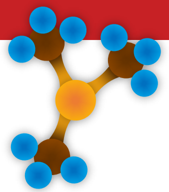
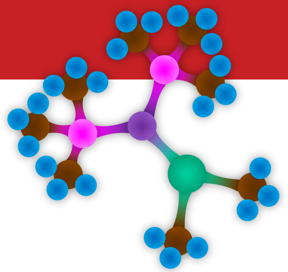
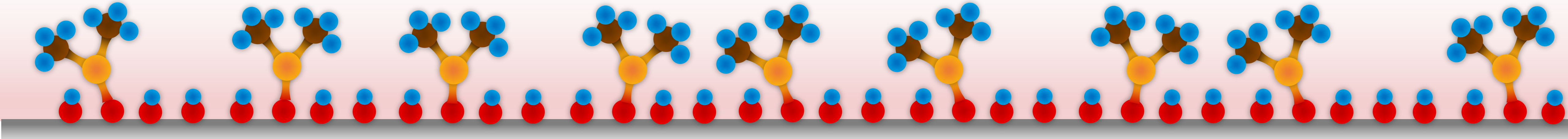
SPATIAL ALD DAY

Tutorial



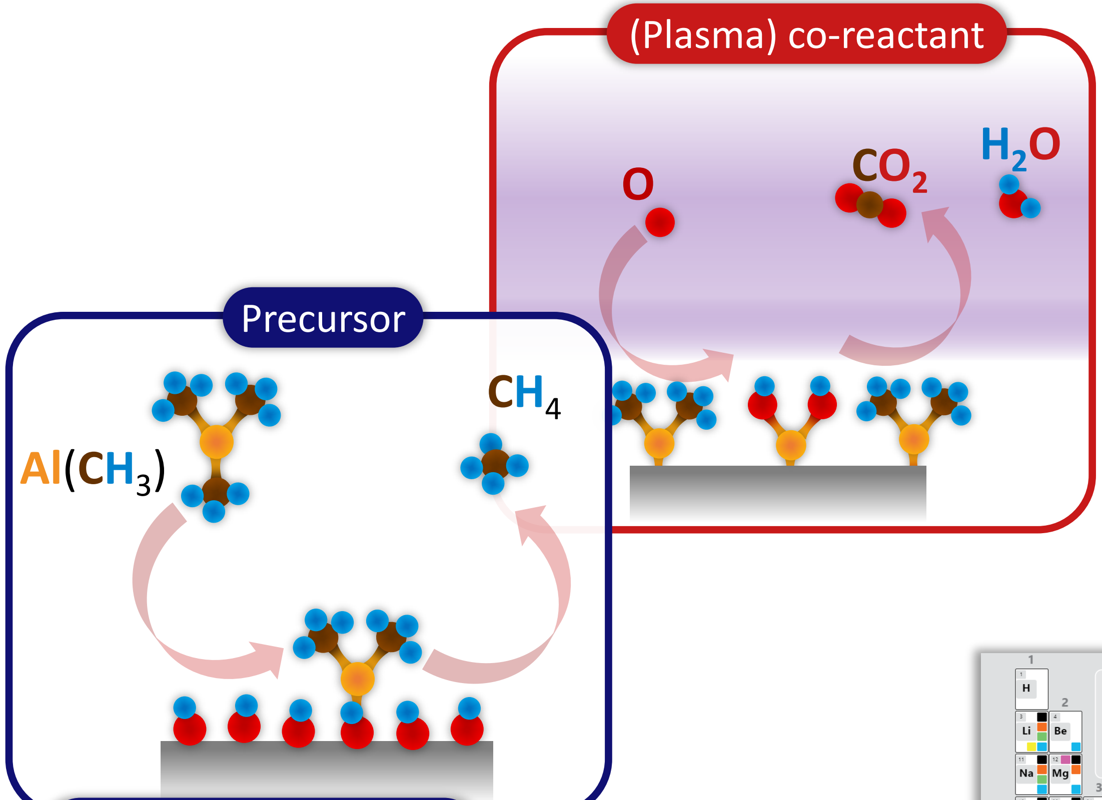


Bart Macco, Paul Poodt



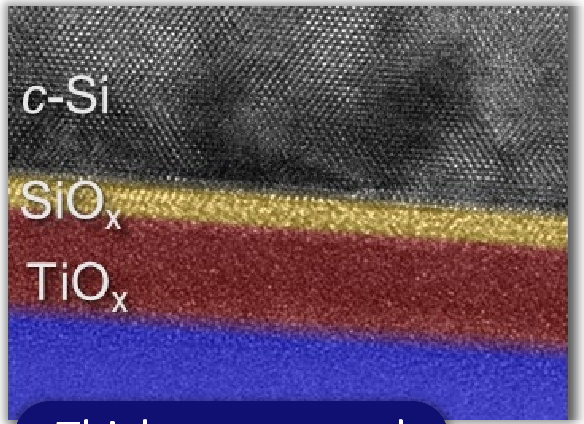
What is Atomic Layer Deposition?

Depositing materials, atomic layer by atomic layer



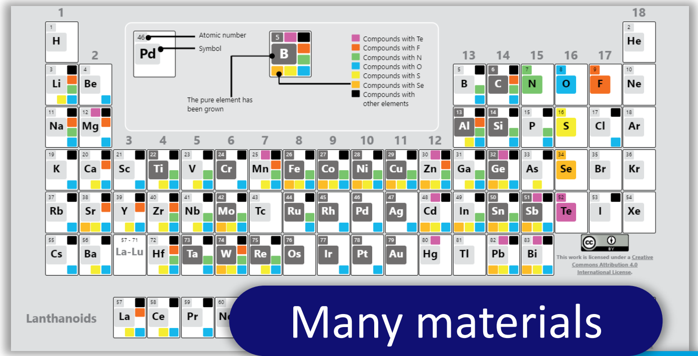
Cyclic exposures

- To precursors and (plasma) co-reactants
- Self-limiting surface reactions



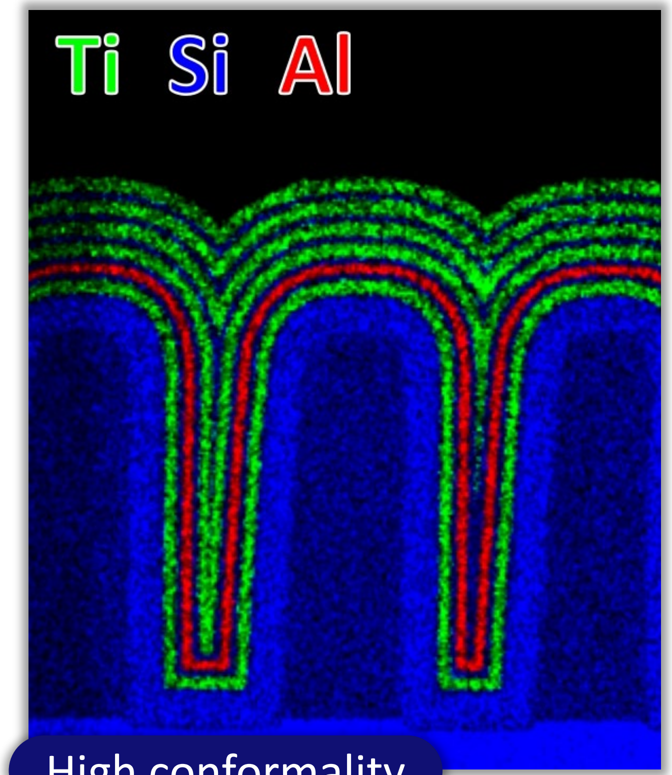
Thickness control

At the Ångstrom-level



Many materials

Metal oxides, nitrides, …



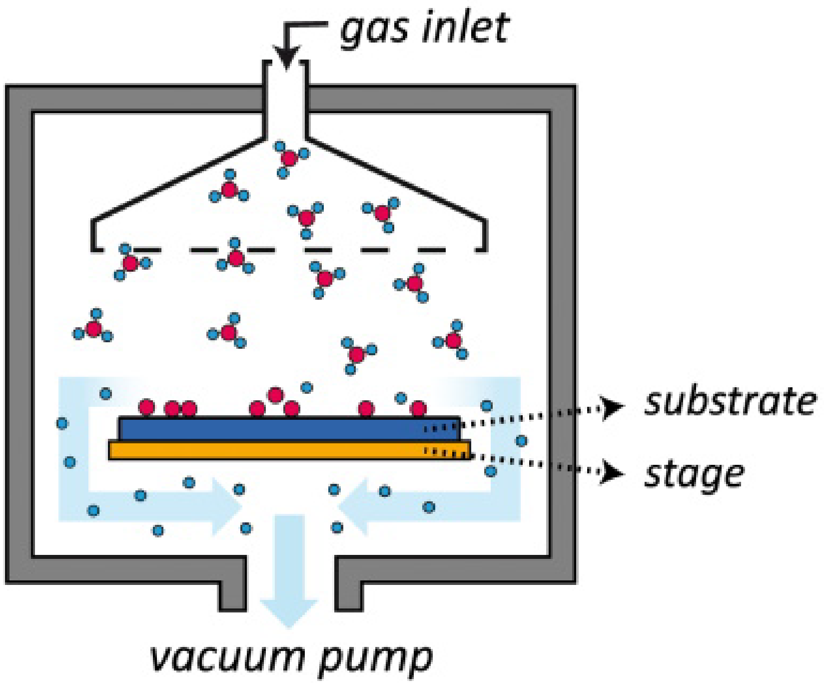
High conformality

Ability to cover 3D structures

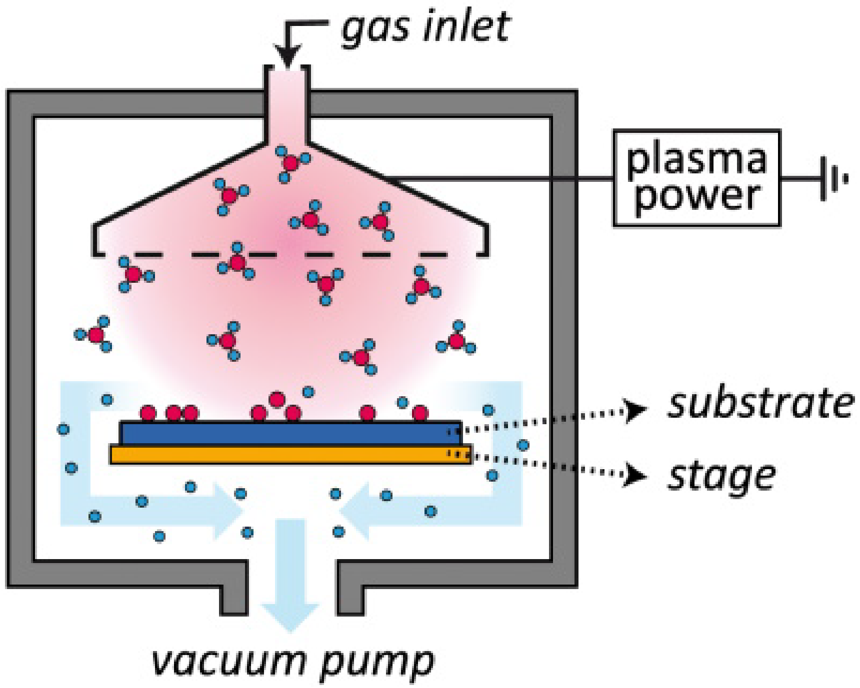
Basics of Atomic Layer Deposition

Typical research lab reactors

Thermal ALD reactor



Plasma ALD reactor

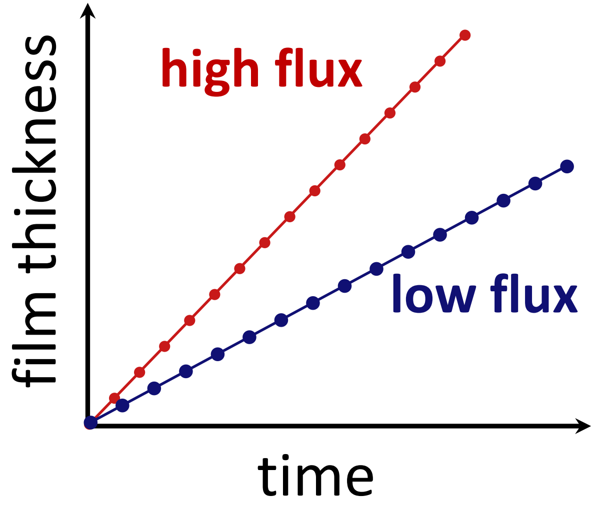


Erwin Kessels, ALD from an application perspective, AtomicLimits (2022)


OXFORD INSTRUMENTS
OpAL
UP
TU/e NANO LAB

Basics of Atomic Layer Deposition

Let’s first look at CVD and PVD



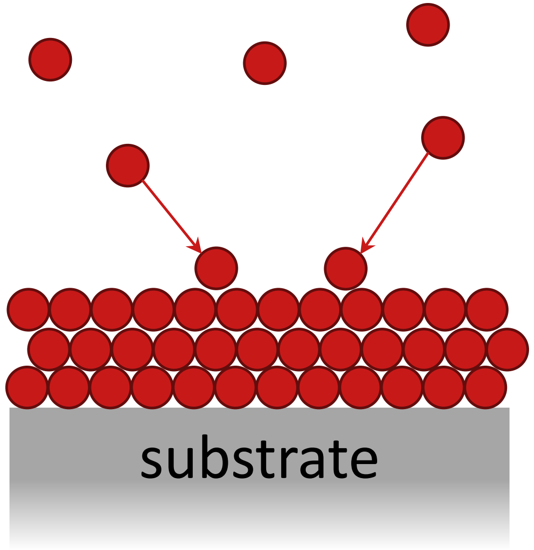
CVD and PVD:

- Gas-phase species collide with surface
- Certain sticking probability *s*
- Film thickness *[nm]* ∝ *flux* *[at. nm^{-2}s^{-1}]* · *s* *[-]* · *time* *[s]* / *density* *[at. nm^{-3}]*

Random flux of species to surface

Known from kinetic gas theory for given gas density n_g, mass m and temperature T

$$\text{flux } \Gamma = \frac{1}{4} n_g \bar{v} \qquad \bar{v} = \sqrt{\frac{8kT}{\pi m}}$$

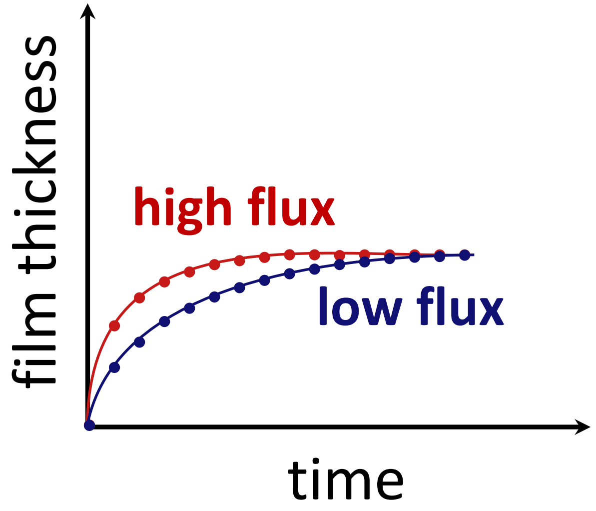


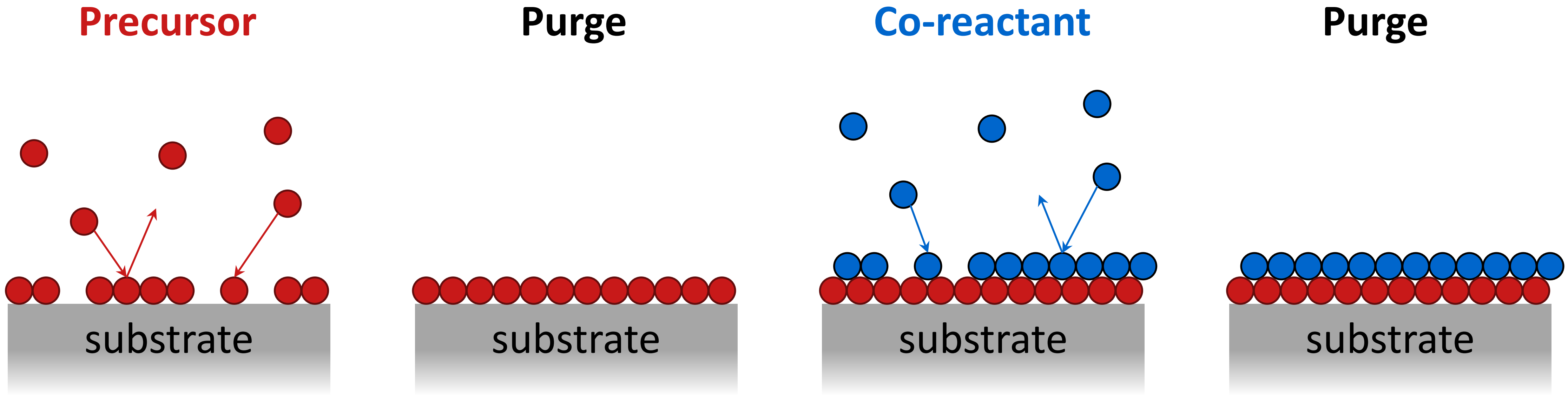
Basics of Atomic Layer Deposition

Why ALD is different from CVD and PVD

ALD:

- Self-limiting surface reactions
- Film thickness $\propto 1 - \exp(-\frac{t}{\tau})$ *(τ scales with flux and s)*



