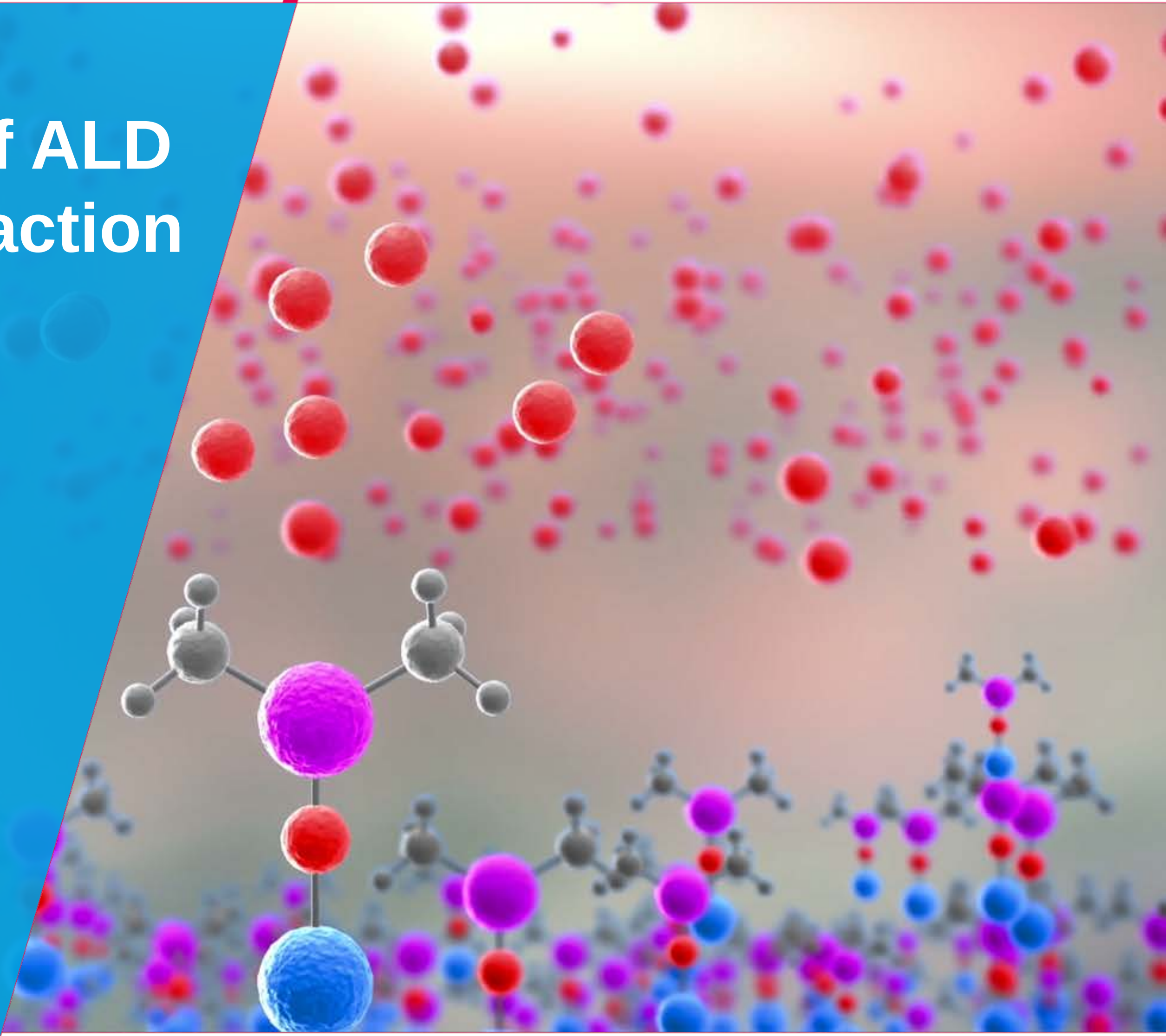
Technische Universiteit
Eindhoven
University of Technology

In situ Studies of ALD Processes & Reaction Mechanisms



Erwin Kessels

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www.tue.nl/pmp

Where innovation starts

This tutorial presentation will give …

(1) an overview of **methods** for *in situ* studies of ALD processes & reaction mechanisms; and

(2) some **insight** into these processes and mechanisms

Don’t expect:

- A comprehensive overview
- Techniques explained in large detail

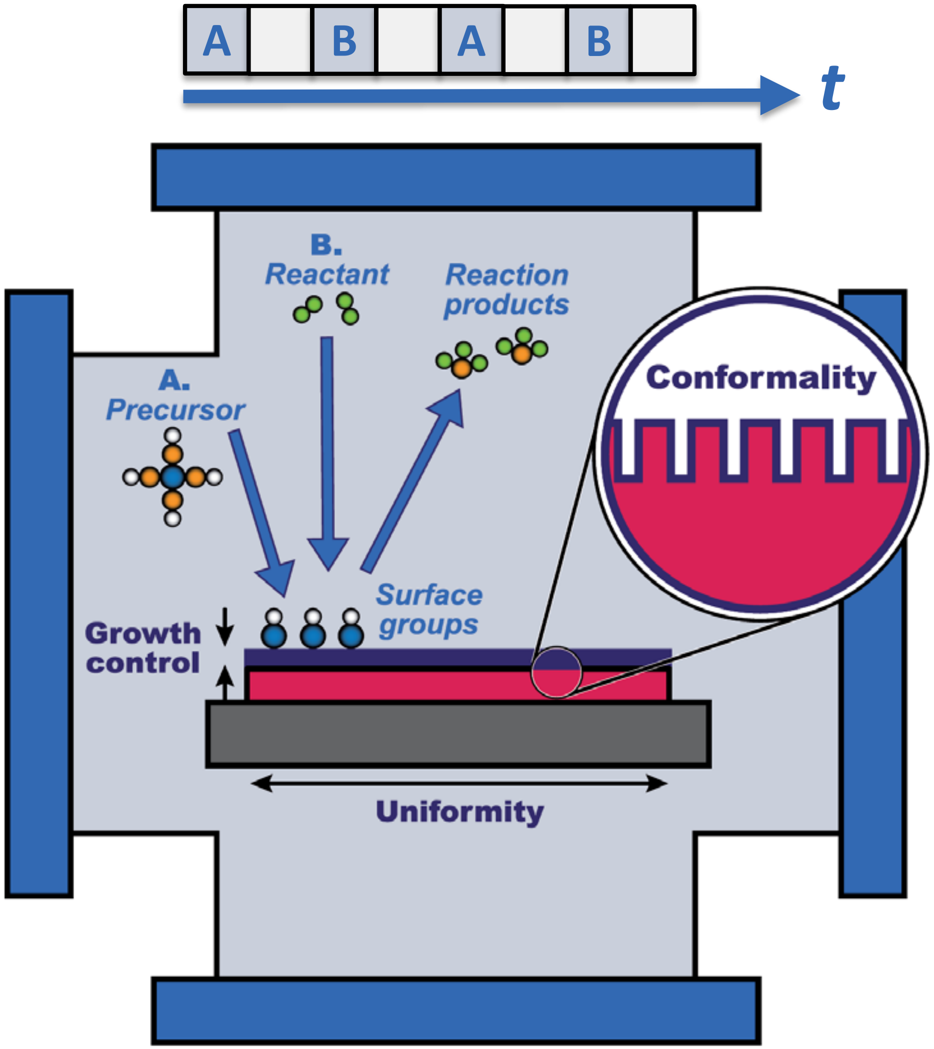
Do expect:

- Focus on what can be learned from the methods
- Their pros and cons articulated & practical comments
- An overview based mainly from own experience

AtomicLimits

For more information & feedback
see blog:
www.AtomicLimits.com

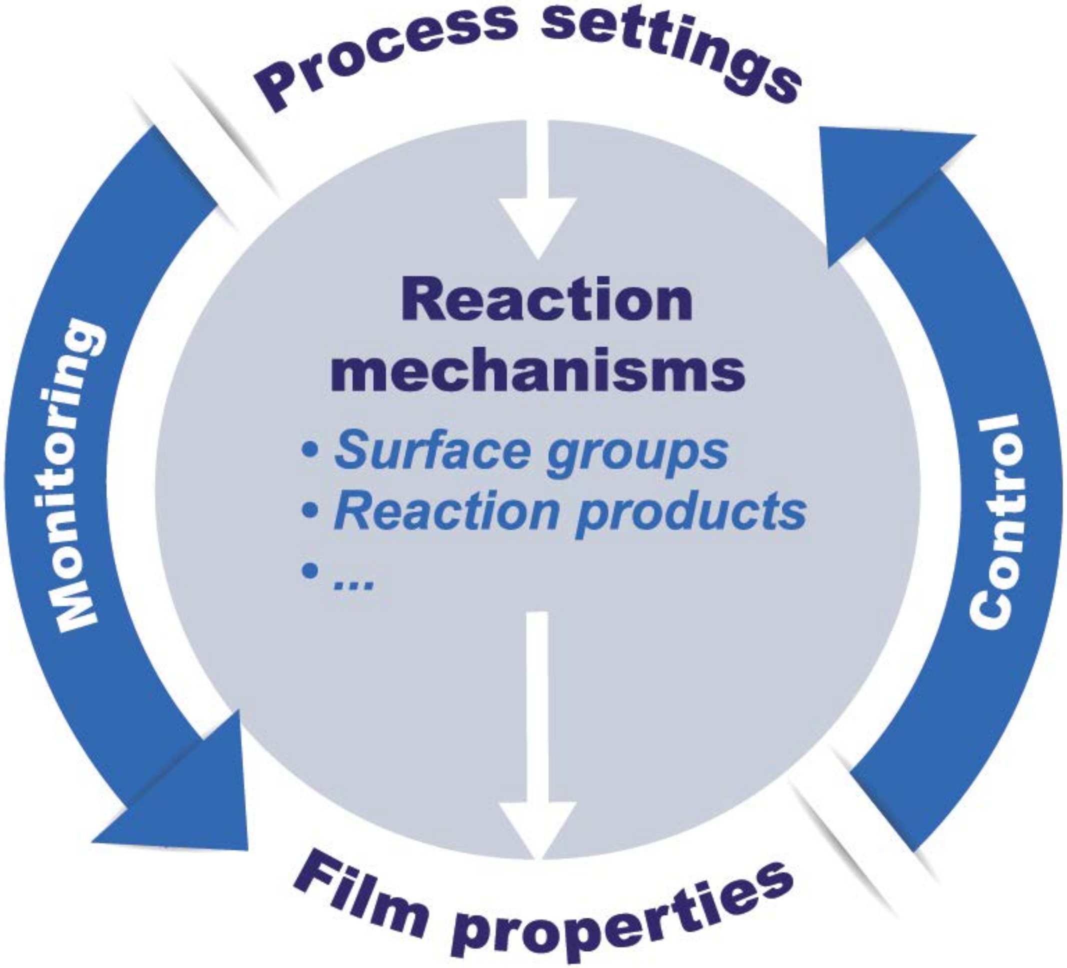
Atomic layer deposition (ALD)



In situ studies:

- Quartz crystal microbalance
- Spectroscopic ellipsometry
- Mass spectrometry
- Gas phase infrared spect.
- Surface infrared spect.
- Optical emission spect.
- X-ray photoelectron spect.
- X-ray diffraction
- Sum-frequency generation
- Adsorption calorimetry
- Scanning tunneling micros.
- …

In situ studies of ALD processes



Discussed **today**:

- **Quartz crystal microbalance**
- **Spectroscopic ellipsometry**
- **Mass spectrometry**
- **Gas phase infrared spect.**
- **Surface infrared spect.**
- **Optical emission spect.**

- X-ray photoelectron spect.
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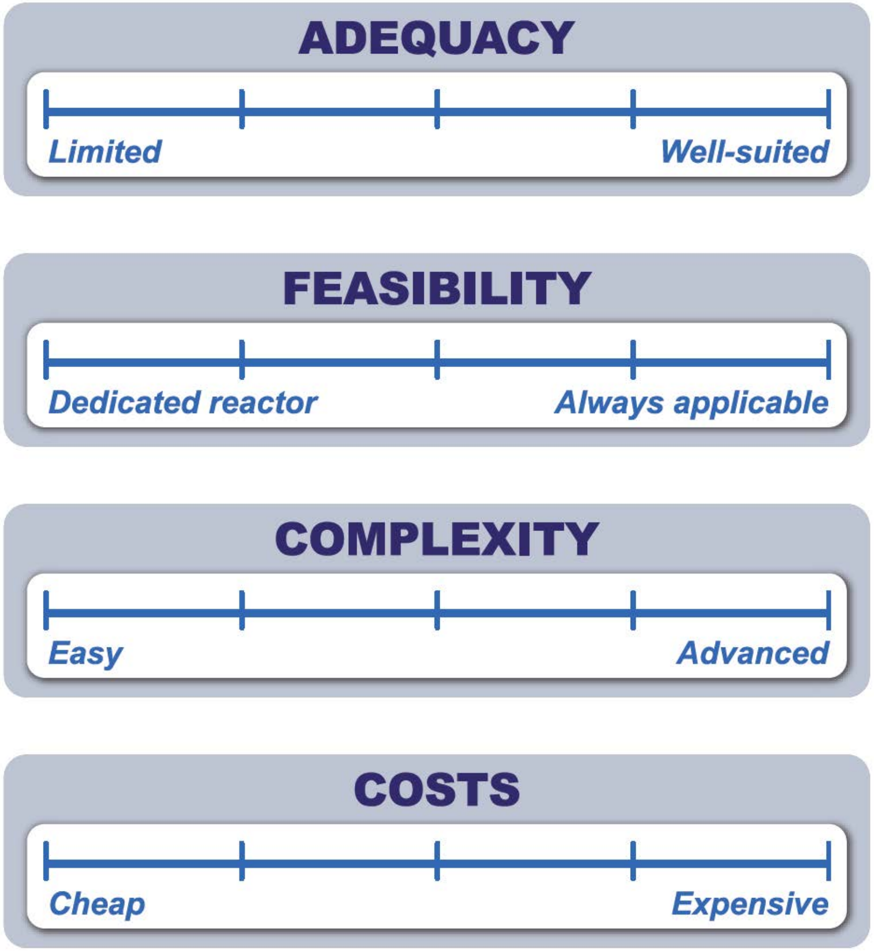
In situ studies of ALD processes



ADEQUACY

Limited — *Well-suited*

FEASIBILITY

Dedicated reactor — *Always applicable*

COMPLEXITY

Easy — *Advanced*

COSTS

Cheap — *Expensive*

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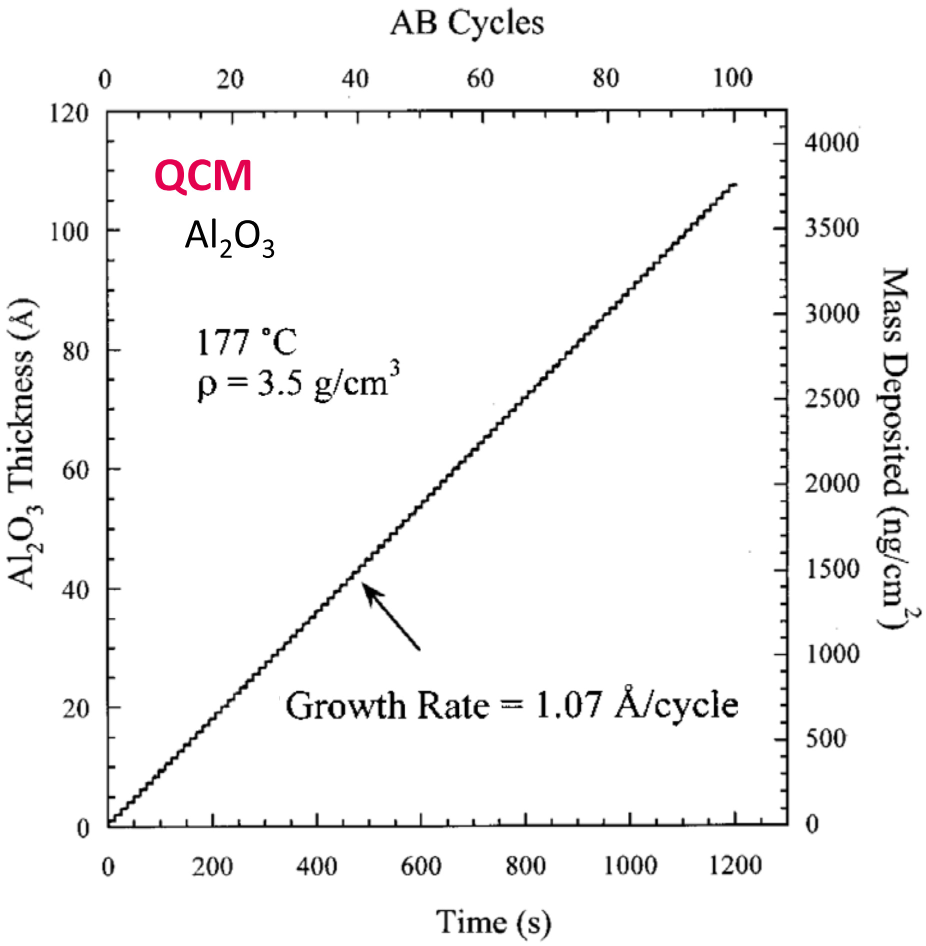
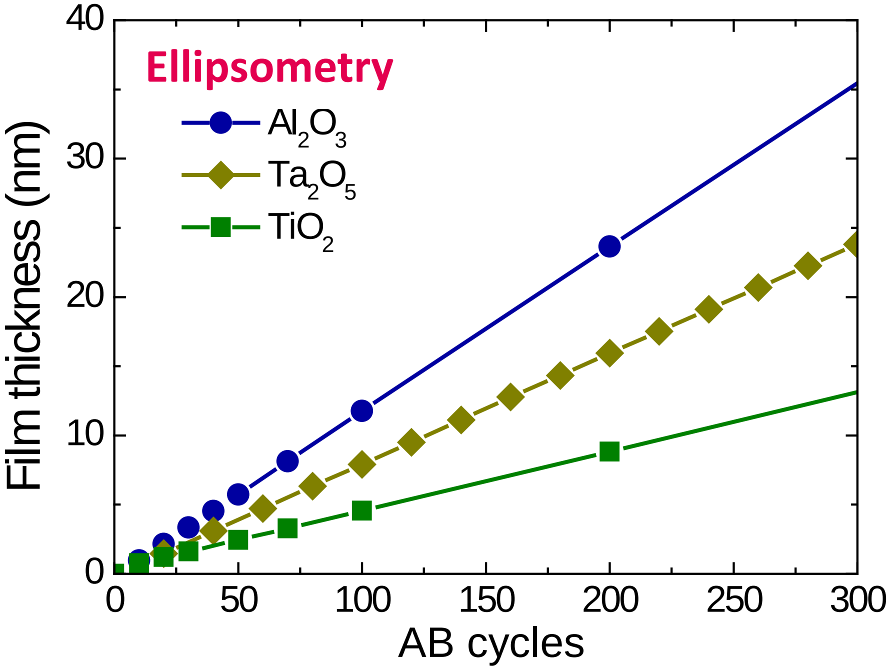
- …

Monitoring (linear) film growth



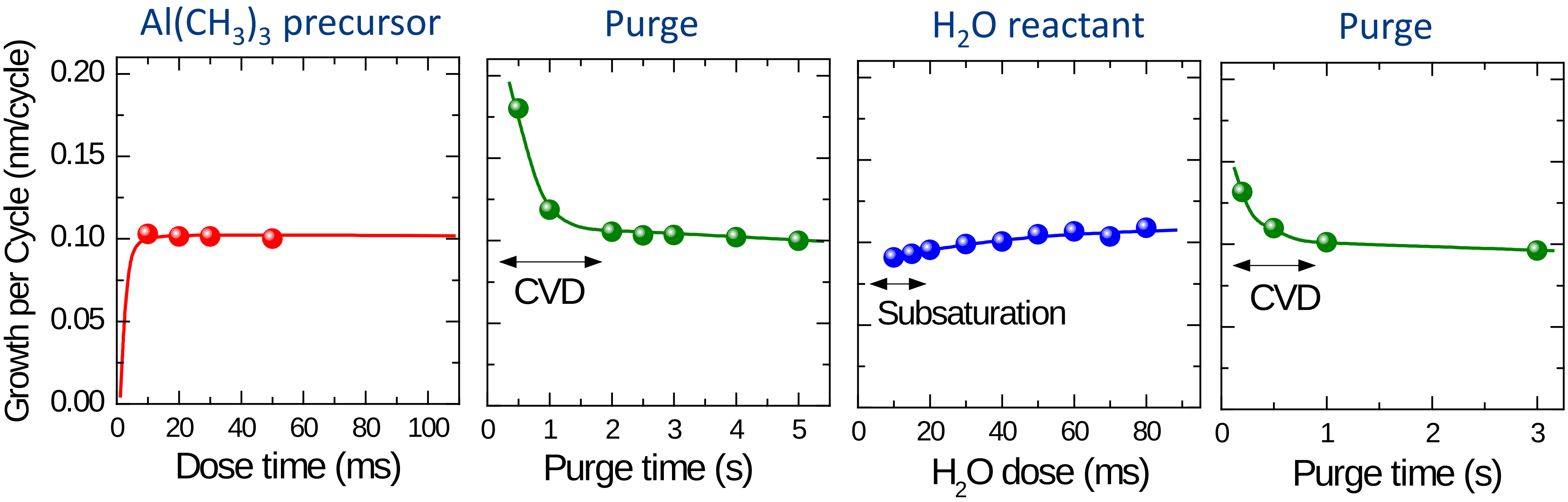


Material	Growth per cycle
Al_2O_3	1.2 Å (100 °C)
Ta_2O_5	0.80 Å (225 °C)
TiO_2	0.45 Å (200 °C)

Elam *et al.*, Rev. Sci. Instr. 73, 2981 (2002).
Langereis *et al.*, J. Phys. D: Appl. Phys. 42, 073001 (2009).

