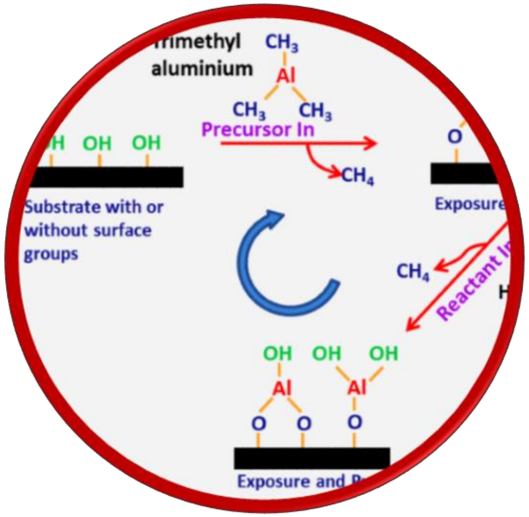
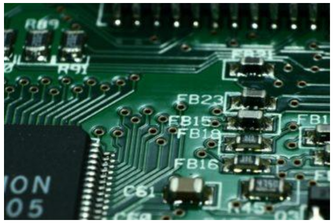
# atomic layer deposition



# application examples



Moisture Protection of PCBs

Optical NIR filter
on a curved lens

Conformal decorative coatings on and watch parts

Anti-tarnishing coating for jewelry

Thin film encapsulation
of moisture sensitive
CsI scintillator plates

Anti-corrosion coating for sensors

Conformal Optical coatings for
high power laser lenses

https://beneq.com/en/coating-services/customer-cases/
https://www.positivecoating.ch/

# content

- Introduction CVD – ALD – PVD
- Timing sequence: ALD vs CVD
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- ALD reactors
- Plasma enhanced ALD
- Spatial ALD
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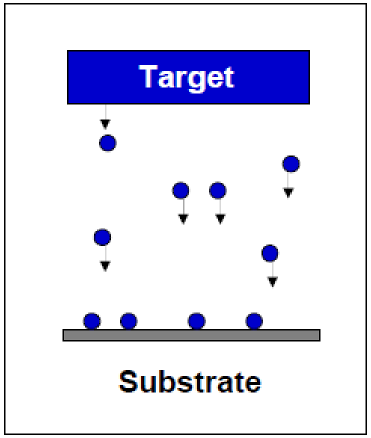
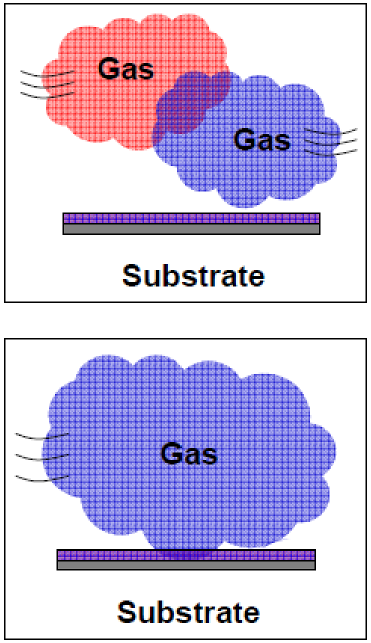
# PVD – CVD - ALD

## Physical Vapor Deposition (PVD)



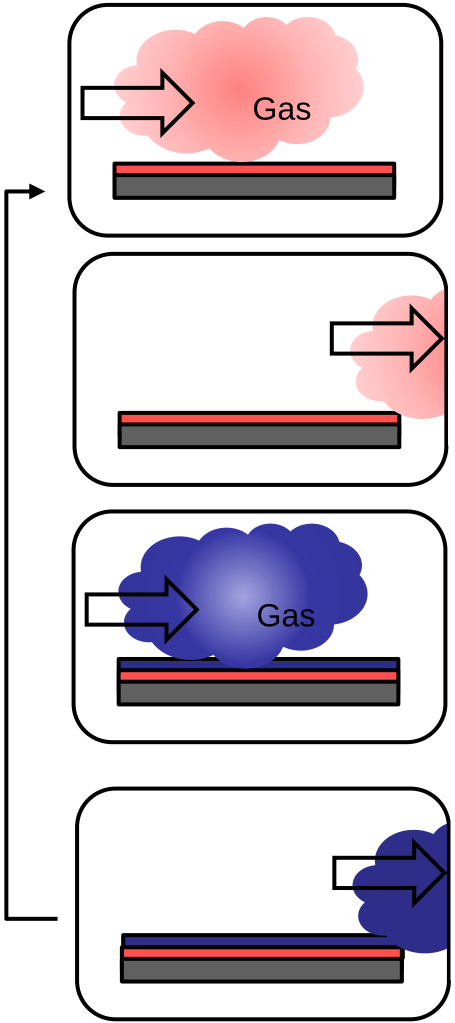
Impingement of atoms or molecular species

## Chemical Vapor Deposition (CVD)



Chemical Reaction Promoted by
Heat
UV
Plasma
Electrons/Ions

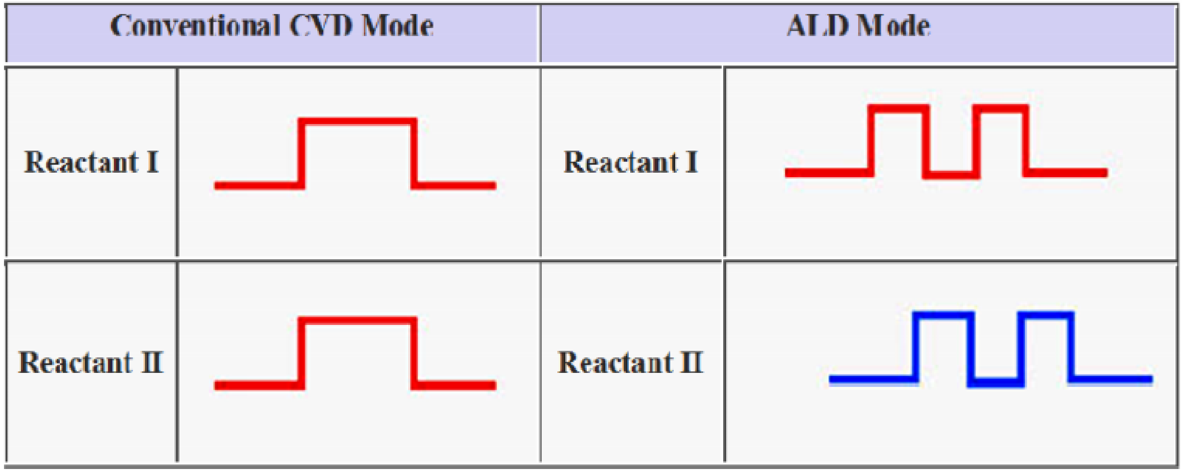
## Atomic Layer Deposition (ALD)



**Surface** Reactions only

# CVD vs ALD

## Timing Sequence : CVD vs ALD



| Conventional CVD Mode | | ALD Mode | |
|---|---|---|---|
| Reactant I | | Reactant I | |
| Reactant II | | Reactant II | |

ALD avoids gas phase reactions by seperating the reactants via sequential pulsing

# physisorption

There are **two aspects of adsorption** that are essential to the understanding of ALD. First, the **bond strength** that binds the gaseous species to the surface varies depending on both the gaseous species and the nature of the surface. Secondly, the **rate at which adsorption occurs** will be finite, and in some cases may be quite slow.

**Physical adsorption** is characterized **by weak bonds** to the solid surface (e.g. heats of adsorption < 20kJ/mole), on the order of **van der Waals** forces, and **rates of adsorption that are fast**.

**A "thermal" ALD process** is defined as one where the desired surface reaction occurs when **both reactants are on the surface at the same time**, but **will not react until the surface is heated to a high enough temperature**.

In all "thermal" ALD processes, temperatures, although lower than in CVD, are high enough to cause weakly bonded monolayers to desorb from the surface. For this reason, "thermal" ALD processes generally **take advantage of chemisorbed monolayers.**

**All gases will physisorb a self-limiting monolayer** under the correct temperature and pressure conditions, **even if they do not chemisorb**. The preferred conditions are **low pressure and moderate temperatures**. For a given pressure, if the **temperature is too low more than one monolayer will adsorb**, and at low enough temperatures a liquid or solid film will be formed. As the **temperature is raised a single monolayer will be left behind** on the surface. Finally, if the temperature is raised enough the single monolayer will be desorbed.

Ohring 2002

# physisorption

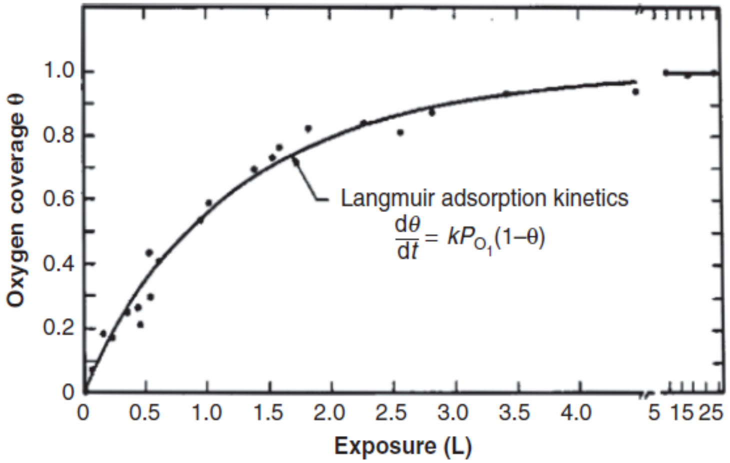
In general, **a single monolayer of a gas will adsorb** to a smooth surface as long as, for the temperature being used, the **pressure stays well below the saturation vapor pressure**. However, when molecules from the gas phase impinge on a surface and begin to stick, a complete (100%) monolayer may not be formed, depending on the pressure or concentration in the gas phase. The simple **Langmuir isotherm, illustrates this effect.**

Langmuir equated the rate of adsorption to the rate of desorption of gas atoms or molecules on a smooth surface, where there is no interaction between adsorbed particles.

The rate of **adsorption is $k_a$ [A](1 – θ)** and the **rate of desorption is $k_{-d}$ θ, where θ is the fraction of surface covered**. Here [A] is the gas phase concentration of the molecular species A. Equating these and defining $K = k_a/k_{-d}$ as an equilibrium constant for the adsorption process, we derive:

$$\theta = \frac{K[A]}{1+K[A]}$$

For low values of [A], the surface coverage varies linearly with the concentration [A] or the gas pressure. For higher pressures, the coverage approaches unity.



.2 Adsorption kinetics of $O_2$ on Rh(111) [9].

Kääriäinen 2013

# chemisorption

Chemisorption is similar to physical adsorption except that **the reactant being adsorbed forms a chemical bond** with atoms on the surface. With this type of bond the forces holding the adsorbed layer in place are on the order of chemical bonds between atoms in a molecule.

The significance of this fact for thermal ALD is that the surface reaction of interest between the two reactants may require a moderately high temperature in order to obtain a rapid reaction.
In this case, the first reactant will have to adsorb and remain bound to the surface until the reaction is complete. Physisorbed reactants will be desorbed by the higher temperatures, because of their weak bonding strength.

Another important consequence of chemisorption for ALD, is **that as a reactant bonds to the surface it will, in general, form just a single monolayer**. Additional reactants arriving at the monolayer coated surface would have to bond to it by van der Waals forces, and the surface temperature would discourage this. Therefore, chemisorption bonding invariably leads to the desired single monolayer of reactant.

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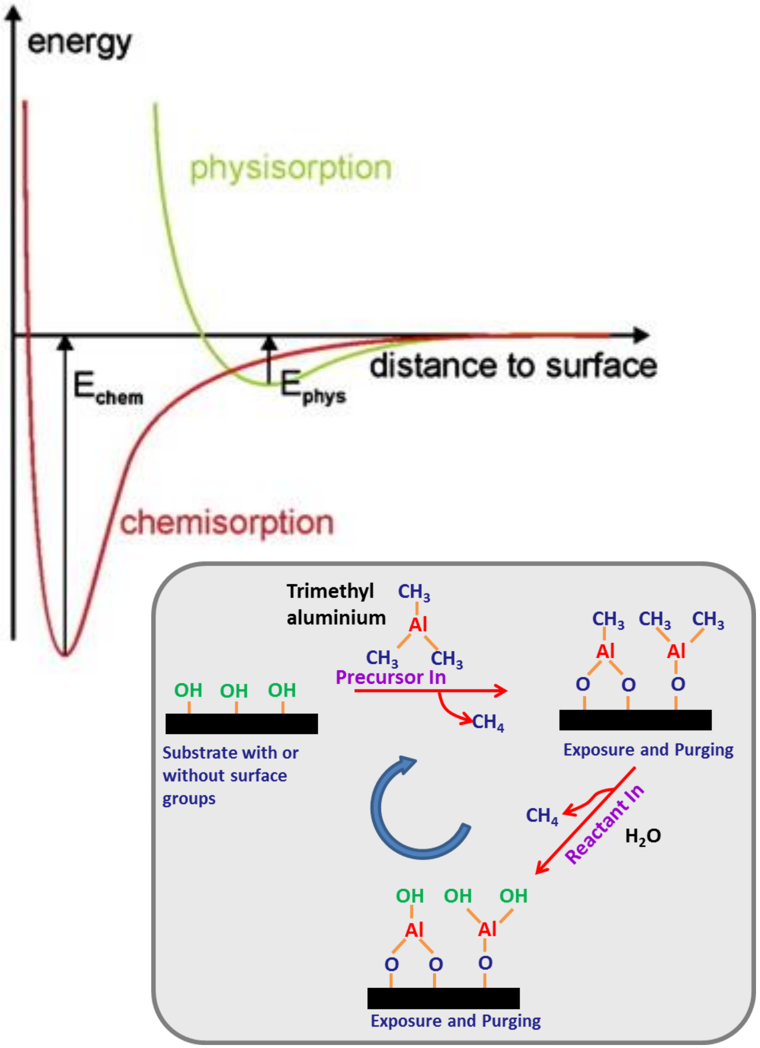
# physisorption & chemisorption



## Chemisorption on reactive surface

- $E_{chem}$ ≈1-10eV (≈ 100-1000 kJ/mol)
- chemical bond
- needs reactive surface site

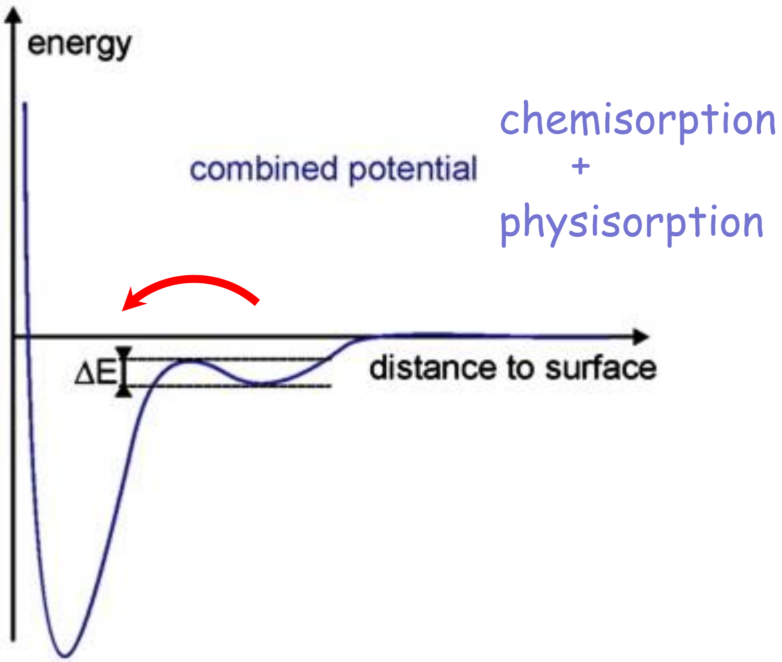
## Physisorption on non-reactive surface

