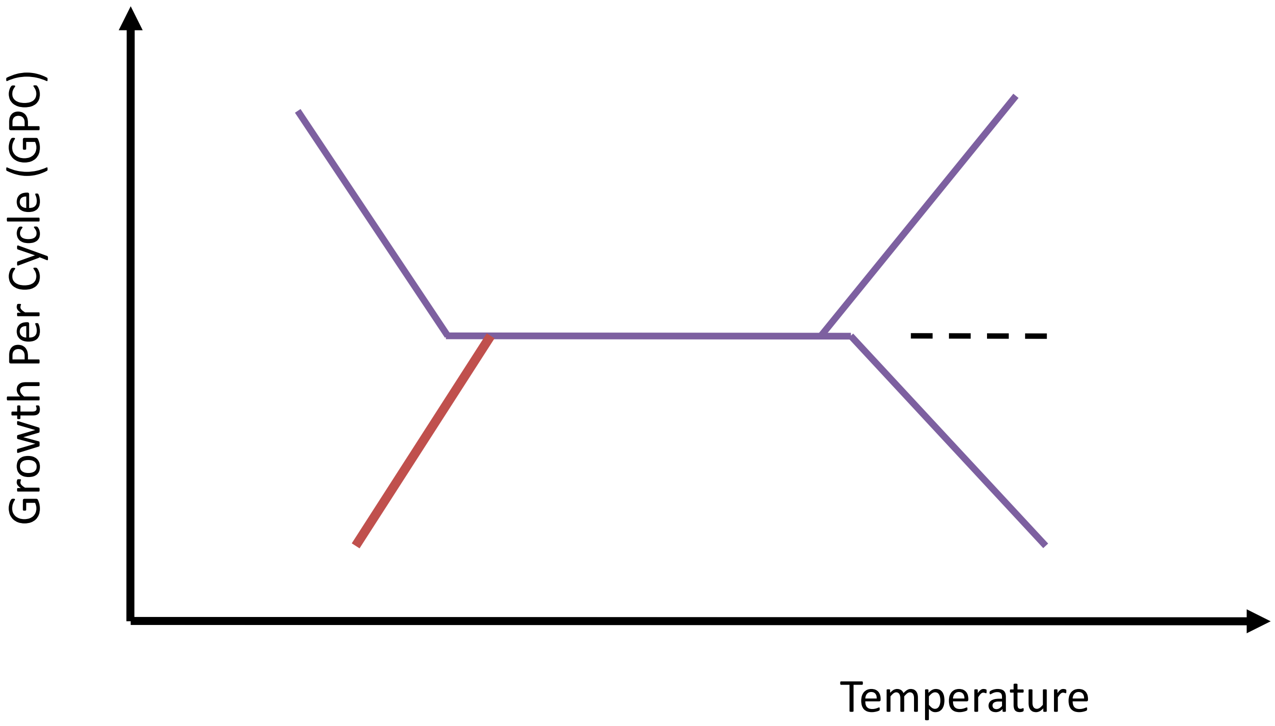
dx.doi.org/10.1021/cm4031057 | *Chem. Mater.* 2014, 26, 1029–1039

Effect of temperature



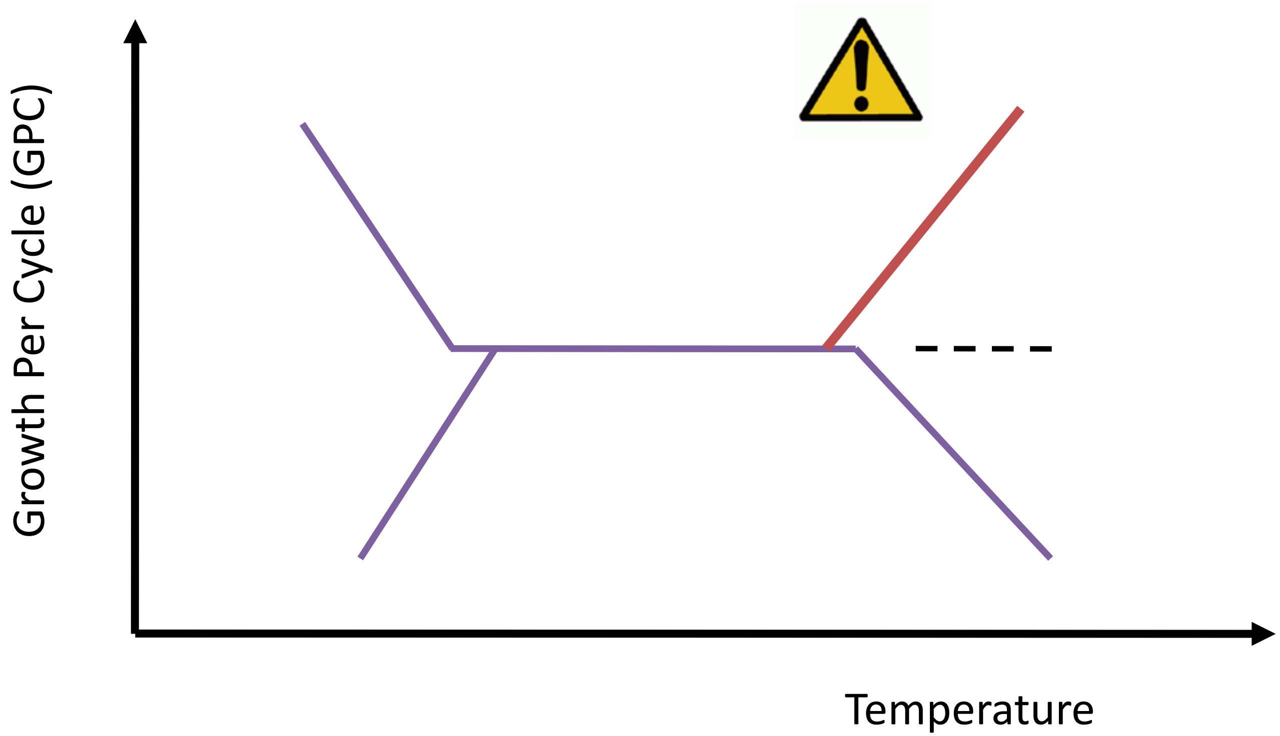
Condensation of the precursors on the substrate surface