ALD saturation curves

ALD of **Al_2O_3** from $Al(CH_3)_3$ and H_2O (200 °C)


$Al(CH_3)_3$ precursor

Purge

H_2O reactant

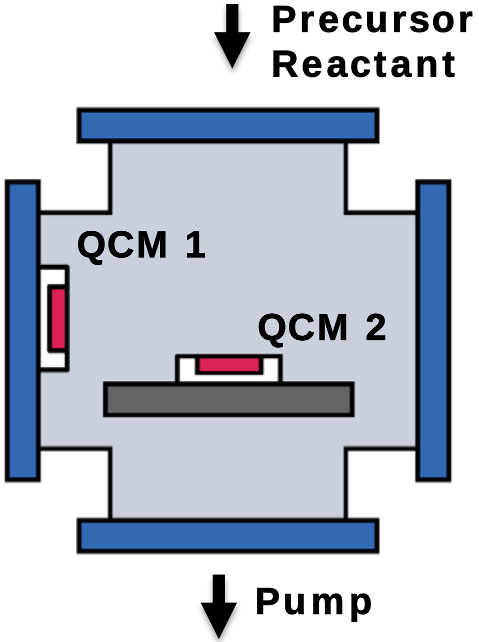
Purge

Vary one parameter while keeping other constant:

$Al(CH_3)_3$ – purge – H_2O – purge

20 ms – 2 s – 40 ms – 1 s

Quartz crystal microbalance (QCM)



QCM sensor = quartz crystal in resonator housing

Measures mass variation of a quartz crystal resonator from its frequency change

▲ • Cheap device and relatively easy-to-implement on many reactors

▲ • Directly measures mass gain/loss in quantitative way

▲ • Very helpful for process development

▼ • Very sensitive to variations in pressure, gas flows and temperature

Elam *et al.*, Rev. Sci. Instr. 73, 2981 (2002).
Rocklein and George, Anal. Chem. 75, 4975 (2003).

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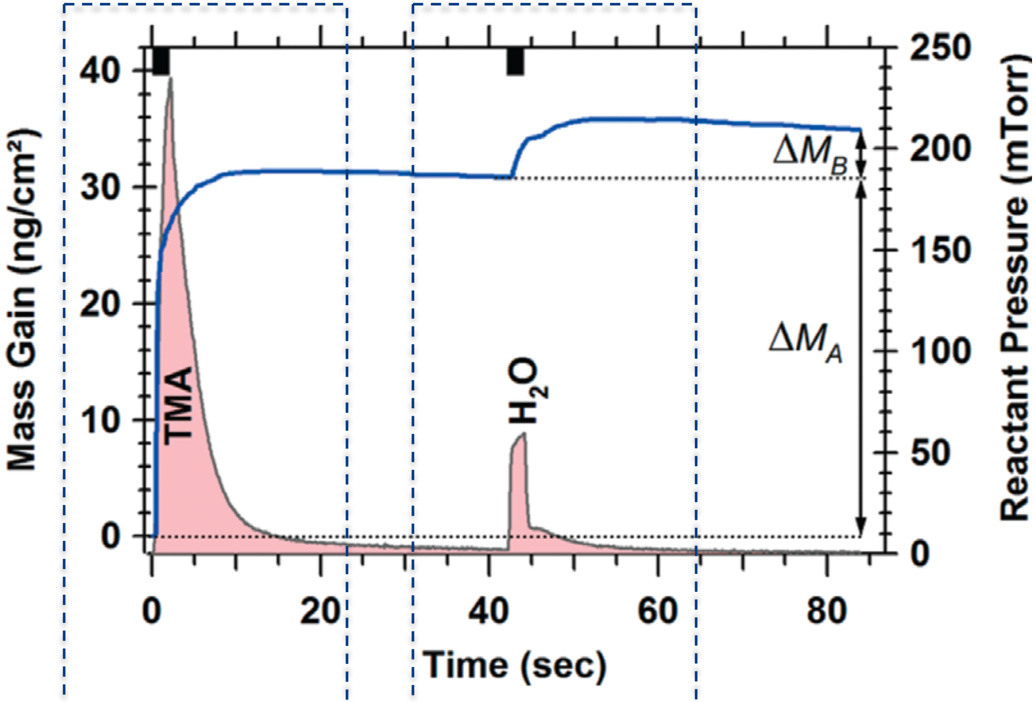
www.inficon.com

QCM – Monitoring mass gain (Al_2O_3)



s-O**H**

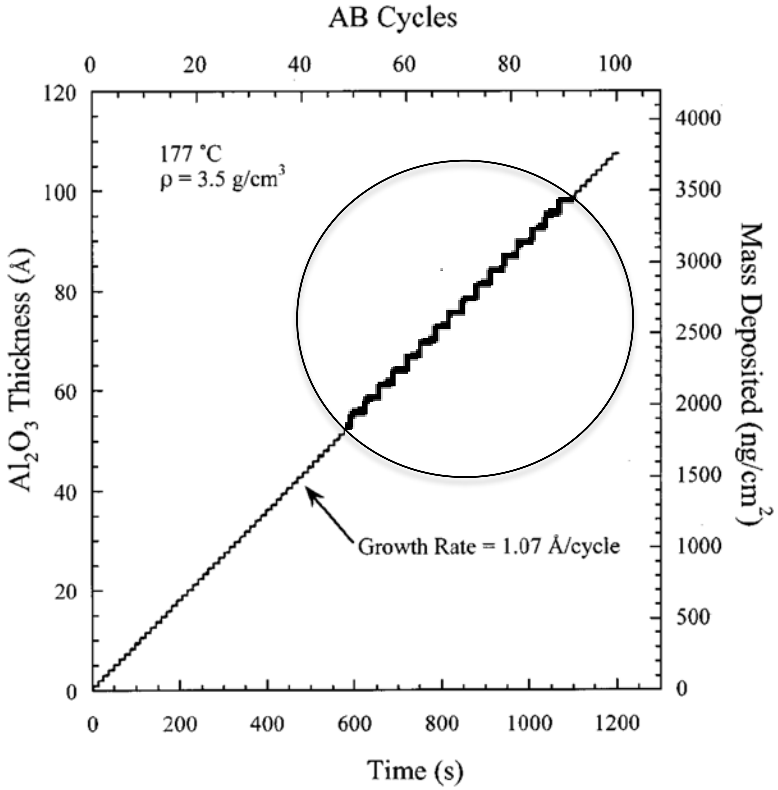
↓

s-O**Al$(CH_3)_x$**

s-Al**CH_3**

↓

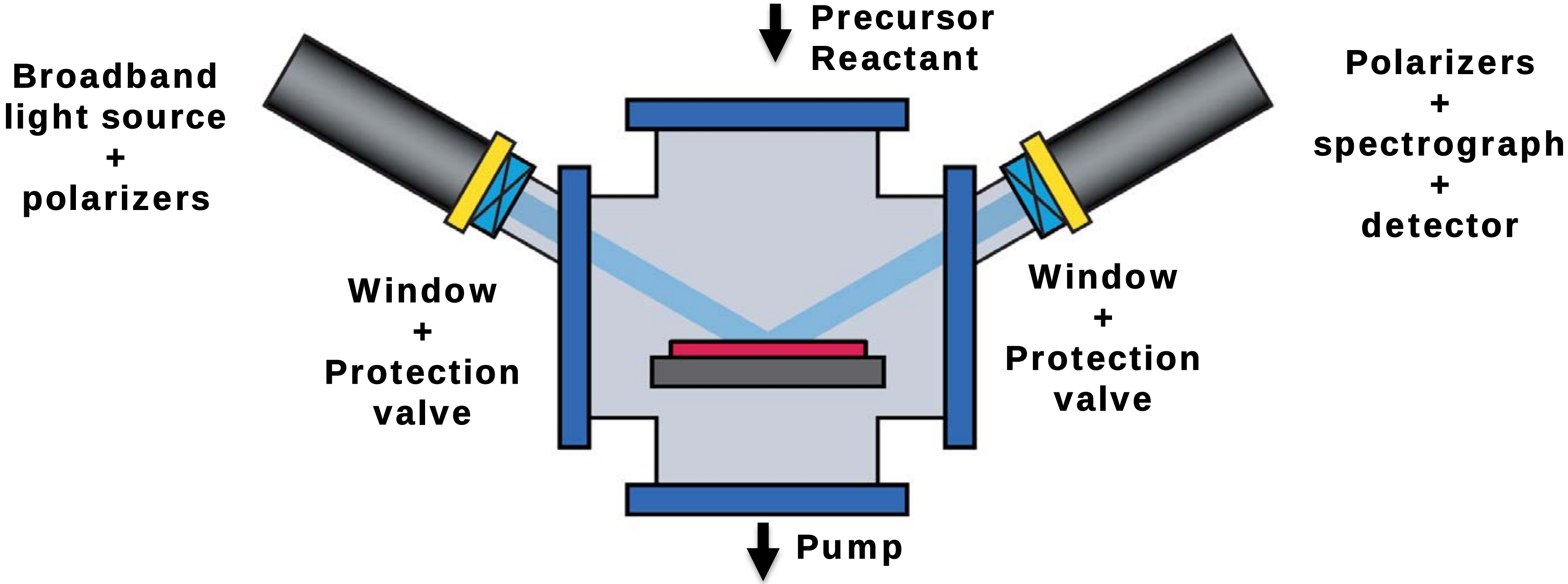
s-Al**OH**



Mass gain/loss can be monitored **per half-cycle**

Elam *et al.*, Rev. Sci. Instr. 73, 2981 (2002).
Wind *et al.*, J. Phys. Chem. A 114, 1281 (2010).

Spectroscopic ellipsometry (SE)



Measures change of polarization of light upon reflection (multiple wavelengths)

- ▲ Directly measures thickness, very helpful for (fast) process development
- ▲ Yields also insight into many other material properties (optical/electrical)
- ▼ Optical modelling can be challenging for some layers/materials
- ▼ Rather expensive and requires special ports for optical access

Langereis *et al.*, J. Phys. D: Appl. Phys. 42, 073001 (2009).
See blog post about ellipsometry & ALD at www.AtomicLimits.com

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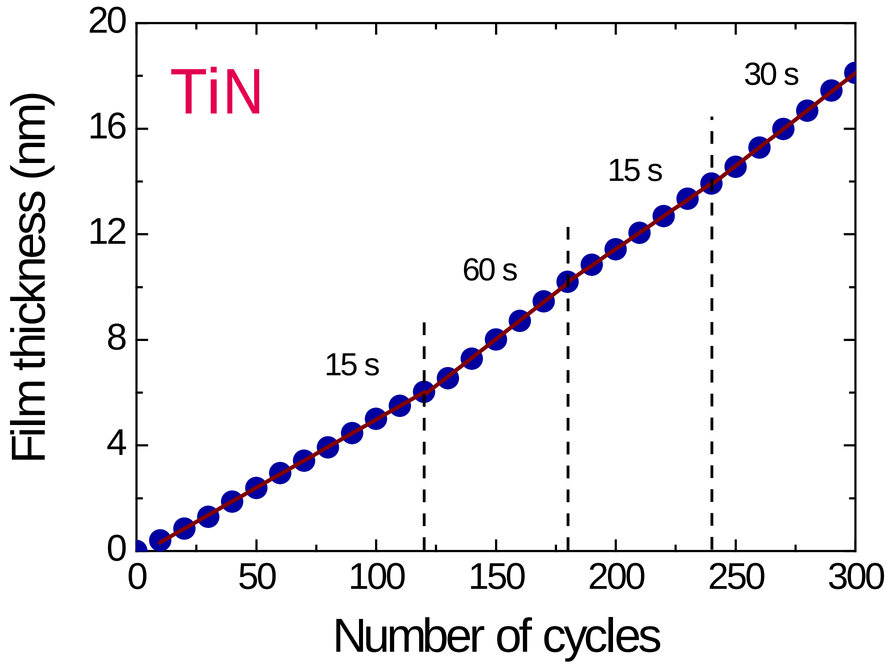
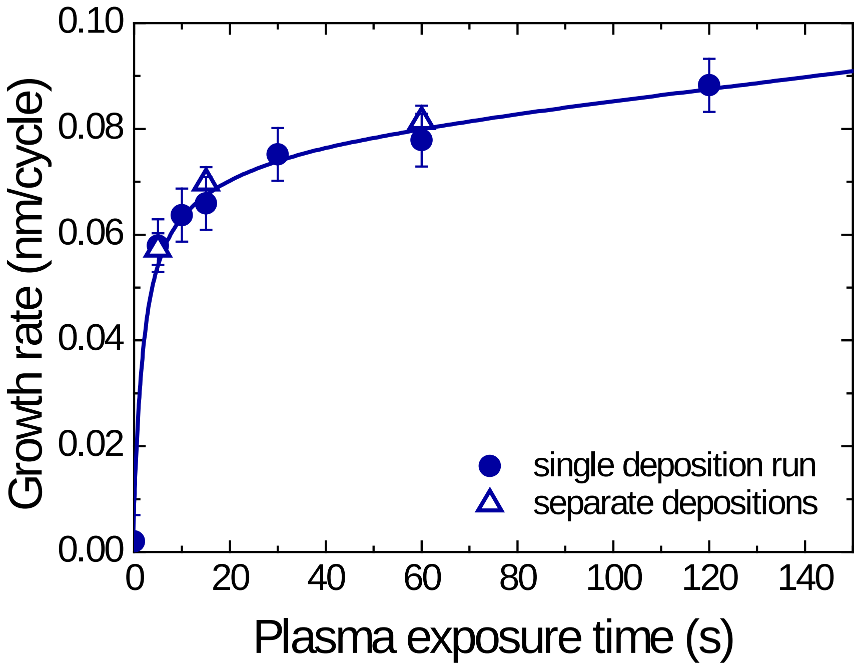
Spectroscopic ellipsometry – Saturation (TiN)



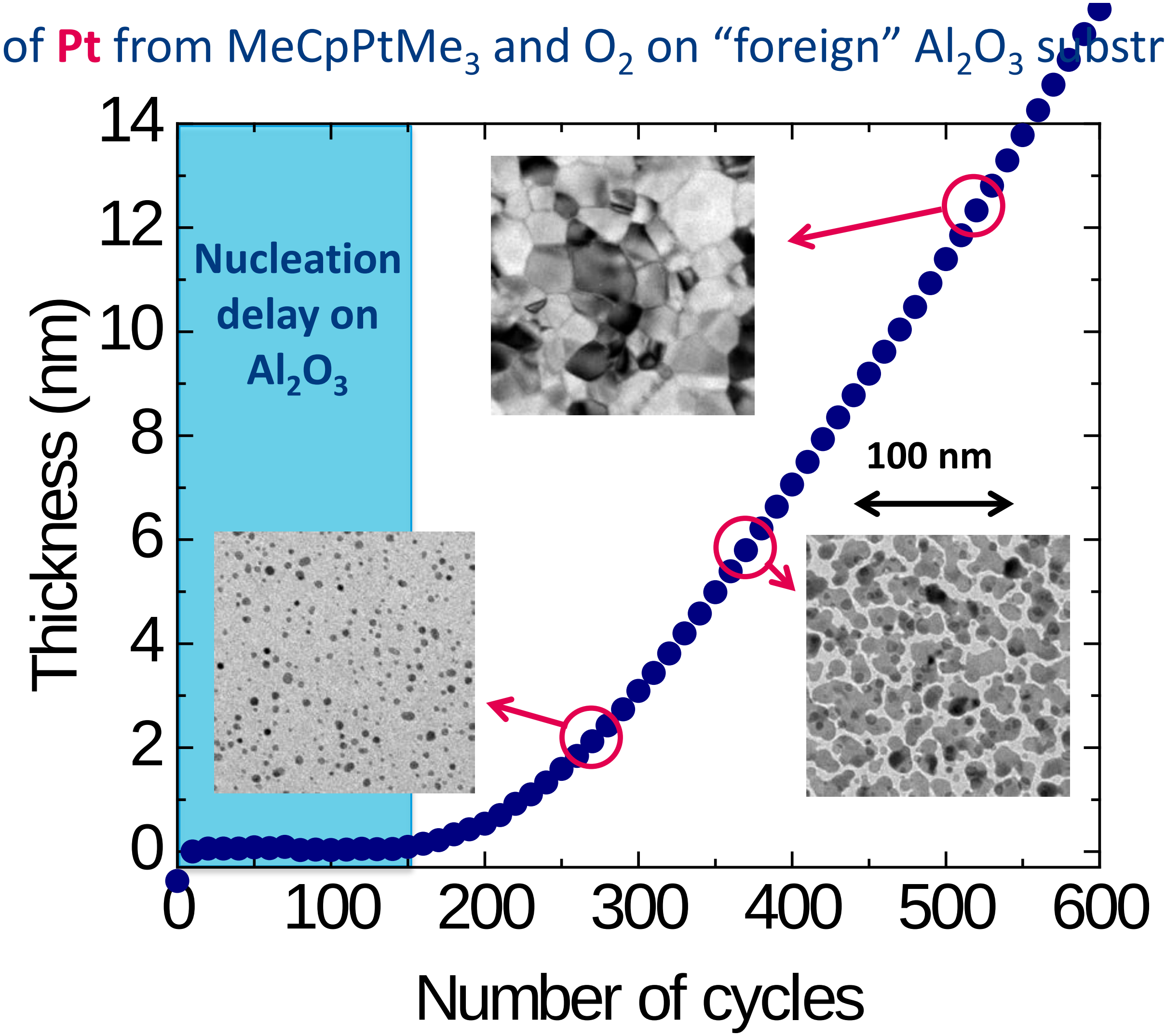


Monitor film thickness while changing precursor/reactant dosing time provides a **fast method to determine saturation curves**

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

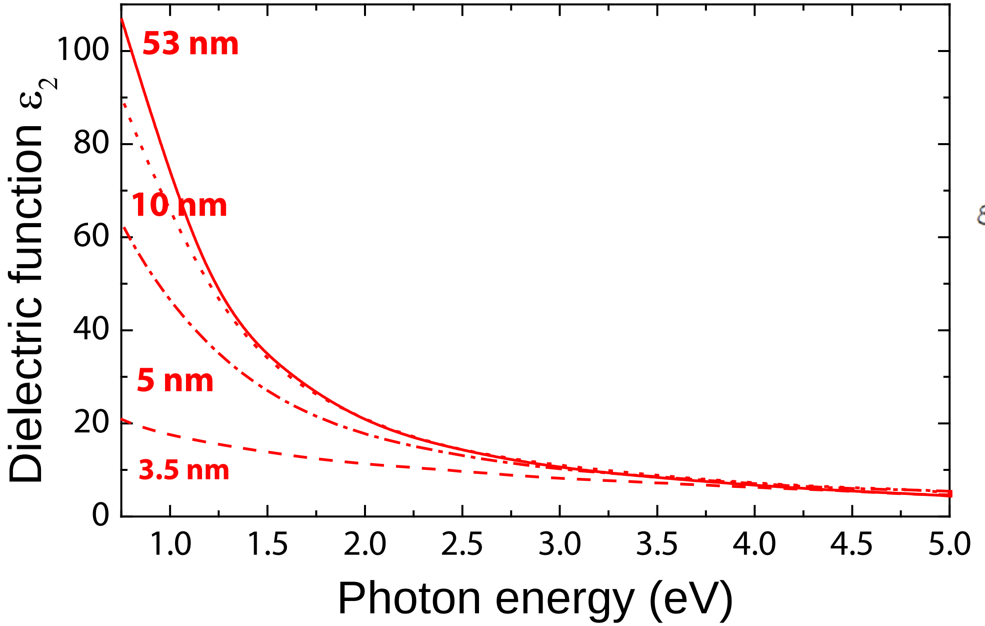
Spectroscopic ellipsometry – Nucleation (Pt)

ALD of **Pt** from $MeCpPtMe_3$ and O_2 on “foreign” Al_2O_3 substrate (300 ^{o}C)



Mackus *et al.*, Chem. Mater. 25, 1905 (2013).