$E_{phys}$ ≈0.1eV (approx. 10 kJ/mol)

Van der Waals Forces
  - non-covalent forces
  - van der Waals energy decays with $1/r^6$

Mechanisms:
Dipole-Dipole (Keesom)
Dipole-polarizable molecule (Debye)
induced dipole moments (London)

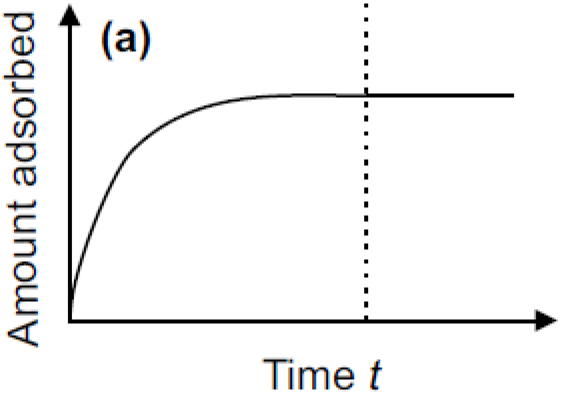
# chemisorption

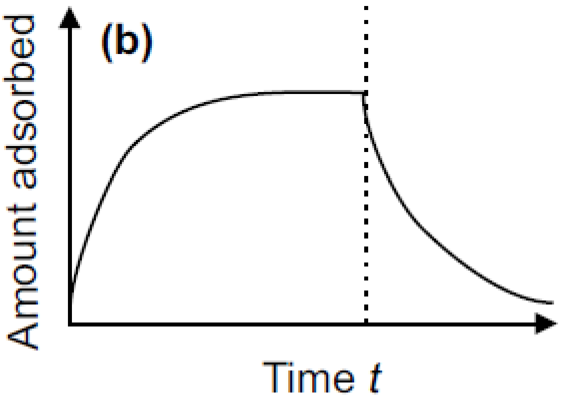


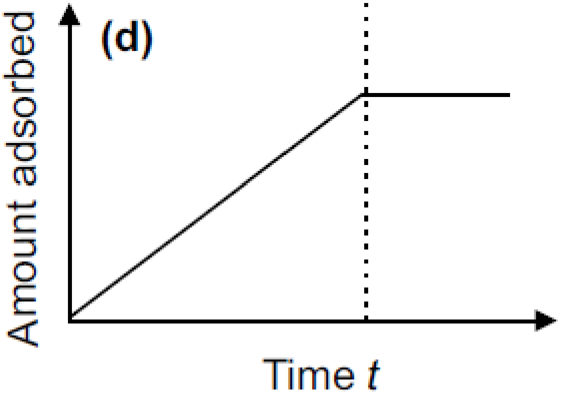
Chemisorption needs to overcome ΔE
→ thermal energy needed
→ substrate heating

Substrate temperature must be smaller than thermal decomposition temperture of the molecule
→ Otherwise we get CVD

# surface saturation







Irreversible saturation ALD reactions:

Surface saturates with a monolayer of precursor, strong chemisorption (=chemical bonds formed)

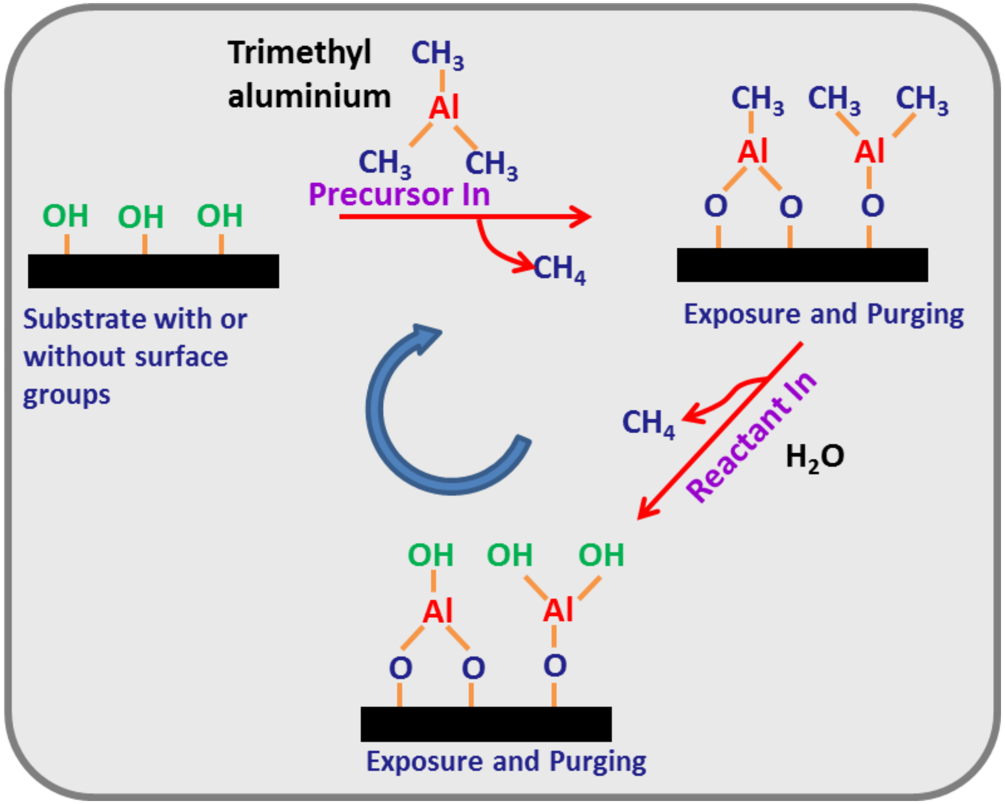
Reversible saturation:

Physisorption only (weak bonds like van der Waals): once precursor flux is stopped, surface species will desorb.

Irreversible non-saturating.

CVD regime:
more reactants in, more film is deposited (continuosly)

# thermal ALD of $Al_2O_3$



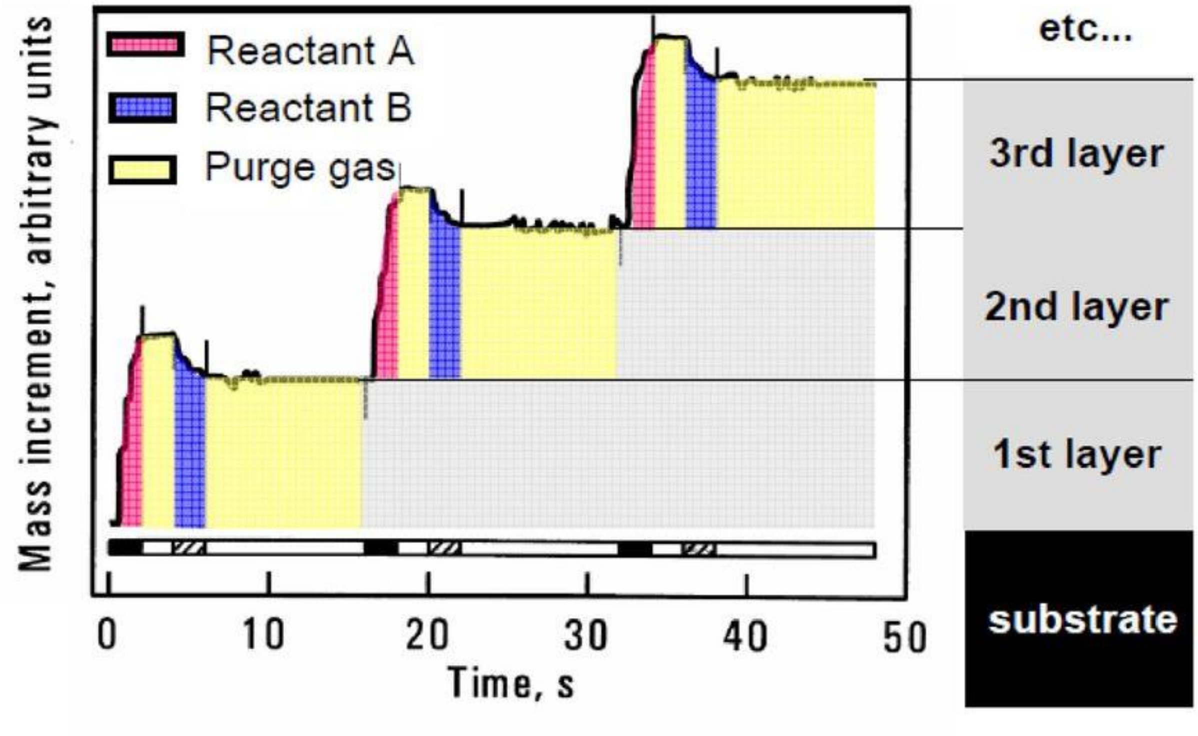
TMA + Water is strongly exothermic reaction

TMA starts spontaneously @ RT to react with humidity and produces powder

Was used as rocket fuel

TMA refill only in dry glovebox under inert atmosphere

# in-situ QCM measurements



Aarik et al., Thin Solid Films 340 (1999) 110, for $HfCl_4/H_2O$ ALD

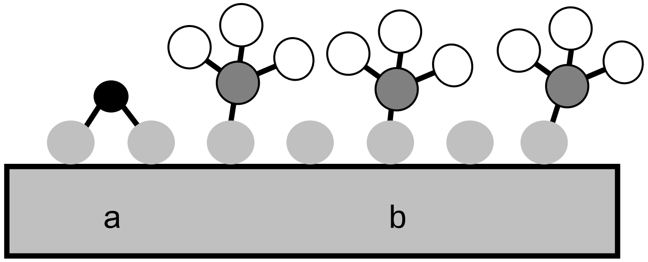
# deposition rate

Basically one atomic layer per pulse

In practise less than an atomic layer because:

a) Inactive surface sites

b) Steric hindrance: a large precursor molecule prevents another precursor molecule from approaching the reactive site



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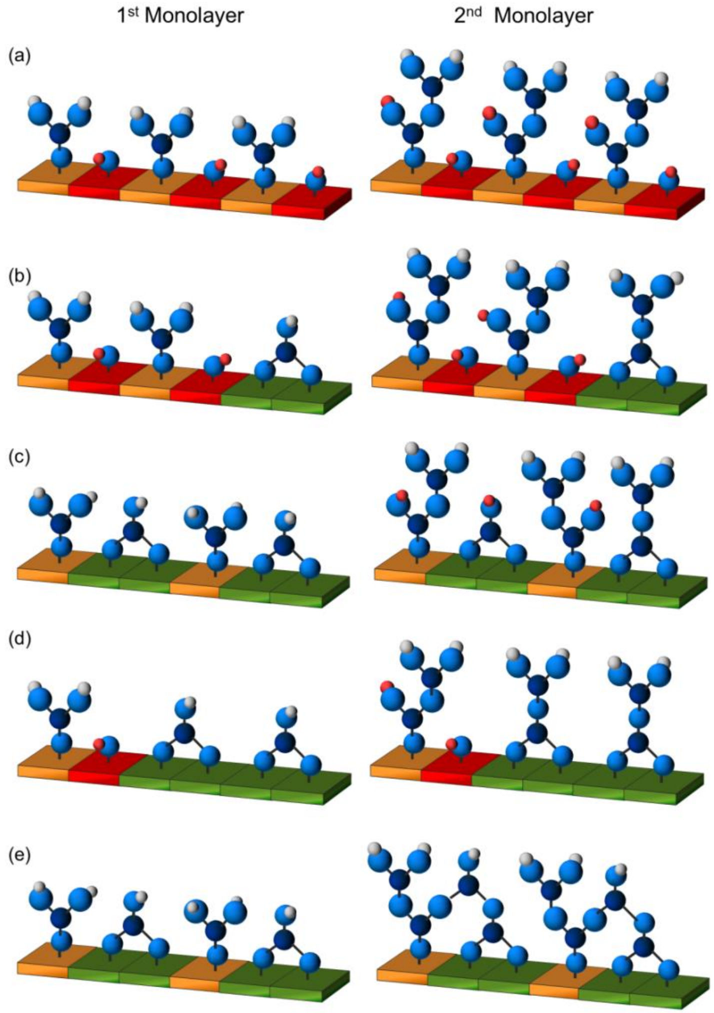
$Al_2O_3$ deposition it is 1.1 Å/cycle (0.11 nm/cycle)

TiN it is 0.2 Å/cycle

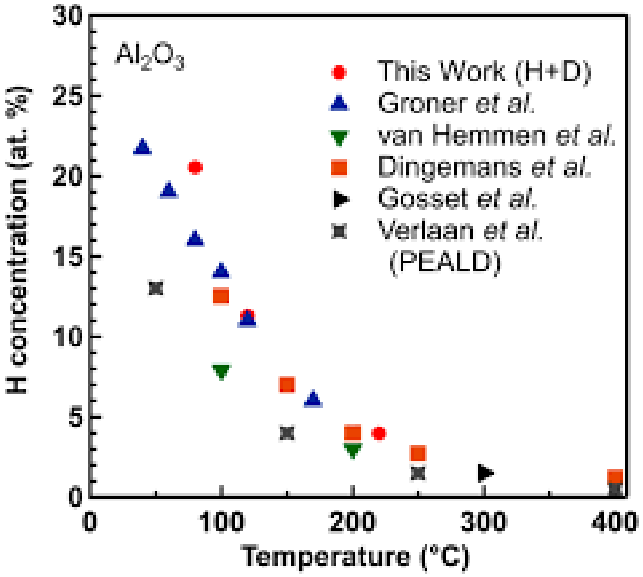
If pulses are one second ➔ 15*monolayer thickness/minute ~ 2 nm/min

If 0.1 second pulses ➔ 20 nm/min max.

