TU/e EINDHOVEN UNIVERSITY OF TECHNOLOGY

Atomic Scale Processing: from Understanding to Innovation

Erwin Kessels

ALD 2019
19th International Conference on Atomic Layer Deposition
July 21-24, 2019 • Bellevue, Washington, USA

ATOMIC LAYER ETCHING
Featuring the 6th International Atomic Layer Etching WORKSHOP

Department of Applied Physics

A big thank you!

- Organizers & past winners
- AVS staff
- ALD steering committee
- The PMP group
  current & past members:
  - Students and postdocs
  - Technical and support staff
  - The PI's
- Collaborators (many of you!)
- Sponsoring companies
- Funding organizations

Plasma & Materials Processing (PMP) group

The PI's: Adriana Creatore[a], Ageeth Bol[b], Richard Engeln, Adrie Mackus, Harm Knoops, Bart Macco[c]

[a] See Tuesday: **AA1-TuM03** by Adriana Creatore
[b] See Wednesday: **NS-WeA03** by Ageeth Bol
[c] See Sunday: Tutorial about **ALD for photovoltaics** by Bart Macco

Outline

1. ALD status report: strong, healthy & growing
2. ALD is big in photovoltaics
3. Plasma ALD has become mainstream
4. Plasma ALD can be very conformal
5. Ion bombardment yields opportunities for ALD
6. Area-selective deposition is trending
7. ALD fundamentals: need for quantitative data
8. Atomic layer etching is becoming vital

More reading on the blog:

www.AtomicLimits.com

Keywords:

Nanoelectronics

Photovoltaics

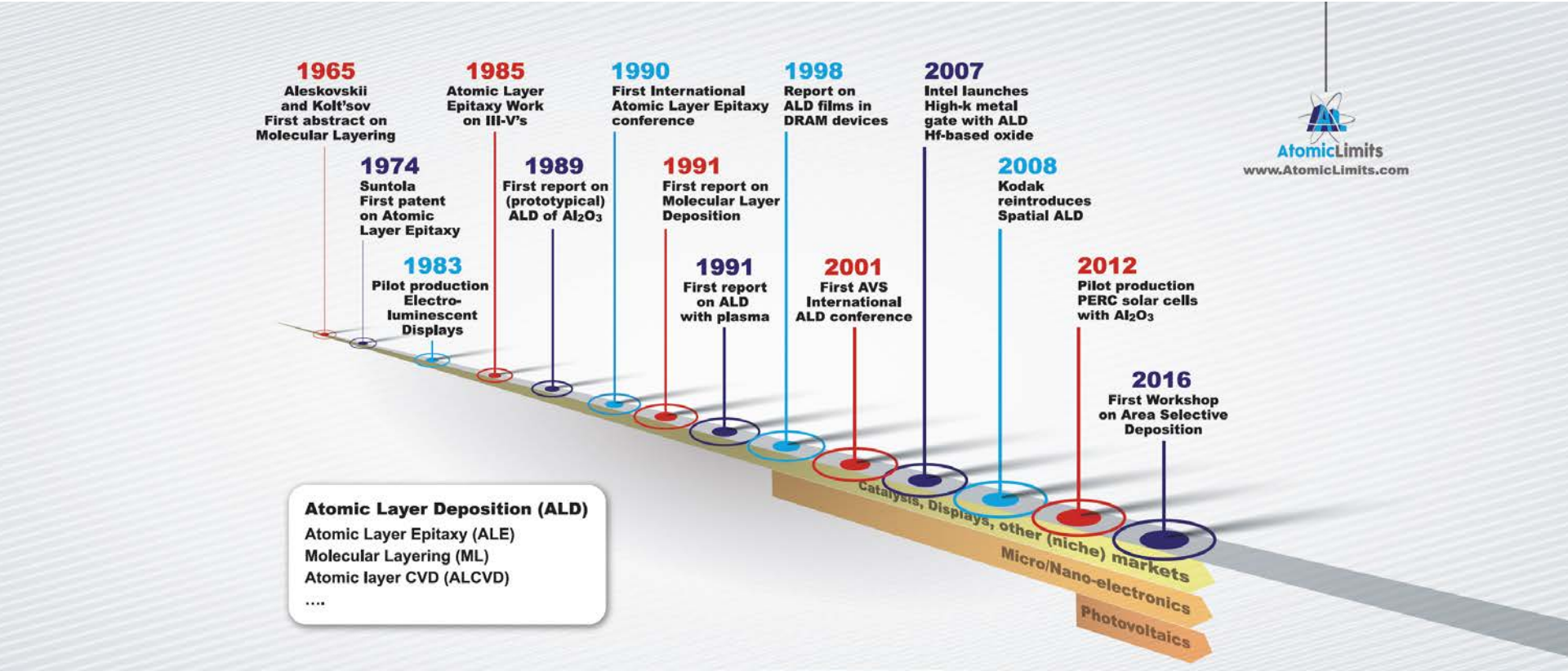
Plasma ALD

ALD fundamentals

1. ALD status report: strong, healthy & growing

- ALD market
- ALD materials
- ALD and ALE databases

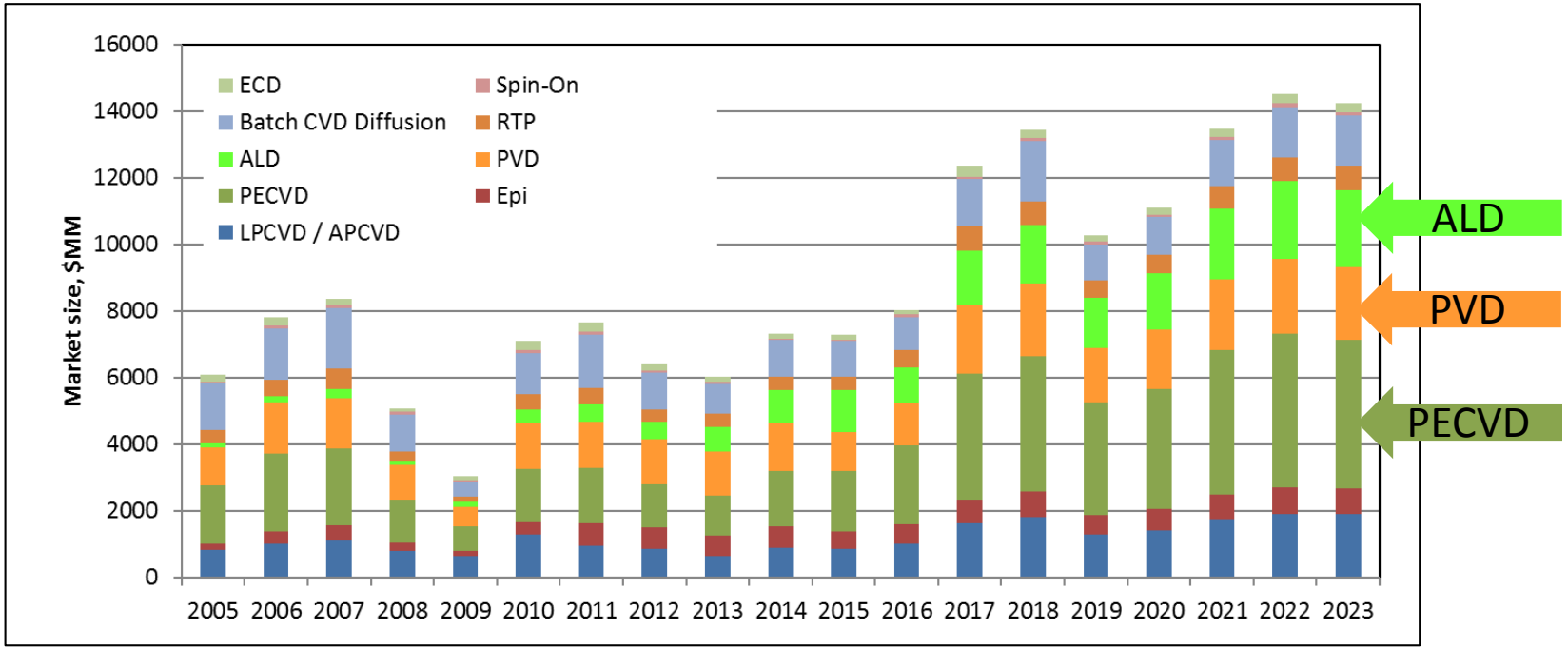
ALD time line – 45+ years of ALD



To appear on www.AtomicLimits.com for downloading

Deposition wafer fab equipment market size

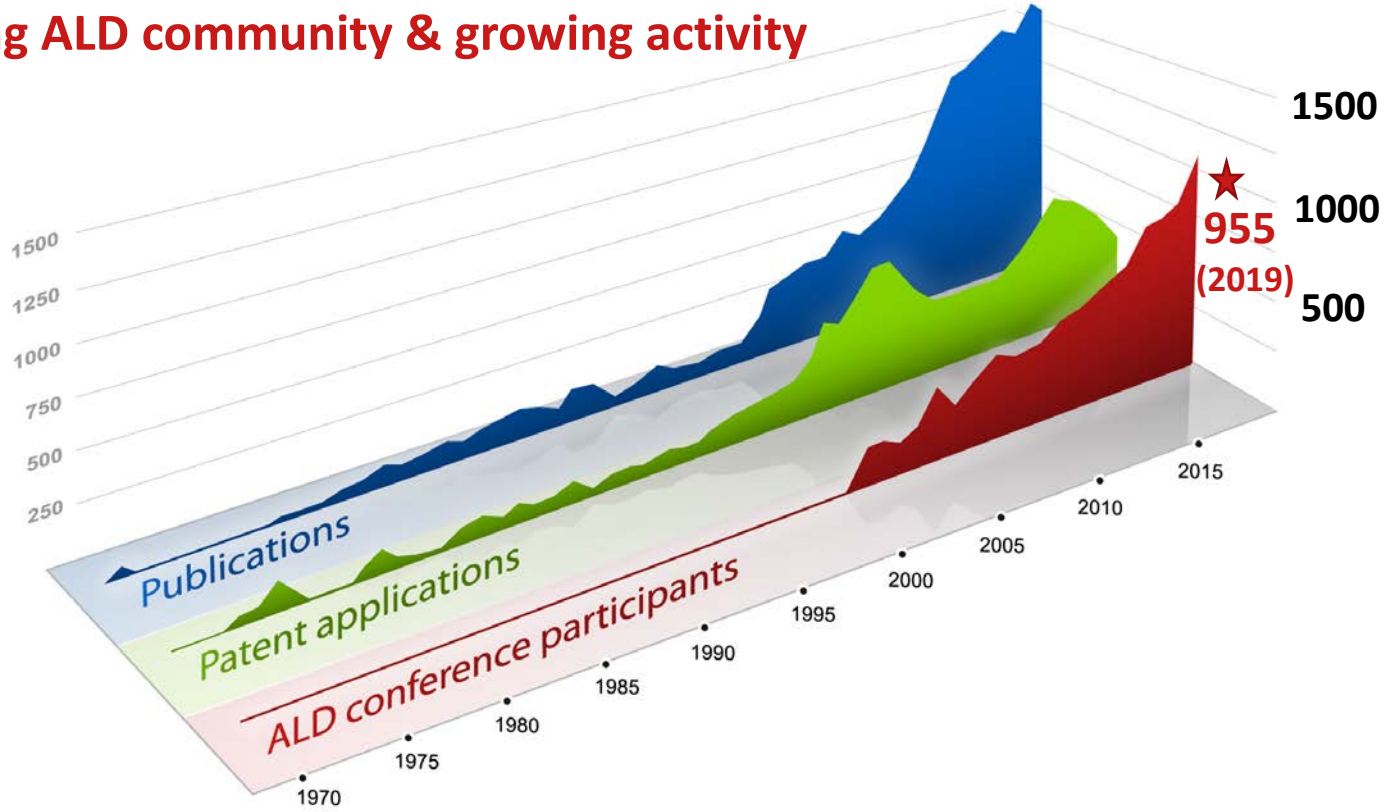
Trends in thin film requirements: thinner, taller, more conformal, lower T



 Data: VLSI Research (March 2019); graph: © ASM 2019, used with permission

Publications, patents, conference participants

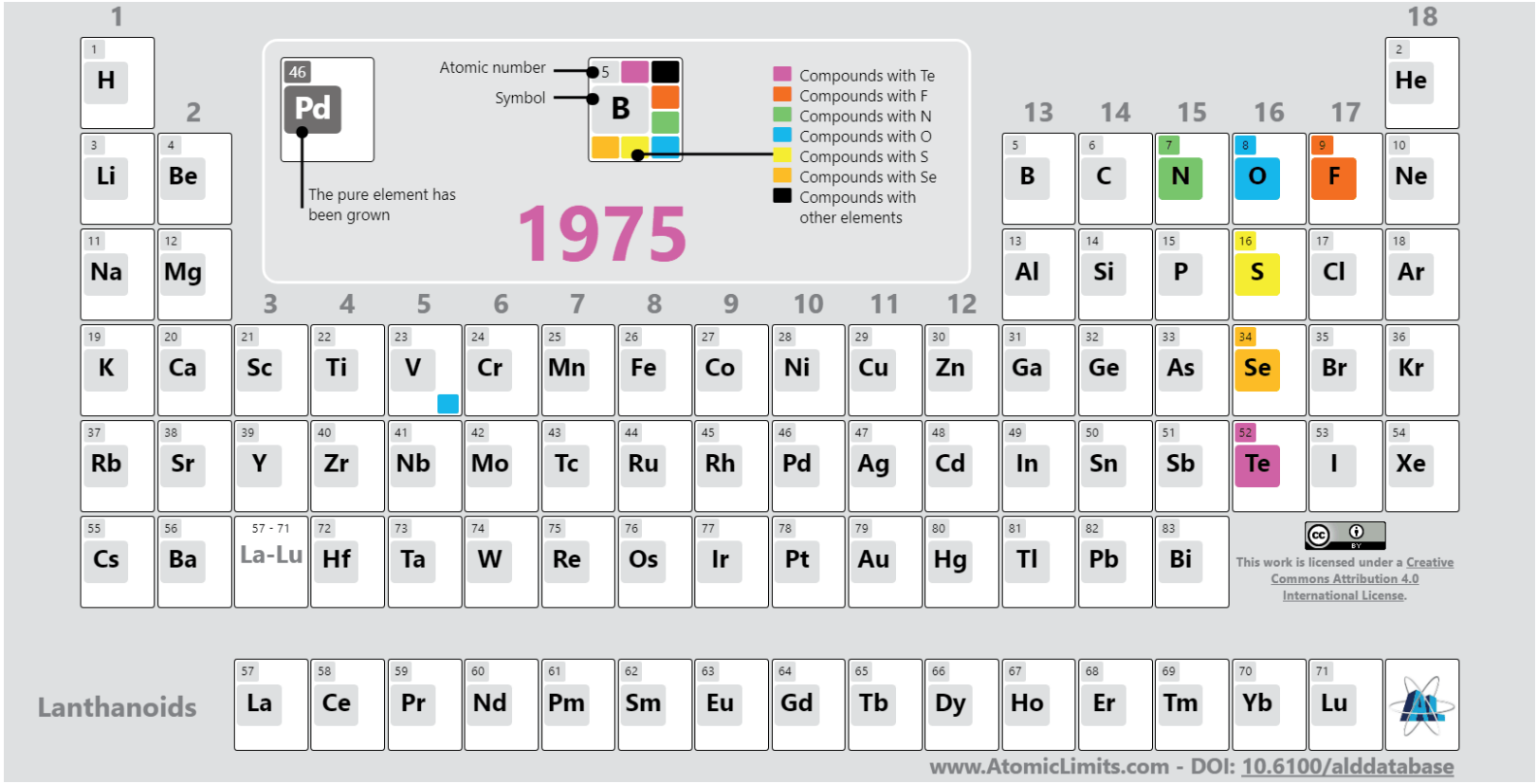
Growing ALD community & growing activity



Data on publications: Harm Knoops/Erwin Kessels using Scopus
Data on patent applications: Jonas Sundqvist – BALD Engineering
Data on ALD conference participants: Della Miller - AVS