Effect of temperature



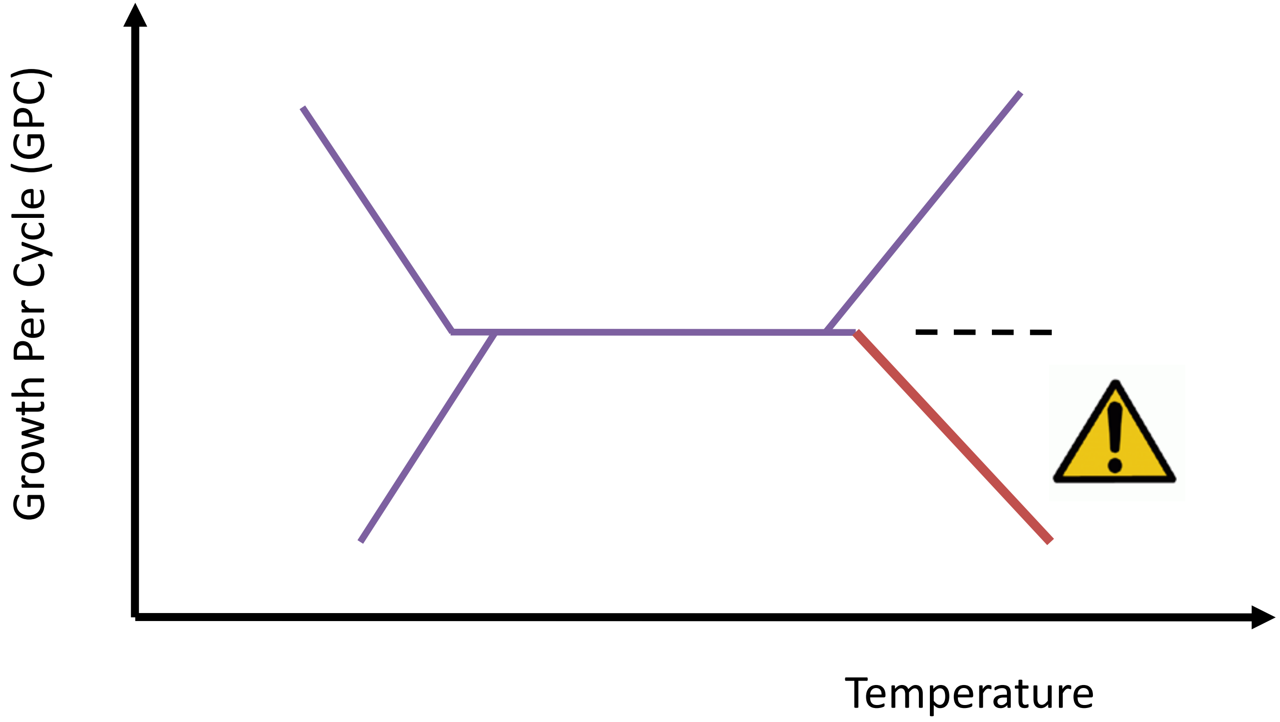
Kinetic regime: activation energy, $v \propto e^{\frac{-E_a}{RT}}$

Effect of temperature



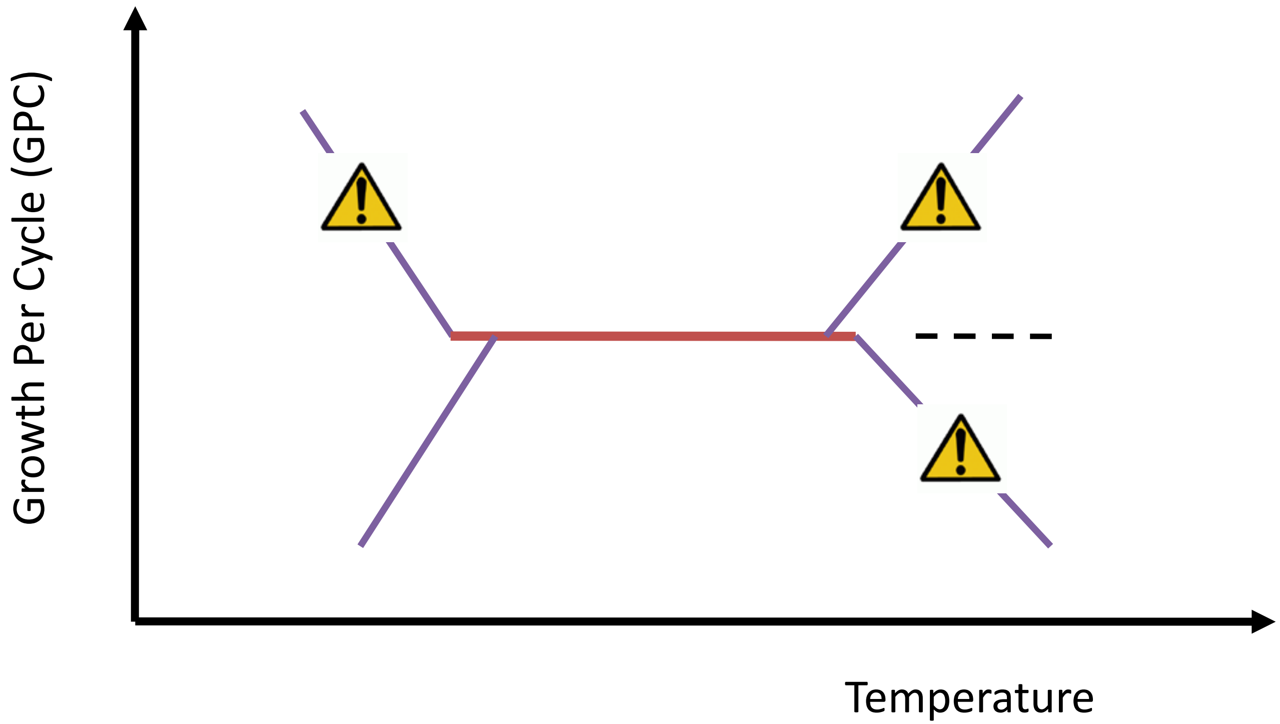
Decomposition of the precursors in the gas phase

Effect of temperature



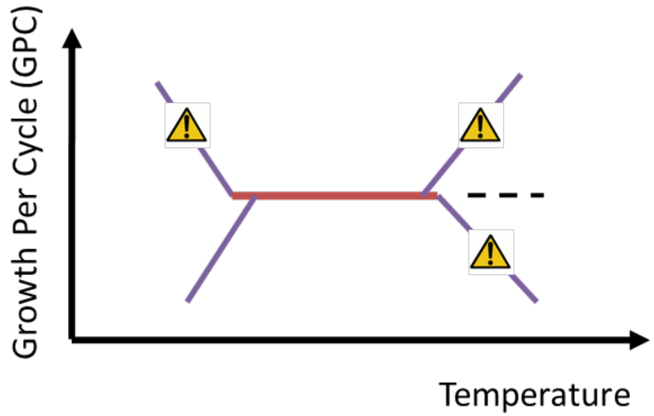
Desorption or sublimation of the deposited material