# incomplete surface reactions



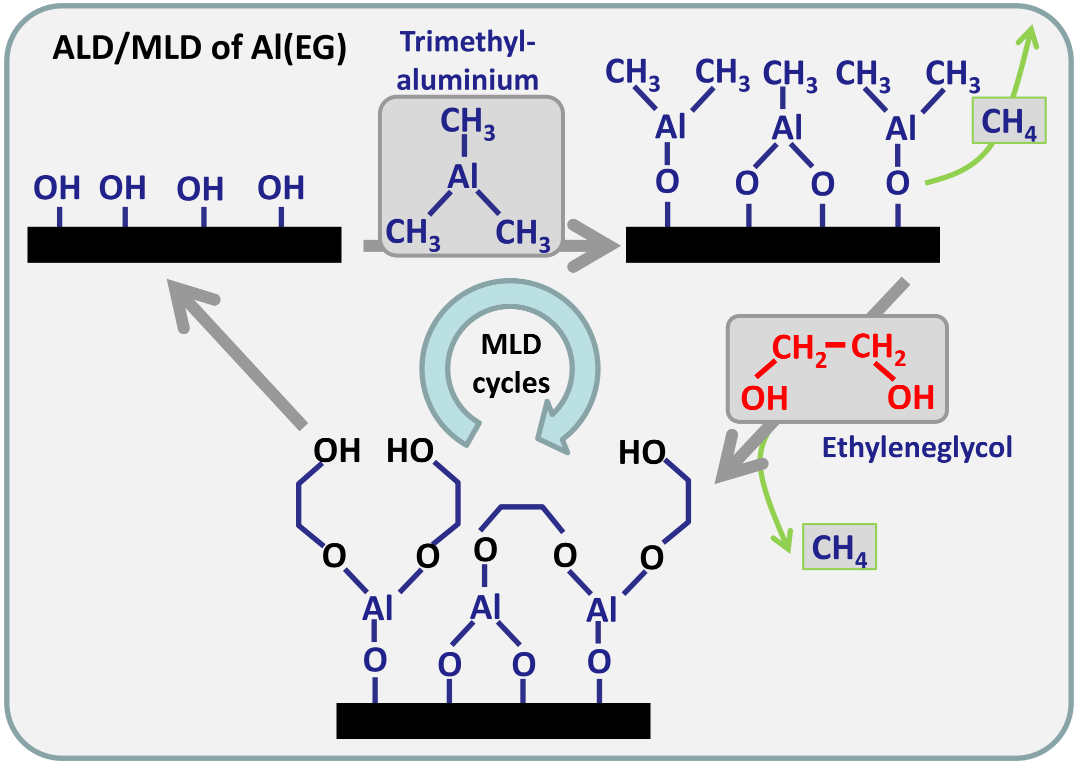
## Hydroxyl Incorporation



*Guerra-Nunez (2017) . Chemistry of Materials, 29, 8690*

# thermal ALD/MLD

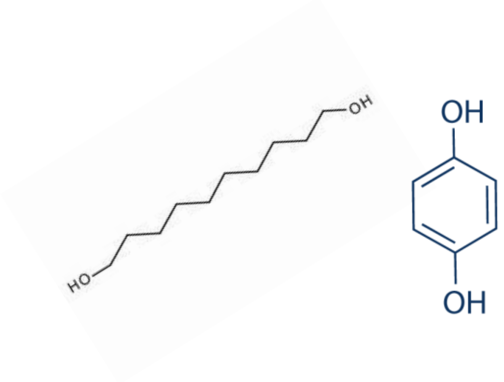
Example: Alucone



MLD: Molecular layer deposition

Hybrid organic-inorganic material

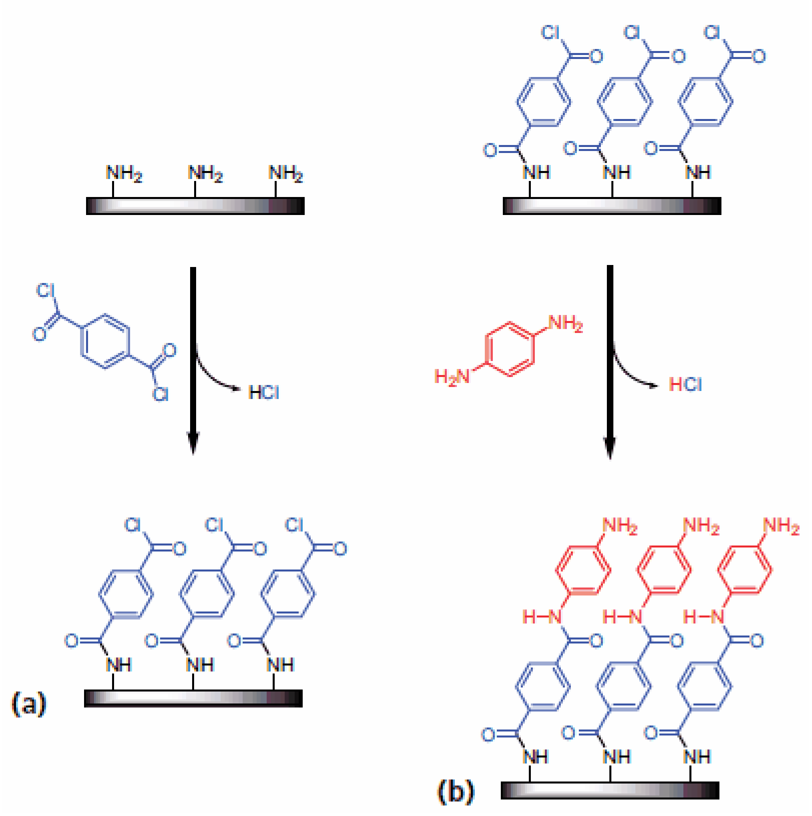
Carbon chain length and structure can be varied



Materials properties can be varied between polymer-like to inorganic

# thermal MLD

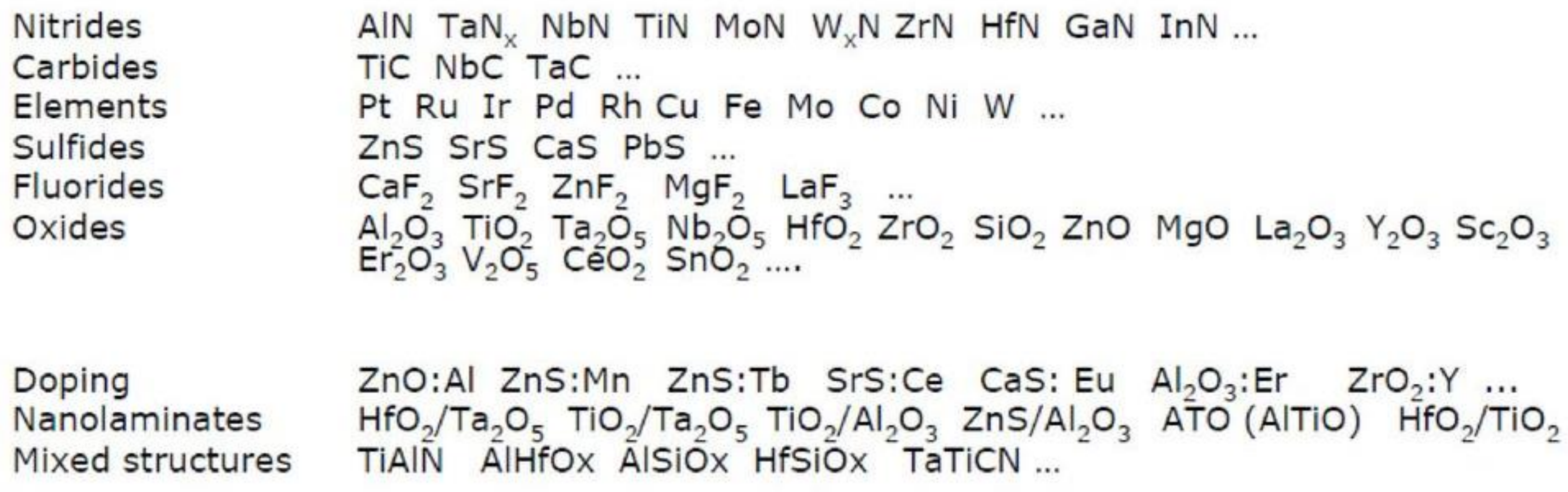
Example: polymer deposition



All reactants are organic compounds

source : ??

# ALD Thin Film Materials



| | |
|---|---|
| Nitrides | AlN $TaN_x$ NbN TiN MoN $W_xN$ ZrN HfN GaN InN ... |
| Carbides | TiC NbC TaC ... |
| Elements | Pt Ru Ir Pd Rh Cu Fe Mo Co Ni W ... |
| Sulfides | ZnS SrS CaS PbS ... |
| Fluorides | $CaF_2$ $SrF_2$ $ZnF_2$ $MgF_2$ $LaF_3$ ... |
| Oxides | $Al_2O_3$ $TiO_2$ $Ta_2O_5$ $Nb_2O_5$ $HfO_2$ $ZrO_2$ $SiO_2$ ZnO MgO $La_2O_3$ $Y_2O_3$ $Sc_2O_3$ $Er_2O_3$ $V_2O_5$ $CeO_2$ $SnO_2$ .... |
| | |
| Doping | ZnO:Al ZnS:Mn ZnS:Tb SrS:Ce CaS: Eu $Al_2O_3$:Er $ZrO_2$:Y ... |
| Nanolaminates | $HfO_2/Ta_2O_5$ $TiO_2/Ta_2O_5$ $TiO_2/Al_2O_3$ $ZnS/Al_2O_3$ ATO (AlTiO) $HfO_2/TiO_2$ |
| Mixed structures | TiAlN AlHfOx AlSiOx HfSiOx TaTiCN ... |

Important missing materials:
- silicon
- silicon nitride

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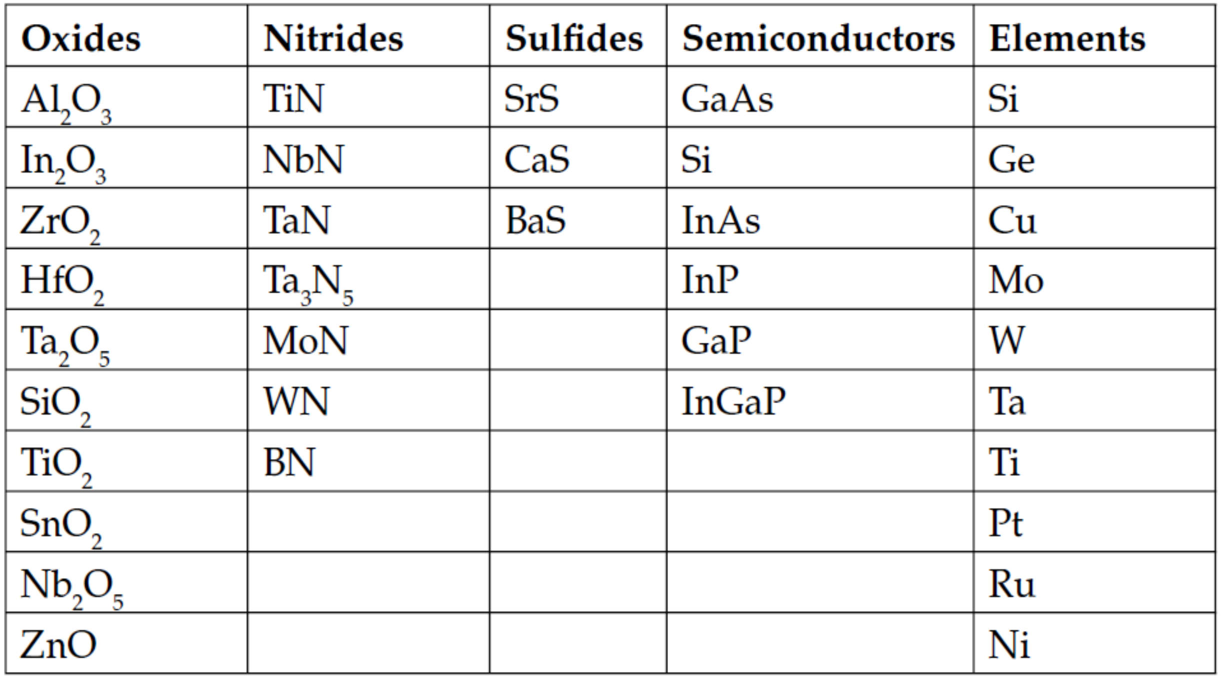
# ALD materials



| Oxides | Nitrides | Sulfides | Semiconductors | Elements |
|---|---|---|---|---|
| $Al_2O_3$ | TiN | SrS | GaAs | Si |
| $In_2O_3$ | NbN | CaS | Si | Ge |
| $ZrO_2$ | TaN | BaS | InAs | Cu |
| $HfO_2$ | $Ta_3N_5$ | | InP | Mo |
| $Ta_2O_5$ | MoN | | GaP | W |
| $SiO_2$ | WN | | InGaP | Ta |
| $TiO_2$ | BN | | | Ti |
| $SnO_2$ | | | | Pt |
| $Nb_2O_5$ | | | | Ru |
| ZnO | | | | Ni |

Missing still: Si, SiN

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# ALD materials

By and large, the first reactant is either a halogen or an organometallic.

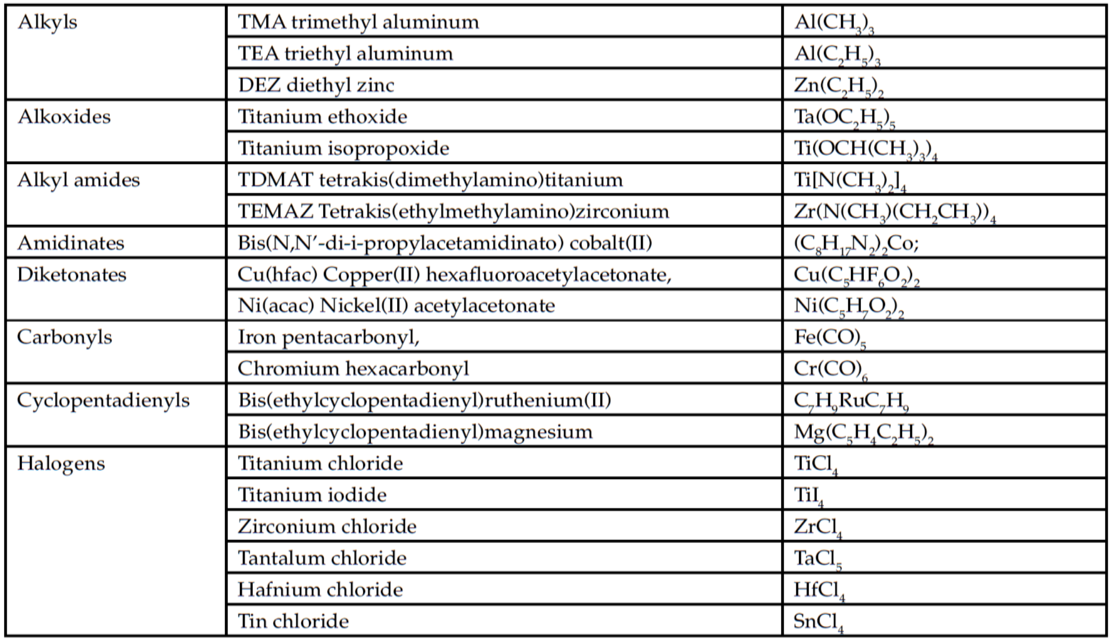
The second reactant:

- often water vapor or ozone.

- Nitrides have been formed using ammonia as the second reactant

- For sulfides, hydrogen sulfide or liquid organo-sulphur compounds are generally chosen as the second reactant.