TU/e

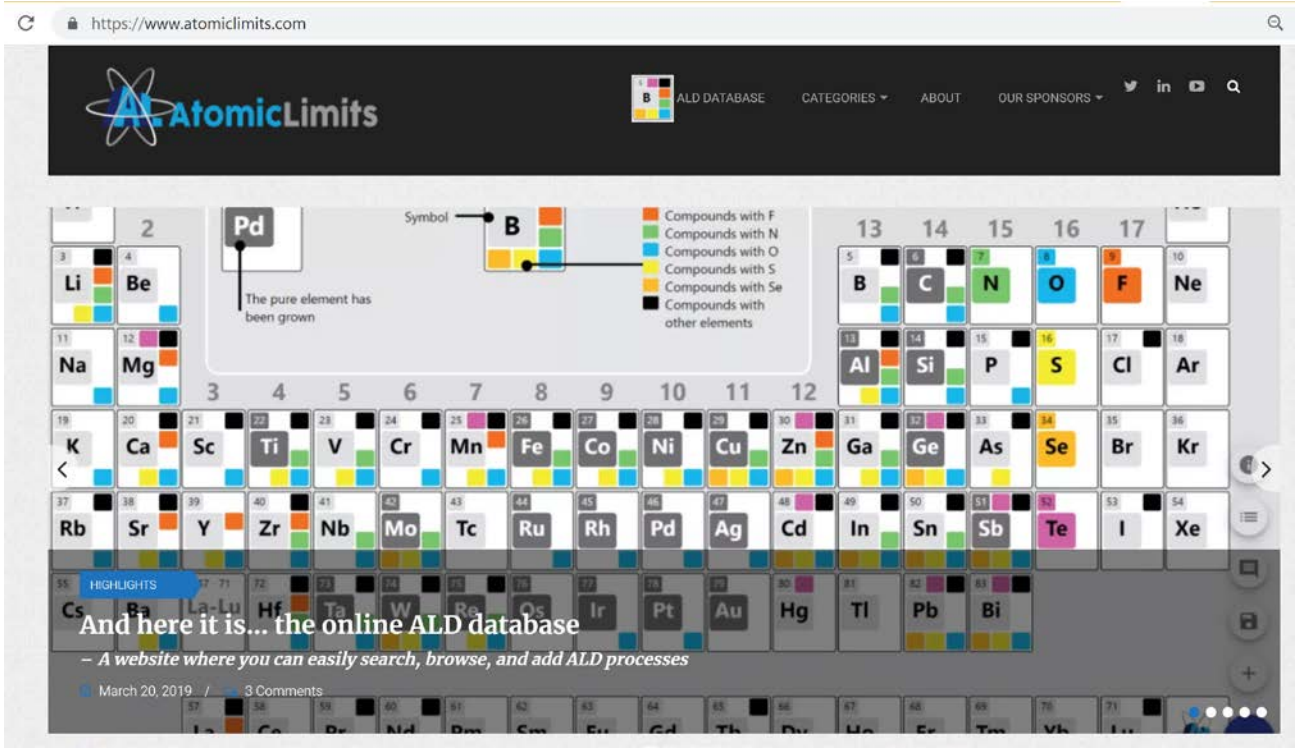
ALD materials over the years



ALD database DOI: https://doi.org/10.6100/alddatabase

The online ALD database – www.AtomicLimits.com

Crowd sourcing: Please add your (new) ALD processes



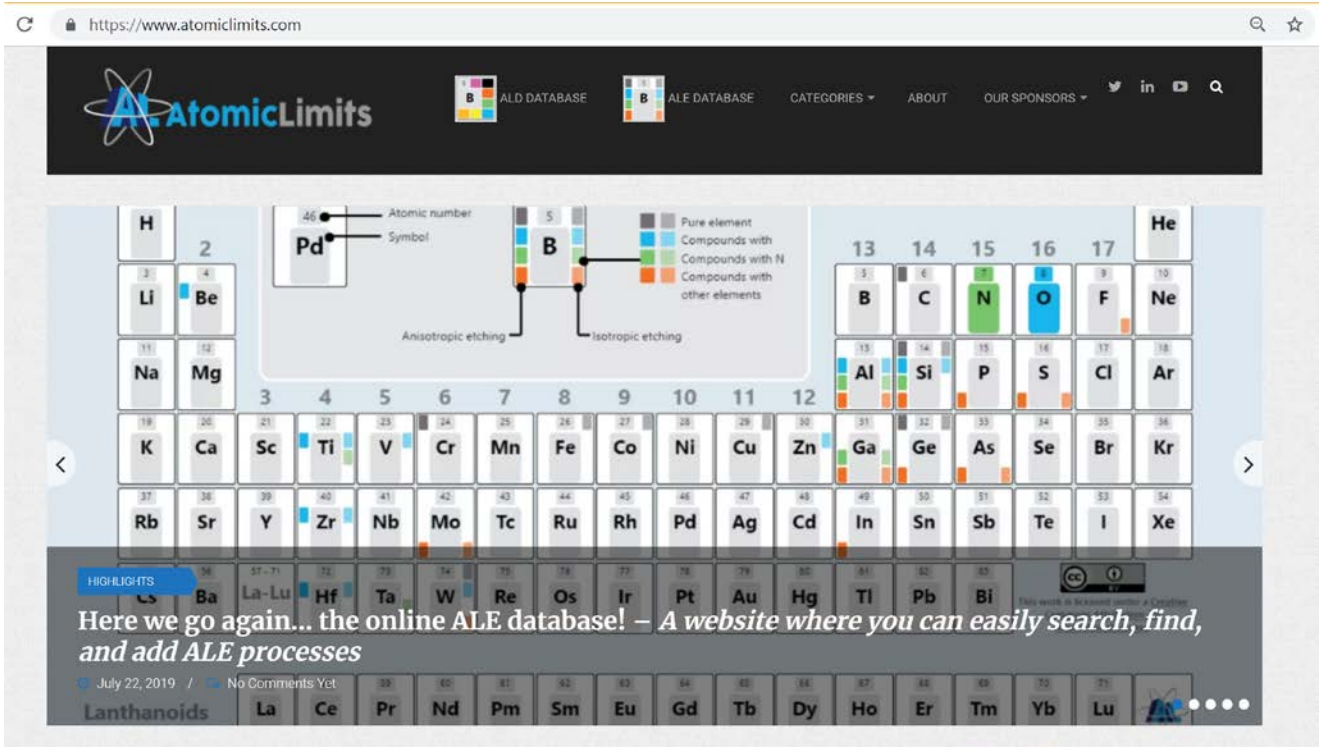
With direct links to publications

ALD database DOI: https://doi.org/10.6100/alddatabase
Content management by Vincent Vandalon, Bart Macco and Harm Knoops

TU/e

The online ALE database – www.AtomicLimits.com

Crowd sourcing: Please add your (new) ALE processes



With direct links to publications

ALE database DOI: https://doi.org/10.6100/alddatabase
Content management by Tahsin Faraz, Nick Chittock, and Adrie Mackus

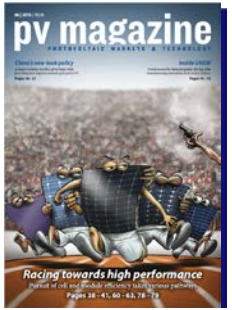
2. ALD is big in photovoltaics

- ALD storms market for PERC (silicon solar cells)
- High-volume manufacturing: batch ALD & spatial ALD
- Emerging: ALD for perovskite solar cells

ALD storms market for PERC (silicon solar cells)

Leadmicro's Kuafu batch ALD

Photo: Leadmicro



June 2019 edition

Atomic layer deposition storms market for PERC

"New Leadmicro Kuafu line designed to passivate 10,000 wafers an hour."

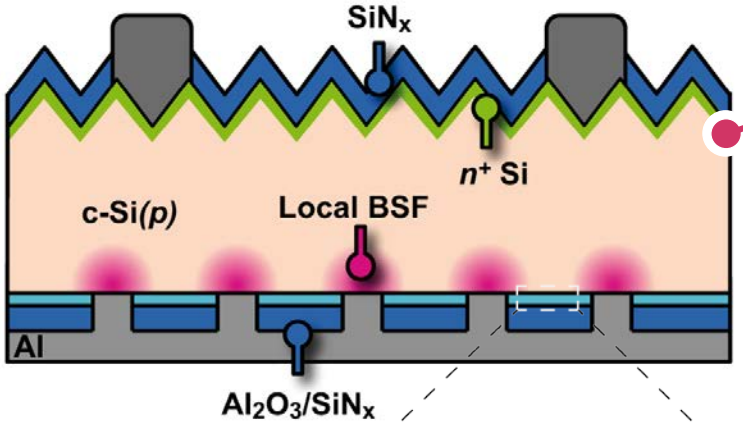
"Almost all major PV cell manufacturers in China now use our system."

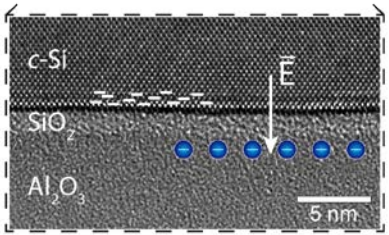
"We have so far equipped over 30 GW of manufacturing lines with ALD"

See Sunday: Tutorial about **ALD for photovoltaics** by Bart Macco

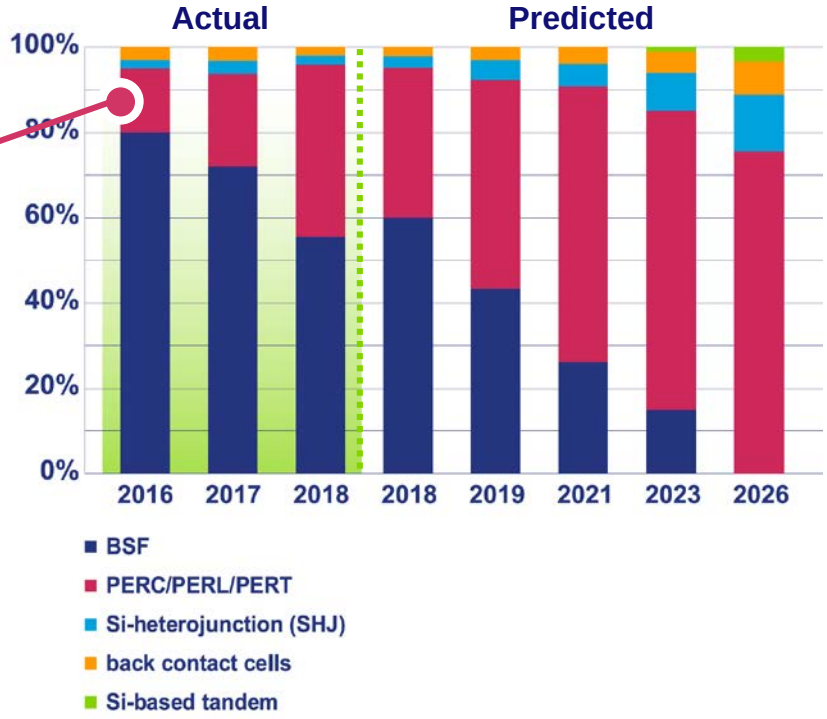
ALD for PERC silicon solar cells

PERC is the new standard in solar panels



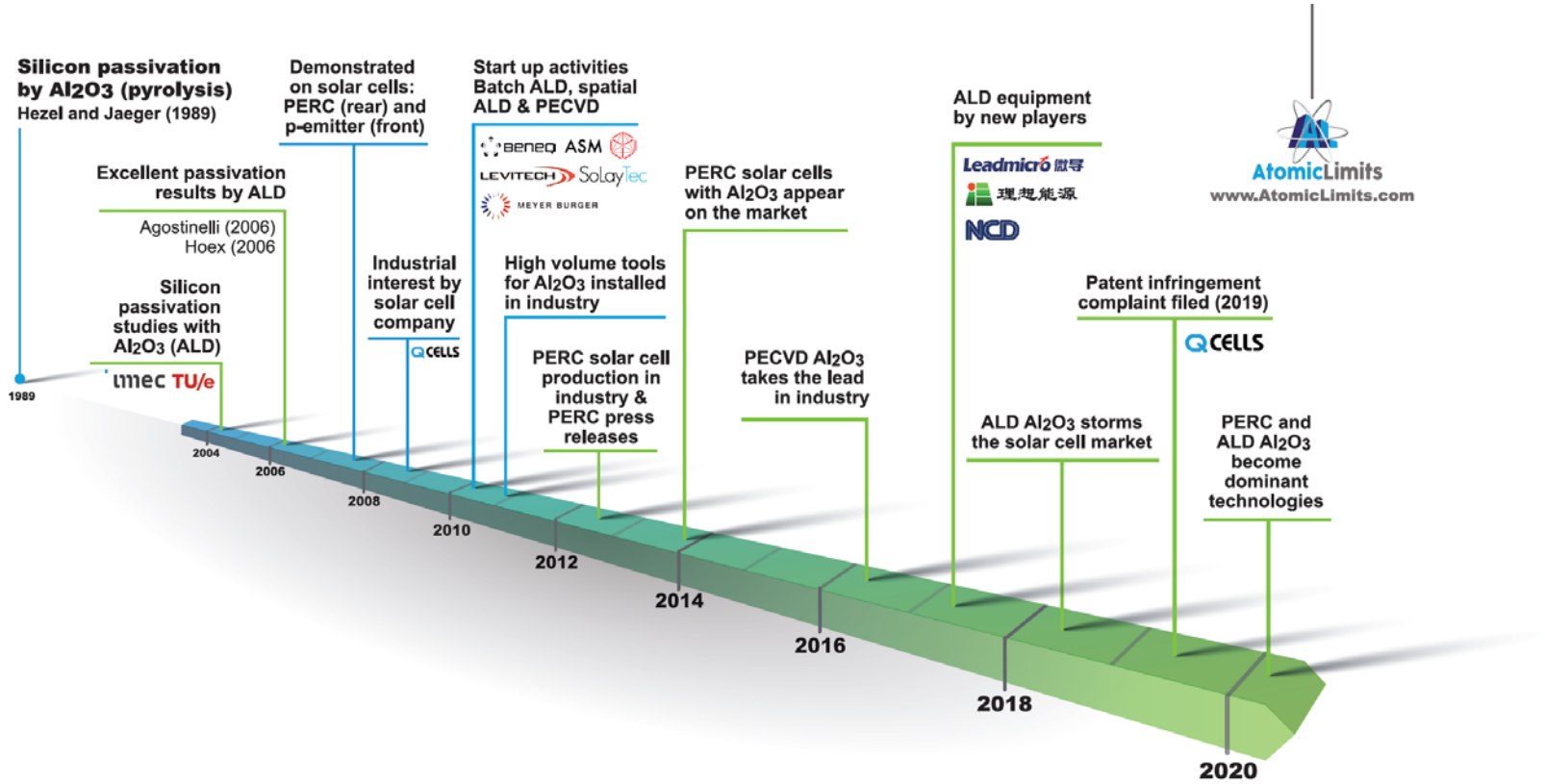


Chemical & field-effect passivation by Al_2O_3 nanolayers



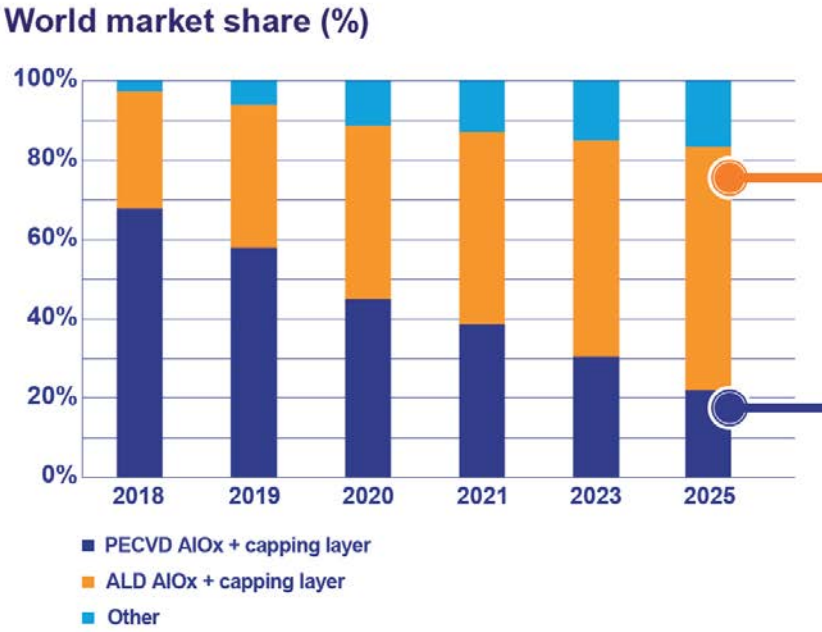
Dingemans *et al.*, J. Vac. Sci. Technol. A 30, 040802 (2012) – Review article
International Technology Roadmap for Photovoltaic, 10th ed. – March 2019