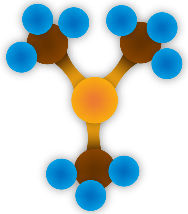


Basics of Atomic Layer Deposition

A real-world example: ALD Al_2O_3 from TMA and H_2O

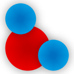
Precursor: metal-center with ligands
trimethylaluminum

$Al(CH_3)_3$



Co-reactant: typically, oxidizing agent
H_2O, O_2, O_3, …

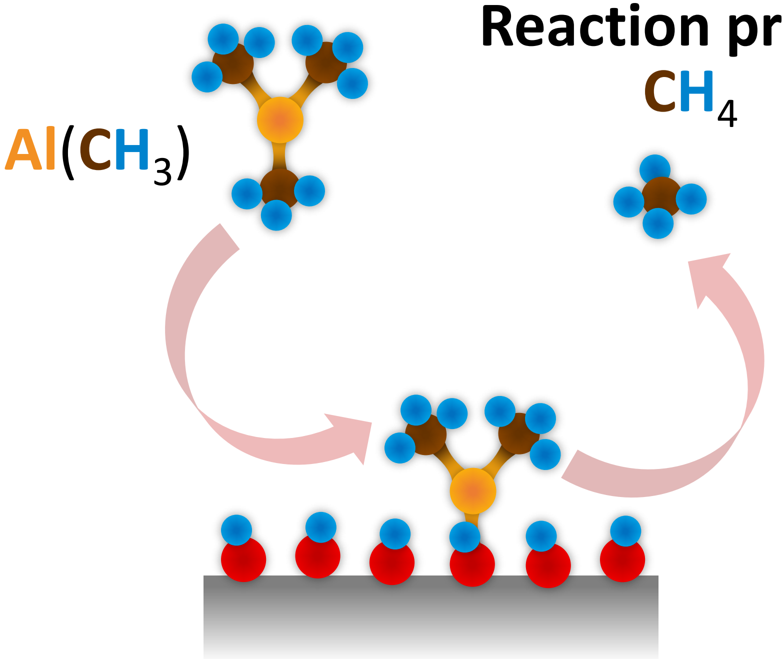
H_2O



Basics of Atomic Layer Deposition

A real-world example: ALD Al_2O_3 from TMA and H_2O

Precursor dose



$Al(CH_3)$

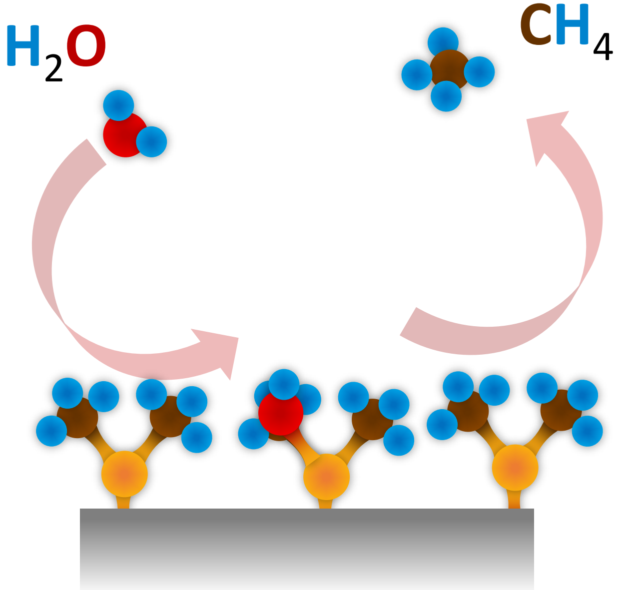
Reaction product

CH_4

Starting surface

OH-groups

Reactant dose



H_2O

Reaction product

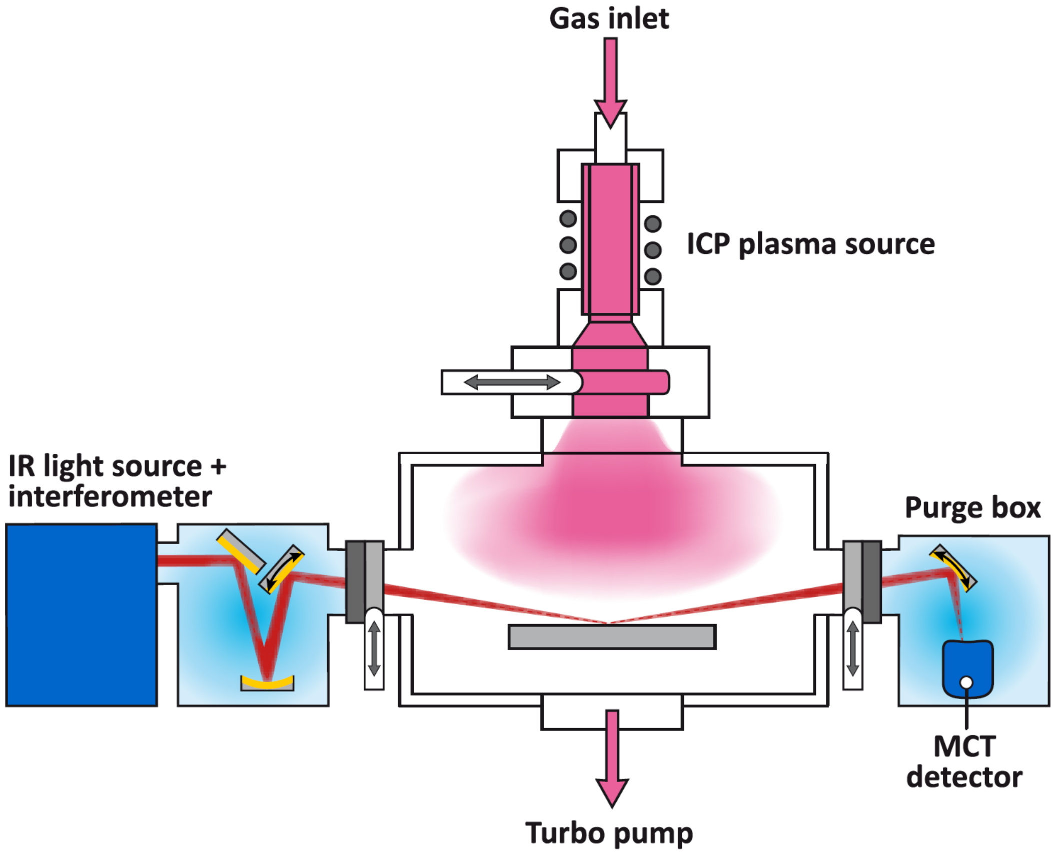
CH_4

Starting surface

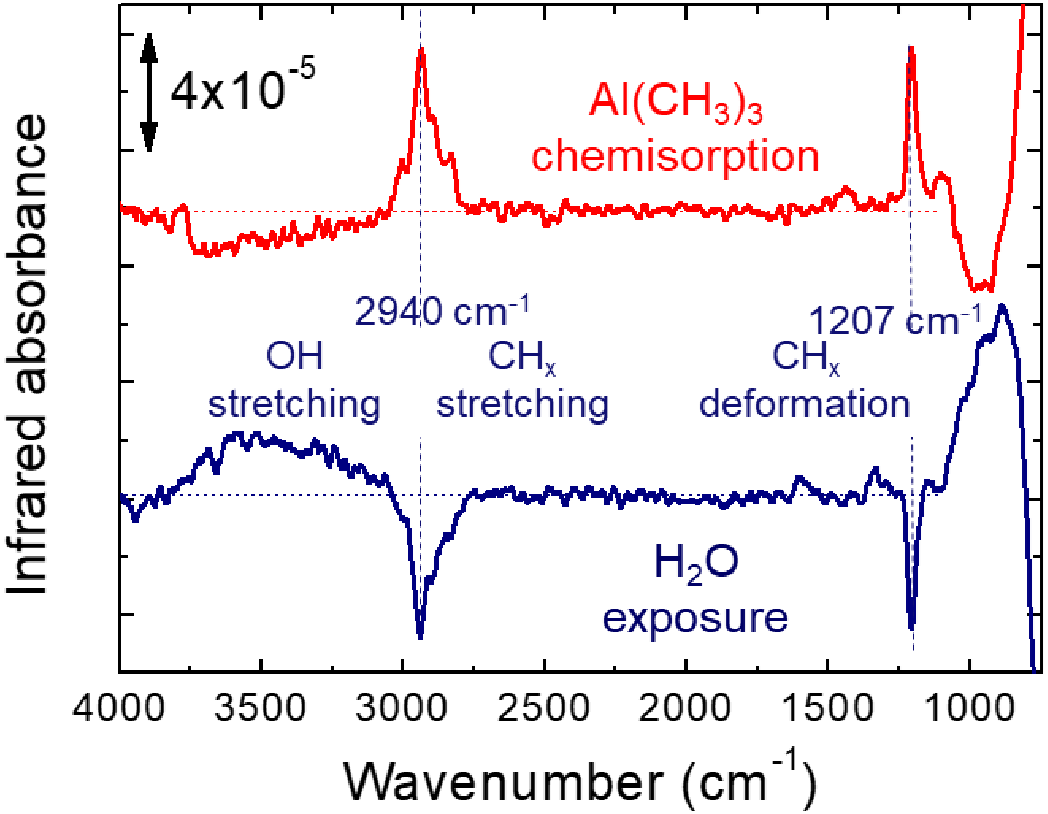
CH_3-groups

Basics of Atomic Layer Deposition

A real-world example: ALD Al_2O_3 from TMA and H_2O



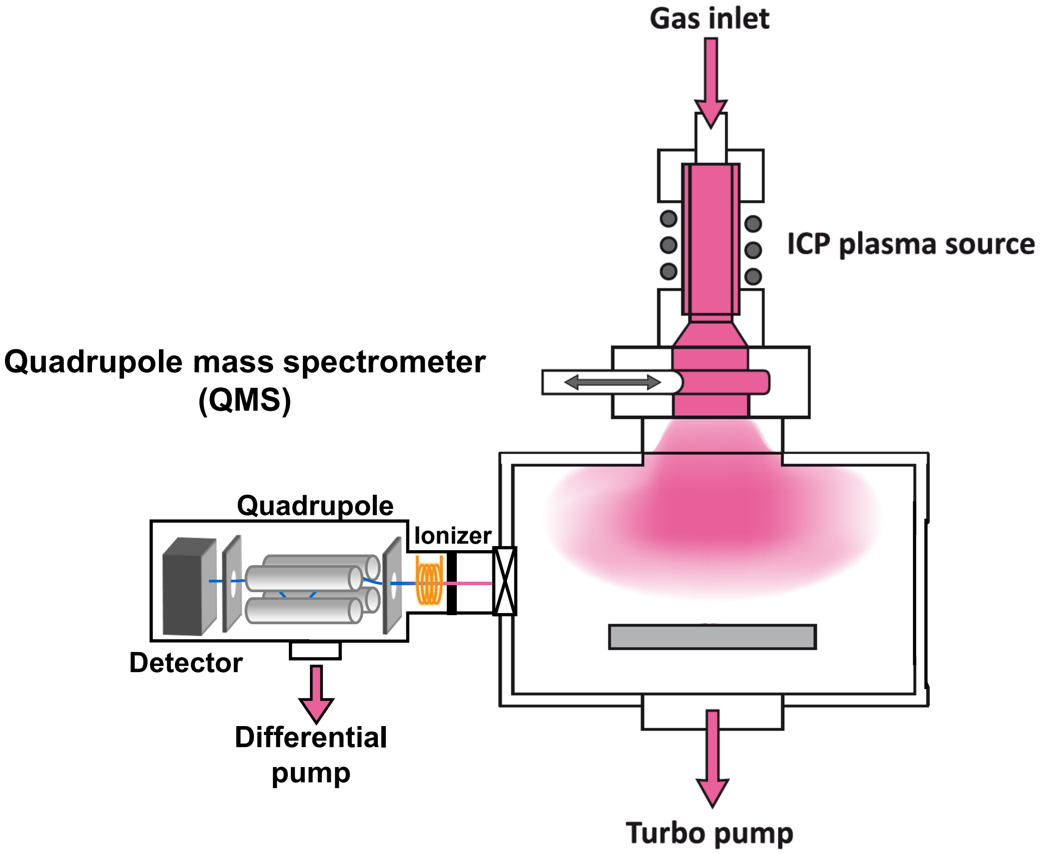
Surface species from surface infrared spectroscopy



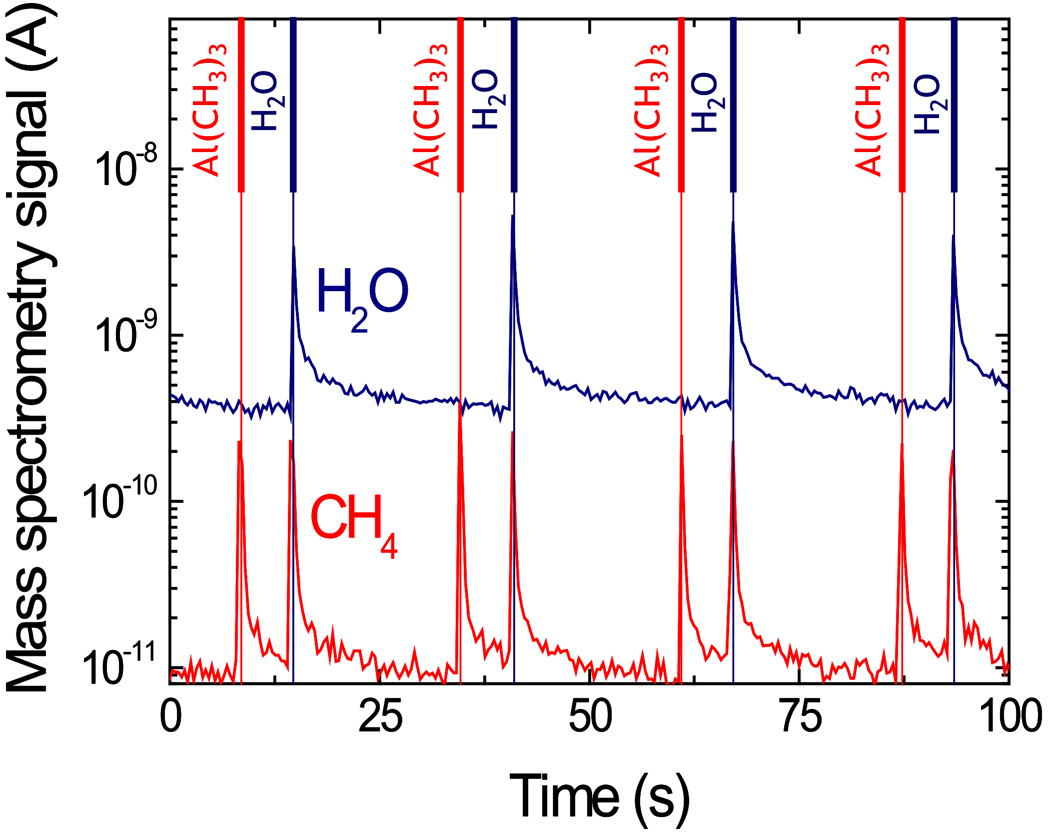
Vandalon and Kessels, J. Vac. Sci. Technol. A 35, 05C313 (2017)

Basics of Atomic Layer Deposition

A real-world example: ALD Al_2O_3 from TMA and H_2O



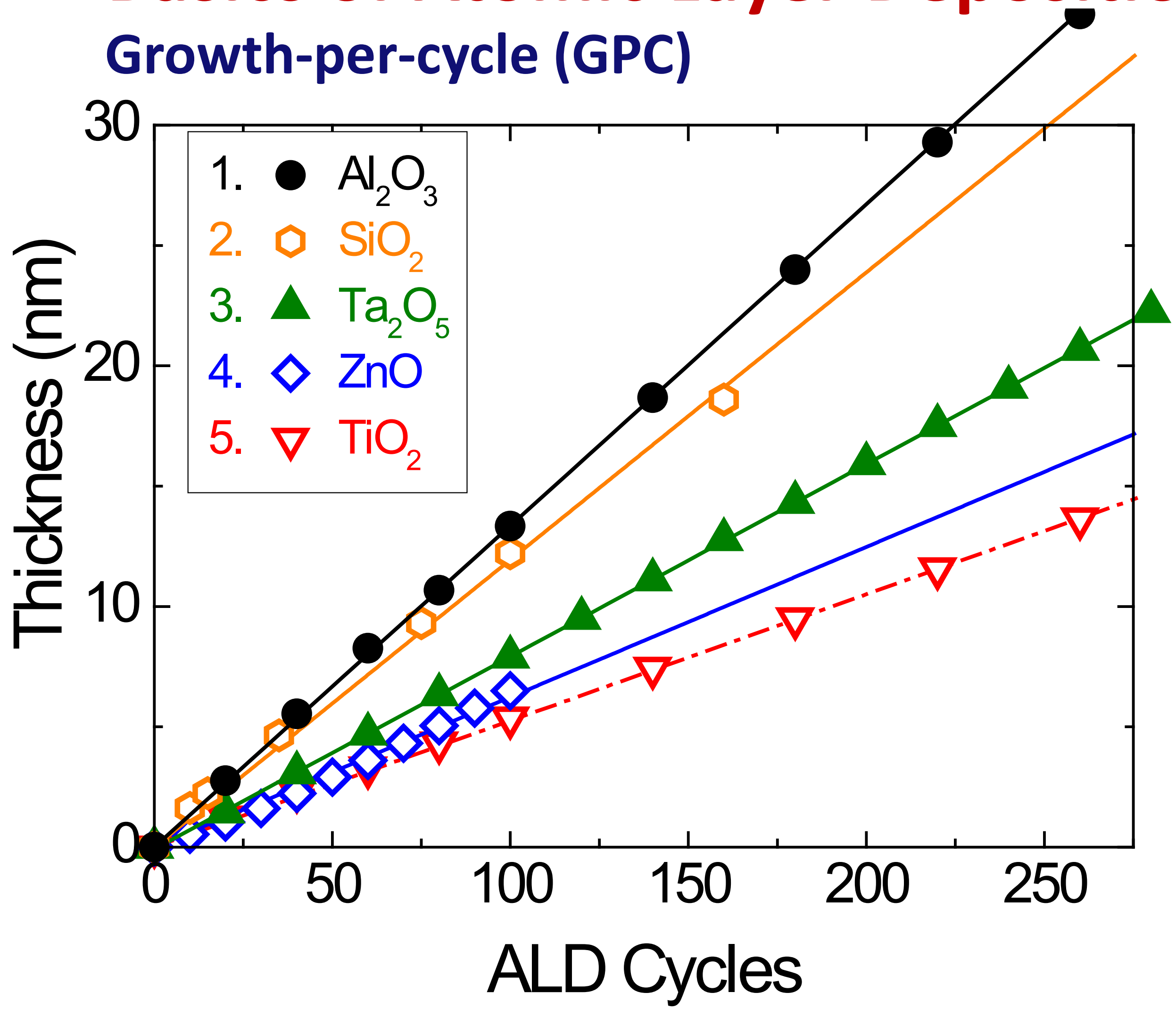
Gas phase (reaction) species from mass spectrometry



Vandalon and Kessels, J. Vac. Sci. Technol. A 35, 05C313 (2017)

Basics of Atomic Layer Deposition

Growth-per-cycle (GPC)



Film thickness is ruled by the **number of cycles** chosen.