- For compound semiconductors, arsine and phosphorous vapor are frequently selected



| | | |
|---|---|---|
| Alkyls | TMA trimethyl aluminum | $Al(CH_3)_3$ |
| | TEA triethyl aluminum | $Al(C_2H_5)_3$ |
| | DEZ diethyl zinc | $Zn(C_2H_5)_2$ |
| Alkoxides | Titanium ethoxide | $Ta(OC_2H_5)_5$ |
| | Titanium isopropoxide | $Ti(OCH(CH_3)_3)_4$ |
| Alkyl amides | TDMAT tetrakis(dimethylamino)titanium | $Ti[N(CH_3)_2]_4$ |
| | TEMAZ Tetrakis(ethylmethylamino)zirconium | $Zr(N(CH_3)(CH_2CH_3))_4$ |
| Amidinates | Bis(N,N′-di-i-propylacetamidinato) cobalt(II) | $(C_8H_{17}N_2)_2Co$; |
| Diketonates | Cu(hfac) Copper(II) hexafluoroacetylacetonate, | $Cu(C_5HF_6O_2)_2$ |
| | Ni(acac) Nickel(II) acetylacetonate | $Ni(C_5H_7O_2)_2$ |
| Carbonyls | Iron pentacarbonyl, | $Fe(CO)_5$ |
| | Chromium hexacarbonyl | $Cr(CO)_6$ |
| Cyclopentadienyls | Bis(ethylcyclopentadienyl)ruthenium(II) | $C_7H_9RuC_7H_9$ |
| | Bis(ethylcyclopentadienyl)magnesium | $Mg(C_5H_4C_2H_5)_2$ |
| Halogens | Titanium chloride | $TiCl_4$ |
| | Titanium iodide | $TiI_4$ |
| | Zirconium chloride | $ZrCl_4$ |
| | Tantalum chloride | $TaCl_5$ |
| | Hafnium chloride | $HfCl_4$ |
| | Tin chloride | $SnCl_4$ |

A growing area of study is into metal-organic films such as the "alucones" where an aluminum precursor reacts with an organic molecule such as glycol to produce an alternating metal and organic structure.

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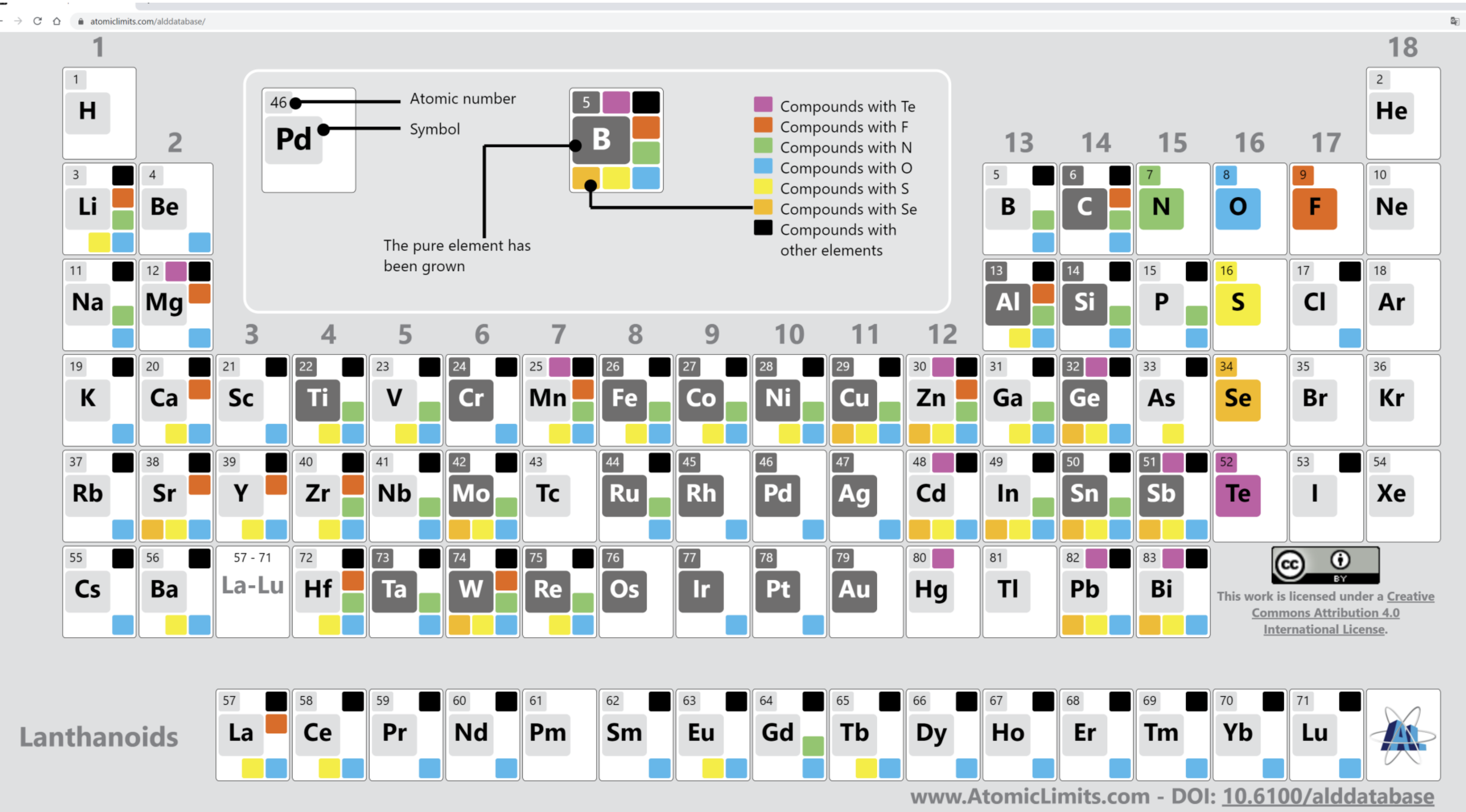
# ALD Thin Film Materials



atomiclimits.com/alddatabase/

46 — Atomic number

Pd — Symbol

The pure element has been grown

🟪 Compounds with Te
🟧 Compounds with F
🟩 Compounds with N
🟦 Compounds with O
🟨 Compounds with S
🟨 Compounds with Se
⬛ Compounds with other elements

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www.AtomicLimits.com - DOI: 10.6100/alddatabase

R. Puurunen, JAP 1997 (2005) & https://www.atomiclimits.com/alddatabase/

# Metal ALD

TABLE VII. Crystallinity studies of ALD element films made by diffraction or spectroscopy.[a]

| Material reactant A | Reactant B | Substrate(s) | Phases | |
|---|---|---|---|---|
| | | | Amorphous | Crystalline |
| Fe | | | | |
| Fe($^t$BuNCMeN$^t$Bu)$_2$ | $H_2$ | $SiO_2$, glass | | 250 °C |
| Co | | | | |
| Co($^i$PrNCMeN$^i$Pr)$_2$ | $H_2$ | $SiO_2$, glass | | 350 °C |
| Co($^i$PrNCMeN$^i$Pr)$_2$ | $H_2$ | $SiO_2$, WN | | 300 °C |
| $CoCp_2$ | $NH_3$[c] | Si | | 300 °C |
| $CoCp(CO)_2$ | $NH_3$[c] | $SiO_2$, Si | | 250–400 °C |
| $CoCp(CO)_2$ | $H_2$[c] | H-Si | | 125–175 °C |
| $Co_2(CO)_8$ | $H_2$[c] | H-Si | 75–110 °C | |
| Ni | | | | |
| Ni($^i$PrNCMeN$^i$Pr)$_2$ | $H_2$ | $SiO_2$, glass | | 250 °C |
| $Ni(acac)_2$ | $H_2$ | Ti, Al, Si | | 250 °C |
| $Ni(hfip)_2$ | $H_2$ | H-Si | | 225 °C |
| Cu | | | | |
| CuCl | $H_2 + H_2O$ | $Al_2O_3$ | | 425 °C |
| CuCl | $H_2$-$H_2O$ | $Al_2O_3$, $SiO_2$ | | 375–475 °C |
| CuCl | $H_2$-$H_2O$ | $Al_2O_3$[d] | | 400 °C |
| CuCl | Zn | $Al_2O_3$ | | 500 °C |
| $Cu(hfac)_2$ | $NH_3$-$H_2O$ | $SiO_2$ | | 283–302 °C |
| $Cu(hfac)_2 \cdot XH_2O$ | formalin | TiN, TaN, Ta | | 300 °C |
| $Cu(hfac)_2 + H_2 + H_2O$ | MeOH | TiN, TaN, Cu, Ta, glass | | 300 °C |
| $Cu(hfac)_2 + H_2 + H_2O$ | EtOH | TiN, TaN, Cu, Ta, glass | | 300 °C |
| $Cu(hfac)_2 + H_2 + H_2O$ | $^i$PrOH | TiN, TaN, Cu, Ta, glass | | 300 °C |
| $Cu(hfac)_2 + H_2 + H_2O$ | formalin | TiN, TaN, Cu, Ta, glass | | 300 °C |
| $Cu(hfac)_2 + H_2 + H_2O$ | CO | TiN, TaN, Cu, Ta, glass | | 300 °C |
| Cu(hfac)(vtmos) | $H_2$[c] | TiN | | 200–300 °C |
| $Cu(acac)_2$ | $H_2$ | Ti, Al, glass | | 250 °C |
| $Cu(acac)_2$ | $H_2$[c] | Si, glass | | 140 °C |
| $Cu(thd)_2$ | $H_2$ | SLG-Pt/Pd, $SiO_2$, glass | | 190–350 °C |
| $Cu(thd)_2$ | $H_2$[c] | Au, $TaN_x$, $SiO_2$ | | 90–250 °C |
| $Cu(dmap)_2$ | $ZnEt_2$ | Si | | 100–120 °C |
| [Cu($^i$PrNCMeN$^i$Pr)]$_2$ | $H_2$ | $SiO_2$, glass, Co, WN | | 190–280 °C |
| [Cu($^s$BuNCMeN$^s$Bu)]$_2$ | $H_2$ | $Al_2O_3$, $SiO_2$, $Si_3N_4$, glass, Ru, Co, Cu, WN | | 150–190 °C |

**Crystallinity of inorganic films grown by atomic layer deposition: Overview and general trends**

Ville Miikkulainen, Markku Leskelä, Mikko Ritala, and Riikka L. Puurunen

https://doi.org/10.1063/1.4757907

| Material reactant A | Reactant B | Substrate(s) | Phases | |
|---|---|---|---|---|
| $Ru(EtCp)(dmp)$ | $O_2$ | Si, Au, Pt, $Al_2O_3$, $SiO_2$, $TiO_2$, TiN | | 230–290 °C |
| $RuCp(CpCH(Me)(NMe_2))$ | $O_2$ | $Al_2O_3$ | | 325–500 °C |
| $Ru(thd)_3$ | $O_2$ | $Al_2O_3$ | | 325–400 °C |
| $Ru(^tBuAMD)_2(CO)_2$ | $O_2$ | O-Si | | 300–400 °C |
| $Ru(^tBuAMD)_2(CO)_2$ | $NH_3$ | WN | | 250–300 °C |
| Rh | | | | |
| $Rh(acac)_3$ | $O_2$ | $Al_2O_3$ | | 250 °C |
| Pd | | | | |
| $Pd(hfac)_2$ | formalin | $Al_2O_3$ | | 200 °C |
| $Pd(hfac)_2$ | $H_2$ | Ir, TaN | | 80–130 °C |
| $Pd(hfac)_2$ | HCOCOOH | tetrasulfide SAM | | 200 °C |
| $Pd(thd)_2$ | $H_2$ | $Al_2O_3$, $SiO_2$ | | 180 °C |
| $Pd(thd)_2$ | $H_2$[c] | Ir, W, Si | 80 °C | |
| Ag | | | | |
| $Ag(O_2C^tBu)(PEt_3)$ | $H_2$[c] | Si, glass | | 140 °C |
| $Ag(hfac)(cod)$ | propanol | glass | | 110–150 °C |
| Sb | | | | |
| $SbCl_3$ | $(Et_3Si)_3Sb$ | Si, SLG | | 95–250 °C |
| Ta | | | | |
| $TaCl_5$ | $H_2$[c] | Si, $SiO_2$ | 25–400 °C | 400 °C[b] |
| $TaF_5$ | $H_2$[c] | $SiO_2$ | | 200–350 °C |
| W | | | | |
| $WF_6$ | $Si_2H_6$ | Si | | 327 °C[b] |
| $WF_6$ | $Si_2H_6$ | $Al_2O_3$ | | 122–177 °C |
| $WF_6$ | $SiH_4$ | TiN, $SiO_2$ | | 300 °C |
| $WF_6$ | $B_2H_6$ | TiN | 300 °C | |
| Ir | | | | |
| $Ir(acac)_3$ | $O_2$ | $Al_2O_3$, $TiO_2$, SS | | 225–375 °C |
| $Ir(acac)_3$ | $O_3$ | Si, SLG, $Al_2O_3$ | | 200–225 °C |
| $Ir(acac)_3$ | $O_3$-$H_2$ | $Al_2O_3$ | | 165–200 °C |
| $Ir(EtCp)(cod)$ | $O_2$ | $SiO_2$, TiN | | 270–290 °C |
| $Ir(EtCp)(cod)$ | $NH_3$[c] | TiN | | 270 °C |
| $Ir(MeCp)(chd)$ | $O_2$ | $Al_2O_3$ | | 225–350 °C |
| Pt | | | | |
| $Pt(MeCp)Me_3$ | $O_2$ | $Al_2O_3$, Ir, Si, $SiO_2$, $ZrO_2$, $SrTiO_3$, $SnO_2$, borosilicate | | 200–300 °C |
| $Pt(MeCp)Me_3$ | $O_2$[c] | Si, $SiO_2$ | | 300 °C |
| $Pt(acac)Me_2$ | $O_3$ | $Al_2O_3$ | | 140–200 °C |

Metal ALD

**Crystallinity of inorganic films grown by atomic layer deposition: Overview and general trends**
https://doi.org/10.1063/1.4757907
Published Online: 08 January 2013, Ville Miikkulainen, Markku Leskelä, Mikko Ritala, and Riikka L. Puurunen