Timeline for (ALD) Al_2O_3 passivation



To appear on www.AtomicLimits.com for downloading

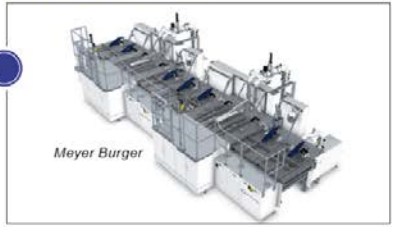
High-volume ALD in photovoltaics



Batch ALD Al_2O_3

Spatial ALD Al_2O_3

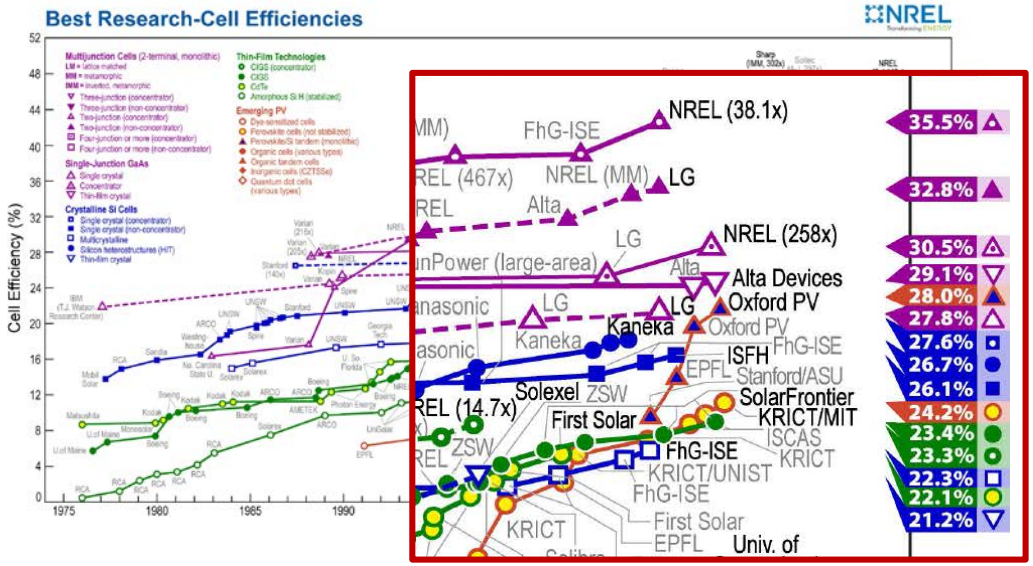
PECVD Al_2O_3



ALD soon to become the dominant technology?

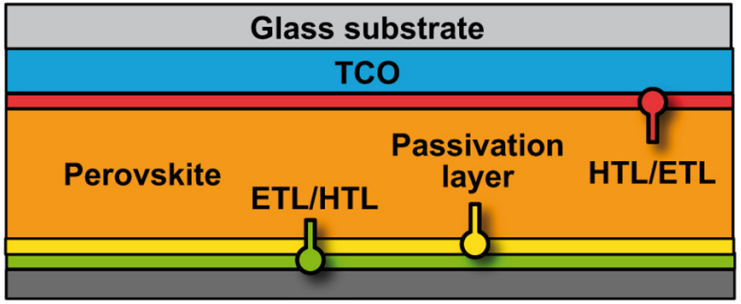
Many potential ALD applications in perovskite solar cells

Hybrid organic-inorganic absorber combined with inorganic nanolayers



Single-junction cells (only perovskite)

Tandem cells (silicon + perovskite)



Inorganic nanolayers (opportunities for ALD):

- Transparent conductive oxides (TCO)
- Electron transport layers (ETL)
- Hole transport layers (HTL)
- Encapsulation layers
- Passivation layers
- Buffer layers

https://www.nrel.gov/pv/cell-efficiency.html

TU/e

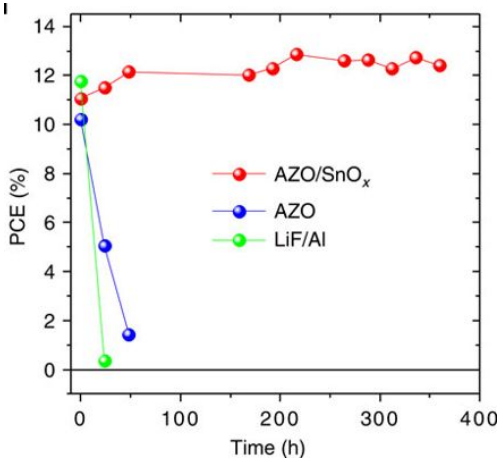
ALD SnO_2 enabling industrial & record perovskite solar cells

ALD SnO_2 is key for environmental stability, conformality, no sputter damage

Industrial upscaling:

Environmental stability is key

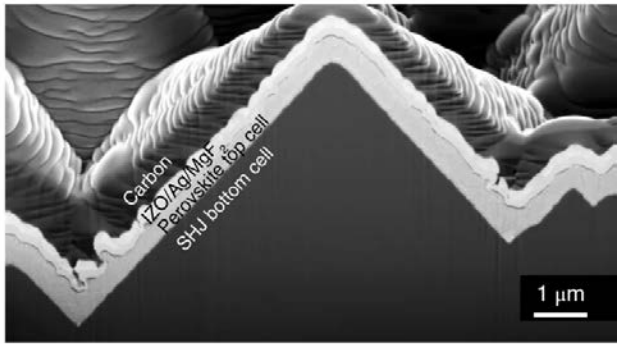
Industry is exploring spatial ALD and roll-to-roll ALD



Tandem-cells:

Conformality & no sputter damage

All recent record efficiency solar cells contain ALD SnO_2



Brinkmann *et al.*, Nat. Commun. 8, 13938 (2017)
Sahli *et al.*, Nat. Mater. 17, 820 (2018)

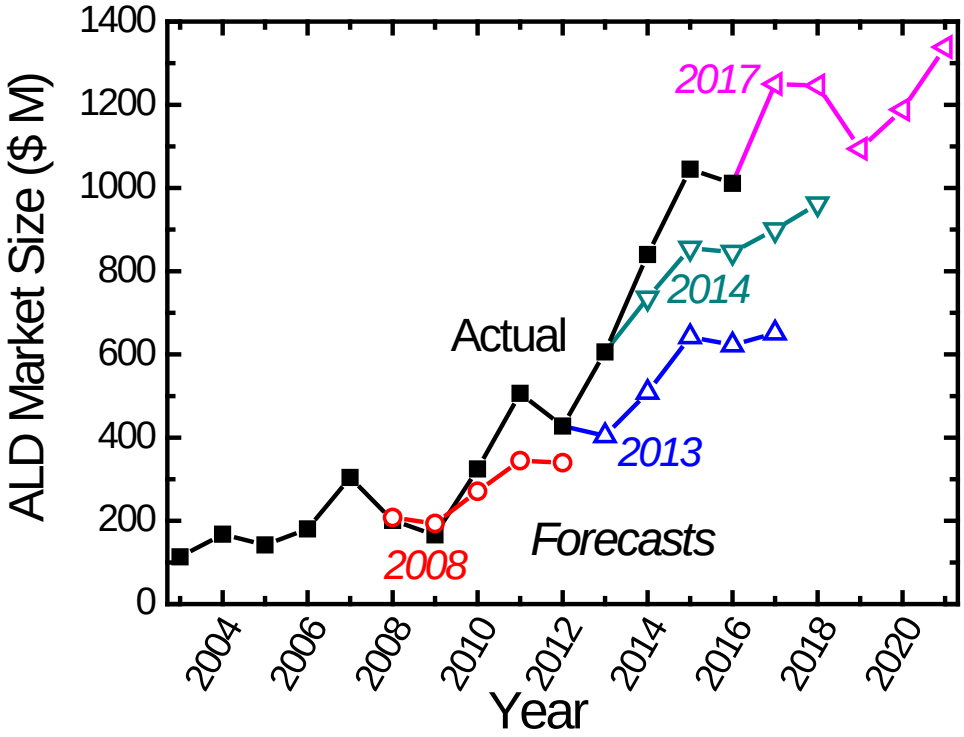
TU/e

3. Plasma ALD has become mainstream

- Self-aligned multiple patterning
- Low temperature deposition
- Trends in plasma ALD tools

ALD wafer fab equipment market size

Predictions have been beaten every time!

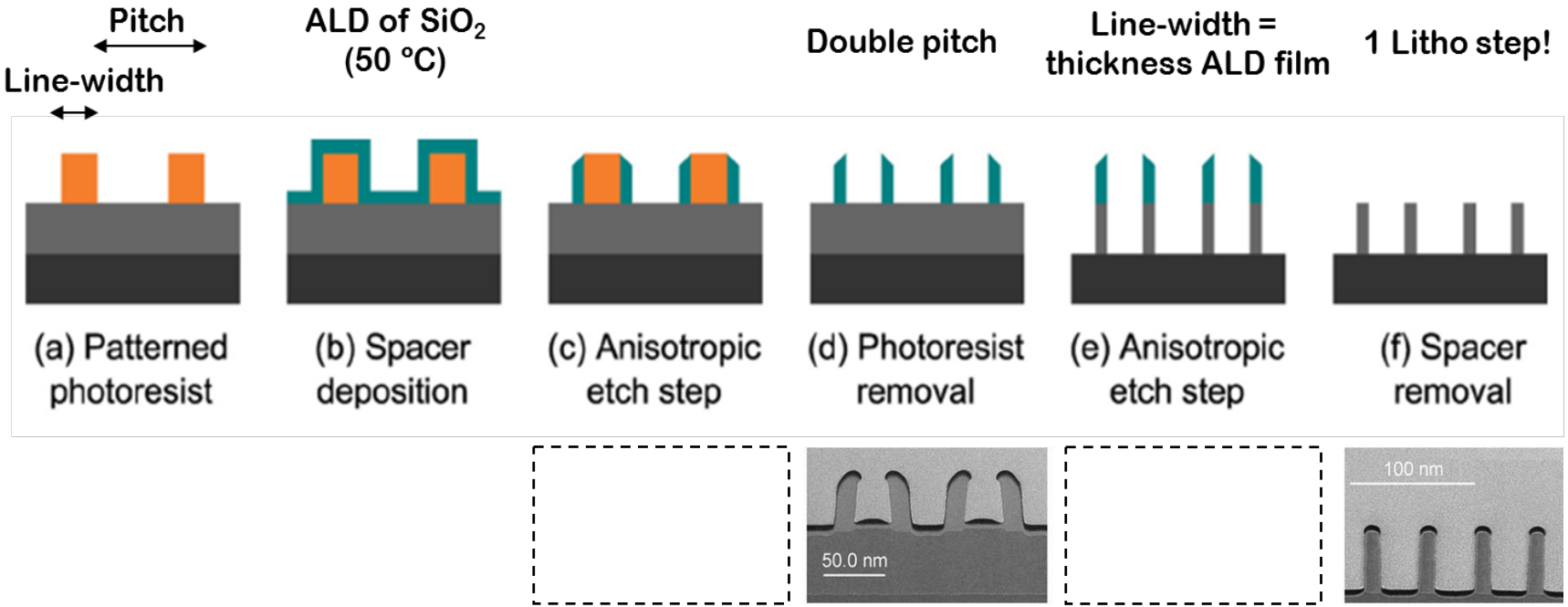


Knoops *et al.*, J. Vac. Sci. Technol. A 37, 030902 (2019) – Review article

TU/e

Patterning – a big (plasma) ALD market

Self-aligned double patterning (SADP) since the 22 nm node



Beynet *et al.*, Proc. of SPIE 7520, 75201J-1 (2009)

Altamirano-Sanchez *et al.*, SPIE Newsroom (2016)

TU/e

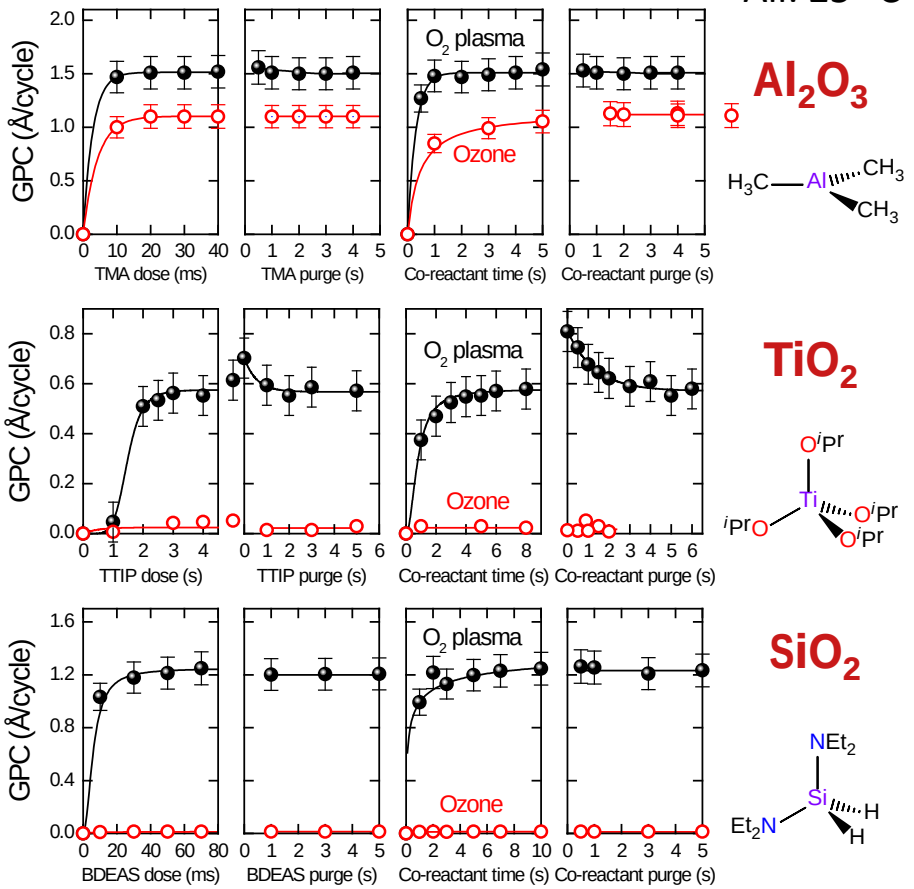
Plasma ALD for low T oxides

Well suited for low temperature ALD

For 25 – 100 ^{o}C range:

1. Processes available ✓
2. High quality films ✓
3. Short cycles with high GPC ✓
4. Excellent conformality (see later) ✓

All: 25 ^{o}C

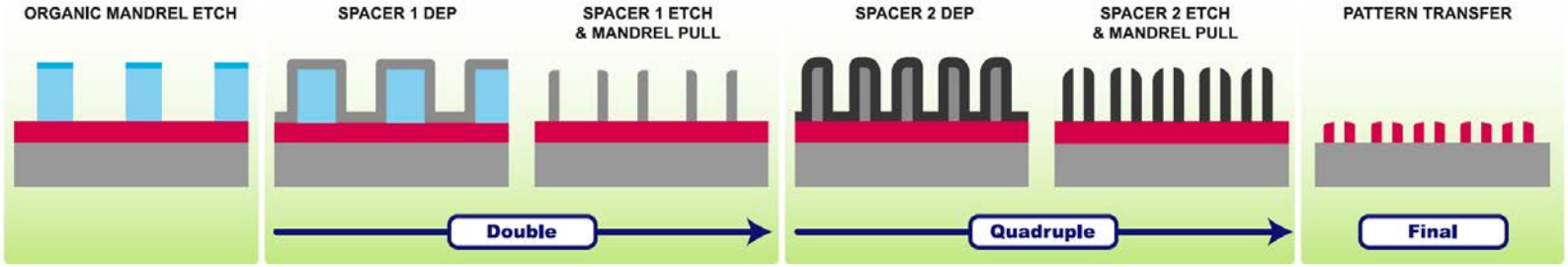


Potts *et al*., Chem. Vap. Deposition 19, 125 (2013)
Potts and Kessels, Coord. Chem. Rev. 257, 3254 (2013)