Spectroscopic ellipsometry – Resistivity (Pt)



Imaginary part of dielectric function ε

$$\varepsilon_2(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 - i\omega/\tau_D} + \sum_{j=1}^{n} \frac{f_j \omega_p^2}{\omega_{0j}^2 - \omega^2 + i\gamma_j \omega}$$

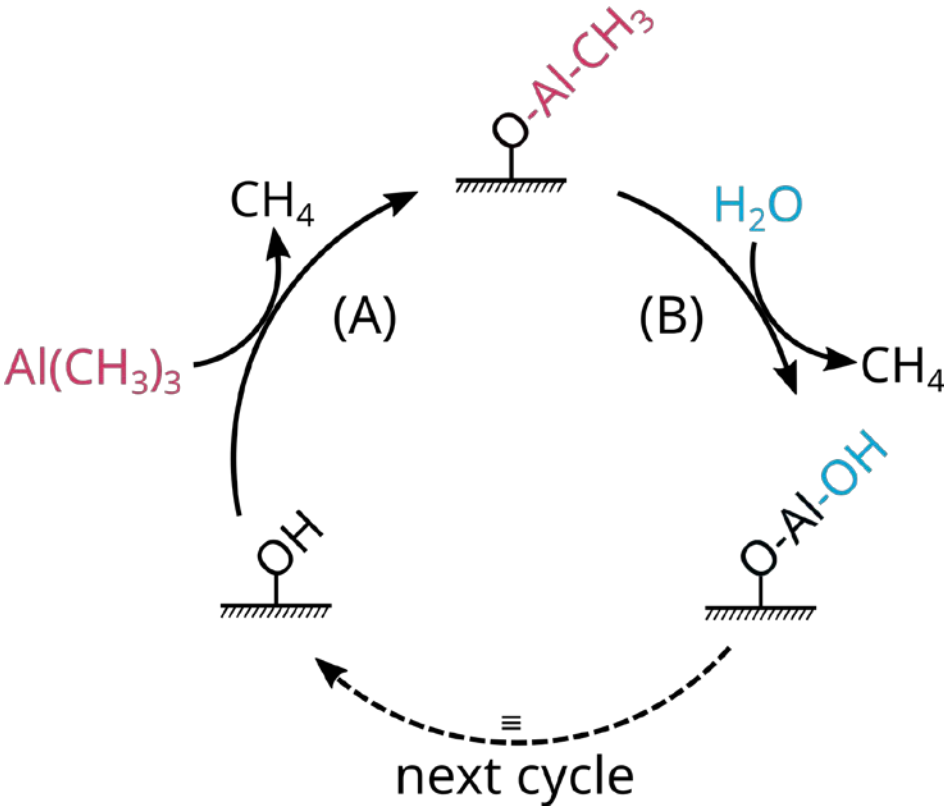
Drude
term
(resistivity)

Lorentz
terms

	Optical resistivity ($\mu\Omega$ cm)	FPP resistivity ($\mu\Omega$ cm)	Bulk resistivity ($\mu\Omega$ cm)
Pt (53 nm)	12.6	13.0 ± 0.2	10.4
Ru (90 nm)	32.8	18.0 ± 0.6	6.7
Pd (42 nm)	67.5	67 ± 1	10.5

Leick *et al.*, J. Phys. D 49, 115504 (2016).

ALD of Al_2O_3 [Case study]



Prototypical ALD process

Precursor:	$Al(CH_3)_3$
Reactant:	H_2O
Temperature:	25-400 °C

Simplified reaction scheme:

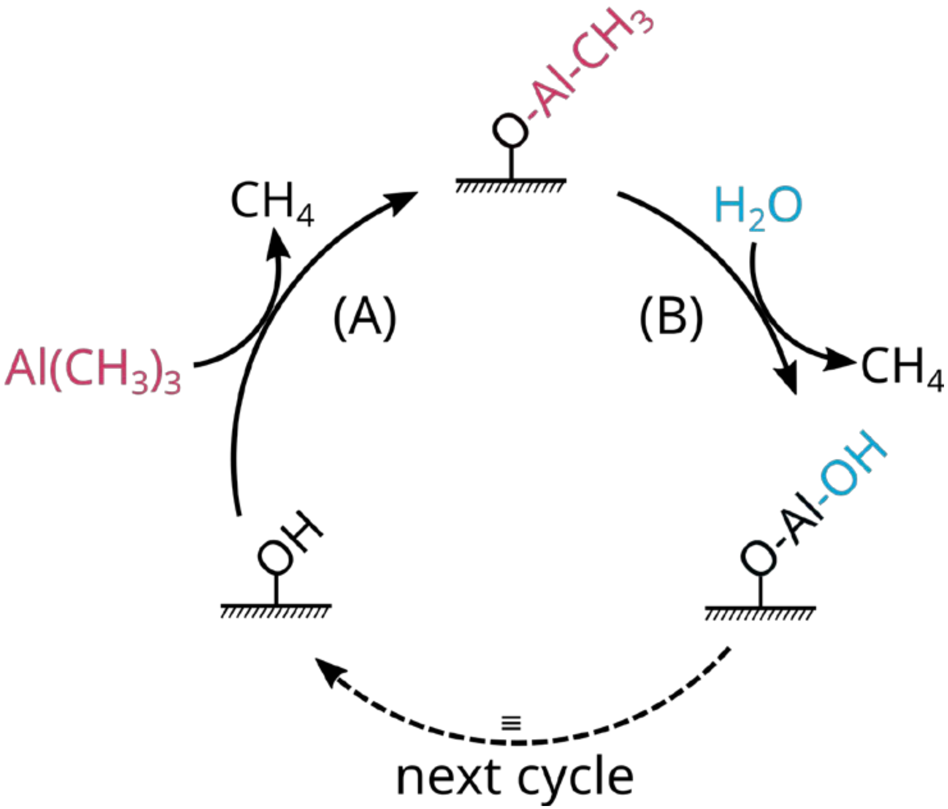
A - 1st Half Cycle

$$\text{s-OH}^* + Al(CH_3)_3 \longrightarrow \text{s-OAl}(CH_3)_2 + CH_4$$

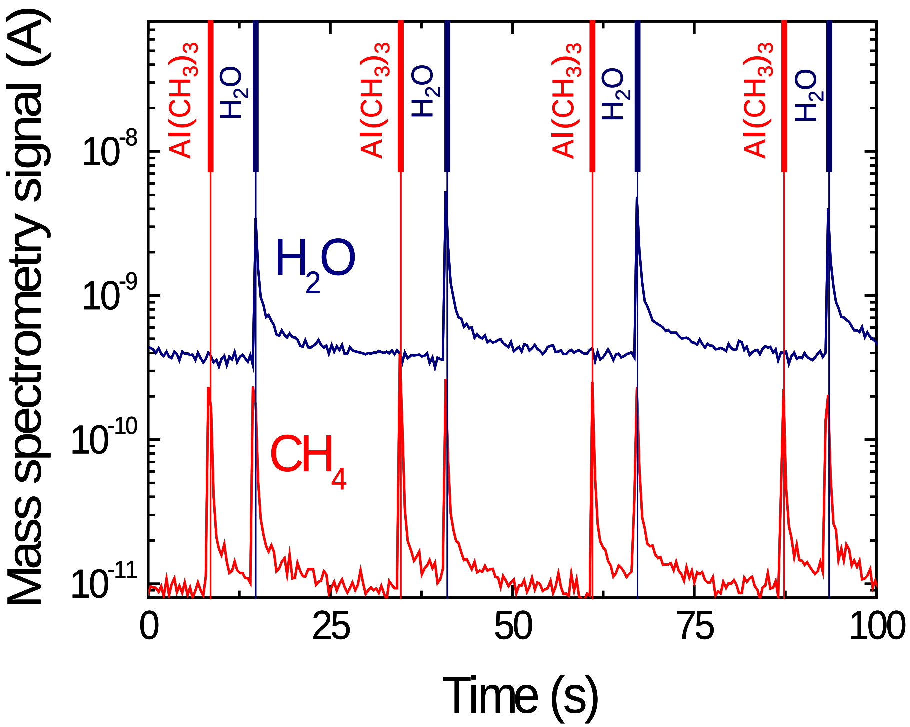
B - 2nd Half Cycle

$$\text{s-AlCH}_3^* + H_2O \longrightarrow \text{s-AlOH} + CH_4$$

Mass spectrometry — Reaction products (Al_2O_3)



Gas phase **reaction products**

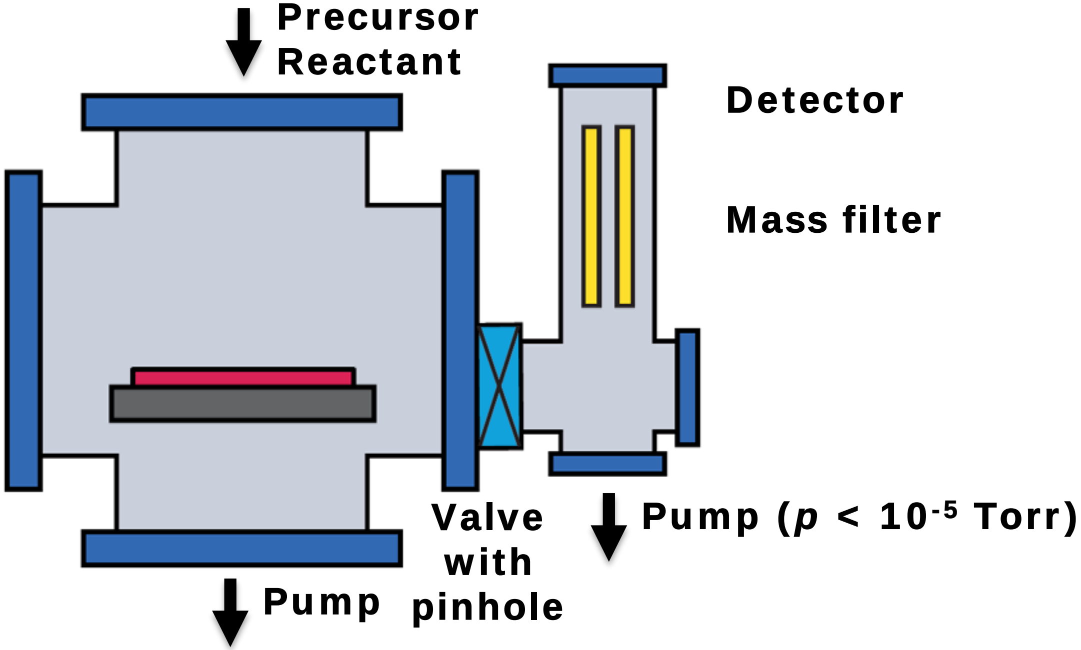


$Al(CH_3)_3$ dosing: **CH_4**

H_2O dosing: **CH_4**

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

Quadrupole mass spectrometry (QMS)



Ionization of gas extracted from the reactor & mass filtering of the ions

- ▲ Easy-to-implement on all types of reactors (with differential pumping)
- ▲ Wide range of species can be detected (but heavy masses difficult)
- ▲▼ All reaction products measured (not only from substrate)
- ▼ QMS cracks molecules into fragments complicating data interpretation

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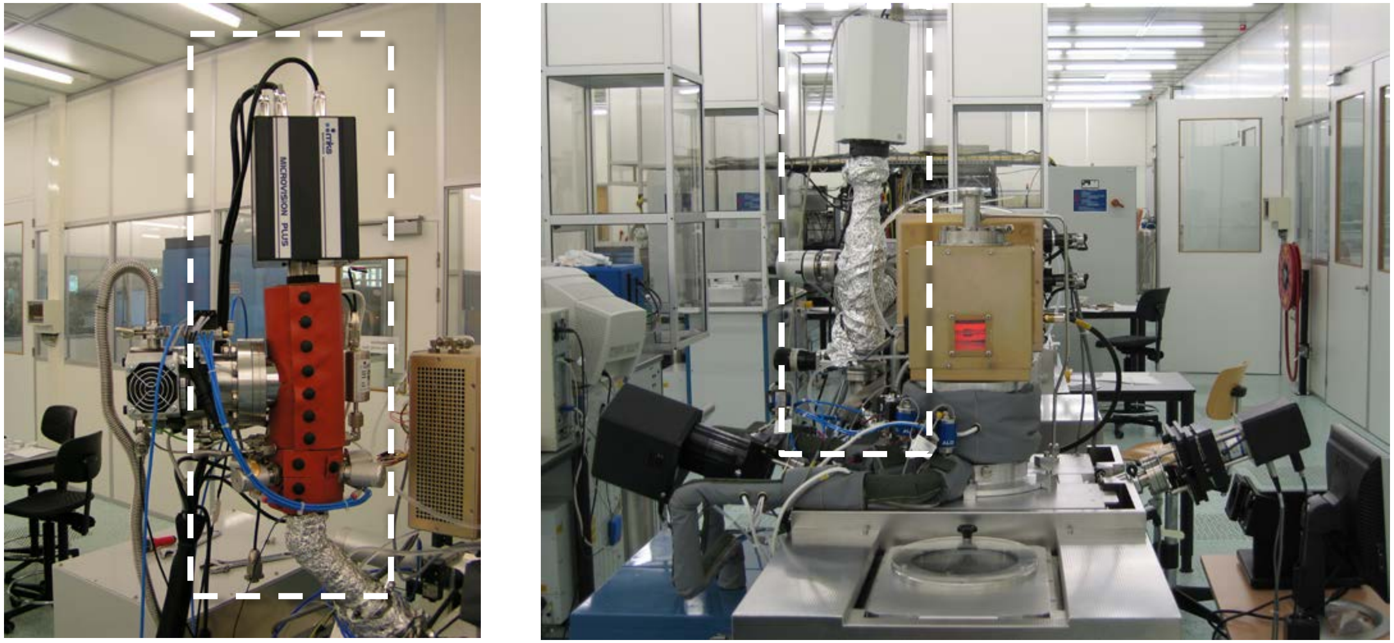

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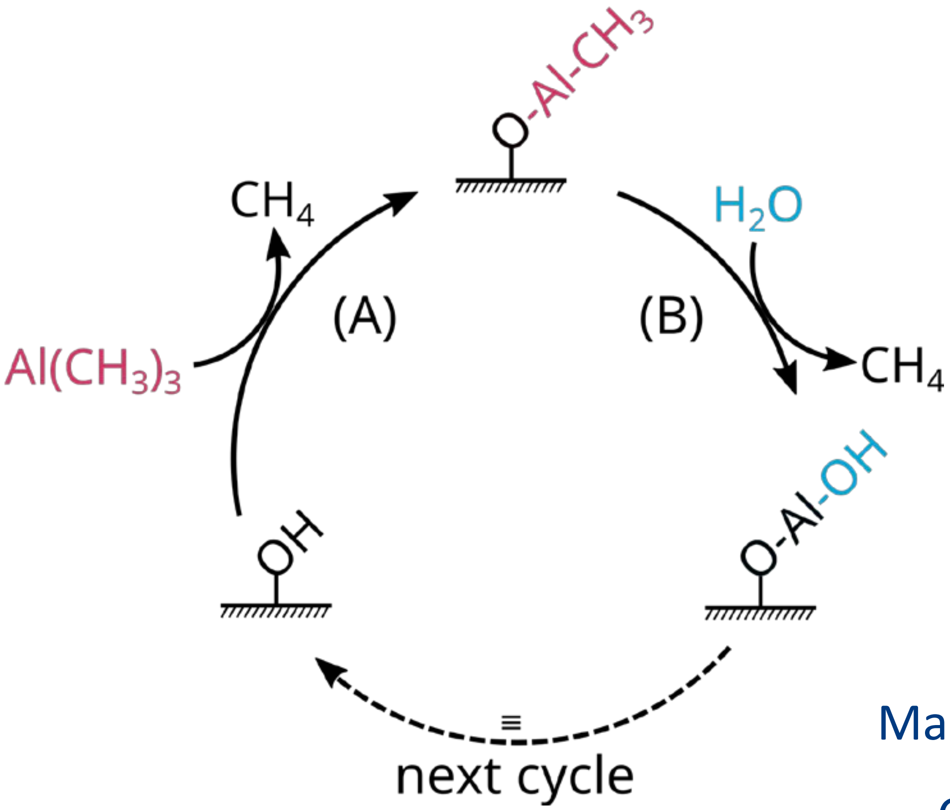
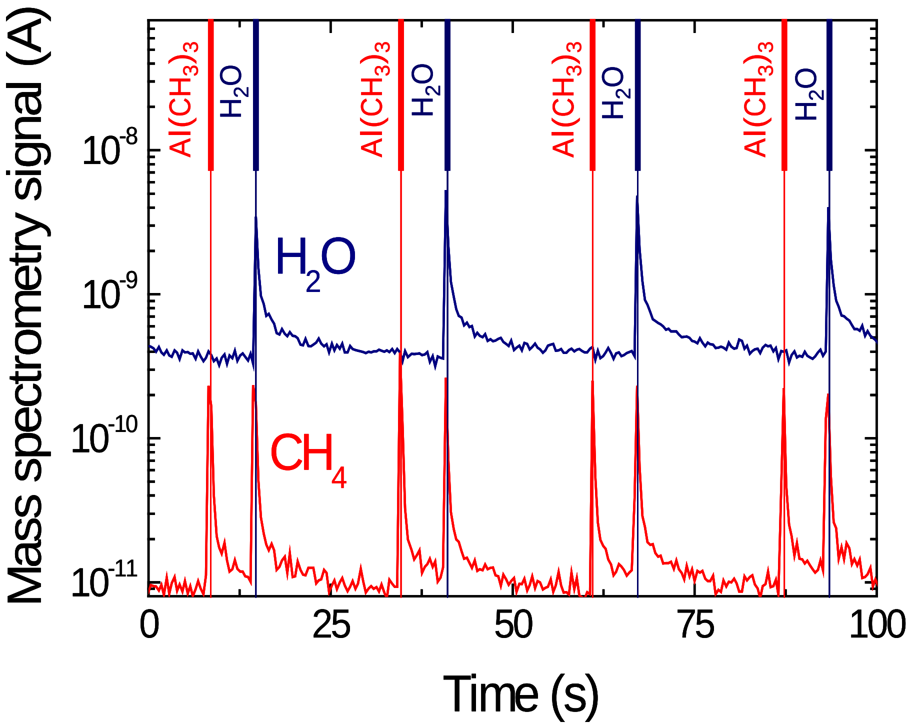




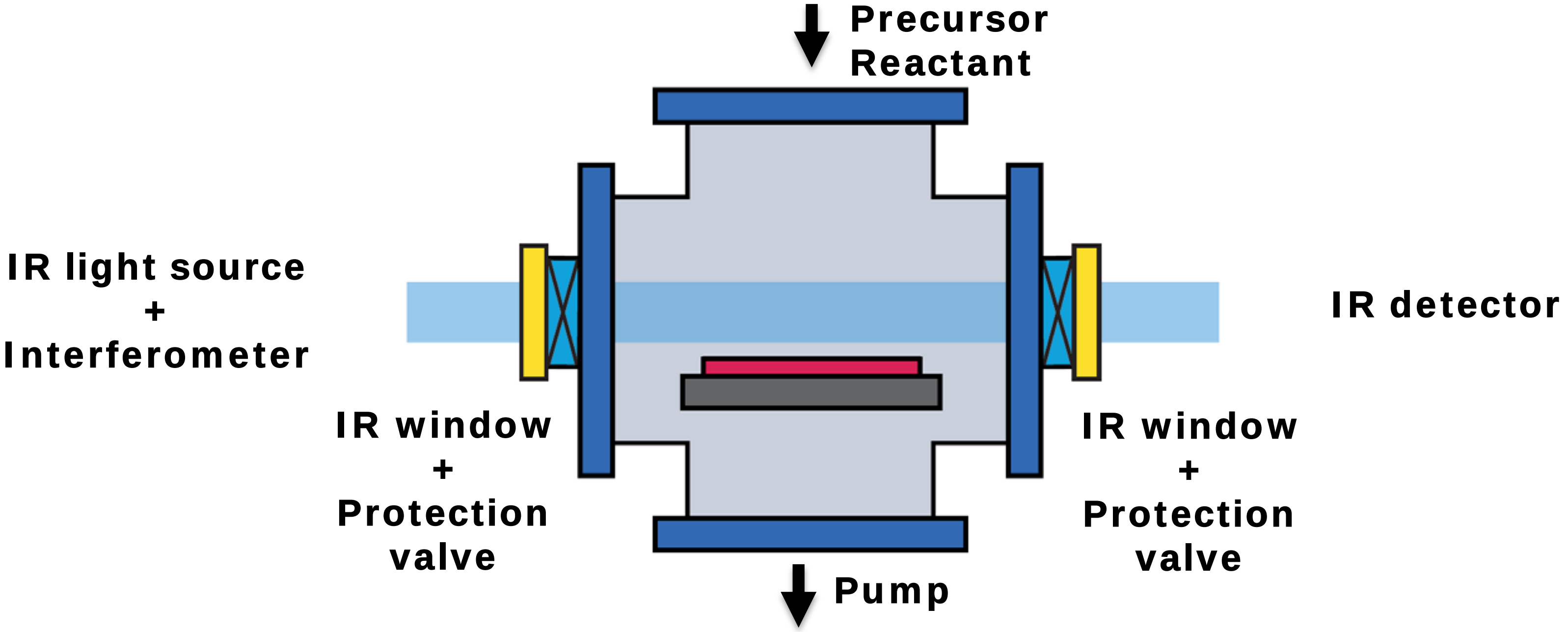
Mass spectrometry probes **mass/charge ratios**

CH_4 probed at **16 (CH_4^+)**; 15 (CH_3^+), etc.