# Metalorganic Molecules for ALD & CVD

## Requirements:

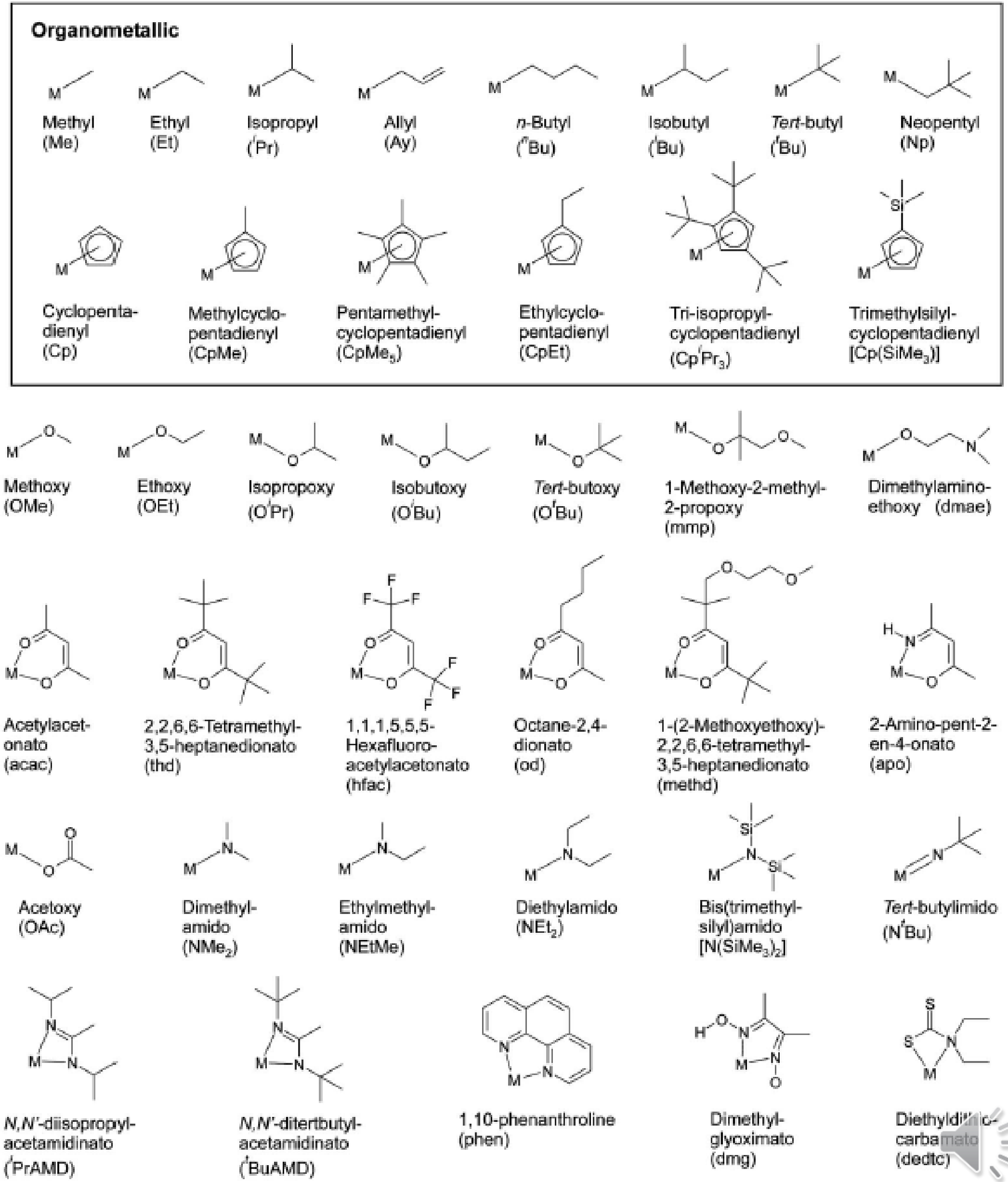
1) Volatility @ «low» Temperature
→ Vapour Pressure

2) Ability to adsorb on surface
→ Physisorption / Chemisorption

3) Ability to dissociate
→ Dissociative Chemisorption

4) Dissociation products volatile
→ Ligand chemistry / Desorption

5) Non-toxic
6) Non-corrosive
7) Stable
(no spontaneous degradation)



R. Puurunen, JAP 1997 (2005)

# ALD process based on:

## Chemisorption

- Suitable temperature for chemical bonding, no thermal decomposition
- Covalent bonding ⇨ excellent adhesion

## Saturation

- Sufficient dosing of precursor material
- Self-terminating reactions ⇨ extremely precise dosing not required

## Surface controlled reactions

- Film thickness is independent of substrate geometry ⇨ conformal film onto deep trenches and 3D structures

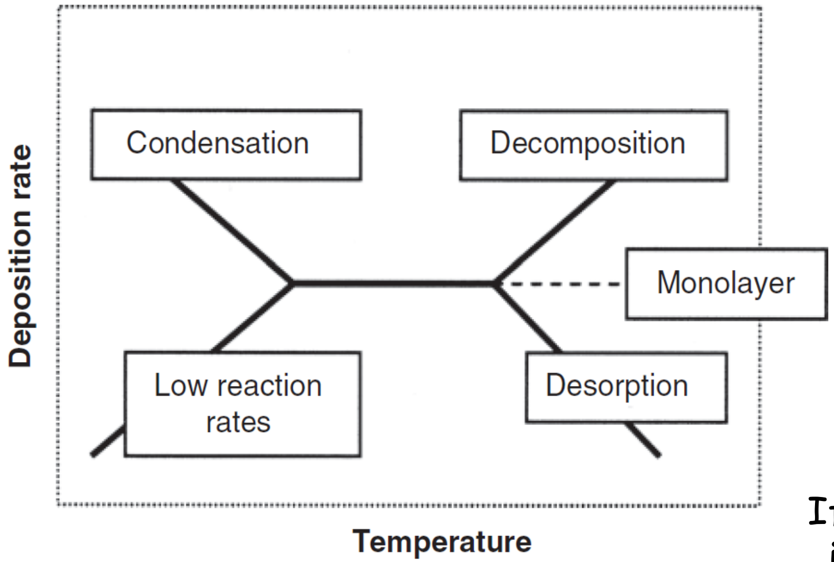
## Sequential

- Digital growth
- Sufficient purging needed between pulses
- Good flow dynamics required to ensure rapid gas changes

# ALD window

if the **temperature is too low**, we may adsorb more than one monolayer per cycle (or even condense a liquid or solid on the surface), and **the deposition rate would be higher** than expected.

If the **temperature is too high**, then first **chemical reactant may decompose** on the surface before having time to react with the second reactant. In this case **the growth rate would be higher** than one would expect from an ALD process.

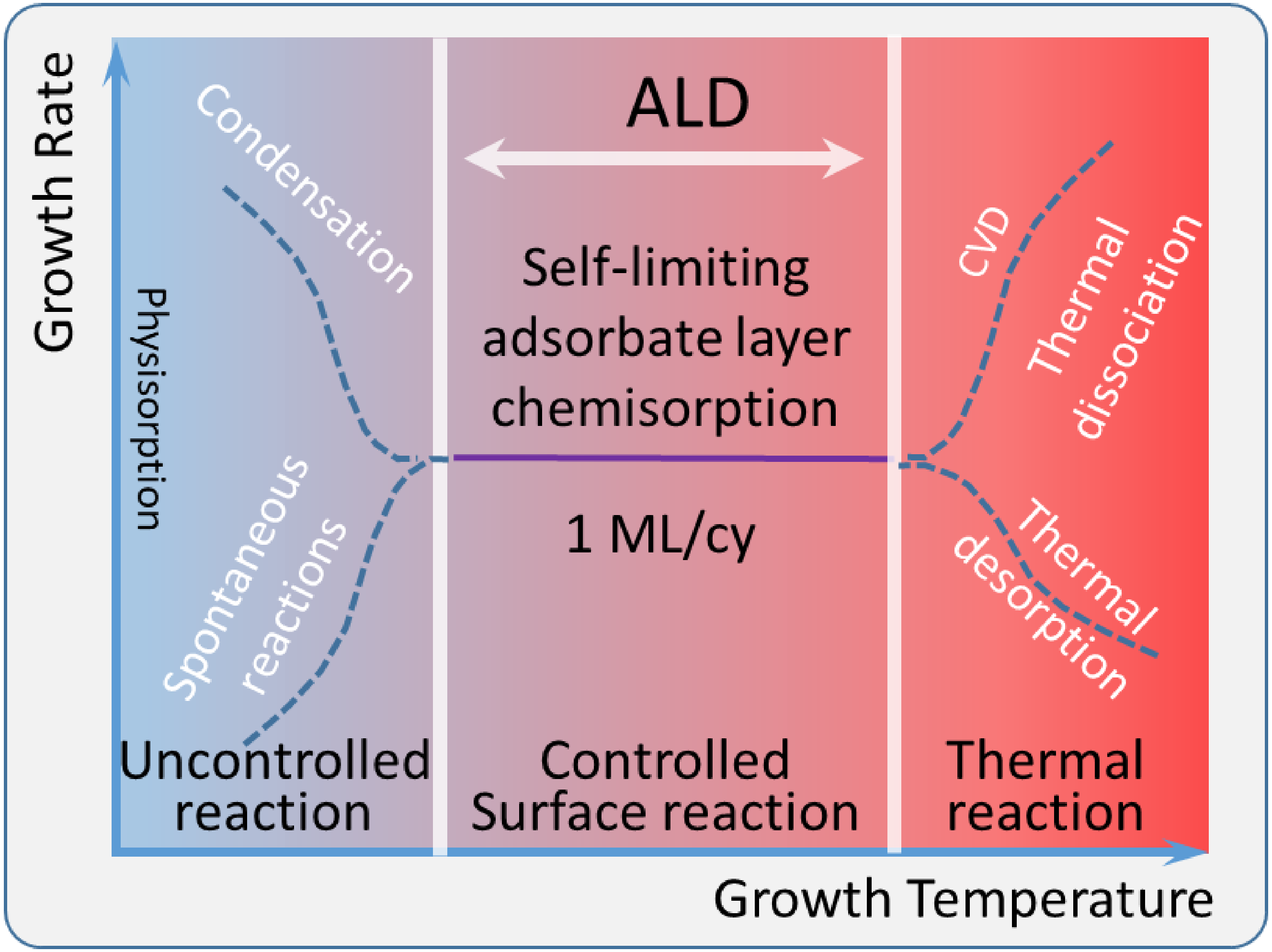


if the **temperature is too low**, the **reaction rate may be so slow** that the reaction time may be too long **compared to a practical cycle time** (e.g. hours rather than seconds).

If the **temperature is too high and if the first precursor is stable** it may still desorb from the surface before having a chance to react with the second reactant. Under this circumstance the **growth rate would be less** than expected.

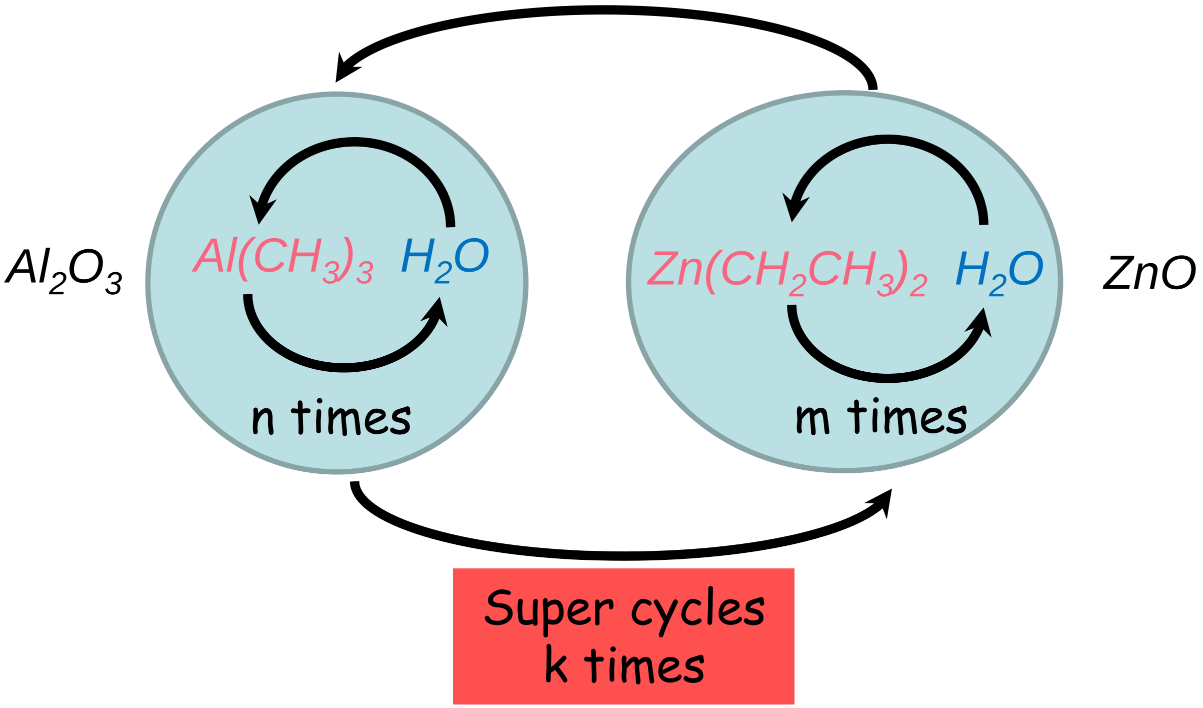
Kääriäinen 2013

# Thermal ALD window

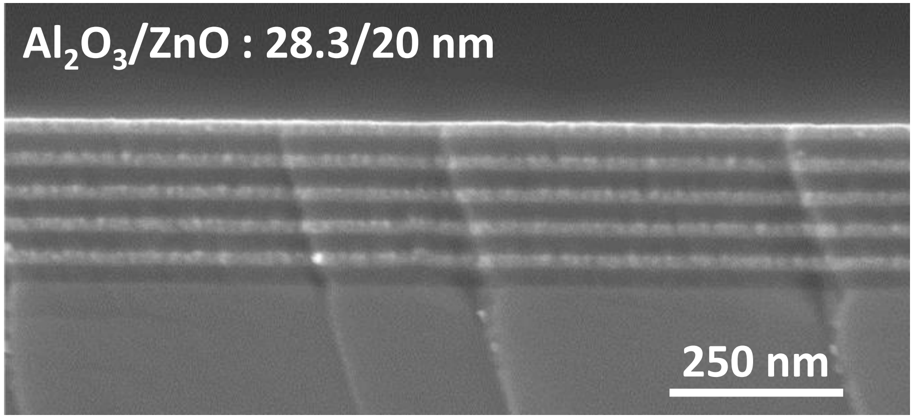


Courtousy, I. Utke, Empa

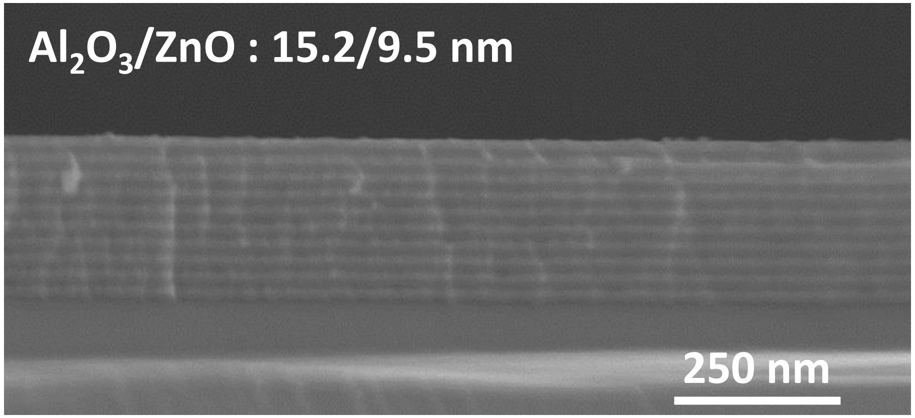
# ALD of $Al_2O_3$/ZnO Multilayers (=Nanolaminates)



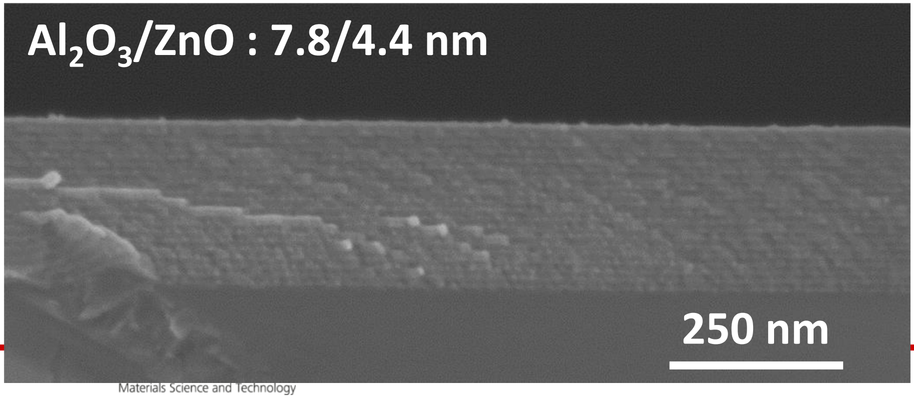
# Structural Characterization of Laminates