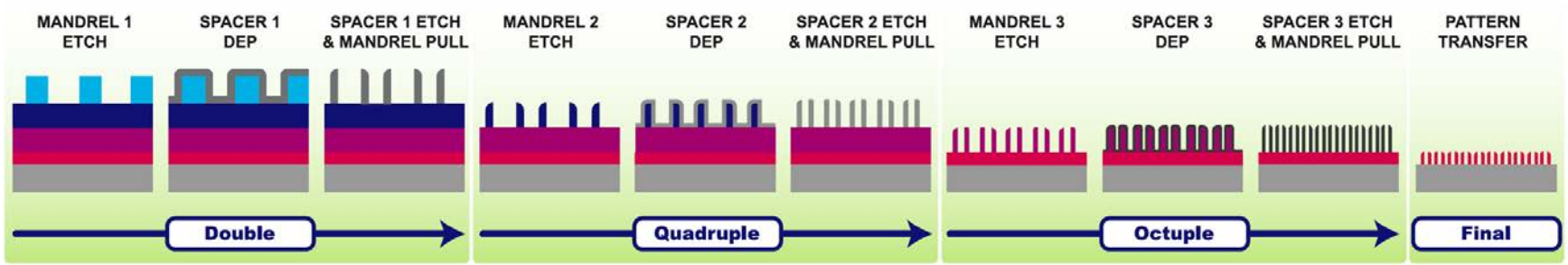
TU/e

Trends in self-aligned multiple patterning (SAxP)

SAQP – since 10 nm node – here: **spacer-on-spacer deposition**



SAOP – for (sub-)5 nm nodes – **193 nm immersion litho outperforms EUV litho**



Decoster *et al.*, Proc. of SPIE 10589, 105890E-1 (2018)

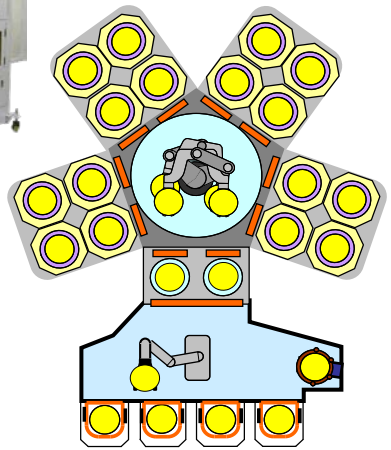
See blog about **ALD-enabled nanopattering** on www.AtomicLimits.com

TU/e

Trends in plasma ALD tools: high-volume direct plasma

Multi single-wafer ALD tools

ASM

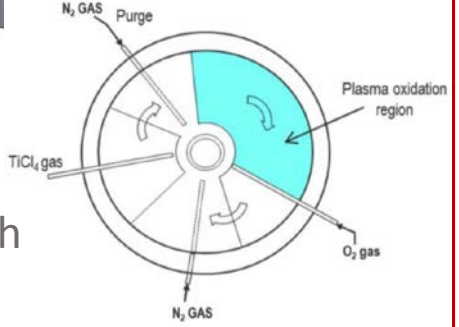


XP8 platform with
4 Quad Chamber
Modules (QCM)

© ASM 2019, used with permission

Spatial multi-wafer ALD tools

TEL



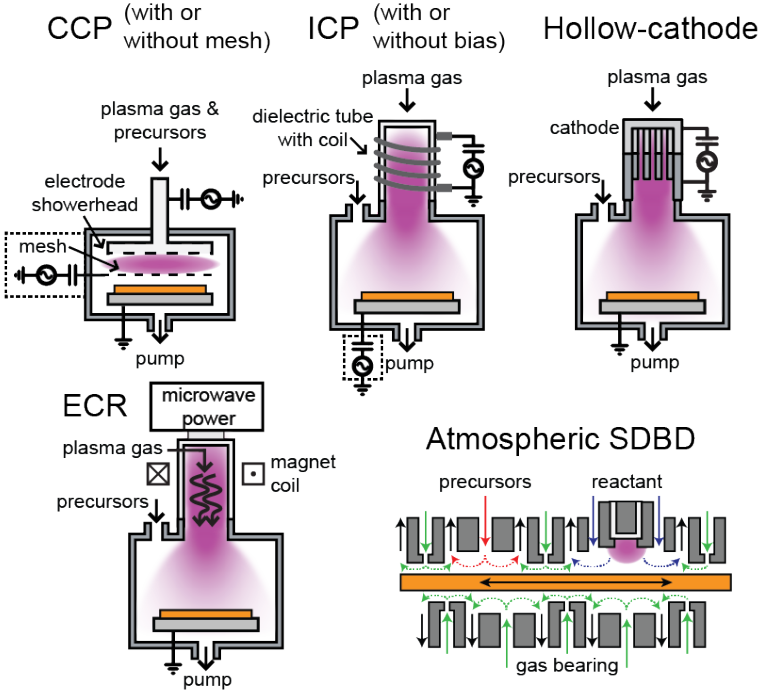
NT333™ with
2 chambers with
6 wafers each

www.tel.com

TU/e

Trends in plasma ALD tools: new plasma sources

Growing variety in plasma sources



Fast remote plasma ALD tools

Atomfab®

www.oxfordinstruments.com

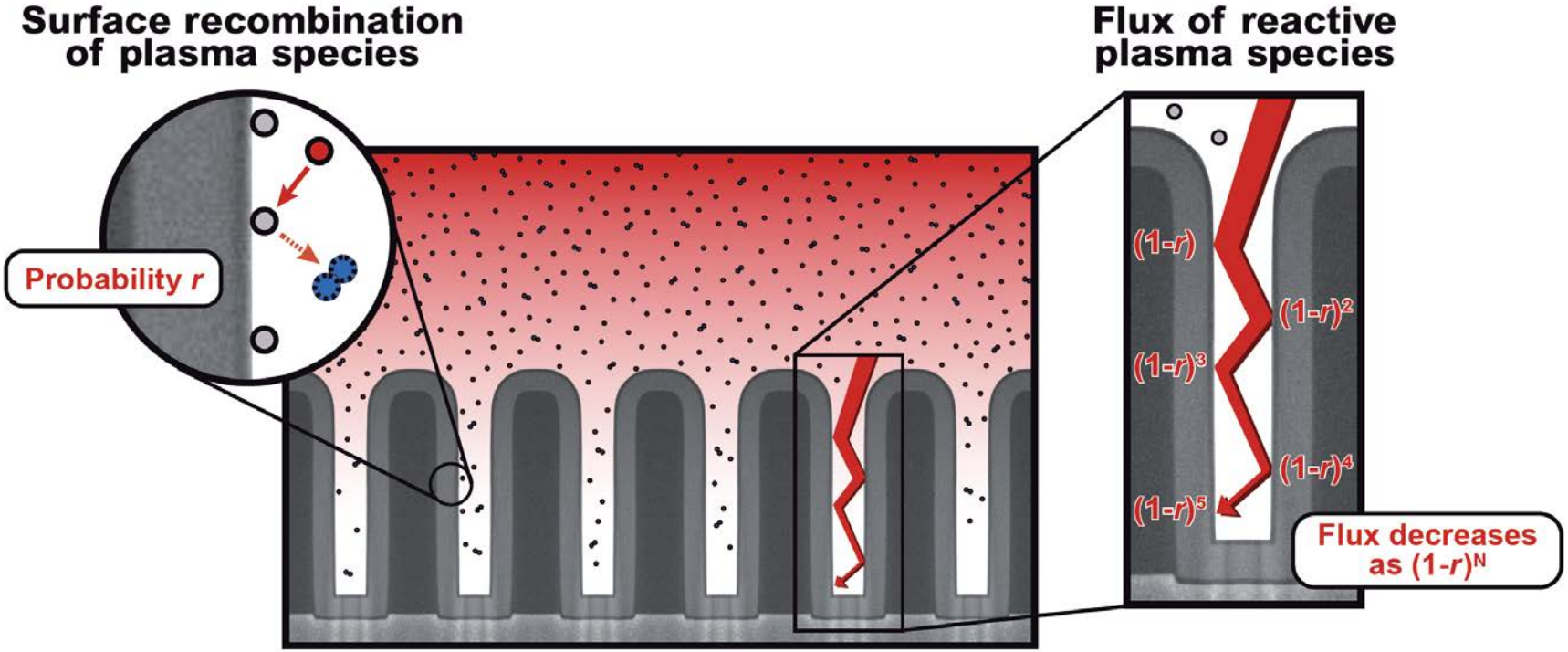
Knoops *et al.*, J. Vac. Sci. Technol. A 37, 030902 (2019) – Review article

4. Plasma ALD films can be very conformal

- Surface recombination probability
- Lateral high aspect ratio structures
- Quantitative data & TEM study

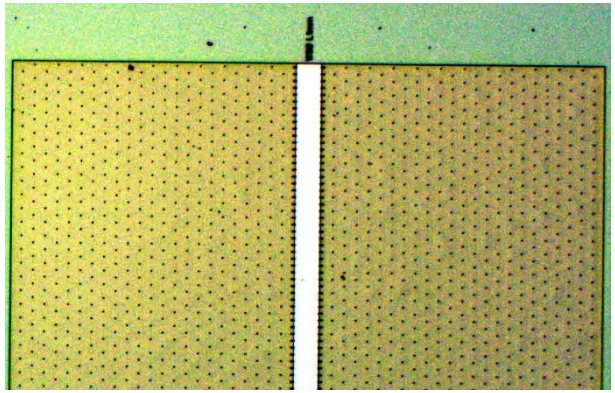
Plasma ALD: limited film conformality?

Surface recombination of plasma species reduces their flux in 3D structures

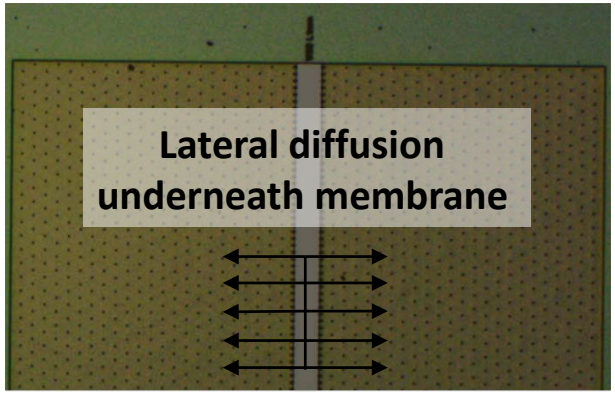


Lateral high aspect ratio structures

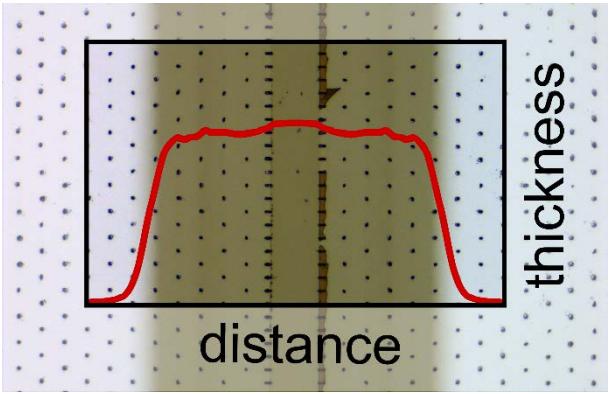
Initial structure

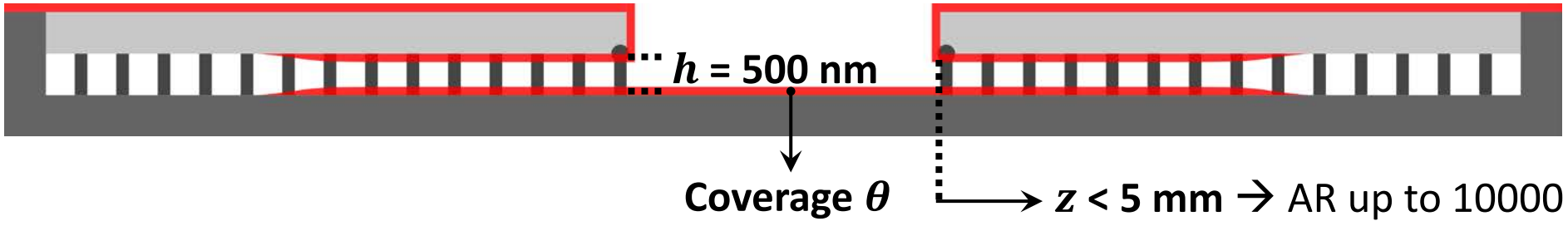


Deposition



Membrane removed





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

Very high conformality can be achieved for plasma ALD

Unpublished result
Please contact: w.m.m.kessels@tue.nl

See Tuesday: **AF-TuA02** by Karsten Arts

Arts *et al.*, to be published (2019)

Plasma ALD of SiO_2-TiO_2-Al_2O_3 laminate on trench

Surface recombination probability r is sufficiently low for demanding applications

Unpublished result
Please contact: w.m.m.kessels@tue.nl

Karsten Arts

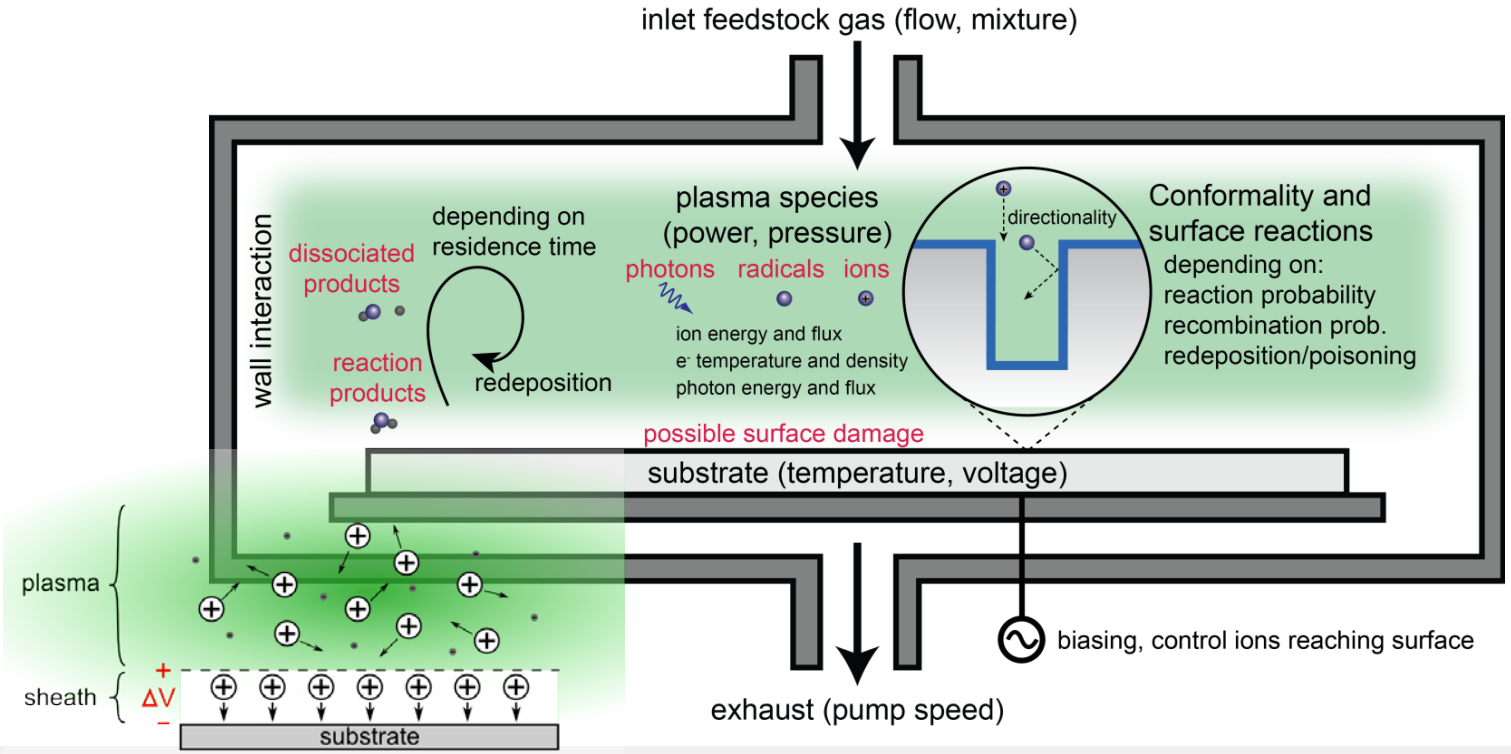
See Tuesday: **AF-TuA02** by Karsten Arts

5. Ion bombardment yields opportunities for ALD

- Plasma-surface interaction
- Ion energy control by rf substrate biasing
- Topographically- and property-selective deposition

Plasma ALD fundamentals

Complex plasma-surface interaction: damage by energetic ions & photons?