The **growth-per-cycle (GPC)** is the thickness increase per ALD cycle.

Typically **0.01 – 0.2 nm/cycle**

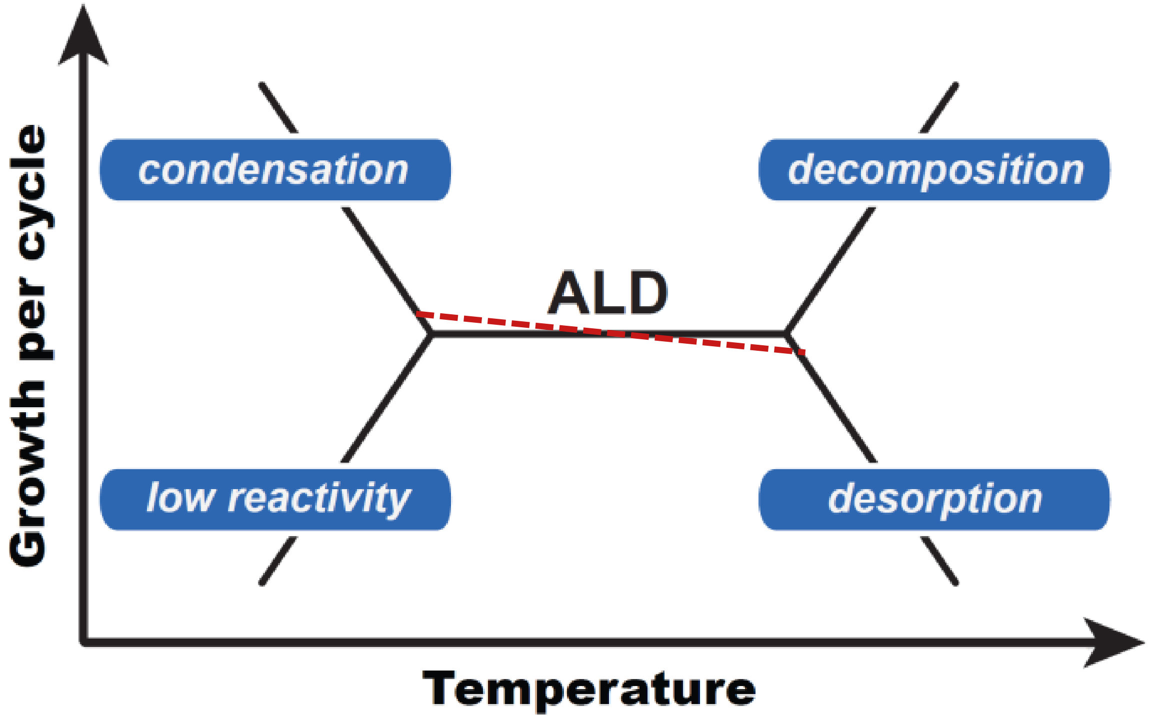
GPC depends on material, precursors & co-reactant, substrate temperature

Potts *et al.*, J. Electrochem. Soc. 157, P66 (2010)

Basics of Atomic Layer Deposition

The ALD window

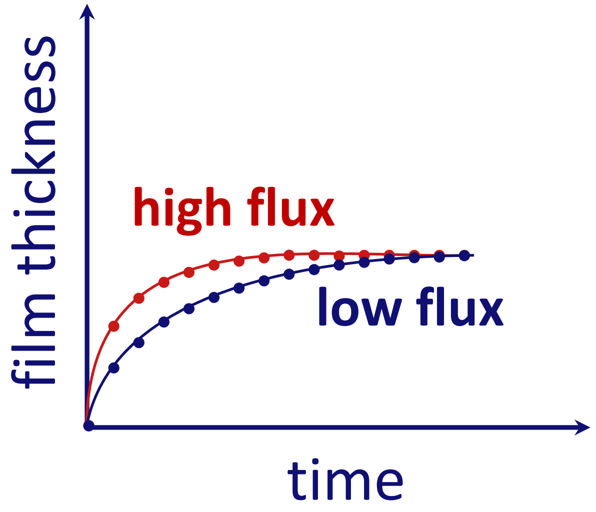
- Temperature range over which you find *well-behaved* ALD
- ALD temperature window not always flat, since equilibrium density of reactive surface sites (e.g., OH), depends on temperature.



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

Basics of Atomic Layer Deposition

Reaction kinetics and saturation curves



How much precursor or co-reactant do you need to dose?

Change in surface coverage → precursors that stick to empty sites

Flux

Fractional coverage of precursor

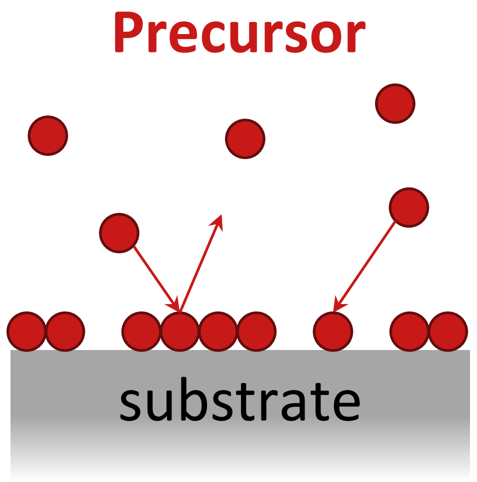
$$n_0' \frac{d\theta}{dt} = \Gamma \, s_0 \, (1 - \theta)$$

Surface site density

Sticking probability

$$\tau = \frac{n_0'}{s_0 \, \Gamma}$$

Solution: $\theta(t) = \left\{ 1 - \exp\left(-\frac{s_0 \, \Gamma}{n_0'} t \right) \right\}$



Basics of Atomic Layer Deposition

Reaction kinetics and saturation curves

$$\boxed{\tau = \frac{n_0'}{s_0\,\Gamma}}$$

Site density n_0'

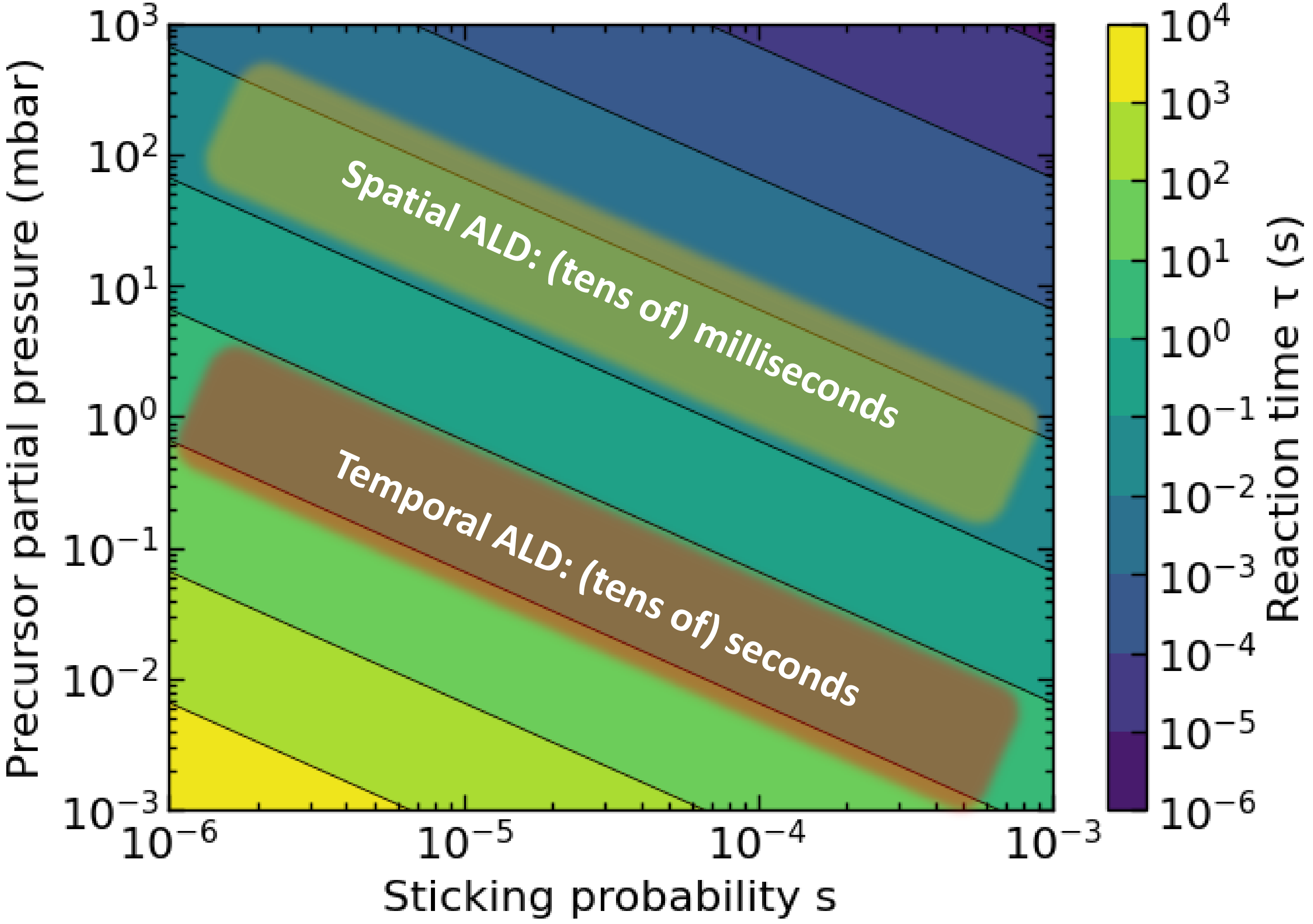
Depends on material, typical ~10^{15} cm^{-2}

Sticking probability s

Depends on precursor, temperature, …
Typical range: 10^{-5} - 10^{-3}

Flux Γ

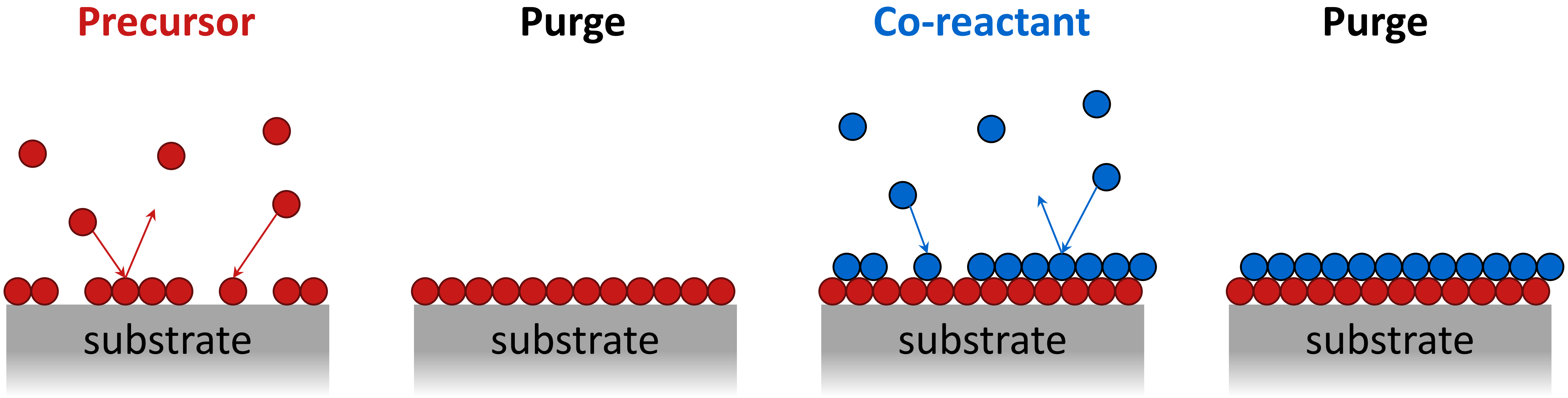
Calculate from pressure, temperature, …



Basics of Atomic Layer Deposition

Reaction kinetics and saturation curves

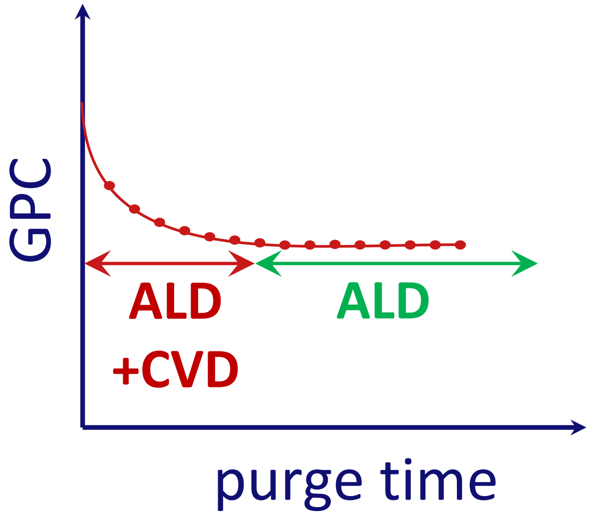
Why do we need to purge after the precursor and co-reactant steps?