20.0 nm
28.3 nm
5 x



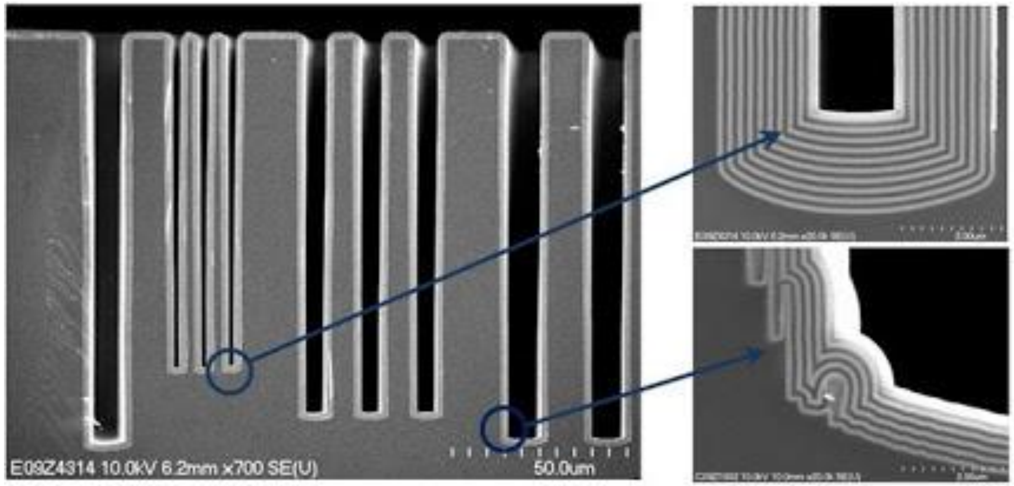
9.5 nm
15.2 nm
10x



4.4 nm
7.8 nm
20x

# ALD conformality

As ALD is self-limited in surface reactions any open porosity structure can be coated uniformly



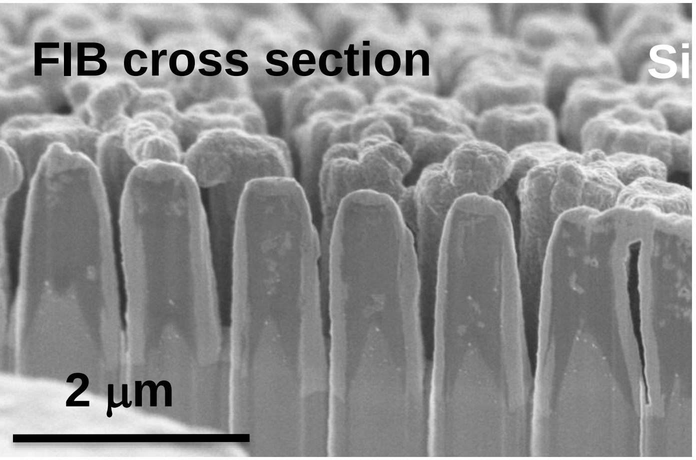
Perfectly conformal coating at trench bottom

Defects are completely encapsulated

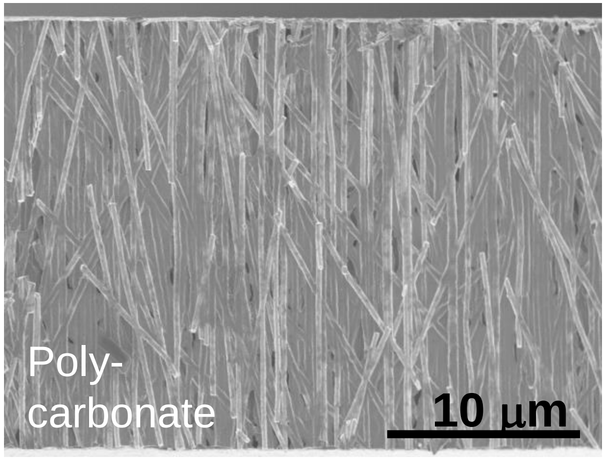
Alternating Layers of $Ta_2O_5$ & $Al_2O_3$ on deep trenches in silicon

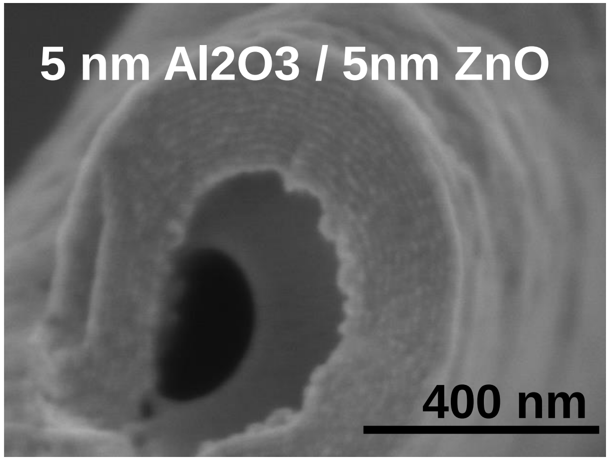
# Conformal coatings on 3D templates

- **Nanocylinder arrays**

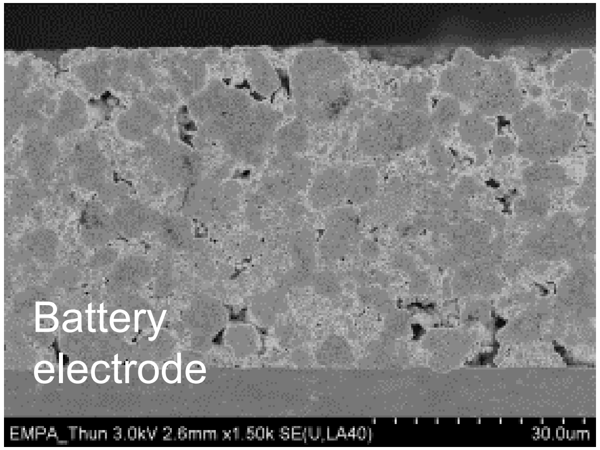


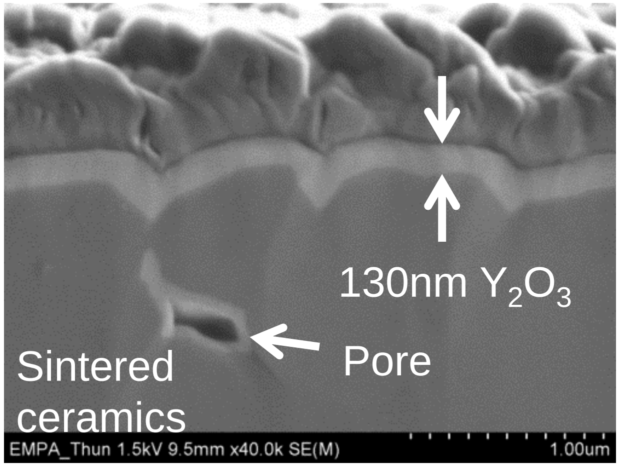
- **Cylindrical Holes**



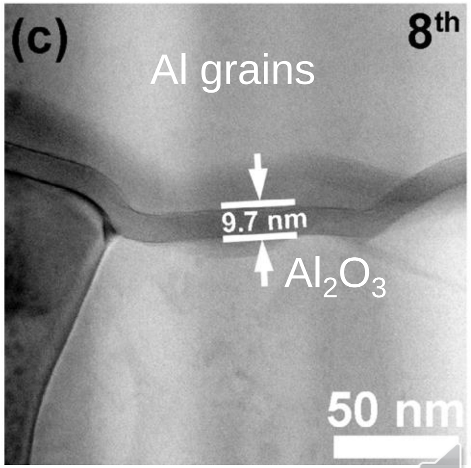


- **Porous Materials**





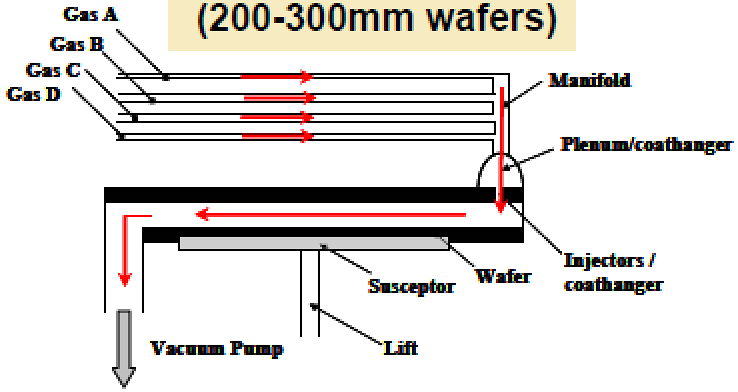
- **Pinhole-free**



# ALD reactors

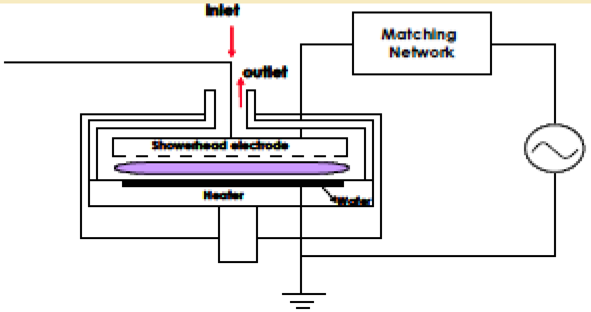
a)

**Cross-flow reactor (200-300mm wafers)**



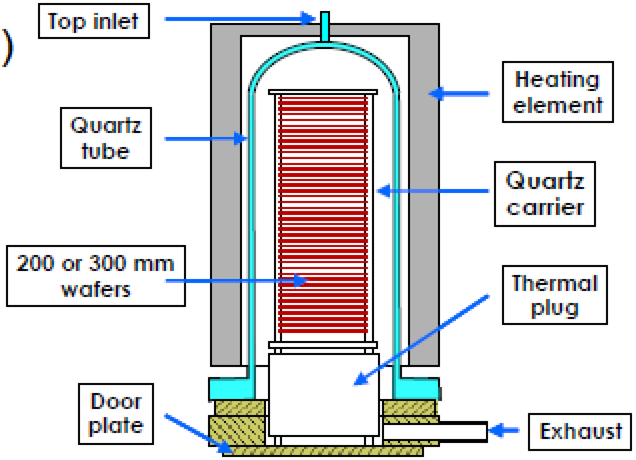
b)

**Showerhead ALD or PEALD reactor (200-300mm wafers)**



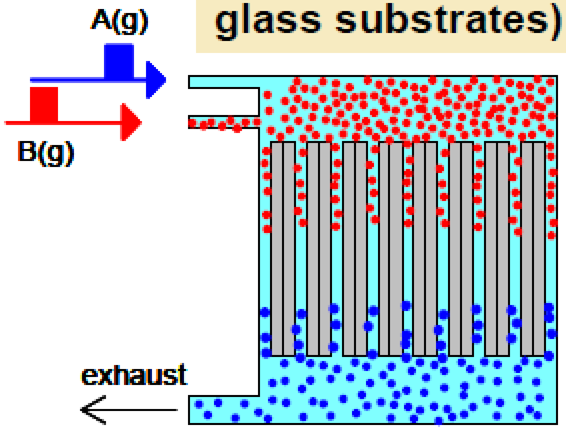
**Batch reactor (200-300mm wafers)**

c)



d)

**Batch reactor (40x50cm² glass substrates)**



Suvi Haukka 2005

# "Radical Enhanced" or Plasma enhanced ALD reactors

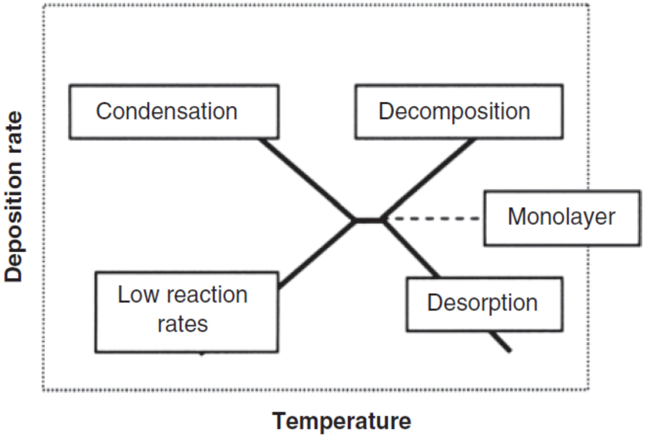
The ALD process takes place within a "**temperature window**" which depends on the stability of the precursor chemicals and their reaction with the surface.

If the **temperature** at which the reaction starts to take place is **too high** then the **temperature window gets shorter and may, in fact, disappear**. Therefore, for many thermal processes, there is no acceptable temperature window.

The approach where one of the reactants is an energetic radical can **maximize this "temperature window"** and even, enable processes at room temperature in some cases.

This is what we will refer to as Radical enhanced ALD (REALD). **All commercial systems** exploit various **plasma sources** available such as capacitive discharges, discharges created by inductive solenoid coils, microwave discharges, etc. Therefore PEALD is used as a synonym for REALD.

Drawbacks of PEALD are **limited conformality** (due to lifetime of radicals) of the films and **more complicated processing**.



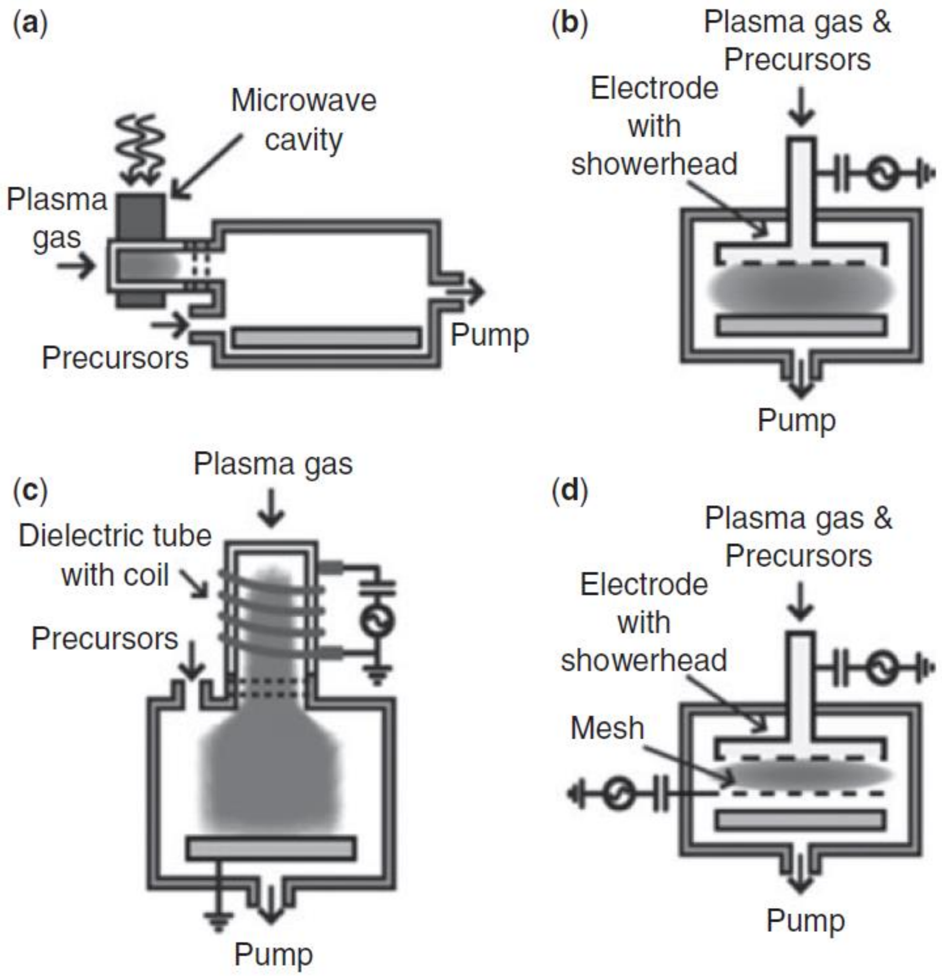
Kääriäinen 2013

# "Radical Enhanced" or Plasma enhanced ALD reactors

Of all of the ways that energetic radicals could be created, the simplest is to generate them in a glow discharge created in a low pressure reactor chamber.