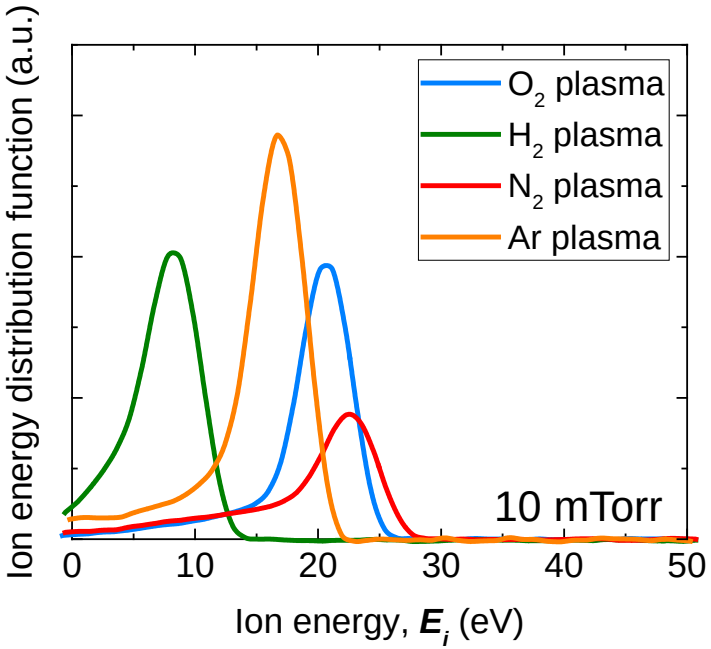


Knoops *et al.*, J. Vac. Sci. Technol. A 37, 030902 (2019) – Review article

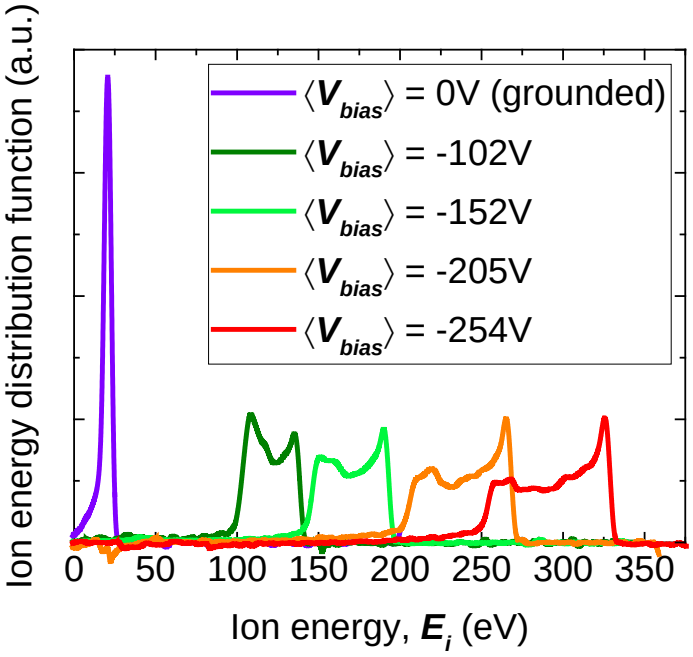
TU/e

Ion energy during plasma ALD (with and without biasing)

Grounded substrate – various plasmas
ion energy < 30 eV



RF substrate biasing – O_2 plasma
ion energy up to 350 eV



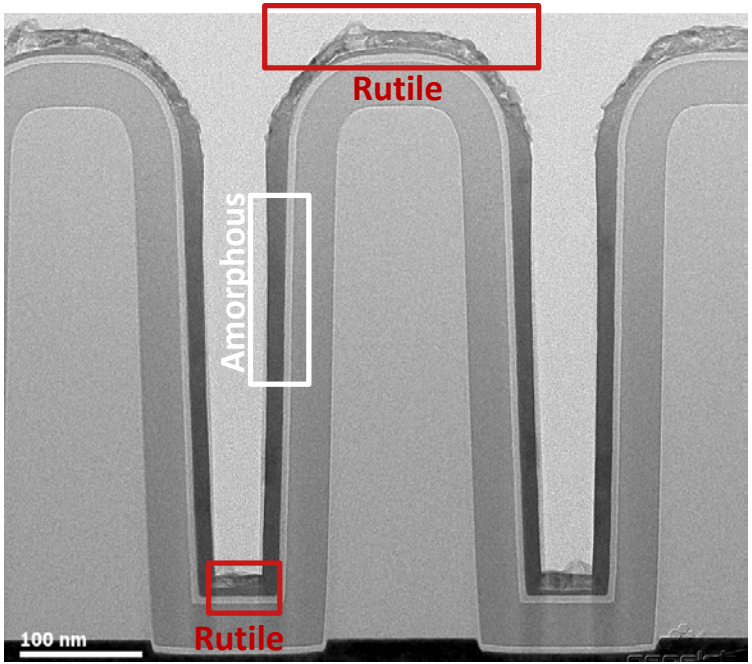
Commercial ALD systems with rf biasing: Oxford Instruments & Sentech
See blog about **substrate biasing during ALD** on www.AtomicLimits.com
Faraz *et al.*, Plasma Sources Sci. Technol. 28, 024002 (2019)

TU/e

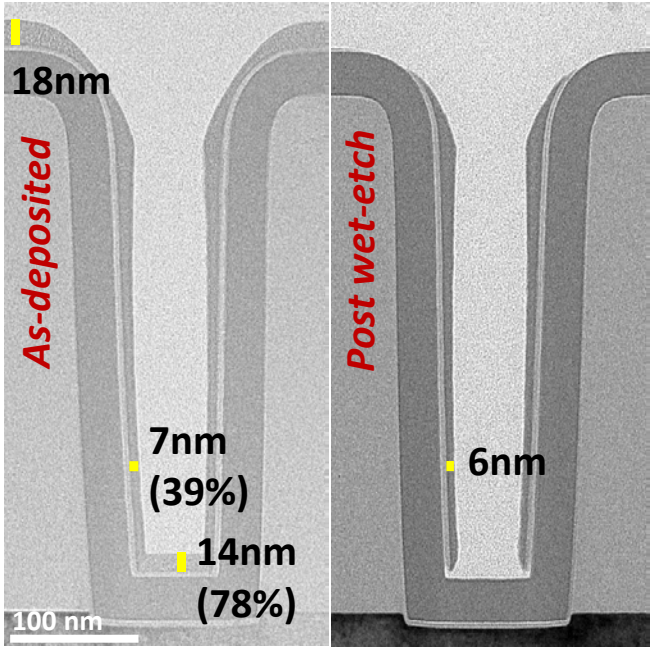
Energetic (directional) ions: Topographically-selective ALD

TEM cross-section (AR = 4.5:1)

TiO_2 with 205 eV directional ions
(Stage temperature = 150 °C)



SiN_x with 65 eV directional ions
(Stage temperature = 500 °C)

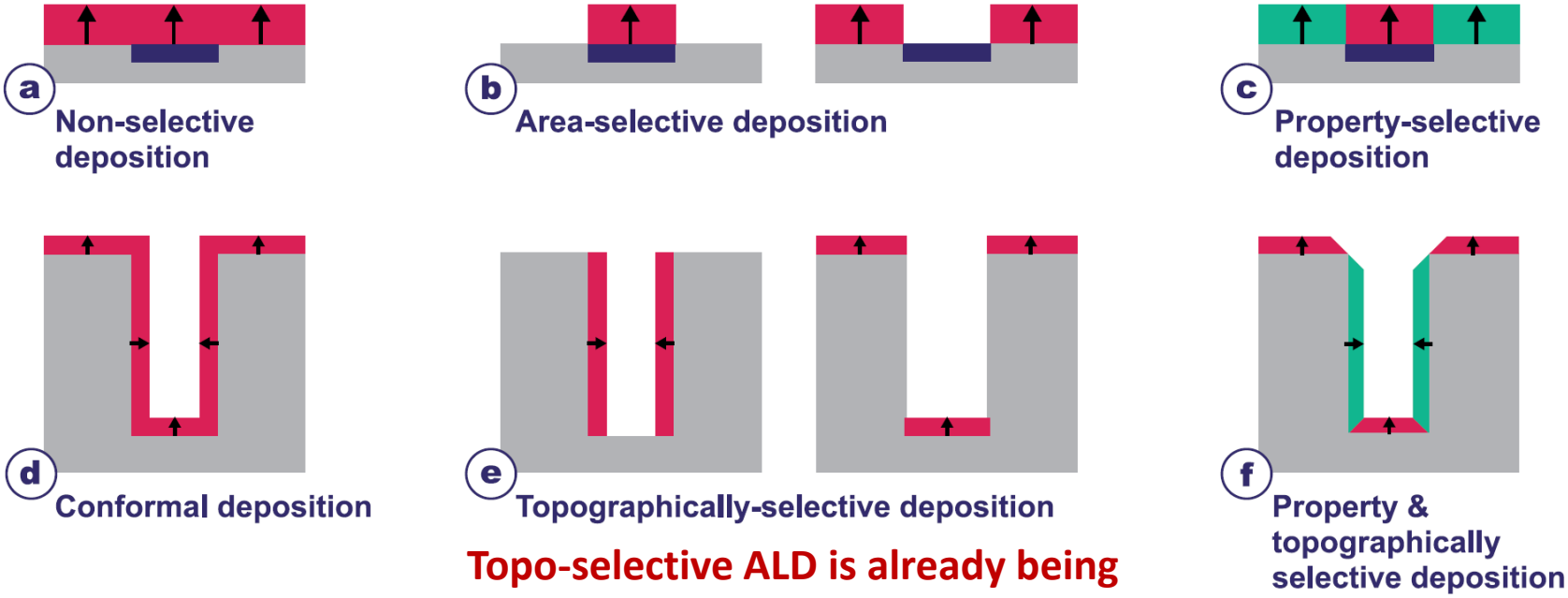


Faraz *et al.*, ACS Appl. Mater. Interfaces 10, 13158 (2018)

TU/e

Toolbox for selective deposition

Trends: Area-selective – Topo-selective – Property-selective – …



Topo-selective ALD is already being used in 3D NAND production

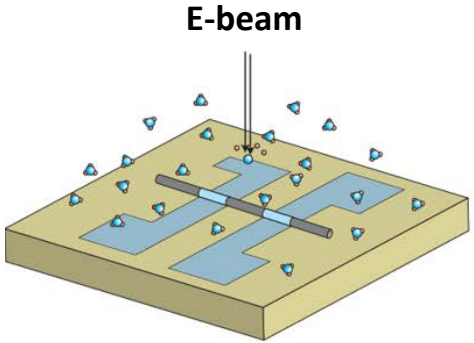
6. Area-selective deposition is trending

- Nanopatterning vs. self-aligned fabrication
- Fully self-aligned via as “killer” application
- Area-selective ALD of SiO_2 and Ru (preview)

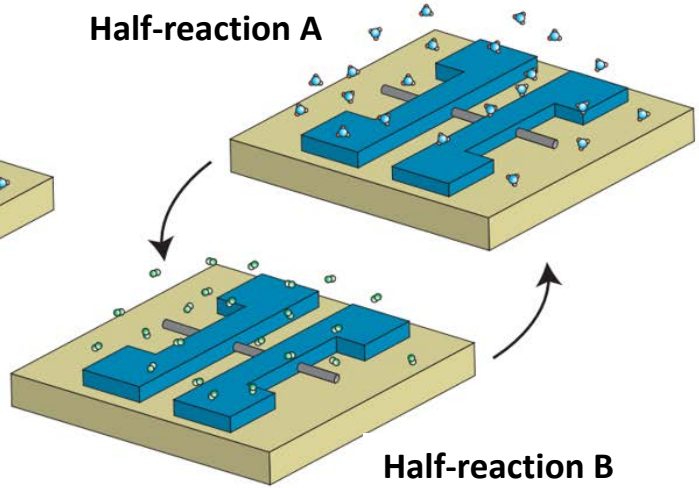
Area-selective ALD & nanopatterning (Pt contacts)

Patterning by e-beam deposition of Pt seed layer followed by area-selective ALD

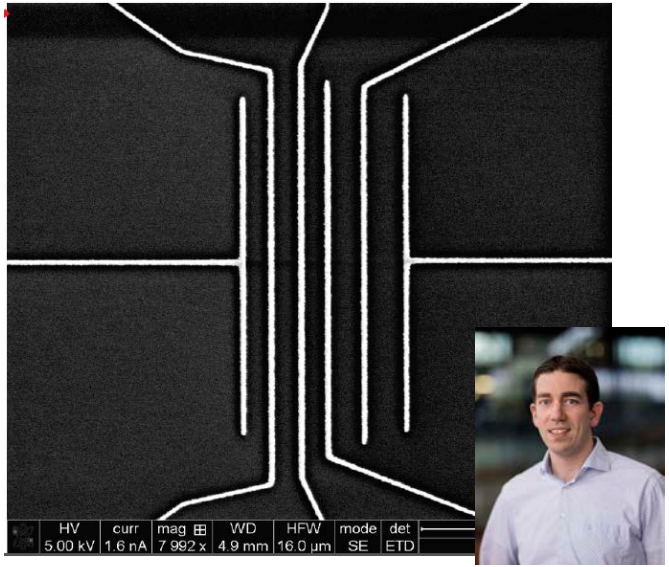
1) Pattern formation



2) Area-selective ALD



Carbon nanotube FET with Pt contacts

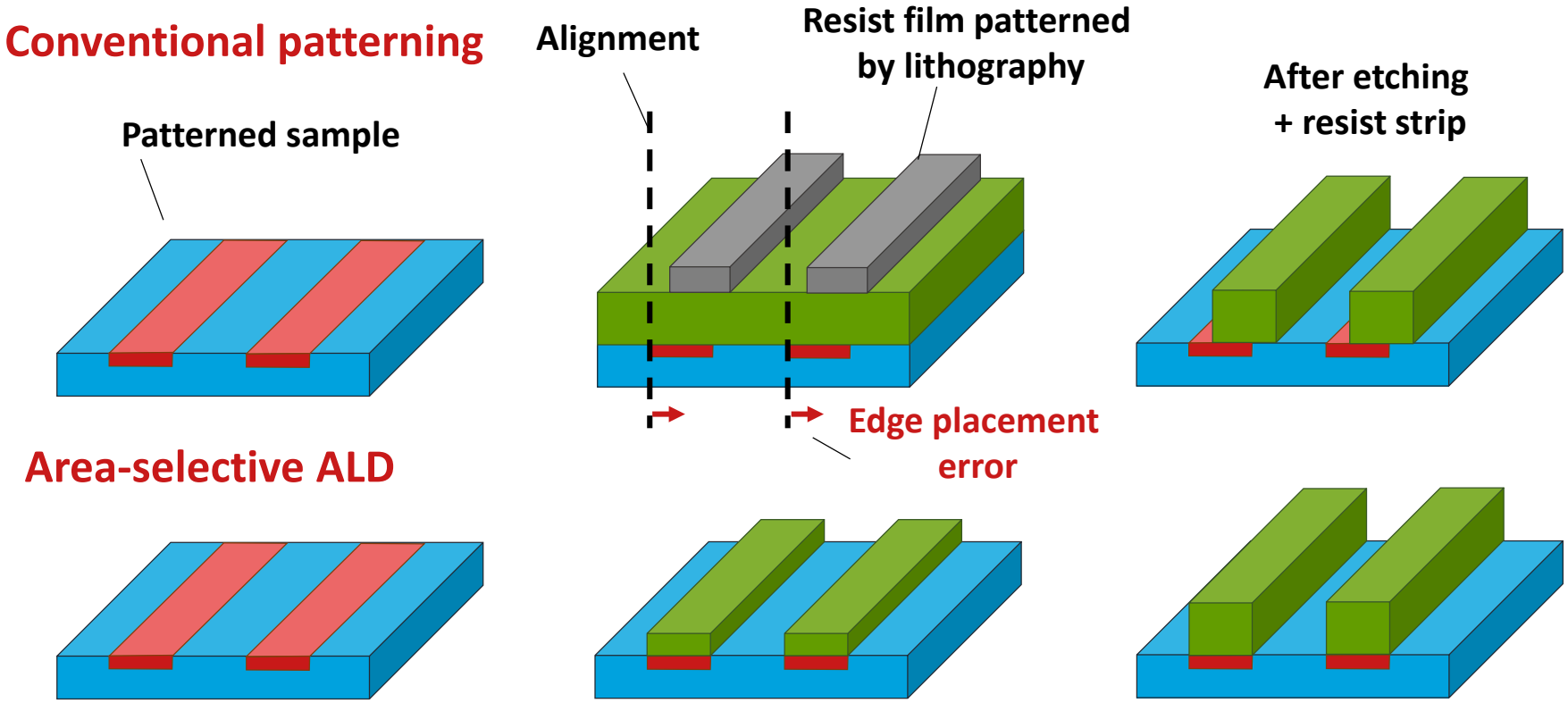


Adrie Mackus

Mackus *et al.*, J. Appl. Phys. 107, 116102 (2010)
Mackus *et al.*, Appl. Phys. Lett. 110, 013101 (2017)