H_2O probed at 18 (H_2O^+); 17 (OH^+); **16 (O^+)**

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

Gas-phase infrared spectroscopy (FTIR)



Precursor Reactant

IR light source + Interferometer

IR detector

IR window + Protection valve

IR window + Protection valve

Pump

Absorption of infrared light (from FTIR interferometer) by rovibrational transitions

- ▲ Calibration is quite straightforward to yield absolute densities
- ▲▼ High sensitivity for certain species but not all species can be detected
- ▲▼ All reaction products measured (not only from substrate)
- ▼ Confinement of reaction products might be necessary for sufficient S/N ratio

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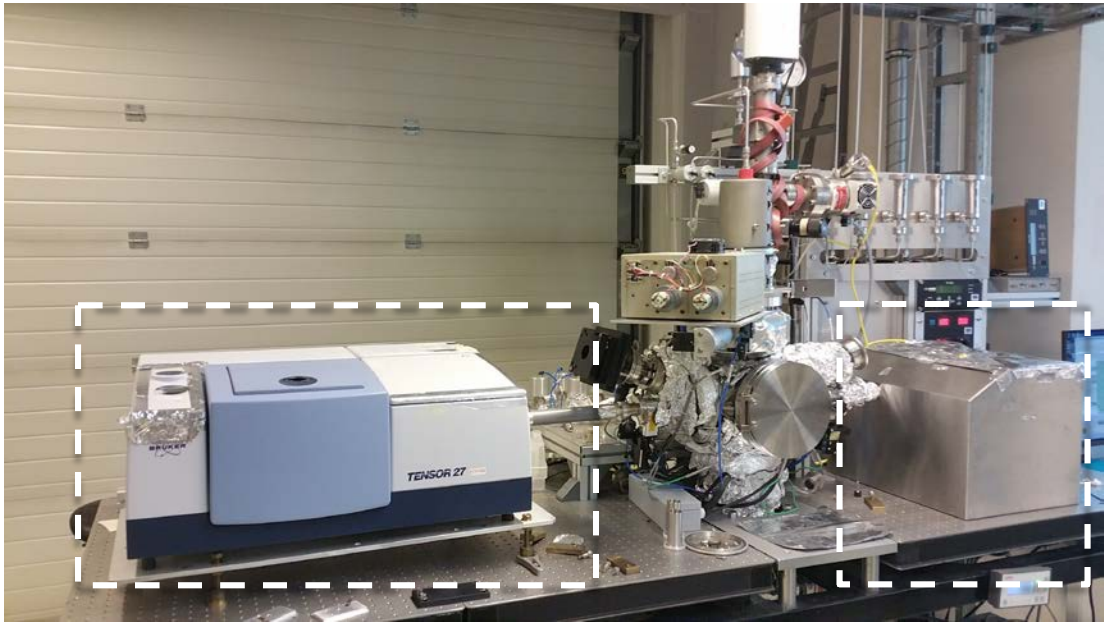

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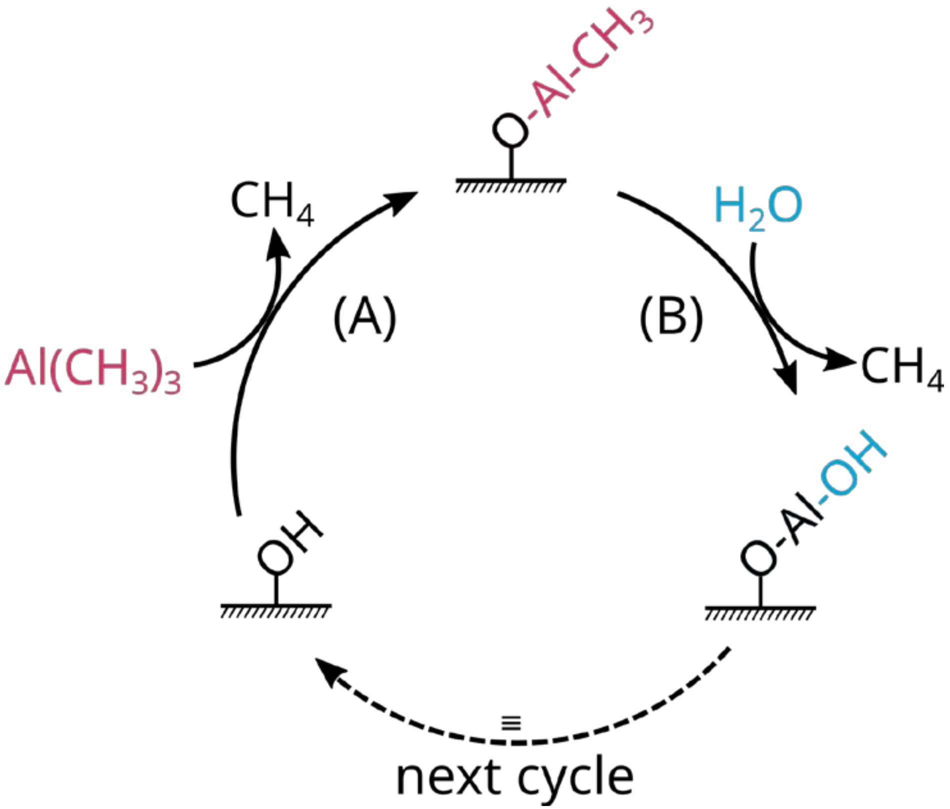
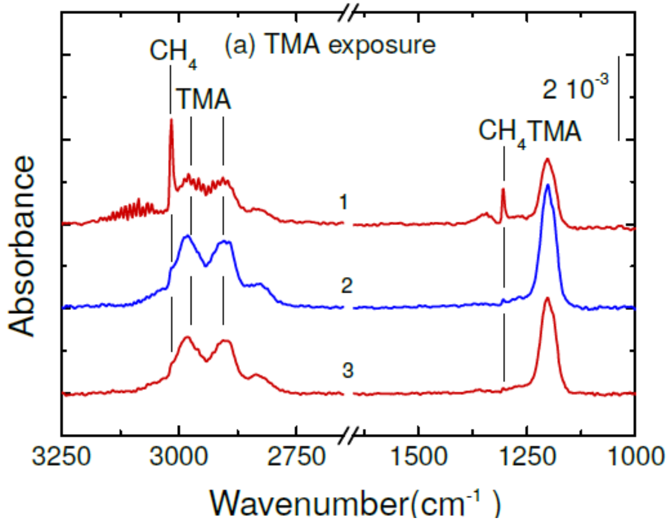
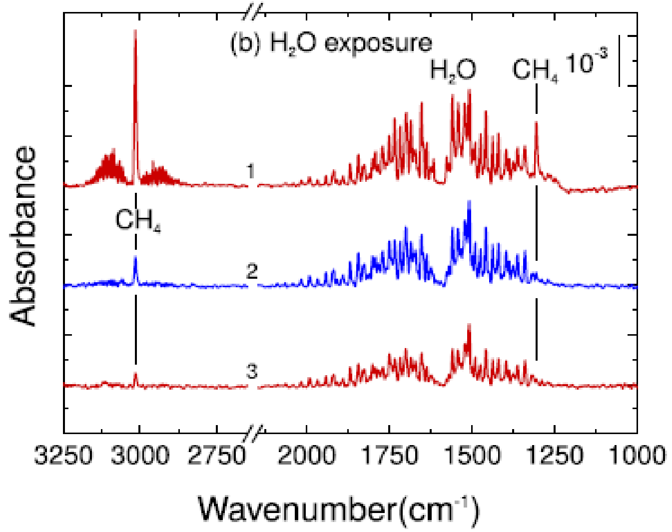
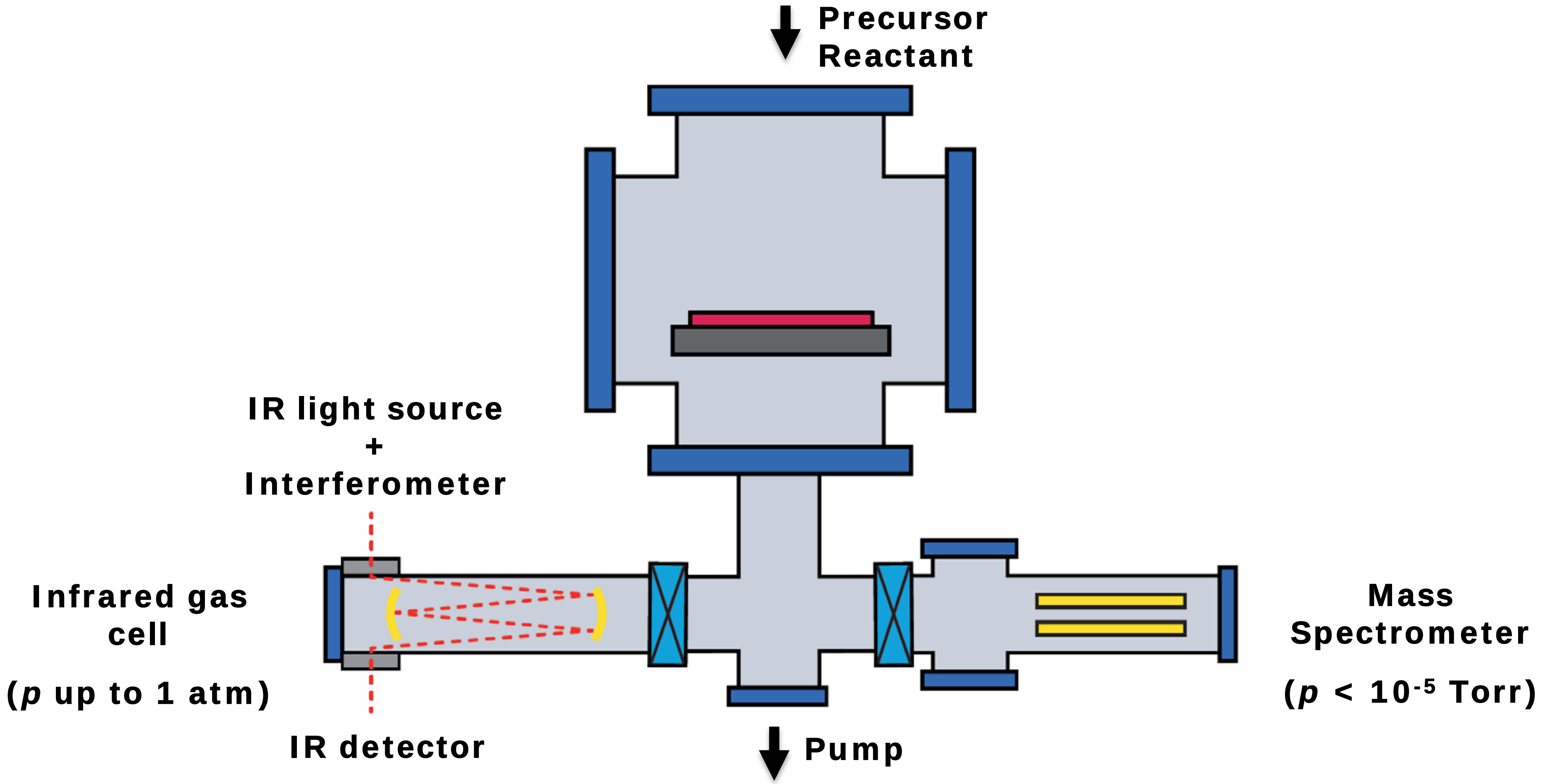






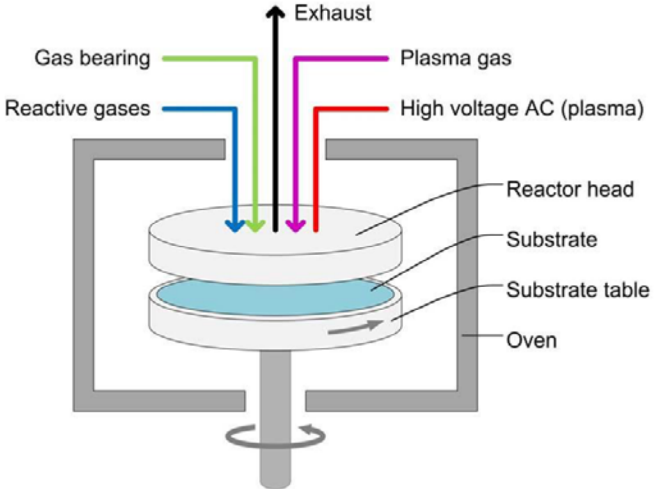
Vandalon and Kessels, J. Vac. Sci. Technol. A 35, 05C313 (2017).

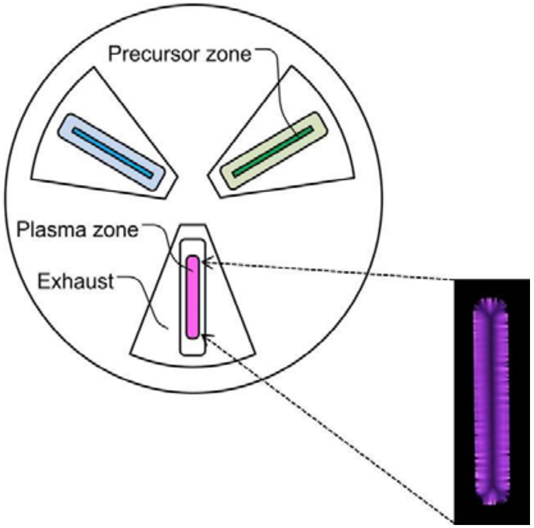
QMS and gas-phase FTIR installed in exhaust



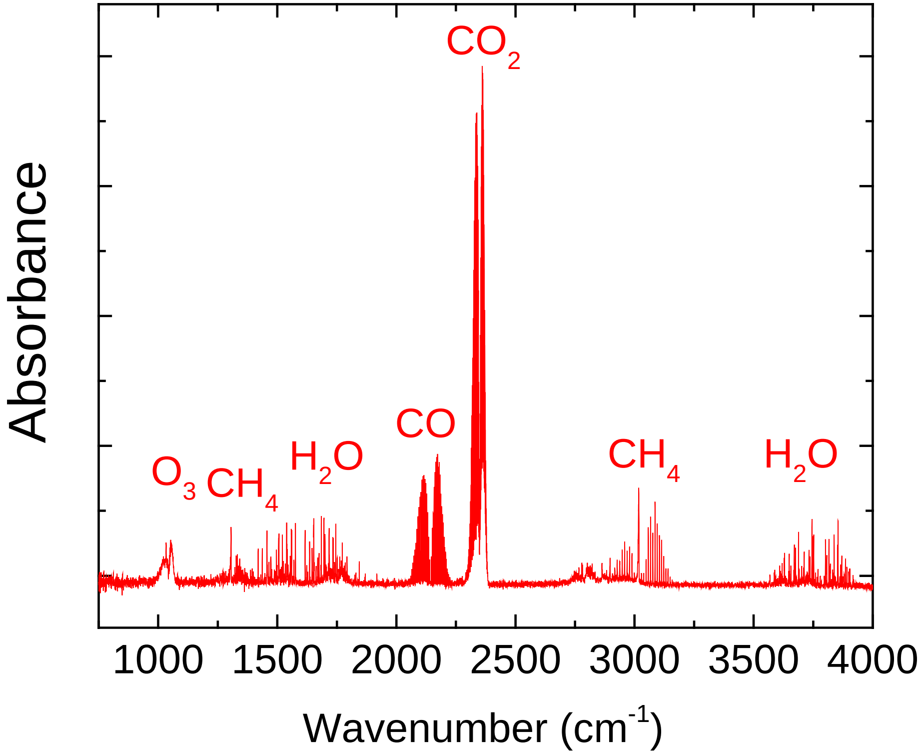
Can quite easily be implemented in **industrial** (**spatial**) ALD equipment

Gas-phase FTIR in exhaust of spatial ALD setup





Spectrum of O_2 plasma reactant step during plasma-assisted spatial ALD of Al_2O_3

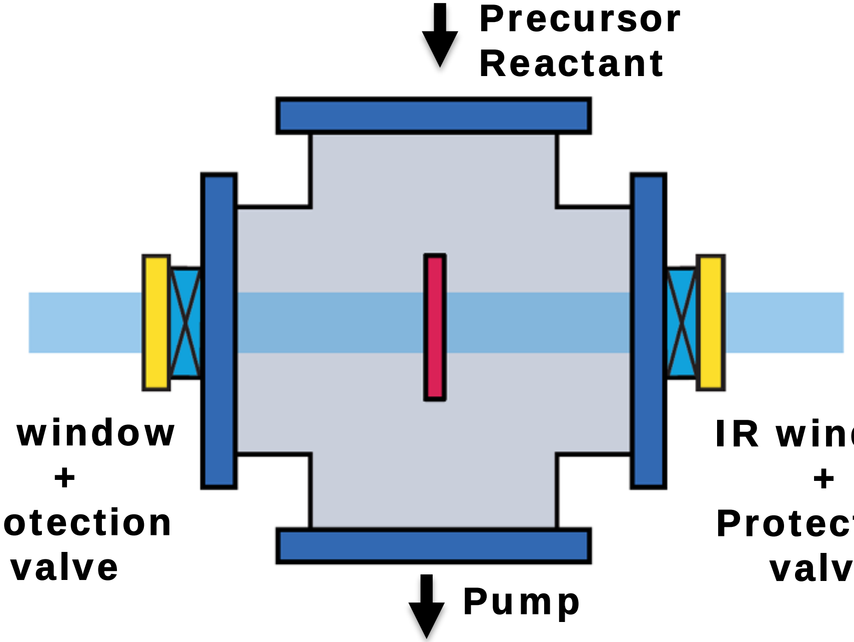


Reaction products:

O_3, combustion products and CH_4

Mione *et al.*, to be published (2018).

Surface infrared spectroscopy (FTIR)



Precursor
Reactant

IR light source
+
Interferometer

IR detector

IR window
+
Protection
valve

IR window
+
Protection
valve

Pump

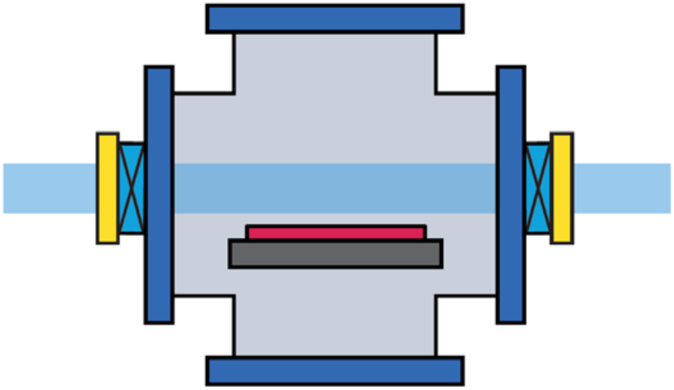
Absorption of infrared light by vibrational transitions by (surface) groups

- ▲ Direct measurement of surface groups created, removed or incorporated
- ▲▼ Probes only surface groups which are changing every (half-)cycle
- ▼ Poor S/N ratio for some species – long integration times required
- ▼ Requires dedicated reactor with optical access and IR-transparent substrate

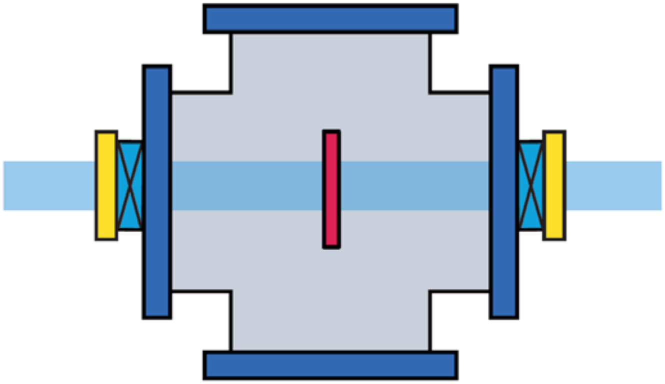
Chabal *et al.*, Surf. Sci. Rep. 8, 211 (1988).