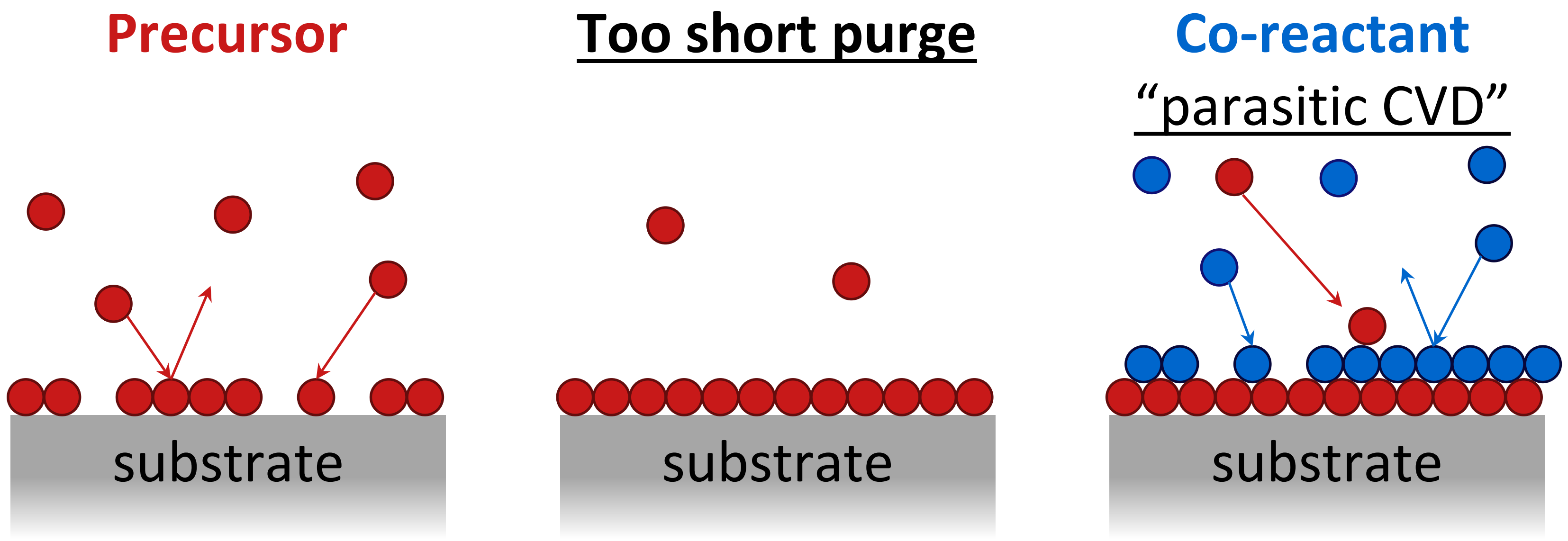


Basics of Atomic Layer Deposition

Reaction kinetics and saturation curves

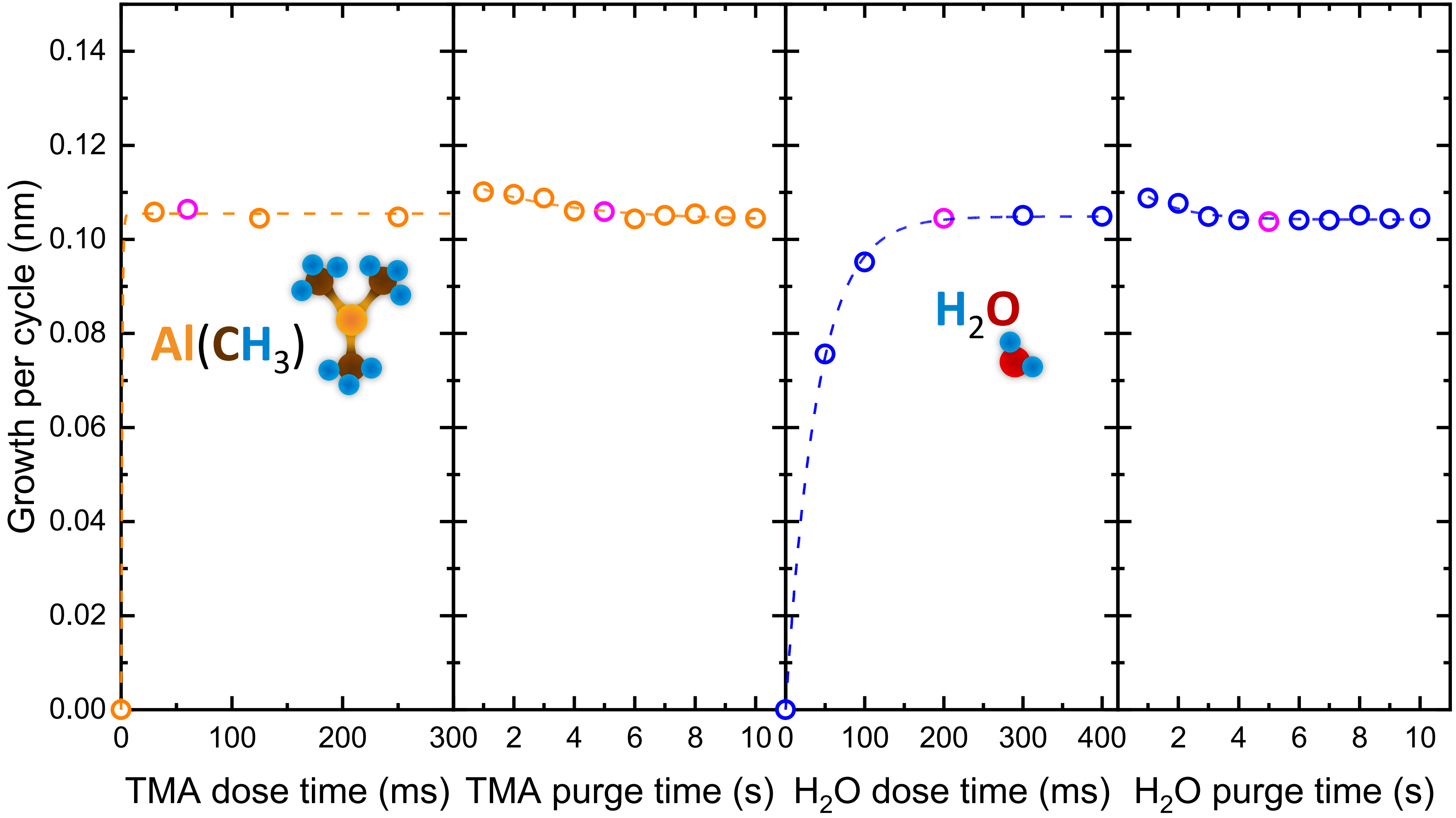
Required purging time determined by gas residence time (chamber volume/pumping speed)**, but also by "stickiness" of species, so surface residence time**





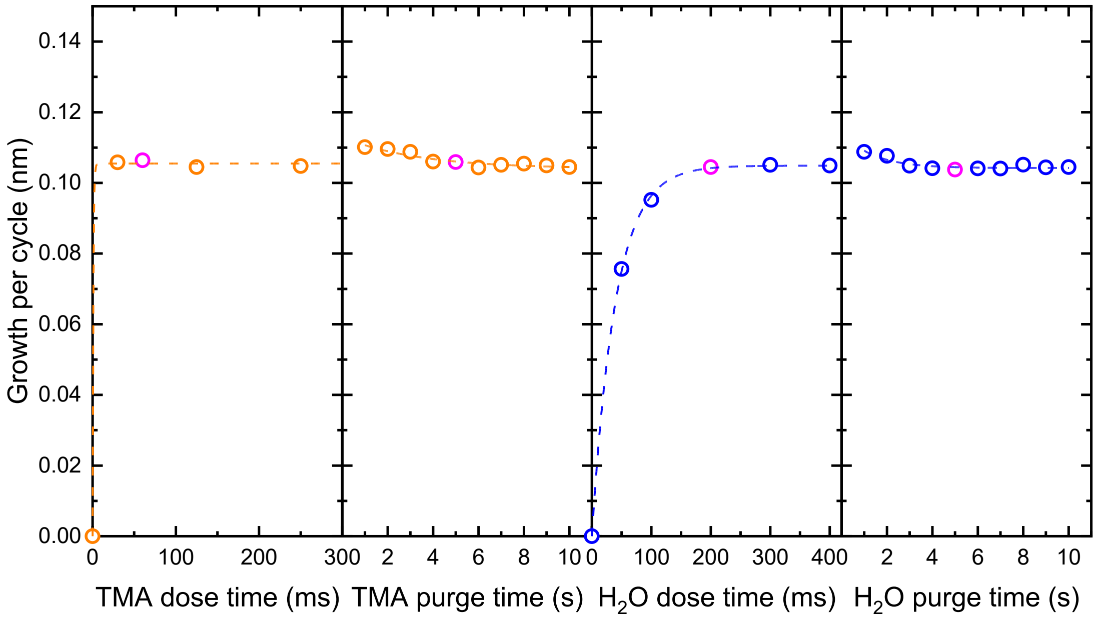
Basics of Atomic Layer Deposition

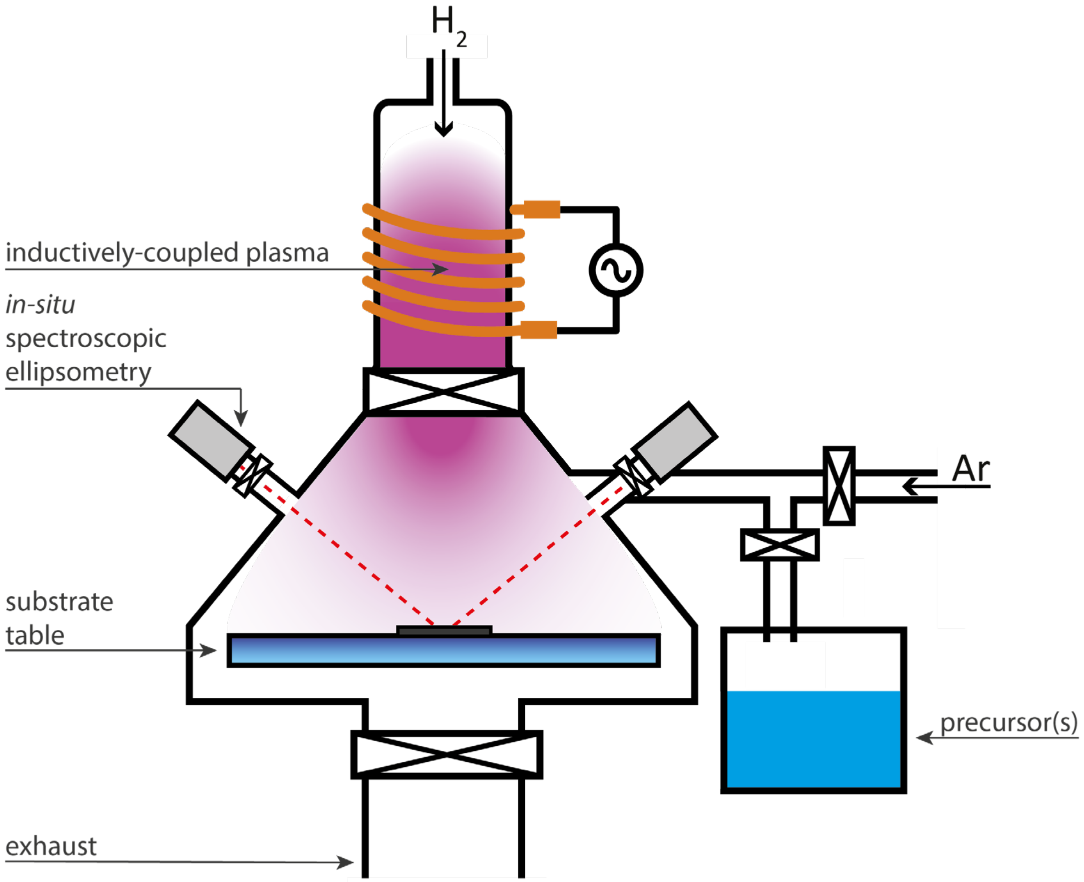
Reaction kinetics and saturation curves



Basics of Atomic Layer Deposition

Reaction kinetics and saturation curves





Spectroscopic ellipsometry during deposition (*in-situ*) is key technique

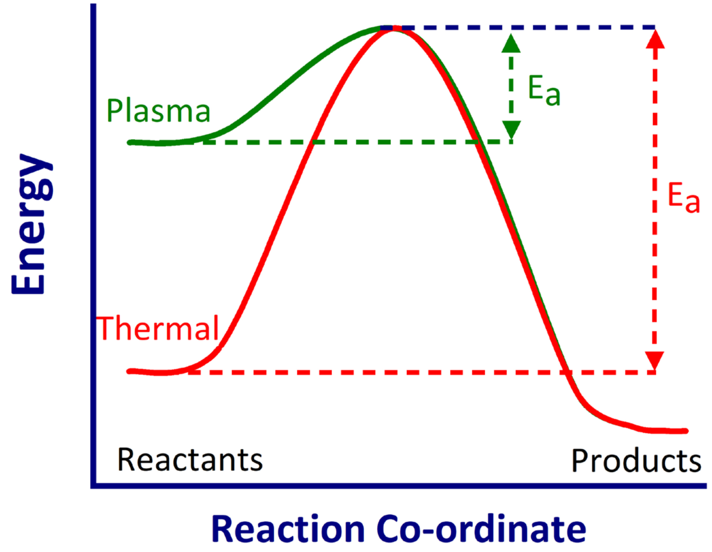
- Optical technique to measure film thickness
- Vary dose/purge time ➔ measure thickness increase ➔ construct saturation curves

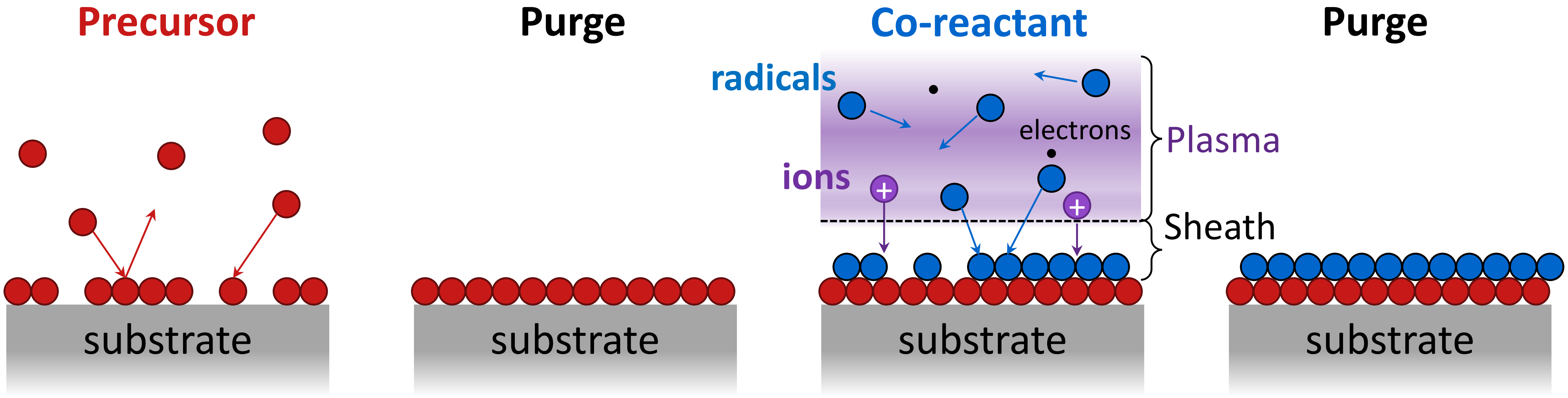
Basics of Atomic Layer Deposition

Plasma-enhanced ALD

Plasma as co-reactant

- More reactive radicals (e.g. O)
- Ions can provide additional energy
- Can enable lower temperatures, new materials, …