TU/e

Area-selective ALD for self-aligned fabrication



Mackus *et al*., Nanoscale 6, 10941 (2014) – Review article

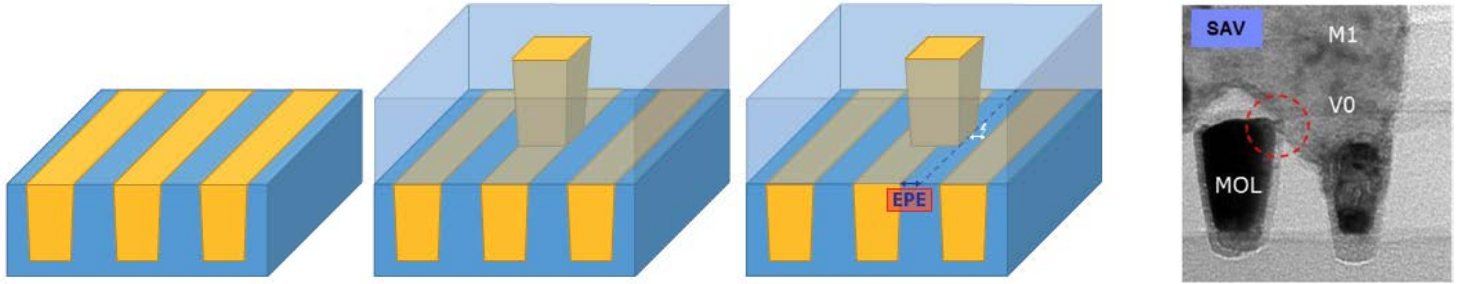
Mackus *et al*., Chem. Mater. 31, 2 (2019) – Perspective article

TU/e

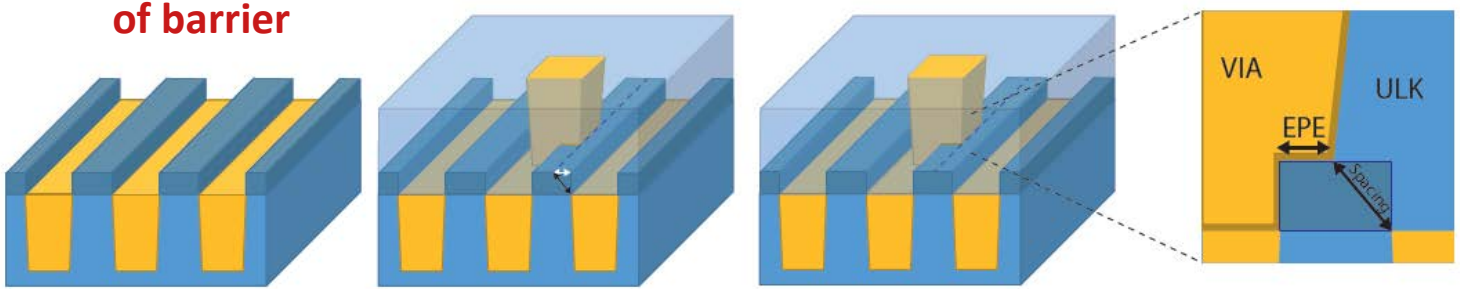
Fabrication of fully self-aligned vias (FSAV)

Desired:
aligned vias

In practice:
Edge placement error (EPE)



Area-selective ALD of barrier

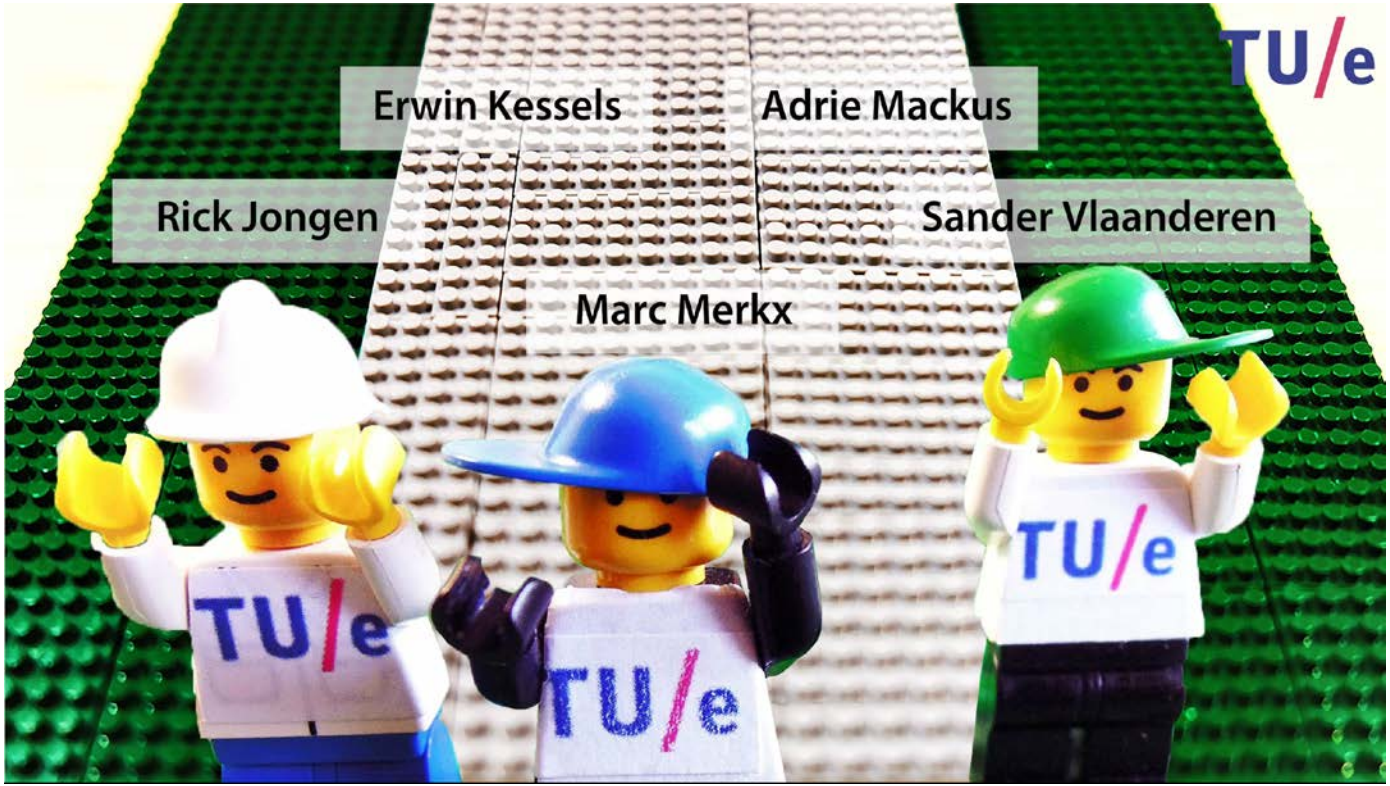


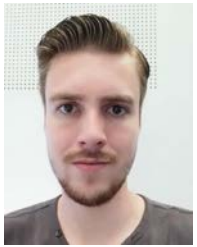
Briggs *et al.*, IEEE, IEDM17-338 (2017)

See blog about **fully self-aligned vias** on www.AtomicLimits.com

TU/e

Selective blocking by inhibitors in ABC cycles (ALD of SiO_2)





Marc Merkx

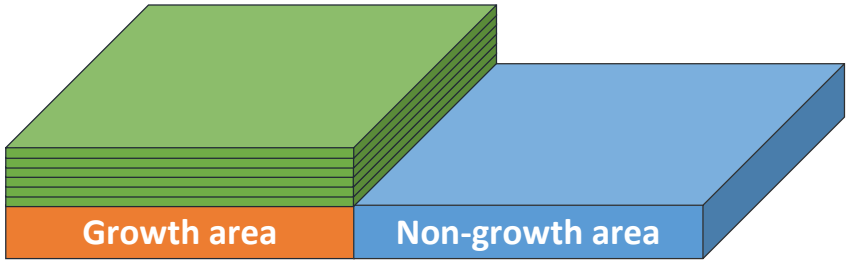
See Tuesday: **AS1-TuA05** by Marc Merkx

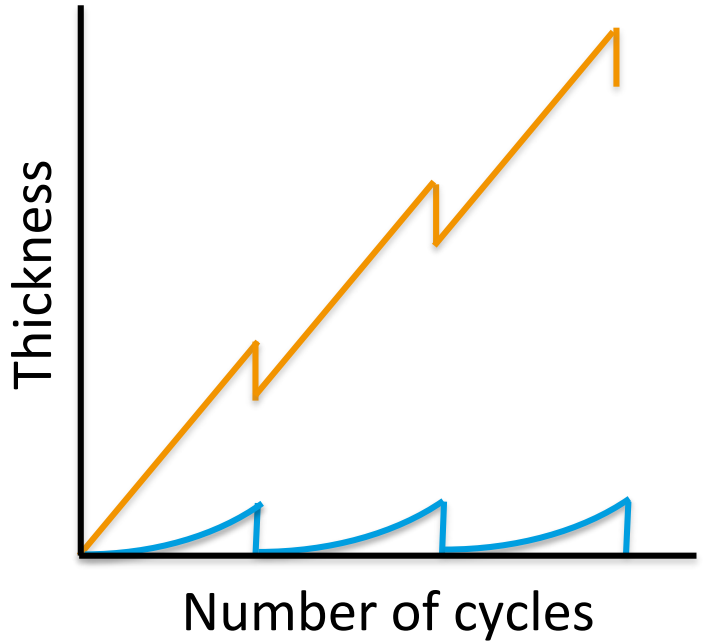
Mameli *et al.*, ACS Nano 11, 9303 (2017)

See blog about **area-selective ALD movie** on www.AtomicLimits.com

TU/e

Combining ALD with etching in supercycles (ALD of Ru)



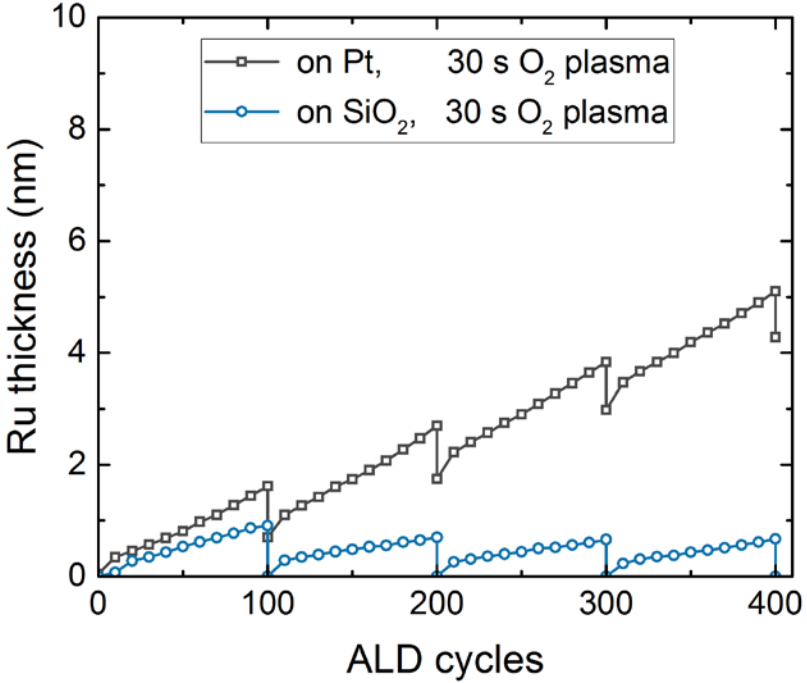


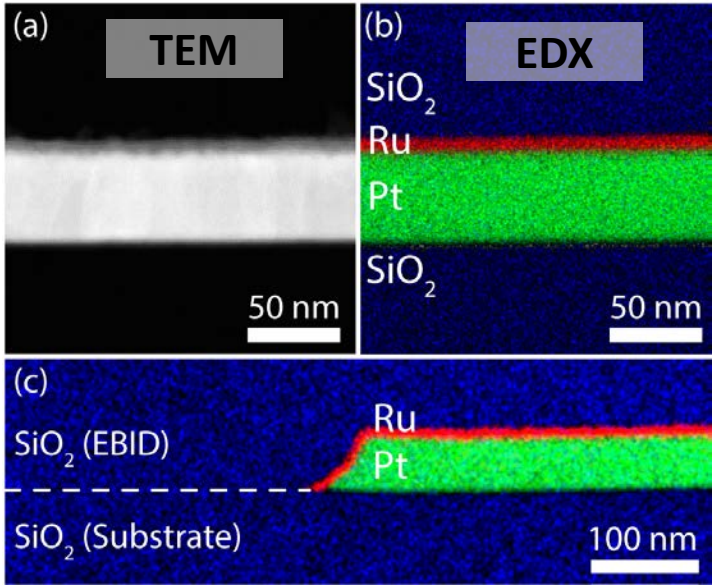
See blog about **area-selective deposition** on www.AtomicLimits.com

Vos *et al*., Chem Mater. 31, 3878 (2019)

Combining ALD with etching in supercycles (ALD of Ru)

Area-selective ALD on Pt (Ru) growth area & not on SiO_2 non-growth area





Martijn Vos

See Tuesday: **AS2-TuA111** by Martijn Vos

Vos *et al.*, Chem Mater. 31, 3878 (2019)

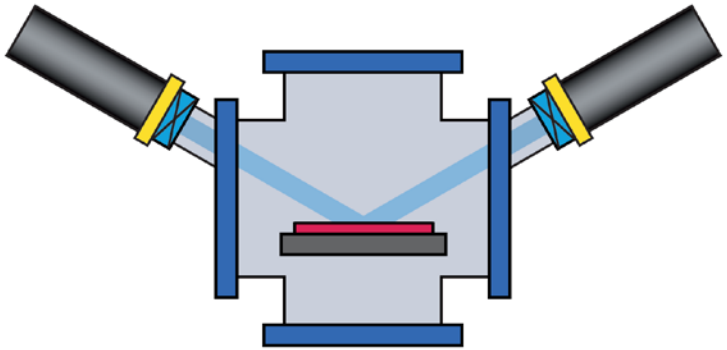
TU/e

7. ALD fundamentals: Need for quantitative data

- *In situ* studies of ALD processes and reaction mechanisms
- Monitoring film growth - *in situ* spectroscopic ellipsometry
- Initial growth & sticking probabilities – broadband sum frequency

In situ studies of ALD processes & reaction mechanisms

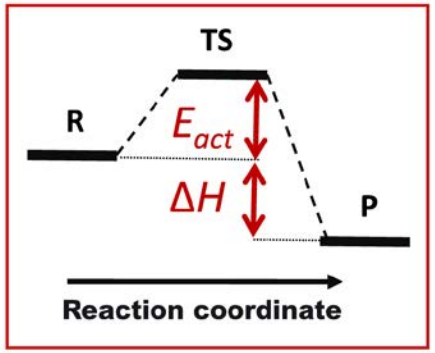
In situ studies

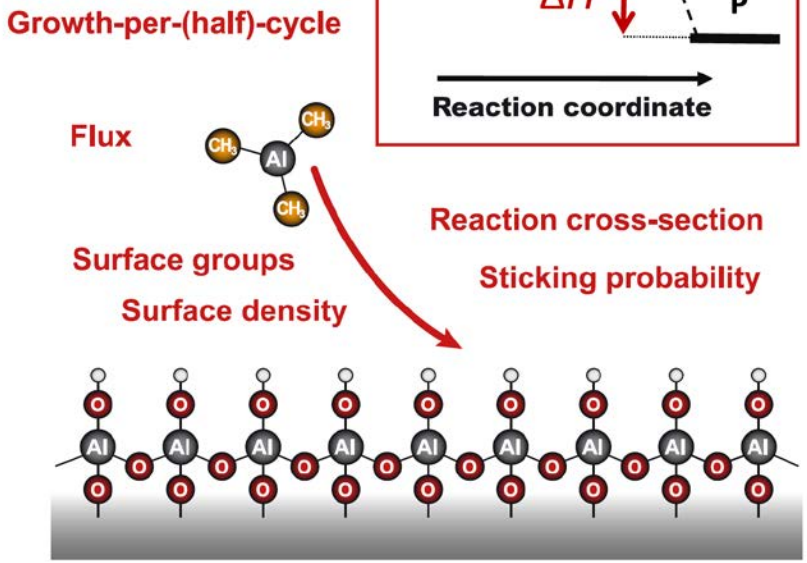


Methods:

- Quartz crystal microbalance
- Spectroscopic ellipsometry
- Gas phase infrared spectroscopy*
- Surface infrared spectroscopy
- X-ray photoelectron spectroscopy
- Etc. etc.