Various configurations infrared spectroscopy

Gas phase species

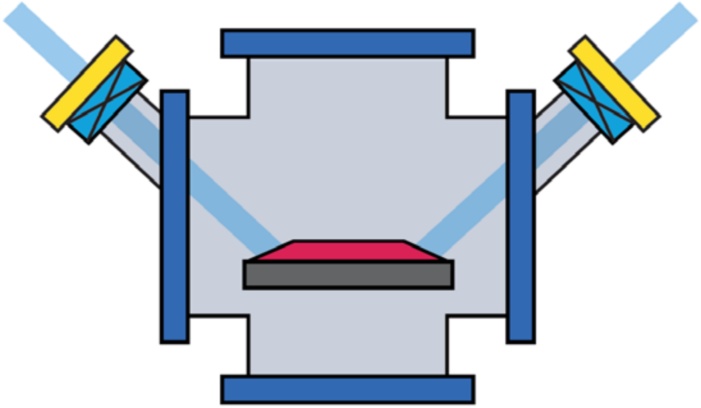


Surface species - wafer



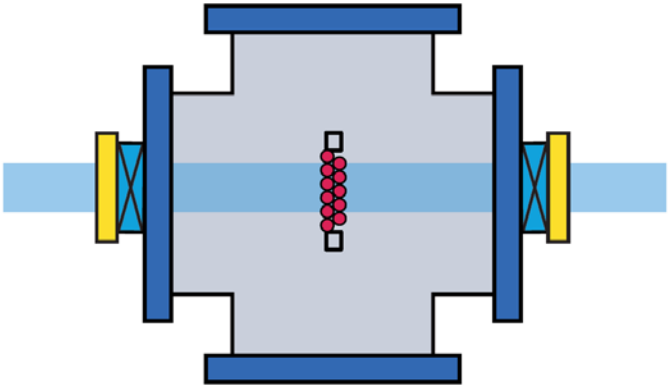
Surface species – ATR element

(multiple reflections at surface)



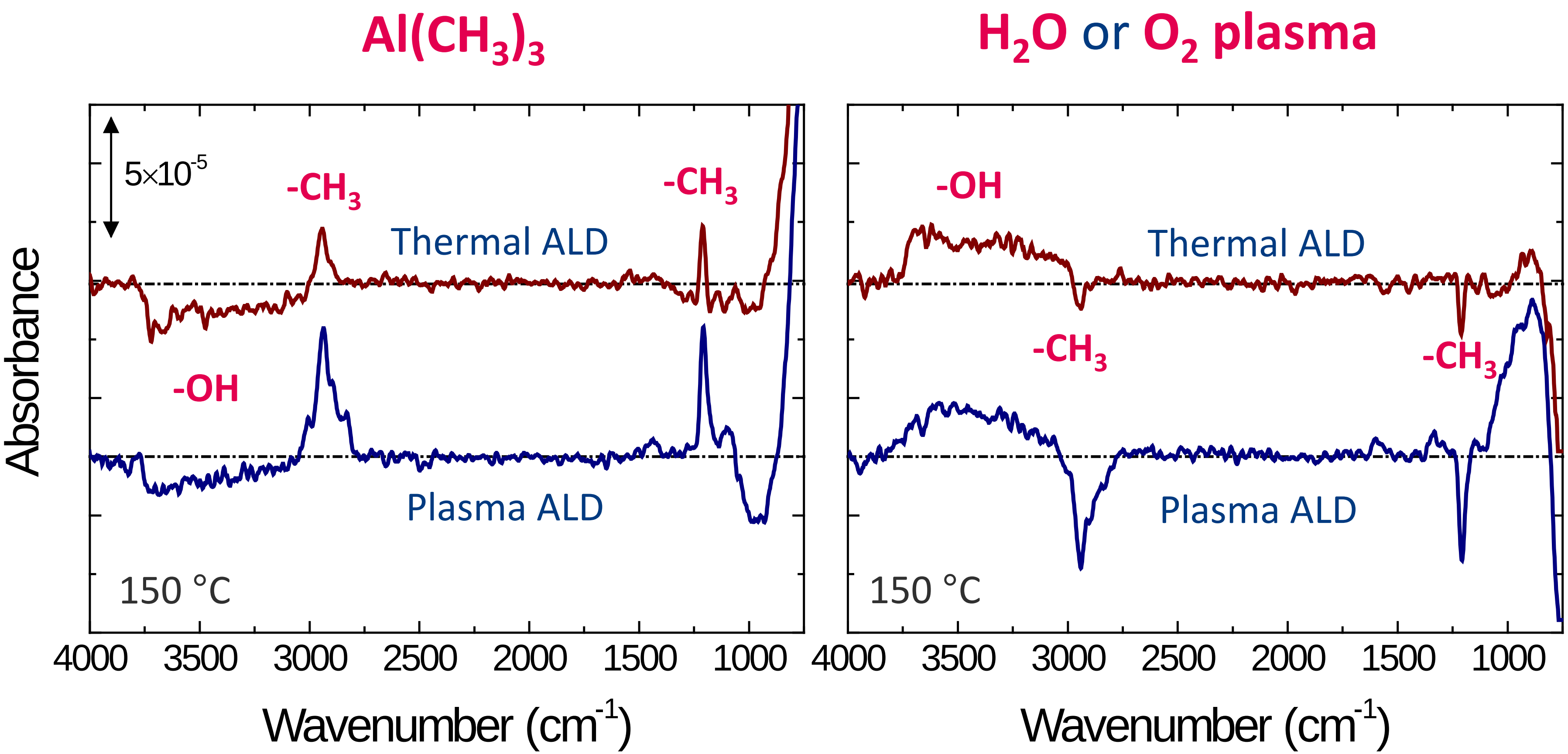
Surface species – particles

(enlarged surface area by particles)



Chabal *et al.*, Surf. Sci. Rep. 8, 211 (1988).

Surface FTIR – Surface groups (Al_2O_3)

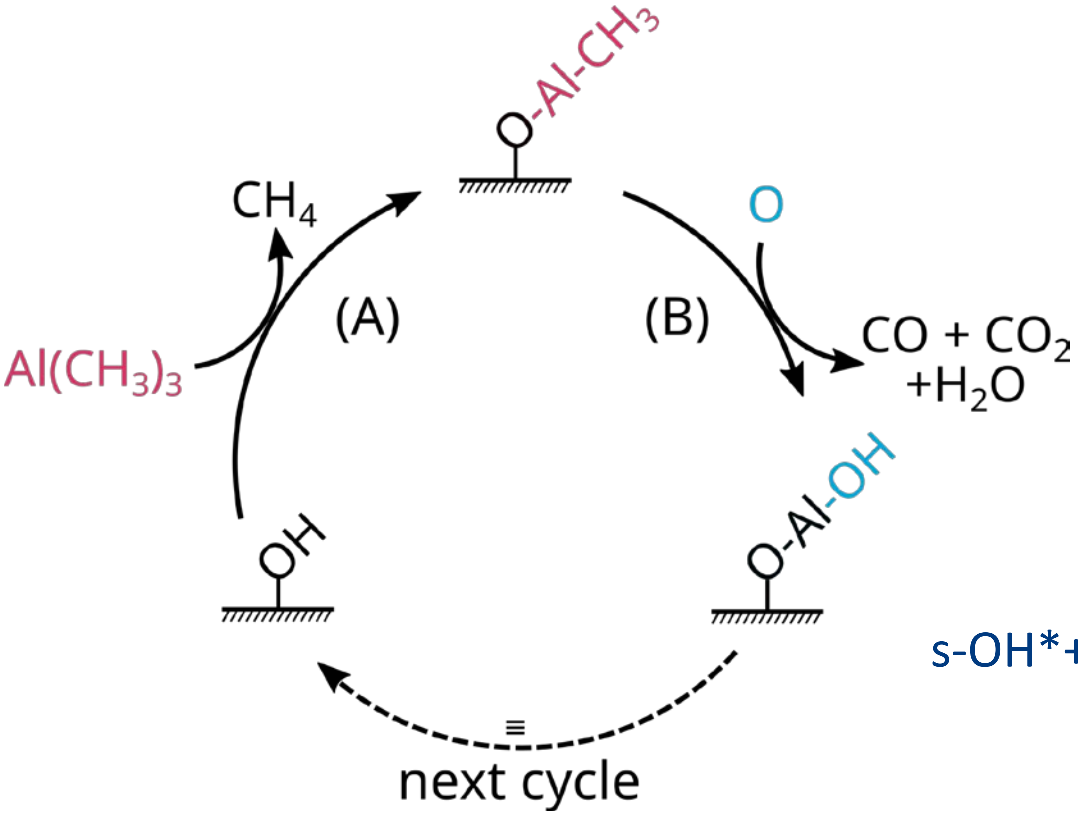


Differential spectra: show changes per half cycle

-CH_3 and **-OH** are surface groups for both thermal and plasma ALD

Langereis *et al.*, ECS Transactions 16, 247 (2008).

Plasma-enhanced ALD of Al_2O_3 [Case study]



Precursor:	$Al(CH_3)_3$
Reactant:	O_2 plasma
Temperature:	25-400 °C

Simplified reaction scheme:

A - 1st Half Cycle

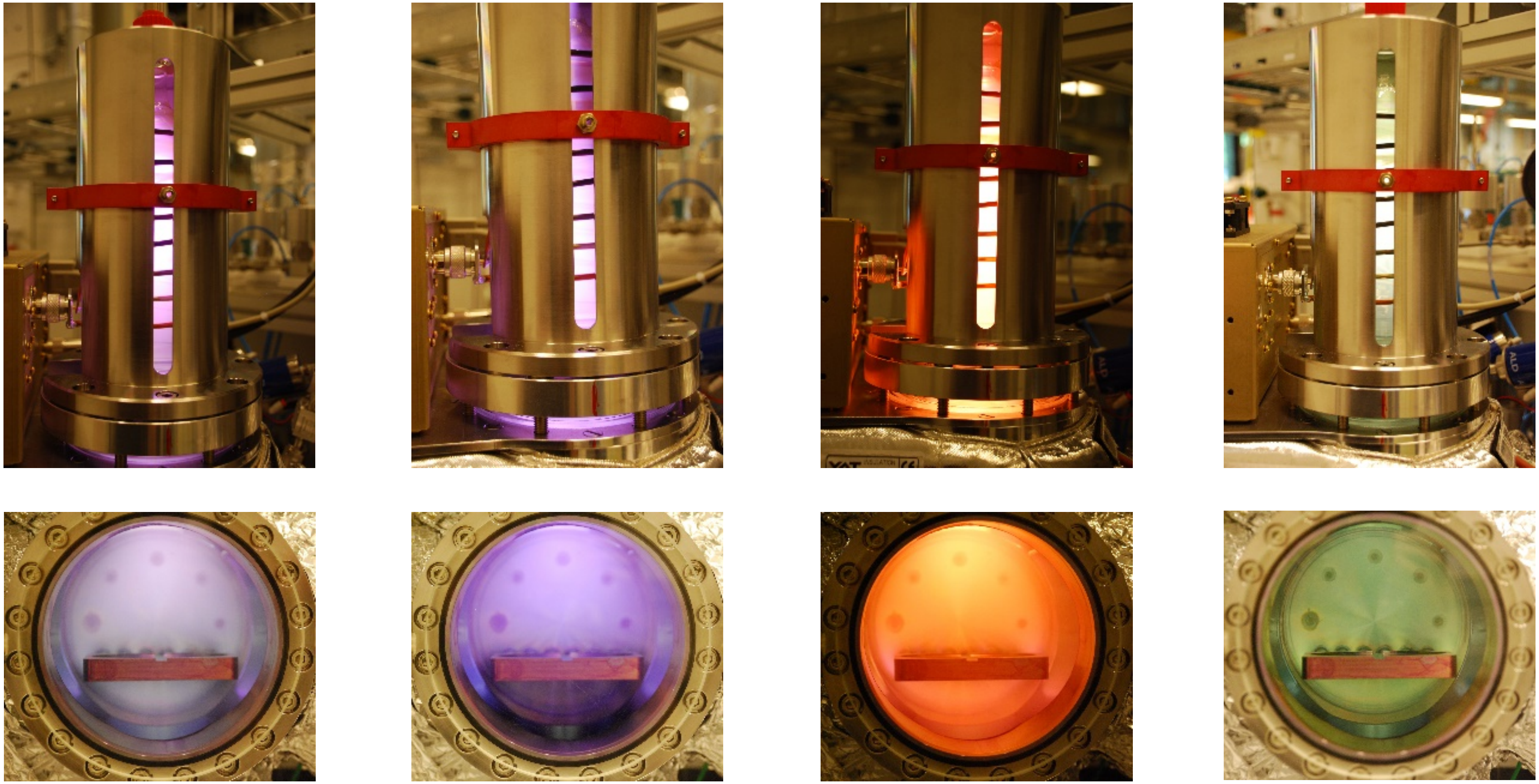
$$\text{s-OH}^* + Al(CH_3)_3 \longrightarrow \text{s-OAl}(CH_3)_2 + CH_4$$

B - 2nd Half Cycle

$$\text{s-AlCH}_3^* + 3O \longrightarrow \text{s-AlOH} + CO + CO_2 + H_2O$$

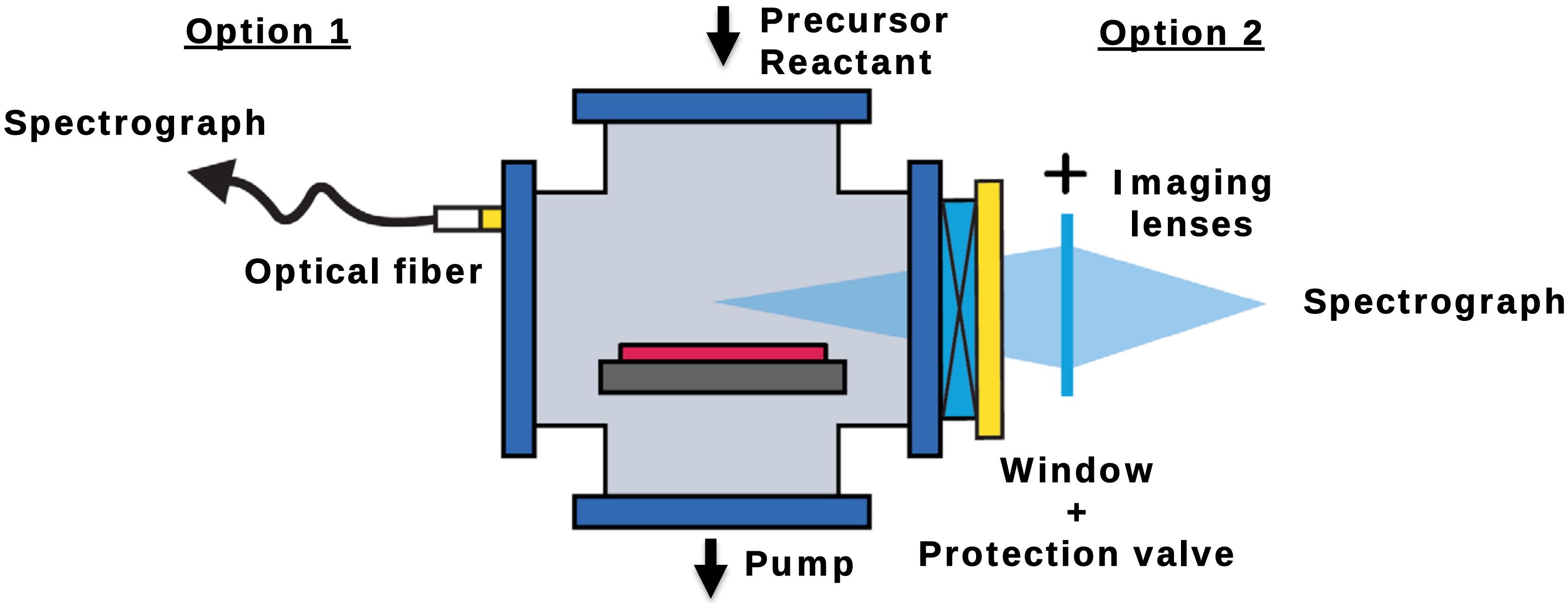
Plasma radiation – feed gas dependent

Ar **H_2** **N_2** **O_2**



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

Optical emission spectroscopy (OES)



Measures (visible) radiation from excited species decaying to lower levels

- 🟩 Ideally suited for process monitoring of plasma-based processes
- 🟩 Extremely easy to implement & cheap
- 🟥 Yields only information about excited species – not ground state species
- 🟥 Typically yields very indirect and qualitative information

Mackus *et al.*, J. Vac. Sci. Technol. A 28, 77 (2010).

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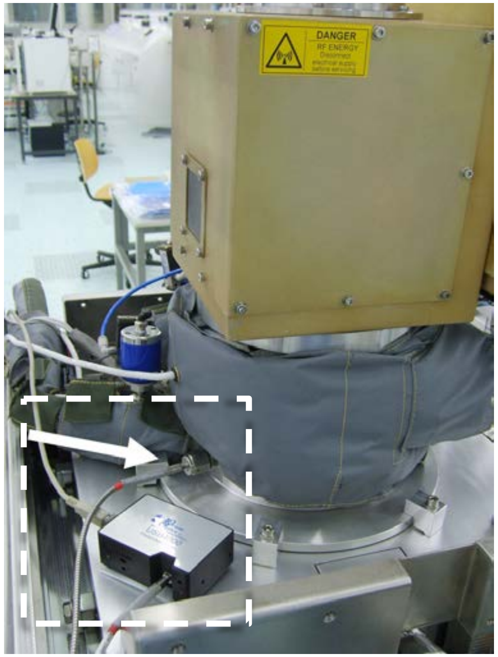

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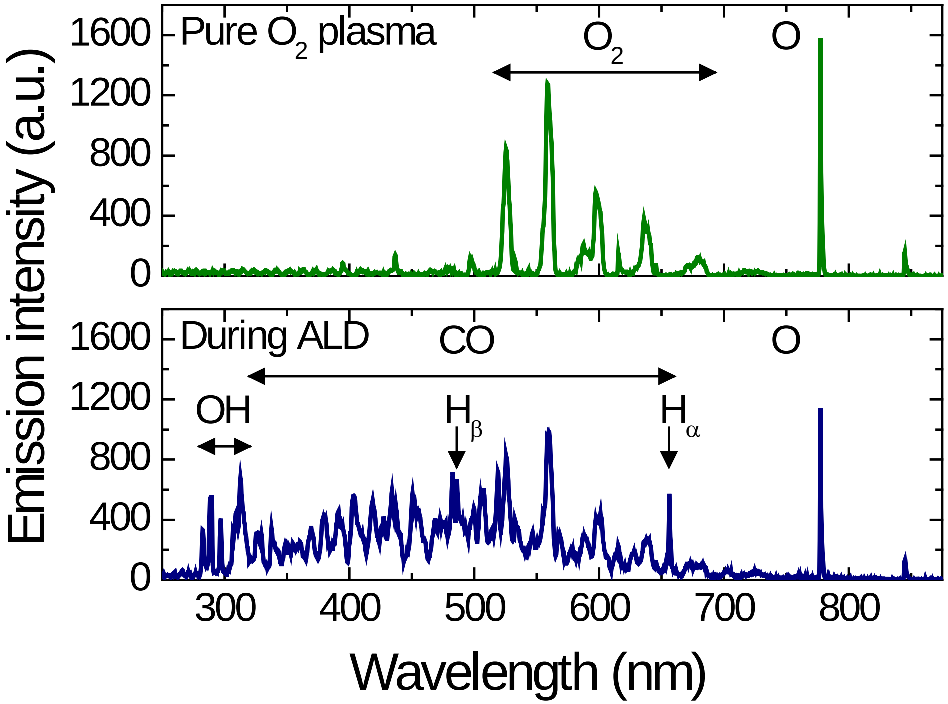
Optical emission spectroscopy – Plasma (Al_2O_3)

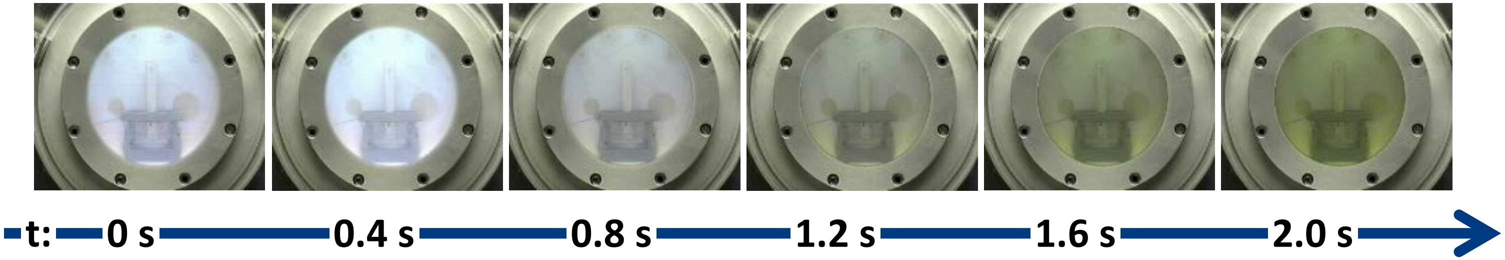


Plasma half-cycle

$AlCH_3^* + 4O \longrightarrow AlOH^* + CO_2 + H_2O$

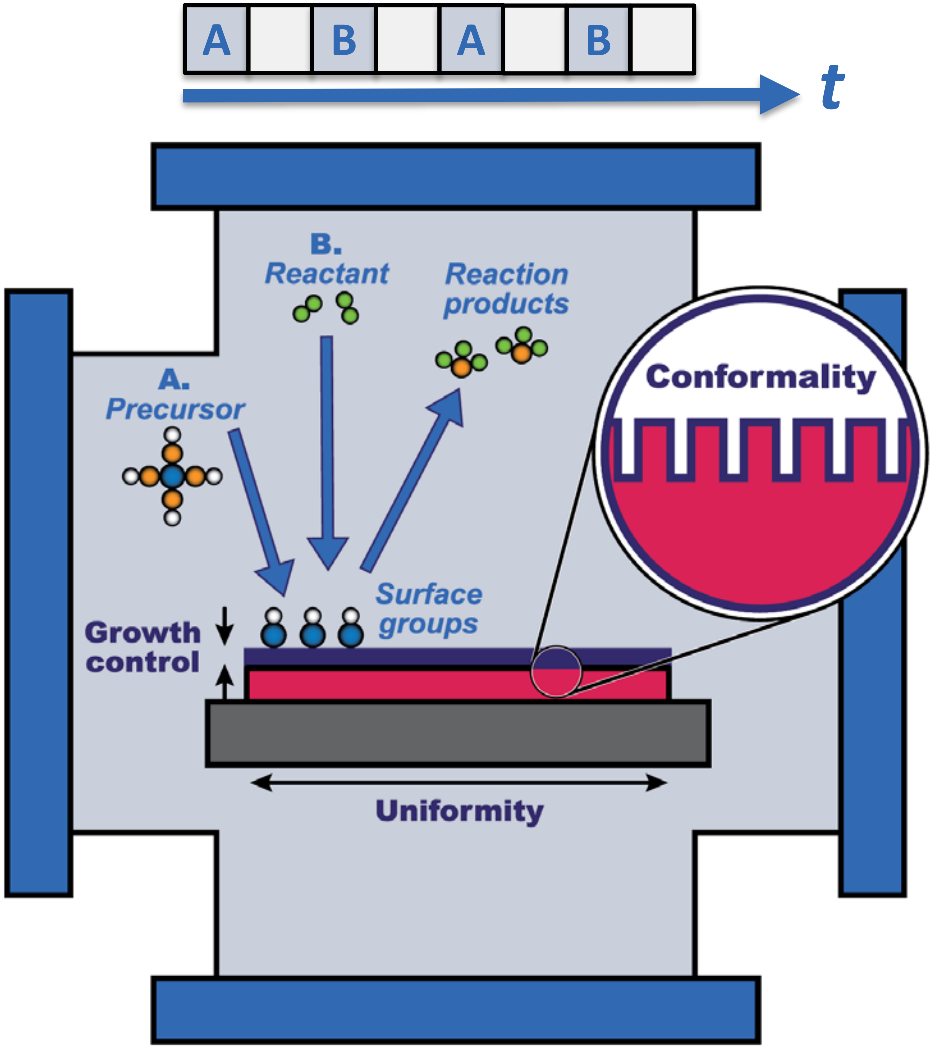
$\boxed{CO_2 + H_2O + e \longrightarrow \mathbf{CO^{ex}} + \mathbf{H^{ex}} + \ldots + e}$

Plasma is "**disturbed**"
by reaction products



Heil *et al.*, Appl. Phys. Lett. 89, 131505 (2006).
Knoops *et al.*, Appl. Phys. Lett. 107, 014102 (2015).