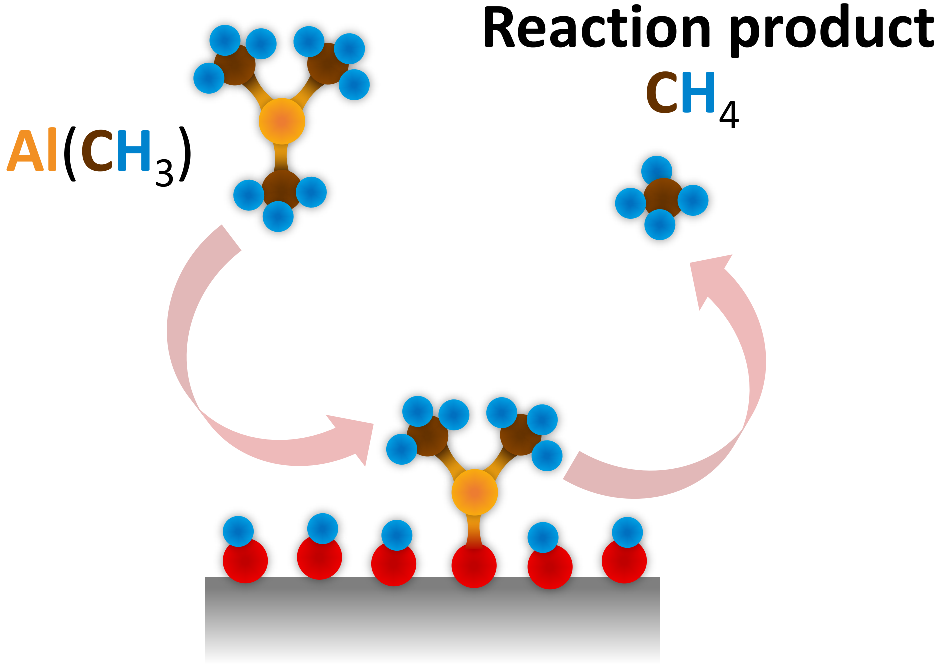




Basics of Atomic Layer Deposition

Plasma-enhanced ALD: Al_2O_3 from TMA and O_2 plasma

Precursor dose

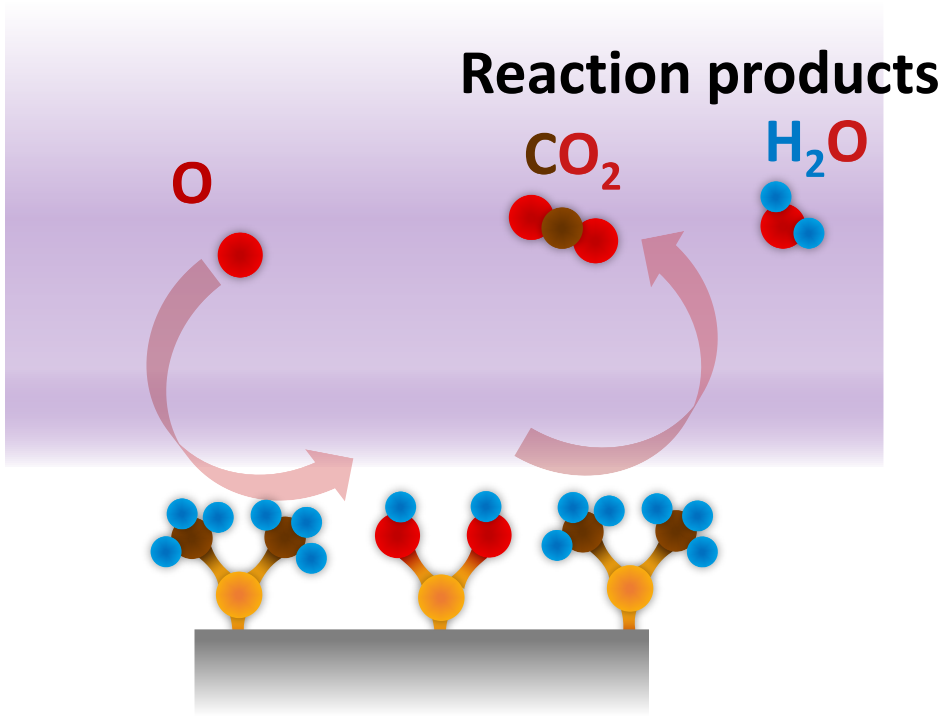


Reaction product
CH_4

$Al(CH_3)$

Starting surface
OH-groups

O_2 plasma dose



Reaction products
CO_2 H_2O

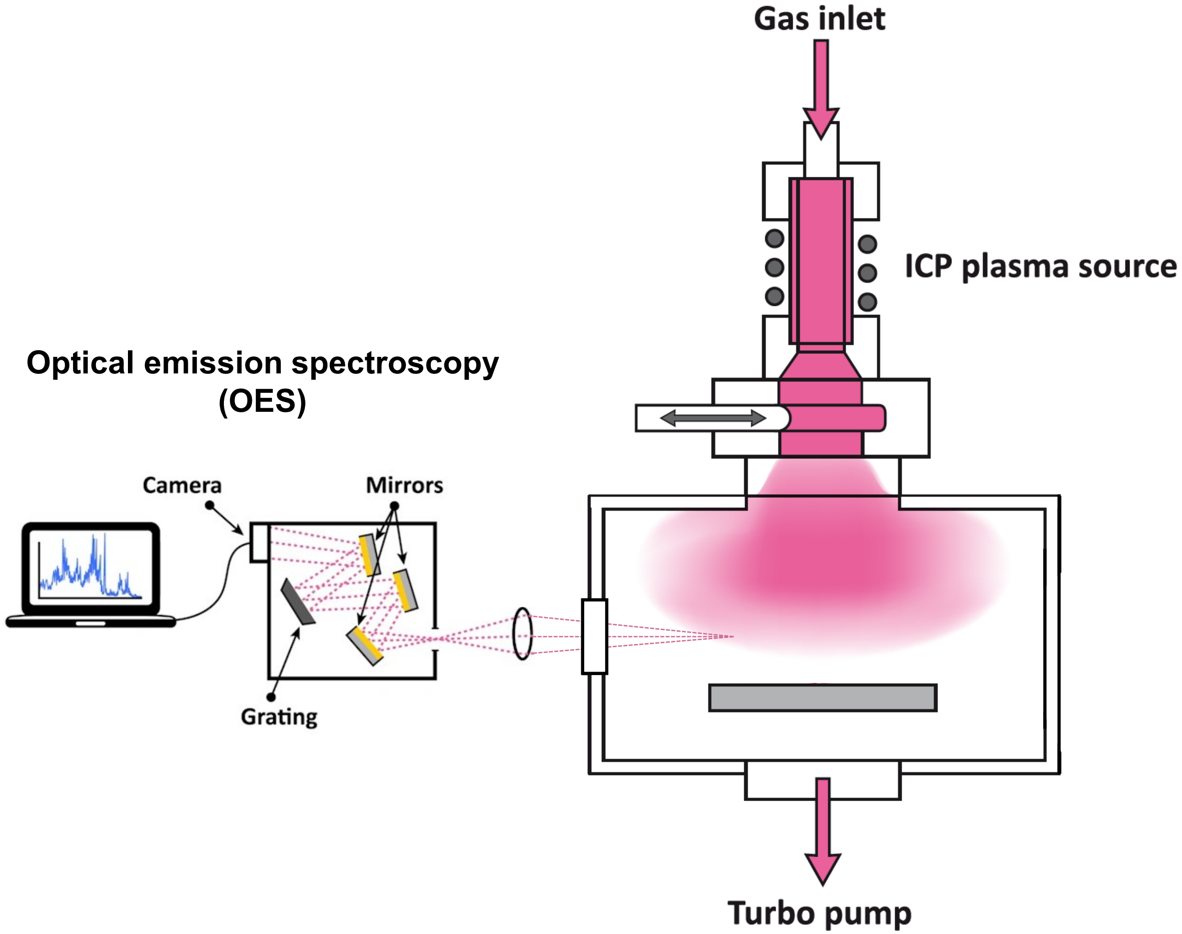
O

Starting surface
CH_3-groups

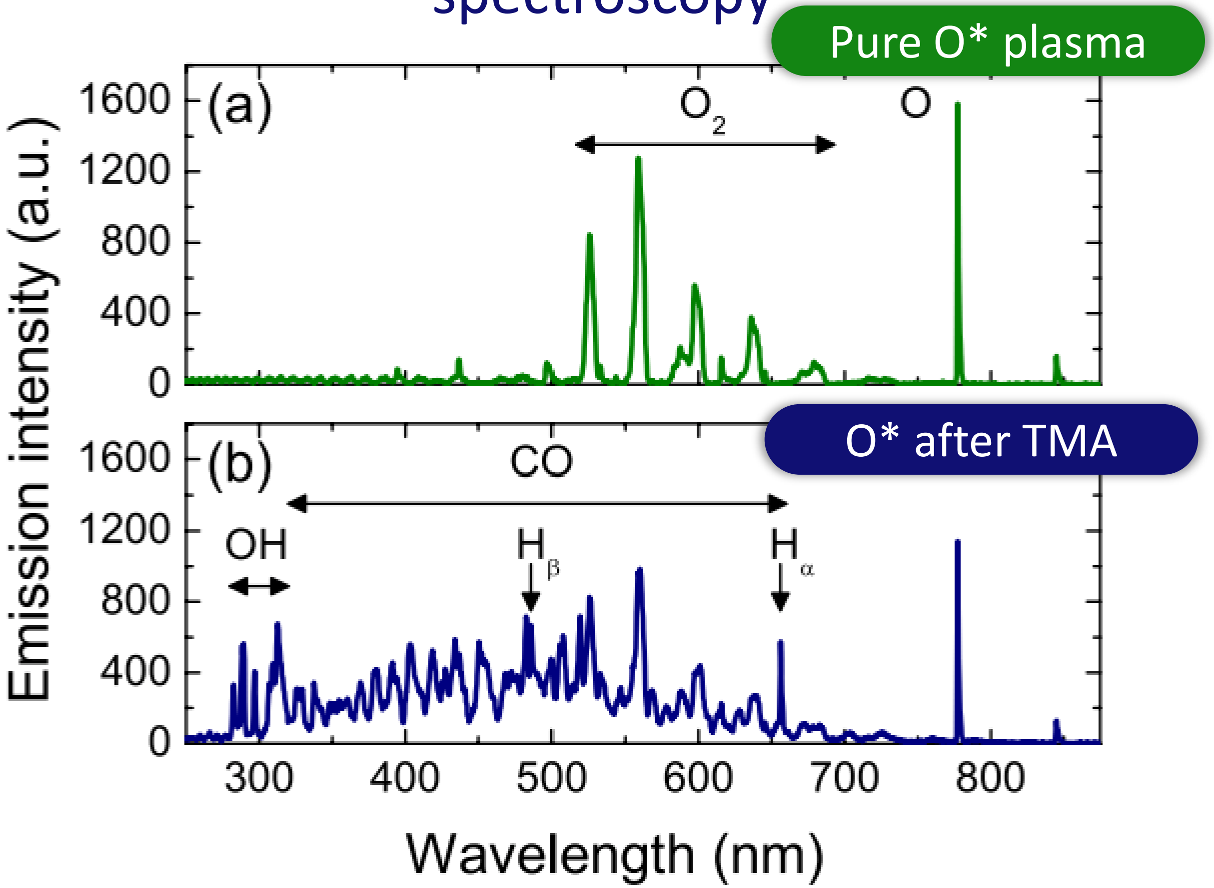
What do you think will be the reaction product(s)?

Basics of Atomic Layer Deposition

Plasma-enhanced ALD: Al_2O_3 from TMA and O_2 plasma



Plasma species from optical emission spectroscopy


Pure O* plasma

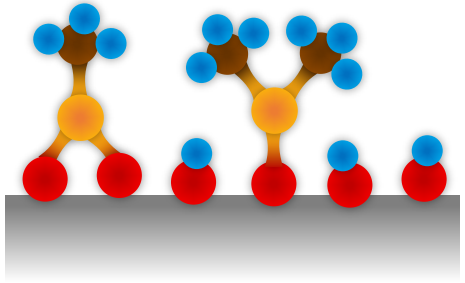
O* after TMA

Common misconceptions about ALD

“You always grow one monolayer”

You typically grow (much) less than a monolayer per cycle!

Monolayer	**~3 Å**
Al_2O_3	**1.1 Å**
ZnO	**1.6 Å**
MoS_2	**0.4 Å**
Pt	**0.5 Å**

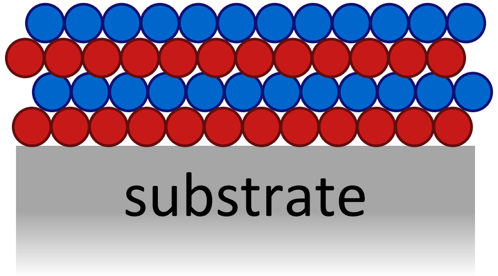


Various factors, often limited by how densely precursors can chemisorb on the surface (steric hindrance)

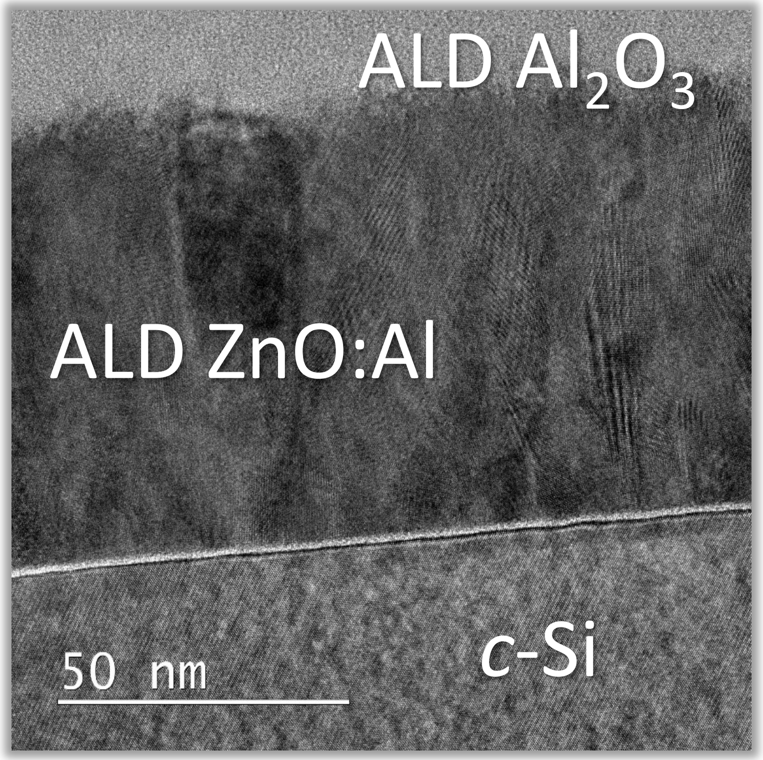
Common misconceptions about ALD

"You always grow a perfect crystal"

Simplistic drawing



versus reality:
polycrystalline ZnO, amorphous Al_2O_3

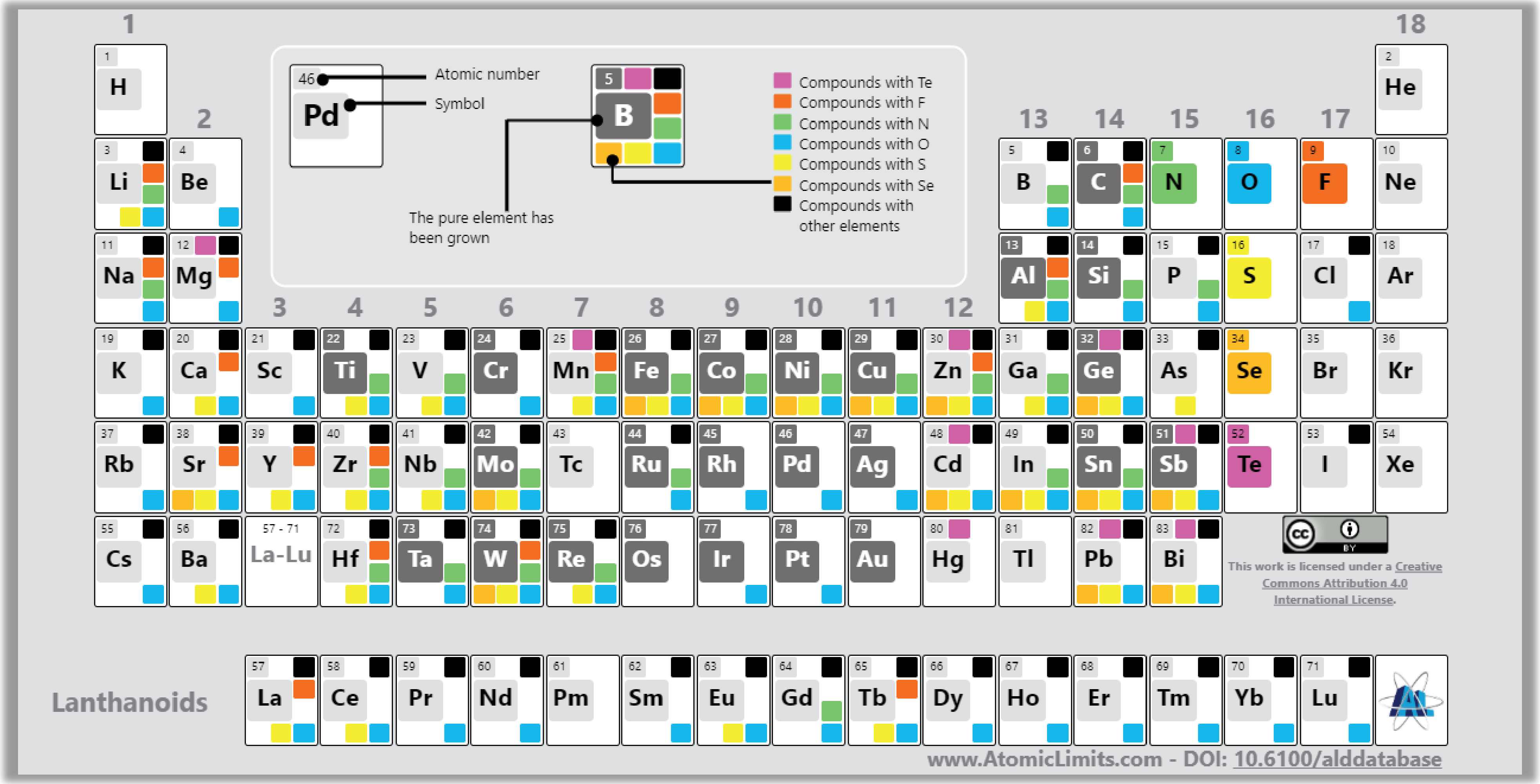


It depends on the material and temperature!

- ZnO (almost) always grows polycrystalline
- Al_2O_3 (almost) always grows amorphous
- In_2O_3 grows polycrystalline above ~100 °C

Basics of Atomic Layer Deposition

The online ALD Database at AtomicLimits.com



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

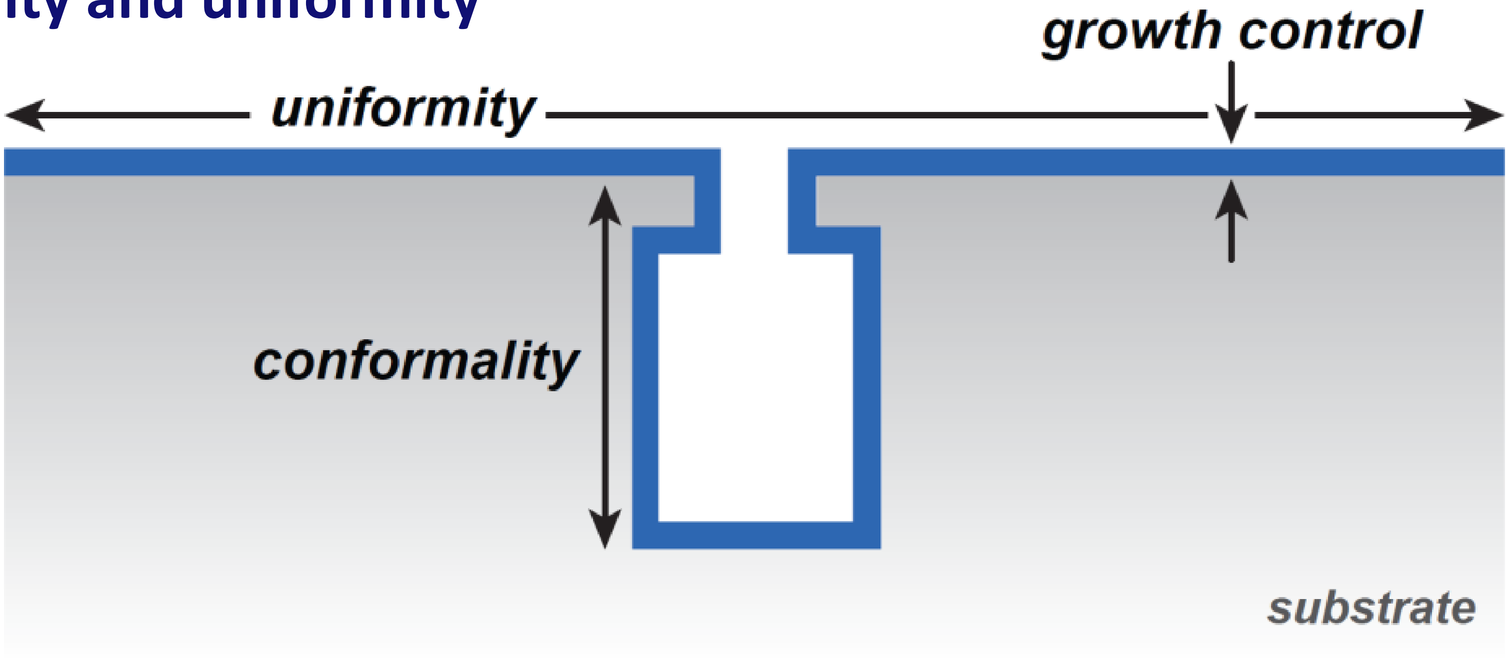
www.AtomicLimits.com - DOI: 10.6100/alddatabase