Data to understand reaction mechanisms



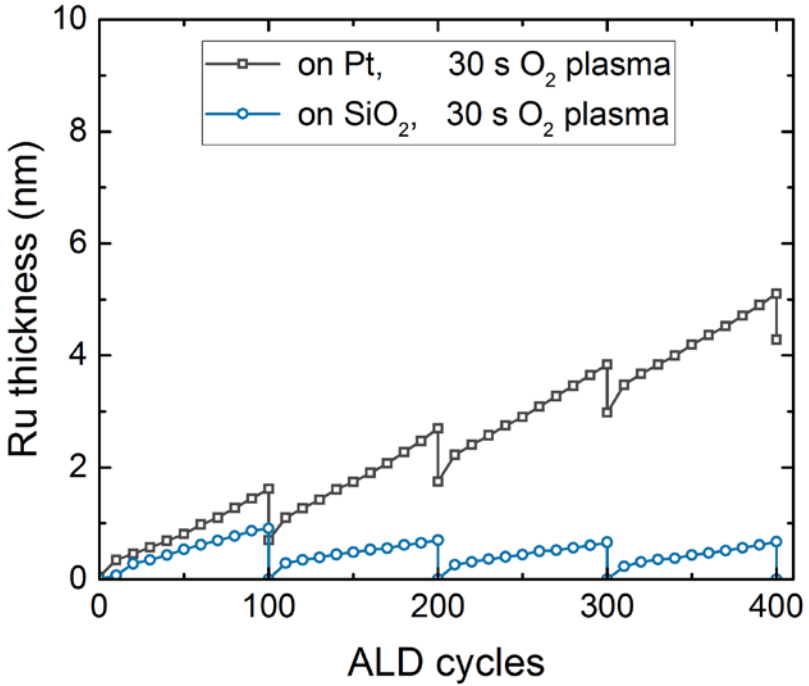


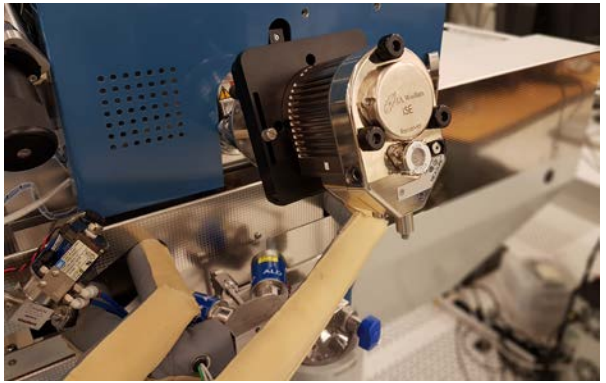
* See Tuesday: **AF1-TuM05** by Maria Mione

See blog about ***in situ* studies of ALD processes** on www.AtomicLimits.com

In situ spectroscopic ellipsometry

Monitoring film growth and material properties





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

See blog about **ellipsometry and ALD** on www.AtomicLimits.com

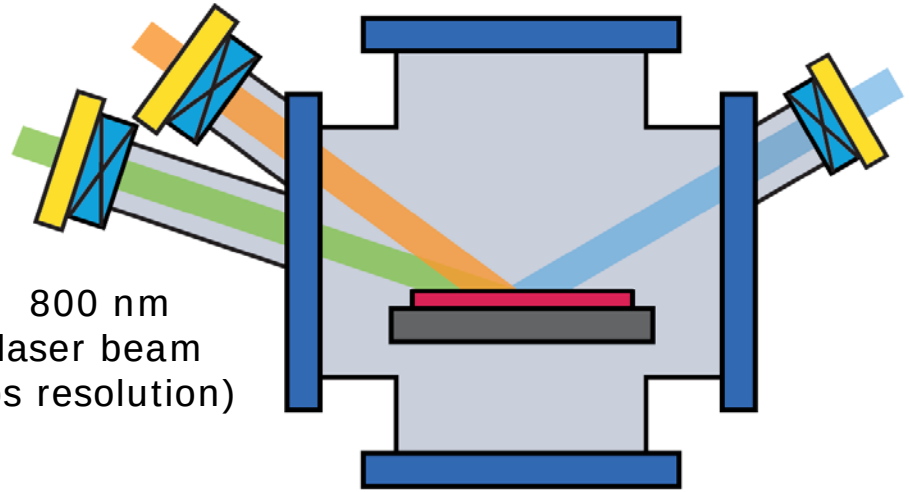
In situ broadband sum frequency generation

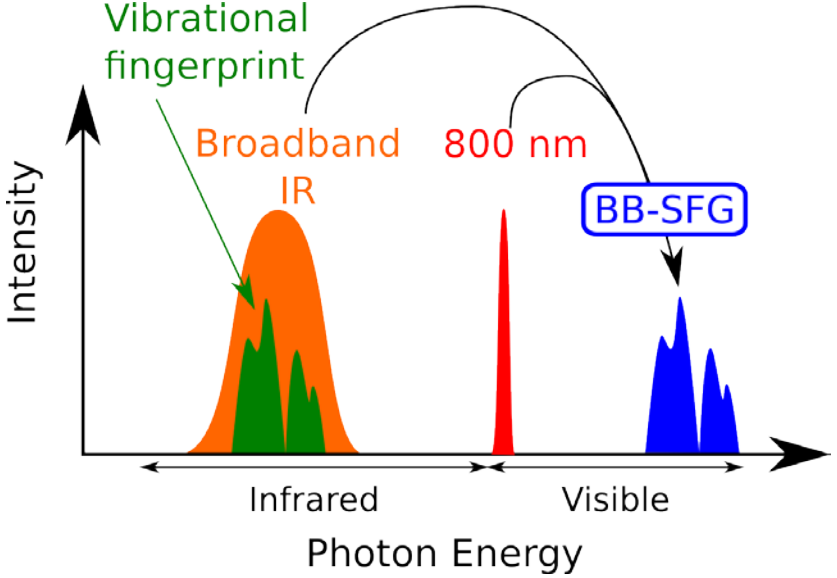
Monitoring surface groups by advanced (highly sensitive) infrared spectroscopy

Tunable IR laser beam
(broadband, fs resolution)

Sum-frequency radiation
(broadband, fs resolution)

$\hbar\omega_{IR} + \hbar\omega_{VIS} = \hbar\omega_{SFG}$



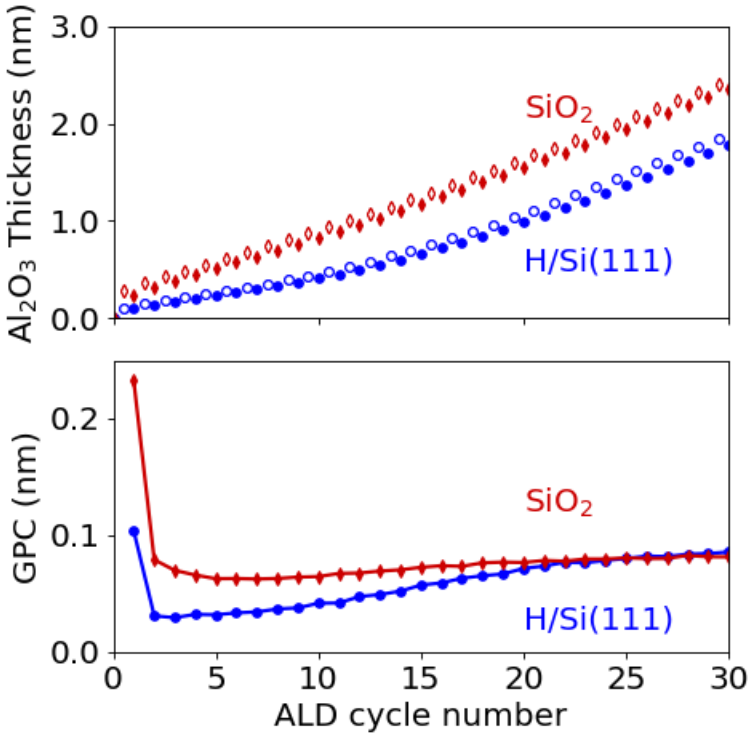


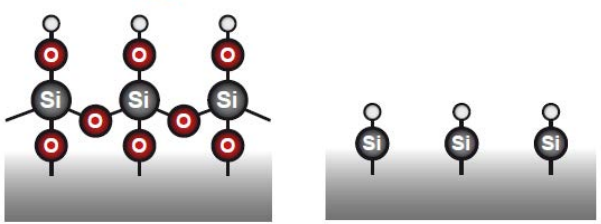
Vandalon and Kessels, Appl. Phys. Lett. 108, 011607 (2016)
Vandalon and Kessels, J. Vac. Sci. Technol. A 35, 05C313 (2017)

TU/e

In situ broadband sum frequency generation

Studying initial growth & extracting sticking probabilities S_0 per cycle





Cycle	SiO_2		Si(111):H	
	S_0^{TMA}	S_0^{H2O}	S_0^{TMA}	S_0^{H2O}
1st	**1.2×10^{-3}**	2.4×10^{-5}	**1.9×10^{-3}**	
2nd	3.6×10^{-3}	2.3×10^{-5}		
3rd	3.6×10^{-3}	2.4×10^{-5}		
Steady regime	3.9×10^{-3}	2.2×10^{-5}	3.9×10^{-3}	2.2×10^{-5}

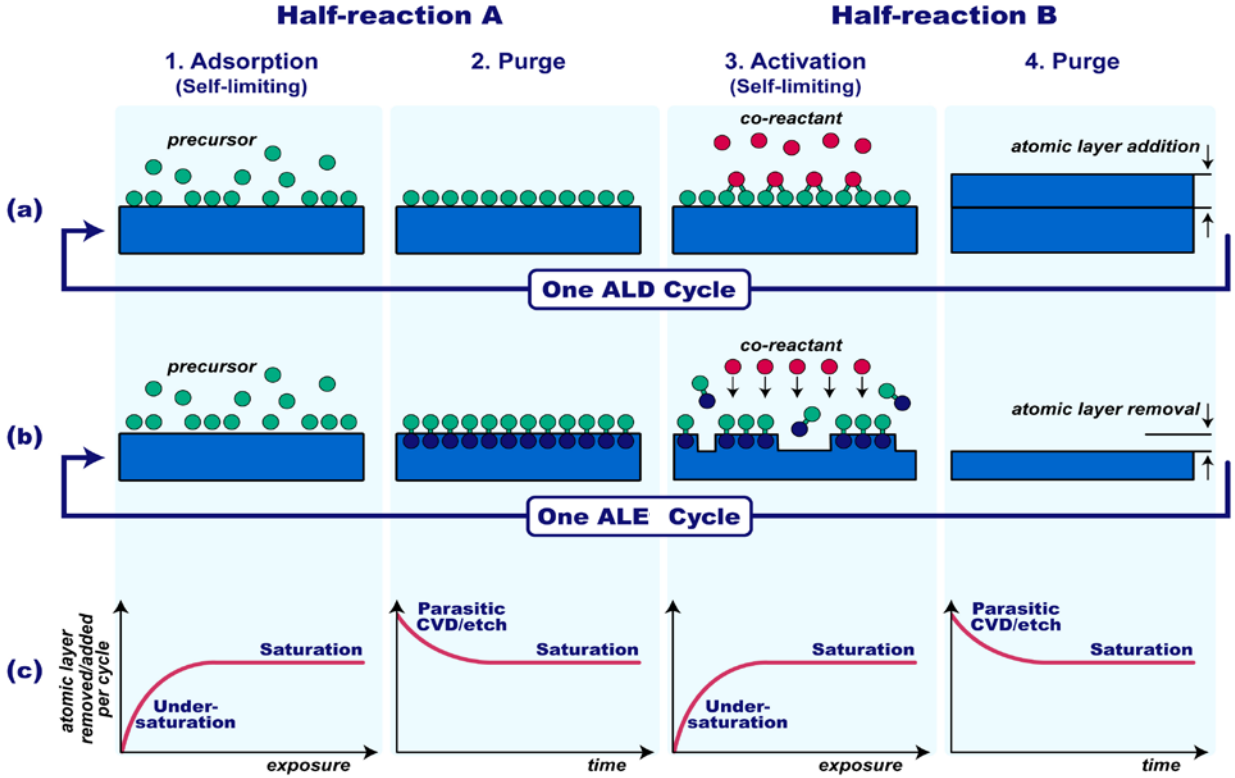
Vandalon and Kessels, J. Vac. Sci. Technol. A 35, 05C313 (2017)
Vandalon and Kessels, Langmuir 35 (2019) - ASAP
(https://doi.org/10.1021/acs.langmuir.9b01600)

TU/e

8. Atomic layer etching is becoming vital

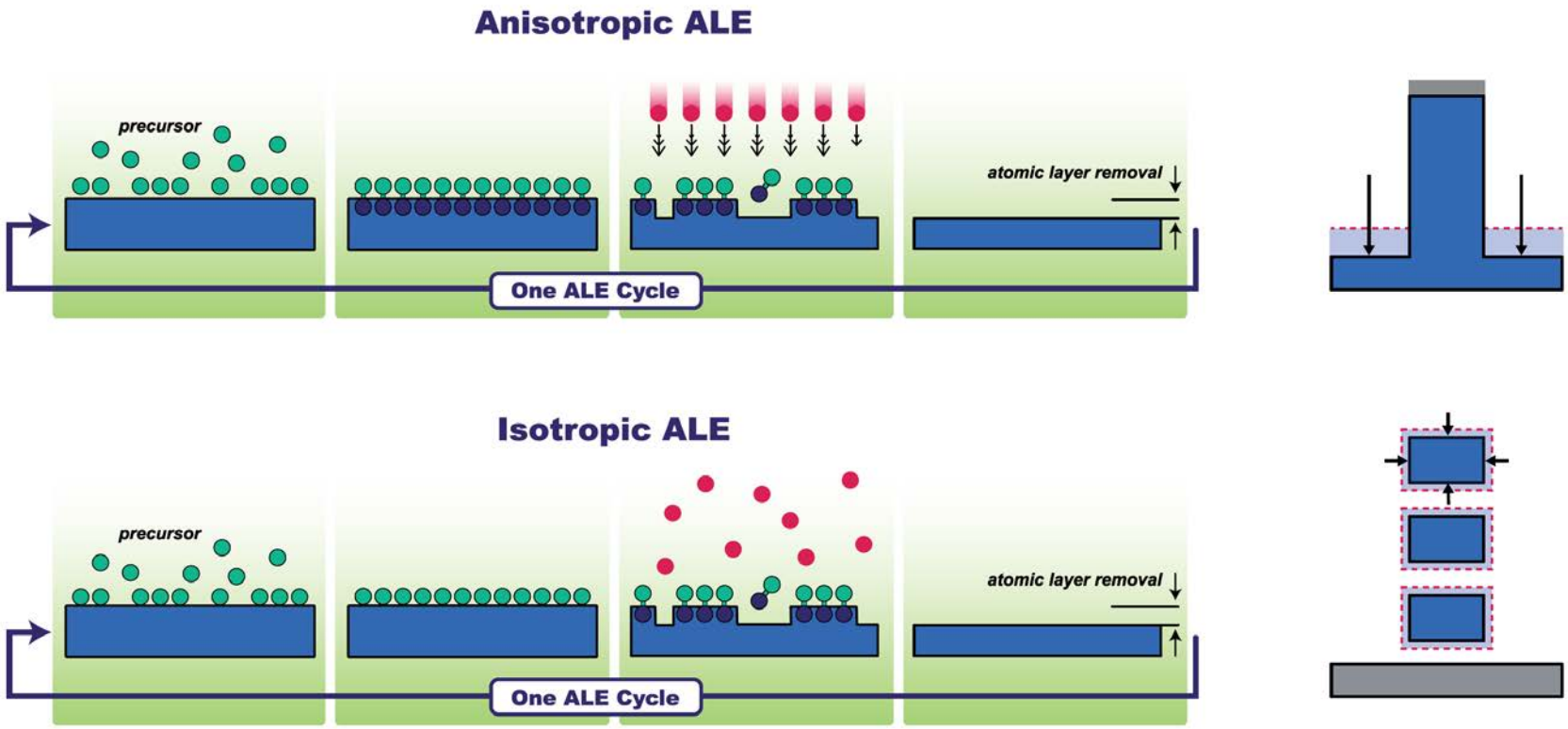
- Anistropic vs isotropic ALE
- Precise ion energy control
- Thermal and plasma-based ALE