Other systems exploit various plasma sources available such as capacitive discharges, discharges created by inductive solenoid coils, microwave discharges, etc.

The actual configuration and placement of the plasma source in the ALD reactor determines the performance of the source in respect to the radical generation efficiency. Remote plasmas need longer cycle times but prevent to a large extent exposure of the growth surface to plasma photons, ions and electrons.



Schematic illustration of plasma-assisted ALD reactor configurations: a) radical- enhanced ALD, b) direct plasma-assisted ALD, c) remote plasma ALD and d) direct plasma reactor with mesh.

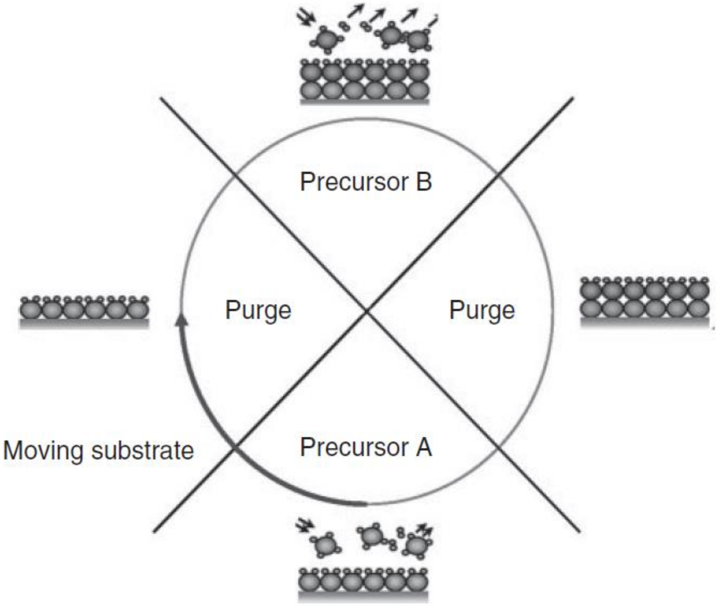
Kääriäinen 2013

# Spatial ALD

In conventional, or batch ALD, precursor pulses must be separated by pulses of purge gas thus giving the familiar precursor, purge, precursor, purge gas sequence.

Some "side-effects" are therefore:
- The gas pulse lengths must be long enough to form a monolayer
- The purge and exhaust pulses must be long enough to ensure that all remaining gas-phase precursors or reaction by-products are removed
- All the internal surfaces of the reaction chamber are coated as well as the substrate

Spatial ALD:
- constant flows of gases in spatially separate zones and physically moving the substrate between these zones.
- allows for continuous in-line process or roll-to-roll web coating
- High deposition rates, no coating on inner chamber surface



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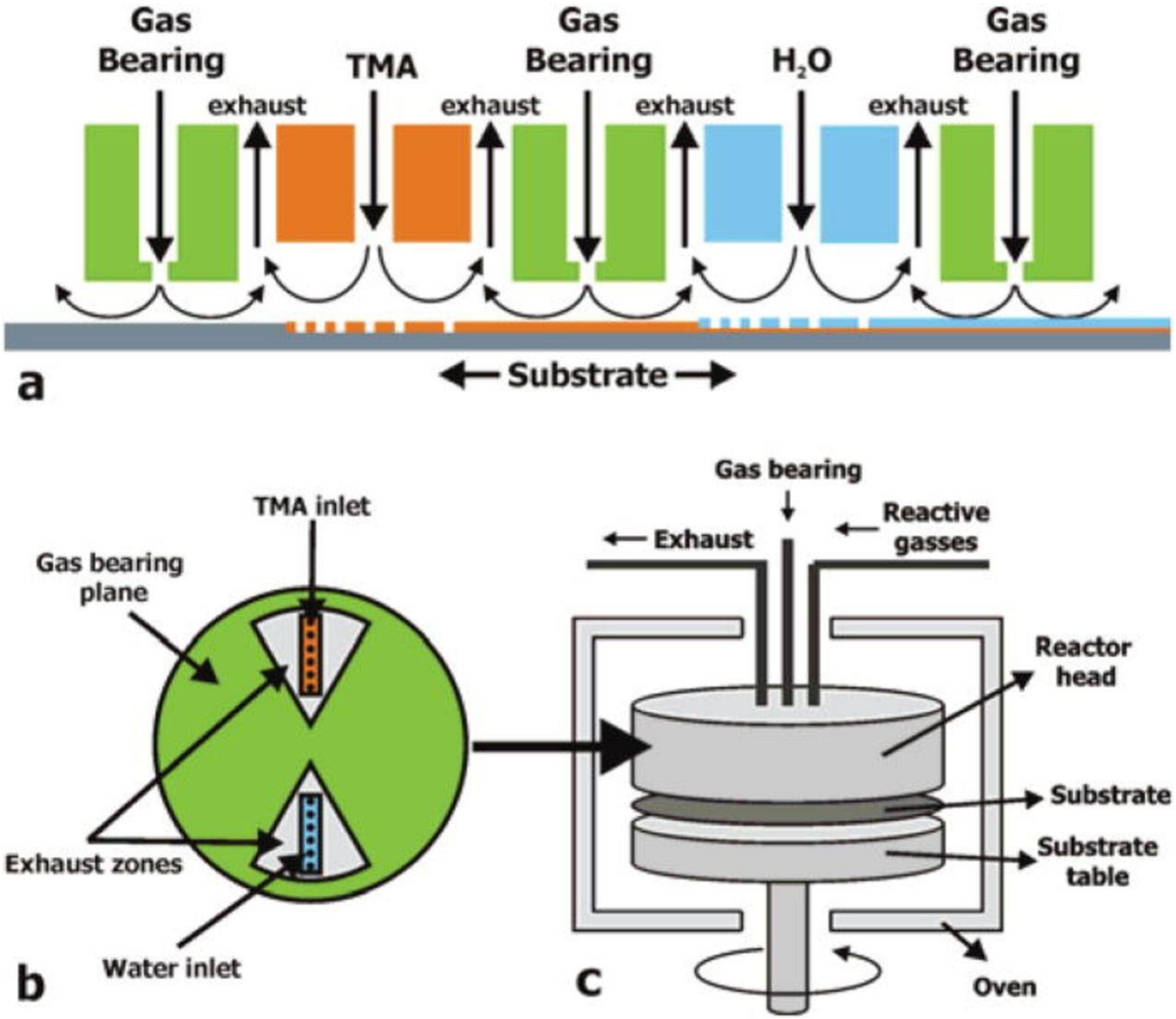
# Spatial ALD



jes.ecsdl.org

# ALD applications

1 nm thick catalysts (Pt, Pd)

2 nm thick TiN barrier layers underneath copper

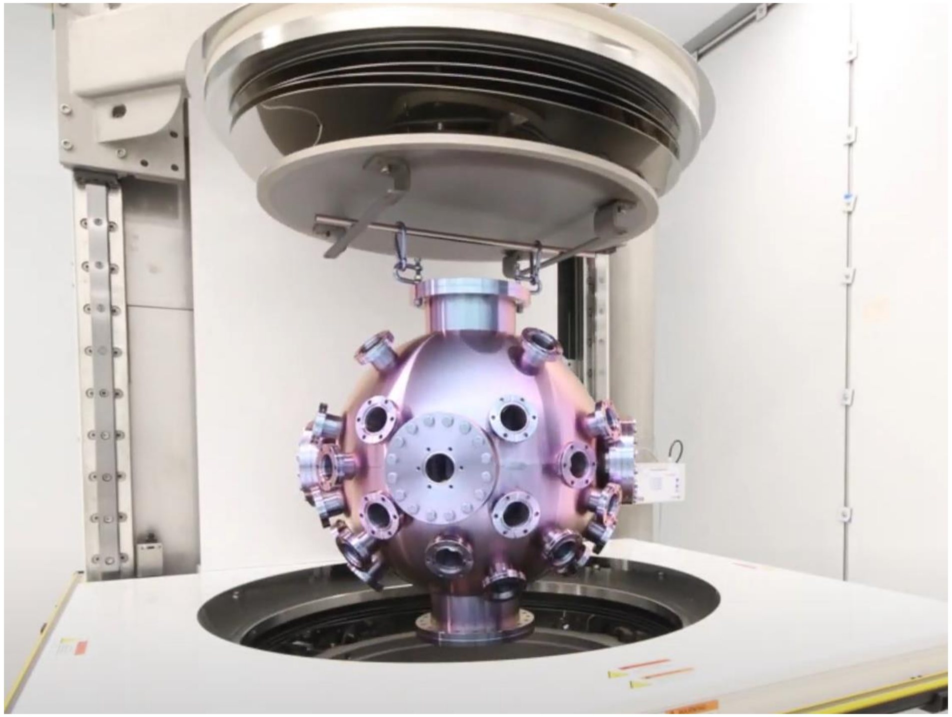
6 nm thick CMOS gate oxides like $HfO_2$

10 nm thick etch masks for plasma etching ($Al_2O_3$)

30 nm thick antireflection coatings in solar cells ($Al_2O_3$)

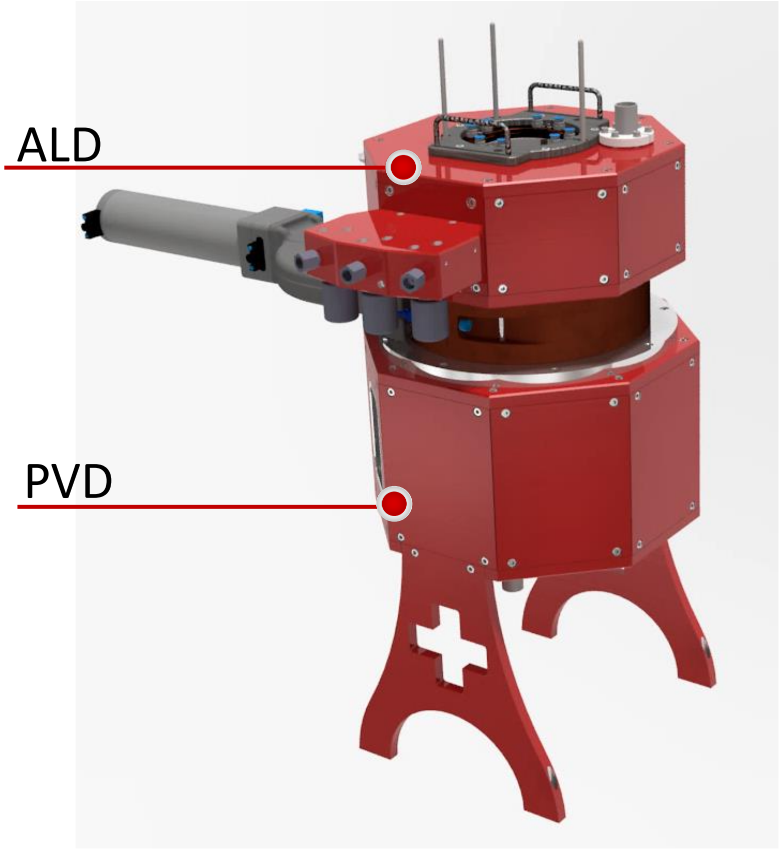
200 nm thick barrier layers in flat panel displays ($Al_2O_3$)

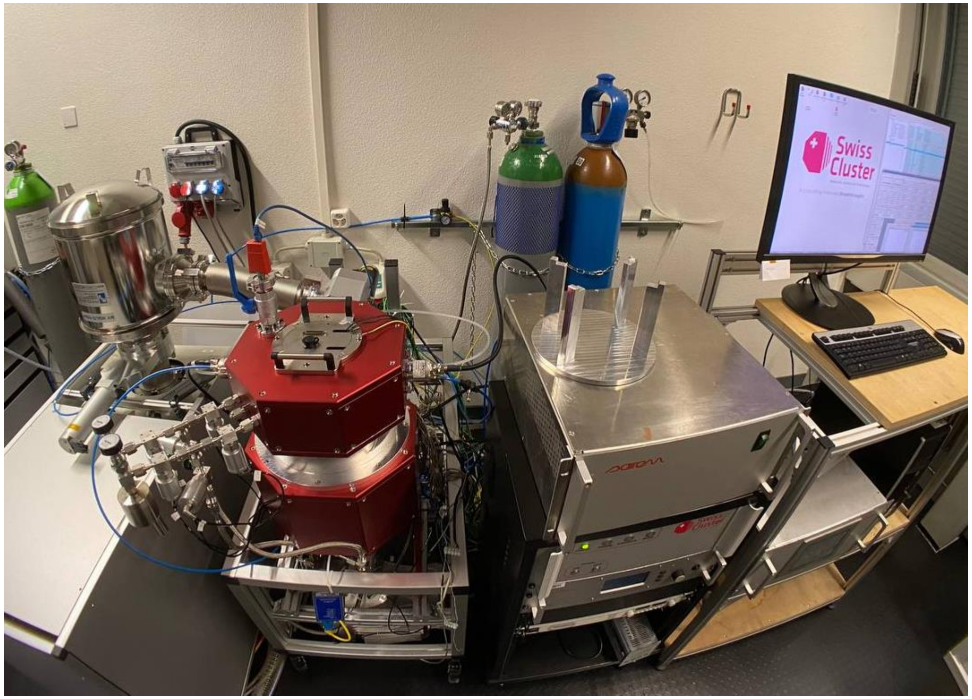
# Swiss Company Portrait: SwissCluster AG