With direct links to publications

https://doi.org/10.6100/alddatabase

Basics of Atomic Layer Deposition

Conformality and uniformity



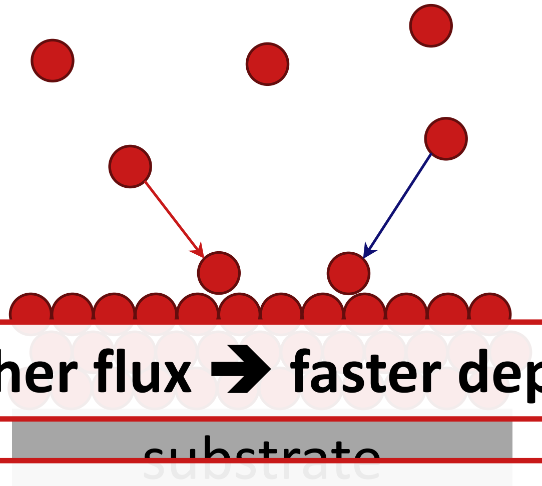
- **Thickness control** at the subnanometer level
- **Uniformity** of the films on large substrates
- **Conformality** for complex surface features

Basics of Atomic Layer Deposition

Flux-controlled vs surface-controlled

CVD and PVD are <u>"flux-controlled"</u>

Thickness $\propto$ *flux* · *time* · *stick. coeff.*

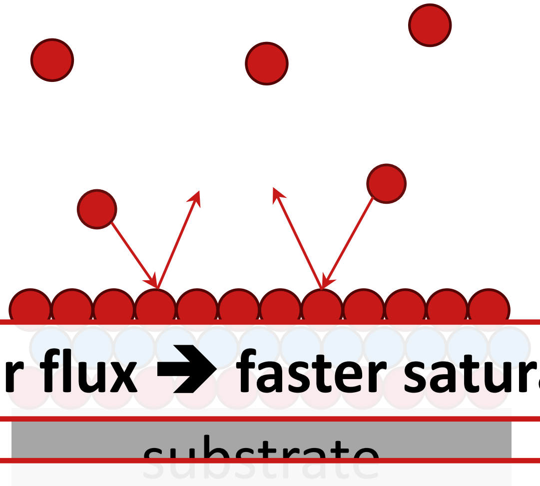


Higher flux → faster deposition

'Analog' thickness control
by deposition time & flux

ALD is <u>"surface-controlled"</u>

Growth-per-cycle $\propto 1 - \exp(-\frac{t}{\tau})$



Higher flux → faster saturation

'Digital' thickness control
by integer number of cycles

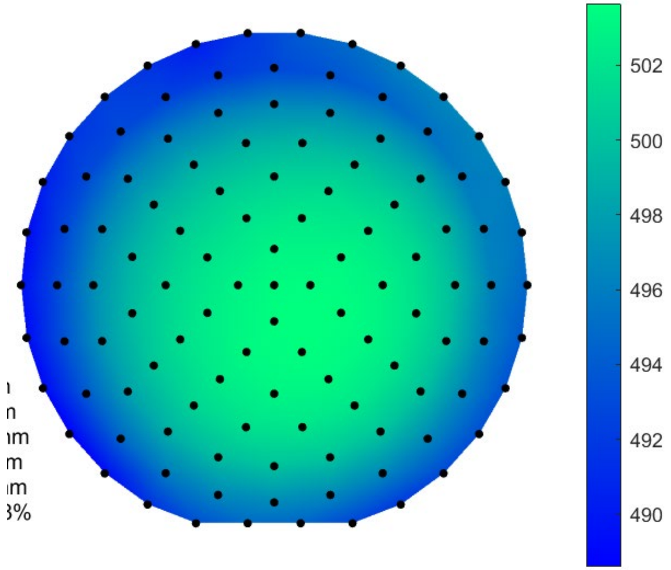
Basics of Atomic Layer Deposition

Flux-controlled vs surface-controlled

CVD and PVD are "flux-controlled"

$\text{Thickness} \propto \mathit{flux} \cdot \mathit{time} \cdot \mathit{stick.\ coeff.}$

Uniformity is sensitive to local changes in flux of species



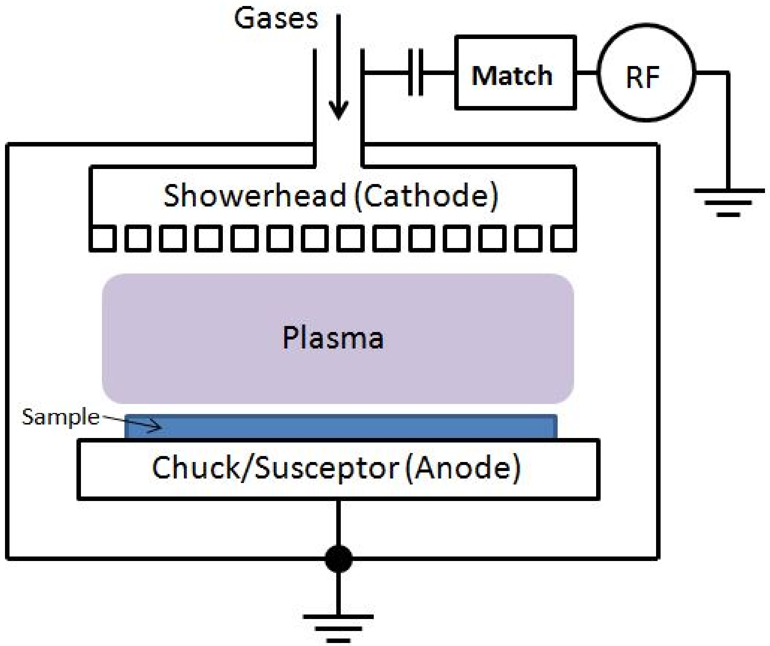
ALD is "surface-controlled"

$\text{Growth-per-cycle} \propto 1 - \exp(-\frac{t}{\tau})$

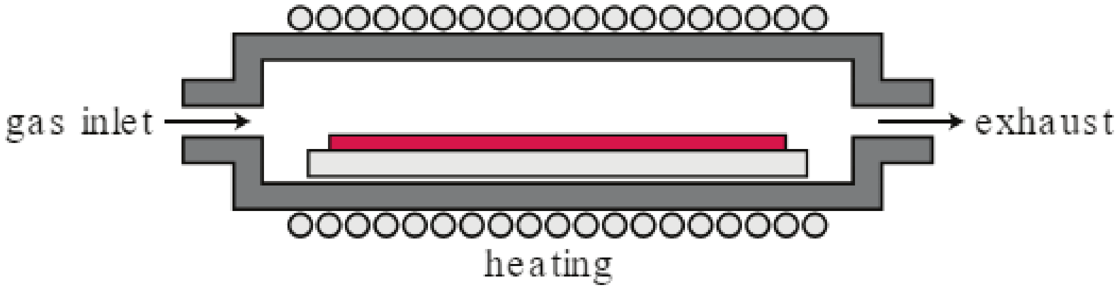
Uniformity is in principle insensitive to local changes in flux of species as long as the whole surface is in saturation

Basics of Atomic Layer Deposition

Flux-controlled vs surface-controlled

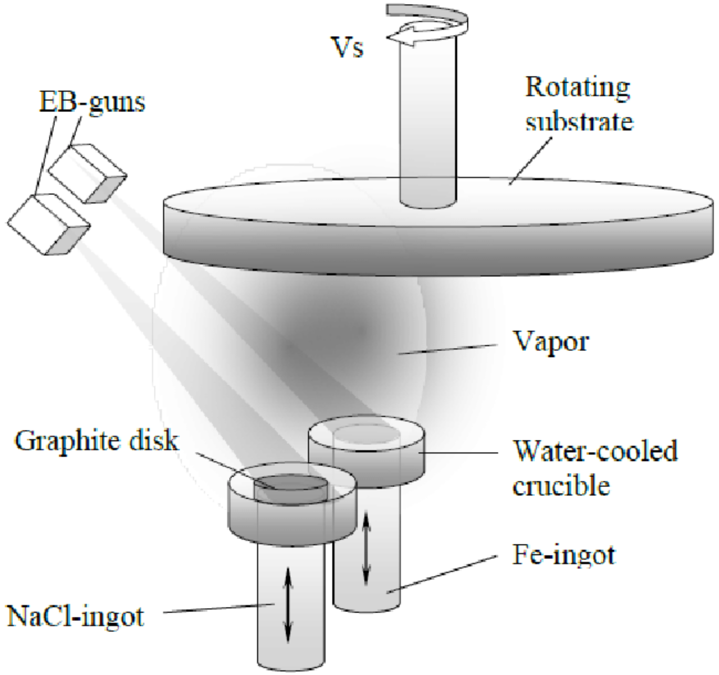


(PE)CVD: Showerheads to uniformly supply gases



ALD: Possible to get good uniformity even with lateral inlet.

PVD: Often the substrate is moved/rotated to average out non-uniformity in fluxes

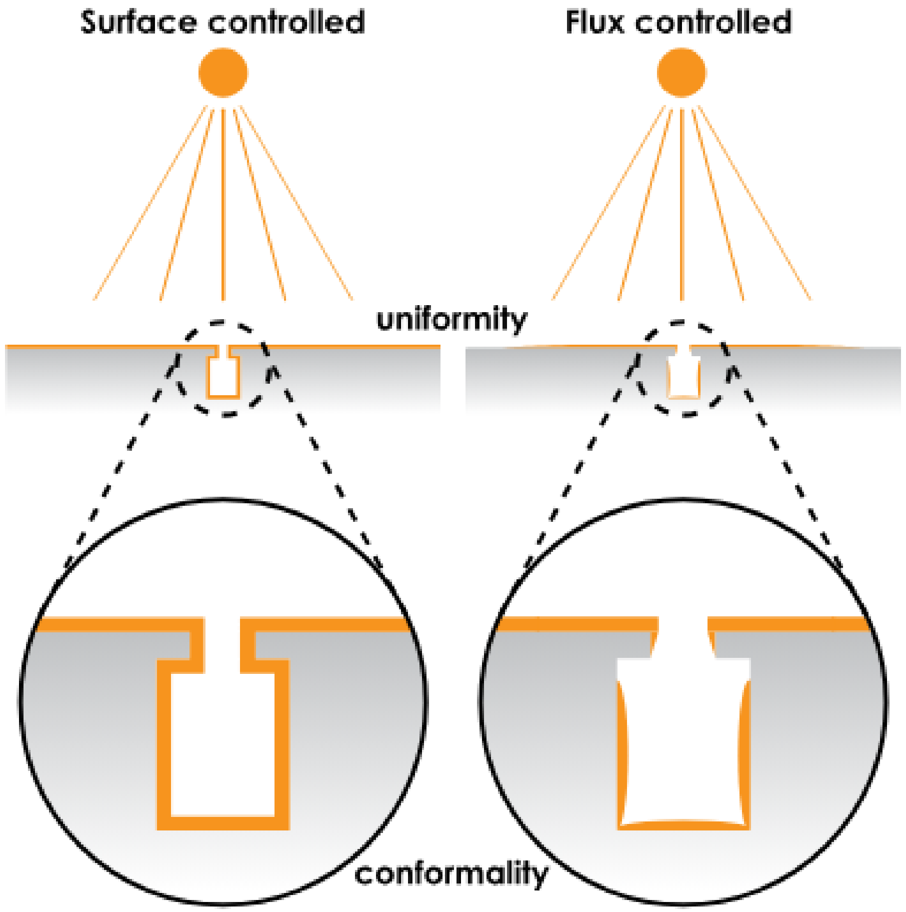


Basics of Atomic Layer Deposition

Conformality and uniformity

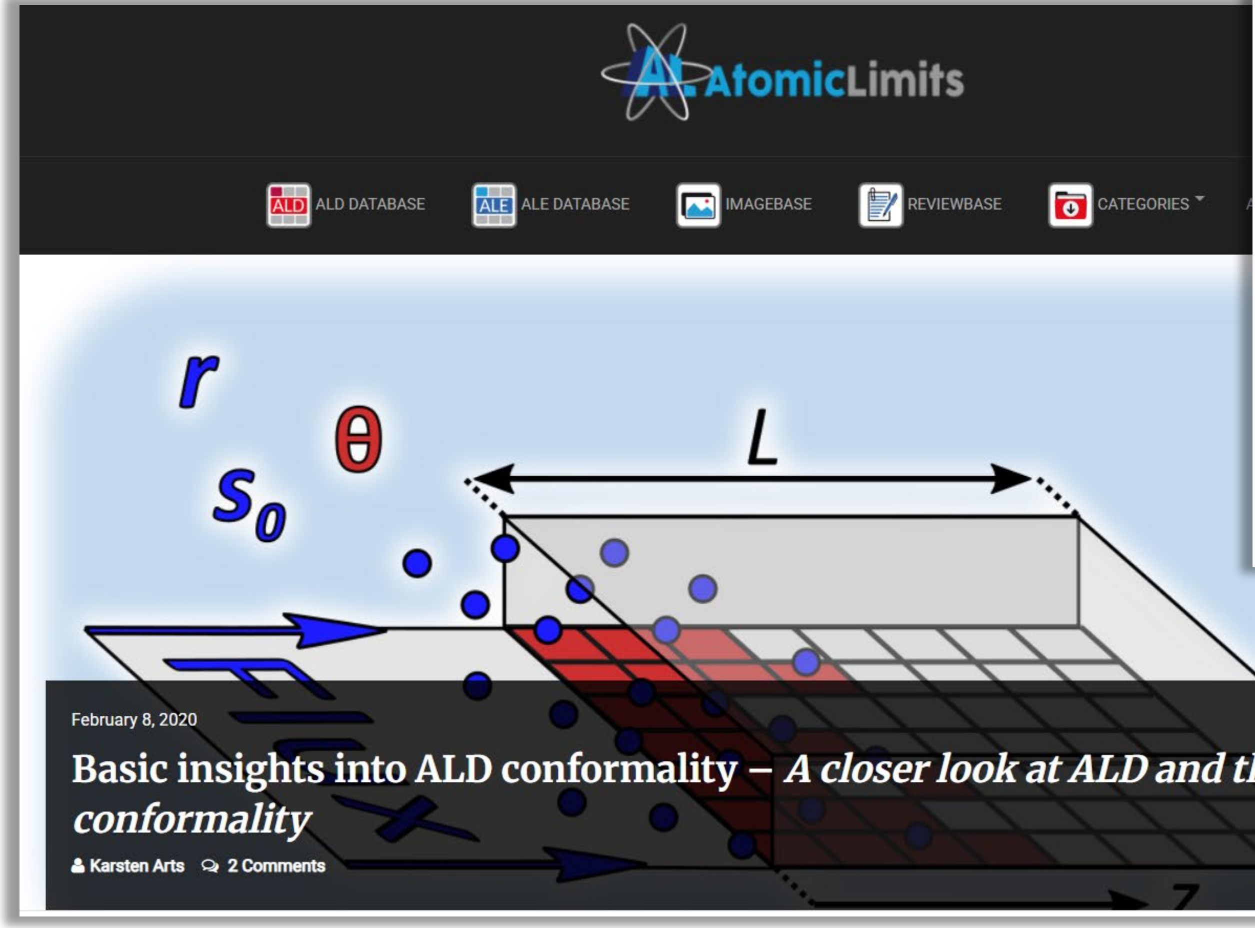
Conformality is the ability to deposit the same film thickness over a 3D structure, e.g. a trench in a wafer

Much like for **uniformity**, conformality is determined by the local exposure (in Langmuirs) that can vary along the trench.