Effect of temperature



ALD window: GPC is constant with T

ALD window



ALD window: GPC is constant with T

	1 monolayer per cycle	**> 1 monolayer per cycle**	**< 1 monolayer per cycle**
ALD window	Ideal case	Gas phase dimerisation of the precursor	**Real case**
	« Small molecule »	Ex= Tantalum ethoxide Tantale TaEtO for Ta_2O_5 deposition	Precursor steric hindrance Surface sites density

Basics

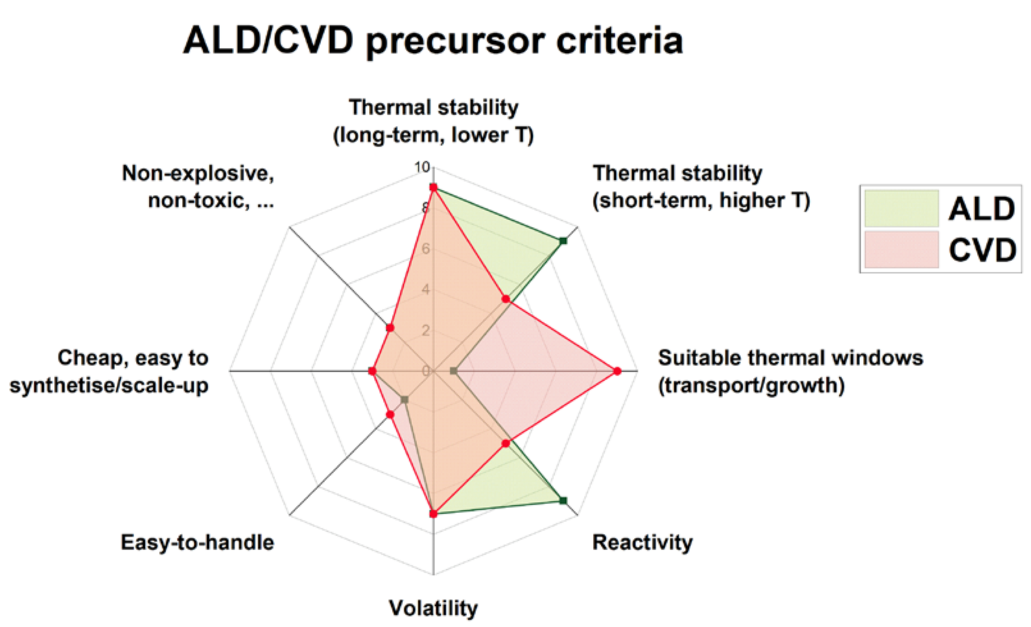
- ❑ Growth temperature optimisation
  - ❑ ALD window
  - ❑ Films properties

- ❑ Optimisation of the precursor dosage
(pulse duration, concentrations- vaporisation temperature)
  - ❑ Under dosing: lower saturated growth rates and poor uniformity
  - ❑ Overdosing : precursor waste and possible CVD component
  - ❑ Normal ALD process is slightly overdosed to ensure good uniformity

- ❑ Purge time optimisation
  - ❑ Too short purge time ⇒ excess precursor overlapping
  - ❑ Too long purge time ⇒ a waste of time and eventual thermal desorption

ALD / Chemical process - Precursors

Precursors dictate film growth conditions and properties



Metal precursors

M – X	M – R	M – N	M – O
$HfCl_4$	TMA ($AlMe_3$) $ZnEt_2$ $RuCp_2$ $Ba(tBu_3Cp)_2$	TDMA-type precursors	TIP-type precursors Diketonate precursors
X = F, Cl, Br, I	R = alkyl Cp = 	TDMA = $(NMe_2)_4$	TIP = $(OiPr)_4$

O, N, S precursors:

- H_2O, O_2, O_3, H_2O_2, O_2, alcohols
- NH_3, N_2 plasma, N_2H_4
- H_2S, S, H_2S plasma

Key points

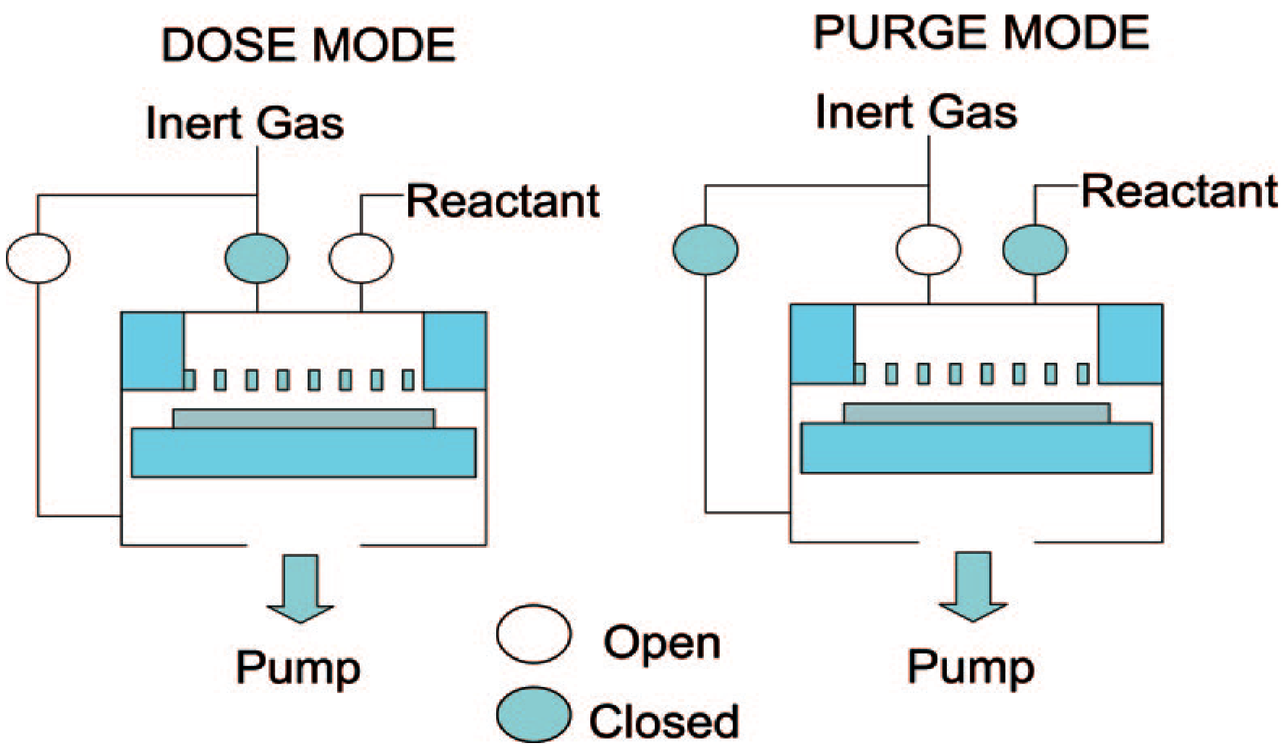
- ALD process =
  - Precursor transport to the reaction zone
  - A precursor chemistry adapted to the substrate (starting surface sites)
  - A specific temperature range: ALD window
  - One surface reaction: precursor saturation on surface sites