Atomic layer deposition (ALD)



Discussed **next:**

ALD merits:

- **Conformality**
- **Uniformity**
- **Growth control**

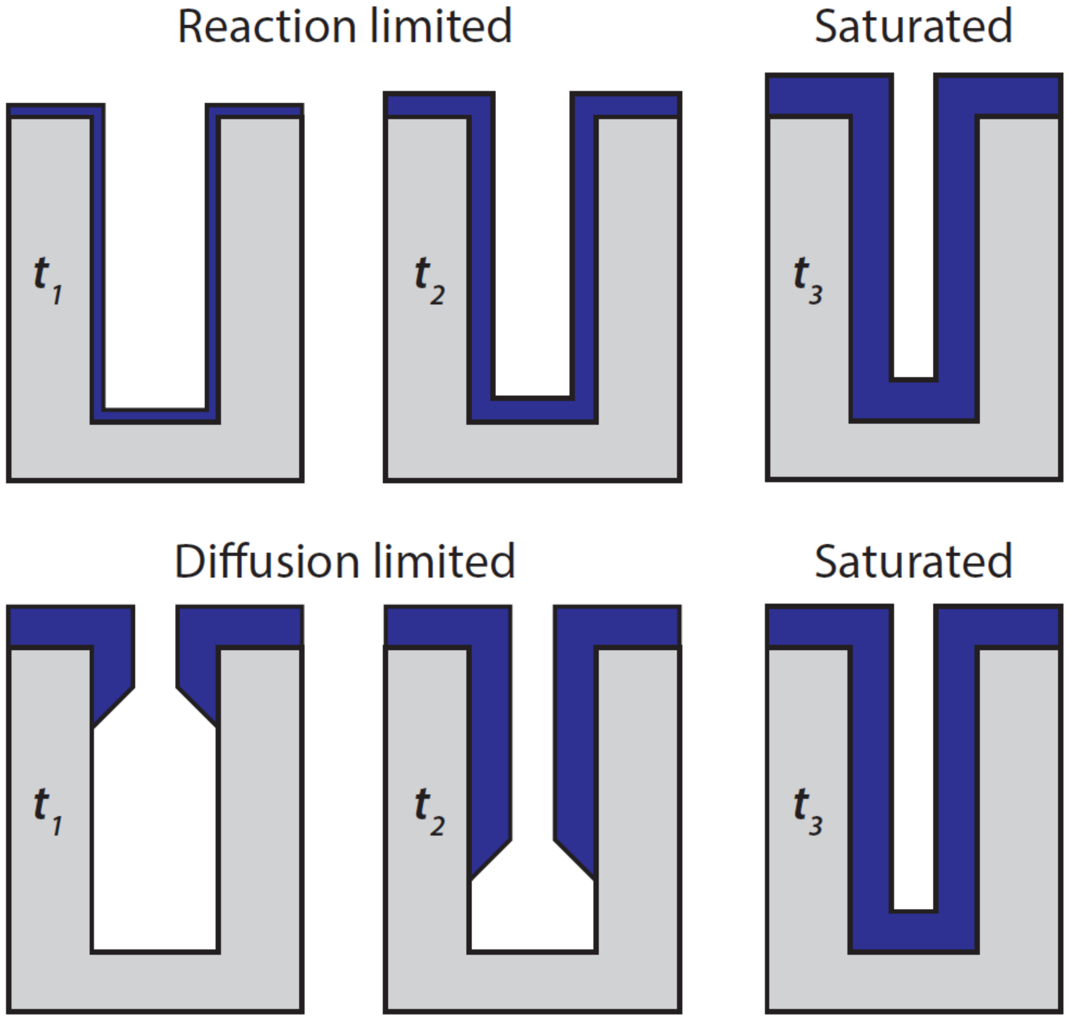
Advanced methods:

- **Sum-frequency generation**
- **Adsorption calorimetry**

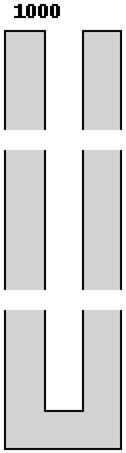
Conformality – Reaction- vs. diffusion-limited

s_0 << 1

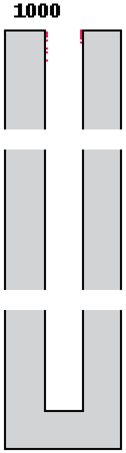
$s_0 \rightarrow 1$



Animation - s_0 << 1



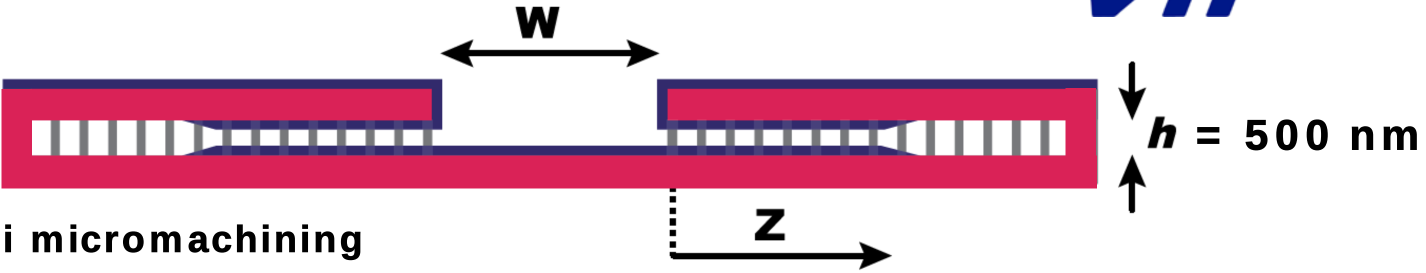
Animation - $s_0 \rightarrow 1$



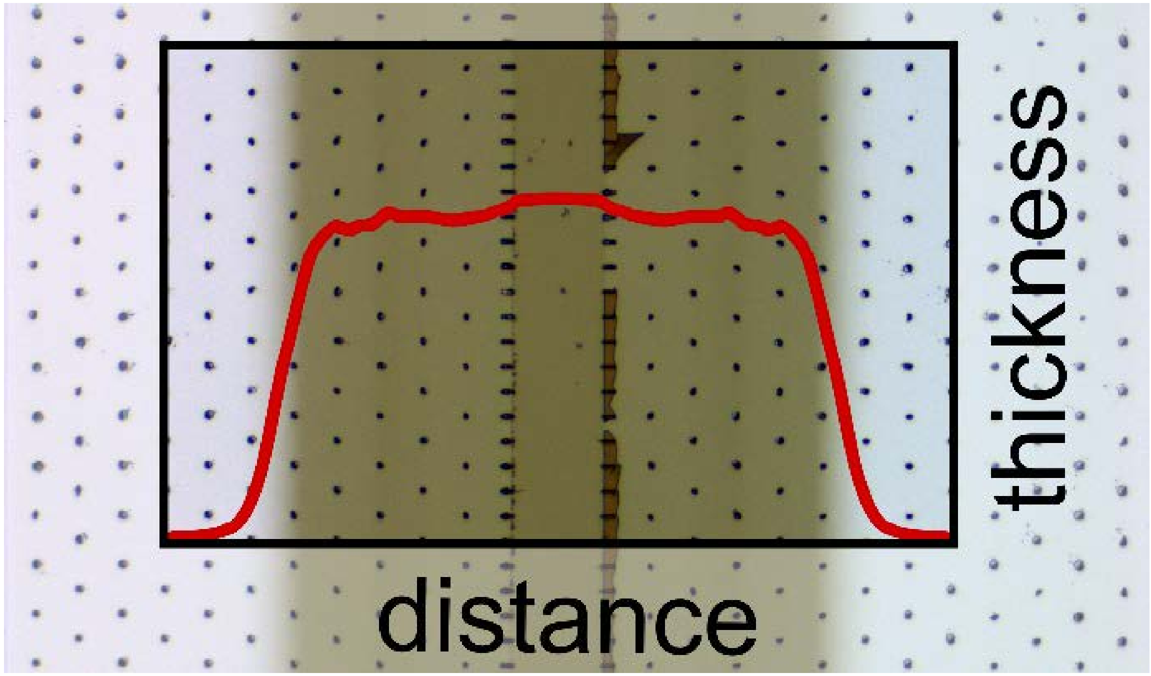
Elam *et al.*, Chem. Mater. 15, 3507 (2003).
Knoops *et al.*, J. Electrochem. Soc. 157, G241 (2010).

Conformality test structures

PillarHall™ LHAR structures



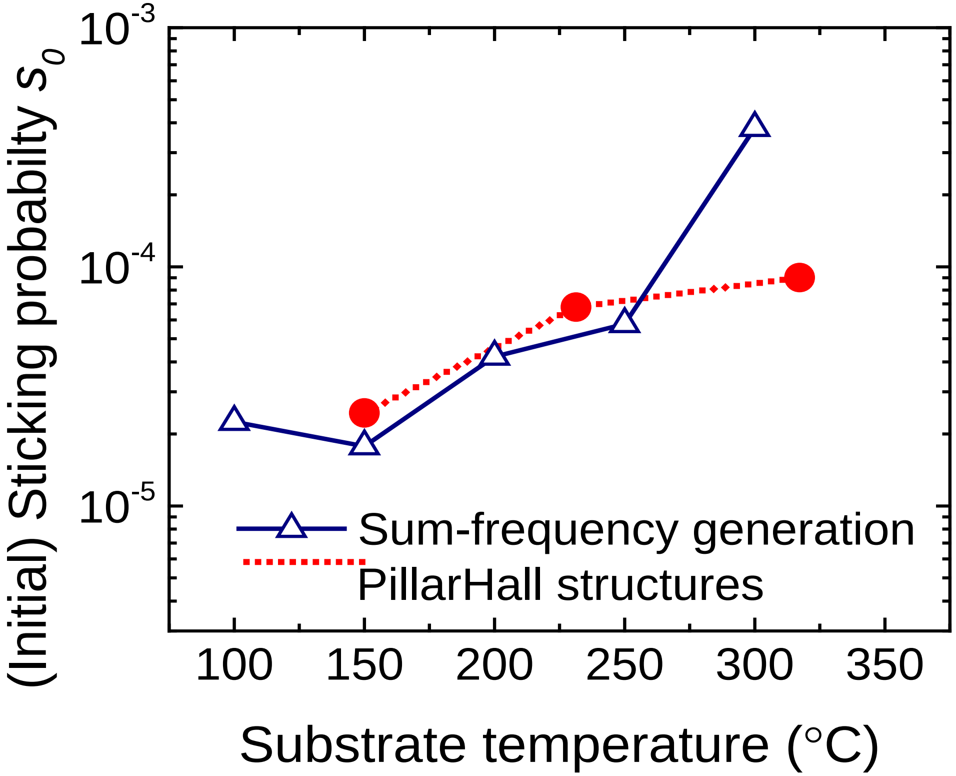
Fabricated by Si micromachining



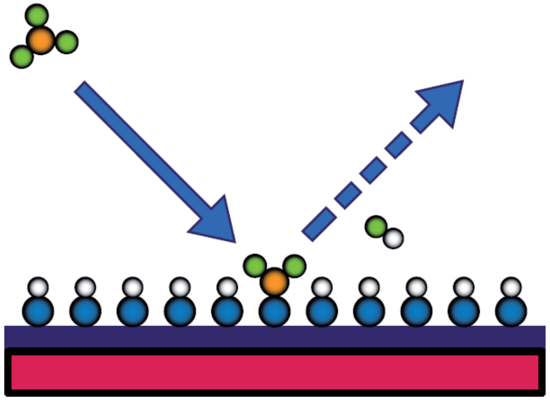
Ylilammi *et al.*, J. Appl. Phys. 123, 205301 (2018).
Gao *et al.*, J. Vac. Sci. Technol. A 33, 010601 (2015).

Conformality tests – sticking probability (Al_2O_3)

Sticking probability of H_2O during H_2O step



Initial sticking probability s_0

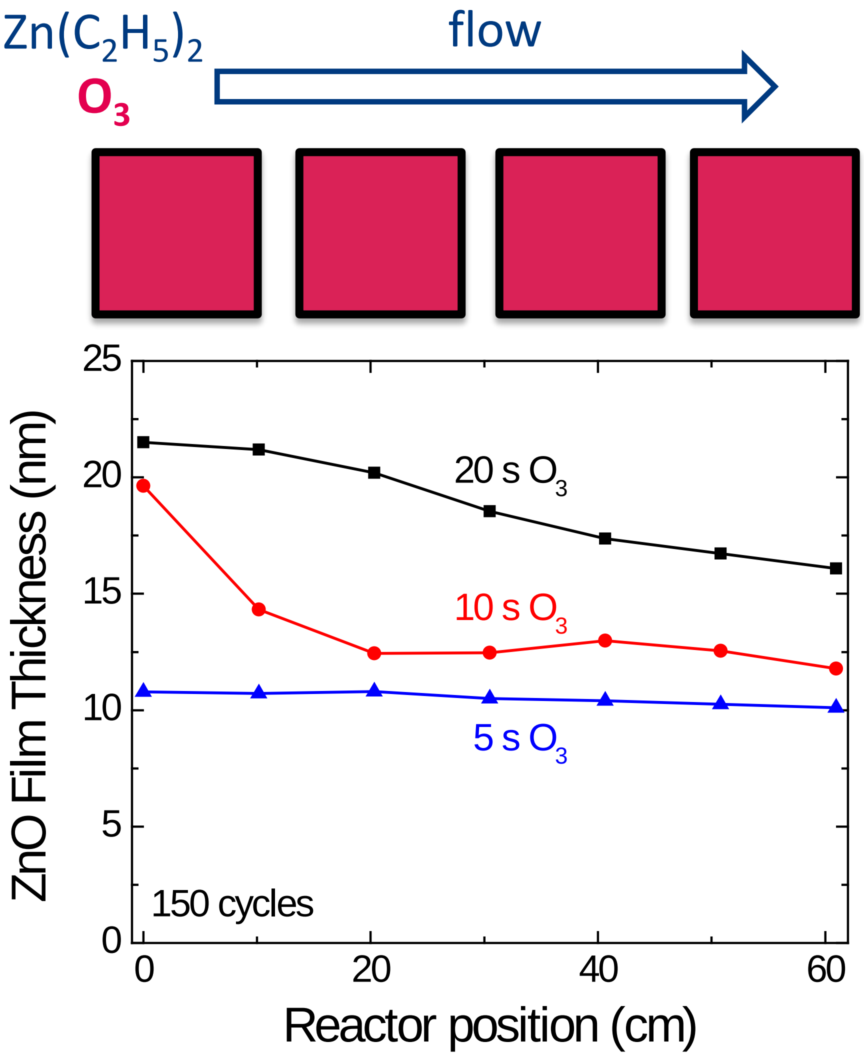


Good agreement with sum-frequency generation (SFG, see later)

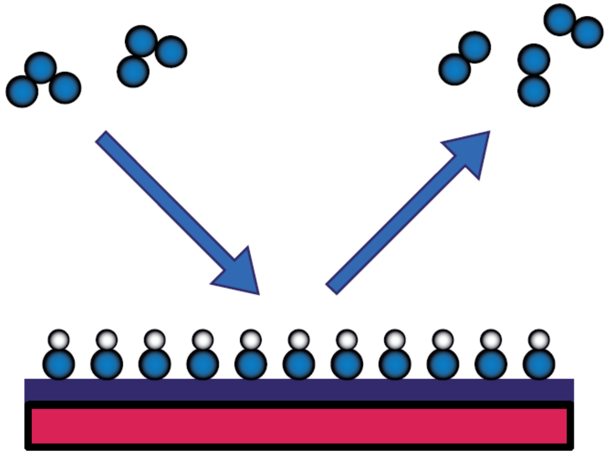
Sticking probability of H_2O **<10^{-4}** ➡ H_2O is **not very reactive** with –CH_3

See presentation Karsten Arts – AF2-Tuesday afternoon at 5 pm
Ylilammi *et al*., J. Appl. Phys. 123, 205301 (2018).

Uniformity – O_3 surface loss (ZnO)



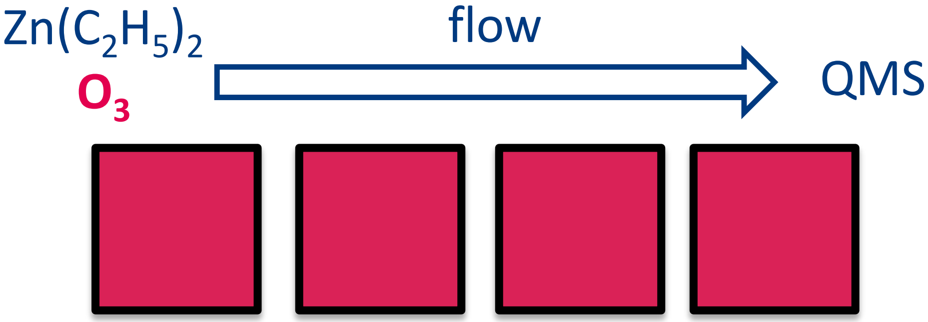
Surface loss/recombination of O_3

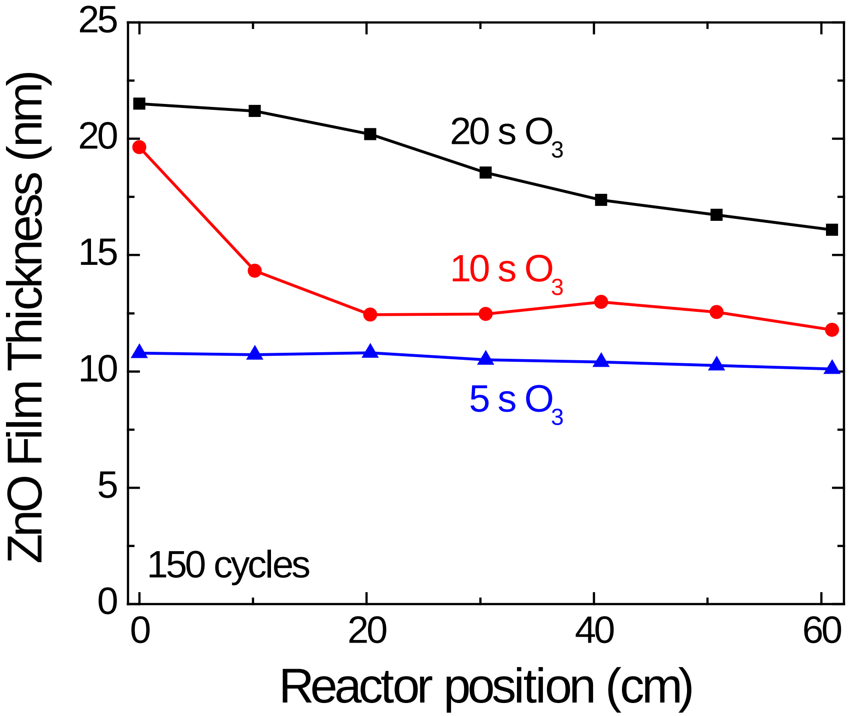


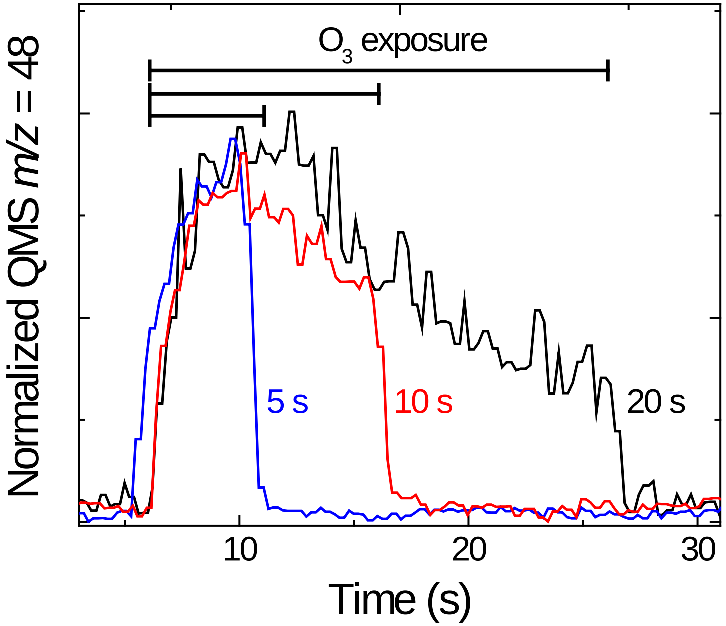
Depends on **surface termination**

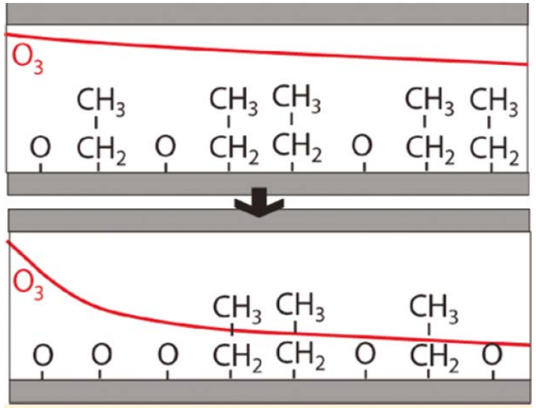
Knoops *et al.*, Chem. Mater. 23, 2381 (2011).