Basics of Atomic Layer Deposition

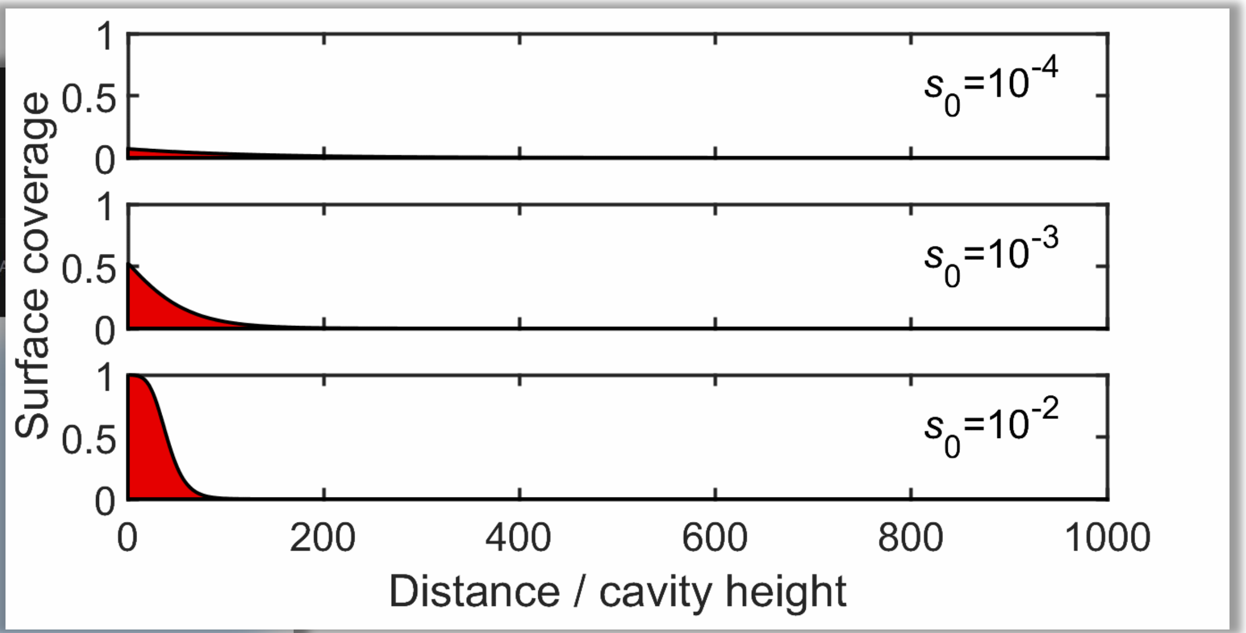
Conformality and uniformity: Further reading



February 8, 2020

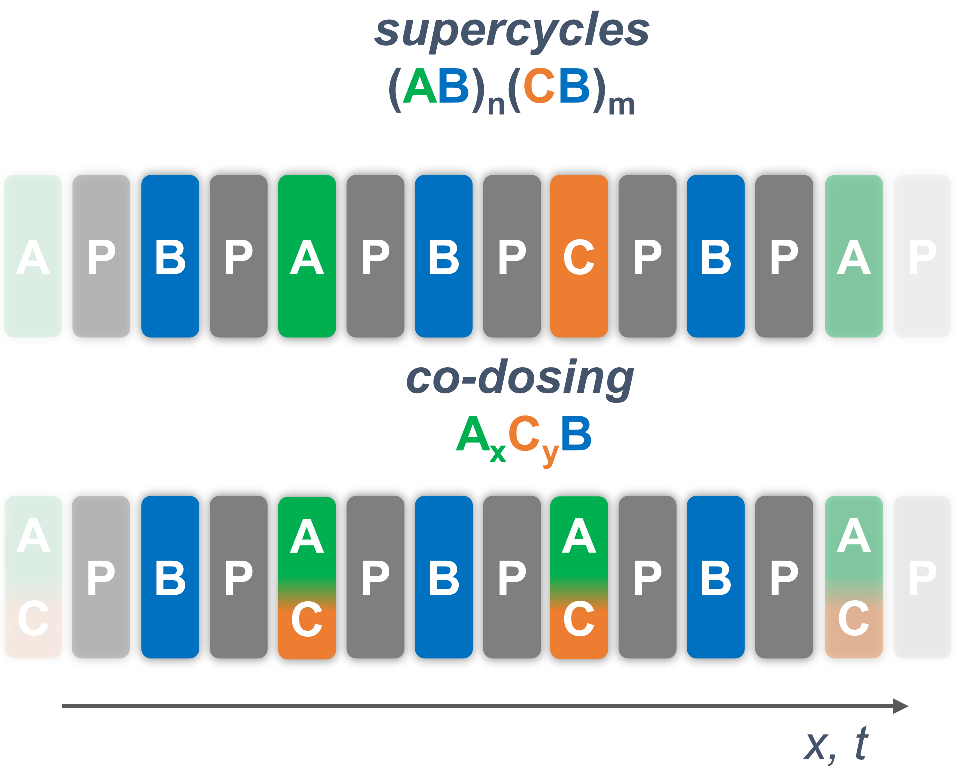
Basic insights into ALD conformality – *A closer look at ALD and thin film conformality*

Karsten Arts 2 Comments

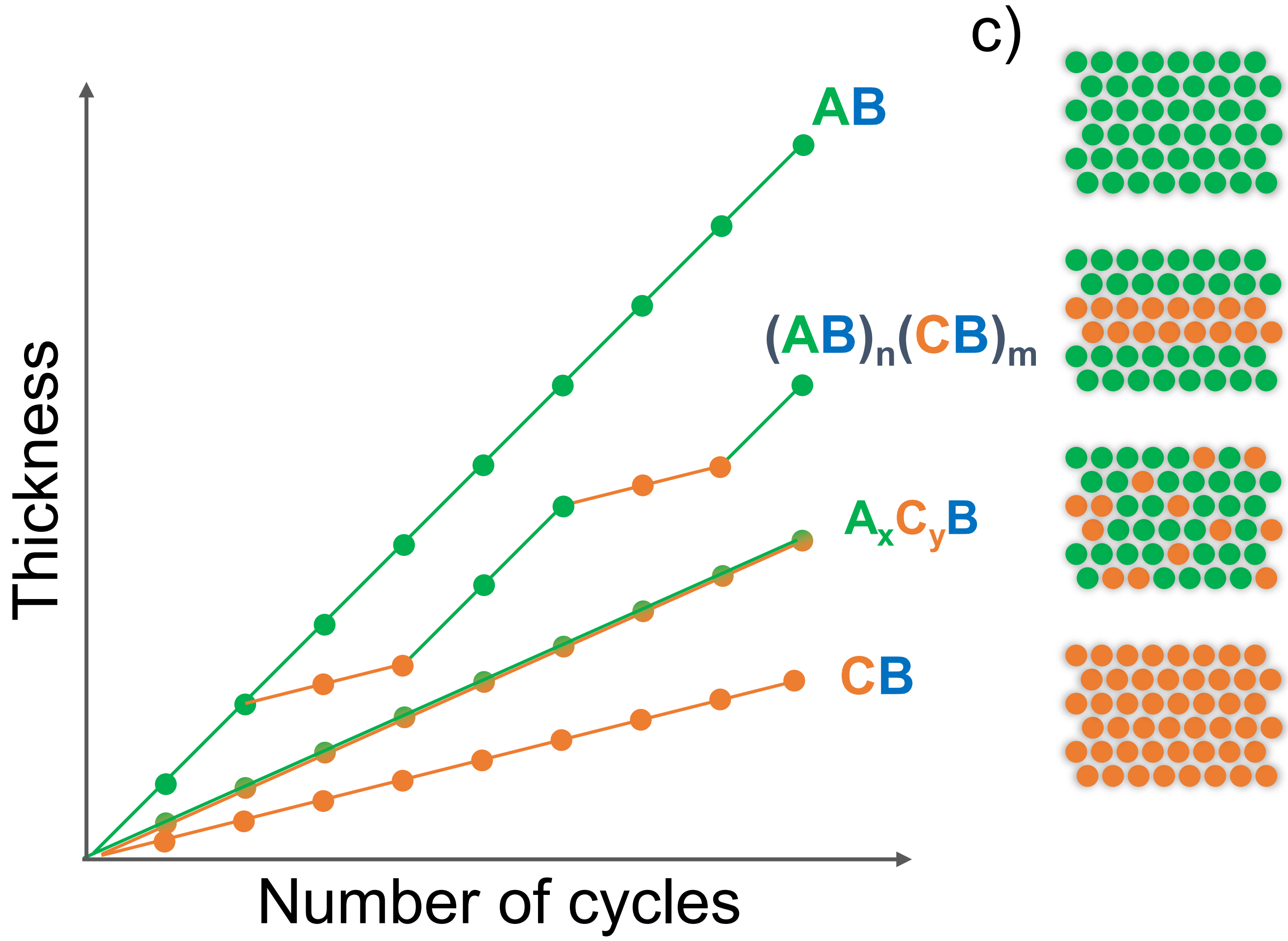


Basics of Atomic Layer Deposition

Doping and alloying



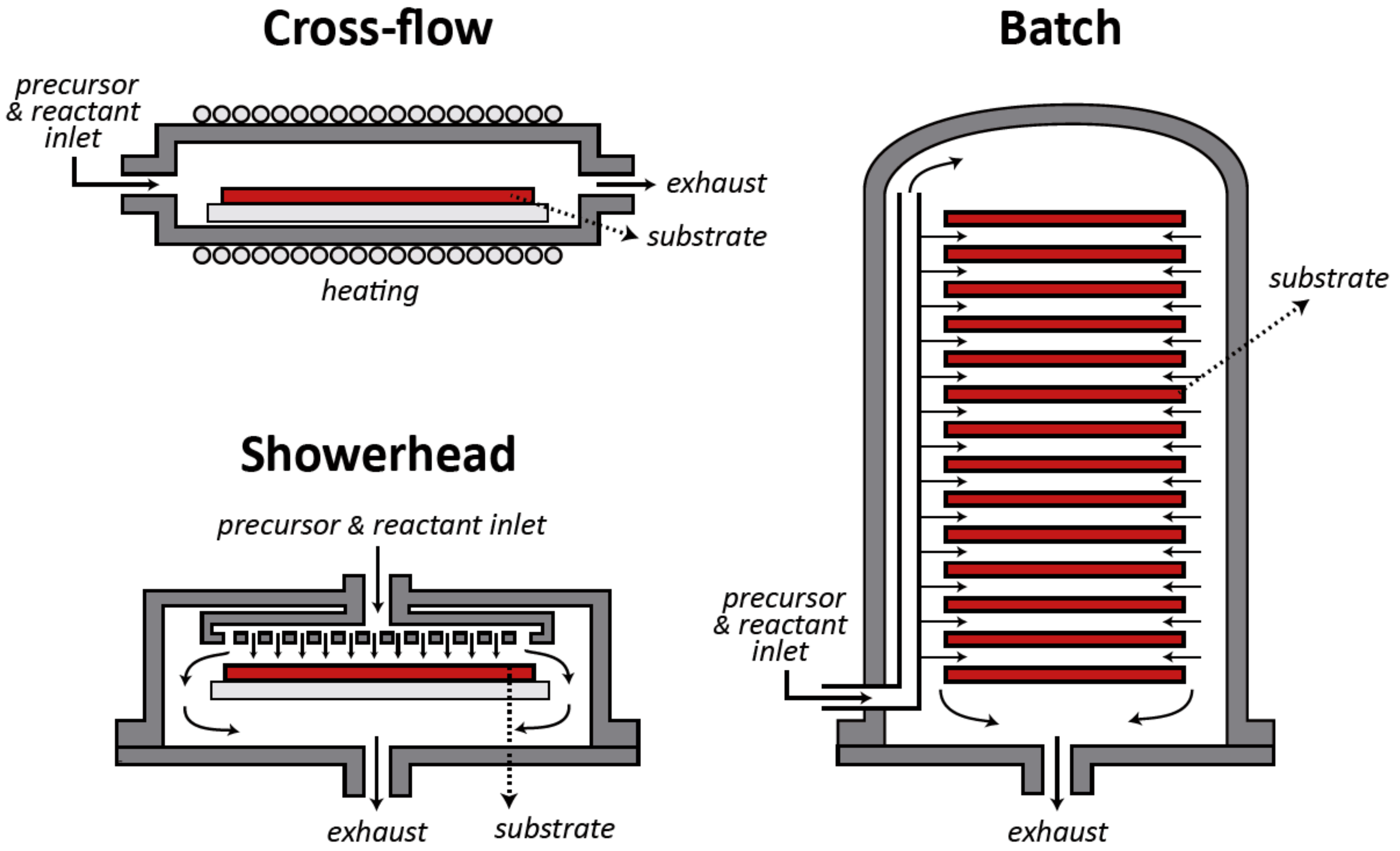
Note: many effects can occur when combining ALD processes. For an overview, see [1]



[1] B. Macco *et al.*, ALD of conductive and semiconductive oxides. *Appl. Phys. Rev.* **9**, 041313 (2022).

How to scale up ALD to many wafers or large area?

Upscaling by batch ALD: Increase throughput by parallel processing



Longer ALD cycles in batch?

Batch: ~30 s | single wafer ~10 s

- **Diffusion** between wafers
- **Large chamber volume**
- **Surface** residence time (sticky H_2O)

Is co-dosing a good idea?

Precursors A and B will have different **reactivity**, **diffusivity** → **non-uniformity**!

Kessels and Putkonen, MRS Bulletin 36, 907 (2011)

How to scale up ALD to many wafers or large area?

Upscaling by batch ALD: Increase throughput by parallel processing

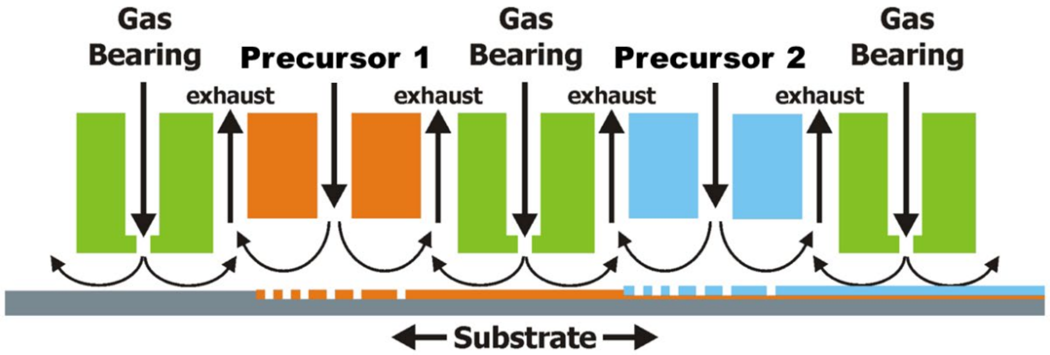
Huge furnaces that can load >10,000 wafers and coat them with ALD Al_2O_3 within an hour!

***Billions** of wafers per year are coated this way for silicon solar cells!*

PV magazine, June 2019 edition
See blog about **ALD for solar cells** on www.AtomicLimits.com

How to scale up ALD to many wafers or large area?

Upscaling by spatial ALD: Increase throughput by serial processing



- Wafers move through **precursor zones**
- Zones are separated by N_2 and **exhausts**
- Typically, at **atmospheric pressure** to allow gas separation
- **Small gap height** (~50-200 µm) keeps **laminar flow** and little intermixing
- **Dosing** and **purging** times are set by the substrate **velocity** and **zone widths**!

Poodt et al., J. Vac. Sci. Technol. A 31(1), 2013

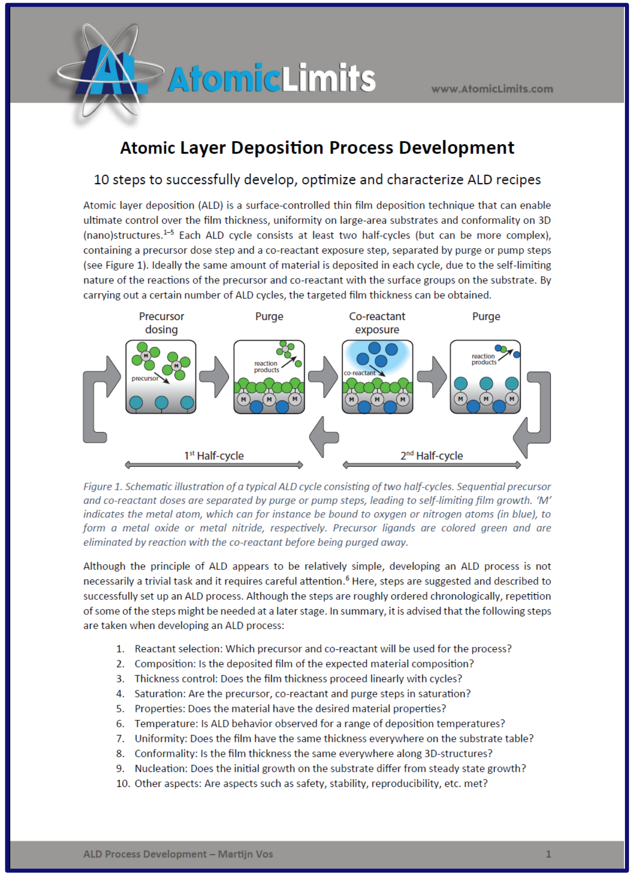
How to scale up ALD to many wafers or large area?