- Characteristics= Temperature = 100-300°C
  Pressure = mbar
  Cycle Time = 1-20 s

  Growth rate= 1 to 10 nm/h

- Reactors

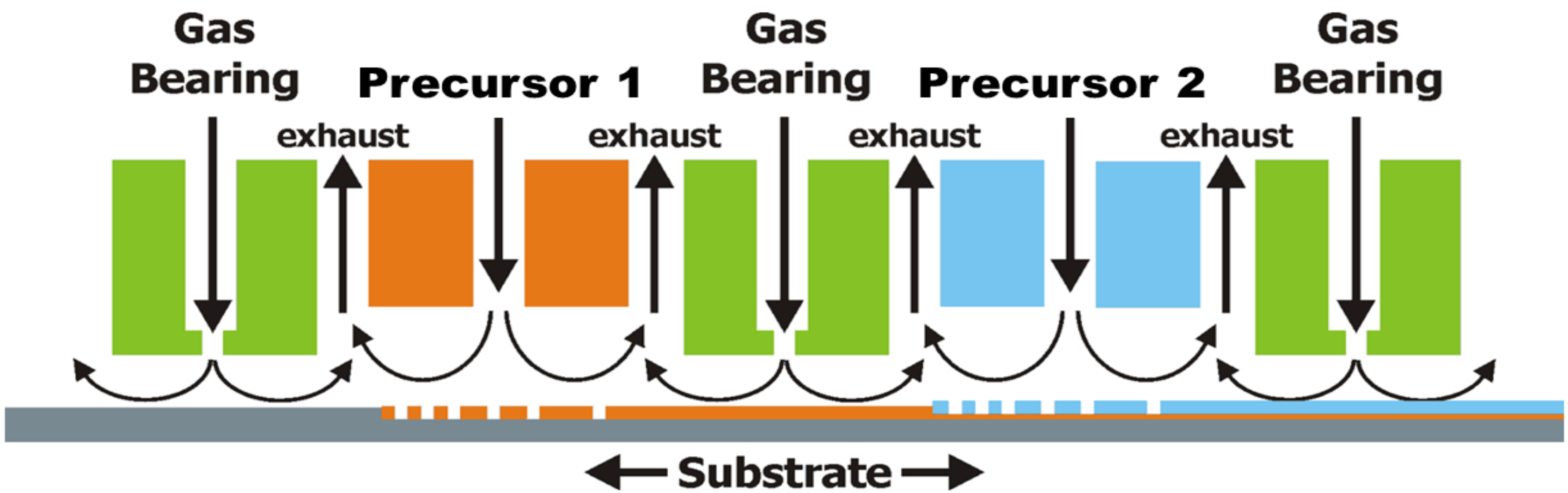
Reactors -



S.M. George , Chemical Reviews, 2010, Vol. 110, No. 1

- ❑Injection close to substrate
- ❑Limited dead zone

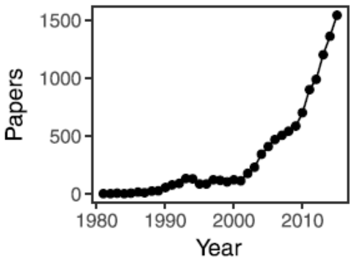
Reactors -



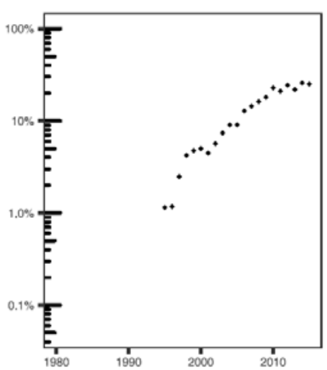
A Spatial ALD reaction scheme where the precursors are dosed simultaneously and continuously in half-reaction precursor zones separated by inert gas zones. Moving the substrate through two half-reaction zones completes one ALD cycle *(Poodt et al., J. Vac. Sci. Technol. A 30, 010802 (2012))*