Uniformity – O_3 surface loss (ZnO)









C_2H_5-term. surface

Low O_3 loss

ZnO surface

High O_3 loss

Knoops *et al.*, Chem. Mater. 23, 2381 (2011).

Growth control - initial growth on foreign surfaces

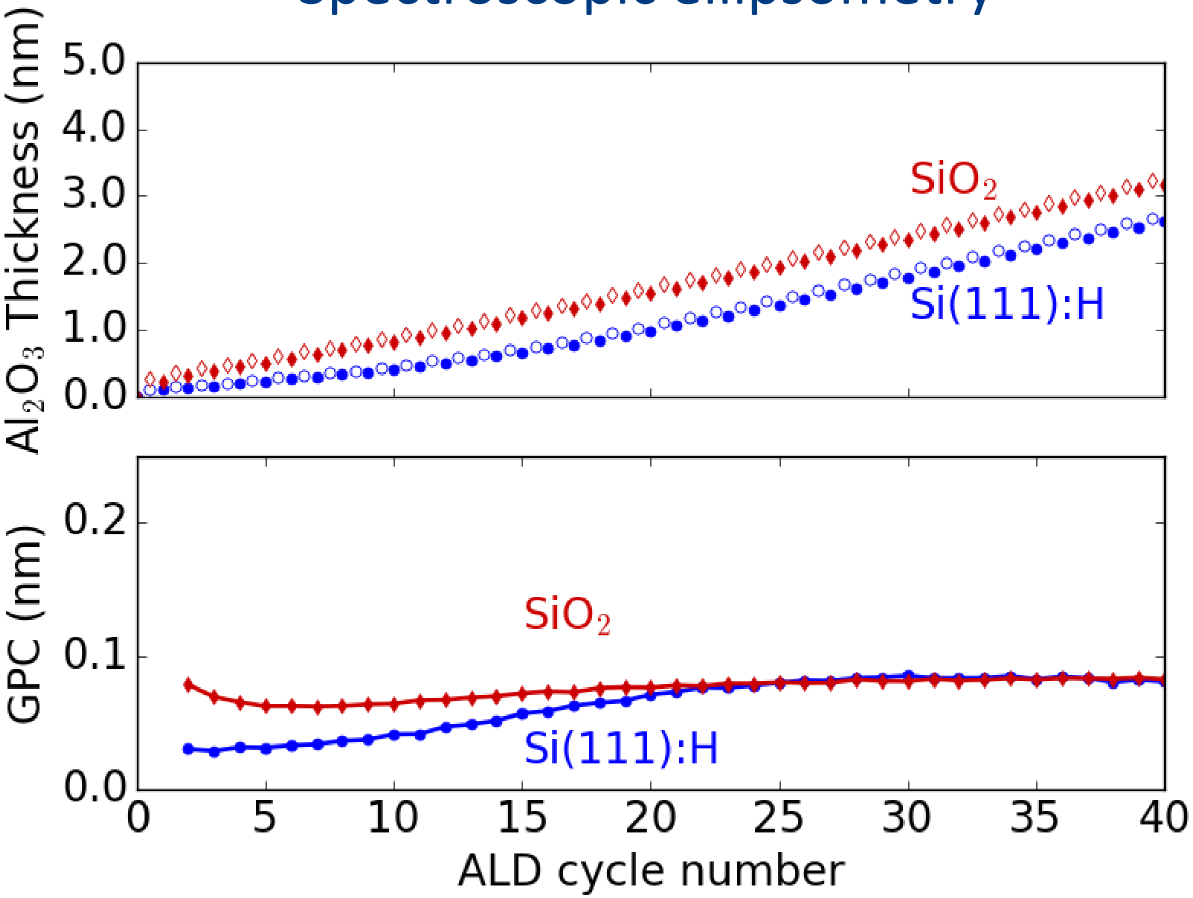
On foreign surfaces initially **no "ideal"** ALD film growth

Additional insight is necessary for

- Ultrathin films
- Area-selective ALD
- Etc.

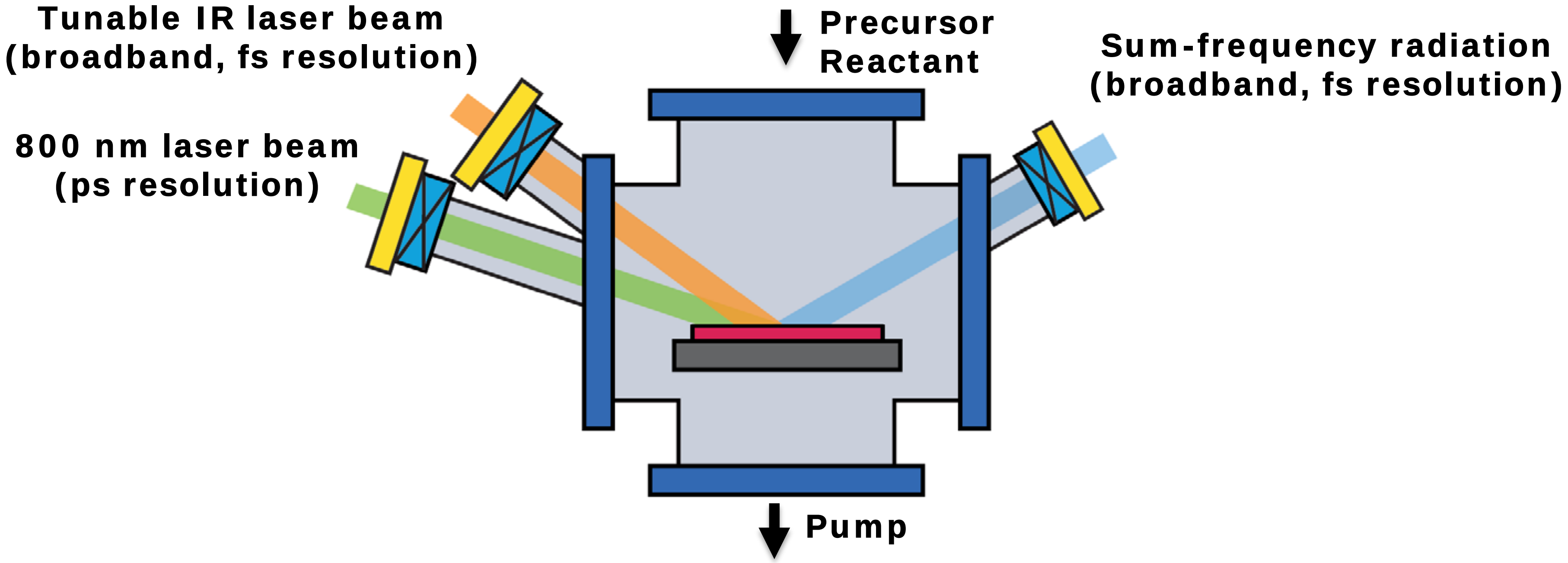
ALD Al_2O_3 on **SiO_2** and **Si(111):H** surfaces

Spectroscopic ellipsometry



Vandalon *et al.*, to be published (2018).

Sum frequency generation (SFG)

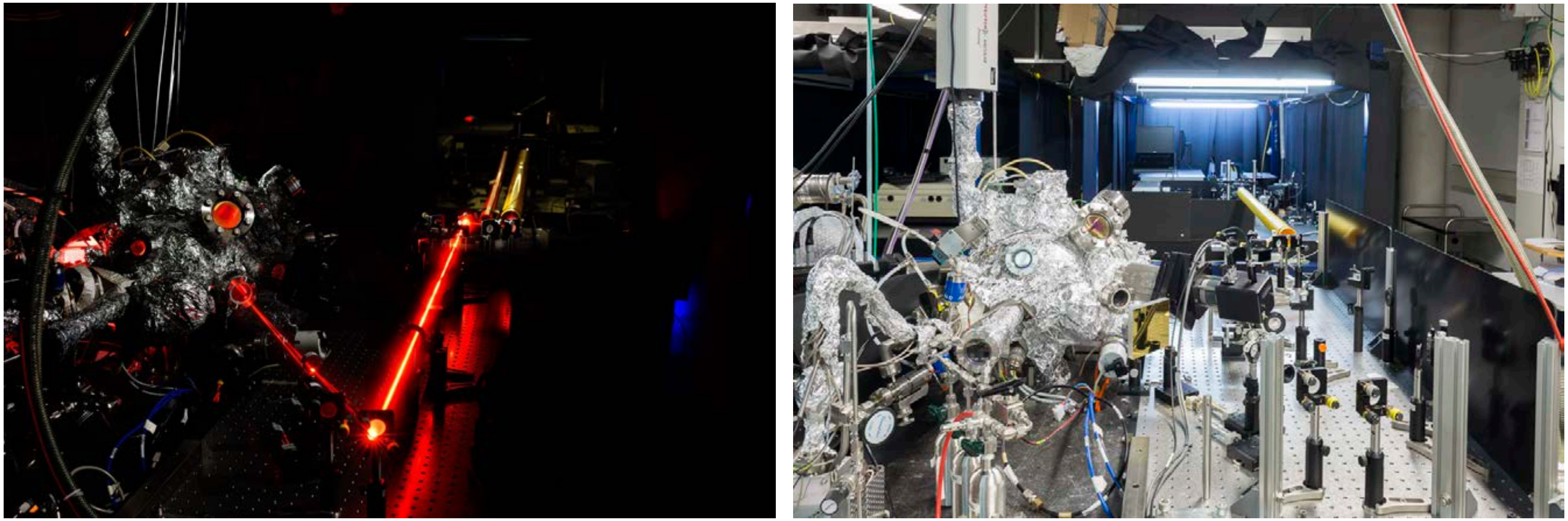


Nonlinear optical technique with 2 laser beams probing vibrational transitions

- ▲ Highly sensitive & specific for surface groups (sub-surface species not probed)
- ▲ Good time resolution, reaction kinetics can be followed in time
- ▲ Can give absolute values of reaction cross-sections/sticking probabilities etc.
- ▼ Very complex method requiring highly dedicated setup with laser-system

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

Sum frequency generation (SFG)



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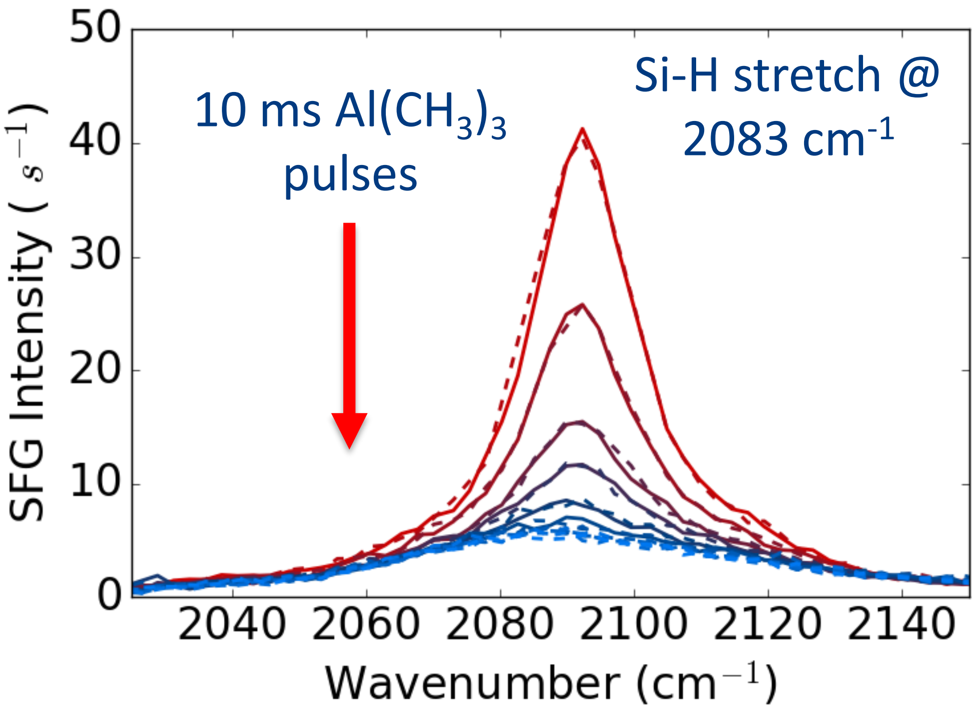
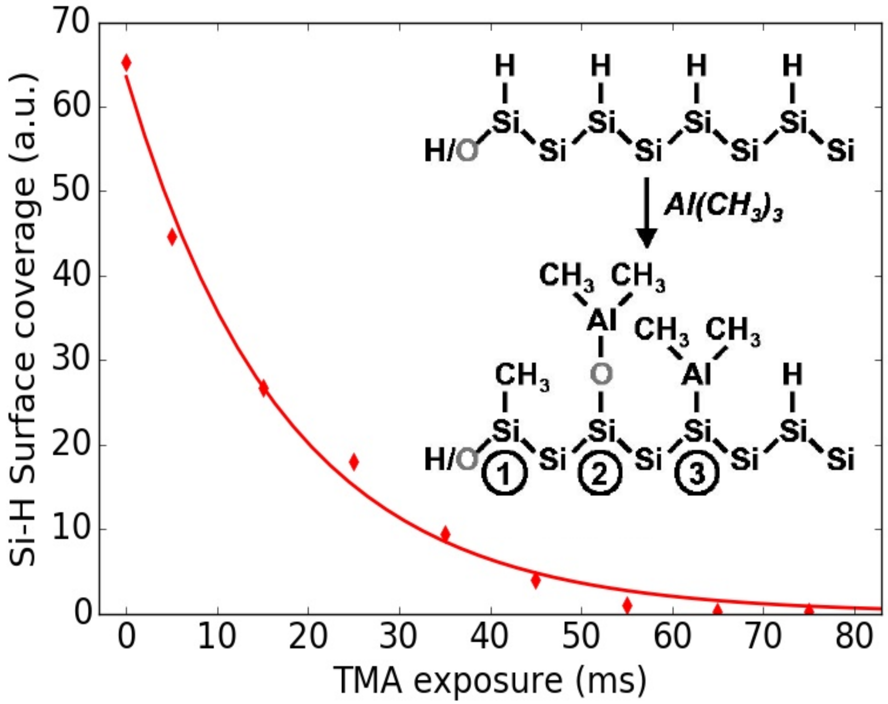
Vandalon and Kessels, J. Vac. Sci. Technol. A 35, 05C313 (2017).

Sum frequency generation – Al_2O_3 on Si(111):H





$Al(CH_3)_3$ reacts with Si(111):H breaking the Si-H bonds

Reaction cross-section $\sigma = (3.1 \pm 0.3) \times 10^{-18}$ cm^2

or translated into sticking probability **$s_0 = (1.9 \pm 0.2) \times 10^{-3}$**

Frank *et al.*, Appl. Phys. Lett. 82, 4758 (2003).
Vandalon *et al.*, to be published (2018).

Initial growth of Al_2O_3 on SiO_2 and on Si(111):H

Initial growth:

1st cyle on Si(111):H

$s_0 = (1.9 \pm 0.2) \times 10^{-3}$

1st cycle on SiO_2

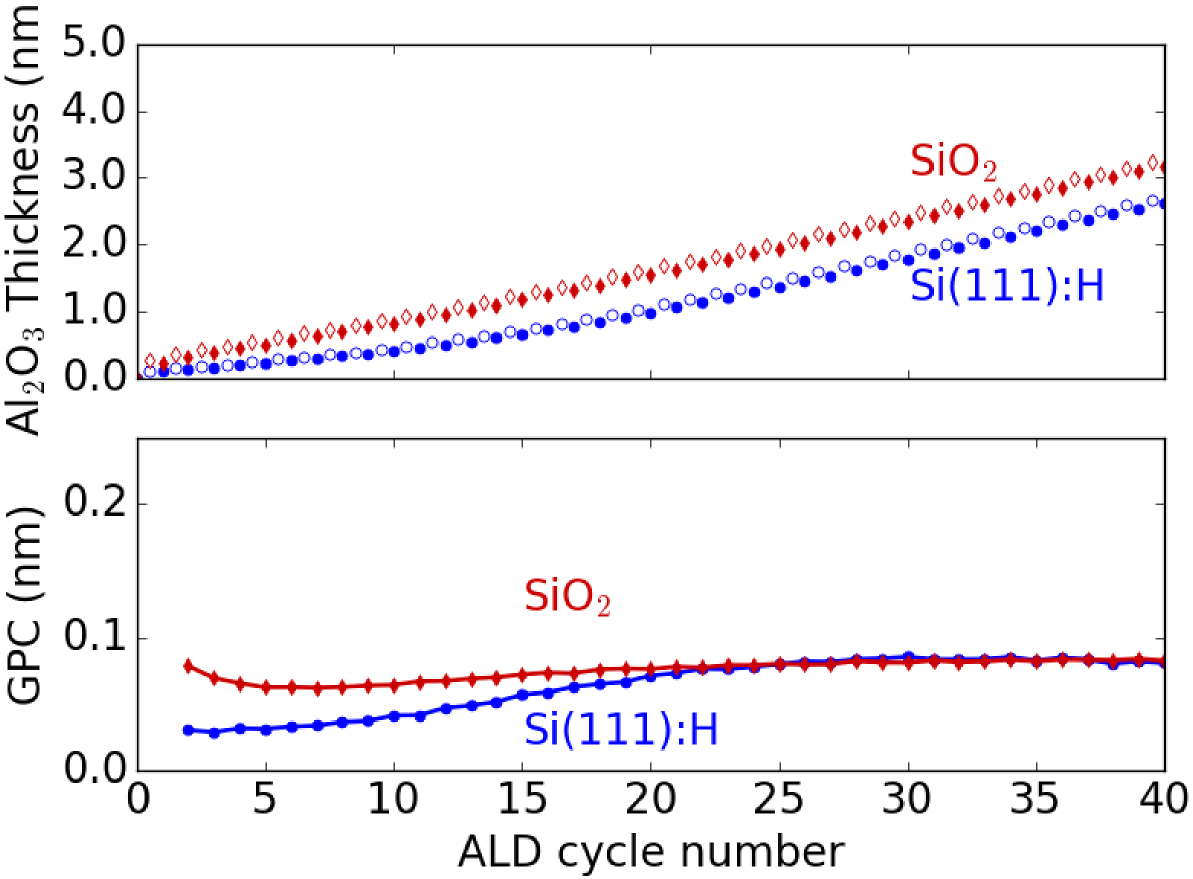
$s_0 = (1.2 \pm 0.1) \times 10^{-3}$

Steady-state growth:

***x*-th cycle (*x*>>1)**

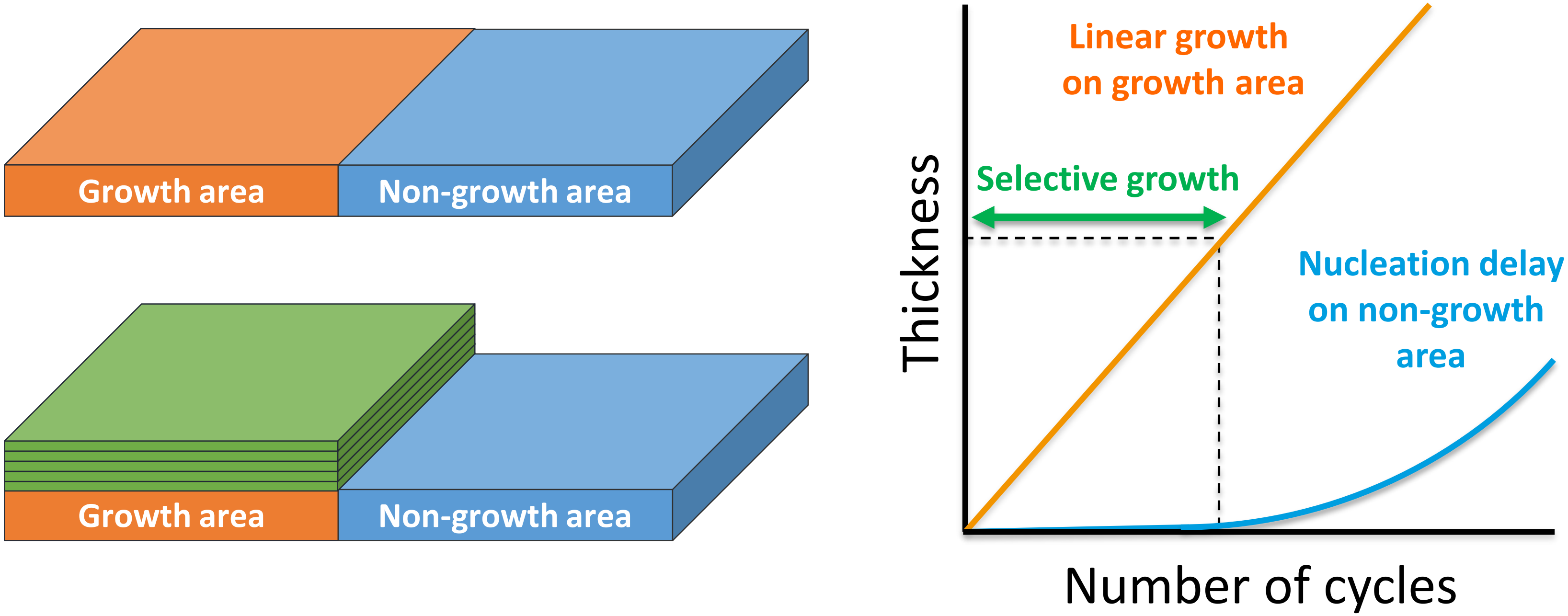
$s_0 = (3.9 \pm 0.4) \times 10^{-3}$

Spectroscopic ellipsometry



Vandalon *et al.*, to be published (2018).