A crude comparison table between batch and spatial ALD

	Batch ALD	Spatial ALD
Deposition on walls	**Yes**	**No**
Thermal budget	**High** (all wafers long in chamber)	**Low** (wafer heated for seconds)
Co-dosing	**No** (non-uniformity)	**Easy**
Supercycles	**Inherently easy**	**Requires dedicated head design**
Tool complexity	**Low** (“oven” + pumps)	**High** (moving parts, …)
Plasma ALD	**Possible, not straightforward**	**Easy** (dielectric barrier discharge)

10 steps to develop an ALD process

www.AtomicLimits.com



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Atomic Layer Deposition Process Development

10 steps to successfully develop, optimize and characterize ALD recipes

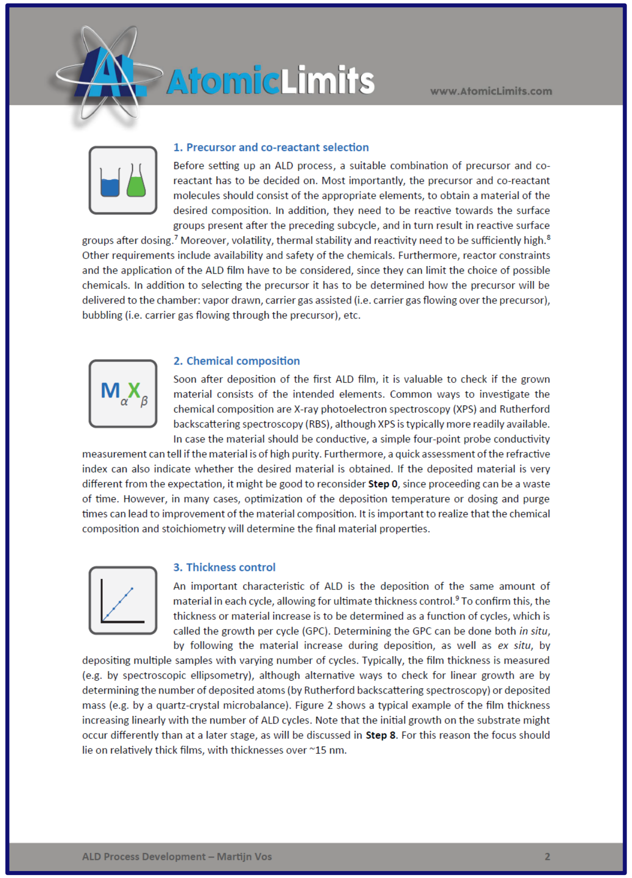
Atomic layer deposition (ALD) is a surface-controlled thin film deposition technique that can enable ultimate control over the film thickness, uniformity on large-area substrates and conformality on 3D (nano)structures.[1–5] Each ALD cycle consists at least two half-cycles (but can be more complex), containing a precursor dose step and a co-reactant exposure step, separated by purge or pump steps (see Figure 1). Ideally the same amount of material is deposited in each cycle, due to the self-limiting nature of the reactions of the precursor and co-reactant with the surface groups on the substrate. By carrying out a certain number of ALD cycles, the targeted film thickness can be obtained.

Figure 1. Schematic illustration of a typical ALD cycle consisting of two half-cycles. Sequential precursor and co-reactant doses are separated by purge or pump steps, leading to self-limiting film growth. 'M' indicates the metal atom, which can for instance be bound to oxygen or nitrogen atoms (in blue), to form a metal oxide or metal nitride, respectively. Precursor ligands are colored green and are eliminated by reaction with the co-reactant before being purged away.

Although the principle of ALD appears to be relatively simple, developing an ALD process is not necessarily a trivial task and it requires careful attention.[6] Here, steps are suggested and described to successfully set up an ALD process. Although the steps are roughly ordered chronologically, repetition of some of the steps might be needed at a later stage. In summary, it is advised that the following steps are taken when developing an ALD process:

1. Reactant selection: Which precursor and co-reactant will be used for the process?
2. Composition: Is the deposited film of the expected material composition?
3. Thickness control: Does the film thickness proceed linearly with cycles?
4. Saturation: Are the precursor, co-reactant and purge steps in saturation?
5. Properties: Does the material have the desired material properties?
6. Temperature: Is ALD behavior observed for a range of deposition temperatures?
7. Uniformity: Does the film have the same thickness everywhere on the substrate table?
8. Conformality: Is the film thickness the same everywhere along 3D-structures?
9. Nucleation: Does the initial growth on the substrate differ from steady state growth?
10. Other aspects: Are aspects such as safety, stability, reproducibility, etc. met?

ALD Process Development – Martijn Vos 1



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1. Precursor and co-reactant selection

Before setting up an ALD process, a suitable combination of precursor and co-reactant has to be decided on. Most importantly, the precursor and co-reactant molecules should consist of the appropriate elements, to obtain a material of the desired composition. In addition, they need to be reactive towards the surface groups present after the preceding subcycle, and in turn result in reactive surface groups after dosing.[7] Moreover, volatility, thermal stability and reactivity need to be sufficiently high.[8] Other requirements include availability and safety of the chemicals. Furthermore, reactor constraints and the application of the ALD film have to be considered, since they can limit the choice of possible chemicals. In addition to selecting the precursor it has to be determined how the precursor will be delivered to the chamber: vapor drawn, carrier gas assisted (i.e. carrier gas flowing over the precursor), bubbling (i.e. carrier gas flowing through the precursor), etc.

2. Chemical composition

$M_\alpha X_\beta$

Soon after deposition of the first ALD film, it is valuable to check if the grown material consists of the intended elements. Common ways to investigate the chemical composition are X-ray photoelectron spectroscopy (XPS) and Rutherford backscattering spectroscopy (RBS), although XPS is typically more readily available. In case the material should be conductive, a simple four-point probe conductivity measurement can tell if the material is of high purity. Furthermore, a quick assessment of the refractive index can also indicate whether the desired material is obtained. If the deposited material is very different from the expectation, it might be good to reconsider **Step 0**, since proceeding can be a waste of time. However, in many cases, optimization of the deposition temperature or dosing and purge times can lead to improvement of the material composition. It is important to realize that the chemical composition and stoichiometry will determine the final material properties.

3. Thickness control

An important characteristic of ALD is the deposition of the same amount of material in each cycle, allowing for ultimate thickness control.[9] To confirm this, the thickness or material increase is to be determined as a function of cycles, which is called the growth per cycle (GPC). Determining the GPC can be done both *in situ*, by following the material increase during deposition, as well as *ex situ*, by depositing multiple samples with varying number of cycles. Typically, the film thickness is measured (e.g. by spectroscopic ellipsometry), although alternative ways to check for linear growth are by determining the number of deposited atoms (by Rutherford backscattering spectroscopy) or deposited mass (e.g. by a quartz-crystal microbalance). Figure 2 shows a typical example of the film thickness increasing linearly with the number of ALD cycles. Note that the initial growth on the substrate might occur differently than at a later stage, as will be discussed in **Step 8**. For this reason the focus should lie on relatively thick films, with thicknesses over ~15 nm.

ALD Process Development – Martijn Vos 2

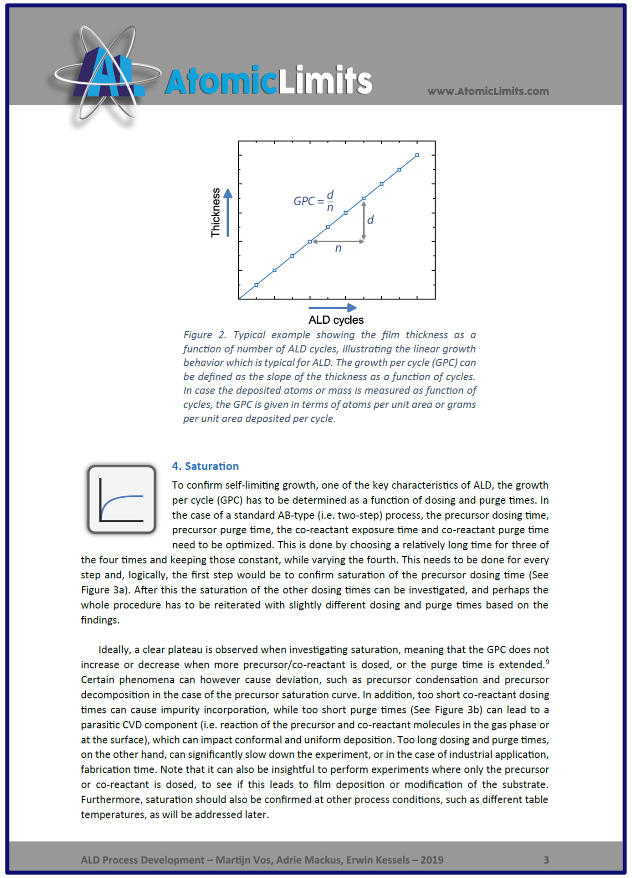

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Figure 2. Typical example showing the film thickness as a function of number of ALD cycles, illustrating the linear growth behavior which is typical for ALD. The growth per cycle (GPC) can be defined as the slope of the thickness as a function of cycles. In case the deposited atoms or mass is measured as function of cycles, the GPC is given in terms of atoms per unit area or grams per unit area deposited per cycle.

4. Saturation

To confirm self-limiting growth, one of the key characteristics of ALD, the growth per cycle (GPC) has to be determined as a function of dosing and purge times. In the case of a standard AB-type (i.e. two-step) process, the precursor dosing time, precursor purge time, the co-reactant exposure time and co-reactant purge time need to be optimized. This is done by choosing a relatively long time for three of the four times and keeping those constant, while varying the fourth. This needs to be done for every step and, logically, the first step would be to confirm saturation of the precursor dosing time (See Figure 3a). After this the saturation of the other dosing times can be investigated, and perhaps the whole procedure has to be reiterated with slightly different dosing and purge times based on the findings.

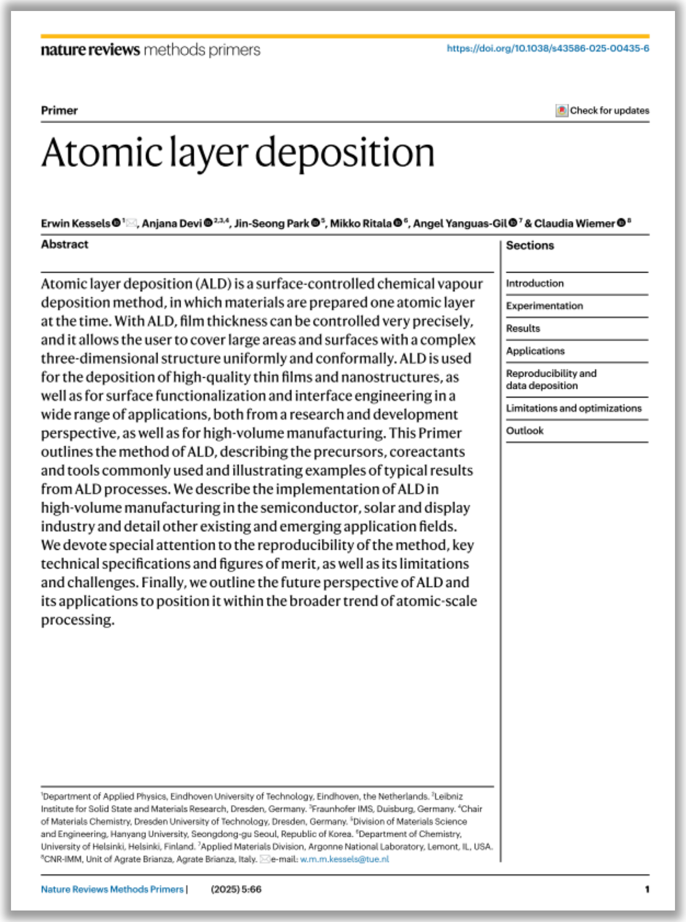
Ideally, a clear plateau is observed when investigating saturation, meaning that the GPC does not increase or decrease when more precursor/co-reactant is dosed, or the purge time is extended.[9] Certain phenomena can however cause deviation, such as precursor condensation and precursor decomposition in the case of the precursor saturation curve. In addition, too short co-reactant dosing times can cause impurity incorporation, while too short purge times (See Figure 3b) can lead to a parasitic CVD component (i.e. reaction of the precursor and co-reactant molecules in the gas phase or at the surface), which can impact conformal and uniform deposition. Too long dosing and purge times, on the other hand, can significantly slow down the experiment, or in the case of industrial application, fabrication time. Note that it can also be insightful to perform experiments where only the precursor or co-reactant is dosed, to see if this leads to film deposition or modification of the substrate. Furthermore, saturation should also be confirmed at other process conditions, such as different table temperatures, as will be addressed later.

ALD Process Development – Martijn Vos, Adrie Mackus, Erwin Kessels – 2019 3

See blog about **ALD process development** (with pdf to download)

Recent review paper

Nature Reviews Methods Primer



nature reviews methods primers

https://doi.org/10.1038/s43586-025-00435-6

Primer

Check for updates

Atomic layer deposition

Erwin Kessels[1], Anjana Devi[2,3,4], Jin-Seong Park[5], Mikko Ritala[6], Angel Yanguas-Gil[7] & Claudia Wiemer[8]

Abstract

Atomic layer deposition (ALD) is a surface-controlled chemical vapour deposition method, in which materials are prepared one atomic layer at the time. With ALD, film thickness can be controlled very precisely, and it allows the user to cover large areas and surfaces with a complex three-dimensional structure uniformly and conformally. ALD is used for the deposition of high-quality thin films and nanostructures, as well as for surface functionalization and interface engineering in a wide range of applications, both from a research and development perspective, as well as for high-volume manufacturing. This Primer outlines the method of ALD, describing the precursors, coreactants and tools commonly used and illustrating examples of typical results from ALD processes. We describe the implementation of ALD in high-volume manufacturing in the semiconductor, solar and display industry and detail other existing and emerging application fields. We devote special attention to the reproducibility of the method, key technical specifications and figures of merit, as well as its limitations and challenges. Finally, we outline the future perspective of ALD and its applications to position it within the broader trend of atomic-scale processing.

Sections

Introduction

Experimentation

Results

Applications

Reproducibility and data deposition

Limitations and optimizations

Outlook

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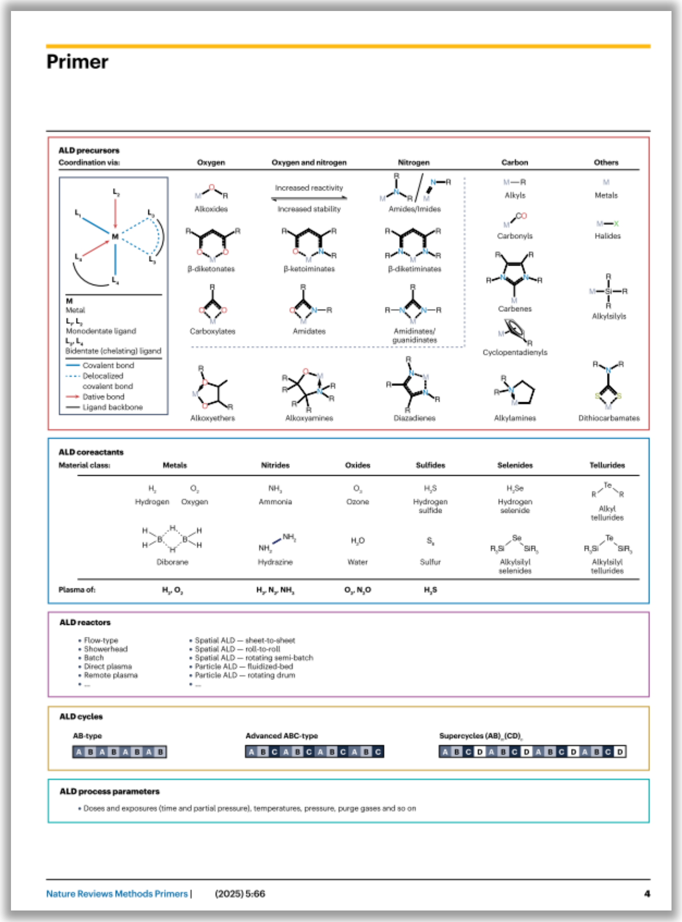

Primer

ALD reactors

- Flow-type
- Showerhead
- Batch
- Direct plasma
- Remote plasma
- ...

- Spatial ALD — sheet-to-sheet
- Spatial ALD — roll-to-roll
- Spatial ALD — rotating semi-batch
- Particle ALD — fluidized-bed
- Particle ALD — rotating drum
- ...

ALD cycles

ALD process parameters

- Doses and exposures (time and partial pressure), temperatures, pressure, purge gases and so on

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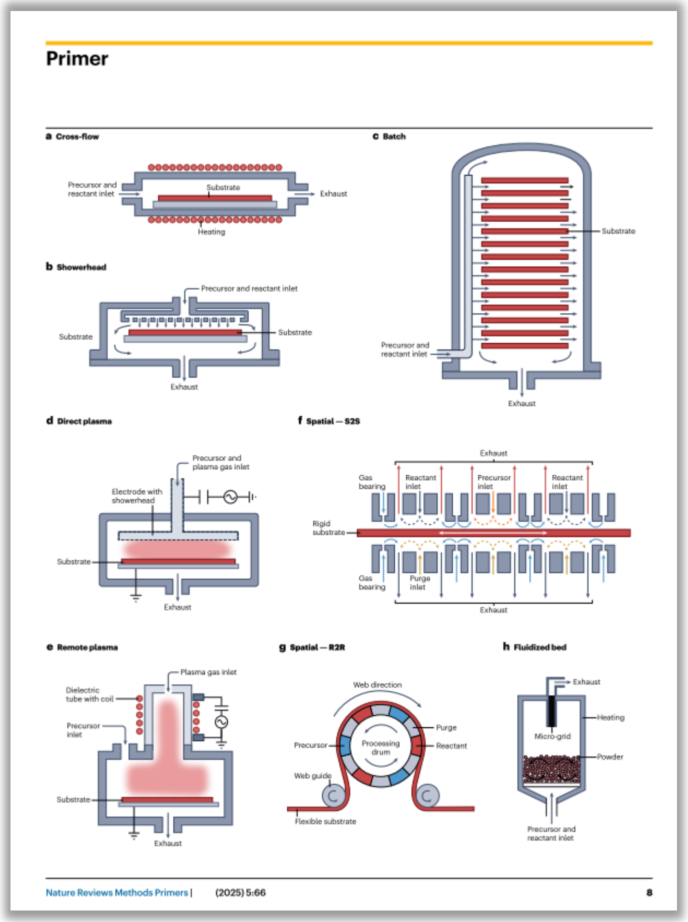

Primer

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W.M.M. Kessels,. *Nature Reviews Methods Primers*, *5*(1), 66, 2025