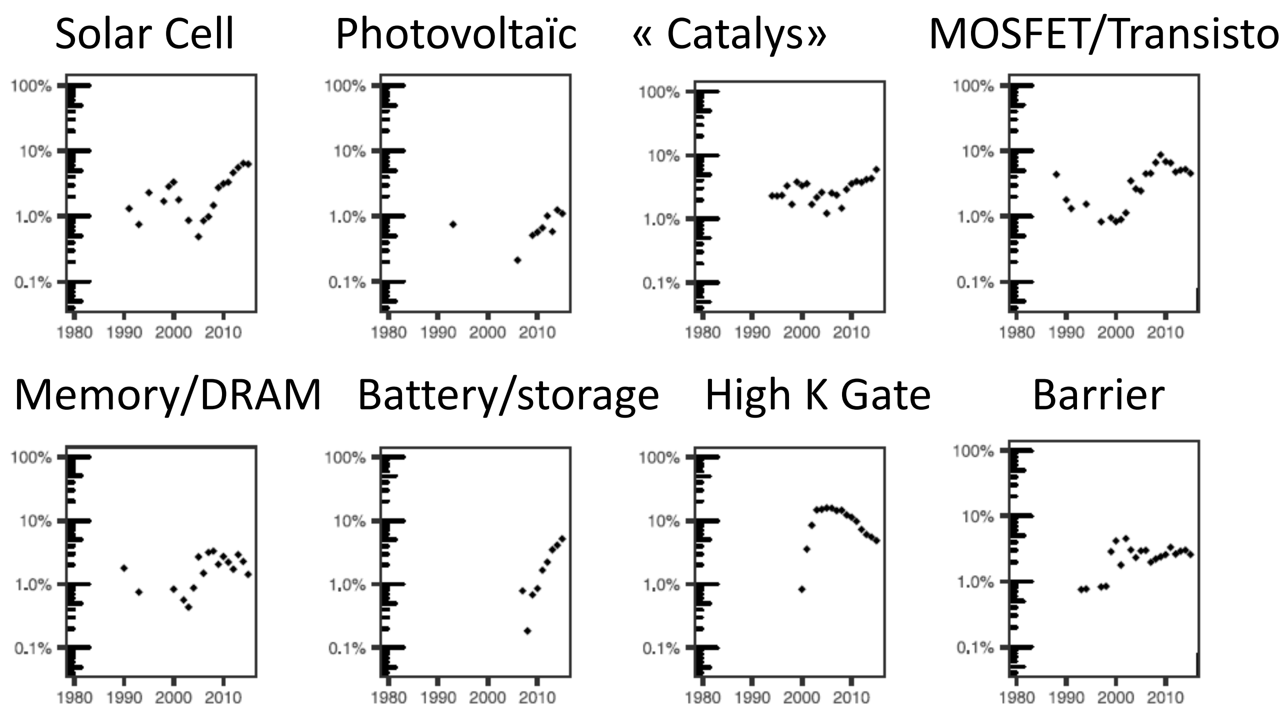
Application Domains

ALD



nano

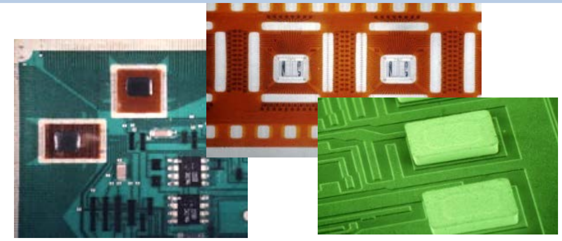




Percentage of ALD papers containing a specific word pertaining to applications in their titles

E. Alvaro, A. Yanguas-Gil (2018)
Characterizing the field of Atomic Layer Deposition: Authors, topics, and collaborations. PLoS ONE 13 (1): e0189137.
https://doi.org/10.1371/journal. pone.0189137

Application Domains



Microelectronics

- -Memories
- -Transistors – microprocessor
- -Capacitors, connections

Display

- -LEDs
- -Screens LCD
- -Screens (O)LED

Energy

- -Batteries
- -Photovoltaïcs
- -PEFMC ful cell

MEMS NEMS

- -Magnetic heads

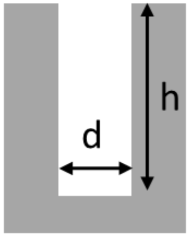
Emerging Applications

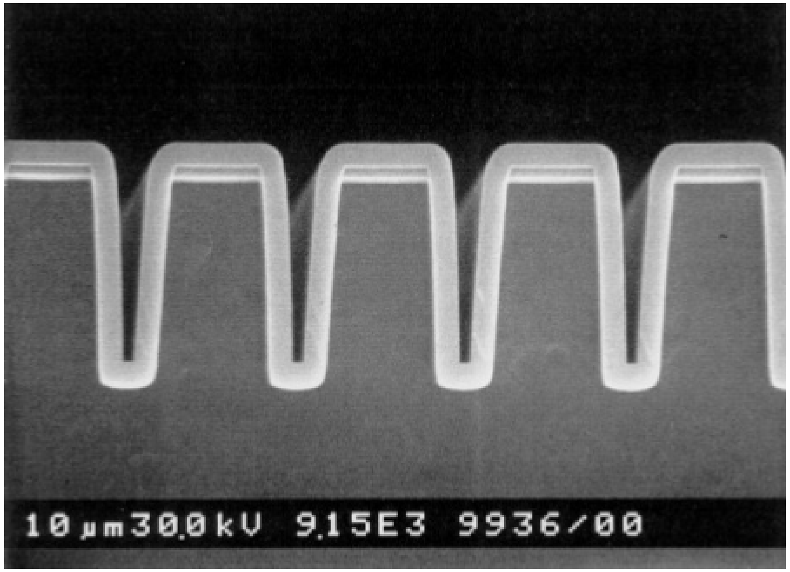
- -Nanomaterials
- -Optoelectronics devices
- -Fibers , textiles
- -Jewelry

F. Donsanti, RAFALD, Grenoble, 2015

ALD Specificities

- **Dense, pinhole-free** films
- Atomic level of **control** on **thickness** and **composition**
- **Soft conditions** (P ~ mbar-atm, T ~ RT-500°C)
- **Conformality** → **well-adapted to any substrates with high aspect ratios**





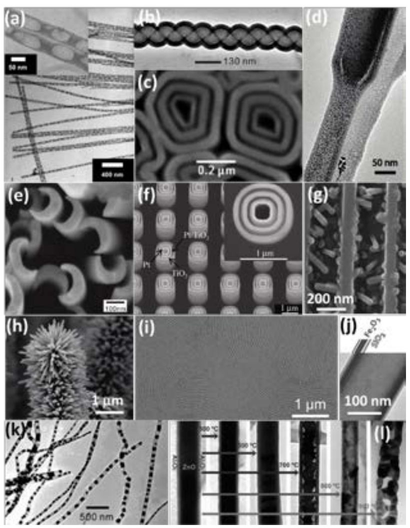
Mikrokemia Oy / University of Helsinki

Amorphous Alumina Al_2O_3

[*http://www.dileepnanotech.com/ALD_Saturating__Chemical_Reaction.htm#top*](http://www.dileepnanotech.com/ALD_Saturating__Chemical_Reaction.htm#top)*, from ref. 1999*

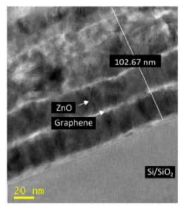
Complex nanostructures

ALD= key technology for the surface modification and the fabrication of complex nanostructured materials



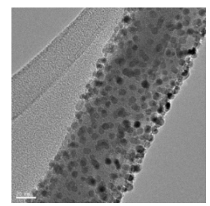
Adv Mater 2012 **24** 1017

Graphene/ZnO Nanolaminates



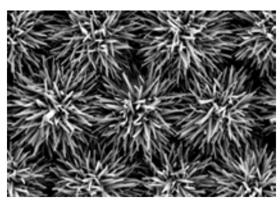
J phys Chem C 2016 **120** 23716

ZnO@Pd



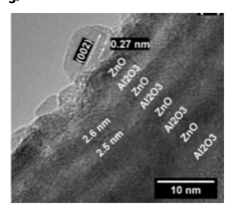
ACS Appl Mater Interfaces 2018 **10** 34765