Area-selective ALD (see tutorial Parsons)

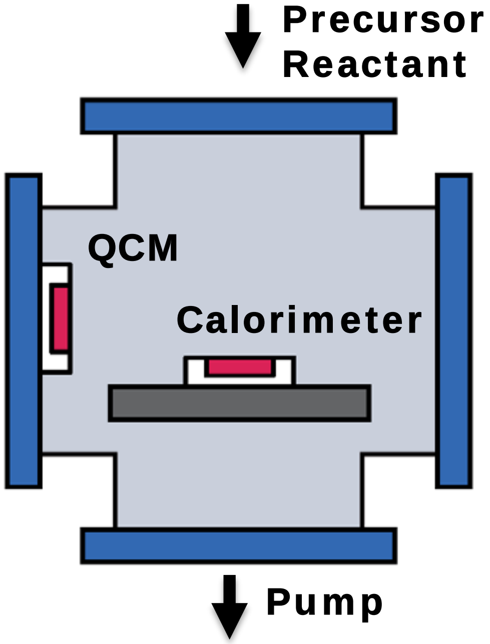


Differences in nucleation behavior (initial growth) are often exploited to achieve area-selective ALD

Fundamental insight (preferable with quantitative information) in initial growth is required

Mackus, ALD2017 tutorial (2017).

Adsorption calorimetry

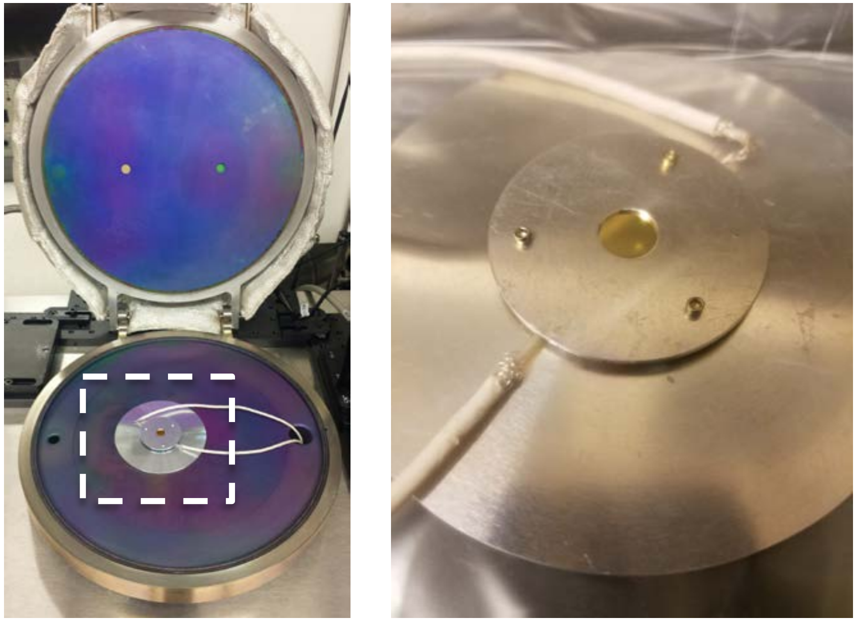


Measures half-cycle reaction heats pyroelectrically using a $LiTaO_3$ crystal disk

- ▲ Provides additional thermodynamic and mechanistic insight
- ▲ Can be used to verify and benchmark (half-cycle) reactions – also from DFT
- ▼ New to the field of ALD – needs follow up work
- ▼ ....

Lownsbury *et al.*, Chem. Mater. 29, 8566 (2017).

Adsorption calorimetry



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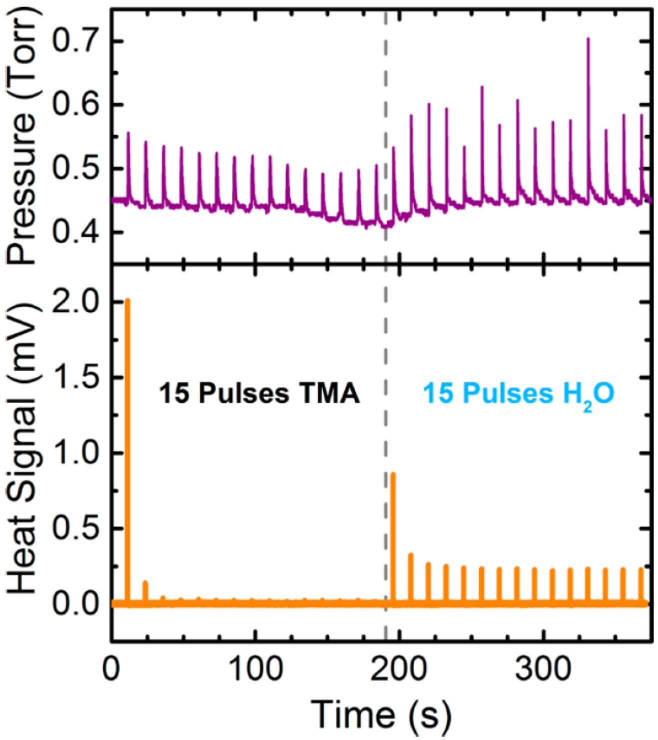
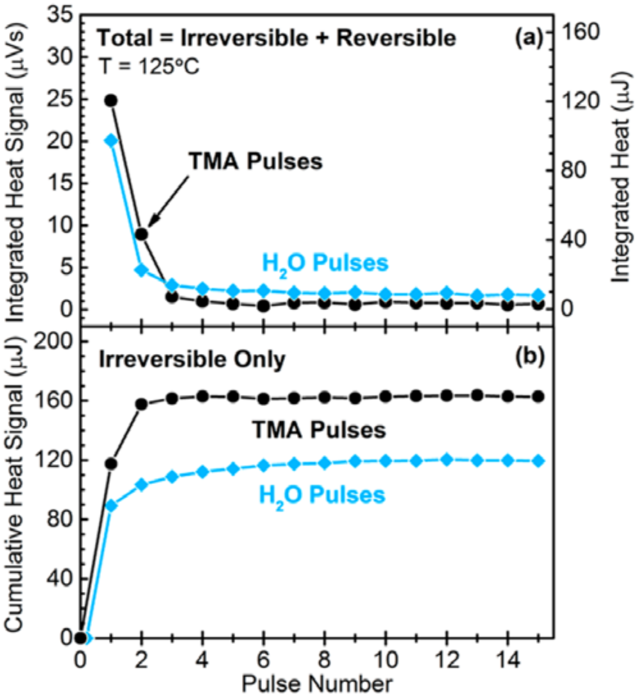
Lownsbury *et al.*, Chem. Mater. 29, 8566 (2017).
Photos courtesy of Alex Martinson (Argonne National Lab)

Adsorption calorimetry – Reaction heats (Al_2O_3)





A - 1st Half Cycle:

$$\text{s-OH*} + Al(CH_3)_3 \longrightarrow \text{s-OAl}(CH_3)_2 + CH_4 \qquad \Delta H = -343\ \text{kJ/mol}$$

B - 2nd Half Cycle:

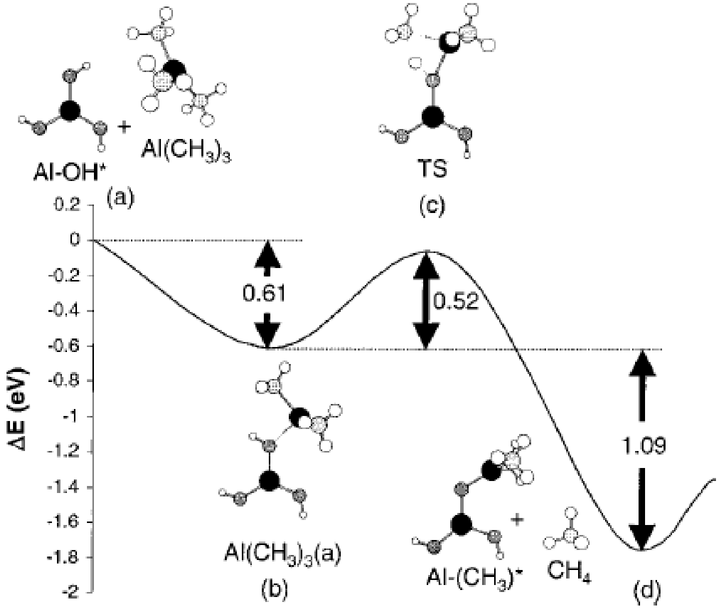
$$\text{s-AlCH}_3\text{*} + H_2O \longrightarrow \text{s-AlOH} + CH_4 \qquad \Delta H = -251\ \text{kJ/mol}$$

Lownsbury *et al.*, Chem. Mater. 29, 8566 (2017).

First-principle calculations

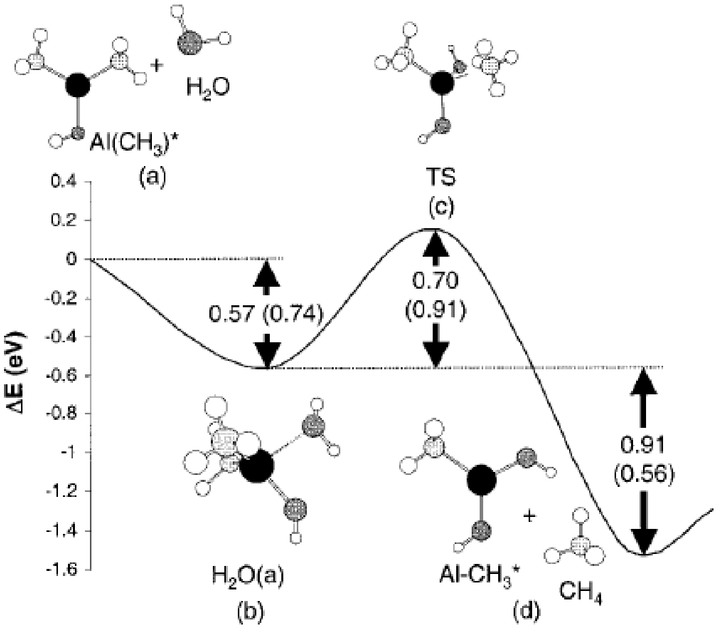
A - 1st Half Cycle

s-OH*+ Al$(CH_3)_3$ ⟶ s-OAl$(CH_3)_2$ + CH_4



B - 2nd Half Cycle

s-AlCH$_3$* + H_2O ⟶ s-AlOH + CH_4

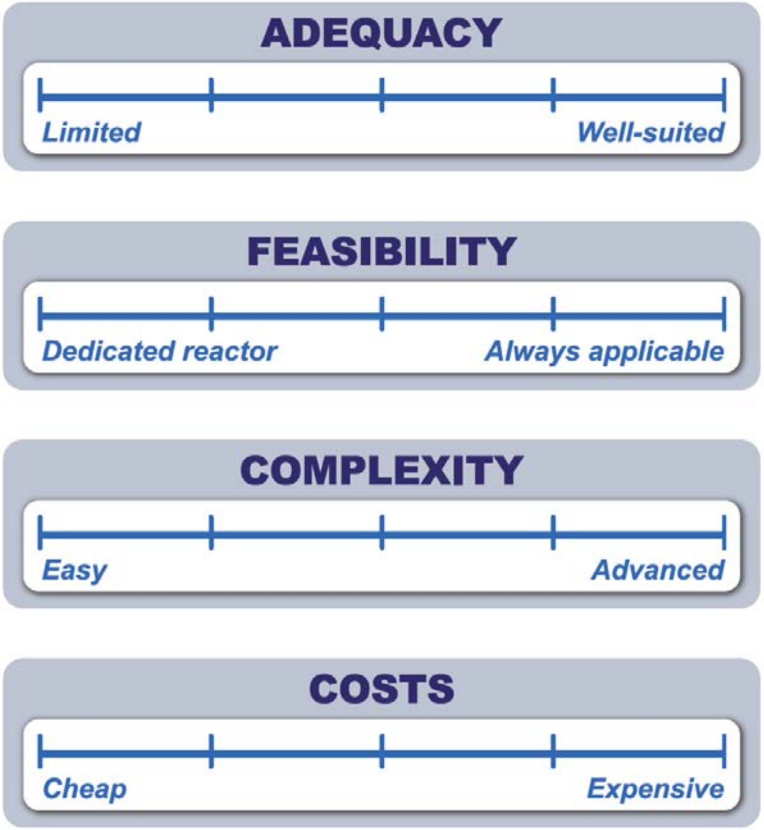


So far calculated reaction heats have remained untested with respect to experiment

Widjaja and Musgrave, Appl. Phys. Lett. 80, 3306 (2002).

Concluding remarks

- Various analytical tools for *in situ* studies of ALD have been discussed
  QMS, gas phase FTIR, QCM, SE, surface FTIR, OES
  Many more exist. Combine tools if you can!



ADEQUACY

Limited — Well-suited

FEASIBILITY

Dedicated reactor — Always applicable

COMPLEXITY

Easy — Advanced

COSTS

Cheap — Expensive

Concluding remarks

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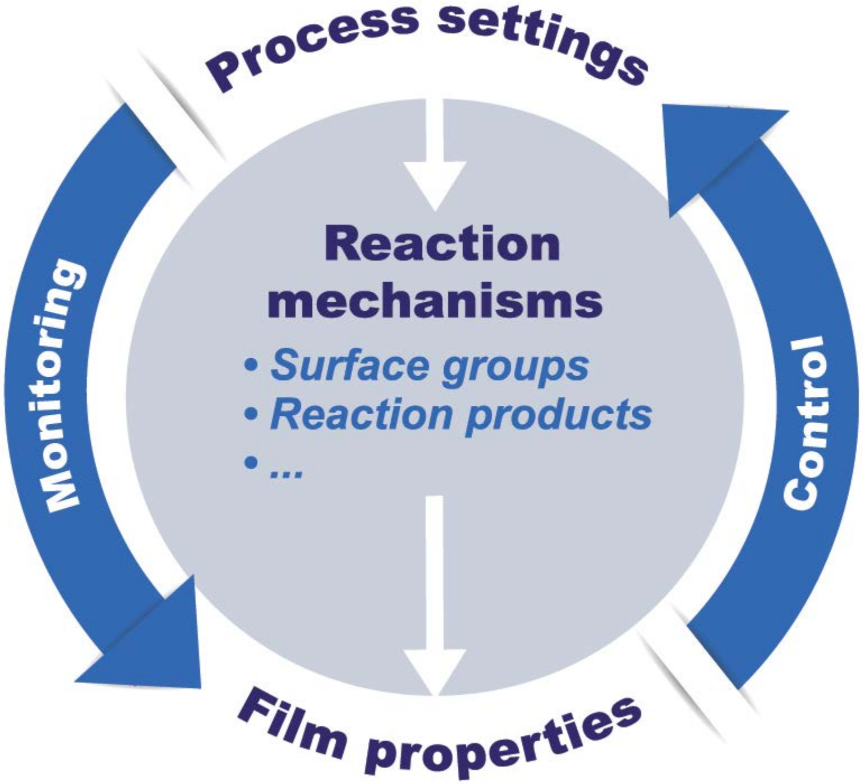
  Many more exist. Combine tools if you can!

- Focus can be on
  - Film growth & properties
  - Reaction mechanisms
  - Process monitoring & control



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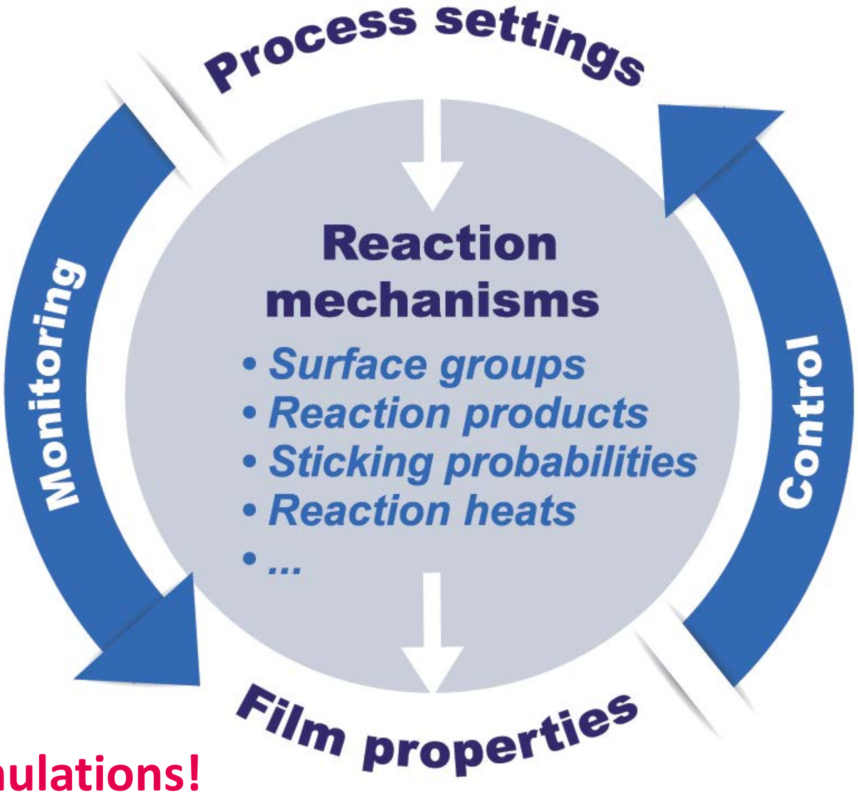
  QMS, gas phase FTIR, QCM, SE, surface FTIR, OES
  Many more exist. Combine tools if you can!

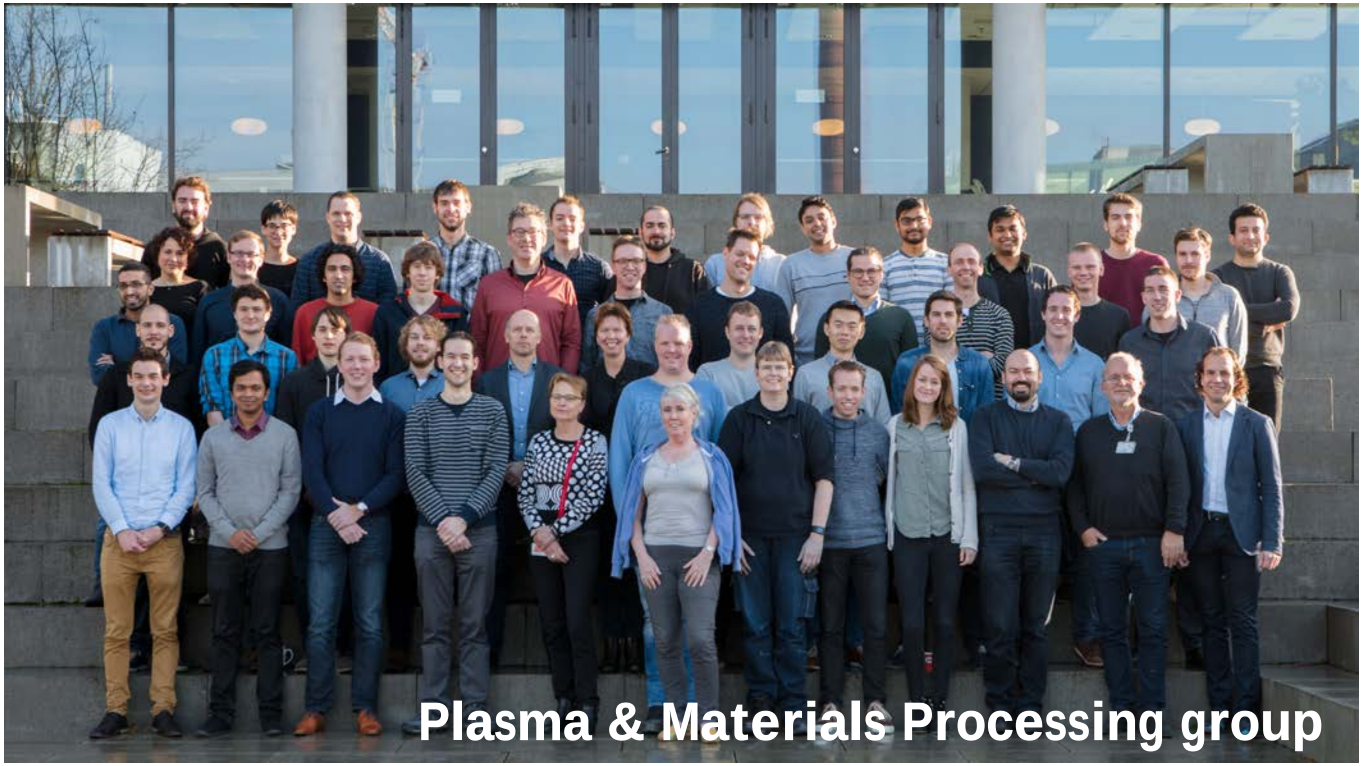
- Focus can be on
  - Film growth & properties
  - Reaction mechanisms
  - Process monitoring & control

- Take it to the next level (**quantitatively**!)
  - Sticking probabilities
  - Reaction heats
  - Transient states
  - ….

  Combine experiments with theory/simulations!



Acknowledgements



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Dr. Marcel Verheijen
Dr. Ageeth Bol
Dr. Adriana Creatore
&
Many PhD students
and postdocs

For more information & feedback
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Mission: educate students and professionals on the principles, applications and future advancements of ALD and related atomic-scale processes.

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