From ALD to ALE



Faraz *et al.*, J. Solid State Sci. Technol. 4, N5023 (2015)

Two flavors: anisotropic and isotropic ALE

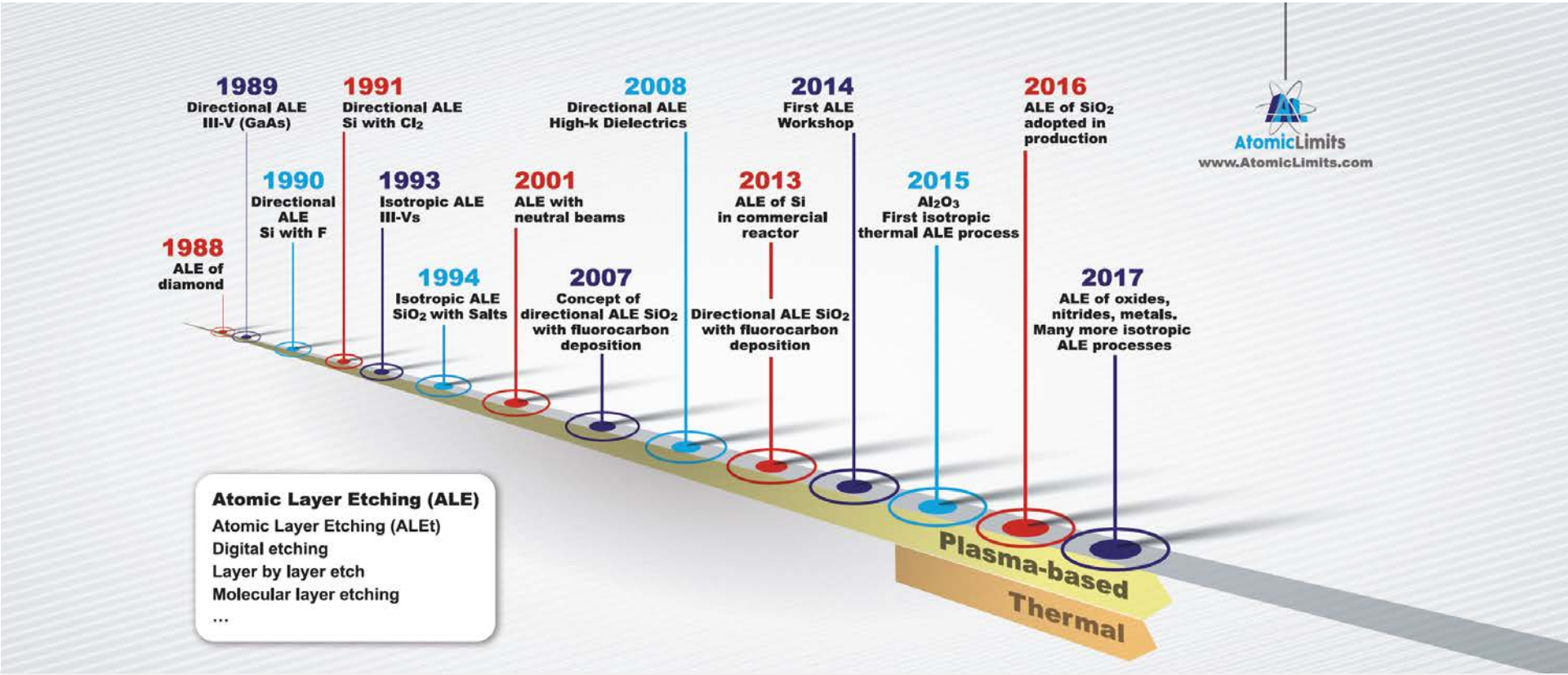


Kanarik *et al*., J. Vac. Sci. Technol. A 33, 020802 (2015)

Faraz *et al*., J. Solid State Sci. Technol. 4, N5023 (2015)

TU/e

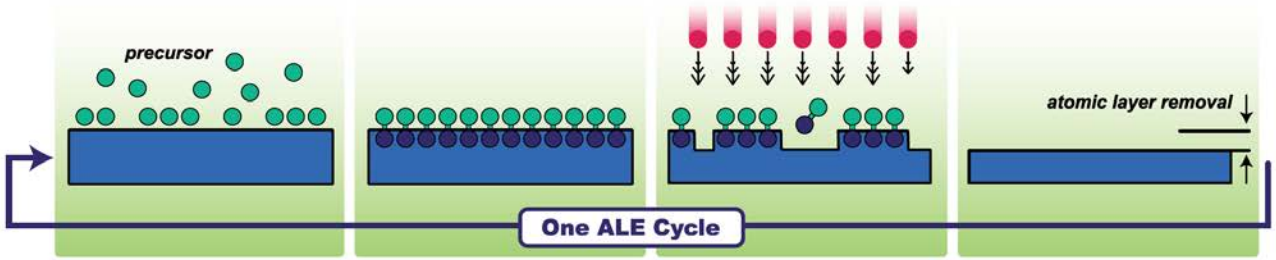
ALE time line – 30+ years of ALE

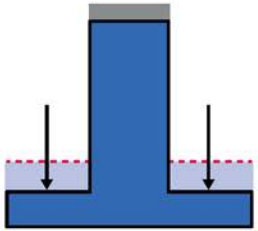


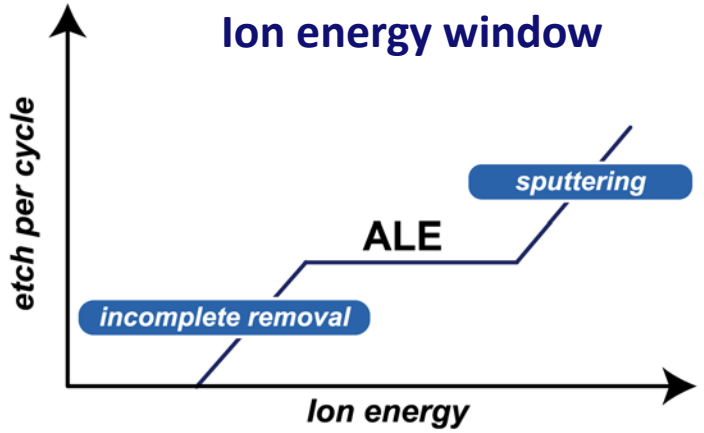
To appear on www.AtomicLimits.com for downloading

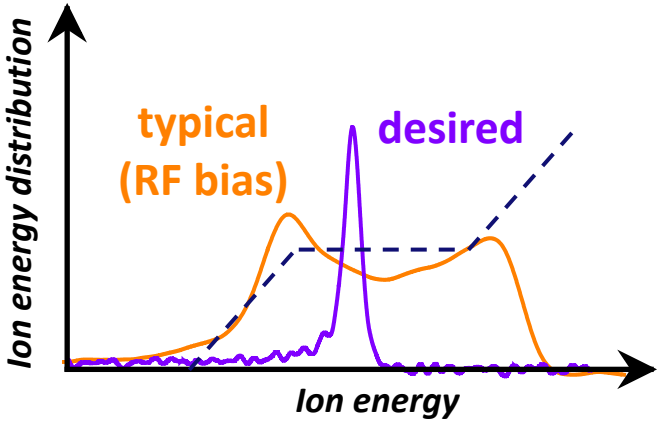
TU/e

Anisotropic ALE – Ion energy window









Kanarik *et al.*, J. Vac. Sci. Technol. A 33, 020802 (2015)
Faraz *et al.*, J. Solid State Sci. Technol. 4, N5023 (2015)

TU/e

Precise ion energy control by innovative substrate biasing

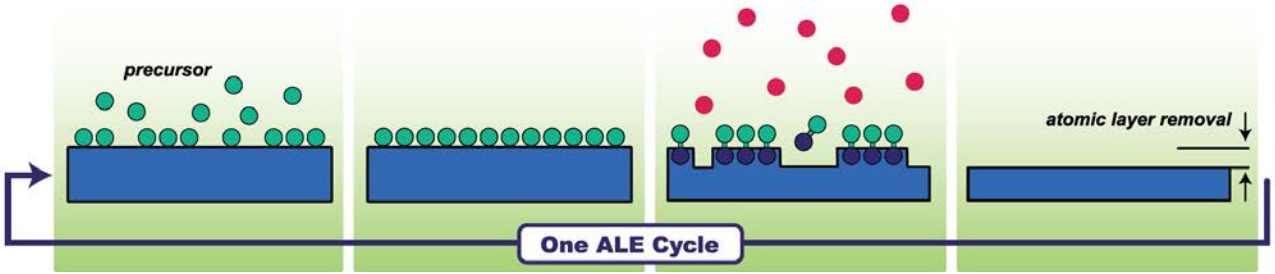
Tailored bias leads to narrow and precisely-controllable ion energy

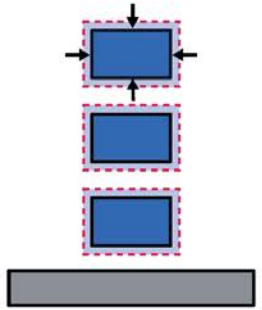
Unpublished result
Please contact: w.m.m.kessels@tue.nl

Wang and Wendt, J. Appl. Phys. 88, 643 (2000)
Blauw *et al*., Electrochem. Sol. State Lett. 10, H309 (2007)
Faraz *et al*., to be published (2019)

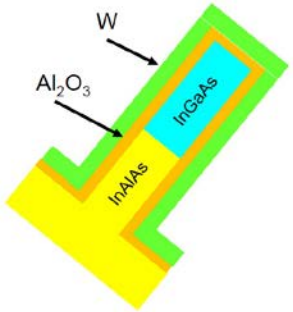
TU/e

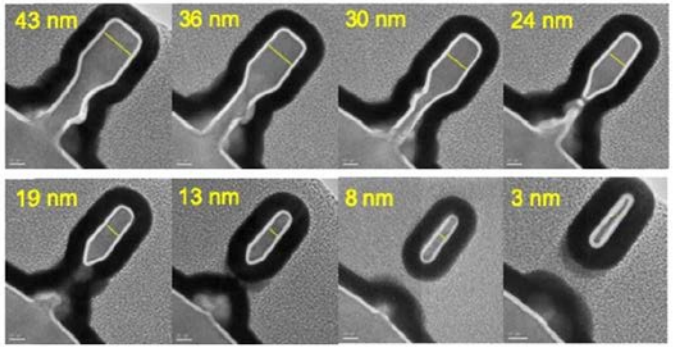
Isotropic ALE – Thermal and plasma-based



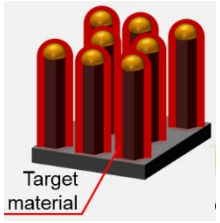


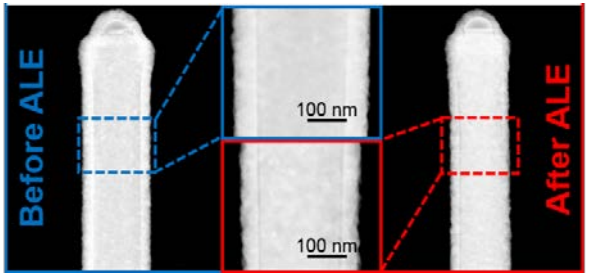
Thermal ALE of InGaAs and inAlAs - **HF** & **$AlCl(CH_3)_2$**





Plasma ALE of ZnO - **Hacac** & **O_2 plasma**

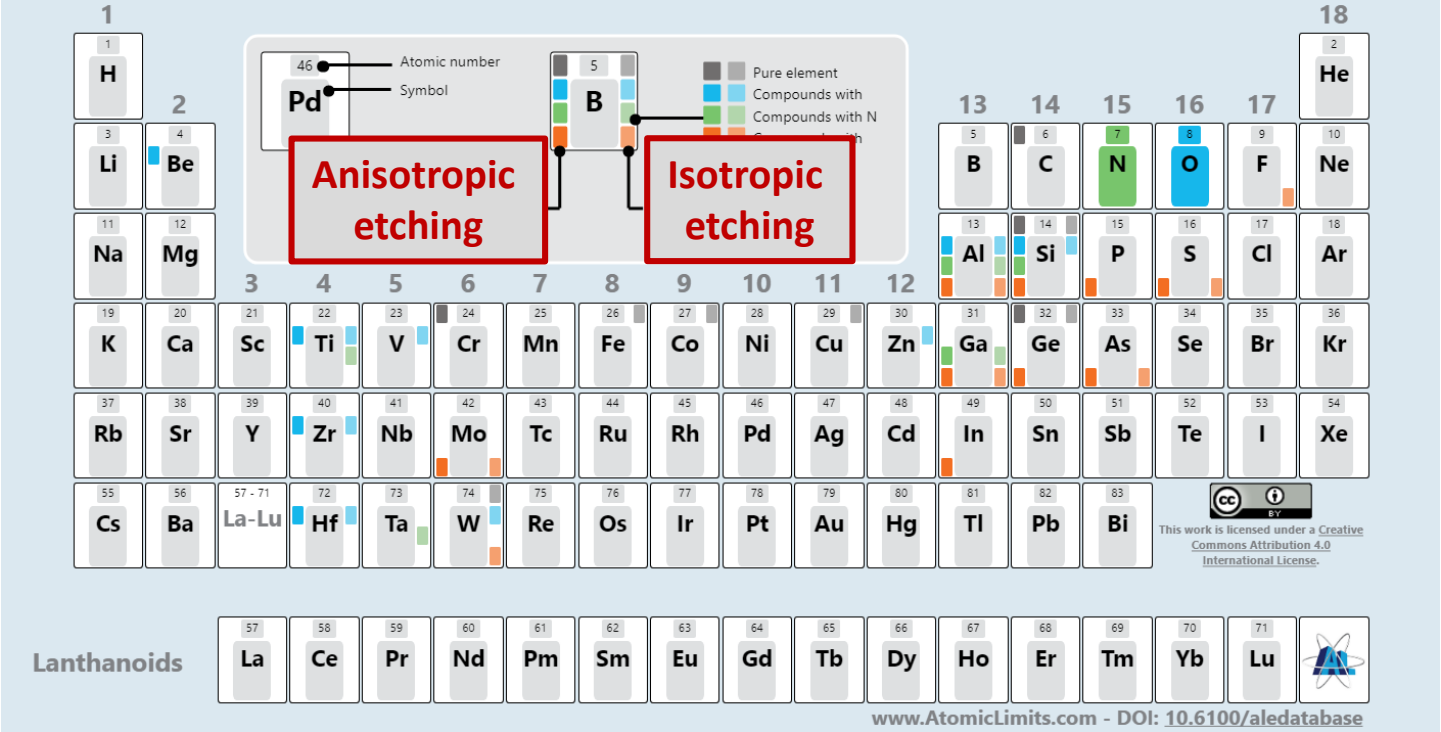




See Sunday: Tutorial about **Thermal Based ALE** by Steve George
Wu *et al.*, to be published in Nano Lett. (2019)
Mameli *et al.*, ACS Appl. Mater. Interfaces 10, 38588 (2018)

The online ALE database – www.AtomicLimits.com

Crowd sourcing: Please add your (new) ALE processes



With direct links to publications

ALE database DOI: https://doi.org/10.6100/alddatabase
Content management by Tahsin Faraz, Nick Chittock, and Adrie Mackus

Summary

1. ALD status report: strong, healthy & growing
2. ALD is big in photovoltaics
3. Plasma ALD has become mainstream
4. Plasma ALD can be very conformal
5. Ion bombardment yields opportunities for ALD
6. Area-selective deposition is trending
7. ALD fundamentals: Need for quantitative data
8. Atomic layer etching is becoming vital

More reading on the blog:

AtomicLimits

www.AtomicLimits.com