ZnO urchin Nws



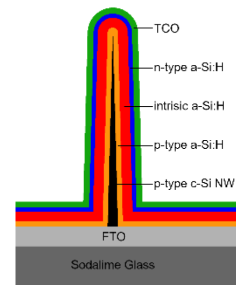
Nano Energy 2012 **1** 696

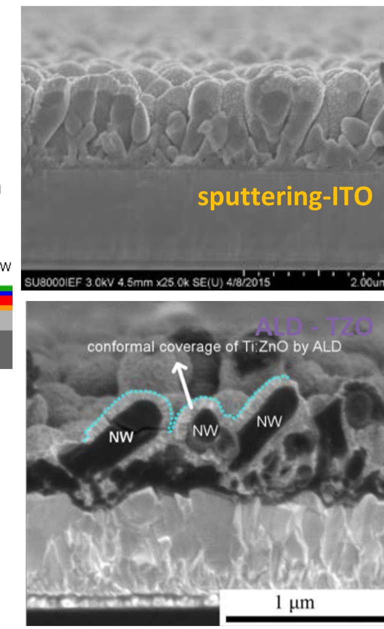
Al_2O_3/ZnO Nanolaminates



J Phys Chem C 2016 **120** 5124

Si NW



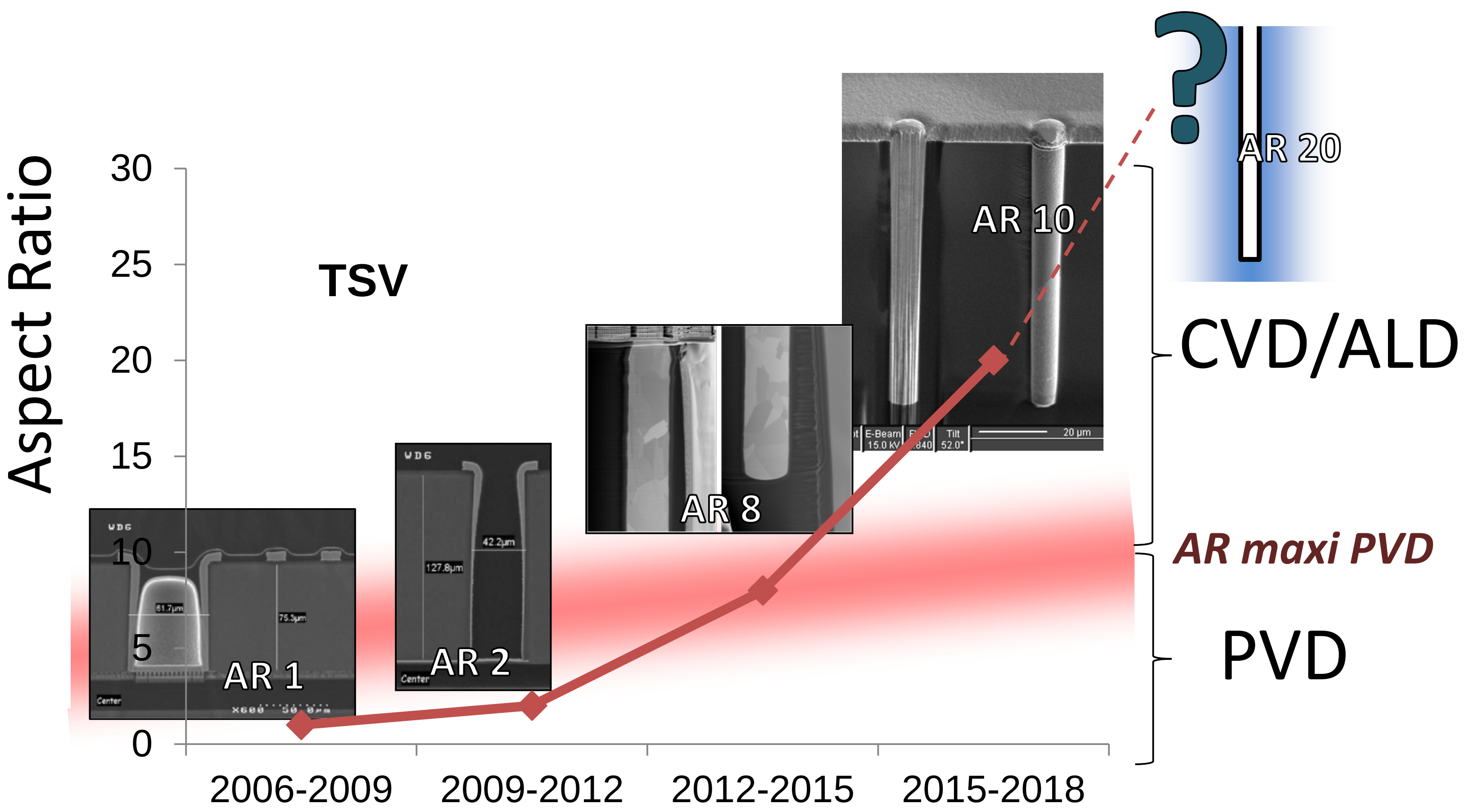


ACS Appl. Mater. Interfaces, **2020**, *12*, 21036

Institut Européen des Membranes

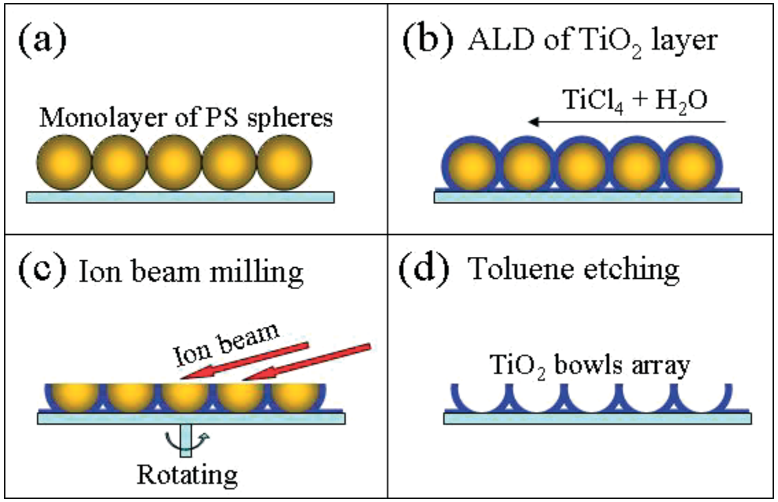
IPVF

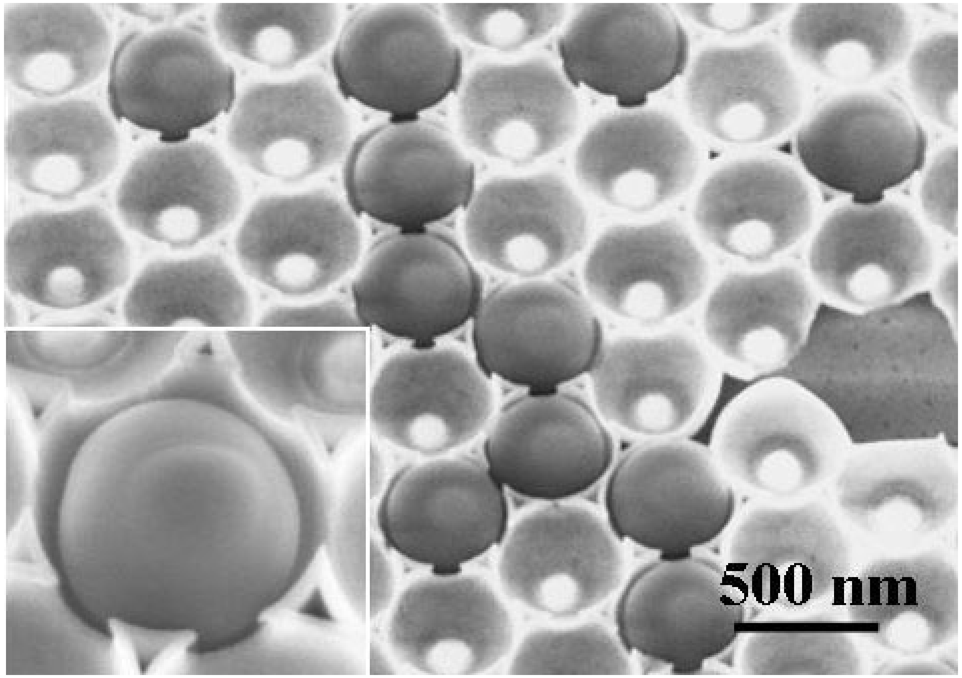
Microelectronics: Through Silicon Via



ALD : only solution for high AR TSV

Sacrificial templates