# SwissCluster AG: Combined deposition techniques

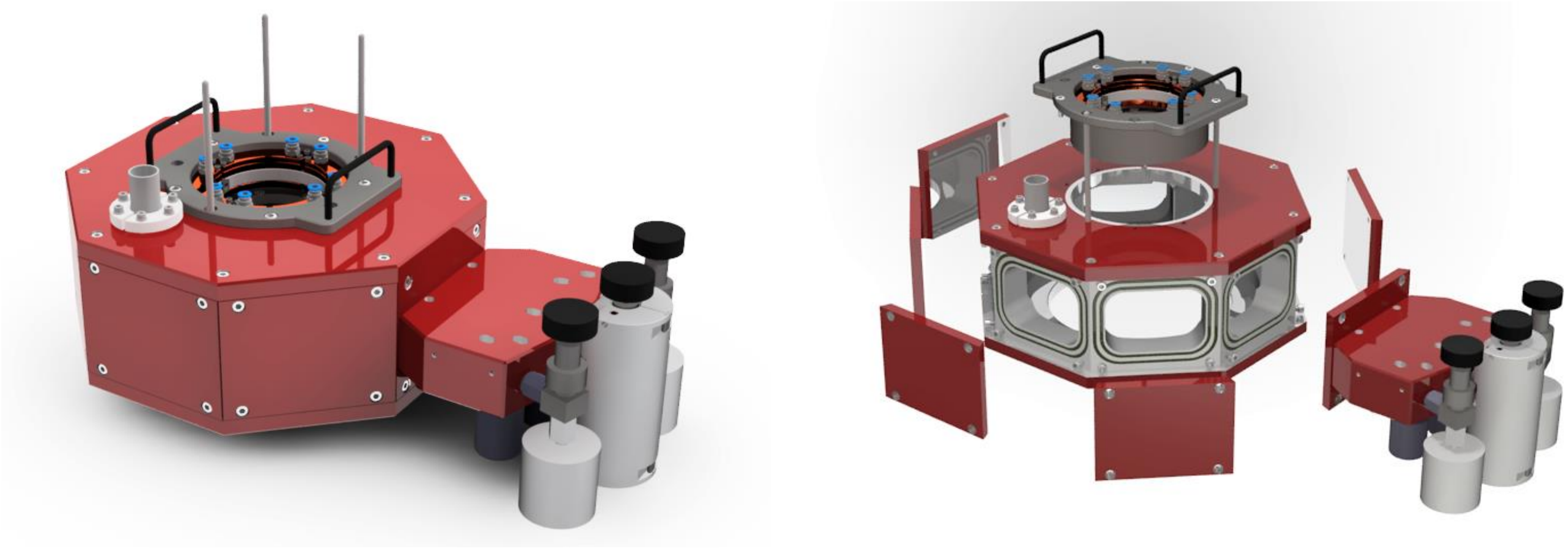
The SC- 1 is the first off-the-shelf cluster system that combines atomic layer deposition (ALD) and physical vapor deposition (PVD) in one compact, modular, and fully automated equipment.
Patent pending.





- Switching between processes without breaking vacuum
- Circumventing native oxidation and surface contamination
- Rapid production of complex multilayer systems

# SwissCluster AG: Modular chamber design

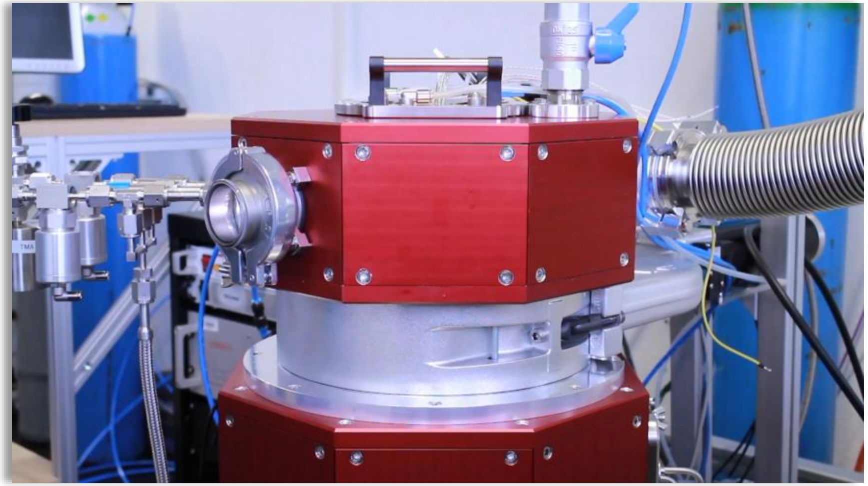


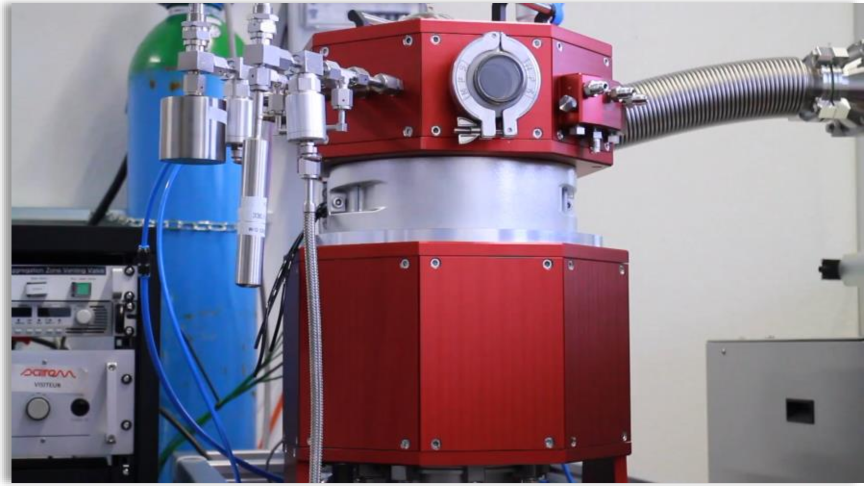
The system includes an ALD chamber and a PVD chamber separated by a gate valve. Due to its modularity, the ALD chamber can host up to 12 gas precursor lines. The PVD chamber can accommodate up to 4 magnetrons.

The system is fully automated and can deposit multinanolayers of multiple material systems from the PVD and ALD materials library of metals, alloys, metal oxides, metal nitrides, etc.

Ohring 2002

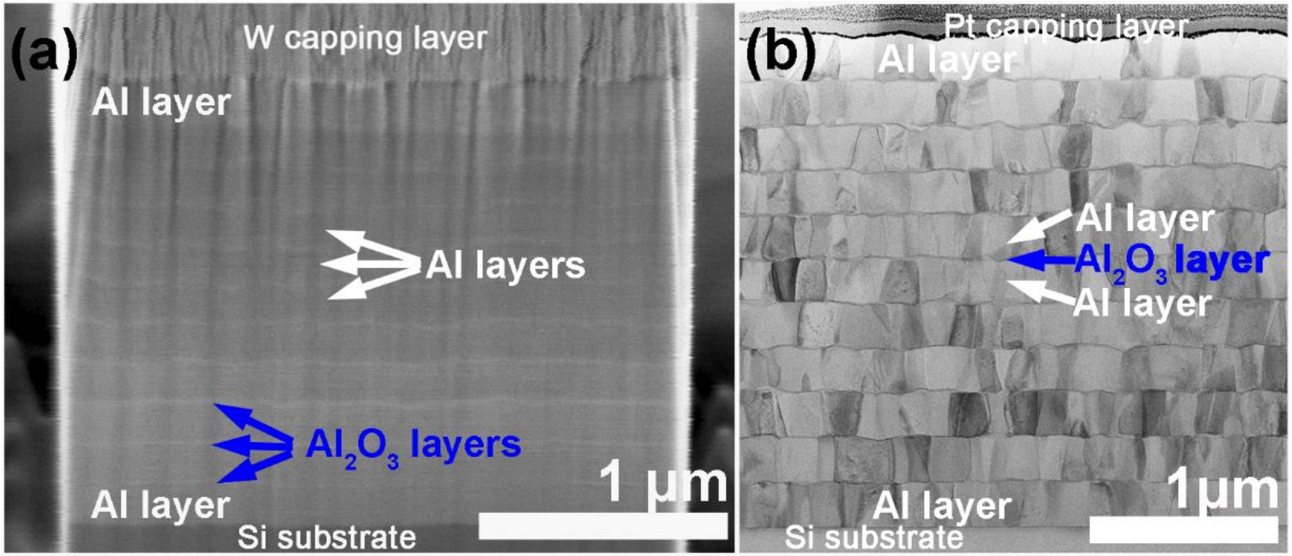
# SwissCluster AG: Videos

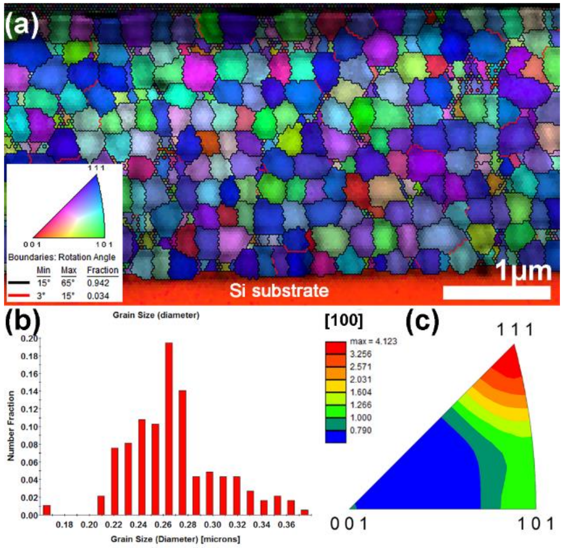


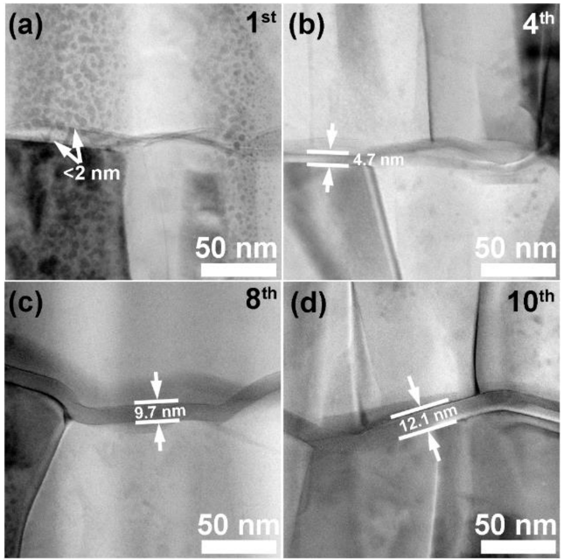


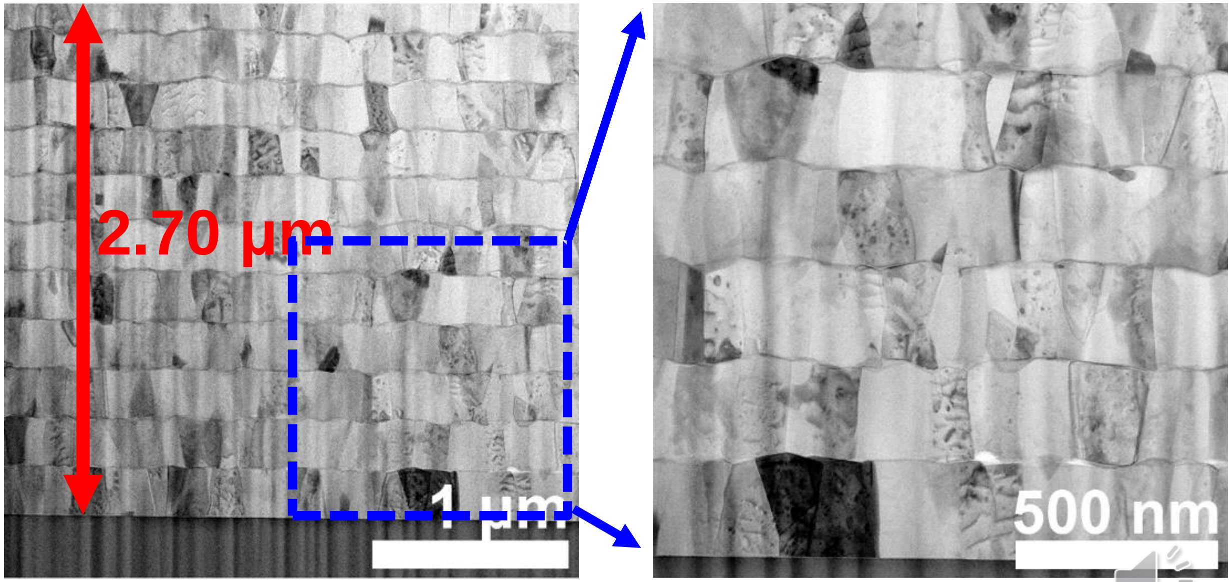
Ohring 2002

# SwissCluster AG: Example thin film system









Empa
Materials Science and Technology

# Summary

- In atomic layer deposition (ALD), the precursor vapors are introduced to the substrates alternately, one at a time, separated by purging periods with inert gas.
- Typical cycle times are from one second to several seconds. Most ALD processes operate between 200°C and 400°C
- ALD and MLD have unprecendented thickness control down to the ML (or atomistic) level with typically half a monolayer per cycle (incomplete coverage)
- Adsorption kinetics described by Langmuir equation, adsorption kinetics (over time) for physisorption and chemisorption
- Energies of physisorption ~0.1eV and Chemisorption 1-10eV,
- Growth rate and steric hindrance, H incorporation at low T
- MLD exploits short organic precursors with OH-group instead water
- The first reactant is either a halogen or an organometallic and the second water vapor or ozone for oxides/ammonia for Nitrides, HS for sulfides.
- Precurser requirements englobe Volatility at low T, ability to physisorb & chemisorb, ability to dissociate and finally non-toxic etc. The success of ALD is built on chemistry, and for each film material an appropriate combination of precursor molecules suited to the ALD process must be found. The requirements for the precursors are contradictory: they must be thermally stable and reactive.
- The ALD window is limited by low reaction rates and condensation at low temperatures and thermal desorption and thermal dissociation at higher temperatures. The reactions should be saturative and no precursor decomposition should take place. Only then is the filmgrowth self-limiting, which is one of the attractive features of ALD
- Self-limiting surface reactions provide for conformal coatings even in high-aspect ratio structures
- Nanolaminate (multilayers) & hybrid organic – inorganic materials possible
- The main stream in ALD is thermal processing, where activation for the surface reaction is brought about by heat. Plasma ALD is increasingly used to provide radicals during the ALD process enabling low deposition temperatures.
- ALD reactor types, range from multilevel batch to flow reactors, PE-ALD reactors and spatial ALD reactors.
- ALD processes have been developed for oxides, nitrides, carbides, fluorides, certain metals, II–VI and III–V compounds, and polymers.
- Applications range from sub-10nm barrier layers or CMOS gate oxides to thick anti-corrosion layers.

# exercises

- Explain the typical process steps of an ALD process of alumina. What are typical cycle times. Why is the film thickness not just the sum of deposited lattice planes in crystalline alumina?
- Draw the function for the adsorption kinetics at the substrate surface.
- Compare energies of chemisorption and physisorption
- Name typical precursors for the two separate ALD cycles
- Which design rules for ALD precursers you know?
- Explain the term ALD window. What happens when process temperatures a re a) too high or b) too low at the substrate surface?
- Why can ALD coatings be conformal despite aspect ratios of surface structures of 1:1000?
- What are typical pressures and temperatures for the ALD process
- What distinguishes ALD from CVD processes – note at least 3 differences
- What are the benefits of PEALD compared to thermal ALD
- Explain the concept of spatial ALD
- Name at least 3 technological applications of ALD thin films

Ohring 2002