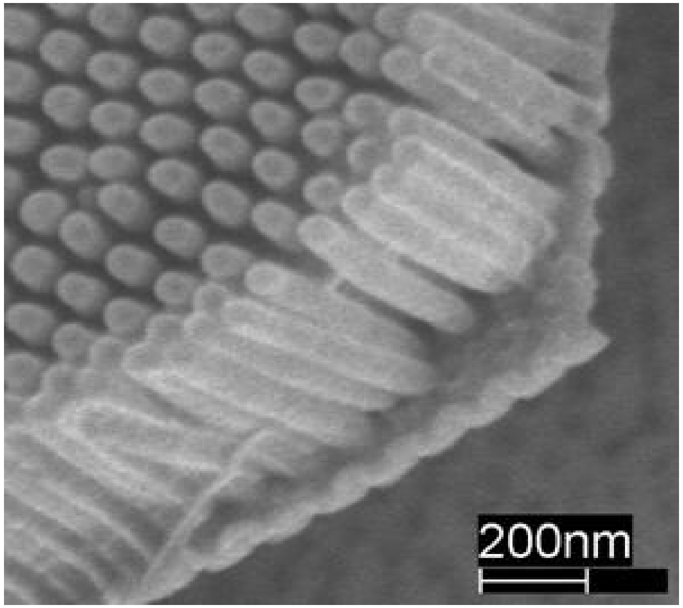




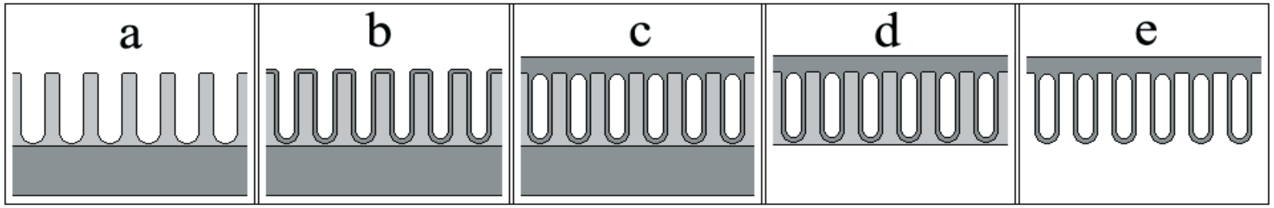
X. D. Wang, E. Graugnard, J. S. King, Z. L. Wang, C. J. Summers, Nano Lett. 2004, 4, 2223.

Examples: sacrificial templates

Nb_2O_5 nanotubes fabricated on a CVD film



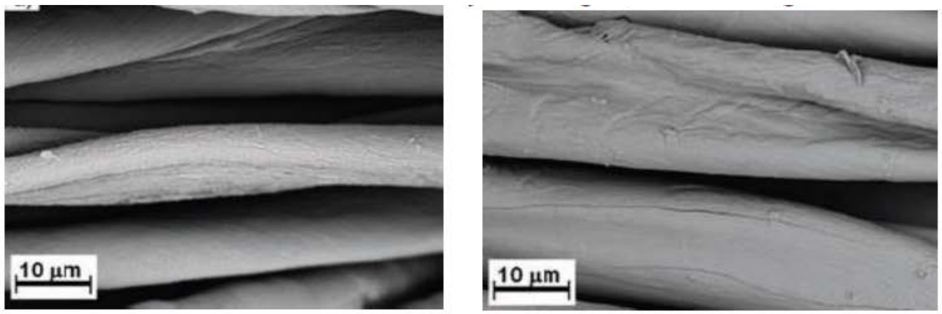
«Template-Based fabrication of Nanostructured Materials »
A. Hårsta , Department of Materials Chemistry, Uppsala University, Sweden



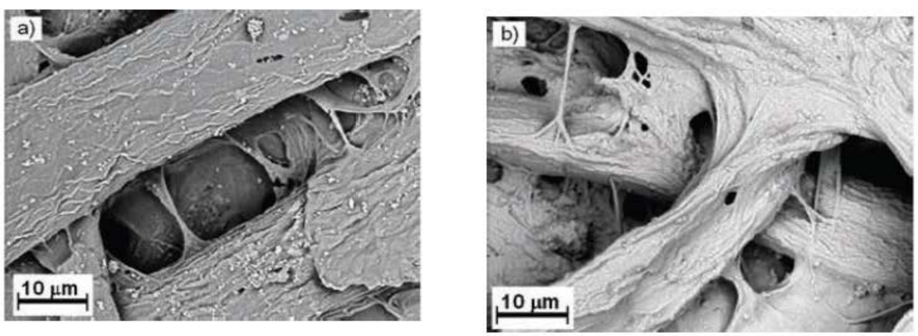
Nanoporous membranes AAO (Anodic Aluminum oxide)

Examples: textile

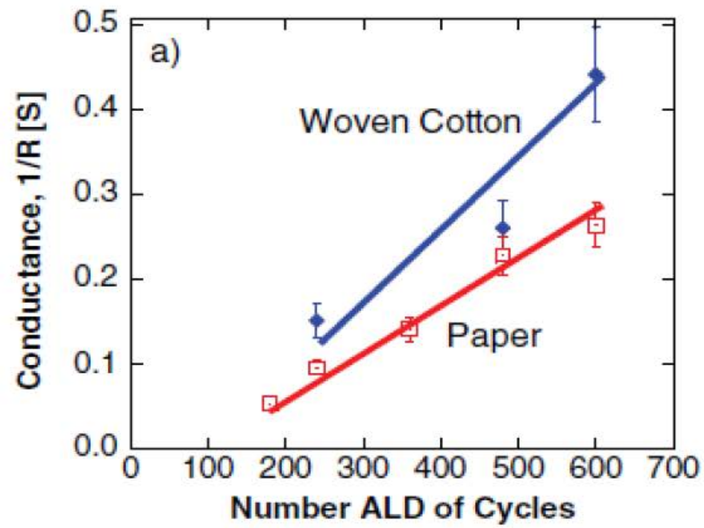
ALD : ZnO on textile fibers



480 cycles ALD ZnO deposited at 115 °C on woven cotton (before and after)



480 cycles ALD ZnO deposited at 115 °C on paper (before and after)



J. S. Jur , W. J. Sweet III , C. J. Oldham , and G. N. Parsons, Adv. Funct. Mater. 2011, 21, 1993–2002

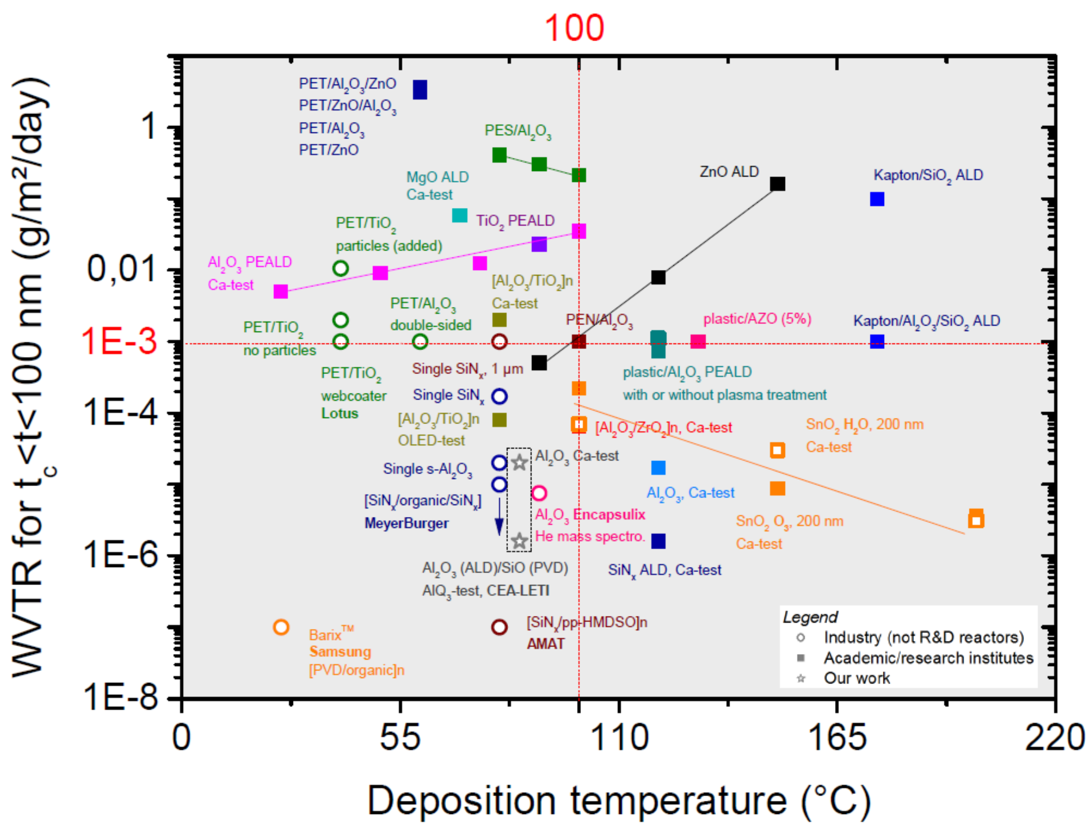
Examples: Paper/ cellulose

Paper to ban plastic but not its functionalities

cilkoa
The barrier solution for paper packaging

PhD Proposal : SIMAP/CILKOA composite optimisation – contact me!

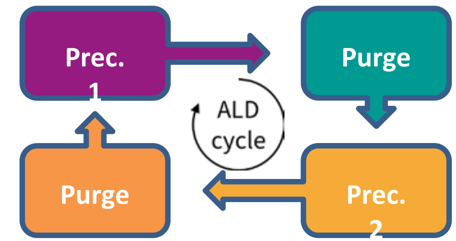
Examples: OLEDs and Organic Electronic components



Source. T. Maindron, CEA, RAFALD, Montpellier, 2017

Take-home messages

ALD is a process based on self-limiting surface reactions
- **atomic level control of film composition and thickness**
- **soft deposition conditions**
- **conformality**



Wide range of aspects

simulations

In situ instrumentation

surface science

molecular synthesis

ALD precursors molecules

ALD functional materials

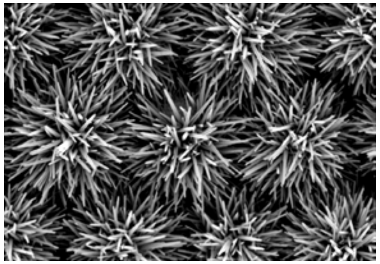
Applications

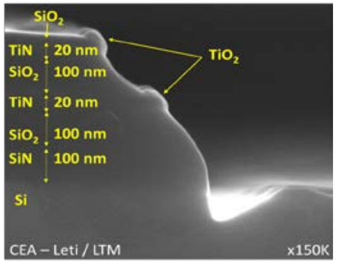
Nanoelectronics
Photonics
Optoelectronics
Quantum technology
Batteries
PV
Fuel cells
Catalysis
Displays
Pharmaceuticals
MEMS
Protective coatings
Biomedical
Optics

Equipments

High throughput reactors, Spatial ALD, Liquid ALD …

Well-adapted for **very thin layer < 50 nm, nanomaterial functionalization**, interface engineering, ….
Largely applied for the synthesis of **oxides materials**
Several **evolutions**: PE-ALD, SALD, MLD, AS-ALD





Techniques de l'Ingénieur, 2016

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workshop:
Lille – IEMN – Nov 2023.